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U.S. DEPARTMENT OF THE INTERIOR
BUREAU OF RECLAMATION

Development of New Tracers to Determine Groundwater Travel Time near Managed Recharge Operations

WateReuse Research Foundation

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About the WateReuse Research Foundation

The mission of the WateReuse Research Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water for various uses through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, reduction of energy requirements, concentrate management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of providing a reliable, safe product for its intended use.

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Abbreviations and Acronyms

^{10}B	boron-10
$BaCl_2 \cdot 2H_2O$	barium chloride dihydrate
Br^-	bromide
CDPH	California Department of Public Health
CDWR	California Department of Water Resources
COM	center of mass
DDW	Division of Drinking Water
FY	fiscal year
GRRP	groundwater replenishment reuse project
GWRS	groundwater replenishment system
HCl	hydrochloric acid
ICP-MS	inductively-coupled plasma mass spectrometer
IPCC	Intergovernmental Panel on Climate Change
KBr	potassium bromide
LACDPW	Los Angeles County Department of Public Works
LACP	Los Angeles coastal plain
LACSD	Los Angeles County Sanitation Districts
MAR	managed aquifer recharge
MDA	minimal detectable activity
MFSG	Montebello Forebay spreading grounds
MSL	mean sea level
NaBr	sodium bromide
NaCl	sodium chloride
Na_2SO_4	sodium sulfate
NG-MIMS	noble gas membrane inlet mass spectrometer
OCCP	Orange County coastal plain
OCWD	Orange County Water District
ppmv	parts per million by volume
pptv	parts per trillion by volume
RHSG	Rio Hondo spreading grounds
SAR	Santa Ana River
SGSG	San Gabriel spreading grounds
SO_4	sulfate
^{35}S	sulfur-35
SF_6	sulfur hexafluoride
TIMS	thermal ionization mass spectrometry
USGS	U.S. Geological Survey
WRD	Water Replenishment District of Southern California

Foreword

The WateReuse Research Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide sustainable sources of high-quality water, protect public health, and improve the environment.

An operating plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities, including water professionals, academics, and Foundation subscribers. The Foundation's research focuses on a broad range of water reuse and desalination research topics including

- Defining and addressing emerging contaminants, including chemicals and pathogens
- Determining effective and efficient treatment technologies to create "fit for purpose" water
- Understanding public perceptions and increasing acceptance of water reuse
- Enhancing management practices related to direct and indirect potable reuse
- Managing concentrate resulting from desalination and potable reuse operations
- Demonstrating the feasibility and safety of direct potable reuse

The operating plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project to provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's project managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The objective of this study was to evaluate new tracers that could be used instead of sulfur hexafluoride (SF_6) for compliance with the California State Water Resource Control Board Division of Drinking Water groundwater replenishment reuse project (GRRP) regulations. The tracers tested were the boron-10 stable isotope (as ^{10}B enriched borate), radio-sulfur (^{35}S), and heat. Results indicate that ^{10}B is retarded relative to the conservative bromide tracer, arriving about 25% later on average, and that ^{35}S and heat have great potential as tracers for managed recharge.

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Executive Summary

Recycling wastewater for potable and nonpotable use by artificially recharging underground aquifers is a decades-old but increasingly common practice. Natural attenuation processes in the subsurface, known as soil aquifer treatment (SAT), purify recycled water during managed aquifer recharge (MAR) and subsequent groundwater flow. Travel time criteria are often used to regulate managed aquifer recharge operations, because degradation is typically time dependent.

The objective of this study was to evaluate two alternative tracers, which could be used instead of sulfur hexafluoride (SF_6) for compliance with the California Division of Drinking Water (DDW), formerly the Department of Public Health (CDPH), groundwater replenishment reuse project (GRRP) regulations. The tracers tested were radio-sulfur (^{35}S) and boron-10 (as ^{10}B-enriched boric acid). We also followed the transport of heat as water temperature changes along with the boron tracer and added the conservative tracer bromide (Br^-), as a control. Therefore, this study investigates three new groundwater tracer methods near MAR operations: a new deliberate tracer (^{10}B) and two intrinsic tracers (heat and ^{35}S dating).

