Partitioning Tracer Tests for Characterizing Immiscible-Fluid Saturations and Interfacial Areas in the Vadose Zone

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ABSTRACT

Contaminant-transport analyses, risk assessments, and site remediations are all constrained by the complexity of the subsurface environment and by our insufficient knowledge of that environment. Most current subsurface characterization methods provide measurements for very small spatial domains, such that they are essentially point values. While such methods can provide accurate and precise data for small scales, their use for characterizing larger domains is generally constrained by sample-size limitations. Thus, methods that provide measurements at larger scales are being developed to complement the point-sampling methods. One such group of methods is based on the use of tracer tests. This review will cover "partitioning" tracer tests, which can be used to measure immiscible-liquid saturation of organic contaminants, soil water content, and fluid-fluid interfacial areas in subsurface systems. The conceptual basis and implementation of these methods will be briefly reviewed, with a focus on vadose zone applications.

Soil AND GROUNDWATER POLLUTION has become one of our most pervasive environmental problems, and remediating contaminated sites has proven to be a formidable challenge. Risk assessments, as well as remediation efforts, are often limited by the complexity of the subsurface environment and by our limited knowledge of that environment. As noted in a National Research Council report, advances in characterizing subsurface properties and processes are essential for improving subsurface assessments and enhancing the success of cleanup technologies (National Research Council, 1994).

The presence of immiscible organic liquids in the subsurface is often the single most important factor limiting remediation of sites contaminated by organic compounds (National Research Council, 1994). Unfortunately, because the distribution of immiscible liquids in the subsurface is complex and heterogeneous, the use of point-sampling methods for their characterization is often problematic. For example, the number of core samples required to accurately characterize the distribution of immiscible liquid in a relatively deep, very heterogeneous vadose zone may be cost prohibitive. In addition, coring is a destructive method, which precludes the ability to measure the identical volume of porous medium more than once.

The problems noted above have generated interest in the use of partitioning tracer tests for characterizing the occurrence, quantity, and distribution of immiscible organic liquids in subsurface systems. Partitioning tracer tests can also be used to measure soil water content and fluid–fluid interfacial areas. In this review, we focus on the conceptual basis and implementation of these tracer tests for vadose zone applications.

CHARACTERIZING IMMISCIBLE ORGANIC-LIQUID CONTAMINATION

Tracer tests have been used in the hydrology and petroleum engineering fields for many decades. The primary applications for these tracer tests have been to measure groundwater velocities and directions, permeabilities, porosities, and dispersivities. In the environmental field, the use of tracer tests has recently been expanded to a variety of new applications. One such application receiving significant attention is the use of partitioning tracer tests to characterize immiscible-liquid saturations of organic contaminants.

Theory

The partitioning tracer method is based on liquidliquid partitioning concepts, the theory for which was originally established in the chromatography field by Martin and Synge (1941). The conceptual and theoretical basis for describing the transport of tracers that partition to immobile, immiscible fluids has been presented in detail elsewhere (e.g., Bouchard et al., 1989; Brusseau, 1992; Jin et al., 1995). Characterizing immiscible-liquid saturation with a partitioning tracer test is typically accomplished by comparing the transport of a tracer that can partition into and out of immiscible liquid (partitioning tracer) to that of a nonreactive (nonpartitioning) tracer. Generally, immobile organic-fluid phases temporarily retain the partitioning tracer, which slows its transport with respect to that of the nonreactive tracer. Thus, retardation of the partitioning tracer indicates the possible presence of immiscible liquid within the zone through which the tracer pulse moved ("swept" zone). When other potential sources of tracer retention, such as sorption by the porous media, are negligible or have been accounted for, the magnitude of retardation of the partitioning tracer is representative of the amount of immiscible liquid present in the swept zone.

The procedure for estimating immiscible-liquid saturation using data collected with a partitioning tracer test involves calculation of a retardation factor (R) for the partitioning tracer, which can be done in a number of ways, as will be discussed below. The R value determined from the tracer test is equated to the mass-balance definition of R, given for aqueous-phase transport as:

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Abbreviations: SVE, soil vapor extraction.

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$$R = 1 + \frac{\rho_{\rm b} K_{\rm d}}{\theta_{\rm w}} + \frac{\theta_{\rm n} K_{\rm n}}{\theta_{\rm w}}$$
[1]

where K_n is the nonaqueous-phase liquid–water partition coefficient (-), K_d is the sorption coefficient (cm³ g^{-1}), ρ_b is bulk density of the porous medium (g cm⁻³), θ_n is volumetric immiscible-liquid content (-), and θ_w is volumetric water content (-). When there is negligible sorption of the tracer by the porous medium, $K_d = 0$ and:

$$R = 1 + \frac{S_{\rm n}K_{\rm n}}{(1 - S_{\rm n})}$$
[2]

where θ_n has been replaced by S_n , the immiscible-liquid saturation (volume of immiscible liquid per volume of pore space). Inspection of Eq. [2] shows that once values are obtained for K_n and R, determined from laboratory experiments and the tracer test, respectively, a value for S_n can be calculated:

$$S_{\rm n} = \frac{R-1}{(R-1) + K_{\rm n}}$$
[3]

