

UC Santa Barbara

UC Santa Barbara Previously Published Works

Title

Gas Transport below Artificial Recharge Ponds: Insights from Dissolved Noble Gases and a Dual Gas (SF₆ and ³He) Tracer Experiment

Permalink

<https://escholarship.org/uc/item/2s42854c>

Journal

Environmental Science and Technology, 39(11)

ISSN

0013-936X

Authors

Clark, Jordan F
Hudson, G Bryant
Avisar, Dror

Publication Date

2005-06-01

DOI

10.1021/es049053x

Peer reviewed

Gas Transport below Artificial Recharge Ponds: Insights from Dissolved Noble Gases and a Dual Gas (SF₆ and ³He) Tracer Experiment

JORDAN F. CLARK,*†,‡
G. BRYANT HUDSON,§ AND
DROR AVISAR‡

Department of Geological Sciences and Institute for Crustal Studies, University of California, Santa Barbara, California 93106, and Chemical Biology and Nuclear Science Division, Lawrence Livermore National Laboratory, Livermore, California 94550

A dual gas tracer experiment using sulfur hexafluoride (SF₆) and an isotope of helium (³He) and measurements of dissolved noble gases was performed at the El Rio spreading grounds to examine gas transport and trapped air below an artificial recharge pond with a very high recharge rate (~4 m day⁻¹). Noble gas concentrations in the groundwater were greater than in surface water due to excess air formation showing that trapped air exists below the pond. Breakthrough curves of SF₆ and ³He at two nearby production wells were very similar and suggest that nonequilibrium gas transfer was occurring between the percolating water and the trapped air. At one well screened between 50 and 90 m below ground, both tracers were detected after 5 days and reached a maximum at ~24 days. Despite the potential dilution caused by mixing within the production well, the maximum concentration was ~25% of the mean pond concentration. More than 50% of the SF₆ recharged was recovered by the production wells during the 18 month long experiment. Our results demonstrate that at artificial recharge sites with high infiltration rates and moderately deep water tables, transport times between recharge locations and wells determined with gas tracer experiments are reliable.

Introduction

Artificially recharging surplus surface or recycled (reclaimed) wastewater into groundwater aquifers has become an important management strategy for increasing the potable water supply in many regions. This practice is especially important in areas with limited surface water storage capacity or highly interannual or seasonal precipitation patterns (1). In order for an artificial recharge system to be successful, facilities must be engineered that have recharge rates significantly higher than are generally observed in natural systems. A common method of achieving these very high

recharge rates relies on constructing spreading basins, shallow ponds that are periodically dried so that the infiltrating surface (pond bottom) can be cleaned of clogging material. An added benefit of artificial recharge is the water quality improvements that are commonly observed between the recharged and the produced waters (e.g., refs 2–5). In fact, the recharge process can be the final treatment step for certain compounds in some projects.

While it is recognized that the quality of recharge water improves during transit in the subsurface, water agencies are often required to document the improvement prior to gaining credit that can be used during the permitting process. To document the in situ changes in the water quality, travel times and paths between the recharge areas and the production wells must be known very well. Recently, Gamlin et al. (6) and Clark et al. (7) developed methods using gas tracers for the direct determination of travel times between recharge areas and wells over the time period of 0–5 years. To follow the movement of recharge water for these long time periods, the authors had to find tracers that could be economically introduced into a large volume of recharge water (>10⁶ m³) at a sufficient concentration to allow quantification after at least a 1000:1 dilution. Furthermore, the tracers had to be nonreactive and their movement not slowed by sorption processes (retardation) within the aquifer. Sulfur hexafluoride (SF₆) and isotopes of xenon (¹²⁴Xe, ¹²⁹Xe, and ¹³⁶Xe) were found to satisfy these conditions (6, 7).

During recharge at spreading ponds, surface water infiltrates into the ground and flows through a vadose or unsaturated zone prior to reaching the water table. The unsaturated zone is composed of three principle phases: soil, water, and soil air. In this zone, gas transfer between the percolating water and soil air will occur. Relatively insoluble gases will partition strongly into the soil air. Thus, during field experiments with gas tracers, such as SF₆ and noble gas isotopes, the tracers should be initially lost from the percolating water to the soil air. This loss will continue until a sufficient amount of tracer has transferred to the soil air and the solubility equilibrium is reached. Once this happens, the gas tracers will be transported through the unsaturated zone without further loss. The time it takes to reach equilibrium is a function of the relative volumes of water and soil air, infiltration rate, Henry's Law coefficient, and gas transfer rate across the air–water interface. Because gas tracers are only injected into the surface water for a short period of time (a few days to weeks), the concentration in the percolating water will decrease (once the gases are no longer added to the surface water), and eventually the gas tracers will transfer from the soil air to the percolating water. Therefore, the expected gas transfer and partitioning between infiltrating water and soil air will act to retard (slow) the movement of the gas relative to the water through the unsaturated zone. This retardation has been demonstrated for a number of gases including SF₆ and He in laboratory experiments (8–10).

Fry et al. (9) proposed that the retardation factor, *R*, for a gas flowing through porous media containing trapped air can be calculated from the dimensionless Henry's Law constant, *H*, and the ratio between the air, *V*_{air}, and water, *V*_{water}, pore volumes

$$R = 1 + H(V_{\text{air}}/V_{\text{water}}) \quad (1)$$

In formulating this relationship, Fry et al. (9) assumed that gas transfer was sufficiently fast to maintain an equilibrium between the trapped gas and the flowing groundwater. Their

* Corresponding author phone: (805) 893-7838; fax: (805) 893-2314; email: jfclark@geol.ucsb.edu.

