Field-Scale Sulfur Hexafluoride Tracer Experiment to Understand Long Distance Gas Transport in the Deep Unsaturated Zone

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A natural gradient SF$_6$ tracer experiment provided an unprecedented evaluation of long distance gas transport in the deep unsaturated zone (UZ) under controlled (known) conditions. The field-scale gas tracer test in the 110-m-thick UZ was conducted at the U.S. Geological Survey’s Amargosa Desert Research Site (ADRS) in southwestern Nevada. A history of anomalous (theoretically unexpected) contaminant gas transport observed at the ADRS, next to the first commercial low-level radioactive waste disposal facility in the United States, provided motivation for the SF$_6$ tracer study. Tracer was injected into a deep UZ borehole at depths of 15 and 48 m, and plume migration was observed in a monitoring borehole 9 m away at various depths (0.5–109 m) over the course of 1 yr. Tracer results yielded useful information about gas transport as applicable to the spatial scales of interest for off-site contaminant transport in arid unsaturated zones. Modeling gas diffusion with standard empirical expressions reasonably explained SF$_6$ plume migration, but tended to underpredict peak concentrations for the field-scale experiment given previously determined porosity information. Despite some discrepancies between observations and model results, rapid SF$_6$ gas transport commensurate with previous contaminant migration was not observed. The results provide ancillary support for the concept that apparent anomalies in historic transport behavior at the ADRS are the result of factors other than nonreactive gas transport properties or processes currently in effect in the undisturbed UZ.

Abbreviations: ADRS, Amargosa Desert Research Site; FEHM, Finite Element Heat and Mass Transfer code; LLRW, low-level radioactive waste; MQI, Millington–Quirk I; MQII, Millington–Quirk II; UZ, unsaturated zone.

Gas diffusion is often considered to be the main mechanism of gas-species transport in natural-gradient arid unsaturated zones (Thibodeaux, 1981; Weeks et al., 1982; Costanza-Robinson and Brusseau, 2006). Characterization of gas diffusion depends on the diffusive and reactive properties of gas-phase constituents, which are typically well established, and the physical characteristics of the soil (Jin and Jury, 1996). The porous medium characteristics together with the free-air diffusion coefficient define the effective diffusion coefficient ($D_{eff}$), which is utilized to mathematically describe spreading along a concentration gradient over time (Webb, 2006). Sound estimates of $D_{eff}$ are important for many waste site management applications that utilize predictive models, including risk assessments of volatilization and migration of chemical waste and remediation performance estimates. In the absence of direct measurements, values of $D_{eff}$ are approximated using empirical relationships developed from theoretical pore-size distribution models (Millington, 1959) or more commonly derived from one-dimensional, laboratory-scale soil column experiments (Millington and Quirk, 1960; Moldrup et al., 2000). Little work has been done to evaluate the suitability of empirical relationships of $D_{eff}$ for field applications involving long distance transport through deep UZs. An exception is the use of trace atmospheric gases to explore the deep UZ (Weeks et al., 1982; Weeks and McMahon, 2007). The atmospheric tracer method is limited to assessing diffusion in the vertical direction, typically
perpendicular to bedding and sediment stratigraphy. The focus of this study, in contrast, is on lateral transport of gases introduced into the subsurface. As pointed out in a review by Werner et al. (2004), additional experimentation is needed for diffusion theory model validation at the field scale, particularly in heterogeneous and structured porous media.

