Title
Nature of Flow and Gas Dynamics Below Spreading Ponds

Authors
Clark, Jordan F
Avisar, Dror
Hudson, G. Bryant

Publication Date
2005-08-01

Nature of Flow and Gas Dynamics Below Spreading Ponds

By

Jordan F. Clark

Dror Avisar

Department of Geology
University of California
Santa Barbara, CA 93106

G. Bryant Hudson

Chemical Biology and Nuclear Science Division
Lawrence Livermore National Laboratory
Livermore, CA 94550

TECHNICAL COMPLETION REPORT

Project Number UCAL-WRC-W-962

August, 2005

University of California Water Resources Center

The research leading to this report was partially supported by the University of California Water Resources Center

Nature of Flow and Gas Dynamics Below Spreading Ponds

Jordan F. Clark, Dror Avisar, G. Bryant Hudson

Abstract

The El Rio Spreading Grounds, an area of artificial recharge, lies within a regional groundwater depression. It consists of ten small ponds surrounded by eight production wells. A deliberate tracer experiment using sulfur hexafluoride (SF_6) and an isotope of helium (^3He) was conducted to determine groundwater flow. The tracer was continuously injected into one pond for one week prior to a ~50 day period of no recharge. At the time of the experiment, the artificial recharge rate through the highly permeable alluvial sediments which underlie the ponds was ~4 m day^{-1} and the water table was ~12 m below the ground surface. Tracer breakthrough curves from the production wells indicate that the plume remained near (within 500 m) the injection site during the 18 month experiment. Its movement was influenced by a number of factors. First, variable groundwater production in the production wells cause frequent changes in the water level, and thus, rates and direction of the plume flow respond to local groundwater cones of depression. Second, additional recharge events, which were free of tracer, create groundwater mounds that block the transport of the tracer to specific production wells. Noble gas concentrations in the groundwater were much higher than in the pond due to the dissolution of trapped air. However, significant retardation (absolute and relative) of the gas tracers was not detected. Breakthrough curves of SF_6 and ^3He at two nearby production wells (within ~10 m of the pond) were very similar and suggest that nonequilibrium gas transfer was occurring between the percolating water and 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 potential dilution caused by mixing within the production well, the maximum concentration observed at this well was ~33% of the mean pond concentration. More than 50% of the SF_6 recharged was recovered by the production wells during this 18 month experiment. The experiment demonstrates 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

Artificial recharge is one of the most important recent developments for managing potable water supplies in California and elsewhere around the word (e.g., Dillion, 2003). It is also used for combating seawater intrusion in some coastal areas such as Los Angeles and Orange Counties. The practice consists of recharging surplus runoff, imported surface water, or recycled wastewater into groundwater aquifers. This is achieved by using injection wells or by enhancing the recharge rate at specially designed facilities such as spreading ponds. The latter are typically small basins that are periodically drained and scraped of clogging material to ensure rapid infiltration. After residing in the subsurface for a period of time, which can be as short as a few days, the recharged water becomes a part of the basin's water supply and can be extracted at municipal, irrigation, or domestic wells.

A common design used in artificial recharge places production wells next to the spreading ponds. This design works well when the main goal is to exploit the recently recharged water without significant dilution with the native groundwater. The water balance near this type of facility is controlled by the relative amounts of recharge and production. In a case of higher long-term well production than recharge, a regional cone of depression will occur trapping the recharged water near the spreading ponds and drawing the native groundwater to the wells. A mound will develop when long-term recharge exceeds production. Because both recharge and production are often seasonal and out of phase, groundwater levels usually fluctuate dramatically near this type of facility with local mounding occurring during parts of the year and a cone depression occurring at other times.

By surrounding spreading ponds with production wells, the travel distance and, consequently, the residence time of the recharged water in the subsurface are often very short. Because of these features, this type of artificial recharge facility has many similarities with river bank filtration, a common practice used in western Europe (Tufenkji et al., 2002). Numerous field studies of river bank filtration have shown that water quality general improves during transit through the groundwater aquifer even when the flow distance is less than 100 m (Schwarzenbach et al 1983; Alain et al 1993; Hiscock and Grischeck, 2002; Tufenkji et al., 2002). Similar improvements in water quality have also been observed down gradient from spreading ponds (Fox et al. 2001; Fox, 2002; Drewes et al. 2002).

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. Documentation of *in situ* biogeochemical processes (water quality changes) that occur requires establishing hydraulic connections between the artificial recharge site and down gradient wells. Moreover, it is important to know where (i.e., beneath the spreading area, within the unsaturated zone, along the flow path) the biogeochemical transformations are occurring. Thus, knowledge about groundwater velocities and hydraulic connections are essential for evaluating the potential transport of contaminants through the aquifer to wells.

A fundamental approach for determining groundwater flow relies on geochemical tracer techniques. Long-term transport can be established using geochemical dating techniques such as the tritium/^{3}He method (Schlosser et al., 1988; Shapiro et al., 1999; Clark et al., 2004). However, because of the typical uncertainty associated with geochemical dating techniques (±2 years), these methods are not well suited for examining short term transport. Recently, Gamlin et al (2001) and Clark et al. (2004) developed methods using gas tracers for the direct determination of travel times between recharge areas and wells over the time period of 0 to 5 years. In order 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 ($>10^{6}$ m^{3}) at a sufficient concentration to allow quantification after at least a 1000:1 dilution. Furthermore, the tracers needed to be non-reactive and their movement not slowed by sorption processes (retardation) within the aquifer. Two gas tracers, sulfur hexafluoride (SF_6) and isotopes of xenon (^{124}Xe, ^{129}Xe, and ^{136}Xe), were found to satisfy these conditions.

During recharge at spreading ponds, surface water infiltrates into the ground and flows through a vadose zone prior to reaching the water table. The vadose zone is composed of three principle phases: soil, water, and soil air. In this zone, gas transfer between the 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 SF_6 and noble gas isotopes, the tracers will be initially lost from the percolating water to the soil air. This loss will continue until sufficient tracer has transferred to the soil air and the solubility equilibrium is reached. Once this happens, the gas tracers will be transported through the vadose 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, the

Henry's Law coefficient, and the 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 eventually become less than the equilibrium value (once the gases are no longer added to the surface water). When this occurs, the gas tracers will transfer from the soil air to the percolating water. Therefore, the expected gas transfer and partitioning between the infiltrating water and soil air will act to retard (slow) the movement of the gas relative to the water through the vadose zone. This retardation has been demonstrated for a number of gases in laboratory experiments (Gupta et al., 1994; Fry et al. 1995; Vulava et al., 2002).

Fry et al. (1995) 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:

$$R = 1 + H\,(V_{air}/V_{water}) \qquad (1)$$

In formulating this relationship, Fry et al. (1995) assumed that gas transfer was sufficiently fast to maintain an equilibrium between the trapped gas and flowing groundwater. Their equation predicts that the transport of most gases will be retarded in 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 $V_{air}/V_{water} > 0.04$. Equation (1) accurately predicts retardation factors determined during laboratory column experiments at low V_{air}/V_{water} ratios, but under predicted retardation at high V_{air}/V_{water} ratios (Fry et al., 1995; Vulava et al., 2002). Kinetic models that included diffusion controlled gas transfer do a much better job matching laboratory experiments at high V_{air}/V_{water} ratios (Donaldson et al., 1997; Vulava et al., 2002). The effect of non-instantaneous gas exchange was to increase the retardation factor. Therefore equation (1) calculates minimum retardation coefficients.

A surprising result of the initial SF_6 and Xe isotope gas tracer experiments performed at artificial recharge facilities in Orange County, CA, was the observation that the gas tracers were transported through the vadose zone to the water table without significant loss or retardation (Gamlin et al., 2001; Clark et al., 2004). Clark et al. (2004) postulated that the absence of retardation indicates that the gas tracers were infiltrating primarily through saturated pathways

contained within the vadose zone. This observation is not universal; significant retardation or loss of gas tracer has been observed elsewhere (Clark et al., 2002; Heilweil et al., 2004).