† Department of Geological Sciences, University of California, Santa Barbara.

‡ Institute for Crustal Studies, University of California, Santa Barbara.

§ Lawrence Livermore National Laboratory.

equation predicts that the transport of most gases will be retarded in the groundwater systems that contain even small amounts of trapped air. For instance, gases with $H > 25$ ($H = 25$ for oxygen at 10 °C) will have retardation factors greater than 2 when $V_{\text{air}}/V_{\text{water}} > 0.04$. Equation 1 accurately predicts retardation factors determined during laboratory column experiments at low $V_{\text{air}}/V_{\text{water}}$ ratios but under-predicted retardation at high $V_{\text{air}}/V_{\text{water}}$ ratios (9, 10). Kinetic models that included diffusion controlled gas transfer do a much better job matching laboratory experiments at high $V_{\text{air}}/V_{\text{water}}$ ratios (10, 11). The effect of noninstantaneous gas exchange include an earlier breakthrough of gases, longer tails, and nonequilibrium between percolating water and soil air.

A surprising result of the initial SF₆ and Xe isotope gas tracer experiments performed at artificial recharge facilities in Orange County, CA was the observation that the gases were transported through the unsaturated zone to the water table without significant loss or retardation (6, 7). Clark et al. (7) postulated that the absence of retardation indicates that the gas tracers were infiltrating primarily through saturated pathways contained within the unsaturated zone. This observation is not universal; significant retardation or loss of a gas tracer has been observed elsewhere (12, 13).

Here, we present results from a dual gas tracer experiment using SF₆ and an isotope of helium, ³He, designed to examine gas transport through the unsaturated zone beneath a spreading pond in more detail than was possible during the Orange County experiments. The dual gas tracer method was initially developed to quantify gas transfer in the ocean and in rivers (14–17). More recently, Vulava et al. (10) suggested that this method could be used to quantify the amount of trapped air in porous media after performing a number of laboratory experiments. Our experiment, which was conducted at the El Rio spreading grounds, Ventura County, CA was designed to quantify gas transfer from the percolating recharge water to the soil air in a field setting. SF₆ and ³He were chosen as tracers because they are conservative, not retarded in saturated porous media (8, 18, 19), have Henry's Law coefficients that differ by about 50%, and are sufficiently inexpensive to tag large volumes of water (typically >10⁶ m³) as is required when performing tracer experiments at artificial recharge sites.

Study Location. Artificial recharge at the El Rio spreading grounds has taken place since their construction in 1955. The spreading grounds are located toward the down gradient end of the Santa Clara–Calleguas aquifer system where the groundwater basin expands forming the permeable alluvial deposits of the Oxnard Plain. Here, the upper aquifer system, which extends to a depth of ~60 m below the ground surface, is composed of discontinuous layers of gravel, sand, and silt (20). At the spreading grounds, the upper 50 m is free of impermeable layers, and thus, the ground has a high infiltration capacity.

Ten shallow ponds (~3 m maximum depth) and a series of distribution channels make up the spreading grounds (Figure 1). Very little surface water recharges from either Pond 1, which is used as a desilting basin, or Pond 9, which is used in the potable supply system. The other eight ponds are scraped periodically to ensure rapid infiltration. During the 1990s, about 40 × 10⁶ m³ of water was recharged annually from the El Rio spreading grounds (21). The source of this water was primarily diverted seasonal runoff from the Santa Clara River and released stored water from a local reservoir, Lake Piru.

The spreading basins are surrounded by nine production wells and a set of seven nested monitoring wells (Figure 1). Because of intensive pumping at the production wells, a regional groundwater depression is found surrounding the spreading grounds (Figure 2), although local mounding beneath the ponds can occur during periods of artificial re-

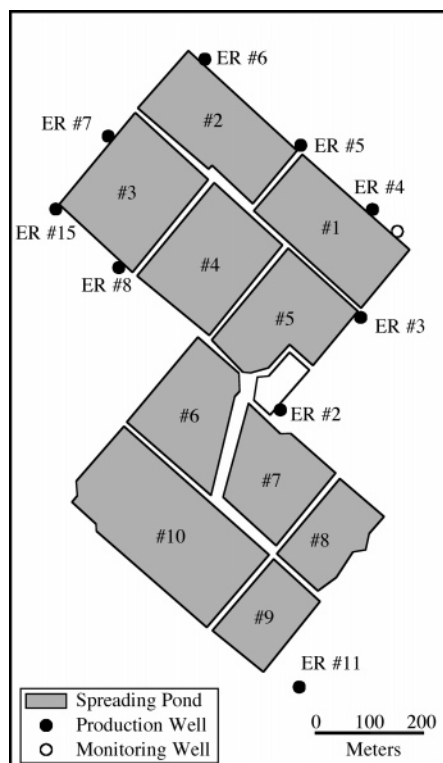


FIGURE 1. Map of the El Rio spreading grounds. The dual gas tracer experiment was conducted from Pond 2 while recharge was occurring from Ponds 2 and 3. The water table elevation was determined at the nested monitoring well. For most of the study period, El Rio #4 was closed.

