Air-water interfacial areas in unsaturated soils: Evaluation of interfacial domains

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[1] A gas-phase miscible-displacement method, using decane as an interfacial tracer, was used to measure air-water interfacial areas for a sand with water contents ranging from \sim 2% to 20%. The expected trend of decreasing interfacial areas with increasing water contents was observed. The maximum estimated interfacial area of 19,500 cm⁻¹ appears reasonable given it is smaller than the measured surface area of the porous medium (60,888 cm⁻¹). Comparison of the experimental data presented herein with literature data provided further insight into the characterization of the air-water interface in unsaturated porous media. Specifically, comparison of interfacial areas measured using gas-phase versus aqueous-phase methods indicates that the gas-phase method generally yields larger interfacial areas than the aqueous-phase methods, even when accounting for differences in water content and physical properties of the porous media. The observations are consistent with proposed differences in interfacial accessibility of the aqueous- and gasphase tracers. Evaluation of the data in light of functional interfacial domains, described herein, yields the hypothesis that aqueous interfacial tracers measure primarily air-water interfaces formed by "capillary water," while gas-phase tracers measure air-water interfaces formed by both capillary and surface-adsorbed (film) water. The gas- and aqueous-phase methods may each provide interfacial area information that is more relevant to specific problems of interest. For example, gas-phase interfacial area measurements may be most relevant to contaminant transport in unsaturated systems, where retention at the airwater interface may be significant. Conversely, the aqueous-phase methods may yield information with direct bearing on multiphase flow processes that are dominated by capillary-phase behavior. INDEX TERMS: 1832 Hydrology: Groundwater transport; 1875 Hydrology: Unsaturated zone; 1866 Hydrology: Soil moisture; KEYWORDS: air-water interface; interfacial tracer

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1. Introduction

[2] The air-water interface has been shown to play a significant role in a number of processes in porous media systems. For example, the air-water interface plays an important role in governing multiphase flow, the significance of interfacial vapor retention for contaminant transport, and mass transfer behavior, including aqueous dissolution, volatilization, and adsorption to the solid phase. A key variable dictating the importance of the interface to such processes is the areal extent of the interface, which is dependent on a number of soil (e.g., texture, packing) and system (e.g., water content and distribution) properties [*Costanza and Brusseau*, 2000]. Qualitatively, a larger interfacial area represents increased adsorption capacity for surface-active compounds and may also decrease mass

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transfer rate limitations. Methods for measuring interfacial areas have been actively sought in order to develop correlations between the air-water interfacial area and system properties and to improve the quantitative understanding of the role of the interface in many processes.

[3] Although several methods for measuring interfacial area have been proposed, each with associated advantages and disadvantages, it is not clear that the methods yield consistent information. It is possible that the various methods probe different physical interfacial domains within the soil, although studies have not specifically examined this phenomenon in detail. The current study was conducted to evaluate in greater detail one of the proposed methods for measuring the air-water interface, a gas-phase interfacial tracer method. Furthermore, the current results will be compared to published data obtained using other interfacial area measurement methods to assess the hypothesis that the various methods may be measuring different physical domains within the porous medium.

2. Background

2.1. Conceptual Models

[4] It is to be expected that the magnitude of the air-water interface in a given system would be dependent upon water

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Figure 1. Proposed relationships between air-water interfacial area and water content. (a) Previously reported relationships; solid and dashed lines adapted from *Reeves and Celia* [1996] and *Or and Tuller* [1999], respectively. (b) Newly proposed relationship. Interfacial areas normalized by the reported maximum interfacial area for the system.

content. While the results of both experiment-based and modeling-based studies show a dependence of interfacial area on water content, there is some disagreement on the exact nature of the relationship. Two general relationships have been proposed for the functional dependence of airwater interfacial area on water content (Figure 1a). For the first proposed relationship (solid line), interfacial area increases from zero at water-saturated conditions to some maximum at relatively low water contents. This maximum interfacial area is considered to correspond to a condition in which pendular rings have formed and dominate the system [e.g., Gvirtzman and Roberts, 1991]. As water content decreases below that associated with maximum pendular ring formation (and resultant maximum interfacial area), the interfacial area decreases to zero. This approach considers only filled pore- and pendular ring contributions to the formation of interfacial area and does not incorporate contributions from adsorbed-water films. The second proposed relationship (dashed line in Figure 1a) is characterized by a nonlinear monotonic decrease in interfacial area with increasing water content [e.g., Cary, 1994]. In addition to filled pores and pendular rings, this approach incorporates the contribution of adsorbed-water films to total interfacial area. Thus, maximum interfacial areas are expected to occur not at the water contents associated with pendular ring formation, but rather at lower water contents where adsorbed water may be most important.

[5] A significant difference between the two theoretical models discussed above is the conceptualization of the source of air-water interfacial area. Capillarity and adsorption are the primary processes that serve to retain water in porous media, influencing water distribution and consequently, the formation of the air-water interface. Capillary processes provide an interfacial domain comprised of menisci of filled or partially filled pores, whereas adsorption processes form an interfacial domain comprised of thin films of water coating solid surfaces. Thus, in addition to water content, it is suggested that water "morphology" will significantly influence interfacial areas. Models that account solely for water held by capillarity (e.g., pendular rings), referred to throughout as "capillary-phase water," yield the approximately parabolic relationship between interfacial areas and water content. Conversely, models that include both adsorbed and capillary-phase water yield the continually decreasing trend.

[6] Both of the proposed conceptualizations regarding air-water interfacial area and its dependence on water content contribute to our understanding of the air-water interface. However, neither model is entirely consistent with our knowledge of the air-water interface in all water content

Model	Processes	$A_{\text{IA}}-\theta_W$ Trend	Surface Area, cm ⁻¹	$\begin{array}{c} \text{Maximum} \mathcal{A}_{\text{IA}},\\ \text{cm}^{-1} \end{array}$
Gvirtzman and Roberts [1991]	С	Parabola	Cubic 65 ^a	40
Cary [1994]	С, А	Nonlinear	Rhomb. 150 ^a Sand 120,000 ^b Silt 1,000,000 ^b	40 120,000* 1,000,000* 2,500,000*
Reeves and Celia [1996]	С	Parabola	NR	2,500,000
Bradford and Leii [1997]	č	-	$82^{a}/2.034^{c}$	160
Or and Tuller [1999] ^e	С, А	Nonlinear	$172^{a}/2,064^{d}$	172*
Silverstein and Fort [2000b]	С, А	Nonlinear	Sand A 604 ^a	182
			Sand B 440 ^a	189
Oostrom et al. [2001]	С, А	Nonlinear	76	70
			$104^{\rm a}/1,181^{\rm d}$	200

Table 1. Summary of Interfacial Area Modeling Results

C, capillarity; A, water adsorption; NR, not reported; *, maximum A_{IA} forced to equal surface area at 0.0 θ_{W}

^aCalculated based on spherical particles and assumed packing.

^bDefined for hypothetical soil.

^c Measured by Krypton/BET methods.

^dMeasured by Nitrogen/BET methods.

^eOr and Tuller present results for a number of soils and soil textures, not discussed here.

regions. A more complete representation of the relationship between interfacial area and water content is obtained if these two conceptualizations are integrated into a model that also incorporates behavior at extremely low water contents (see Figure 1b), which is not accounted for in the two existing models. Generally, the magnitude of the maximal air-water interfacial area would be expected to correlate in some manner to the surface area of the medium. This maximum interfacial area would typically be associated with water contents wherein the porous-medium surfaces are uniformly solvated by a thin film of water. The interfacial area should be smaller than the maximum value at water contents below that required for formation of a uniform water film, becoming zero when no water is present. Likewise, interfacial area should also decrease at water contents greater than that required for uniform film coverage, becoming zero at saturation.

[7] While the general description of the interfacial-area/ water-content relationship illustrated in Figure 1b is consistent with current understanding of the air-water interface in porous media, the specifics of the relationship, such as the water content associated with the maximum interfacial area and the magnitude of change of the interfacial area as a function of water content, will likely depend on properties of the specific system of interest. In addition, there may be practical constraints to measuring the proposed behavior over the entire range of water contents. For example, as will be described in more detail in a later section, all current interfacial-area measurement methods rely on the porous medium being completely solvated by water. The subuniform water film region discussed above does not conform to this experimental requirement. The presence of exposed mineral grains under conditions of subuniform film coverage would constrain current methods from accurate interfacial area measurements.