Task I developed and evaluated the ^{35}S-SO_4 method as a new MAR groundwater dating tool at two Southern California field sites: (1) Rio Hondo spreading grounds (RHSG), Pico Rivera, and (2) Orange County Water District (OCWD) Groundwater Recharge MAR facilities, Anaheim. ^{35}S-SO_4 travel times are compared to those determined by Clark's (2011, 2014) deliberate tracer experiments, which used SF_6, conducted at these two sites.

Task II evaluated (1) the possible retardation of the now more affordable boron isotopic deliberate tracer ^{10}B relative to conservative flow as represented by Br^- transport and (2) the potential for heat flow to interpret residence time through temperature time series collected hourly in high-quality well loggers. Task II was conducted at the U.S. Geological Survey (USGS) research test basin at the northern extent of San Gabriel spreading grounds (SGSG), Pico Rivera.

These tasks are discussed and the three tracers are evaluated in detail in the body of the report. Ideal tracers are nonreactive and do not sorb readily to aquifer material. In general, two of the three may not be conservative enough for DDW, due to retardation (^{10}B) or dilution between young and old groundwater (^{35}S dating), resulting in an overestimation of groundwater travel time. Conversely, heat as recorded by temperature changes show great promise but requires additional studies. For microbiological contaminants, public health agencies require a tracer that is conservative and does not overestimate travel time. For some wells, there was a large discrepancy in subsurface travel time observed for the ^{35}S-SO_4 tracer compared to the SF_6 tracer. The ^{35}S-SO_4 activity could overestimate the time by a factor of four. Large values for counting error in the analysis of ^{35}S-SO_4 activity introduce a significant uncertainty and make interpretation of the results difficult. The ^{35}S method requires repeated testing, because the results varied by season. It is useful to answer the question if a fraction of the well water arrived within a year of recharge.

Chapter 1

Groundwater Tracers for Managed Recharge

1.1 Introduction

Water quality concerns are raised when recycled wastewater is a portion of managed aquifer recharge (MAR) source waters. Facilities that use recycled water as a portion of their MAR source waters are examples of indirect potable reuse. Understanding the fate and transport of potential contaminants in MAR operations is paramount for protecting public and environmental health. Only from this understanding can robust, cost-effective, and appropriate regulations be developed.

Results of detailed water quality studies and numerical models near MAR operations have shown that one of the most important hydrologic parameters is subsurface residence time (e.g., Fox and Makam, 2009; Laws et al., 2011). Some potential contaminants of public health concern, such as infective micro-organisms, are naturally removed or become inactive with time and distance in the subsurface (e.g., Yates and Yates, 1987; Fox et al., 2001; Drewes et al., 2002; Hiscock and Grischeck, 2002; Laws et al., 2011). Natural attenuation processes, collectively known as soil aquifer treatment (SAT), further improve the quality of recharged water for subsequent potable and nonpotable reuse.

Current California regulations for groundwater replenishment reuse projects (GRRP) require specific subsurface residence times prior to extraction for potable use (Johnson, 2009; California Division of Drinking Water (DDW), 2014). Minimum residence times, from infiltration at spreading ponds to extraction at drinking water wells, are based on the degree of aboveground treatment technologies before recharge. Minimum time for tertiary-treated recycled water can be as little as 2 months of response retention time (if the minimum pathogen removal is achieved aboveground via treatment processes) or could exceed 6 months if tertiary recycled water is surface spread. DDW considers deliberate (or artificial/added) tracer experiments as the best method for establishing retention times for surface spreading projects.

1.2 Need for New Tracers

DDW requires deliberate tracer experiments for establishing retention times underground from MAR facilities using recycled water. Deliberate tracers introduced into the water system are distinguished from intrinsic (or environmental) tracers that already exist in the ground and recharge waters (Davis et al., 1985; Holmbeck-Pelham et al., 2000). Ideal tracers are soluble, mobile, and behave conservatively (i.e., are nonreactive and do not sorb readily to aquifer material). Artificial recharge demands a tracer capable of dating on <1.0 year timescales at minimum cost and is also in compliance with environmental and health permitting.