The ADRS in southwestern Nevada (Fig. 1a) serves as a field-scale laboratory for investigating long-distance gas transport in arid unsaturated soils and sediments. This site has been well characterized over many years of study (e.g., Fischer, 1992; Andraski, 1997; Andraski and Stonestrom, 1999). A low-level radioactive waste (LLRW) disposal facility adjacent to the ADRS serves as the source of numerous gas-phase contaminants. From 1962 to 1992, the facility buried commercial waste in a series of 22 unlined trenches ranging from 2 to 15 m deep. Contaminants from the buried waste have migrated through the thick UZ and have been consistently measured in ADRS boreholes since measurements first began about 20 yr ago (Stonestrom et al., 2004; Baker et al., 2012; Maples et al., 2013). The ADRS deep unsaturated boreholes were drilled and instrumented to various sampling depths (UZB-1, 47.9 m; UZB-2, 108.8 m; UZB-3, 103.9 m) in November 1992, September 1993, and December 1999, respectively (Fig. 1b). Tritium concentrations in water vapor and core water collected from the UZ at the ADRS (Prudic and Striegl, 1995; Prudic et al., 1997) greatly exceed concentrations predicted by accepted analytical tritium transport models (i.e., Smiles et al., 1995) applied across the estimated ranges of geological, hydrological, and chemical conditions at the site (Striegl et al., 1996). Simulations conducted using multidimensional, multiphase flow and transport numerical models (Walvoord and Stonestrom, 2004; Mayers et al., 2005) also underestimate the measured tritium migration from the LLRW facility. Several other gas-phase constituents derived from buried waste, including chlorofluorocarbons, hydrocarbons, and radioactive carbon dioxide, exhibit enhanced long distance (>100 m) lateral transport at the ADRS (Striegl et al., 1996; Baker et al., 2012). Vertical profiles of elemental mercury gas display abrupt concentration changes with depth, suggesting preferential lateral migration that is not captured by conventional modeling approaches based on simple transport by gas diffusion alone (Walvoord et al., 2008).

Here we describe the results and analyses of a gas tracer test in the deep UZ under natural-gradient conditions at the ADRS. The temporal and spatial (both depth and longitudinal) scales investigated by this field study exceed those addressed by previous gas transport experiments (Werner et al., 2004; Tick et al., 2007). The primary objectives of this experimental study were to: (i) evaluate the general utility of laboratory-derived empirical formulations of diffusivity for field-scale application and (ii) improve the physical framework for interpreting both apparent anomalous historic contaminant transport data as well as recent data collected via regular monitoring. “Expected” tracer results (i.e., those displaying gas-phase Fickian diffusion well matched to model predictions) would suggest that laboratory-derived empirical formulations of diffusivity may be appropriately applied to field scales larger than previously tested. Expected results would further suggest that historic apparent anomalies cannot be explained by current ambient conditions, pointing to site history and contaminant-specific partitioning to explain transport evolution. “Unexpected” tracer results would shed light on the limitations of standard diffusivity models as applied to long-distance transport in the deep UZ. Unexpected results could also help substantiate observed enhanced gas-phase transport at the ADRS and provide insight into pervasive processes controlling anomalous transport at this and other LLRW sites (Dirkes et al., 1999).

![Fig. 1. (a) Location of the Amargosa Desert Research Site (ADRS) and the low-level radioactive waste (LLRW) facility in southwestern Nevada, as well as (b) the ADRS deep unsaturated zone boreholes adjacent to the LLRW facility.](image-url)
In situ methods for evaluating gas-diffusion transport properties include, but are not limited to, single-well and cross-well tracer tests with instantaneous and continuous point sources as reviewed by Werner et al. (2004). Single-well gas tracer injection tests (Werner and Höhener, 2003; Tick et al., 2007) are rapid, require few soil gas measurements, and yield transport property information for a small, usually poorly defined, volume of soil near the well. Cross-well gas tracer tests (Kreamer et al., 1988; Nicot and Bennett, 1998) offer a distinct advantage over single-well tests in that a larger volume of subsurface material is investigated, but they require more gas concentration measurements and a longer monitoring duration. An instantaneous point-source test has operational advantages over a continuous point-source test in that a slow, constant release rate of the tracer gas is difficult to maintain over long periods of time.