It is critical to recognize that the saturation values obtained from partitioning tracer tests are "large-scale" values, representing an integration of saturations distributed throughout the swept volume. The magnitude of the observed retardation, and thus the calculated immiscible-liquid saturation, is a function of the volume of immiscible liquid in the zone interrogated by the tracer test. The scale of measurement corresponds to the size of the swept zone, which is generally controlled by the placement of the injection and observation points. Thus, the tracer method provides a measure of immiscible-liquid saturation at scales larger than the traditional, point-sampling methods. By sampling a much larger volume of the subsurface compared with that sampled with individual cores or monitoring wells, the partitioning tracer method generally has a greater opportunity of encountering immiscible liquid and thus detecting its presence. This enhanced detection potential is a major advantage of the method. Other advantages of the method include no significant limits to the depth of application and the ability to tailor the scale of measurement to the objectives of the study.

The use of partitioning tracer tests to measure immiscible organic-liquid saturation in the subsurface was developed in the petroleum industry during the 1970s as a means to determine residual oil saturation in oil fields (Cooke, 1971; Deans, 1971). Since then, numerous partitioning tracer tests have been conducted for this purpose, as reviewed by Tang (1995). The use of the partitioning tracer method for measuring immiscible-liquid contamination in environmental systems was initially demonstrated in the laboratory by Jin et al. (1995) and Wilson and Mackay (1995). Both groups of investigators showed that partitioning tracer tests provided accurate estimates of the volume of chlorinated solvents emplaced in sand-packed columns. Several pilot-scale partitioning tracer tests have been conducted in studies to evaluate innovative subsurface remediation technologies (e.g., Rao et al., 1997; Annable et al., 1998a; Jawitz et al., 1998; McCray and Brusseau, 1998; Blanford et al., 1999; Brown et al., 1999; Falta et al., 1999a, 1999b; Cain et al., 2000; Meinardus et al., 2002). The first full-scale field application of the partitioning tracer method for characterizing immiscible-liquid contamination was conducted at a Superfund site in Tucson, AZ (Nelson and Brusseau, 1996).

Gas-Phase Partitioning Tracer Tests for Vadose Zone Characterization

The applications referenced above involved tracer tests conducted in water-saturated systems using aqueous-phase tracer solutions, which has been the primary mode of application. A similar approach could also be used to measure immiscible-liquid saturation in the vadose zone. However, a more practical approach would be to conduct gas-phase partitioning tracer tests. The major difference between gas- and aqueous-phase tracer tests is the selection of the tracers to reflect the gas phase as the mobile fluid. For this case, the retardation factor, assuming retention only by the immiscible liquid, is defined as:

$$R = 1 + \frac{S_{\rm n}K_{\rm ng}}{(1 - S_{\rm n} - S_{\rm w})}$$
[4]

where K_{ng} is the immiscible-liquid–gas partition coefficient (-) and S_w is water saturation (-). The use of gasphase partitioning tracer tests to determine residual oil saturation in gas-saturated petroleum reservoirs was introduced by Tang and Harker (1991). More recently, the use of gas-phase partitioning tracer tests to measure immiscible-liquid contamination in water-unsaturated systems has been examined in the laboratory (Whitley et al., 1999) and in the field (Mariner et al., 1999; Deeds et al., 1999; Simon et al., 1998; Brusseau et al., 2003).

The first gas-phase vadose zone partitioning tracer test was conducted by Mariner et al. (1999) at a chlorinated-solvent contaminated site in New Mexico. The test was conducted in a region located beneath two solvent disposal trenches to estimate the amount of immiscible liquid trapped within the vadose zone. This information was used to help plan and evaluate remedial activities for the site. A gas-phase vadose zone partitioning tracer test was conducted for similar purposes at a chlorinated solvent–contaminated Superfund site in Tucson, AZ (Simon et al., 1998). No comparison was made of the partitioning tracer results to independent measures of immiscible-liquid contamination for either study.

Such a comparison was reported by Deeds et al. (1999), who conducted gas-phase partitioning tracer tests in the vadose zone of a fuel-contaminated site at Kirtland Air Force Base in New Mexico. The tests, using methane as the nonreactive tracer and four perfluorocarbons as partitioning tracers, were conducted before and after a pilot-scale demonstration of radio frequency–enhanced soil vapor extraction. Based on the results of the tracer tests, the mass of contaminant removed, measured as total petroleum hydrocarbons, was estimated to be 63% of the initial mass. This value is similar to the massremoved value of 52% determined by analysis of core samples collected before and after the demonstration test, indicating the tracer method provided a reasonable measure of immiscible liquid volume.