Sulfur hexafluoride (SF_6), a nontoxic (Lester and Greenberg, 1950) and nonreactive synthetic gas, has been the principle deliberate tracer for work near MAR sites (e.g., Gamlin et al., 2001; Clark et al., 2004, 2005; Avisar and Clark, 2005; McDerrmott et al., 2008). SF_6 emission is regulated in California because it is a strong greenhouse gas (approximately 23,000 times stronger than CO_2 on a per molecular basis; IPCC, 1996). Despite SF_6 having a significantly lower atmospheric mixing ratio compared to CO_2 (2013 mixing ratio: ~ 7 parts per trillion volume (pptv) and ~400 parts per million volume (ppmv) for SF_6 and CO_2, respectively) and contributing very little to the total greenhouse forcing, the future of SF_6 as a tracer remains in doubt and will require additional permitting from the California Air Resources Board.

Standard shallow-groundwater dating techniques using intrinsic tracers, such as tritium/helium-3 ($T/^3He$) and chlorofluorocarbon (CFC) methods, have uncertainties of typically ± 2 years, too large to effectively determine <6 month travel times which is a significant benchmark in the GRRP regulations. Furthermore, these techniques are often difficult to interpret at long-screened production wells where mixing of multiple flowpaths (generally inside the well) complicate the age interpretation (e.g., McDermott et al., 2008). Noble gas isotopes, such as helium and xenon, have been used successfully as deliberate tracers to determine subsurface residence times (Hudson, 1994; Davisson et al., 1998; Clark et al., 2004, 2005), but are still impractical due to high analysis costs and long analysis times. However, Lawrence Livermore National Laboratory continues to make progress on this front and their new noble gas membrane inlet mass spectrometry (NG-MIMS) system has significantly reduced the cost and increased the throughput of samples (Visser et al., 2013).

A major disadvantage to the application of deliberate tracers is the significant field and laboratory effort that is necessary to obtain sufficient data for robust breakthrough curves. Deliberate tracers also work best in areas with many monitoring wells. Without sufficient monitoring points and sampling frequency, the tracer patch could pass without detection. Deliberate tracer techniques are also highly dependent on the hydrologic conditions during the experiment. If local hydraulic gradients change in response to changes in recharge or pumping, a second tracer experiment may be needed to reevaluate groundwater travel times. Finally, dilution can limit the application of these experiments. Budgets may constrain the ability to tag large spreading ponds with a deliberate tracer due to the substantial amount of mass needed to raise concentrations in large volume settings.

Intrinsic tracers have higher repeatability and do not require a physical injection but are considered by DDW to be less reliable than deliberate tracers. Currently, intrinsic tracers can only be used for travel time estimations during project planning purposes and not final residence time determination to receive credit for pathogen removal, which requires a deliberate tracer (Johnson, 2009; DDW, 2014).

The utilization of intrinsic tracers, including radionuclides of atmospheric origin (e.g. tritium, ^3H or T, and krypton-85, ^{85}Kr), has been a useful approach to determining subsurface travel times in shallow aquifers (e.g., Ekwurzel et al., 1994; Solomon et al., 1992). However, the half-lives of these tracers (12.43 years for T, and 10.76 years for ^{85}Kr) do not allow for groundwater dating on the 6-month to 1-year time scale of interest to MAR managers and regulators. Due to the effort and timescale limitations of current tracer techniques, the development of new tracer methods that require minimal field and laboratory work and that can resolve subsurface residence times on timescales of <1 year will improve the development of MAR facilities and reaffirm indirect potable reuse as a safe option for increasing local water supplies.