Here, we present results from a dual gas tracer experiment using SF_6 and an isotope of helium, ^3He, designed to examine gas transport through the vadose 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 (Watson et al., 1991; Wanninkhof et al., 1993; Clark et al., 1994). More recently, Vulava et al. (2002) 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. SF_6 and ^3He were chosen as tracers because they are conservative, not retarded in saturated porous media (Carter et al., 1959; Gupta et al., 1994; Wilson and Mackay, 1996), and have Henry's Law coefficients that differ by about 50%.

Study Location

The El Rio Spreading Grounds are located near Oxnard, CA and are managed by the United Water Conservation District (UWCD). This public agency supplies high quality water for both agriculture and municipal uses. The district encompasses about 87,00 hectares of central Ventura County, CA and manages the groundwater supply contained in the Santa Clara-Calleguas Hydrologic unit. In order to maintain a high-quality groundwater supply, UWCD has implemented a number of management practices including artificial recharge, which began in the 1920s.

The hydrology of the Santa Clara-Calleguas hydrological unit was recently examined in detailed by Hanson et al (2003) as a part of the US Geological Survey RASA program. This study determined that natural groundwater recharge occurs primarily through infiltration of stream flow within the major rivers and numerous arroyos that drain the mountain fronts of the basin. Direct recharge of precipitation on bedrock outcrops and the valley floor contribute a lesser amount. For the period 1984-93, natural recharged averaged about 140 MCM/yr (1 MCM = $1x10^6$ m^3). Artificial recharge at the three spreading grounds (El Rio, Saticoy and Piru) and irrigation return flow contribute together about the same amount of water to the groundwater

system. During the years of 1984-93, artificial recharge and irrigation return flow averaged about 70 MCM/yr and 63 MCM/yr, respectively.

The gas tracer experiment was preformed in the El Rio Spreading Grounds (Figure1), which have a maximum wetted surface area of 40 hectares (UWCD, 2001). The percolation rate, which averages about 4 m^3/s, varies significantly. It is at a maximum in recently cleaned ponds and decrease with usage as the pond bottom becomes clogged. The facility consists of ten ponds (Figure1)**.** Pond 1 is used as a desilting basin, and thus has a very low percolation rate. Pond 9 is closed and will be used in the potable supply system as a storage reservoir of chlorinated water. The other eight ponds are scrapped periodically to ensure rapid infiltration. During the 1990s, about 40 MCM was recharge annually from the El Rio Spreading Grounds (UWCD, 2001). The source of the recharge water was primarily diverted seasonal run-off from the Santa Clara River and released stored water from Lake Piru, a reservoir located to northeast of the spreading grounds.

The El Rio Spreading Grounds are located towards the down gradient end of the Santa Clara River watershed where the groundwater basin expands forming the permeable alluvial deposits of the Oxnard Plain. The upper aquifer (late Pleistocene and Holocene age) system is composed of discontinuous layers of gravel, sands, and silts (Hanson et al. 2003), generally found at a depth of approximately 30 to 70 m below the surface of the land. The absence of low-permeability confining layers between surface recharge sources and the underlying aquifer allows effective recharge of the basin. As a result, this aquifer system is the main source of recharge to the Oxnard Plain (UWCD, 2000).

The spreading basins are surrounded by nine production wells (Figure 1). Due to intensive pumping at these wells, a regional groundwater depression is found in the vicinity of the ponds (Figure 2). As a result, groundwater flow is towards the spreading grounds. Within the spreading area, much steeper cones of depressions can form around each well during periods of intense pumping and mounding beneath the ponds occur during recharge events. 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 very complex pattern of flow beneath the El Rio Spreading Grounds.

Methods

In September 2002, about 24 MCM of water was released from Lake Piru down Piru Creek and into the Santa Clara River. A portion of this water was diverted into the El Rio Spreading Grounds (about 6 MCM), flooding Ponds 2 and 3 for almost five weeks between 7-Sept-02 and 8-Oct-02 (Figure 3). Except for a two weeks period in August when deep groundwater was released into Pond 2, the spreading area had been essentially dry for more than 6 months prior to the release.

During the September recharge event, the water depth in both Pond 2 and 3 was initially less than 0.3 m, despite the very high influx of surface water, 1.3 m^3/s (Figure 3), demonstrating the very high percolation rates of these ponds. After about two weeks**,** the water level in Pond 2 rose in response to the increasing flow into the spreading area and a water depth of about1.2 m was maintained for the tracer experiment.

For a period of eight days (27-Sept to 4-Oct, 2002), a gas mixture containing SF_6 (~0.9 m^3) and ^3He (~0.001 m^3) was injected into Pond 2 by bubbling through a diffusion stone that was placed in a water depth of about 1.2 m. During this time, the average percolation rate of surface water into the ground was 1.8 m^3/s or 4 m/day (vertical velocity), significantly higher than the average because little recharge had occurred since the last cleaning. The mean residence time of water in the pond was about 0.3 day. While the tracer injection was in progress, an additional 1.7 m^3/s was percolating into the ground from Pond 3.

The release point of SF_6 in Pond 2 was close to the inlet pipe (~10 m offshore) but away from the "white water" (to minimize the gas lost), which was observed immediately downstream from the pipe (Figure 4, 5). The injection rate was maintained using a battery operated switcher valve (an 8-port, 2-way valve) set to release about 1.5 cc STP of the gas mixture per min. Approximately 17 liters (105 gr) of SF_6 was injected into the pond during this experiment.

Pond samples for SF_6 analysis were collected every two days, ~10 cm below the surface in 15 ml Vacutainers at eleven designated locations during the injection period (Figure 4). 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 also collected in 15 ml Vacutainers prior to, during, and after the tracer injection from eight production wells located in the spreading grounds (Figure 1). The production wells have

relatively long screened intervals that ranged between 40 and 70 m in length and, with the exception of El Rio #11, they were located within 600 m from Pond 2. During the first 3 months, groundwater samples were collected every 3 to 7 days. Monthly samples were collected for the next nine months. Thereafter, samples were collected every two months.

All of the SF_6 samples were analyzed on a gas chromatograph (GC) using the head-space method described by Clark et al. (2004). SF_6 was separated from other gases with a Molecular Sieve 5a column held at room temperatures. The GC detector response was calibrated about every 10 samples with standards (~148 pptv, ~524 pptv and ~1947 pptv) prepared by Scott-Marrin Inc. (Riverside, CA, (909) 653-6780). The precision and detection limits of this method were ±5% and 0.04 pmol l^{-1}, respectively.

^{3}He samples were collected only at three stations within the pond (5, 6, and 7) and from only two wells (El Rio #5, #6). These samples were collected in 3/8 inch 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 ^{3}He/^{4}He isotope ratio and the concentrations of ^{4}He 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 ^{3}He/^{4}He isotope ratio, the ^{4}He, Ne, and Ar concentration, and the Kr and Xe concentration measurements were ±0.5%, ±1%, and ±2%, respectively.

Results

Water Balance

During the 18-month study, about 47 MCM of water was recharged during four distinct periods at the El Rio Spreading Grounds (Figure 3). During the first period, which resulted from the managed release of surface water from Lake Piru, only Pond 2 and 3 were wet and the tracer experiment was begun. The second period of recharge coincided with the start of the seasonal precipitation. Sufficient runoff was produced by the middle of November 2002 (day 55[1]) to divert significant volumes of water into El Rio. During the next seven months, approximately 33 MCM of surplus runoff was artificially recharged from six of the eight ponds. The wetting

[1] Time in days is report from the start of the tracer inject on 27-Sept-02.

history for each pond differed. After a dry summer, recharge began once again on day 351, following a second release from Lake Piru. The final period of recharge was initiated by the return of the seasonal precipitation on day 402.