For the purposes of better understanding field-scale gas transport in the deep UZ, a cross-well instantaneous point-source approach was selected, taking advantage of existing monitoring infrastructure at the research site. Sulfur hexafluoride (Table 1) was chosen as the tracer gas due to its conservative physiochemical properties (Rattray et al., 1995; Maiss et al., 1996). Sulfur hexafluoride is primarily anthropogenic and is found in relatively low concentrations in the atmosphere (<10 pptv) and in the UZ under natural conditions. Concentrations can be detected at atmospheric levels with high precision using a gas chromatograph equipped with an electron capture detector and following rigorous procedures to prevent contamination and instrumental noise (Busenberg and Plummer, 2000). For measuring concentrations well above background levels, procedures need not be as rigorous, and a gas chromatograph with an electron capture detector that is relatively easy to transport can be used for on-site analysis.

**Materials and Methods**

**Study Site**

The present climate in the Amargosa Desert is arid-thermic, with precipitation averaging 108 mm yr⁻¹ from 1981 to 2011 (Arthur et al., 2012). The dominant vegetation is creosote bush (Larrea tridentata [Sessé & Moc. ex DC.] Coville), a highly water-efficient North American desert shrub. Continuous monitoring at the ADRS since 1987 under native vegetation indicates that evaporative processes confine infiltrating precipitation-induced wetting fronts to within 1.2 m of the land surface (Andraski, 1997; Tumbusch and Prudic, 2000). Native plants at the ADRS maintain extremely low matric potentials at the base of their ~1-m-deep root zone (≤ 4 MPa), preventing deeper percolation. This shallow monitoring data together with modeling of measured chloride, matric potential, and stable isotope (²H and ¹⁸O in water) profiles of the deep UZ strongly suggests that liquid fluxes below the root zone and above the water table are negligible (Walvoord et al., 2004).

**Table 1. Properties of sulfur hexafluoride (SF₆).**

<table>
<thead>
<tr>
<th>SF₆ property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight, g mol⁻¹†</td>
<td>146.06</td>
</tr>
<tr>
<td>Density, g L⁻¹†</td>
<td>6.164</td>
</tr>
<tr>
<td>Free-air diffusion coefficient, m²d⁻¹†</td>
<td>0.77</td>
</tr>
<tr>
<td>Vapor pressure at 22°C, MPa†</td>
<td>2.26</td>
</tr>
<tr>
<td>Air–water partitioning constant (mol m⁻³ air/mol m⁻³ water) at 10°C†</td>
<td>105</td>
</tr>
<tr>
<td>Air–water partitioning constant (mol m⁻³ air/mol m⁻³ water) at 15°C†</td>
<td>126</td>
</tr>
</tbody>
</table>

† Tick et al. (2007).
‡ Werner and Höhener (2003).

Depth to groundwater at the ADRS ranges from 85 to 115 m (Fischer, 1992). Sediments in the UZ consist of unconsolidated and poorly sorted debris-flow, fluvial, and alluvial-fan deposits (Nichols, 1987). Deep sediments include playa and lacustrine deposits (Taylor, 2010). Beneath the surface soil, sediment composition is almost entirely sand and gravel, with minor amounts of silt and clay. However, layers with more abundant fine-grained sediment were observed at or near the surface and between depths of 79 and 85 m. Borehole cores analyzed for texture were all classified as gravelly to very gravelly sand to sandy loam. A generalized layered stratigraphy for the site was conceptualized (Fig. 2a) and implemented for previous modeling studies (Mayers et al., 2005; Walvoord et al., 2008). Volumetric water contents are relatively low, ranging from 0.05 to 0.14 m³ m⁻³, and estimated porosities range from 0.18 to 0.32 m³ m⁻³ (Mayers et al., 2005). Very low unsaturated hydraulic conductivity and thus negligible water flux (on the order of 10⁻² mm yr⁻¹) in the deep UZ render gas-phase transport an important mechanism for the movement of water vapor and volatile constituents. In this study, we test the hypothesis that diffusion is the main mechanism of gas-phase transport at this site.