Gas-phase partitioning tracer tests were conducted at a fuel depot in Tucson, AZ to evaluate the utility of the partitioning tracer method for characterizing organic immiscible-liquid contamination in the vadose zone (Brusseau et al., 2003). One test, using sulfur hexafluoride as the nonreactive tracer and bromochlorodifluoromethane as the partitioning tracer, was conducted after 30 mo of operation of a soil vapor extraction (SVE) system within the boundaries of an existing fuel dispensing island and former underground fuel tank facility. Analysis of hydrocarbon concentrations in the SVE effluent indicates that approximately 355 000 L of hydrocarbons were recovered during the 30-mo operation period. Comparing this value to the initial volume of hydrocarbons present, estimated to be approximately 454 000 L based on core data, produces an estimate of 99 000 L of hydrocarbons remaining within the area influenced by the SVE system. Extrapolation of the tracer test results to the SVE-impacted zone produces an estimate of 107 000 L of hydrocarbon present. The two values are similar, again suggesting the tracer method provided a reasonable measure of immiscible liquid volume.

MEASURING SOIL WATER CONTENT

Characterizing soil water content is important to many activities, including those associated with agriculture, forestry, hydrology, and engineering. For example, knowledge of soil water content is especially important for management of agricultural resources and for flood control. It is also central to describing water flow and contaminant transport in the vadose zone. There are several methods with which to measure soil water content, such as neutron thermalization, time domain reflectometry, and gravimetric analysis of core samples. These methods have a history of successful use. However, the majority of methods in current use provide point values of soil water content (i.e., small sample volumes). While this is an advantage for obtaining accurate information at small scales, it is a disadvantage for determining soil water contents for larger (field) scales. The partitioningtracer concept can be applied in this situation to develop a larger-scale method for measuring soil water content, as discussed by Brusseau et al. (1997).

Theory

In this case, gas-phase tracer tests are conducted using a tracer that remains in the gas phase (nonreactive tracer) and one that partitions to water. The retardation factor for gas-phase transport of a tracer that is retained solely by water can be written as:

$$R = 1 + \frac{\theta_{\rm w}}{\theta_{\rm g} K_{\rm h}} = 1 + \frac{S_{\rm w}}{(1 - S_{\rm w}) K_{\rm h}}$$
[5]

where K_h is the gas–water partition coefficient (nondimensional Henry's Law coefficient) and θ_g is volumetric gas porosity.

Inspection of Eq. [5] shows that once a value for R is obtained from a partitioning tracer test, a value for θ_w can be determined when K_h and θ_g are known. Furthermore, S_w can be determined without knowledge of θ_g . Values for K_h are generally available in the literature and can also be measured in the laboratory. As described above for immiscible-liquid saturation, the soil water content measurements obtained with the partitioning tracer method are large-scale values, representing an integration of the soil water contents distributed within the tracer-swept zone.

Previous Applications

The application of gas-phase partitioning tracer tests for measuring soil water contents has been recently evaluated for both laboratory and intermediate-scale systems. Brusseau et al. (1997) conducted column experiments using He as the nonreactive tracer and CO₂ as the water-partitioning tracer. The transport of CO₂ was retarded compared with that of He because of the retention of CO_2 by the immobile water phase. The soil water content determined from the retardation of CO_2 was 0.14, which is relatively close to the gravimetrically measured value of 0.16. Kim et al. (1999a) conducted column experiments using methylene chloride and chloroform as water-partitioning tracers. They found good correspondence between the tracer-derived soil water contents and the gravimetrically measured values for a range of soil water contents.

The water-partitioning tracer method has been tested at the intermediate scale with a series of experiments conducted in a large (4.0 m deep, 2.5-m diameter) weighing lysimeter (Nelson et al., 1999a; Carlson et al., 2003). The lysimeter contains a homogeneous packing of fine sand, and is instrumented with multiple devices with which to measure soil water content. Experiments were conducted at three soil water contents using SF_6 as the nonreactive tracer and various halogenated methanes as water-partitioning tracers. For the first set of tests, soil water contents of 0.04, 0.06, and 0.06 were estimated using the tracer data collected at the effluent sampling location with bromochlorodifluoromethane, dibromodifluoromethane, and trichlorofluoromethane, respectively, as the water-partitioning tracers. The latter two values were identical to independently measured values of soil water content obtained using gravimetric analysis of core samples and time domain reflectometry. For the second set of tests, a soil water content of 0.12 was estimated using the tracer data collected at the effluent sampling location with trichlorofluoromethane as the water-partitioning tracer. This value is 80% of the independently measured values obtained using time domain reflectometry (0.15), neutron scattering (0.15), and conversion of soil-tension data (0.15). For the third set of tests, a soil water content of 0.07 was estimated using the tracer data collected at the effluent sampling location with difluoromethane as the partitioning tracer. This value is identical to the independently measured values obtained using time domain reflectometry, neutron scattering, and conversion of soil-tension data.