During the first 250 days (8 months) of the study, El Rio #2, #3, #5, #6, and #11 were usually operated at least 15 hours per day whereas El Rio #4, #7, #8, and #15 were rarely on. Total groundwater production average 0.60 m^3/s and 13 MCM were pumped. El Rio #4 was closed due to equipment problems for 10 months between day 21 and 345 (18 Oct 02 to 7 Sept 03). After day 250 (4 June 03), El Rio #7, #8 and #15 were operated 20-24 hours per day and production at well #3 decreased significantly (Table 2). El Rio #2, #5, #6, and #11 were still pumped heavily. The average pumping rate was slightly higher, 0.63 m^3/s, and 12 MCM were produced.

The water balance below the El Rio Spreading Grounds depends on two major components: artificial recharge and groundwater production. At the monitoring well which is located next to Pond 1 (Figure 1), static groundwater levels show a rapid response to recharge at the spreading ponds. 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 the 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 three months prior to and during the September recharge event. Hence, water level measurements at these times were not affected by local pumping. The high correlation between recharge and water table rise indicates very fast recharge velocities. In the absence of artificial recharge, water levels slowly dropped due to groundwater production and the dissipation of the recharge mound. Although not shown at the monitoring well, large local cones of depression form near actively pumped production wells. The size and duration of these cones is highly variable and depends on the rate of production.

SF_6 Input Function

During the injection period, SF_6 concentrations within Pond 2 ranged between 0 and 286 pmol/l (1 pmol/l = 10^{-12} mol/l). Although the pond was never well mixed, the distribution of SF_6

did exhibit a consisted pattern defined by the pond's circulation, location of the diffusion stone (injection point), and gas lost across the air-water interface (Figure 4). The highest concentrations were found towards the northwestern end of the pond at stations 3, 4, 6, 7, 10, and 11. Station 5, which was the closest to the injection point, showed the highest variability. At stations 2, 8, and 9, SF_6 concentrations were generally below 5 pmol/l at stations and the tracer was never detected at station 1. These four stations were located at the southeastern end of the pond to both sides of the injection point and apparently received mostly water that was not tagged with the gas tracers.

The mean concentration of SF_6 in the pond, about 32 pmol/l, remained relatively constant during the injection period. Similarly, the mean concentration at the northwestern end, about 41 pmol/l, was also relatively constant. Based on the mean concentration, the mean percolation rate, and the length of time of the injection period, approximately 0.033 moles (4.8 gr) of SF_6 were transported to the subsurface by the recharging water. This is <5% of the total amount released. Thus, most of the tracer was lost to the atmosphere, demonstrating the inefficiency of bubbling SF_6 into shallow water bodies. Gamlin et al. (2001) reported similar losses during the Orange County tracer experiment. A day after the injection was stopped, the concentration of SF_6 decreased to <0.1 pmol/l. This decrease is consistent with the very short resistance time of water within the pond.

Tracer Breakthrough Curves

By monitoring tracer concentration at wells, initial and peak travel times can be determined from the breakthrough curves (Figure 6,7). The initial arrival time represents the fastest flow paths between the well and where the tracer was introduced (Pond 2). At narrow screened monitoring wells, the arrival time of the peak concentration represents the mean travel time of the tracer patch and can be used to calculate groundwater velocities. However, during this experiment only production wells were available. Because these wells draw water in from along the entire length of the screen and can dilute the patch concentrations by an unknown amount (by drawing in untagged groundwater), velocities determined with peak concentrations do not necessarily represent the mean groundwater velocity.

Tracer was first observed at El Rio #6, five days after the start of the injection period and maximum concentrations were observed about two weeks later (Figure 6a). El Rio #6 is located

within 10 m of Pond 2 near its northwestern corner (the high concentration end) and is screened between 50 m 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 SF_6 was 10 m day^{-1}. At its maximum, 10.6 pmol l^{-1}, the groundwater SF_6 concentration was ~25% of the mean concentration in the high concentration end and ~33% of the mean concentration for the entire pond.

The second well to receive 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 m to 90 m below ground surface) as El Rio #6. SF_6 was first detected on day 17 and the concentration reached a maximum on day 82 (Figure 6b). 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 SF_6 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 10s of meters from were 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.

Following the initial detections, tracer has been observed in all samples collect from El Rio #6 and #5. Tracer concentration in both wells decreased nearly exponentially after peaking (Figure 6). This gradual decrease can be explained by the local water balance. Untagged water that was recharged after the tracer injection (especially from Pond 2) acted to push the tagged water away from these two wells and to deeper depths of the aquifer. Counteracting this was groundwater production that would draw the tagged water towards these wells.

The amount of SF_6 recovered at each well can be calculated from the daily pumping rates and concentrations, interpolated between measurement days. At El Rio #6, approximately 18% of the total amount of SF_6 that entered the ground was recovered. Slightly more, approximately 22%, was recovered at El Rio #5. Thus, 40% of the tracer contained in the recharge water was produced at essentially the same location as where it infiltrated into the ground.

The very long period of detection and the very high recovery rates indicates that the tagged groundwater remained nearby these wells during the study period despite the large amount of

artificial recharge that occurred during the winter and spring. The regional cone of depressions that surrounds the El Rio Spreading Grounds and groundwater extraction at the eight production wells prevented the tracer from being transported away from the spreading grounds.

The breakthrough curves of excess ^3He and SF_6 were very similar at El Rio #5 and #6, showing simultaneous first detections and nearly simultaneous maxima (Figure 6). At El Rio #6, the local concentration minimum observed during the second week 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, SF_6 arrived one sample prior to ^3He (6 days earlier) while at El Rio #5, ^3He arrived one sample prior to SF_6 (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 time (about 15 minutes 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, SF_6 and ^3He maxima occurred simultaneously.

The ratio of excess $^3He/SF_6$ 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. There is a slight excess of SF_6 on the falling limb.

At the more distant wells (#2, #3, #7, #8, and #15), the tracer appeared at different times and concentrations. It was not detected at El Rio #11 during the 18-month long experiment. Recharge rates, location, and production rates seem to be the principle factors governing detection of SF_6. At El Rio #2 and #3, SF_6 was detected after 100 days for a relatively short period of time (Figure 7a). The arrival occurred about two months after the start of the second recharge period. These two wells lie to the south of Pond 2 on the far side of Pond 1, the desilting basin and Pond 5. The brief detection (~50 days) may be related to the second recharge event. For 50 days after the end of the injection period the patch was free to spread "radially" from the injection point. However after the initiation of the second recharge period, mounding occurred below the spreading basins creating flow barriers and in some place reversing the direction of flow. We speculate that the patch split and a portion moved towards the southern wells. The rest of the patch flowed to the north and east and remained near the northern wells.

SF_6 was detected at El Rio #7, #8 and #15 multiple times during the study. These wells lie to the west of Pond 2 on the far side of Pond 3 and they produced very little groundwater until day 250 (summer 2003). At #7 and #15, tracer was detected during the first 80 days of the experiment, prior to the second recharge episode (Figure 7b). It was also detected during the summer 2003 after the rate of recharge slowed and pumping at these wells significantly increased. At El Rio #8, tracer was periodically observed after day 80 (Figure 7c). It was only consistently detected after day 250, when intensive pumping began at this well.

The history of SF_6 at El Rio #7 (Figure 7c) clearly illustrates the effects of intensive local production on the groundwater flow and upon the tracer's detection at wells. SF_6 was first detected here after 26 days (24 Oct 02). This well is approximately 50 m from the northwestern corner (high concentration end) of Pond 2. The concentration remained steady (0.5–0.7 pmol) for about two weeks while little water was produced from this well. On day 41 (7 Nov 02), intensive pumping was switch from El Rio #6 to #7 for three weeks. During this time, SF_6 concentrations increased significantly at El Rio #7 reaching a peak (9.8 pmol/l) a month later (day 68). Moreover, immediately after the intensive pumping stopped at El Rio #7, SF_6 concentrations decreased rapidly to less than 0.3 pmol/l. This decrease also coincided with the initiation of the second recharge period.