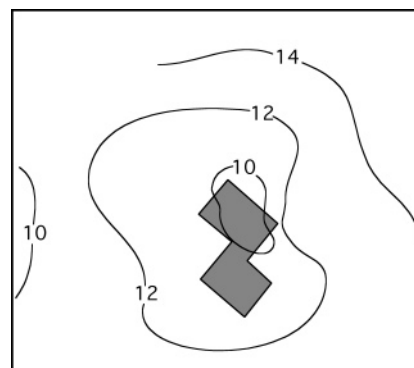


FIGURE 2. Regional water table (meters above sea level) near the El Rio spreading grounds (shaded area) determined for November 2002.

charge. Within the spreading area, much steeper cones of depressions can form around each well during periods of intense pumping. On average, groundwater production is higher during the summer, and artificial recharge is higher during the winter and spring. The seasonality in the recharge and production combined with the very steep local hydraulic gradients create a complex pattern of flow beneath the El Rio spreading grounds.

Materials and Methods

Tracer Injection. In September 2002, about 24 × 10⁶ m³ of water was released from Lake Piru down Piru Creek and into the Santa Clara River. About 20% of this water was diverted into the El Rio spreading grounds, flooding Ponds 2 and 3 for 35 days (Figure 3), beginning on September 8, 2002, day –19 of the experiment (time is referenced to the start of the tracer injection: day 0 = September 27, 2002). The spreading

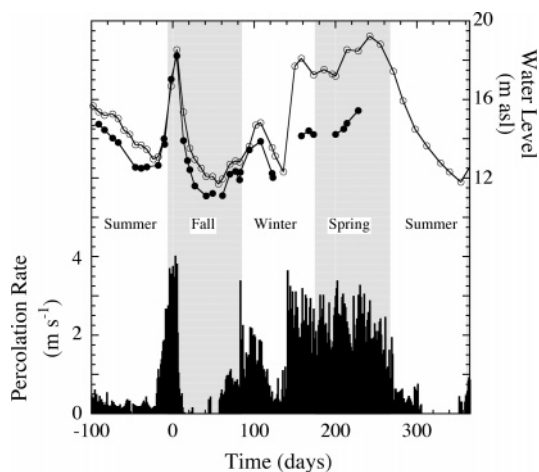


FIGURE 3. Rate of artificial recharge and the local water table elevation at the El Rio spreading grounds. The bottom of Pond 2 is about 30 m above sea level. Time zero is September 27, 2002. Water level measurements collected at El Rio #7 during periods of pumping were removed and are indicated by the absence of connecting lines. Open circles = water level at the monitoring well and filled circles = water level at El Rio #7.

area had received very little water for the 3 months prior to this release. For a period of 8 days (September 27 to October 4, 2002), a gas mixture containing SF₆ (~900 L) and ³He (~1 L) was injected into Pond 2 (surface area = 3.8 ha) by bubbling through a diffusion stone that was placed in a water depth of about 1.2 m. During this time, the average recharge rates from Ponds 2 and 3 were 1.8 and 1.7 m³ s⁻¹, respectively. The September percolation rate was about an order of magnitude higher than the mean because the ponds had recently been cleaned of clogging material. The release point of the gases was about 10 m offshore of the inlet pipe, away from the white water (to minimize the gas lost), which was observed immediately downstream. The injection rate was maintained using a battery operated switcher valve (an 8-port, 2-way valve) set to release 1.5 cm³ STP of the gas mixture per minute. Approximately 17 L (0.72 mol) of SF₆ was injected into the pond, tagging ~1.1 × 10⁶ m³ of water.

Sampling Strategy. During the injection period, pond samples were collected every 2 days, ~10 cm below the surface at 11 designated locations. These samples were collected to determine the tracer concentration and spatial distribution in the pond so that its input function to the groundwater could be determined. Groundwater samples were collected prior to, during, and after the tracer injection from eight of the nine production wells located in the spreading grounds (Figure 1). During the first 2 months, groundwater samples were collected every 3–7 days. For the next 6 months, they were collected every 2–4 weeks. Thereafter, samples were collected every 6–8 weeks. The wells were located up to 900 m away from Pond 2 and have relatively long screened intervals (40–70 m).

Laboratory Procedures. The SF₆ samples were collected in 15 mL Vacutainers and analyzed on a gas chromatograph (GC) using the headspace method described by Clark et al. (7). SF₆ was separated from other gases using a Molecular Sieve 5a column held at room temperature. The GC detector response was calibrated about every 10 samples with standards (~148 and ~524 pptv) prepared by Scott-Marrin Inc. (Riverside, CA). The precision and detection limits of this method were ±5% and 0.04 pmol L⁻¹, respectively.

³He samples were analyzed at only one pond station and from only two wells (El Rio #5 and #6). They were collected in 20 cm long, 3/8 in. copper tubes (~10 mL) that were sealed

with steel pinch-off clamps. In the laboratory, the copper tubes were attached to a high vacuum inlet system that led to a VG5400 noble-gas mass spectrometer. The ³He/⁴He isotope ratio and the concentrations of ⁴He and the heavier noble gases (Ne, Ar, Kr, and Xe) were determined. The mass spectrometer was calibrated with equilibrated water samples and known quantities of air. The uncertainties of the ³He/⁴He isotope ratio; the ⁴He, Ne, and Ar concentration; and the Kr and Xe concentration measurements were ±0.5, ±1, and ±2%, respectively.