Water-partitioning tracer tests have been conducted at the field scale, in association with gas-phase partitioning tracer tests designed to characterize immiscibleliquid contamination in vadose zone systems (Mariner et al., 1999; Deeds et al., 1999; Simon et al., 1998). However, the soil water contents obtained in these tests were not compared to independently measured values. The first field-scale application of the water-partitioning tracer method wherein the results were compared with independent measures of soil water content was recently conducted by Keller and Brusseau (unpublished data, 2003). The tracer tests were conducted before and after a controlled infiltration event. An injection-extraction well couplet spaced 7.3 m apart was used to conduct the tests, using SF₆ and difluoromethane as the nonreactive and water-partitioning tracers, respectively. The soil water content estimated from the tracer test conducted before the infiltration event is 0.086, which is identical to the mean of the values measured using gravimetric analysis of core samples, neutron scattering, and borehole ground-penetrating radar. The soil water content estimated from the tracer test conducted after the infiltration event is 0.10, which is 83% of the mean of the independently measured values.

Interestingly, the results obtained from the field tests are similar to those obtained from the lysimeter experiments. The soil water contents obtained from the partitioning-tracer tests were identical to the independently measured values for the tests conducted at the lower soil water contents of 0.06 to 0.09. These water contents are equivalent to water saturations of approximately 13 and 23% for the lysimeter and field site, respectively. Conversely, the soil water contents derived from tracer tests were approximately 80% of the independently measured values for the tests conducted at the higher water contents, which are equivalent to water saturations of approximately 32%. The reduced efficacy at the highest water saturation may reflect the impact of advectivediffusive mass transfer constraints on gas-phase transport (Keller and Brusseau, unpublished data, 2003).

Generally, the results presented above suggest that the gas-phase partitioning tracer method holds promise as a means to measure soil water content at the field scale, especially for sites with moderate to low water contents. The method may be particularly appropriate for sites with extensive vadose zones, such as those found in arid and semiarid environments, for which the use of traditional methods would be cost prohibitive. Implementation of tracer tests in conjunction with a limited number of point-measurement devices may be a viable approach for applications requiring long-term monitoring of water contents, such as those associated with vadose zone waste disposal facilities. While the point-measurement devices serve as sentinels characterizing temporal changes in water content, the partitioning tracer test would provide information regarding total volumes of water present at any given time.

MEASURING FLUID-FLUID INTERFACIAL AREAS

The interfaces between immiscible organic liquid and water, between organic liquid and air, and between wa-

ter and air are of great significance for contaminant transport in the subsurface. The interfacial areas are, in part, reflections of the pore-scale distribution of the fluids in the porous medium. As such, knowledge of the interfacial areas could provide insight into the disposition (e.g., morphology) and movement of the fluids in the system. In addition, mass transfer across an interface is a function of the interfacial area. Thus, knowledge of the interfacial areas would provide greater understanding of mass-transfer phenomena, such as dissolution and evaporation of immiscible organic liquids. Fluid-fluid interfaces may also directly influence the retention behavior of volatile organic contaminants. For example, accumulation of organic contaminants at the air-water interface has been shown to influence their retention and transport behavior in unsaturated systems (e.g., Costanza and Brusseau, 2000).

The magnitude and disposition of fluid-fluid interfaces in porous media is clearly of great significance. Unfortunately, measuring interfacial areas in porous media has been problematic. A recent surge of interest in this topic, however, has led to several potentially viable approaches. Static and continuous flow-through column methods based on the use of surfactants have recently been proposed as a means to measure interfacial areas (Karkare and Fort, 1993; Anwar et al., 2000; Schaefer et al., 2000). In addition, experimental methods based on visualization techniques have been proposed (e.g., Montemagno and Gray, 1995). These methods have shown promise for estimating or measuring interfacial areas for simplified, well-controlled laboratory systems, which will enhance our ability to examine flow and transport processes. However, given the limitations inherent to these methods, it is unlikely that they can be used routinely for complex systems or for in situ applications. The interfacial "partitioning" tracer test is an alternative method that may be better suited for these latter applications.

Theory

It is well known that many organic compounds will tend to accumulate at the interface between two fluids. The accumulation of a surface-active compound at the interface of mobile and immobile fluids will retard its transport with respect to that of a non-surface-active compound (e.g., a nonreactive tracer residing in the mobile fluid) in a manner analogous to that of a bulkphase partitioning tracer. The magnitude of retardation of the surface-active compound will be a function of the interfacial partition coefficient and the interfacial area. Thus, it is possible to measure interfacial areas using an interfacial partitioning tracer test. Such an approach was recently proposed by Rao and colleagues (Saripalli et al., 1997; Kim et al., 1997), who used aqueous-phase tracers, and by Brusseau et al. (1997), who used gas-phase tracers.