The concentration and duration of detection at the five distant wells were lower than at El Rio #5 and #6. Thus, the amount of SF_6 recovered by these wells was lower. Nevertheless, 7.8% and 3.7% of the total amount of SF_6 that infiltrated were produced by El Rio #8 and #15, respectively. El Rio #2, #3, and #7 each produced less than 0.6%. The total recovery fraction at the seven wells where tracer was detected was 53.3%. This very high recovery fraction resulted from the very high groundwater production and the trapping of the patch near the ponds by the regional cone of depression.

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 ~18° C (the pond temperature was not measured). Relative to the pond water, all five gases were enriched in the groundwater samples (Figure 8). This enrichment is due to the dissolution of trapped air and is commonly referred to as 'excess air' (Heaton and Vogel, 1981). The ratio of the noble gases in the excess air is not

identical to that of the atmosphere assuming a constant recharge temperature (Figure 8). 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 (Aeschbach-Hertig et al., 2000). 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 ~1.1 x 10^{-9} cc STP gr^{-1} to ~1.3 x 10^{-9} cc STP gr^{-1} during the measurement period. This change in concentration is equivalent to ~5° C decrease in temperature, assuming the amount excess air remained constant and reflects changes in the season of recharge.

Discussion

The very short residence time of water in the pond (~0.3 day) combined with the location of the injector created a complicated spatial input function of the tracer to the groundwater system. Therefore, direct measurements were required to define this function. These measurements showed SF_6 was successfully introduced into the recharge water but significant variations in concentrations existed within the pond. Most importantly, the surface water monitoring revealed that parts of the pond received very little or no tracer. This spatial variability did contribute to the late arrival of tracer to El Rio #5 relative to El Rio #6. Placing the diffusion stone closer to the inlet pipe would decrease this variation, although more of the SF_6 would be lost via air-water gas transfer in the white water immediately downstream of the inlet. This lose could be offset by increasing the injection rate of tracer.

After infiltrating, the tracer was transported more than 10 m through the unsaturated zone to the water table. The unsaturated zone contains three principle phases: sediment, water, and soil air. During transport, gas exchange between the water and soil air will occur. Thus, there is the potential of losing gas tracers from the tagged recharge water to the soil air during percolation. The amount of loss is dependent on the volume ratio of water and soil air, the percolation rate, and the duration of the tracer experiment (Fry et al., 1995; Heilweil et al., 2004). The transfer direction reverses, once the dissolved tracer becomes under-saturated with respect to the soil air. This occurs after the tracer injection period, assuming that recharge continues. The net effect of

gas transfer within the unsaturated zone is retardation, the slower movement of the gas tracers relative to the water (Fry et al., 1995).

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 ($[Ne]_{measured}/[Ne]_{equilibrium}$-1), the amount of excess air formed here (Ne excess > 100%) is larger than generally observed under conditions of natural recharge (Ne excess < 50%; Wilson et al., 1997; Stute and Schlosser, 2000) suggesting 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 (Stute and Talma, 1998). The increase in 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 144% ± 9% of 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 cm^3 of excess air. During the September recharge event, ~3 x 10^6 m^3 of surface water was recharged from Pond 2, thus more than 3 x 10^7 liters of air was dissolved during excess air formation. The source of this air was the vadose zone below the pond. Assuming a porosity of 33% and a 12 m thick vadose 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.

Although the noble gas data clearly show that the infiltrating recharge water came in contact with trapped air, a number of lines of evidences suggest that loss of gas tracer within the unsaturated zone was small during the El Rio tracer experiment. 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 SF_6 and He have high Henry's law coefficients, respectively, 143 and 95 at 17.5° C (Fry et al., 1995) and partition strongly into the air. At equilibrium approximately 60% of the mass of SF_6 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 equation (1), the equilibrium model of Fry et al. (1995), are greater for SF_6 than for He and exceed 2 when the amount of trapped air is greater than ~1% of the pore volume (Table 1). At 2% air, the retardation factors for SF_6 and He are 3.9 and 2.9, respectively.

Breakthrough curves at both El Rio #5 and #6 indicates that the two gas tracers were traveling at the same rate; SF_6 was not traveling 30% to 50% slower (see Table 1) than ^3He as expected if retardation by trapped air were 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 (Carter et al., 1959; Gupta et al., 1994, Wilson and Mackay, 1996; Vulava et al., 2002). At El Rio #6 where vertical flow dominates, the infiltrating water traveled ~12 m through the vadose 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 vadose 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. Tracer first arrived to El Rio #6 between day 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 ratio 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 non-equilibrium gas transfer is occurring between the percolating water and trapped air. However, the non-ideal 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% to 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., 10) was not observed during El Rio field experiment. Both of these lines of evidence suggest that the trapped air volume was small.

Quantification of the amount of trapped air is not possible because of uncertainties in the amount of mixing of tagged and untagged groundwater within the production wells and the vertical groundwater velocity between the water table and screen top. Nevertheless, the lines of evidence discussed above strongly suggest that the volume of trapped air was small, less than 10%. At the Sandy Hollow Reservoir experimental recharge basin, Heilweil et al. (2004) 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. In this site, Heilweil et al. (2004) determined the trapped air fraction of the pore space to be between 7% and 26%. Their experiment was conducted one 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 excess air volumes determined with the noble gas data indicate that a significant fraction of the trapped air (> 25% of the pore volume) 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 preformed early in the recharge event should show more retardation than those preformed later. Analysis of the tracer data from all of the production wells during the 18 months study indicates that the tracer plume has remained very close to its point of entry and more than half of the recharged SF_6 was recovered. Having the spreading groundwater within a regional cone of depression trapped the recharge water near the ponds where it could be produced. This type of design could be used for storing high quality surface water in aquifers that contain low quality or saline groundwater. Maintaining the regional cone of depression by extracting the low quality or saline water would be necessary.

The movement of the tracer within the spreading area was influenced by two major factors. First, pumping at production wells located within the spreading grounds cause frequent changes in the water level by creating steep cones of depression, and thus, influence the direction of the plume flow. Second, additional recharge events (lacking tracer) that occurred during winter 2002-3, diluted and moved the tracer plume. In some cases, additional recharge created barriers (mounds) that prevented the plume from reaching wells. These effects were demonstrated during the summer 2003, when a significant decrease in the amount of recharge water at the ponds, accompanied by increasing the pumping rate, allowed the tracer plume to been drawn towards El Rio #7, #8 and #15.

Implications for Tracing Recharge Water

The dual gas tracer experiment results indicate that gas tracers were not slowed significantly during transit through the vadose zone to the water table. The small amount of trapped air, the very high infiltration rate, and moderately deep water table 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. (2004). 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. (2001) and Clark et al. (2004) for determining travel times between recharge locations and wells with gas tracers are reliable at recharge sites with relatively high infiltration rates. Therefore, 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

The authors thank Tony Blankenship and his field workers for assisting us in the field and answering many questions about the plumbing of the El Rio Spreading Grounds. Steve Bachman and Daniel Detmer of the United Water Conversation District provided valuable information and data. 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.

References

Alain, C. M. B. and Bertin C., 1993, Biogechemical processes during the infiltration of river water into an alluvial aquifer, *Environmental Science and Technology*, 27, 661-666.

Aeschbach-Hertig, W.; Peeters, F.; Beyerle, U.; and Kipfer R., 2000, Palaeotemperature reconstruction from noble gases in ground water taking into account equilibration with entrapped air, *Nature*, 405, 1040-1044.

Carter, R. C.; Kaufman, W. J.; Orlob, G. T.; and Todd, D. K., 1959, Helium as a ground water tracer, *Journal of Geophysical Research*, 64, 2433-2439.

Clark, J. F.; Wanninkhof, R.; Schlosser, P.; and Simpson, H. J., 1994, Gas exchange in the tidal Hudson River using a dual tracer technique, *Tellus*, 46B, 274-285.