**Experiment Design**

The gas tracer study at the ADRS made use of existing instrumented boreholes located 9.00 m apart (Fig. 2b,c). UZB1, designed for water potential monitoring, contained tubes with removable thermocouple psychrometers similar to those described by Tumbusch and Prudic (2000). Borehole completion of UZB-1 enabled ground surface access to four discrete depths (Prudic et al., 1997). UZB-1 air-sampling ports have specially constructed stainless-steel screens that connect directly to 6-mm nylon tubing reaching the ground surface and thus enabling access. Tracer was injected at two of these port locations, 14.9 and 47.9 m below the ground surface, via the psychrometer access tubes. The UZB-2 borehole was used to monitor concentration breakthrough curves at available gas ports. UZB2, designed for gas sampling, was described by Prudic et al. (1997). For the shallow injection port in UZB-1, the closest horizontal monitoring ports in UZB-2 were offset by ~3 m above (11.9 m) and below (18.0 m). For the deeper
injection port in UZB-1, there was a UZB-2 monitoring port at the same depth (47.9 m).

A 99.99% pure SF₆ tracer was used to minimize the amount of pressure disturbance to the system while introducing the desired amount of tracer. Tracer was injected simultaneously at each of the two UZB-1 ports on 27 Apr. 2005 at an approximate rate of 15.38 mL min⁻¹ over 78 min to achieve total injection volumes of 1200 mL. Manual injection was accomplished using polypropylene 60 mL-syringes with three-way stopcocks connected to the 6-mm access tubes associated with the two UZB-1 ports at depths of 14.9 and 47.9 m. Twenty syringes were needed for each injection location to deliver the desired tracer amount. Immediately following tracer introduction, 120 and 240 mL of air were injected at the shallow and deep injection ports, respectively, to clear the psychrometer-access tubes of residual SF₆ tracer and introduce all tracer into the sediment.

Before tracer injection, gas samples were collected from the UZB-1 and UZB-2 ports to establish background concentrations. Beginning 1 d after tracer injection, gas samples from the UZB-2 monitoring borehole were collected twice daily for the first 2 wk of the experiment, after which the sampling frequency was gradually reduced during the remainder of the year. Each 6-mm monitoring tube was purged by removing approximately two pore tube volumes (individually calculated for the depth of each port) before sample collection. Samples were collected in 20-mL nylon syringes equipped with a three-way polycarbonate stopcock.

Sample syringes were flushed with gas from the collection depth four times before the actual sample was retained. Positive pressure was applied to the closed-off syringe containing the gas sample to minimize dilution before gas chromatograph analysis. Duplicate samples were collected. Gas samples were analyzed by on-site gas chromatography for the first 2 wk of the experiment. Subsequent samples were shipped to the USGS in Denver, CO and analyzed within 1 to 2 d of collection. All samples were analyzed using a PerkinElmer gas chromatograph equipped with a dual electron capture detector, which was transported to the site before tracer injection and returned to Denver 2 wk post injection. Ultra-pure N₂ gas was used as the carrier gas. Gas passed through moisture and oxygen traps before entering the chromatograph. Peak separation of SF₆ was accomplished by injecting 0.5 mL of the collected sample or standards with the N₂ carrier gas at a rate of 30 mL min⁻¹ through a 80/100 Porapak Q 3.175-mm (1/8-inch) column. Settings included an oven temperature of 35°C, injector temperature of 100°C, and electron capture detector temperature of 100°C, following those used by Rattray et al. (1995). Standards of National Institute of Standards and Technology (NIST)-traceable SF₆ in air were run before every round of sample analysis to establish calibration curves. The standards were chosen to span the expected range of concentration values for the field samples and yielded a detection limit of 1 nL L⁻¹. Periodic blanks and duplicates were run for quality assurance.