The retardation factor is defined for this case as (neglecting sorption by porous media and partitioning to the bulk "immobile" fluid):

$$R = 1 + \frac{A_i K_i}{\theta_{w,g}}$$
[6]

where A_i is the specific area of the fluid–fluid interface $(cm^2 cm^{-3})$, $K_i (= \Gamma/C_{w,g})$ is the partition coefficient between the interface and water (w) or air (g) (cm), and Γ is surface excess (moles of surface-active compound at interface divided by the area of the interface). With knowledge of the interfacial partition coefficient and the soil water content or gas porosity, the interfacial area can be calculated. It should be noted that this value is an effective, global interfacial area, reflecting the influence of system properties (e.g., tracer behavior, fluid distribution) on the gross retention and transport of the interfacial tracer.

Previous Applications

The application of the aqueous-phase interfacial partitioning tracer method has recently been illustrated with several laboratory investigations conducted using sand-packed columns. Saripalli et al. (1997) used a surfactant (sodium dodecylbenzenesulfonate) as a tracer to measure interfacial areas for decane-water and airwater systems. Kim et al. (1997) used the same surfactant to measure air-water interfacial areas for several soil water contents. Saripalli et al. (1998) and Kim et al. (1999b) used two surfactants to measure interfacial areas between several organic immiscible liquids and water. Kim et al. (1998) used two alcohols to measure air-water interfacial areas. In all cases, the results of the experiments, which were conducted with water as the mobile phase, produced interfacial areas that were similar to those estimated using geometric and thermodynamic models. The aqueous-phase tracer method was recently applied in the field in a pilot-scale experiment conducted at Hill Air Force Base (Annable et al., 1998b). An interfacial partitioning tracer was used in conjunction with a bulk-phase partitioning tracer to examine the distribution of a multiple-component immiscible liquid within a 3 by 5 m encapsulated portion of aquifer. The results of these laboratory and field experiments indicate that the aqueous-phase interfacial partitioning tracer test holds promise for characterizing fluid-fluid interfacial areas in porous media.

Brusseau et al. (1997) used a gas-phase partitioning tracer method to measure air-water interfacial areas in unsaturated packed columns. They used the interfacial area determined from the partitioning tracer (heptane) test to successfully predict the retardation and transport of trichloroethene in the same system. This information was used to help evaluate the relative contributions of (solid-phase) sorption, retention in bulk water, and interfacial accumulation to retardation of volatile organic contaminants during gas-phase transport in unsaturated porous media. Kim et al. (1999a) used decane as a gas-phase interfacial partitioning tracer and observed increasing interfacial areas as soil water content decreased. In addition, the interfacial areas obtained with the gas-phase method were generally larger than those obtained using the aqueous-phase tracer method for the same porous medium.

Gas-phase tracer tests, using decane as an interfacial tracer, were conducted by Costanza-Robinson and Brusseau (2002) for a sand-packed column with soil water contents ranging from approximately 2 to 20%. The expected trend of decreasing interfacial areas with increasing water contents was observed, and the maximum estimated interfacial area of 19 500 cm⁻¹ was approximately one-third of the measured surface area of the porous medium (60 888 cm⁻¹). These results were integrated with literature data to provide further insight into the characterization of the air-water interface in unsaturated porous media. Specifically, comparison of interfacial areas measured using gas-phase vs. aqueous-phase methods indicates that the gas-phase method generally yields larger interfacial areas than do the aqueous-phase methods, even when accounting for differences in soil 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 yielded the hypothesis that aqueous interfacial tracers measure primarily airwater interfaces formed by capillary water, while gasphase tracers measure air-water interfaces formed by both capillary and surface-adsorbed (film) water (Costanza-Robinson and Brusseau, 2002). 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.

IMPLEMENTATION

The tracers to be used in a partitioning tracer test are selected to meet several criteria. The magnitude of retardation of the partitioning tracers is a key factor. The retardation should be large enough to be measurable with some level of certainty, but should be small enough such that the length of the test remains practical. The length of the test will depend on the size of the target domain and the planned flow rates, as well as the magnitude of retardation. The magnitude of retardation is a function of the immiscible-liquid saturation and the partition coefficient. If an approximate range of saturations expected to be encountered is known a priori, the partitioning tracers can be selected according to their partition coefficients to provide retardation factors within the desired range. If the immiscible-liquid saturation is unknown, it is useful to use multiple partitioning tracers spanning a range of partition coefficients, thus providing a range of potential retardation. The partitioning tracers, as well as the nonreactive tracers, should have low toxicity at the concentrations employed, be resistant to transformation processes, and have robust analytical properties (e.g., low detection limits, low background concentrations).