Results

Water Balance. The water table below the El Rio spreading grounds responds very rapidly to artificial recharge. The groundwater surface, which had been falling, rose by more than 6 m, reaching a maximum of ~18.5 m above sea level (asl) during the September 2002 recharge event (Figure 3). This rise was recorded at one monitoring well and at one production well, El Rio #7. The monitoring well is located approximately 220 m southeast of Pond 2, while El Rio #7 is located approximately 70 m west of Pond 2, adjacent to Pond 3. The infiltration rate of Pond 3 was similar to Pond 2 during this recharge event. El Rio #7 was rarely pumped for the 3 months prior to and during the September recharge event. Hence, water level measurements at these times were not affected by local pumping. The depth to water below Pond 2 was ~12 m at the maximum water table rise.

Following the September recharge event, the groundwater surface fell due to local pumping and the dissipation of the recharge mound. Significant recharge began again in mid-November (day 55) at the start of the 2002–2003 wet season and continued through June 2003. Variations in the amount of recharge during this time were caused by variations in the amount of surface water available for diversion into the spreading grounds.

Total groundwater production at the spreading grounds averaged ~0.6 m³ s⁻¹ during the tracer experiment. During the first 250 days (8 months) of the study, El Rio #2, #3, #5, #6, and #11 were usually operated at least 15 h per day, whereas El Rio #4, #7, #8, and #15 were rarely on. After day 250 (June 4, 2003), El Rio #7, #8, and #15 were operated 20–24 h per day, and production at well #3 decreased significantly. El Rio #2, #5, #6, and #11 were still pumped heavily.

Initial Pond Concentration. Because of the location of the diffusion stone, the short residence time of water, and slow mixing, Pond 2 was not well-mixed, and significant gradients in the SF₆ concentration were observed during the injection period. The highest SF₆ concentrations were found near the diffusion stone and toward the northwestern end of the pond. To the right and left of the injection point, the concentration was typically below the detection limit. Apparently, these areas received mostly water that was not tagged with the gas tracers. The mean SF₆ concentrations in the pond and in the northwestern half were 32 pmol L⁻¹ (1 pmol L⁻¹ = 10⁻¹² mol L⁻¹) and 41 pmol L⁻¹, respectively. On the basis of the mean concentration, the mean percolation rate (1.8 m³ s⁻¹), and the length of the injection period, approximately 0.033 mol of SF₆ was transported to the subsurface by the recharging water.

Tracer Breakthrough Curves. The tracer was first observed at El Rio #6, 5 days after the start of the injection period, and maximum concentrations were observed about 2 weeks later (Figure 4A). El Rio #6 is located within 10 m of Pond 2 near its northwestern corner (the high concentration end) and is screened between 50 and 92 m below the ground surface. Hence, water flowed vertically to this well. The calculated groundwater velocity of the leading edge based on the first arrival of SF₆ was 10 m day⁻¹. At its maximum, 10.6 pmol L⁻¹, the groundwater SF₆ concentration was ~25%

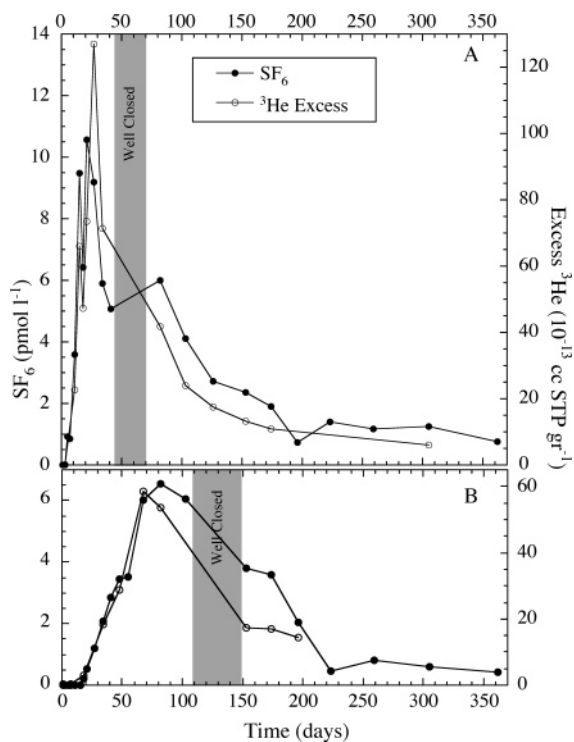


FIGURE 4. Breakthrough curves at (A) El Rio #6 and (B) El Rio #5. El Rio #5 and #6 were closed and not pumping (shaded areas) for about one month starting on day 109 and 42, respectively.

of the mean concentration in the high concentration end and 33% of the mean concentration for the entire pond. The amount of SF₆ produced was calculated from the daily pumping rates and concentrations, interpolated between measurement days. At El Rio #6, approximately 18% of the total amount of SF₆ that entered the ground was recovered.