2.2. Previous Modeling Efforts

[8] Several mathematical models have been proposed to quantify the specific air-water interfacial area in a variety of real and hypothetical porous media systems. As discussed above, the models fall into two general categories, according to which of the two proposed relationships between interfacial area and water content they predict. The general "parabolic" relationship between interfacial area and water content is predicted by models presented by Gvirtzman and Roberts [1991] and Reeves and Celia [1996], while the nonlinear decreasing trend is predicted by models presented by Cary [1994], Or and Tuller [1999], Tuller et al. [1999], Silverstein and Fort [2000a, 2000b], and Oostrom et al. [2001]. An interfacial area model proposed by Bradford and Leij [1997] does not fall into either category because the model is not applicable to the low water-content region that differentiates between parabolic and nonlinearly decreasing behavior. The Gvirtzman and Roberts and Reeves and Celia models do not account for adsorbed-water contributions to interfacial area, while the others do. As discussed by Or and Tuller [1999], adsorbed water may contribute the bulk of the air-water interfacial area in some systems. Thus, failure to account for adsorbed-water contributions could result in artificially low predicted interfacial areas.

[9] A summary of published interfacial area modeling efforts is provided in Table 1. From inspection of the data, it is clear that models which include adsorbed water predict air-water interfacial areas that are largest at very low water contents, and that decrease in a general nonlinear manner toward zero as water content increases to saturation. Models that do not include adsorbed water predict the parabolic trend. Most of the models predict interfacial areas that are less than measured or calculated surface areas, which lends some support for the model values. Only the Bradford and Leij [1997] model yielded interfacial area estimates that exceed reported (calculated) surface areas. Due to the variety of methods used to measure and calculate surface areas and the fact that certain models force interfacial areas to equal surface areas, it is difficult to draw firm conclusions from the modeling data regarding the influence of surface area on interfacial areas. This issue will be addressed in greater detail with regard to comparisons of experiment-based interfacial areas and both measured and calculated surface areas.

2.3. Previous Interfacial Area Measurement Efforts

[10] No well-tested and accepted method exists for direct measurement of air-water interfacial areas. Without such a method, interfacial retention cannot be predicted with confidence nor its significance in a system completely evaluated. To date, there are at least five proposed approaches to the measurement of interfacial areas. Each method will be briefly described below. A more detailed review of the methods was presented by *Costanza and Brusseau* [2000].

[11] Two of the methods make use of well-established procedures used for miscible-displacement column experiments. Interfacial tracers are used as the solute, allowing correlation between experimentally measured retardation factors and interfacial areas. *Brusseau et al.* [1997], *Silva* [1997], *Enright* [1998], and *Kim et al.* [1999] have conducted gas-phase tracer experiments, using heptane and decane as interfacial tracers. Silva and Kim et al. performed experiments at three or more water contents, while Brusseau et al. and Enright present data for only one or two water contents, respectively.

[12] An aqueous-phase interfacial tracer method, analogous to the gas-phase tracer method, with the exception that water is the mobile phase carrying the interfacial tracer, has also been proposed. *Saripalli et al.* [1997] and *Kim et al.* [1997, 1998] have demonstrated the surfactant interfacial tracer technique for measuring air-water interfacial areas in laboratory-scale porous media systems. Sodium dodecyl benzene sulfonate (SDBS) was used as the aqueous interfacial tracer, and six experiments were performed at water saturations ranging from 11% to 100%.

[13] A static method developed by Karkare and Fort [1993, 1994, 1996], Karkare et al., [1993], and Silverstein and Fort [1997] relies on the principles of capillary action, and the use of a surfactant that forms a solid monolayer at the air-water interface. With this method, a horizontally positioned column is packed with uniformly wetted porous media. As surfactant is added to one half of the column, accumulating at the air-water interface, the water redistributes 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 greater than the initial. This water mobilization is observed only for surfactant concentrations greater than a critical value, corresponding to monolayer coverage. Thus, knowledge of the area per molecule (inverse of surface excess) at which the mobilization occurs and the minimum amount of surfactant needed to achieve this critical mobilization concentration, allows the calculation of the interfacial area. Interfacial areas were measured for sand and glass bead systems at several water contents ranging from 5 wt % to near saturation. Additionally, Silverstein and Fort [1997] made use of the method in estimating interfacial areas for three glass bead systems with different average particle diameters over a range of water contents.

[14] Anwar et al. [2000] proposed a surfactant mass balance method to measure air-water interfacial areas. The method involves saturating a soil-packed column with a surfactant (SDBS) solution and then draining the column to the desired water content. The solution is then passed through the column, maintaining the desired water content. The column effluent is continually recycled back through the column, until the effluent surfactant concentration remains constant. When no additional surfactant mass is retained in the column, it is assumed that equilibrium distribution of the surfactant in the system has been achieved. Experiments were conducted in three soil columns containing different size-fractions of glass beads.

[15] Schaefer et al. [2000] proposed a method that, similarly to the mass balance method, is based on the premise of mass conservation in the system. However, it relies upon surfactant diffusion, rather than advection of a surfactant solution, to deliver the surfactant to the air-water interfaces. Thus, the assumption of chemical equilibrium is integral to this method. A column is filled with a surfactant solution, to which sand is added. After packing, a pool of surfactant solution remains at the top of the column. The column is then drained into a reservoir, connected to the bottom of the column, to obtain the desired water content. This allows the system to be set to a given water content either by drainage or imbibition. After the desired water content has been set, the surfactant solution in the reservoir is monitored for concentration changes. When no concentration change is detected, it is assumed that any initial aqueous-phase concentration gradient caused by accumulation of surfactant molecules at the interface has been satisfied, and that equilibrium has been reached. The column is unpacked and an extraction and mass balance is performed similarly to that described by Anwar et al. [2000]. Experiments were conducted under both drainage and imbibition conditions at several water contents, and using several SDBS concentrations to examine the effects of surface tension changes on measured interfacial areas.

[16] As note above, several approaches have been described for measurement of air-water interfacial areas in porous media, and all appear to have potential for furthering the current understanding of the gas-water interface in porous media and its complex dependence on system properties (e.g., water content, grain size). Table 2 provides a summary of the experimental measurements reported in the literature. It is clear that the air-water interfacial areas measured using the gas-phase method are significantly larger that those obtained with the aqueous-phase methods. Although water contents were different among experiments, this fact does not account for the clear difference between results obtained from the gasand aqueous-phase methods. For example, when the Kim et al. [1999] data are compared only to systems with similar calculated surface areas and similar water contents, such as the data reported by Anwar et al. and Schaefer et al. (see Table 2), it is seen that the maximum interfacial areas obtained with the gas-phase method are approximately an order of magnitude larger than the aqueous-based values. This may suggest that for comparable surface area systems, the gas-phase tracers are measuring a different interfacial-area domain than are the aqueous-phase methods.