The partitioning tracer test is conducted similarly to nonreactive tracer tests. Partitioning tracer tests can be implemented in a number of ways, varying in the methods of injection, extraction, and sampling. The simplest configuration involves a single well, wherein the tracer pulse is first injected into and then extracted from the subsurface (push-pull test). Samples for analysis of tracer concentrations are collected at the well. Because of the reversible retention of the partitioning tracers used in a partitioning tracer test, the standard analysis approach based on tracer separation cannot be used for this system. Thus, a specialized approach must be used for single-well push-pull tests. The primary method used in the petroleum engineering field, as described by Deans (1971), involves the use of a partitioning tracer that hydrolyzes to a compound that has a different magnitude of immiscible-liquid partitioning. After the tracer pulse is pumped into the subsurface, the pulse is allowed to remain in the system for a period of time to allow transformation to occur (the so-called "shut-in" period). The pulse is then pumped back to the well, and samples are analyzed for concentrations of both the parent and product compounds. This method allows the two tracers to start at the same position within the subsurface, thus providing an opportunity for separation to occur during transport back to the recovery well. Use of this method for environmental applications has so far been constrained by a lack of suitable tracers. Recently, Istok et al., (2002) evaluated the use of single-well push-pull partitioning tracer tests wherein immiscible-liquid saturations are estimated based on differences in apparent dispersion of tracers with different magnitudes of retardation.

A variation of the single-well system is the borehole dissipation test. With this method, which, for example, has been used for gas-phase diffusive tracer tests, a small tracer pulse is injected into the well under naturalgradient conditions. Samples are then collected from the well to monitor the rate of decline in tracer concentration (dissipation), which will be influenced by the magnitude of retardation of each tracer. This approach has been used recently in laboratory and intermediatescale (lysimeter) gas-phase experiments to measure immiscible-liquid saturation in water-unsaturated systems (Werner and Hohener, 2002).

Another variation of the single-well approach involves the use of multiple well screens and vertical circulation (i.e., vertical-circulation well). The placement of two or more screened intervals within a single well allows one interval to be used for injection and one interval for extraction. A vertical dipole is created with this configuration, which produces vertically oriented flow. This system can be used to conduct single-well partitioning tracer tests, as demonstrated by Chen and Knox (1997) for a sand-tank system.

Another type of well configuration involves the use of a single pumping well and one or more non-pumping wells. One variation of this configuration involves a single extraction well and one or more nonpumping injection wells, where the injection wells are used to introduce the tracer pulse into the flow field created by the extraction well, which is used for sampling. Another variation of this configuration involves a single pumping injection well and one or more monitoring wells surrounding the injection well. Given the use of separate injection and extraction points, the standard analysis method based on the separation of tracers with different magnitudes of partitioning is suitable for either of these configurations.

The final general well configuration for tracer tests, the interwell tracer test, involves a combination of pumping injection and extraction wells. The use of this configuration was first proposed for the partitioning tracer method by Cooke (1971) and is the most common method for environmental applications. The well field for this approach may comprise a single injection– extraction well couplet, two or more injection and extraction wells configured in a line-drive system, or more complex variations.

The interwell method generally provides greater hydraulic or pneumatic control and measures larger areas. Conversely, tests based on single-well methods may be less expensive to conduct and provide more localized information. The method used at a given site will depend on the objectives and constraints associated with that site.

The use of monitoring wells is rarely addressed in the petroleum-reservoir applications of partitioning tracer tests. However, monitoring wells are a common feature at environmental field sites, and can be useful for partitioning tracer tests. For example, there is a limit to the sensitivity of the partitioning tracer method. The sensitivity depends in part on the ratio of immiscible-liquid volume to swept volume. The swept volume of an extraction well can be very large. Thus, a small, localized volume of immiscible liquid could have a very small impact on retardation as measured at an extraction well. This small signal could be lost in the noise typically associated with field experiments. Conversely, the swept volume for monitoring wells is significantly smaller. Thus, a relatively small, localized volume of immiscible liquid may be more accurately measured by analysis of monitoring well data. However, the larger swept zone associated with an extraction well provides a much larger zone of interrogation, which, as discussed above, is an advantage when using the partitioning tracer method to search for immiscible liquid. Thus, it is beneficial to use both monitoring and extraction wells for sampling.

As noted above, monitoring wells, given their smaller swept volumes, can be used to focus on specific sections of the total swept zone associated with the injection– extraction wells. This provides an opportunity to examine the areal spatial distribution of immiscible liquids. In addition, multilevel sampling devices or depth-specific monitoring wells can be used to examine the vertical distribution of immiscible liquids. Thus, the spatial distribution of organic-liquid contamination or of soil water can be characterized with partitioning tracer tests (e.g., Nelson and Brusseau, 1996; Sillan et al., 1998; Falta et al., 1999a; Meinardus et al., 2002).