Clark, J. F., 2002, Defining transport near ASR operations using sulfur hexafluoride gas tracer experiments. In: Dillon, P. J. (ed.) *Management of Aquifer Recharge for Sustainability*, Swets & Zeitlinger Publishers, 257-260.

Clark, J.F.; Hudson, G. B.; Davisson, M. L.; Woodside, G.; and Herndon, R., 2004, Geochemical imaging of flow near an artificial recharge facility, Orange County, CA, *Ground Water*, 42, 167-174.

Dillion, P. J., 2003, *Management of Aquifer Recharge for Sustainability*, Balkema Publishers, Exton, Pennsylvania, p.

Drewes, J. E.; Heberer, T.; Rauch, T.; and Reddersen, K., 2002, Fate of pharmaceuticals during ground water recharge, *Ground Water Monitoring and Remediation*, 23(3), 64-72.

Donaldson, J. H.; Istok, J. D.; and O'Reilly, K. T., 1997, Development and testing of a kinetic model for oxygen transport in porous media in the presence of trapped gas, *Ground Water*, 35, 270-279.

Fry, V. A.; Istok, J. D.; Semprini, L., O'Reilly, K. T.; and Buscheck, T. E., 1995, Retardation of dissolved oxygen due to a trapped gas phase in porous media, *Ground Water*, 33, 391-398.

Fox, P., 2002, Soil Aquifer Treatment: An assessment Of Sustainability. In Dillion, P. J. (ed) *Management of Aquifer Recharge for Sustainability*. Balkema Publishers, Exton, Pennsylvania, 21-26.

Fox, P. K.; Narayanaswamy, A.; Genz, A.; and J. E. Drewes, 2001, Water quality transformations during soil aquifer treatment at the Mesa Northwest Water Reclamation Plant, USA, *Water Science and Technol*ogy, 43, 343-350.

Gamlin, J.D.; Clark, J. F; Woodside, W.; and Herndon, R., 2001, Large-scale tracing of ground water with sulfur hexafluoride, *Journal of Environmental Engineering* 127, 171-174.

Gupta, S. K.; Lau, L. S.; Moravcik, P. S., 1994, Groundwater tracing with injected helium, *Ground Water*, 32, 96-102.

Hanson, R.T.; Martin, P.; and Koczot, K. M., 2003, Simulation of ground-water/surface-water flow in the Santa Clara-Calleguas ground-water basin, Ventura County, California. U.S., Geological Survey Water-Resources Investigation Report 02-4136, 157 p.

Heaton, T. H. E. and Vogel, J. C., 1981, 'Excess-air' in groundwater. *Journal of Hydrol*ogy, 50, 201-216.

Heilweil, V. M.; Solomon, D. K.; Perkins, K. S.; and Ellett K. M., 2004, Gas-partitioning tracer test to quantify trapped air during recharge, *Ground Water*, 42, 589-600.

Hiscock K. M. and Grischeck T., 2002, Attenuation of groundwater pollution by bank filtration, *Journal of Hydrology*, 266, 139-144.

Schlosser, P.; Stute, M.; Dorr, H.; Sonntag, C.; and Munnich, K. O., 1988, Tritium/^{3}He dating of shallow groundwater, *Earth and Planetary Science Letters*, 89, 352-363.

Shapiro, S. D; LeBlanc D.; Schlosser, P.; and Ludin, A., 1999, Characterizing a sewage plume using the ^{3}H-^{3}He dating technique, *Ground Water*, 37, 861-878.

Schwarzenbach, R. P.; Giger, W.; Hoehn, E.; and Schnelder, J. K., 1983, Behavior of organic compounds during infiltration of river water to ground water. Field studies, *Environmental Science and Technology* 17, 472-479.

Stute M. and Schlosser, P., 2000, Atmospheric noble gases. In *Environmental tracers in Subsurface Hydrology*: Cook, P., Herczeg, A. L., Eds. Kluwer: Boston, 349-377.

Stute M. and Talma, S., 1998, Glacial temperatures and moisture transport regimes reconstructed from noble gases and O-18, Stampriet aquifer, Namibia. In *Isotope Techniques in Studying Past and Current Environmental Changes in the Hydrosphere and the Amosphere*, IAEA: Vienna, 307-318.

Tufenkji, N.; Rayen, J.; and Elimelech, M., 2002, Bank filtration: A simple technology may inexpensively clean up poor-quality raw surface water, *Environmental Science and Technology* 36 423A-428A.

United Water Conservation District, 2001, *Surface and Ground water Conditions Report Water Year 2000 Supplement*. Ground Water Resources Department, UWCD, Ventura County, CA, 60p.

Vulava, V. M.; Perry, E. B.; Romanek, C. S.; and Seaman J. C., (2002) Dissolved gases as partitioning tracers for determination of hydrogeological parameters, *Environmental Science & Technology*, 36, 254-262

Watson, A. J.; Upstill-Goddard, R. C.; and Liss, P. S., 1991, Air-sea exchange in rough and stormy sea, measured by a dual tracer technique, *Nature*, 349, 145-147.

Wanninkhof, R; Asher, W.; Weppernig, R.; Chen, H.; Schlosser, P.; Langdon, C.; and Sambrotto, R., 1993, Gas transfer experiment on Georges Bank using two volatile deliberate tracers, *Journal of Geophysical Research*, 98, 20,237-20,248.

Wilson, G. B. and McNeill, G. W., 1997, Noble gas recharge temperatures and the excess air component, *Applied Geochemistry*, 12, 747-762.

Wilson, R. D. and Mackay, D. M., 1996, SF_6 as a conservative tracer in saturated media with high intragranular porosity or high organic carbon content, *Ground Water*, 34, 241-249.

Table 1: Fraction at equilibrium partitioned into the air volume and retardation coefficients calculated for SF_6 and He at 17.5° C with differing amounts of trapped air. In the calculations, H_{SF_6} and $H_{^3He}$ were 143 and 95, respectively (Fry et al., 1995). The retardation coefficients were calculated with the equilibrium model of Fry et al. (1995) using equation (1).

	Air Fraction ($V_{air}/(V_{water}+ V_{air})$					
	0.005	0.01	.02	0.05	0.10	0.20
$[SF_6]_{air}/[SF_6]_{total}$	0.43	0.60	0.75	0.89	0.94	0.97
$[^3He]_{air}/[^3He]_{total}$	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
$R_{^3He}$	1.5	2.0	2.9	6.0	11	25