**Numerical Modeling Approach**

To compare the SF₆ tracer observations with expected results for Fickian gas diffusion, a two-dimensional radial forward modeling approach was implemented using the UZ framework developed in previous ADRS studies and standard empirical formulations for diffusivity calculations. The model design followed the methodology described in Walvoord et al. (2008) to simulate radial transport of a conservative gas at the ADRS. The Finite Element Heat and Mass Transfer Code (FEHM; Zyvoloski et al., 1997) was used to simulate non-isothermal vapor and liquid movement and SF₆ transport in the 110-m thick UZ for 1 yr following tracer injection at UZB-1. The model domain extended 110 m vertically (the entire UZ) and 200 m in the horizontal (radial) direction away from the injection borehole; variable grid spacing of 0.25 to 2 m was used, resulting in a 11,640 node (97 × 120), 11,424 rectangular elemental grid. Layered heterogeneity in soil properties observed at the ADRS, as illustrated in Fig. 2a and listed in Table 2, was implemented in the model following Mayers et al. (2005) and Walvoord et al. (2008). Initial conditions for the transport simulations represent 16,000 yr of transient UZ drying based on water potential and pore water concentrations of Cl⁻, ²H, and ¹⁸O.
measured at the ADRS (Walvoord et al., 2004). The resulting water content and air-filled porosity profiles, together with total porosity, are shown in Fig. 2d. Initial SF$_6$ concentrations for the simulation were set at 0 nL L$^{-1}$ before tracer injection. Temperatures varied linearly between 21.8°C at the surface to 26.8°C at the water table.

Two Millington–Quirk formulations were used to evaluate their effect on simulation results. Effective diffusion coefficients ($D_{eff}$) for SF$_6$ were calculated by the model for each model node at each time step based on the Millington–Quirk I and II formulations (Millington 1959; Millington and Quirk, 1960; Jin and Jury, 1996),

### Millington–Quirk I (MQI): $D_{eff} = D^0 a^{(10/3)}/\varphi^2$  \hspace{1cm} [1]

### Millington–Quirk II (MQII): $D_{eff} = D^0 a^{2}/\varphi^{(2/3)}$  \hspace{1cm} [2]

where $D^0$ is the vapor diffusion coefficient for SF$_6$ in air: 0.77 m$^2$ d$^{-1}$ (Werner and Höhener, 2003); $a$ is air-filled porosity; and $\varphi$ is total porosity. Sulfur hexafluoride was modeled as a conservative gas species. Sulfur hexafluoride was injected as a rate of 15.38 mL min$^{-1}$ over a 78-min injection period at depths of 14.9 and 47.9 m, commensurate with the field experiment. Simulations were run on a 0.1-h time step for 1 yr after the injection period to correspond with the duration of the tracer test monitoring period.

### Results and Discussion

#### SF$_6$ Tracer Data

Background concentrations of SF$_6$ in monitoring borehole UZB-2 were determined using samples collected before tracer injection in UZB-1 (time = 0 d in Table 3), and values ranged between 3 and 18 nL L$^{-1}$. These background values are about 600 to 3000 times the 2005 atmospheric SF$_6$ concentration, as a result of migration from SF$_6$–containing waste in the adjacent LLRW area. Such large background concentrations preclude applying the method of Weeks et al. (1982) to discern soil diffusion parameters and warrant the use of pure SF$_6$ for tracer injection to easily distinguish the injected tracer from ambient site concentrations. Measured SF$_6$ concentration profiles in UZB-2 through time following simultaneous tracer injections at shallow (14.9 m) and deep (47.9 m) ports in UZB-1 illustrate the migration of the shallow and deep plumes (Fig. 3; Table 3). UZB-2 concentrations measured over the first week following tracer injection showed no systematic increases. Mean concentrations for Days 1 through 7 are listed in Table 3. At Day 8, the SF$_6$ concentration increased by about an order of magnitude above background concentration at the UZB-2 11.9-m depth, which is vertically offset from the UZB-1 shallow injection port by 3.0 m. A similar increase at the 18.0-m monitoring depth, which is vertically offset from the shallow injection port by 3.1 m, was not detected until Day 13. The earlier arrival of the shallow plume at the 11.9-m versus 18.0-m monitoring depth suggests that SF$_6$ tracer movement was more strongly affected by sediment stratigraphy than density effects by the time the plume reached UZB-2.