The second well to receive the tracer was El Rio #5. This well is located approximately the same distance from Pond 2 and is screened over approximately the same depth interval (45–90 m below ground surface) as El Rio #6. SF₆ was first detected on day 17, and the concentration reached a maximum on day 82 (Figure 4B). The relatively late arrival times at El Rio #5 resulted from poor mixing in Pond 2. While El Rio #6 was located near the high concentration end of the pond, El Rio #5 was located at the low concentration end. The concentration of SF₆ in the southeastern corner where El Rio #5 is located was always below the detection limit. Therefore, because of the poor mixing within the pond, this well was located tens of meters from where the tracer was recharged. The exact distance is unknown because of the relatively large spacing between pond stations. Tagged water, thus, had to flow both vertically and laterally to reach El Rio #5. Intensive production at this well that created a local cone of depression probably contributed to this lateral flow. Approximately 22% of SF₆ transported to the subsurface was produced by this well.

At five of the six distant wells (#2, #3, #7, #8, and #15), the tracer was detected, although at different times and concentrations. It was never detected at the most southern well, El Rio #11. Artificial recharge rates, well location, and groundwater production rates seem to be the principle factors governing the movement of the tracer plume. The regional cone of depression and intense groundwater production prevented the plume from moving away from the spreading grounds. All though less SF₆ was produced at the distant wells than at El Rio #5 and #6, their combined recovery was significant, accounting for about 12% of the amount that percolated during the injection period.

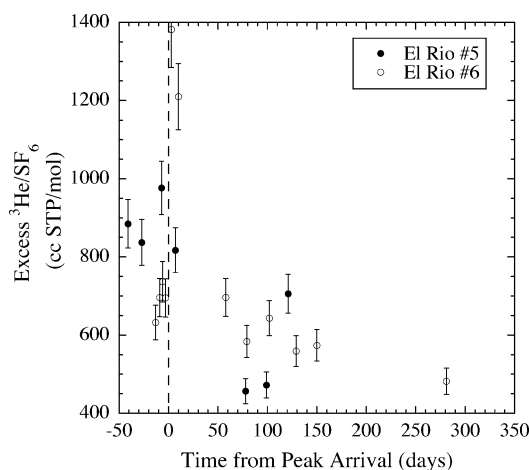


FIGURE 5. Excess ³He/SF₆ ratios observed in well samples plotted relative to the arrival of the peak.

The breakthrough curves of excess ³He and SF₆ were very similar at El Rio #5 and #6, showing simultaneous first detections and nearly simultaneous maxima (Figure 4). At El Rio #6, the local concentration minimum (day 18) was seen on both breakthrough curves. Apparently, this well was drawing in a greater fraction of untagged water from the September recharge event or a greater fraction of deeper old groundwater at this time. The arrivals of peak concentrations were not coincident; at El Rio #6, SF₆ arrived one sample prior to ³He (6 days earlier), while at El Rio #5, ³He arrived one sample prior to SF₆ (14 days earlier). Because the observed maxima did not necessarily occur at the time of the maximum groundwater concentration (i.e., we sampled the shoulders of the peak), the difference in the arrival times may not be significant. Furthermore, the samples were collected at different times (about 15 min apart), and the wells may have been drawing in a slightly different percentage of relatively deep (untagged) and shallow (tagged) groundwater due to their long screen intervals. Within the experimental uncertainties, SF₆ and ³He maxima occurred simultaneously.

The ratio of excess ³He/SF₆ was a maximum during the peak arrivals. Ignoring the peak interval, the ratio decreased with time reaching a minimum at the end of the observation period (Figure 5). There is an excess of SF₆ on the falling limb.

Dissolved Noble Gases. Dissolved noble gas (He, Ne, Ar, Kr, and Xe) concentrations in Pond 2 were in equilibrium with the atmosphere assuming a water temperature of ~17.5 °C (the pond temperature was not measured). Relative to the pond water, all five gases were enriched in the groundwater samples. This enrichment is due to the dissolution of trapped air and is commonly referred to as excess air (22). Average excesses (defined here as $([X]_{\text{measured}}/[X]_{\text{equilibrium}} - 1)$) were for He, 153 ± 27%; Ne, 130 ± 26%; Ar, 42 ± 10%; Kr, 22 ± 5%; and Xe, 10 ± 4%. The ratio of the noble gases in the excess air is not identical to that of the atmosphere assuming a constant recharge temperature (Figure 6). If the trapped air bubbles completely dissolved, then the ratio of the noble gases would be the same as the atmosphere. Thus, the excess air is formed by the partial dissolution of the air bubbles (23). The amount of excess air as measured by the excess Ne concentration varied with time but not in a linear fashion. In contrast, the Xe concentration, which is more strongly dependent on temperature than excess air, increased from $\sim 1.1 \times 10^{-9}$ to $\sim 1.3 \times 10^{-9}$ cm³ STP g⁻¹ during the measurement period. This change in concentration is equivalent to ~5 °C decrease in temperature, assuming that the amount of excess air remained constant.

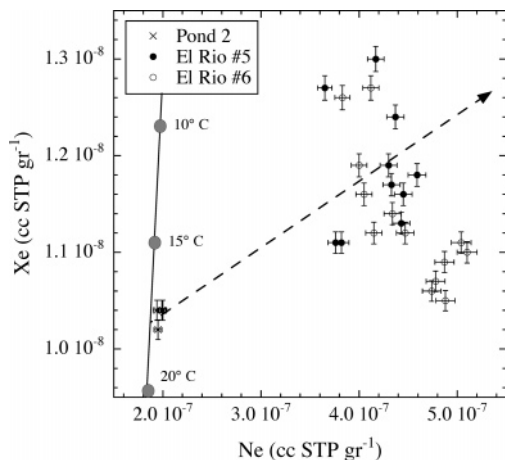


FIGURE 6. Ne and Xe concentrations in Pond 2 and groundwater samples. The nearly vertical line shows atmospheric equilibrium concentrations at different temperatures, and the dashed arrow shows the increase in concentration caused by excess air formations assuming complete bubble dissolution.