[17] Interfacial areas are influenced by porous-medium texture [*Cary*, 1994; *Karkare and Fort*, 1996; *Silverstein and Fort*, 1997; *Anwar et al.*, 2000]. Specifically, porous media with larger surface areas tend to have larger interfacial areas at a given water content. Thus, it is possible that some of the variation in interfacial area values observed in Table 2 is due to differences in the surface areas of the various porous media used in the experiments. However, direct evaluation of the impact of surface area differences is difficult for the entire set of published data because of the different types of surface area information reported. The two

(cm^{-1})	$\frac{\text{Measured SA}}{(\text{cm}^{-1})}$	$\begin{array}{c} \text{Maximum } A_{\text{IA}} \\ (\theta_W) \ (\text{cm}^{-1}) \end{array}$	Method
Sand: 190	NR	145 (0.07)	SM
ass beads: 288	NR	224 (0.07)	
NR	NR	61,095 (0.16)	GT
NR	11,136	3,662 (0.05)	GT
300-500	NR	130 (0.25)	AT
180	2,064	46.4 (0.11)	AT
A: 290	NR	164 (0.11)	SM
B: 604		302 (0.11)	
C: 440		345 (.011)	
110 ^a	28,200 ^b	13,301 (0.05)	GT
180	2,064	1,500 (0.01)	GT
A: 148	NR	90 (0.03)	SMB
B: 76		72 (0.01)	
C: 51		50 (0.01)	
104	1,181	I: 181 (0.01)	SD
	·	D: 235 (0.01)	
	alculated SA (cm ⁻¹) Sand: 190 ass beads: 288 NR 300–500 180 A: 290 B: 604 C: 440 110 ^a 180 A: 148 B: 76 C: 51 104	alculated SA (cm ⁻¹) Measured SA (cm ⁻¹) Sand: 190 NR ass beads: 288 NR NR NR NR 11,136 300-500 NR 180 2,064 A: 290 NR B: 604 2,064 C: 440 110 ^a 180 2,064 A: 148 NR B: 76 C: 51 104 1,181	alculated SA (cm ⁻¹) Measured SA (cm ⁻¹) Maximum A_{IA} (θ_W) (cm ⁻¹) Sand: 190 NR 145 (0.07) ass beads: 288 NR 224 (0.07) NR NR 61,095 (0.16) NR 11,136 3,662 (0.05) 300-500 NR 130 (0.25) 180 2,064 46.4 (0.11) A: 290 NR 164 (0.11) B: 604 302 (0.11) C: 440 345 (.011) 110 ^a 28,200 ^b 13,301 (0.05) 180 2,064 1,500 (0.01) A: 148 NR 90 (0.03) B: 76 72 (0.01) 50 (0.01) 104 1,181 I: 181 (0.01) D: 235 (0.01) 255 (0.01) 245 (0.01)

Table 2	2.	Summary	of	Measured	Interfacial	Areas

SA, surface area; NR, not reported; S, sand; GB, glass beads; GT, gas-phase tracer; SM, surfactant mobilization; AT, aqueous-phase tracer; SMB, surfactant mass balance; SD, surfactant diffusion; I, imbibition; D, drainage.

^aCalculated from average particle size data provided by the author using the method described by *Haughey and Beveridge* [1969].

^bAssumed to be N₂/BET measurement, but not stated explicitly by author.

methods of determining surface area that were reported in the literature were calculations based on geometric arguments and the assumption of smooth spherical particles, and N₂-adsorption data analyzed according to the BET isotherm. The latter values would reflect the impacts of intraparticle porosity, surface roughness, and nonspherical particles on surface area and are, therefore, expected to be much larger than the surface areas calculated assuming smooth, spherical particles. For example, Kim et al. [1997] reported a calculated surface area of 180 cm⁻¹ for a selected porous medium, while *Kim et al.* [1999] reported a N_2 /BET-measured surface area of 2064 cm⁻¹ for the same porous medium. Similarly, Schaefer et al. [2000] report calculated and N_2 /BET-measured surface areas of 104 and 1181 cm⁻¹, respectively, for the same porous medium. Despite these limitations, sufficient information exists to evaluate the relative magnitudes of measured interfacial areas in comparison to calculated and N₂/BET-measured surface areas.

[18] Interfacial areas obtained using the gas-phase tracer method are generally larger than and, therefore, inconsistent with smooth-sphere calculated interfacial areas (see Table 2). Conversely, in only 2 of 12 instances are aqueous-surfactant-based interfacial area measurements larger than the calculated surface areas. In fact, it generally holds that gas-phase methods yield interfacial area values that are comparable to the N₂/BET-measured surface areas, while aqueous-surfactant methods yield values comparable to smooth-sphere calculated surface areas. This may support the hypothesis that gas-phase and surfactant-based methods access different physical domains and, therefore, yield interfacial area measurements for different fractions of the total interfacial area.

[19] It is likely that the advective surfactant methods primarily measure only those interfacial-area domains that bound contiguous advective water pathways. This would generally exclude interfacial area bounding immobile or "isolated" water, water that does not participate in advective flow. In an unsaturated porous medium, this immobile water fraction would likely include water held as adsorbed water in drained or partially drained pores. Thus, the advective surfactant methods may not measure significant amounts of air-water interfacial area associated with adsorbed water. In fact, interfacial areas measured using the advective surfactant methods are similar to the interfacial area values predicted with the models that consider only capillary-phase contributions to interfacial area (see Tables 1 and 2). Conversely, these model-based results, like the smooth-sphere calculated surface areas, are inconsistent with the interfacial areas measured with the gas-phase tracer method. Models that do include adsorbed-water contributions to interfacial area force the maximum interfacial area to equal the surface area. Thus, these modeling results will differ depending on whether smooth-sphere calculated or N2-BET-measured surface areas are used as model-input values. If smooth-sphere calculated areas are used in such models, the results will be more representative of the magnitude of interfacial area measured by aqueousphase experiments. Conversely, the use of N₂/BET-measured surface areas as input values will produce estimates similar to those measured by gas-phase tracers. The issues introduced above will be further addressed in light of the results obtained from the current study.

3. Materials and Methods

3.1. Porous Medium and Tracer Properties

[20] Experiments were conducted using a natural porous medium, Vinton fine sand. The texture and multipoint nitrogen BET specific surface areas are reported with additional physical properties in Table 3. Methane was used as a nonreactive tracer (100 ppmv), while heptane (100 ppmv) and decane (2 ppmv) were evaluated for use as interfacial tracers. These correspond to approximate concentrations of 66, 411, and 12 mg·L⁻¹, respectively (1 atm, 25°C). A significantly lower vapor pressure was used for decane compared to the other compounds due to its much lower saturation vapor pressure. The tracer gases were each custom-mixed in a balance of nitrogen to the desired input concentration and introduced into the system via high-pressure gas

 Table 3. Physical Properties of Porous Medium

5 1	
Texture: ^a % sand, silt, clay	97, 1.8, 1.2
Organic carbon content, wt/wt % ^a	0.01
Particle density, g·cm ⁻³	2.69
Average pore diameter (adsorption/desorption), ^b Å	128.4/167.7
Total specific surface area, b m ² ·g ⁻¹	3.54
Internal specific surface area, ^{b,c} m ² ·g ⁻¹	2.83
External specific surface area, ^{b,d} m ² ·g ⁻¹	0.71
Total internal pore volume, ^{b,e} cm ³ ·g ⁻¹	0.00958

^aSoil, Water, and Plant Analysis Laboratory, Tucson, AZ.

^bMicromeritics Instrument Corporation, Norcross, GA.

^cInternal area, defined as surface area contained within pores of 17 to 3000 Å diameter.

^dExternal area defined as difference between total and internal surface areas.

 $^{\rm e}$ Internal pore volume, defined as volume contained within pores of 17 to 3000 Å diameter.

cylinders (Air Products, Long Beach, CA; Spectra Gases, Branchburg, NJ; or Air Liquide, Houston, TX).

[21] Literature values were available for Henry's constants and interfacial adsorption coefficients. However, values for solid-phase sorption coefficients (K_D) depend on properties of the porous medium and therefore, require soil-specific measurement or estimation. Saturated-phase sorption coefficients were estimated for heptane and decane, since available experimental measurement methods were not compatible with the extremely high Henry's coefficients of these compounds. Many correlations between sorption coefficients and properties of the porous medium (e.g., fraction of organic matter) and of the chemical (e.g., octanol-water partition constant) are available in the literature. Although it is recommended that a correlation be chosen that is specific to the class of compounds of interest, none were available for alkanes. Furthermore, while such correlations are often referenced to organic carbon or organic matter contents, few correlations have been developed for porous media with low organic-carbon fractions, such as used in the current study. Since no single estimation method was specifically tailored to the porous medium and the sorbates of interest in this research, a total of four correlations were used and their results were averaged. The uncertainty in the estimation was then taken as the standard deviation of the results. For more detail concerning the estimation method, readers are referred to Costanza-Robinson [2001]. The resulting estimated mean K_D values for heptane and decane, as well as select physicochemical properties of all compounds used are contained in Table 4.