As expected, concentration changes in UZB-2 associated with the UZB-1 shallow (14.9 m) injection were most pronounced at the 11.9- and 18.0-m sampling depths throughout the monitoring period. Similarly, concentration changes in UZB-2 associated with the deep (47.9 m) injection were most prominent in the sample depths of 47.9 m and 57.6 m throughout the monitoring period.

Breakthrough curves for UZB-2 monitoring depths are illustrated in Fig. 4a. The maximum shallow-plume SF$_6$ concentration measured at 11.9 m was 927 nL L$^{-1}$ at 42 d, and the maximum at 18.0 m was 761 nL L$^{-1}$ at 70 d. The sampling frequency during this period imposes about a 1-wk margin of error on the peak concentration arrival estimate. Deep plume concentrations began increasing at the UZB-2 47.9-m depth ~12 d after the UZB-1 tracer injection. The peak deep-plume SF$_6$ concentration at 47.9 m reached 1312 nL L$^{-1}$ at 70 d and that for the 57.6-m depth was 249 nL L$^{-1}$ at 89 d.

Gas samples from the UZB-1 tracer injection ports at 14.9 and 47.9 m were also collected and analyzed beginning 56 d after injection. Samples from UZB-1 were not withdrawn before that time to minimize near-field disturbance of the tracer test. During the post injection period from Days 56 and 357, a total of seven gas samples at each injection port were collected and analyzed for SF$_6$ concentration (Fig. 4b, Table 4). Although equivalent SF$_6$ volumes were injected simultaneously at the two injection ports at the beginning of the tracer test, the Day 56 concentration for the deep port (54,373 nL L$^{-1}$) was nearly three times that for the shallow port (18,542 nL L$^{-1}$). Greater concentrations for the deeper port (factors of 2.3 to 4.1) persisted throughout the UZB-1 sample collection period. By the end of the tracer test, SF$_6$ concentrations had decreased to 174 and 471 nL L$^{-1}$ at 14.9 and 47.9 m, respectively.

Comparisons of the UZB-2 breakthrough curves (Fig. 4a) and the UZB-1 declines in SF$_6$ at the injection ports (Fig. 4b) support the interpretation that spreading of the shallow plume is faster.
Table 3. Sulfur hexafluoride concentrations in the unsaturated zone monitoring borehole, UZB-2, at various depths and through time subsequent to tracer injection at the shallow (14.9 m) and deep (47.9 m) ports in UZB-1.

<table>
<thead>
<tr>
<th>Time since injection</th>
<th>Sampling depth in UZB-2†</th>
<th>SF&lt;sub&gt;6&lt;/sub&gt; Conc, nL L&lt;sup&gt;−1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>5.5 m</td>
<td>11.9 m</td>
</tr>
<tr>
<td></td>
<td>18.0 m</td>
<td>24.1 m</td>
</tr>
<tr>
<td></td>
<td>34.1 m</td>
<td>47.9 m</td>
</tr>
<tr>
<td></td>
<td>57.6 m</td>
<td>94.2 m</td>
</tr>
<tr>
<td>0 (background) †</td>
<td>3.4</td>
<td>5.7</td>
</tr>
<tr>
<td>1–7 (mean)</td>
<td>2.8</td>
<td>7.5</td>
</tr>
<tr>
<td>8</td>
<td>3.2</td>
<td>58.0</td>
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<td>9</td>
<td>7.1</td>
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<td>357</td>
<td>88.5</td>
<td>144.4</td>
</tr>
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</table>

† Samples were also collected at depths of 106.4, and 108.8 m, but are not shown here, since tracer test influence was not detected in concentrations from these samples. ‡ Samples collected before tracer injection. § Sample not collected.