The methods discussed above are based on the introduction of exogenous tracers into the subsurface. However, under certain conditions, resident compounds may also be used as partitioning tracers. This was illustrated by Hunkeler et al. (1997) in their application of a partitioning-tracer method to measure diesel-fuel saturation at a site in Switzerland. In their approach, the distribution of a naturally occurring radioactive isotope (²²²Rn) at the contaminated site was characterized, comparing concentrations in groundwater samples collected within the fuel-contaminated zone to values measured for samples collected up gradient of the contaminated zone. The differences in ²²²Rn concentrations, assumed to be due to partitioning of the ²²²Rn into the diesel fuel, were used as a basis to estimate an average diesel-fuel saturation for the site. This value (1.5%) is similar to the value of 1.9% obtained from analysis of a single core sample. The use of Rn to characterize immiscible-liquid contamination was also recently examined by Semprini et al. (2000) and Davis et al. (2002), the latter using a pushpull method combining an injected nonreactive tracer and the naturally occurring Rn.

The primary method of data analysis for a partitioning tracer test involves a comparative moment analysis of the breakthrough curves measured for the tracers. In this approach, the retardation factor is defined as the quotient of the mean travel times of the partitioning and nonreactive tracers. When multiple partitioning tracers are used, the travel-time analysis can be conducted using the various pairs of partitioning tracers, as well as the partitioning–nonreactive pairs (e.g., Jin et al., 1995). This approach can in some cases increase the robustness of the results.

Travel times or retardation factors can also be obtained by methods other than the use of moment analysis. For example, with the landmark method (e.g., Tang, 1995), calculation of travel times is based on comparing specific points of the respective breakthrough curves, such as times of first arrival, times of peak arrival, or times of selected magnitudes of mass recovery. Calibration of mathematical models to measured breakthrough curves can also be used to obtain retardation factors. The advantage of the moment method is that it may be less sensitive to nonideality factors (rate-limited mass transfer, heterogeneity effects) than the landmark method, and it is not dependent on a suite of assumptions as are modeling-based analyses. However, the moment method is susceptible to error, especially when breakthrough curves are incomplete, when mass-transfer constraints are significant, and, in some cases, when mass loss occurs. An example of a protocol for conducting partitioning tracer tests is presented by Jin et al. (1997). An analysis of uncertainty in estimated saturations due to errors associated with measurement of concentrations, partition coefficients, and retardation factors is presented by Dwarakanath et al. (1999) and Meinardus et al. (2002).

POTENTIAL CONSTRAINTS

The performance of a partitioning tracer test can potentially be constrained by several factors, such as ratelimited mass transfer, multiphase retention, variable distribution of immiscible liquid, subsurface heterogeneity (e.g., spatially variable hydraulic conductivity), and tracer mass loss. These factors can confound data collection and analysis, and in general can cause the partitioning tracer test to yield measurements that are less than the true values. Thus, it is critical to understand how these factors may influence the efficacy of the partitioning tracer method, and to elucidate the conditions under which they may be important.

Liquid–liquid (or gas–liquid) partitioning is generally treated as an instantaneous, linear, reversible process for partitioning tracer test applications. The degree to which mass transfer of a partitioning tracer will be rate limited during a tracer test will depend on the relative magnitudes of the characteristic times of mass transfer and advective transport. Mass transfer is influenced by the velocity of the mobile phase, fluid saturations, fluidfluid interfacial areas, and porous-media characteristics. The degree to which mass transfer of partitioning tracers may be rate limited, and the resultant potential impact on the efficacy of the partitioning tracer method, has not been rigorously evaluated for complex field systems. However, the fact that the saturations or volumes of immiscible liquid estimated from partitioning tracer tests have compared favorably to independent measures for the relatively few cases where they have been compared suggests that rate-limited mass transfer may not have had a significant impact on tracer-test performance for those cases. A more direct evaluation of mass transfer behavior can be obtained by analyzing partitioning tracer transport data with mathematical models that incorporate rate-limited mass transfer. Such an evaluation was recently done for field data reported by Cain et al. (2000), who conducted a series of pilot-scale partitioning tracer tests at Hill AFB in Utah. The results of the analysis, employing a model that explicitly incorporates ratelimited mass transfer of a partitioning tracer (Brusseau, 1992), indicate that mass transfer of the partitioning tracers could be treated as being essentially instantaneous for that tracer-test application (unpublished data).