3.2. Laboratory System Overview

[22] Tracer gases were introduced via high pressure cylinders. All gases passed through a partially water filled gas washing bottle (Pyrex, Ace Glass, Vineland, NJ) prior to contacting the wetted porous medium to prevent drying of the porous medium. Separate humidification bottles were used for the carrier gas (ultra-high-purity nitrogen) and the tracers (reactive and nonreactive) to avoid background contamination. The temperature and relative humidity of the gases were measured using a thermohygrometer probe (Dwyer Instruments, Inc., Michigan City, IN) inserted into a custom-made humidity chamber that was connected in-line through a column bypass line. The column bypass line also allowed for various system variables (e.g., flow rate, C_0

voltage) to be measured or set without precontamination of the porous medium.

[23] A horizontally mounted 10.5-cm (7.06-cm i.d.) stainless steel column (MODcol, St. Louis, MO) was used with dispersion plates (nominal 20-µm pore size) fitted at both ends to allow an even distribution of vapor across the column cross-section. Bed-support frits (2- to 4-µm pores) were also inserted between the porous medium and the diffusion plates to prohibit grains from clogging the dispersion plates and to minimize column dead-volume. Stainless steel three-way valves (Whitey, Arizona Valve and Fittings Co., Phoenix, AZ) were used to switch between the tracer and carrier gases. All system components through which gases flowed were connected with 1/8'' stainless steel tubing and 1/8'' stainless steel Swagelok fittings (Arizona Valve and Fittings Co., Phoenix, AZ). High-resolution metering valves (Cole Parmer, Vernon Hills, IL), gage- and differential pressure gauges (Dwyer Instruments, Inc., Michigan City, IN), and third-stage high precision pressure regulators (Model 44-4660S24, Tescom, Elk River, MN or Model 8310, Porter Instrument Company, Inc., Hatfield, PA) were used to control flow rates and monitor pressures in the system. A 25-mL bubble flowmeter (Kimble-Kontes, Vineland, NJ) or digital flowmeter (ADM2000, J&W Scientific, Folsom, CA) was inserted at the detector outlet to measure flow rates.

[24] The column effluent stream passed directly to an online flame ionization detector (FID) (Varian 3700 or 3400, Varian Associates, Inc., Walnut Creek, CA) for analysis. The column effluent was split and only 20 mL·min⁻¹ was directed to the FID. The stream was split to maintain the flame in the detector, as well as to remain within the linear detection range. Air and hydrogen were supplied to the FID at 300- and 30 mL·min⁻¹, respectively, and the detector was heated to 300°C. The FID signal was routed to a digital voltmeter (Micronta, Fort Worth, TX) that was interfaced to a personal computer using Wedge software (T.A.L. Enterprises, Philadelphia, PA). This configuration allowed concentration (voltage) versus time data to be collected real-time at any specified time interval, typically between 20 s and 1 min. A detailed schematic of the system is presented elsewhere [Costanza-Robinson, 2001].

3.3. Packed-Column Experimental Methods

[25] The experimental system, including all tubing, valves, and connectors, was initially flushed for several minutes with

Table 4. Physicochemical Properties of Compounds

	Methane	Heptane	Decane
CAS no.	74-82-8	142-82-5	124-18-5
MW, g·mol ⁻	16.0	100.2	142.3
C_W sat a mg·L ⁻¹	24	3.1	0.04
P_0 , ^a atm	275	0.062	0.002
K_D^{sat} , mL·g ⁻¹	na	0.7°	2.9°
$K_H(-)^a$	27	82	264
$K_{\rm IA}, {\rm cm} \times 10^{-5}$	na	2.33 ^b	22.4 ^b
$\log K_{OW}(-)$	1.09 ^a	4.66^{a}	5.67 ^d
D_a , cm ² ·s ⁻¹	0.205 ^a	0.069 ^a	0.058^{a}

Values given at 25°C; na, not applicable.

^a From Schwarzenbach et al. [1993].

^bFrom *Hoff et al.* [1993].

^cEstimated (see text).

^dFrom Lyman [1990].

methanol to remove any residual machine oil or other organic contamination and was then rinsed with deionized, organic-free water. The water-filled sections were then weighed, emptied, oven-dried, and weighed again to determine the dead-volume contained in various portions of the system. The total system dead volume measured in this manner was 4.5 cm³, which is approximately 3% of the total column pore volume.

[26] The porous medium was heated overnight at 105°C to dry the porous medium and remove any volatile contaminants. The media was allowed to cool under vacuum in a desiccator. The media was then uniformly mixed with the desired amount of water and packed wet into the column. The porous medium was tamped in the column at small increments, typically 1-cm, to minimize the formation of particle-size layering in the column. Aliquots of the wet porous medium were collected before and after packing to gravimetrically determine initial water contents. After the experiment, the column was unpacked and a small (<20 g) aliquot was taken from near the column inlet, three points along the axis of flow, and near the column outlet for gravimetric water content measurement. In addition, the remainder of the column porous medium was used to measure a composite column-averaged water content. The average final water content was consistently close to the water content measured before the experiment, indicating minimal loss of water during the experiments. This was confirmed by the insignificant change in the column mass observed throughout the duration of each experiment.

[27] In order to achieve a constant-concentration tracer input pulse, the water in the humidification bottle had to be saturated with the compound of interest prior to introduction of the gas to the column. Saturation was achieved by passing the gas through the humidification bottle and the column bypass line until a steady FID signal was observed. Prior to each tracer experiment, the nitrogen carrier gas was flushed through the packed column until a steady FID baseline was achieved. The carrier flow rate was matched to the tracer gas flow rate. Multitracer experiments could not be conducted due to the use of flow-through detection (i.e., no analytical separation). Therefore, tracer experiments were conducted sequentially, using identical experimental conditions. Experiments were conducted at least in duplicate, and often in triplicate.

[28] The tracer pulse was introduced to the system by switching between the tracer and carrier gas line using a 3-way directional switching valve. The input pulse was continued until a relative concentration, defined as the ratio of actual concentration (*C*) to input concentration (*C*₀), of one was achieved. Upon switching back to the tracer-free (nitrogen) gas line, a significant pressure surge was created due to backpressure in the system. Use of a high-precision third-stage regulator minimized this surge, but it could not be completely eliminated. The surge is manifested in the breakthrough curves as a temporary increase in solute concentration above $C/C_0 = 1$.

[29] Experiments were conducted at a nominal column flow rate of 50 cm³·min⁻¹, with 20 cm³·min⁻¹ directed to the FID and the remainder vented prior to the detector via the split vent line. The chosen column flow rate corresponds to pore velocities within the wide range of velocities reported as typical for soil vapor extraction remediation systems. Total

column flow rate was measured as the sum of flow at the FID outlet and the split vent. Actual column volumetric flow rates were slightly smaller due to gas expansion associated with the post column pressure drop. Gas expansion, and consequent concentration gradient effects, along the length of the column were not considered to be important, given that the induced pressure gradient along the column was only 3%. Gases were introduced at a pressure of 3 psi (\sim 210 cm of water). This relatively high inlet pressure was required to overcome backpressure created by the online gas-washing bottles.

[30] Sorption of compound vapors to the column system apparatus was considered and corrected for in the analysis of the data. Sorption to the apparatus, versus retention by the porous medium, was characterized by conducting tracer experiments using an empty column. The magnitude of retention observed for the system without porous media was then subtracted from the total retention measured in systems with porous media.

3.4. Data Analysis

[31] Breakthrough curves were plotted as relative concentration (C/C_0) versus eluted pore volume. A single pore volume represents the gas-filled volume contained in the packed column. The breakthrough curves were analyzed using comparative moments analysis, in which the transport of the reactive tracers are compared to the transport of the nonreactive tracer. Comparative moments analysis is useful either when the exact pore- and dead volumes of the system are not known or when pressure gradients and gas-expansion complicate the relationship between average linear gas velocity, time, and volumetric flux. This latter consideration served as motivation for use of a comparative analysis. The retardation factor is defined as the ratio of the travel time of a given compound and the travel time of a nonreactive tracer.

$$R_r^{\rm EXP} = T_r / T_{nr} \tag{1}$$

Thus, by definition, the retardation factor of a nonreactive tracer is one. Results of previous research indicate that this assumption is valid for our system [*Brusseau et al.*, 1997].