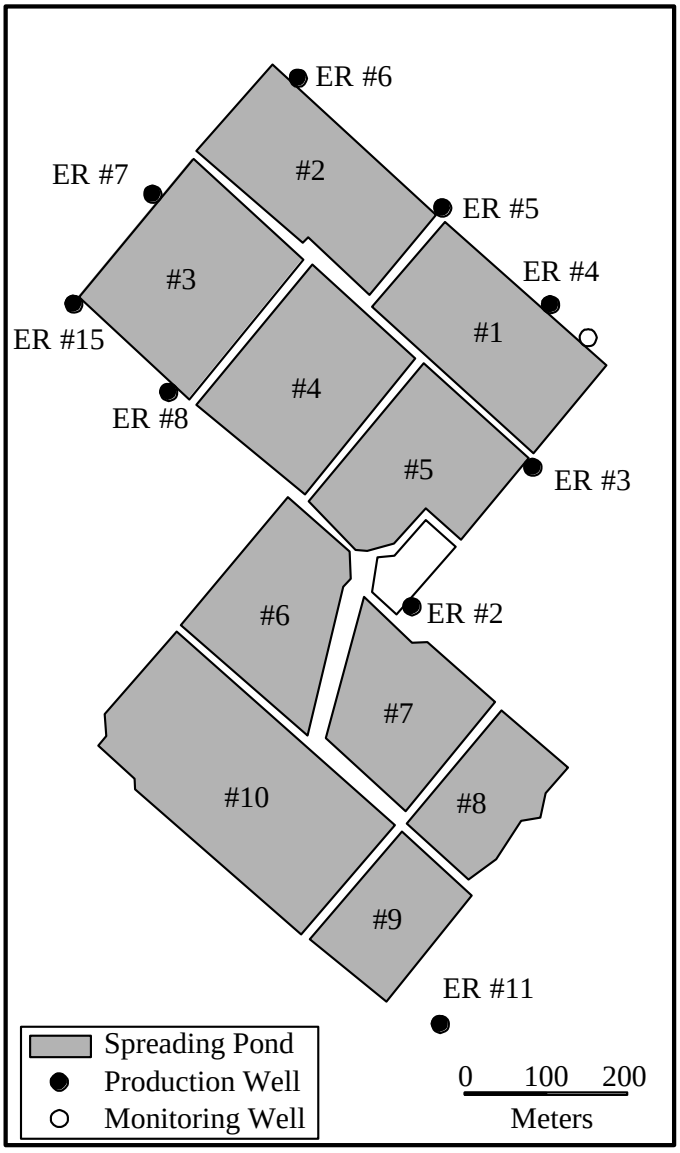

Figure 1: Map of the El Rio Spreading Grounds. The dual gas tracer experiment was conducted from Pond 2 while recharge was occurring from Pond 2 and 3. The water table elevation was determined at the nested monitoring well. For most of the study period.

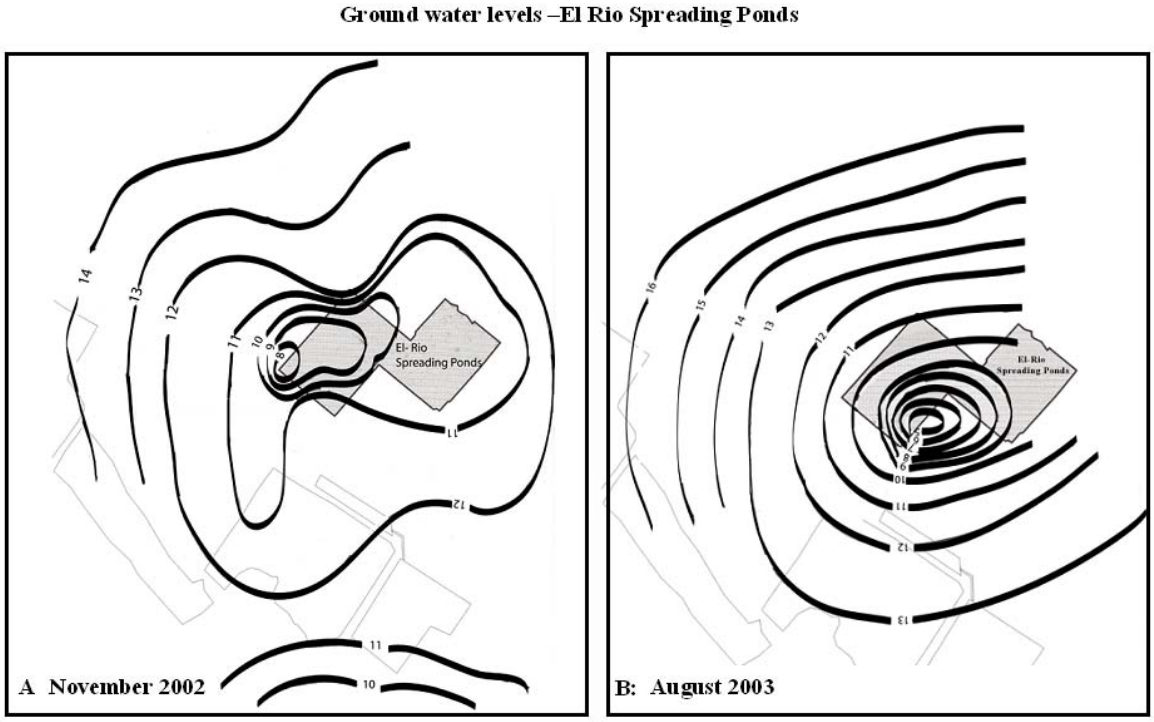

Figure 2: Ground water levels maps near the El-Rio Spreading Grounds at two different dates. A: November 2002 and B: August 2003.

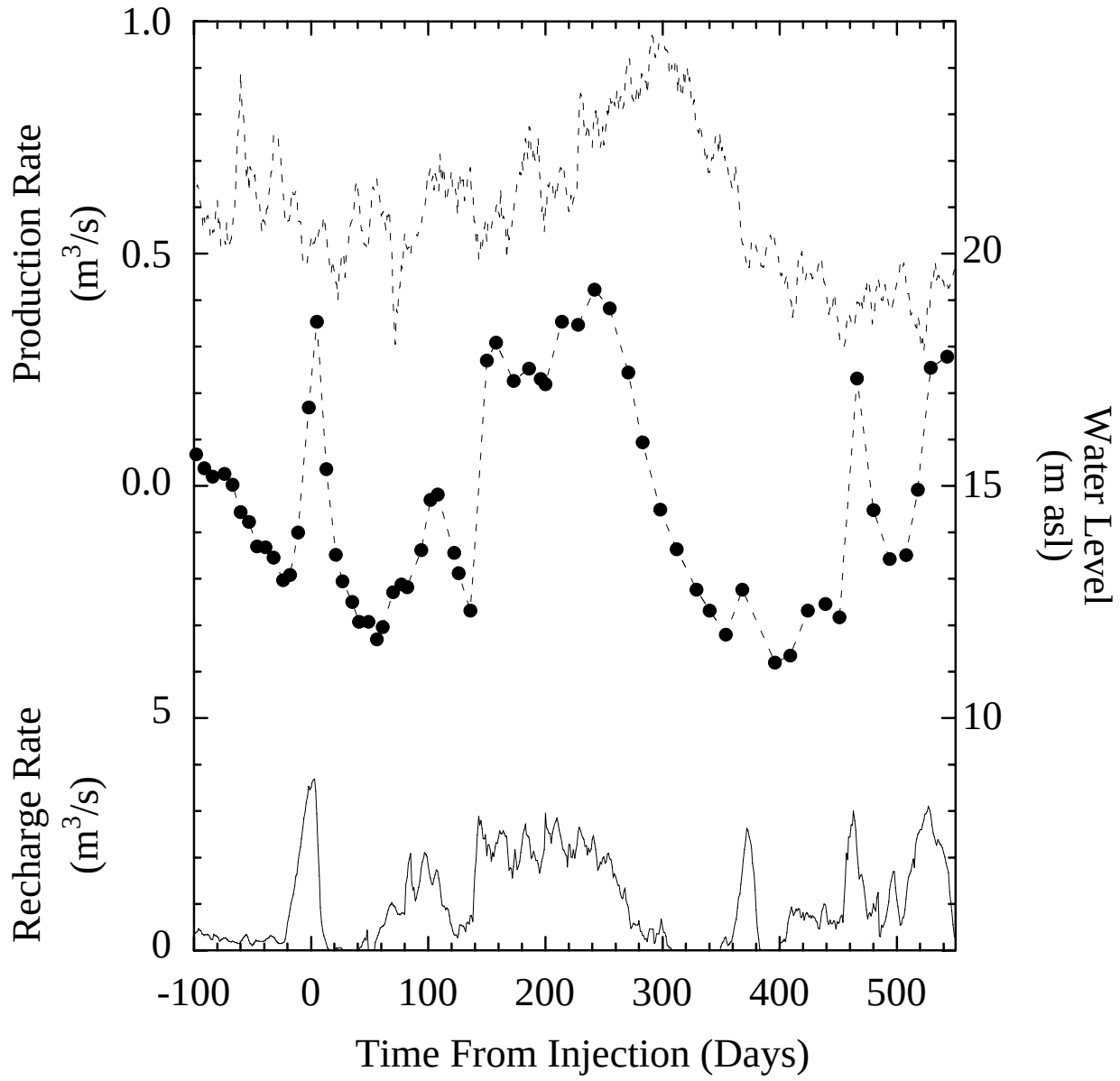

Figure 3: The rate of artificial recharge (solid line), water table elevation measured at the monitoring well (solid dots with dashed line), and total ground water production rate (dashed line) at the El Rio Spreading Grounds. The bottom of Pond 2 is about 30 m above sea level. Time zero is Sept 27, 2002.