Fig. 3. Sulfur hexafluoride concentrations through time in gas samples collected in the UZB-2 monitoring borehole. Time (t) represents time since tracer injection at shallow (14.9 m) and deep (47.9 m) ports in nearby UZB-1 borehole. Arrows indicate time advancing trend in shallow and deep plume concentration.
than the deep plume. The shallow plume arrives at the UZB-2 11.9-m depth before the deeper plume arrives at the 47.9-m depth, despite the vertical offset in the shallow plume injection monitoring depths. The concentration peak of the shallow plume also occurs earlier in time (42 d) than the peak of the deep plume (70 d). The magnitudes of the UZB-2 concentration peak and the UZB-1 concentration decline are both greater for the deep plume than those for the shallow plume. The more rapid arrival and lower ultimate peak concentrations in the shallow plume may result from variations in porosity and tortuosity in the UZ sediments, but may also indicate greater dispersion from effects of minor advective oscillations induced by atmospheric pressure variations (Kuang et al., 2013).

### Modeling Results

The radial transport results for the SF$_6$ tracer simulations for four selected times since tracer injection at UZB-1 (the origin) are shown in Fig. 5. Results shown here correspond to the simulation that utilized the MQI formulation to calculate $D_{\text{eff}}$ at each node; however, results from the MQII are visually identical to MQI results when displayed at the same scale. Despite the modeled layered heterogeneity in the system, the diffusive plumes display little difference from what would be expected in a homogeneous system. This is due to the relatively large magnitude of diffusion coefficients for gases like SF$_6$ (0.77 m$^2$ d$^{-1}$, in air). For comparison, the diffusion coefficient of SF$_6$ in pure water at 25°C is on the order of 1.04 $\times$ 10$^{-5}$ m$^2$ d$^{-1}$ (King and Saltzman, 1995), and differential diffusion resulting from layered heterogeneity for a saturated system would be more pronounced.

In accordance with this study’s main objective of broadly evaluating diffusive transport in a deep desert UZ, results of the SF$_6$ transport modeling, without calibration or other adjustments, were compared with tracer test data. Figure 6 illustrates the comparison
between observations and simulated results for the four UZB-2 monitoring ports closest in depth to the UZB-1 injection points, and similar correspondence was observed for the other monitoring depths. In general, the comparisons between observed data and model results are reasonable, suggesting that gas transport in the deep UZ at the ADRS is controlled by Fickian diffusion, and standard formulations for representing diffusivity are good first approximations. However, notable discrepancies between expectations (model results) and observations exist. The most prominent discrepancy is the models’ underprediction of peak tracer concentrations. For all UZB-2 monitoring ports, only the model results for the 5.5-m (not shown) and 57.6-m (Fig. 6d) locations closely reproduce observed peak concentrations.

With respect to the timing and concentration associated with the advancing plume fronts, the MQII model reproduces the data better than the MQI model. The MQII model also shows more favorable comparison than the MQI model with the breakthrough curve falling limb concentrations, although declining concentrations for the shallow plume (Fig. 6a,b) are better matched than those for the deep plume (Fig. 6c,d). The MQI model tends to overpredict concentrations related to the shallow and deep plume breakthrough curve falling limbs as compared to observations.

Comparison of the commonly used MQI model results with the observations indicates slightly faster than expected migration of SF$_6$. The slightly faster transport relative to the diffusion-based model predictions may result from long-range advection, advective oscillations, or errors in the estimates of $D_{\text{eff}}$. Long-range advection can be ruled out based on results of Maples et al. (2013), who showed minimal movement of the tritium plume’s center of mass in a study between 2001 and 2011. Because the direction of contaminant movement from the buried waste was perpendicular to the line between UZB-1 and UZB-2, any advective transport in this direction would tend to create the appearance of slower transport and smaller peaks. Testing the potential effects of advective oscillations and structure of diffusivity on SF$_6$ migration are topics of a subsequent study.