[32] The total retardation factor for heptane and decane may be influenced by several retention processes and is written as:

$$R_T = 1 + \frac{\rho_b K_D}{\theta_a K_H} + \frac{\theta_w}{\theta_a K_H} + \frac{K_{\rm IA} A_{\rm IA}}{\theta_a} + R_{\rm SS}$$
(2)

where ρ_b refers to the bulk density of the packed column [g·cm⁻³]; K_D , K_H , and K_{IA} are the saturated-phase sorption coefficient [cm³·g⁻¹], Henry's constant [–] and the airwater interfacial adsorption coefficient [cm], respectively; θ_a and θ_W are the volumetric air-porosity and water content, respectively [–]; A_{IA} refers to the specific air-water interfacial area [cm⁻¹], and R_{SS} is a correction factor accounting for any uptake of the tracers by the system hardware (e.g., tubing and column walls). The "one" on the RHS of equation (2) represents retention in the gas-phase pore volume. Thus, an R_{SS} -corrected retardation factor for heptane and decane can be written as:

$$R'_{T} = R_{T} - R_{SS} = 1 + R_{S} + R_{W} + R_{I}$$
(3)

Experiment	θ_T (-)	θ_W (-)	θ_a (-)	$g \cdot cm^{-3}$	PV, cm ³	Q, PV·min ⁻¹	v, cm·min ⁻¹
1	0.361	0.019	0.341	1.720	155.7	3.1	3.2
2	0.366	0.026	0.330	1.705	155.0	3.1	3.3
3	0.358	0.031	0.327	1.726	149.1	3.0	3.4
4	0.375	0.052	0.323	1.682	147.1	2.9	3.4
5	0.401	0.076	0.325	1.611	148.3	3.0	3.4
6	0.396	0.097	0.299	1.625	136.2	2.7	3.7
7	0.403	0.136	0.266	1.607	121.5	2.4	4.1
8	0.397	0.169	0.235	1.603	107.2	2.1	4.7
9	0.393	0.196	0.197	1.631	90.0	1.8	5.6

Table 5. Packed-Column Specifications and Flow Conditions

PV, column air-filled pore volume; Q, volumetric flowrate; v, average linear velocity.

where R_S , R_{IV} , and R_I refer to the retention due to sorption to the solid phase, dissolution into bulk water, and interfacial adsorption, respectively. The corrected retardation factor will be used in the following analyses and, for convenience, will simply be termed the retardation factor (*R*). R_S and R_W are calculated from known physicochemical constants related to the porous medium and the solute (equation (2)). Finally, R_I is calculated using a mass balance approach as the difference between the total retardation factor and the sum of the contributions from other processes.

[33] Once the various terms are known, an estimated specific interfacial area can be calculated from the heptane or decane retardation factor as $A_{IA} = R_I \theta_a / K_{IA}$. An ideal interfacial tracer will be retained in the porous media system by a single retention process, adsorption at the air-water interface. Therefore, it is instructive to calculate the relative magnitude of the various contributions to heptane and decane retention. The percent contributions to retention of the individual processes are calculated as:

$$F_S = \frac{R_S}{R_T' - 1} \times 100 \tag{4}$$

$$F_W = \frac{R_W}{R_T' - 1} \times 100 \tag{5}$$

$$F_I = \frac{R_I}{R'_T - 1} \times 100 \tag{6}$$

4. Results and Discussion

4.1. Transport and Retention

[34] Miscible displacement experiments were conducted at nine water contents ranging between $\sim 2\%$ and $\sim 20\%$. The measured specifications and flow conditions for each experiment are given in Table 5. Postexperiment profiles indicate that water contents were uniform throughout the column for each experiment (Figure 2), while experiment reproducibility is demonstrated in Figure 3. Sorption to the stainless steel system was measurable for both heptane and decane. R_{SS} values of 0.148 and 0.849 were used to correct heptane and decane retardation factors, respectively. Because the retention of heptane in the packed column was minimal (Table 6), sorption to stainless steel is observed to dominate total heptane retention, as discussed in the following paragraphs. To the contrary, decane retention to stainless steel comprises 25% of the measured retardation factor at the highest soil-water content, and decreases to <6% at the lowest soil-water contents where the air-water interfacial area becomes significant. Thus, in the soil-water content region of primary interest, sorption to stainless steel represents a relatively minor contribution to total retention of decane.

[35] As shown in representative examples (Figure 3), heptane breakthrough curves exhibit relatively sharp and symmetric arrival and elution waves, indicating relatively ideal transport. Decane curves exhibit significant tailing in both the arrival and elution waves in virtually all experiments. The tailing observed for decane is much greater than that observed for heptane and is likely due to the additional



Figure 2. Water content profiles for all experiments.



Figure 3. Replicate tracer breakthrough curves.

apparent dispersion caused by greater solute retention and longer residence time, as discussed in detail elsewhere [*Costanza-Robinson*, 2001]. The recovery and retention data for heptane and decane are summarized in Table 6. Recoveries are greater than 98% for all experiments, except for decane in experiment-set 1, which had an average recovery of only 93%. The relatively large retardation factors for those experiments (R = 14) and the comparatively long experiment duration may have contributed to lower mass recoveries. Therefore, a water content of approximately 2% might be considered as the lower limit of the appropriate range for using decane as an interfacial tracer.

[36] Heptane and decane retention are strongly dependent on water content (see Table 6). Both tracers exhibit the expected inverse relationship between the magnitude of retention and water content. This trend is expected because interfacial areas have been shown to be inversely proportional to water content in porous media. Although decane and heptane show similar trends in retention as a function of water content, decane has a significantly greater magnitude of retention at all water contents. This is expected given that decane's interfacial partition coefficient is approximately an order of magnitude larger than heptane's. In fact, the retardation factor for heptane is calculated as less than one for experiment-set 8 (R = 0.96) and 9 (R = 0.97). This may indicate slight overestimation of the retention of heptane by the system hardware (R_{SS}) or may reflect the difficulty of quantifying such minimal retention, due to inherent uncertainty in experimental parameters (e.g., flow rates, temperature). The highest retardation factor for heptane is 1.5, measured at the lowest water content (1.9%) and drops to 1.1 at the slightly higher water content of 2.6%. Thus, in a higher water-content range more typical of a field scenario, the retardation factor for heptane is so small as to be difficult to quantify. This is a clear drawback to the use of heptane as an interfacial tracer.

[37] The appropriateness of heptane and decane as interfacial tracers can be further examined in light of the fraction of their porous-media-associated retention that is due to processes other than adsorption at the air-water interface. The absolute (i.e., R_S , R_W , and R_I) and percent contributions (i.e., F_S , F_W , and F_I) of each retention process to total retardation, calculated according to equations (2) and (4), (5), and (6), respectively, were determined for heptane and decane. This analysis showed that sorption to the solid phase contributed significantly to heptane retention. In fact, at all but two water contents, sorption was the greatest source of porous-media-associated retention of heptane. Hence, once dissolution into bulk water and sorption to the solid phase are accounted for, interfacial adsorption is observed to be negligible at all but the lowest three water contents. In the 1.9%, 2.6%, and 3.1% θ_W experiments, interfacial adsorption is shown to contribute 27%, 41%, and 71%, respectively, of the total retardation. Thus, as discussed in greater

Table 6. Heptane and Decane Retardation Factors

Exercision and 0			Heptane	Decane			
Experiment	01	% Recovery	$R \pm stdev$	n	% Recovery	$R \pm$ stdev	n
1	0.019	99.6	1.538 ± 0.009	4	93.2	14.179 ± 1.541	2
2	0.026	99.6	1.146 ± 0.004	2	99.4	5.371 ± 0.023	2
3	0.031	98.8	1.124 ± 0.025	3	100.0	5.194 ± 0.120	2
4	0.052	99.5	1.042 ± 0.002	3	98.8	3.324 ± 0.042	3
5	0.076	99.7	1.007 ± 0.005	3	100.0	2.735 ± 0.043	3
6	0.097	99.4	1.008 ± 0.004	3	99.1	2.861 ± 0.049	2
7	0.136	99.0	1.070 ± 0.008	2	98.6	2.879 ± 0.022	2
8	0.169	99.5	0.958 ± 0.019	2	100.5	2.464 ± 0.072	2
9	0.196	99.5	0.973 ± 0.012	3	101.8	2.515 ± 0.041	2

 Table 7. Process Contributions to Total Retardation Factor for Decane

Experiment	θ_W	$R'_{\rm TOT}$	R_S	R_W	R_I	F_S	F_W	\mathbf{F}_{I}
1	0.019	14.18	0.06	0.00	13.12	0.4	0.0	99.6
2	0.026	5.37	0.06	0.00	4.31	1.3	0.0	98.7
3	0.031	5.19	0.06	0.00	4.13	1.4	0.0	98.6
4	0.052	3.32	0.06	0.00	2.26	2.5	0.0	97.5
5	0.076	2.74	0.06	0.00	1.66	3.2	0.1	96.7
6	0.097	2.86	0.06	0.00	1.80	3.3	0.1	96.7
7	0.136	2.88	0.07	0.00	1.81	3.6	0.1	96.3
8	0.169	2.46	0.08	0.00	1.39	5.2	0.2	94.6
9	0.196	2.52	0.09	0.00	1.42	6.1	0.2	93.7

detail by *Costanza-Robinson* [2001], these results indicate that heptane was not an optimal interfacial tracer for this system.