Discussion

The water balance and, thus, groundwater flow beneath the El Rio spreading grounds is forced strongly by artificial recharge and groundwater production. At the monitoring well that is located next to Pond 1 (Figure 1), static groundwater levels show a rapid response to recharge at the spreading ponds (Figure 2). This high correlation indicates very fast recharge velocities. In the absence of artificial recharge, water levels fall due to groundwater production and the dissipation of the recharge mound. Analysis of the tracer data from all of the production wells during the 18 month study indicates that the tracer plume remained very close to its point of entry, and more than half of the recharged SF₆ was recovered from wells within the spreading grounds. SF₆ was observed at El Rio #5 and #6 continuously after its initial appearance for over a year. At the more distant wells, SF₆ was detected episodically in response to groundwater production and artificial recharge. Despite the mounding that occurred during recharge events, the tracer plume was unable to move away from the spreading grounds because of the regional cone of depression and the pumping at the production wells. The very complicated local groundwater flow system must be considered when interpreting the tracer breakthrough curves at El Rio #5 and #6.

The noble gas data clearly show that the infiltrating recharge water exchanged gases with trapped air, which was pressurized above atmospheric, at the El Rio spreading grounds. As measured by the Ne excess, the amount of excess air formed here (Ne excess > 100%) is larger than generally observed under conditions of natural recharge (Ne excess < 50%; refs 24 and 25), indicating excess air may prove to be a good tracer of artificial recharge water from spreading basins. Ne excesses as large or larger than observed below the El Rio spreading grounds have been found in a few aquifers away from spreading ponds, most notably in the Stampriet aquifer, Namibia (26). The increase in the Xe concentration observed during the first 200 days of the experiment reflects the migration of cooler water that recharged after the tracer injection during the winter and spring.

During excess air formation, oxygen and other components of air will dissolve along with the noble gases, and therefore, the recharge process will also increase their concentrations above equilibrium values. In terms of solubility and diffusion rate, the noble gas most similar to oxygen is Ar. Groundwater Ar concentrations were 142 ± 10% of

TABLE 1. Fraction at Equilibrium Partitioned into Air Volume and Retardation Coefficients Calculated for SF₆ and He at 17.5 °C with Differing Amounts of Trapped Air^a

	air fraction ($V_{\text{air}}/(V_{\text{water}} + V_{\text{air}})$)					
	0.005	0.01	0.02	0.05	0.10	0.20
$[\text{SF}_6]_{\text{air}}/[\text{SF}_6]_{\text{total}}$	0.43	0.60	0.75	0.89	0.94	0.97
$[\text{He}]_{\text{air}}/[\text{He}]_{\text{total}}$	0.32	0.49	0.66	0.83	0.91	0.96
R_{SF_6}	1.7	2.4	3.9	8.5	17	36
R_{He}	1.5	2.0	2.9	6.0	11	25

^a In the calculations, H_{SF_6} and H_{He} were 143 and 95, respectively (9). The retardation coefficients were calculated with the equilibrium model of Fry et al. (9) using eq 1.

saturation. Dissolved oxygen concentrations should have increased by a similar amount, demonstrating the importance of excess air formation on the biogeochemistry near sites of artificial recharge by surface percolation.

Each liter of groundwater contained more than 10 cm³ of excess air. During the September recharge event, ~3 × 10⁶ m³ of surface water was recharged from Pond 2; thus, more than 3 × 10⁷ L of air was dissolved during excess air formation. The source of this air was the unsaturated zone below the pond. Assuming a porosity of 33% and a 12 m thick unsaturated zone, air from more than 25% of the pore volume dissolved. Hence, the amount of trapped air was significantly reduced during the recharge event. The tracer experiment was conducted at the end of the September recharge event when the amount of trapped air was at its minimum.

How trapped air will affect the arrival times of gas tracers at wells depends on the Henry's Law coefficient, the amount of trapped air, and the duration of the tracer injection. Both SF₆ and He have high Henry's Law coefficients, respectively, 143 and 95 at 17.5 °C (9), and partition strongly into the air. At equilibrium, approximately 60% of the mass of SF₆ and 50% of the He will partition into the gas phase when the pore space contains only 1% air (Table 1). At 5% air, 88 and 83% of these gases will partition into the air volume. Retardation coefficients calculated using eq 1, the equilibrium model of Fry et al. (9), are greater for SF₆ than for He and exceed 2 when the amount of trapped air is greater than ~1% of the pore volume (Table 1).

Breakthrough curves at both El Rio #5 and #6 indicates that the two gas tracers were traveling at approximately the same rate; SF₆ was not traveling 30–50% slower (see Table 1) than ³He as expected if retardation by trapped air was operating uniformly along the flow path. However, trapped air is only expected above the water table, and hence, for most of the distance, the gas tracers were transported through saturated material where these tracers are not retarded (8, 10, 18, 19). At El Rio #6 where vertical flow dominates, the infiltrating water traveled ~12 m through the unsaturated zone to the water table (as recorded at the monitoring well and El Rio #7) and then ~38 m through saturated media to the top of the screen. The average recharge rate in Pond 2 was ~4 m day⁻¹. Assuming a porosity of 33%, the vertical velocity and travel time in the unsaturated zone was ~12 m day⁻¹ and ~1 day, respectively. These estimated values are maxima because the depth to the water table in the middle of the pond could have been less than observed at the monitoring well and El Rio #7. In fact, saturated columns could exist below the pond. Thus, the travel time to the water table may have been less than a day.