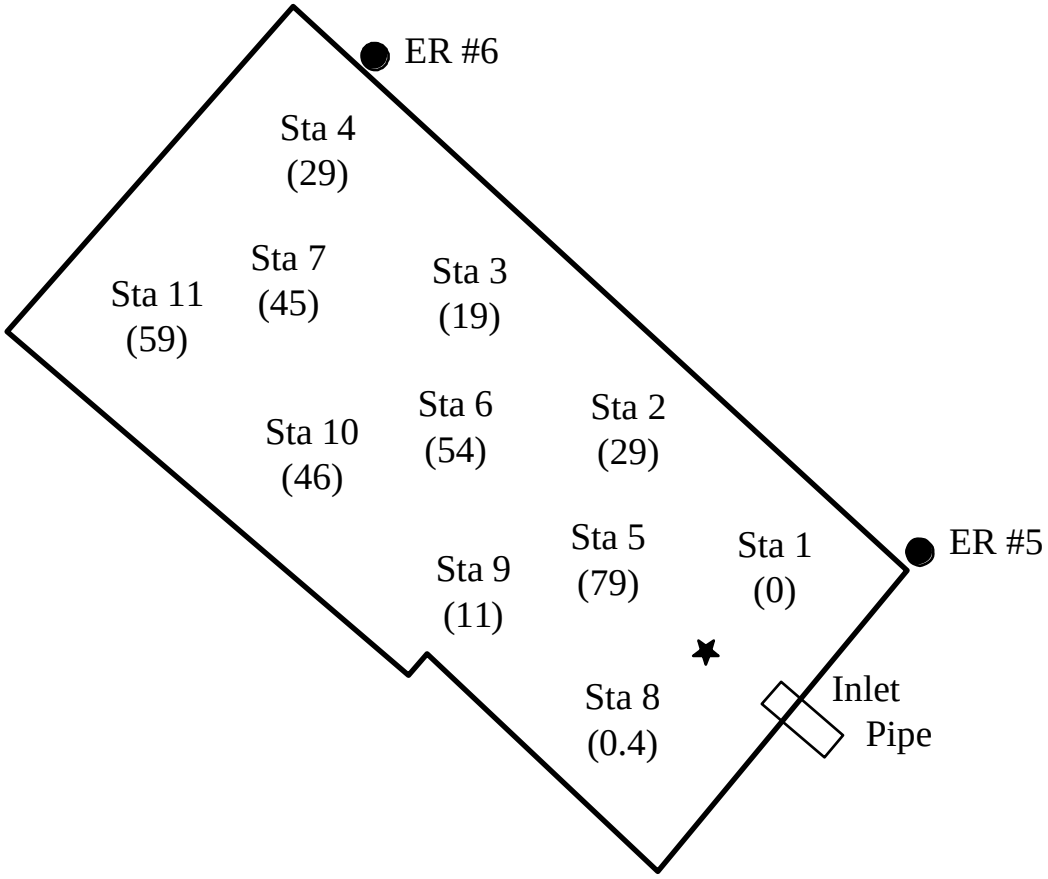

Figure 4: Location of the sampling stations within Pond 2 during the injection period. Below each station number is the mean SF_6 concentration (pmol/l). The gas tracers were injected at the star about 10 m offshore of the inlet pipe.

Figure 5: Photograph of the inlet pipe to Pond #2, the gas cylinder containing the mixture of SF_6 and ^3He, and El Rio #5.

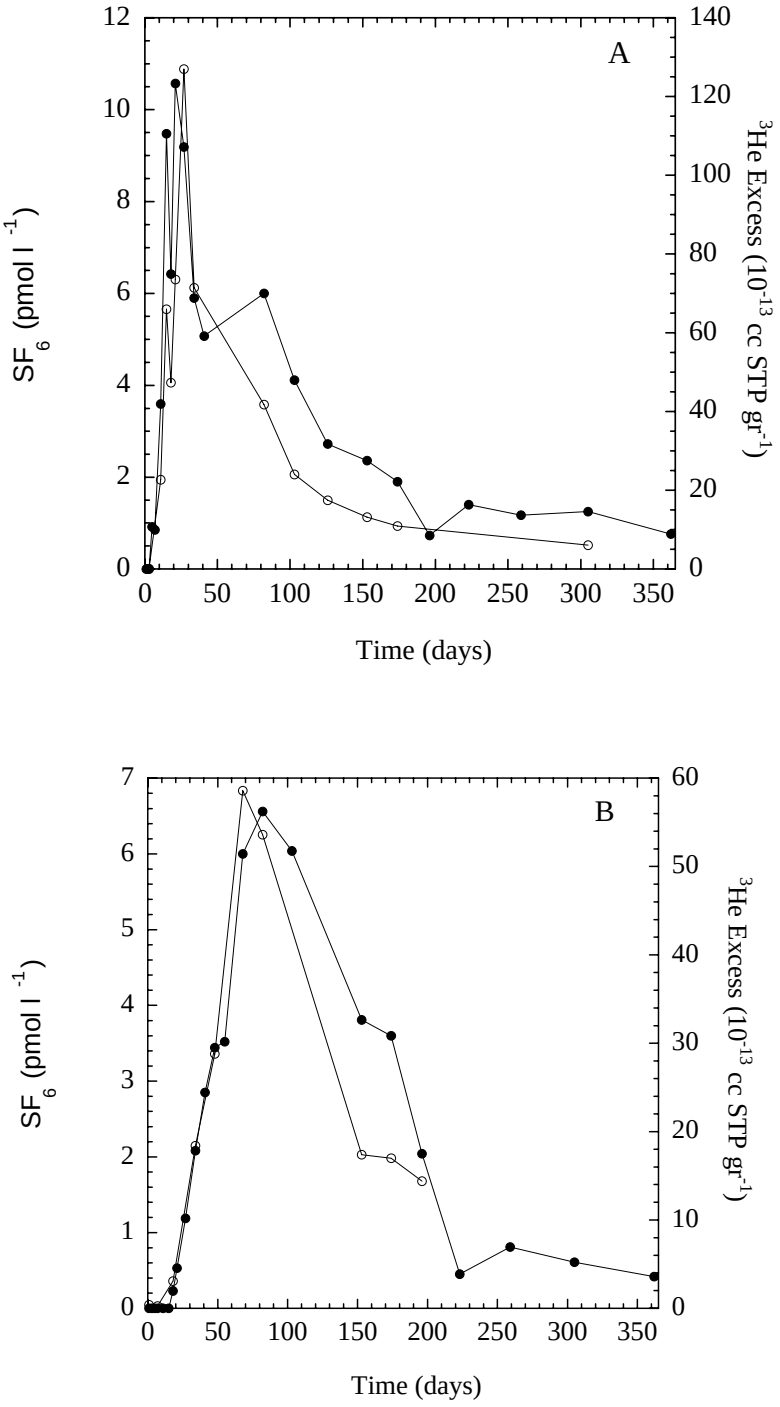

Figure 6: Tracer breakthrough curves at (A) El Rio #6 and (B) El Rio #5.