[38] Contrary to the arguments against the use of heptane as an interfacial tracer, data provided in Table 7 lend support for the viability of decane as an interfacial tracer. Adsorption at the air-water interface is shown to contribute no less than 92% of the total retardation. Sorption to the solid phase contributes secondarily to retention, but at levels of no more than 7% of the total. In addition, aqueous dissolution is shown to be of little importance. Thus, decane shows promise as an interfacial tracer, and its potential to yield information regarding air-water interfacial areas will be further examined.

4.2. Measured Air-Water Interfacial Areas

[39] The air-water interfacial areas calculated from analysis of the decane breakthrough curves are shown as a function of water content in Figure 4. The measured air-water interfacial areas range from approximately 1000 to 20,000 cm⁻¹, and, as expected, are inversely proportional to water content. The maximum interfacial area of ~19,500 cm⁻¹ is less than, and therefore consistent with, the N₂/BET-measured surface area of the porous medium (~60,888 cm⁻¹). Typical specific surface area units of cm²·g⁻¹ are converted to the cm²·cm⁻³ units used for interfacial areas by multiplying by the bulk density of the porous medium. The N₂/BET measurement of specific surface areas is expected to capture some of the molecular-scale surface roughness of the sand grains. Therefore, measured surface areas should be higher than estimated interfacial areas, since water will tend to mask microscale surface roughness when the water films extend beyond a few monolayers. Thus, the decane-derived air-water interfacial area estimates appear reasonable given the properties of our porous medium.

[40] As discussed previously, calculated surface areas based on smooth-sphere assumptions are often reported in conjunction with interfacial area data presented in the literature. Smooth-sphere surface areas (*S*) for Vinton sand were calculated using [*Haughey and Beveridge*, 1969]:

$$S(cm^{-1}) = \frac{6(1-n)}{d}$$
(7)

where *n* refers to the porosity of the packed porous medium system [-] and *d* is an average particle diameter [cm]. Using an average porosity for all packed columns of 0.377 and an average particle diameter of 0.0234 cm derived from particle-size distribution data [Young et al., 1997], the smooth-sphere surface area of the Vinton sand is calculated to be 160 cm⁻¹. This value is significantly smaller than even the lowest measured interfacial area. This indicates that calculated smooth-sphere surface areas may not serve as an appropriate point of comparison for the interfacial domain measured by gas-phase interfacial tracers. This point will be discussed in detail in the following section.

[41] A potentially important source of uncertainty in the current study involves the use of an estimated value for the decane K_D . The lack of estimation correlations tailored to the compound class of interest, here straight-chain alkanes, increased the uncertainty in the estimation. Furthermore, the available estimation methods rely on soil-organic matter referenced correlations, while the porous medium of interest has a very small fraction of organic-matter (0.01%). The uncertainty in the K_D value, taken as the relative standard deviation of four estimation methods was 39%. Because solid-phase sorption accounts for such a small fraction of the total decane retardation factor, even a more conservative 50% uncertainty in K_D has only a slight effect on the interfacial area estimates.



Figure 4. Measured air-water interfacial areas (calculated from decane retardation factors) as a function of water content.



Figure 5. Maximum measured air-water interfacial areas versus N_2 /BET-measured porous-medium surface areas. Data include those from the current study and literature data obtained using the gas-phase method. The linear regression has been forced through the origin.

[42] Another means of assessing the possible error in the sorption coefficient is to note that as water content increases, the contribution of interfacial adsorption to decane retention decreases. Extrapolating to complete water saturation, the only retention processes that can influence the system are aqueous dissolution and sorption to the solid phase. Therefore, an estimate of the sorption coefficient can be obtained by extrapolating the decane-retention/water-content function to complete saturation. The retardation equation for watersaturated conditions is written as:

$$R_T = 1 + \frac{\rho_b K_D}{\theta_a K_H} + \frac{\theta_w}{\theta_a K_H}$$
(8)

The extrapolated retardation factor and knowledge of the remaining physicochemical properties allows equation (8) to be solved for K_D . Both linear and exponential extrapolations of the data to saturation ($\theta_W = 37.5\%$) fit the data well and yield similar estimates of 1.7 and 1.9 for the total decane retardation factor at saturation, which correspond to sorption coefficients of 0.3 and 0.5 for the linear and exponential extrapolations, respectively [Costanza-Robinson, 2001]. These values are approximately an order of magnitude smaller than the values estimated from the correlations (Table 4) and used throughout this analysis. However, the smaller extrapolated K_D values have little effect on calculated interfacial area values because the contribution of sorption to total retention is extremely low for either set of K_D values. The largest change in interfacial area values due to either general uncertainty in the K_D estimation or the extrapolated sorption coefficient was 14%.

[43] In assessing the validity of the current method for measuring specific air-water interfacial areas, it is also important to determine whether any other sources of tracer retention may be occurring within the system that are not being explicitly accounted for in the analysis. The only potential process that was not incorporated into the current analysis is capillary phase separation (CPS), which involves "condensation" of organic vapors in small, water-saturated intraparticle pores. There is limited research into the occurrence of CPS in porous media/contaminant systems, but preliminary data suggest that for CPS to occur, high relative vapor pressures, as well as pore diameters on the order of molecular dimensions, are required [*Bartell and Donahue*, 1952; *Miyahara et al.*, 1997]. In the current system, the relative vapor pressures used for decane, which were the highest of all compounds, were extremely low ($\sim 0.10\%$). It is highly unlikely that CPS could occur under such conditions and, thus, it appears reasonable to exclude CPS in the analysis.

4.3. Comparison With Literature Data

[44] Kim et al. [1999] used decane as an interfacial tracer to measure air-water interfacial areas at several water contents. The reported retardation factors were all less than 2 for water contents ranging between 5% and 17%. Although this represents a similar water content range as examined in the current research, the retardation factors reported by Kim et al. are significantly lower than those reported here (see Table 6). The discrepancy in retardation factors may be readily explained by the large difference in specific surface areas of the porous media used in the two studies. Kim et al. report a nitrogen/BET-measured surface area of 1200 cm²·g⁻¹, while the specific surface area of the porous medium used herein is 35,400 cm²·g⁻¹. Consistent with their lower surface area, Kim et al. report air-water interfacial areas of 80-1500 cm⁻¹, which are smaller than those reported here. Thus, the Kim et al. results appear both self-consistent and consistent with the data reported herein.

[45] To assess whether the gas-phase tracer method is sensitive to variations in porous medium surface area, as would be expected, the maximum interfacial areas (regardless of water content differences) reported in the literature and the current study are plotted against the N₂/BETmeasured surface areas (Figure 5). There is a clear positive correlation ($r^2 = 0.93$) between the maximum measured interfacial area and measured surface area. Thus, it appears that the gas-phase tracer method is sensitive to the impact of surface-area variations on the magnitude of the associated air-water interfacial areas.



Figure 6. Measured surface-area-normalized air-water interfacial areas versus water content for data obtained using the gas-phase interfacial tracer method. Measured surface areas obtained using the N_2 /BET method.