Because El Rio #5 and #6 have relatively long screens that begin significantly below the water table, interpretation of the arrival times (initial and peak) is difficult. Furthermore, plug flow, as observed during laboratory column experiments, does not exist below the spreading grounds. Nevertheless, transport times of the peak and plume front were short. The

tracer first arrived to El Rio #6 between days 3 and 5, implying that the front of the tracer plume was moving at a rate greater than 10 m day^{-1} , comparable to the infiltration rate. The concentration peaked after ~ 24 days. Because the vertical velocity below the table water should be less than the infiltration rate due to horizontal spreading and because the mixing portions of tagged and untagged water produced by the well should change as the plume migrates to deeper depths, it is not possible to directly relate the peak arrival to the infiltration rate and retardation. Therefore, the relative arrival times of SF_6 and ^3He and the shapes of the breakthrough curves must be used. The decrease in the ratio (Figure 5) indicates that trapped air is presented and is affecting the transport of the gas tracers. The very early first arrival and long tail suggests that nonequilibrium gas transfer is occurring between the percolating water and the trapped air. However, the nonideal transport of the tracers below the water table, the mixing of different aged water within the production well, and rating limiting gas transfer into the trapped air make it difficult to quantify the amount of trapped air.

As is evident by the large fraction of SF_6 recovered at the production wells, the bulk of the gas tracer dissolved in the pond was transferred across the water table. Loss of tracer to the gas phase was small despite the very high Henry's Law coefficients of SF_6 and He. Further evidence for little transfer out of solution comes from the maximum concentration at El Rio #6. Despite the potential for mixing between tagged and untagged water within this well, the maximum SF_6 concentration was 25–33% of the pond concentration. The very large reduction in gas concentration observed during laboratory column experiments with trapped air volumes greater than a few percent (e.g., ref 10) was not observed during the El Rio field experiment. Both of these lines of evidence suggest that the trapped air volume was small.

At the Sandy Hollow Reservoir experimental recharge basin, Heilweil et al. (12) observed that the transport of He gas was significantly (an order of magnitude) slower than bromide. They also observed significant He loss during percolation. Relative to the Br maximum, maximum He concentrations were on the order of 100 times lower in the groundwater than in the recharge basin, and the total recovery of He was very low. In this site, Heilweil et al. (12) determined the trapped air fraction of the pore space to be between 7 and 26%. Their experiment was conducted 1 month after the first wetting of an experimental infiltration pond when the mean infiltration rate was about 0.05 m/day and the depth to water was about 20 m. The fate of the gas tracers was very different at the Sandy Hollow Reservoir and the El Rio recharge sites.

The excess air volumes determined with the noble gas data indicate that a significant fraction of the trapped air ($>25\%$ of the total pore space) dissolved during the 5 week long recharge event. The effect of trapped air on the transport of gases decrease with time as the air volume dissolved into the recharging water. Hence, tracer experiments performed early in the recharge event should show more retardation than those performed later.

Implications for Tracing Recharge Water. The dual gas tracer experiment results indicate that gas tracers were not slowed significantly during transit through the unsaturated zone to the water table. The very high infiltration rate, moderately deep water table, and noninstantaneous gas exchange between the percolating water and trapped air at the El Rio spreading grounds limited the effects of retardation and loss of tracer from solution. In other settings with deeper water tables and slower recharge rates, the effects of trapped air on gas tracers could be much greater as shown by Heilweil et al. (12). Another factor that needs to be considered is how long and maybe how frequently recharge occurs. Excess air formation is an important process that lowers the amount

of trapped air. The techniques established by Gamlin et al. (6) and Clark et al. (7) for determining travel times between recharge locations and wells with gas tracers are reliable at recharge sites with relatively high infiltration rates. Thus, gas tracer experiments can be used during the permitting procedure where a minimum travel time needs to be established to meet drinking water regulations.

Acknowledgments

We thank Tony Blankenship for assisting in the field. Steve Bachman and Daniel Detmer provided valuable information and data about the operations of the El Rio Spreading Grounds. We thank three anonymous reviewers for their helpful and careful reviews. This work was supported by the United Water Conservation District, the Water Resources Center of the University of California (W-962), and the University Collaborative Research Program at Lawrence Livermore National Laboratory (03-GS-024). This is contribution 0682 of the Institute for Crustal Studies at the University of California, Santa Barbara.