As noted above, liquid–liquid and gas–liquid partitioning is usually assumed to be linear. This may be generally true for many of the systems encountered in environmental applications. However, it is possible that partitioning may be nonlinear in some cases. For example, a partitioning tracer could possibly exhibit nonideal behavior in the immiscible-liquid phase, depending on the latter's composition. In such cases, the magnitude of partitioning could be dependent on the tracer concentration (e.g., concentration-dependent activity coefficient) or the composition of the immiscible liquid, which may be spatially or temporally variable. The influence of nonlinear partitioning on the application of partitioning tracer tests is discussed by Wise (1999) and Wise et al. (1999).

The partition coefficient is generally treated as a temporally and spatially constant parameter; however, this may not be the case for some situations. The magnitude of the partition coefficient is determined by the physicochemical properties of the tracer and the immiscible liquid. Thus, for a given tracer, the partition coefficient is a function of the composition of the immiscible liquid. This composition may vary as a function of space and time due to a number of factors. Hence, partition coefficient values may be spatially and temporally variable. For example, the magnitude of the partition coefficient was shown to change after a multiple-component immiscible liquid was flushed several times with a solubilization-enhancing agent (Lee et al., 1999) and after the application of soil venting (Deeds et al., 1999). This behavior should be considered in the application of partitioning tracer tests, especially for mixed-waste systems.

The partitioning tracer method is usually employed assuming that the retardation of the selected partitioning tracer is due only to retention by the target phase. However, if the partitioning tracer is in fact retained by one or more additional phases (e.g., sorption by aquifer solids), and if this additional retention is not accounted for, the partitioning tracer test may yield erroneously large measurements. The potential for multiphase retention may be difficult to evaluate for some complex systems.

The potential impact of the partitioning tracer test on the disposition of the target phase should be considered when designing a test and when analyzing its results. Under certain conditions, a partitioning tracer test could cause a change in the mass, morphology, or distribution of the target phase, such that the measured system is not fully reflective of the original, natural state. For example, this can be a concern for tests conducted at sites contaminated by immiscible liquids that have relatively high aqueous solubilities or vapor pressures, such that an appreciable amount of contamination is solubilized or evaporated during the test. The dissolution or evaporation associated with a tracer test may cause a change in the composition of multiple-component immiscible liquids. The potential impact of tracer tests on system properties may be of special concern for the application of interfacial tracers, which, because of surface accumulation, could possibly decrease interfacial tensions sufficiently to alter fluid distributions.

Tracer recovery can be influenced by transformation processes, such as biodegradation and abiotic reactions. Differential degradation of the tracer suite can influence the measurement and calculation of immiscible-liquid saturation (Annable et al., 1998a; Cain et al., 2000). This is of special significance given that alcohols, which are generally prone to biodegradation, have been the most widely used partitioning tracers to date for aqueousphase tracer tests. Recovery of the tracer can also be influenced by hydraulic- or pneumatic-related factors, such as failure to capture all injection-well flow lines. While the impact of such factors on tracer recovery should be considered, one purpose of using a nonreactive tracer is to attempt to account for the impact of such factors.

The performance of a partitioning tracer test can potentially be influenced by heterogeneity-related factors. For example, immiscible-liquid distribution at most sites is expected to be spatially nonuniform, with zones of residual immiscible-liquid saturation adjacent to zones free of immiscible liquid, along with the possible occurrence of pockets of higher immiscible-liquid saturation (e.g., pools). In such cases, the advecting fluid may flow

primarily around (bypass) the zones of high immiscibleliquid saturation due to the reduced relative permeabilities associated with these zones. Such bypass flow may limit the contact of the tracer pulse to the periphery of the immiscible-liquid zone, thereby resulting in an underestimation of immiscible-liquid volume under certain conditions. Porous-media heterogeneity (e.g., spatially variable permeability) may also constrain the effectiveness of partitioning-tracer tests. For example, immiscible liquids present in lower-permeability zones within or adjacent to higher-permeability zones may not be fully measured due to the preferential flow that occurs in such systems. The effectiveness of partitioning tracer tests under such conditions will depend on specific site properties (e.g., degree of heterogeneity, immiscible-liquid distribution) and conditions of the test (e.g., tracer selection, input pulse size, well-field configuration) (e.g., Nelson et al., 1999b; Meinardus et al., 2002).

SUMMARY

The partitioning tracer methods discussed here provide measurements at a scale that is larger than that associated with point-measurement methods. This is an advantage for economical characterization of relatively large areas. In addition, the scale of measurement can be tailored to the sampling objectives by modifying the tracer sampling network (e.g., distances between wells). The tracer methods can therefore serve to complement the point-sampling methods currently available.

The partitioning tracer methods have been tested at laboratory and intermediate (pilot) scales. In addition, a few full-scale field tests have been conducted. The results of these tests indicate the partitioning tracer method can provide robust information that is extremely useful for site characterization and remediation performance assessment. While these methods have great promise, it is clear that their performance is potentially influenced by various factors. Thus, additional research, especially at the field scale, is needed to more fully evaluate the efficacy of these methods under a wide range of potentially limiting conditions.

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