[46] In order to account for differences in surface area of the porous media used for experiments reported in the literature, interfacial areas obtained using the gas-phase interfacial tracer method are normalized by measured surface areas and plotted against water content (Figure 6). There is considerable variation among the studies presented, possibly due to differences in water-retention properties of the various media examined or the impact of additional forms of retention (e.g., solid-phase sorption and sorption to system hardware) that were explicitly accounted for in the current study. However, all studies show the same general trend with respect to water content, and the results of the current research appear to be generally consistent with the literature data.

[47] Aside from the gas-phase tracer method, the remaining methods for measuring interfacial are aqueous-phase, surfactant-based methods. The surfactant studies generally report smooth-sphere calculated surface areas, rather than N₂/BET-measured surface areas. Therefore, in order to compare the current data to literature data derived from the surfactant methods, the Vinton sand smooth-sphere surface area must be used (160 cm⁻¹). Figure 7 compares maximum reported interfacial areas versus calculated surface areas for the current research and all literature data (gas and aqueous-phase) for which calculated surface areas were available. Open squares in Figure 7 represent data derived from gas-phase studies, while aqueous-phase data are represented by the filled squares.

[48] Gas-phase tracer-derived interfacial areas are observed to be consistently larger than aqueous-based values for similar calculated surface areas. *Kim et al.* [1999] noted that the gaseous and aqueous tracer methods may probe different physical domains within a porous medium, due to limitations in hydrodynamic access of the aqueous-based surfactant tracers. It is further hypothesized here that this difference in domain access may account for the much larger interfacial areas measured by the gaseous tracers. Specifically, it is hypothesized that the gas-phase tracers are able to access interfacial area formed by adsorbed-water films, whereas access to this domain is most likely constrained for the advective-surfactant methods due to the immobile nature of water in these domains. This would lead to larger gas-phase measured interfacial areas if adsorbedwater contributions to total interfacial area are significant. The current data adds to the mounting evidence that interfacial areas measured using gas-phase interfacial tracers are generally higher than those measured using aqueousphase methods.

[49] To examine the aqueous-surfactant data in greater detail, it is useful to plot the calculated surface areanormalized interfacial areas versus water content for the surfactant methods (Figure 8). The filled squares represent data reported by Schaefer et al. [2000], obtained using an aqueous-phase surfactant method based on diffusive rather than advective transport. The remaining aqueous-phase surfactant methods (e.g., aqueous tracer, surfactant mass balance, and surfactant-induced water mobilization) rely on advective processes and are represented by the open squares. It is clear that the diffusion method yields larger normalized interfacial areas than the advective methods. This behavior suggests that the diffusion-based method may have greater access to nonadvective interfacial domains relative to the advective-based methods. Non-advective interfacial domains would include relatively immobile water films formed by water adsorption on solid surfaces. While the surfactants transported advectively may only access a small fraction of the water-film interfacial domain, surfactant molecules may be able to diffusively access some portion of this domain, thereby measuring a larger fraction of the air-water interface bounding these films.

[50] Based on the previous discussions, it appears possible that differences in interfacial accessibility may explain the differences in air-water interfacial areas obtained from the gas-phase versus aqueous-phase methods, as well as the differences between aqueous-advective and aqueous-diffusive methods. Thus, it is useful to compare in a single figure interfacial areas obtained using all three methods. Figure 9 shows surface area-normalized interfacial areas versus water



Figure 7. Maximum air-water interfacial areas versus calculated porous-medium surface areas for the current and literature data. Open squares represent data from gas-phase studies [*Enright*, 1998; *Kim et al.*, 1999; this study], while filled squares represent data from aqueous-phase surfactant studies [*Kim et al.*, 1997; *Saripalli et al.*, 1997; *Silverstein and Fort*, 1997; *Kim et al.*, 1998; *Anwar et al.*, 2000; *Schaefer et al.*, 2000]. Inset shows aqueous-phase data alone. Calculated surface areas based on "smooth-sphere" assumption.

content for studies representing all three interfacial area measurement methods, wherein the N_2 /BET-measured surface areas are used for normalization. At the highest water contents, all three methods appear to be trending toward similar normalized interfacial areas. At higher water con-

tents, capillary-phase water is thought to contribute significantly to the total air-water interfacial area. Convergence of the three methods may indicate relatively equal access of the gas-phase tracers and aqueous-surfactant tracers to airwater interfaces formed by capillary water.



Figure 8. Calculated surface-area-normalized air-water interfacial areas versus water content for literature data obtained using aqueous-phase methods. Aqueous-diffusive data are adapted from *Schaefer et al.* [2000]; aqueous-advective data are adapted from *Kim et al.* [1997], *Saripalli et al.* [1997], *Silverstein and Fort* [1997], *Kim et al.* [1998], and *Anwar et al.* [2000]. Calculated surface areas based on "smooth-sphere" assumption.



Figure 9. Measured surface-area-normalized air-water interfacial areas versus water content for all three types of measurement methods. The gas-phase tracer method is represented by the current data, *Silva* [1997], and *Kim et al.* [1999]. Aqueous-phase advective and diffusive methods are represented by *Kim et al.* [1997] and *Schaefer et al.* [2000], respectively. Measured surface areas obtained using the N₂/BET method.

[51] At intermediate water contents, however, the differences increase among the three methods. This divergence increases significantly at the lowest water contents, where the gas-phase method measures significantly larger normalized interfacial areas. In this same region, the surfactant diffusion method maintains a linear trend in interfacial areas. Kim et al. [1997] do not report interfacial areas for the low water content region; however, because the Kim et al. data fit well within the larger data set of all advectivesurfactant methods (see Figure 8), it may be assumed that the Kim et al. aqueous-surfactant data would also maintain a linear trend in the low water contents region. The linearity of the interfacial-area/water-content function for the aqueous-based methods results in much smaller measured interfacial areas compared to the gas-phase method for the lowest water-content region. Because adsorbed water is expected to contribute most significantly to the formation of air-water interfaces at low water contents, these results may indicate that the surfactant methods cannot measure the entire adsorbed-water interfacial domain.

[52] In summary, these data suggest the gas-phase method provides the largest measured air-water interfacial areas, consistent with the hypothesis that they can access much of the interfacial area associated with adsorbed water, as well as the interfacial area associated with the capillary-phase domain. In comparison, the aqueous-surfactant methods clearly measure smaller interfacial areas, consistent with the hypothesis that they access a smaller fraction of the total air-water interface, most likely because of limited access to interfaces formed by adsorbed water.

4.4. Evaluation of Proposed Interfacial Domains

[53] The hypothesis that the gas-phase interfacial tracer method and the aqueous-phase, surfactant-based methods probe different physical interfacial domains has been discussed above. Two process-linked interfacial domains were discussed, specifically air-water interfaces associated with adsorbed water, and interfaces associated with capillaryphase water. In order to assess the robustness of this hypothesis in relation to experimental data, it is useful to define "functional" interfacial domains. It is proposed that the following functional domains may contribute to the total air-water interface in unsaturated porous medium systems: (1) air-water interfaces contained within unsaturated intraparticle porosity; (2) air-water interfaces bounding advective-gas pathways; (3) air-water interfaces bounding advective-water pathways; (4) isolated air-water interfaces (i.e., inaccessible to advective gas and water). The relative contribution of these four functional domains to the total air-water interfacial area would likely be a function of the porous-medium texture, the fluid-phase distributions, and the saturation history.

[54] Domain 1 is unlikely to contribute significantly to total interfacial area, except at extremely low water contents, due to water filling of small intraparticle pores via capillary forces. For example, for the Vinton sand used herein, the intraparticle porosity was measured via nitrogen adsorption to be 0.00958 cm³·g⁻¹ (Table 3), which corresponds to approximately 7.5 cm³ of intraparticle volume for a packed column. For the lowest water-content experiment conducted (1.9% θ_W), a total of 8.7 cm³ of water was present in the column. If it is assumed that all the intraparticle porosity is water-filled, the remaining 1.2 cm³ of water would be sufficient to solvate the external surface area of the particles to the equivalent of approximately 8 monolayers of water. Thus, even at very low water contents, there is sufficient water present to saturate the intraparticle porosity and satisfy the favorable energetics of adsorption to dry mineral surfaces.