Fig. 6. Comparison of observed breakthrough curves for selected locations in UZB-2 and modeled responses using Millington–Quirk I (MQI) and Millington–Quirk II (MQII) formulations for diffusivity calculations.
Implications for Contaminant Gas Transport Prediction and Evaluation

Predicting migration of contaminants in the gas phase is especially critical in deep arid UZs where much of the United States’ low-level radioactive waste and chemical waste are interred. Gas diffusion is a primary transport process enabling the spreading of contaminants present in the gas phase through the UZ beyond the spatial footprint of low-level radioactive and chemical waste burial facilities. The utility of standard diffusion theory has not been validated at the depth and scales (both spatial and temporal) relevant to long-distance arid UZ transport. Results from the field-scale ADRS gas tracer study suggest that the use of empirical lab-scale formulations, such as the Millington–Quirk expressions for representing diffusivity, is a reasonable primary approach even in deep heterogeneous structured UZs. This assessment confirms the conclusions of an alternative method that tested this utility via atmospheric gas tracer diffusion into deep UZs on the decadal timescale (Weeks et al., 1982). Overall, the less common MQII model represents deep UZ diffusion in this large-scale field experiment better than the widely used MQI model. This result is in agreement with earlier findings of Jin and Jury (1996), who compared laboratory measured relative diffusion coefficients with those derived from commonly used empirical models and found the MQII model to excel compared to the MQI and other models investigated. In terms of this study’s objectives, the difference between formulations has a relatively minor impact.

Contrasting with previously documented anomalous (theoretically unexpected) long-distance (>100 m) lateral transport of vapor-phase tritium through the deep UZ at the ADRS, the SF6 tracer experiment results were consistent with existing theory. The SF6 tracer data were evaluated for excursions reflective of processes that could explain enhanced tritium transport from a LLRW disposal area, but no such excursions are identified. The slight differences in apparent rates of migration of SF6 versus theoretical estimates are not sufficient to explain the long distance tritium transport at the site. For example, Striegl et al. (1996) and Mayers et al. (2005) increased diffusion coefficients by an order of magnitude in forward model runs and still were not able to match the extent of tritium transport during the lifetime of the facility. The SF6 results confirming transport controlled by gas diffusion at the ADRS are consistent with those of a recent 10-yr field study (2001–2011) of tritium plume dynamics in the shallow (upper 2 m) UZ at the research site (Maples et al., 2013). In that study, limited advancement of the plume was consistent with theoretical estimates, and it was concluded that the observed widespread distribution of tritium (>400 m from trenches) primarily resulted from transport before 2001. Maples et al. (2013) proposed that waste-source gas generation within LLRW burial sites may have contributed to the pre-2001 transport of tritium from the LLRW area into the adjacent UZ. These relative comparisons between the shallow and deep UZ results are incomplete and uncertain, but they provide support for the hypothesis that the documented anomalies in long-distance transport at the ADRS are the result of early time perturbations rather than ongoing processes and/or time-independent transport properties.

Conclusions

The in situ experimental gas tracer test described here represents transport over greater temporal and spatial scales than those addressed by typical laboratory-scale soil column studies and other in situ UZ tracer tests reported in the literature to evaluate soil transport parameters. In general, “tried and true” empirical relationships for estimating effective diffusion coefficients that were originally developed at the lab scale adequately describe gas transport measured in this study’s field-scale experiment in the deep UZ. However, minor discrepancies were noted. Future work should address these discrepancies by introducing multiple approaches of conceptualizing the spatial variability of diffusivity and evaluating the effect of natural forcings in the UZ.

Under natural conditions, the migration of volatile and semivolatile chemicals within arid UZs is often assumed to be dominated by gas-phase diffusion. For conditions associated with buried waste sites, this assumption may be called into question. Waste burial can impose large gradients in temperature and pressure on the ambient regime, producing advective and thermal transport that is difficult to predict or hindcast with insufficient data. The results from the SF6 tracer test at the ADRS offer confirmation of transport rates similar to those of gas diffusion under current conditions and at a distance of ~160 m from the nearest buried waste trench. The gas transport behavior observed during the year-long tracer test performed 13 yr after LLRW facility closure suggests that the natural conditions and UZ soil properties at the ADRS are likely not responsible for the anomalous vapor-phase transport observed soon after facility closure. By process of elimination, the results further suggest that early-time conditions or phase disequilibrium may play critical roles in contaminant migration through the deep UZ near buried waste facilities. Careful early-time monitoring is needed to capture perturbations and reconcile excursions from predicted diffusive transport.

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