Literature Cited

- Dillion, P. J. *Management of Aquifer Recharge for Sustainability*; Balkema Publishers: Exton, PA, 2003.
- Schwarzenbach, R. P.; Giger, W.; Hoehn, E.; Schnelder, J. K. Behavior of organic compounds during infiltration of river water to groundwater. Field studies. *Environ. Sci. Technol.* **1983**, *17*, 472–479.
- Fox, P.; Narayanaswamy, K.; Genz, A.; Drewes, J. E. Water quality transformations during soil aquifer treatment at the Mesa Northwest Water Reclamation Plant, USA. *Water Sci. Technol.* **2001**, *43*, 343–350.
- Tufenkji, N.; Ryan, J. N.; Elimelech, M. Bank filtration. *Environ. Sci. Technol.* **2002**, *36*, 423A–428A.
- Drewes, J. E.; Heberer, T.; Rauch, T.; Reddersen, K. Fate of pharmaceuticals during groundwater recharge. *Ground Water Monit. Rem.* **23** (3), 64–72.
- Gamlin, J. D.; Clark, J. F.; Woodside, G.; Herndon, R. Large-scale tracing of groundwater with sulfur hexafluoride. *J. Environ. Eng.* **2001**, *121*, 171–174.
- Clark, J. F.; Hudson, G. B.; Davisson, M. L.; Woodside, G.; Herndon, R. Geochemical imaging of flow near an artificial recharge facility, Orange County, CA. *Ground Water* **2004**, *42*, 167–174.
- Gupta, S. K.; Lau, L. S.; Moravcik, P. S. Groundwater tracing with injected helium. *Ground Water* **1994**, *32*, 96–102.
- Fry, V. A.; Istok, J. D.; Semprini, L.; O'Reilly, K. T.; Buscheck, T. E. Retardation of dissolved oxygen due to a trapped gas phase in porous media. *Ground Water* **1995**, *33*, 391–398.
- Vulava, V. M.; Perry, E. B.; Romanek, C. S.; Seaman, J. C. Dissolved gases as partitioning tracers for determination of hydrogeological parameters. *Environ. Sci. Technol.* **2002**, *36*, 254–262.
- Donaldson, J. H.; Istok, J. D.; O'Reilly, K. T. Development and testing of a kinetic model for oxygen transport in porous media in the presence of trapped gas. *Ground Water* **1997**, *35*, 270–279.
- Heilweil, V. M.; Solomon, D. K.; Perkins, K. S.; Ellet, K. M. Gas-partitioning tracer test to quantify trapped air during recharge. *Ground Water* **2004**, *42*, 589–600.
- Clark, J. F. Defining transport near ASR operations using sulfur hexafluoride gas tracer experiments. In *Management of Aquifer Recharge for Sustainability*; Dillon, P. J., Ed.; Balkema Publishers: Exton, PA, 2002; pp 257–260.
- Watson, A. J.; Upstill-Goddard, R. C.; Liss, P. S. Air–sea exchange in rough and stormy sea measured by a dual tracer technique. *Nature* **1991**, *349*, 145–147.
- Wanninkhof, R.; Asher, W.; Weppernig, R.; Chen, H.; Schlosser, P.; Langdon, C.; Sambrotto, R. Gas transport experiment on Georges Bank using two volatile deliberate tracers. *J. Geophys. Res.* **1993**, *98*, 20,237–20,248.
- Clark, J. F.; Wanninkhof, R.; Schlosser, P.; Simpson, H. J. Gas exchange rates in the tidal Hudson river using a dual tracer technique. *Tellus* **1994**, *46B*, 274–285.
- Clark, J. F.; Schlosser, P.; Stute, M.; Simpson, H. J. SF_6 – ^3He tracer release experiment: A new method of determining longitudinal dispersion coefficients in large rivers. *Environ. Sci. Technol.* **1996**, *30*, 1527–1532.

- (18) Carter, R. C.; Kaufman, W. J.; Orlob, G. T.; Todd, D. K. Helium as a groundwater tracer. *J. Geophys. Res.* **1959**, *64*, 2433–2439.
- (19) Wilson, R. D.; Mackay, D. M. SF₆ as a conservative tracer in saturated media with high intragranular porosity or high organic carbon content. *Ground Water* **1996**, *34*, 241–249.
- (20) Hanson, R. T.; Martin, P.; Koczot, K. M. Simulation of groundwater/surface water flow in the Santa Clara-Calleguas basin, Ventura County, CA. United States Geological Survey Water Resources Investigation Report 02-4136, 2003; p 157.
- (21) United Water Conservation District. *Surface and Groundwater Conditions Report, Water Year 2000 Supplement*; 2001, p 60.
- (22) Heaton, T. H. E.; Vogel, J. C. Excess air in groundwater. *J. Hydrol.* **1981**, *50*, 201–216.
- (23) Aeschbach-Hertig, W.; Peeters, F.; Beyerle, U.; Kipfer R. Palaeotemperature reconstruction from noble gases in groundwater taking into account equilibration with entrapped air. *Nature* **2000**, *405*, 1040–1044.
- (24) Wilson, G. B.; McNeill, G. W. Noble gas recharge temperatures and the excess air component. *Appl. Geochem.* **1997**, *12*, 747–762.
- (25) Stute, M.; Schlosser, P. Atmospheric noble gases. In *Environmental tracers in Subsurface Hydrology*; Cook, P., Herczeg, A. L., Eds.; Kluwer: Boston, 2000; pp 349–377.
- (26) Stute, M.; Talma, S. Glacial temperatures and moisture transport regimes reconstructed from noble gases and ¹⁸O, Stampriet aquifer, Namibia. In *Isotope Techniques in Studying Past and Current Environmental Changes in the Hydrosphere and the Atmosphere*; IAEA: Vienna, 1998; pp 307–318.

Received for review June 22, 2004. Revised manuscript received March 13, 2005. Accepted March 21, 2005.

ES049053X