[55] Assuming that the intraparticle porosity is, indeed, water-filled, the surface area associated with this domain would be unable to contribute to interfacial area. Therefore,



Figure 10. Measured air-water interfacial areas versus water content for gas- and aqueous-phase methods. Adapted from *Kim et al.* [1997, 1999].

it may be more appropriate to use only the external fraction of the total surface area as a point of comparison for interfacial areas. However, even this comparison is not perfect, since the menisci of filled intraparticle pores will also contribute to "external" interfacial area, rendering the external surface area a low estimate of expected maximum external interfacial area. In the Vinton soil, the internal and external surface areas are 47,827 and 11,999 cm^{-1} , respectively (Table 3), compared to the maximum measured interfacial area of 19,500 cm^{-1} . The measured interfacial area is closer to, but larger than the external surface area. It is unlikely that the additional 7500 cm^{-1} of interfacial area is contributed solely by the menisci of filled intraparticle pores. Thus, it remains possible that partially filled intraparticle pores may also be contributing to interfacial areas. However, based on the amount of water present and on the significantly smaller interfacial areas compared to internal surface area, it will be assumed in the following analysis that Domain 1 does not contribute significantly to interfacial area in the current system.

[56] In general, the potential contribution of domain 4 (isolated air-water interface) to total interfacial area may be difficult to evaluate. Oostrom et al. [2001] examined this functional domain in an analogous saturated system, where NAPL served as the nonwetting fluid rather than air. Their modeling results indicated that there may be systems in which this domain is significant. Due to its isolation from both aqueous and gaseous advective flow, it is possible that the currently proposed interfacial area measurement methods may not measure all of the interfacial area associated with this domain. However, the following analysis is restricted to comparison of just the advective gas- and aqueous-phase methods and neglects Domain 4 as a significant contributor to interfacial area. This assumption appears reasonable for the data discussed herein given that they were obtained using relatively ideal (e.g., homogeneous) systems.

[57] Based on the assumptions discussed above, domains 2 and 3 remain as the major sources of differences between the advective gas- and aqueous-phase interfacial area measurement methods. As discussed above, it is likely that domain 2 is dominated by adsorbed-water contributions to interfacial area. However, it is also quite likely that at the lower water contents, where interfacial areas become significant, tracers transported in the gas-phase will also have relatively unhindered access to interfaces formed by capillary water. Domain 3 is likely dominated by capillary-phase water contributions to interfacial area, which is supported by the general observation that models that do not include adsorbed-water contributions to interfacial area yield values of comparable magnitude to the interfacial areas measured with the aqueous-phase methods (see Tables 1 and 2). Moreover, adsorbed water-associated interface would be less readily accessed by aqueous-phase tracers at the low water contents of interest, due to discontinuity of the aqueous phase. Therefore, in the current analysis, it will be assumed that Domain 3 is comprised solely of capillary water air-water interfaces, while Domain 2 includes both capillary- and adsorbed water interfaces.

[58] Given the assumptions above, the interfacial area results reported by Kim et al. [1997, 1999] for gas- and aqueous-phase methods, respectively, can be analyzed to arrive at a first-order approximation of the relative contributions of the two domains to total air-water interfacial area. Clear differences were observed between the results of the two methods when applied to the same porous medium, as shown in Figure 10. Kim et al. [1999] discussed the differences between the results of the gas- and aqueous-phase measurement methods and suggested interfacial mobility, caused by a surfactant-induced decrease in surface tension inherent to the aqueous-tracer method, as the cause of the difference. Specifically, interfacial areas measured using the aqueous-phase method were hypothesized to be erroneously small due to nonzero velocities of surfactant molecules retained at the air-water interface. Although the surfactantinduced surface tension decrease may be significant and may influence surfactant transport behavior, the results of the studies discussed above suggest that this factor is unlikely to be the only source of the differences in interfacial areas measured by the two methods. For example, the aqueous-diffusion based method proposed by Schaefer et al. [2000] is presumably immune to the potential interfacialmobility problems associated with the aqueous-advection methods. As noted above, the interfacial areas obtained



Figure 11. Estimated thin-film (adsorbed water) and pendular-ring (capillary water) contributions to interfacial area.

using the diffusion-based aqueous-surfactant method were larger than interfacial areas obtained using the advectivebased aqueous-surfactant methods. Thus, the impact of interfacial mobility on interfacial areas measured using the advective-based methods provides an alternative explanation for the observation that the diffusive-based method vields higher normalized interfacial areas than the advective-based methods. However, the differences in the two sets of measured interfacial areas are relatively small (see Figure 8). Furthermore, the interfacial areas obtained with the gas-phase method are significantly larger than the areas obtained with either aqueous-phase method at the lowest water contents. These results suggest that the majority of the differences between maximum interfacial areas measured by gas- and aqueous-phase methods are due to differences in interfacial domain accessibility.

[59] The interfacial areas obtained using the aqueousphase method were described by a linear equation, converted here from units of water saturation to water content [*Kim et al.*, 1997]:

$$A_{\rm IA} \ ({\rm cm}^{-1}) = -170.03\theta_W + 63.524 \ {\rm r}^2 = 0.972$$
 (9)

Extrapolation of the regression over the water content range examined using the gaseous tracer allows a first-order estimate of capillary-water contributions to interfacial area, while the difference between the gas- and aqueous-phase experiments yields an estimate of the adsorbed-water contributions. Linear extrapolation of the aqueous-phase data to lower water contents is supported by the linearity in results of all other aqueous surfactant-based methods (see Figure 8). Calculated in this manner, the relative contributions of the two types of air-water interface are plotted against water content in Figure 11.

[60] At the lowest water contents, adsorbed water is estimated to contribute more than 90% of the interfacial area measured by the gas-phase tracer. This decreases to approximately 50% at the highest water content for which gas-phase data were available ($\sim 22\% \theta_W$). These results are relatively consistent with model-simulation results pre-

sented by *Or and Tuller* [1999] for a sand system, wherein they predict that adsorbed-water contributions overwhelm capillary-contributions at all water contents. Specifically, adsorbed water is predicted to contribute no less than 95% of the total interfacial area at water contents ranging from zero to 35%. While differences in porous-media properties used in the two studies may account for the differences in relative contributions, it is clear that both studies indicate that adsorbed-water films contribute significantly to total air-water interfacial area.

5. Conclusions

[61] Decane was observed to demonstrate relatively ideal interfacial tracer properties, including that its dominant retention mechanism was adsorption at the air-water interface. The interfacial areas measured using decane displayed the expected trend of decreasing interfacial area with increasing water content. The maximum estimated interfacial area of 19,500 cm⁻¹ appears reasonable in that it is smaller than the measured total specific surface area of the medium, and is in the same range as the measured external surface area.

[62] Comparison of the measured data presented herein with literature data provided further insight into the characterization of the air-water interface in unsaturated porous media. Specifically, comparison of gas- and aqueous-phase data indicates that the gas-phase method generally yields larger interfacial areas than do the aqueous-phase methods, even when accounting for differences in water content and physical properties of the porous media. The observations are consistent with proposed differences in interfacial accessibility of the aqueous- and gas-phase tracers. Evaluation of the data in light of functional interfacial domains leads to the hypothesis that aqueous interfacial tracers measure primarily air-water interfaces formed by "capillary water" (Domain 3), while gas-phase tracers measure air-water interfaces formed by both capillary and adsorbed water (Domain 2). The data further indicate that Domain 2 may comprise a larger fraction of the total air-water interfacial area for

systems examined here. A deeper understanding of the functional interfacial domains and their link to existing interfacial area methods will serve to improve the methods and the interpretation of their results.

[63] The surfactant- and gaseous tracer methods appear complimentary, in that the two are most readily applied to 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. In addition, the gas- and aqueous-phase methods may each provide interfacial area information that is more relevant to specific problems of interest. For example, gas-phase interfacial area measurements may be most relevant to contaminant transport in unsaturated systems, where retention at the air-water interface may be significant. Conversely, the aqueous-phase methods may yield information with direct bearing on multiphase flow processes that are dominated by capillary-phase behavior.

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