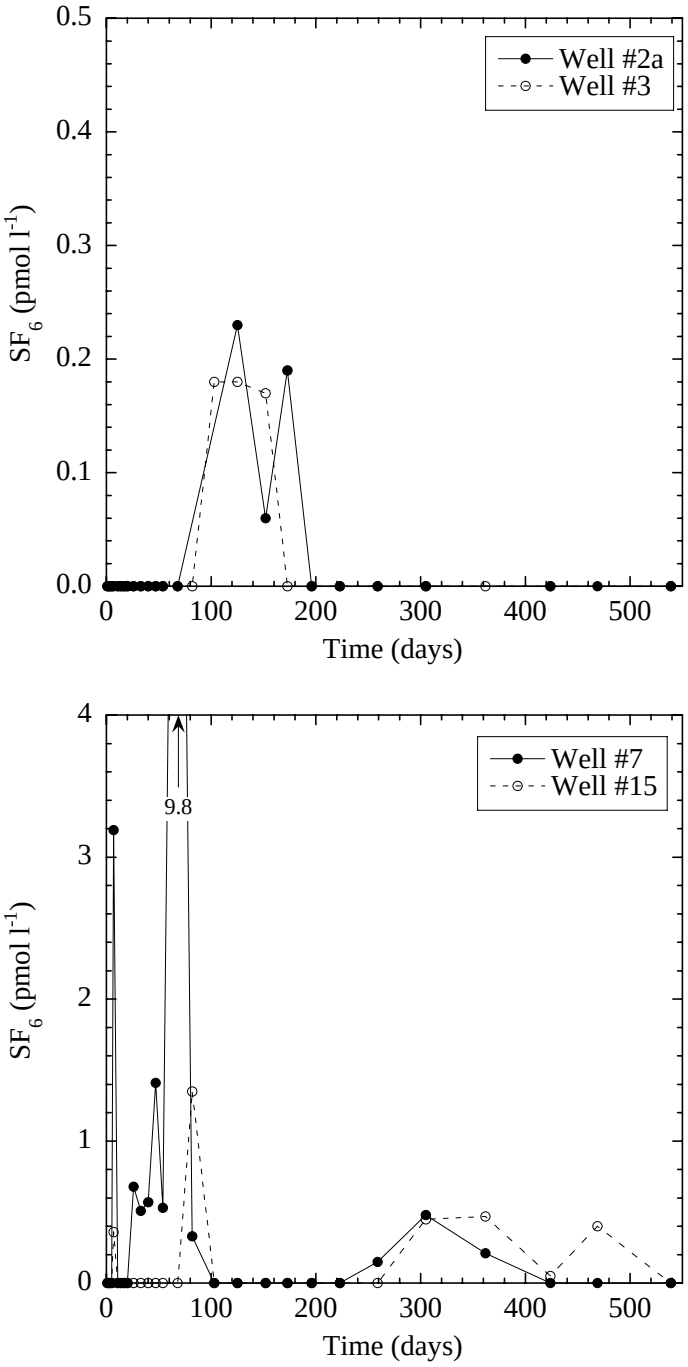

Figure 7a&b: Tracer breakthrough curves at El Rio #2a, #3 #7 and #15.

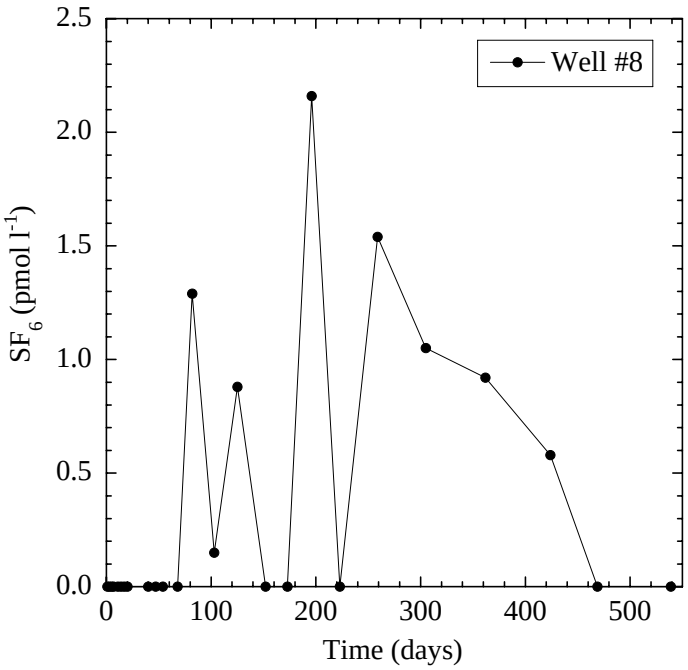

Figure 7c: Tracer breakthrough curve at El Rio #8.

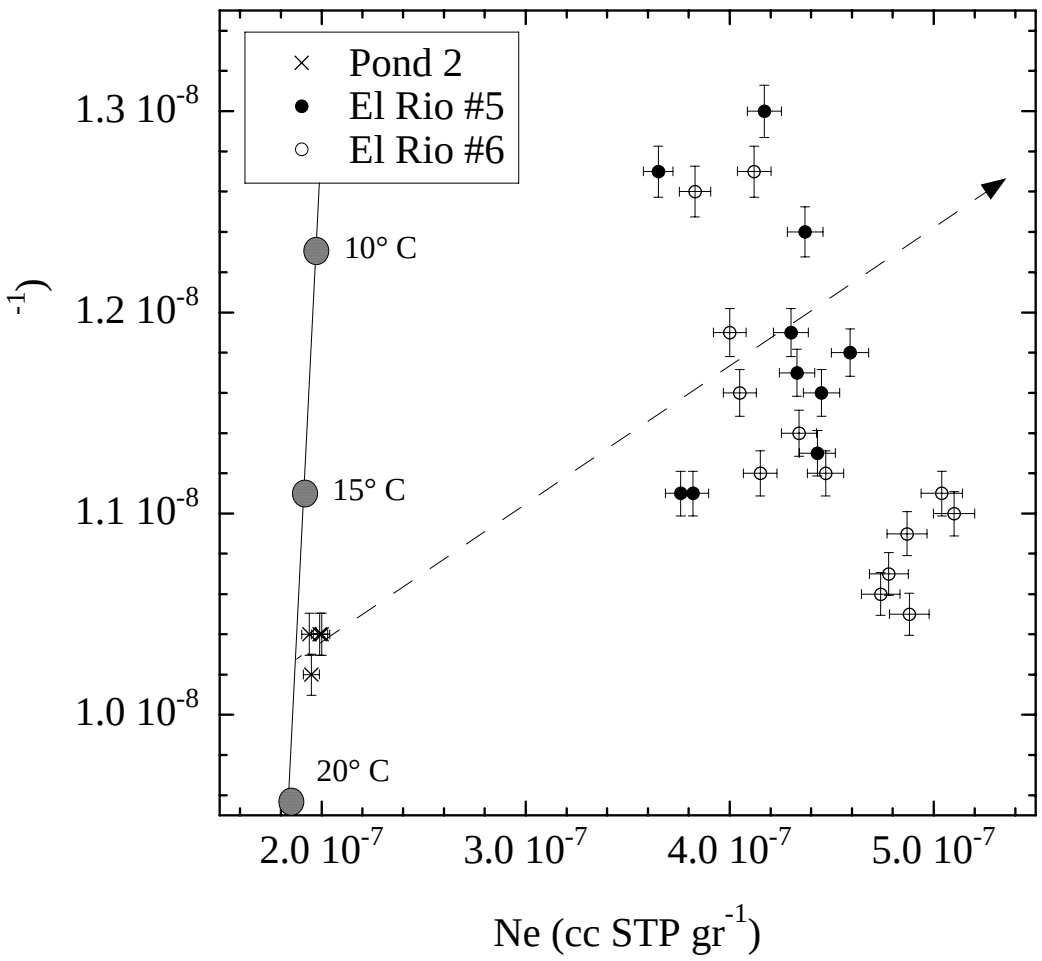

Figure 8: Ne and Xe concentrations in Pond 2 and groundwater samples. The nearly vertical line shows atmospheric equilibrium concentrations at different temperatures and the dashed arrow shows the increase in concentration caused by excess air formation assuming complete bubble dissolution.