1.2.1 Sulfur-35 in Dissolved SO_4

Sulfur-35 (^{35}S) is a natural radionuclide produced in the upper atmosphere by cosmic rays interaction with argon. After its production, ^{35}S rapidly oxidizes to $^{35}S\text{-}SO_2$ and eventually to $^{35}S\text{-}SO_4$ and is transferred to groundwater as dissolved $^{35}S\text{-}SO_4$, mainly through recharge of precipitation (e.g., Tanaka and Turekian, 1991, 1995; Michel et al., 2000). For investigating groundwater travel time near MAR sites ^{35}S is an ideal intrinsic radionuclide due to its short half-life of 87.5 days (Friedlander et al., 1981).

Dissolved ^{35}S-SO_4 has been employed in hydrologic studies as an intrinsic tracer for atmospheric SO_4 for more than two decades (Cooper et al., 1991; Tanaka and Turekian, 1991, 1995; Burns et al., 1998; Sueker et al., 1999; Michel et al., 2000; Shanley et al., 2005). Because of dilution with ^{35}S-dead SO_4 (SO_4 containing no detectable ^{35}S), the application typically has been restricted to high-elevation (mountain) basins where groundwater residences times are <1 year, biogeochemical cycling and water/rock interactions are minimal, stream and snow SO_4 concentrations are low, and the hydrologic SO_4 budget is dominated by atmospheric inputs (Cooper et al., 1991; Sueker et al., 1999; Michel et al., 2000; Shanley et al., 2005).

Application of the ^{35}S-SO_4 method as an intrinsic tracer to lowland aquifers, including MAR facilities, is limited due to potential dilution of the atmospheric signal with SO_4 from anthropogenic sources that are ^{35}S-dead. Few measurements of ^{35}S-SO_4 exist from the low-elevation regions of large river basins. Although both wet and dry atmospheric deposition will continue to contribute ^{35}S-SO_4 to rivers downstream of the headwaters and SO_4 concentrations are typically higher in rivers that collect municipal wastewater effluent or agricultural return water because of anthropogenic inputs, dilution is a concern that may prevent the application of ^{35}S in these settings.

In addition to atmospheric deposition of ^{35}S-SO_4, a number of different reservoirs (soil zone, minerals, and biota) contribute SO_4 to groundwater and rivers; however, the continental sources are typically ^{35}S-dead due to >1-year long residence times (four half-lives). Activities of ^{35}S-SO_4 in the lower parts of these river systems are expected to be lower than in the headwaters due to the dilution of atmospherically produced ^{35}S-SO_4 with ^{35}S-dead SO_4. The activity of ^{35}S also decreases due to radioactive decay during transit downstream. This effect is significant when portions of the river pass through reservoirs with water storage times greater than 3 months (one half-life) as may happen in many aqueduct systems such as the Colorado River Aqueduct that delivers water to Southern California.

The aim of this study was to develop and evaluate the ^{35}S-SO_4 method as a new groundwater tracer technique to determine subsurface travel times near MAR facilities, which are likely to have high SO_4 concentrations and low ^{35}S activity. Travel times for ^{35}S-SO_4 are compared to those determined with deliberate tracer experiments (Clark, 2009, 2014) at two Southern California field sites: (1) Rio Hondo spreading grounds (RHSG) in Los Angeles County and (2) Orange County Water District (OCWD) Groundwater Recharge MAR facilities in Orange County. One of the primary benefits of this new environmental tracer method is the potential for repeatable measurements that could be used to assess how different hydraulic conditions affect travel time. In particular, ^{35}S-SO_4 could be used to examine how travel times respond to the seasonality of recharge and well production.

1.2.2 Boron-10 and Bromide

Hydrogeological applications of boron isotopes began in recent decades with studies tracing sources of groundwater contamination (Davidson and Bassett, 1993; Vengosh et al., 1994; Leenhouts et al., 1998). Boron is useful for this purpose due to distinct isotopic signatures between end members and its prevalent nature (Bassett, 1990). Isotopic tracers can be favorable for evaluating groundwater recharge due to low analytic detection limits (Quast et al., 2006). Boron occurs naturally as two stable isotopes, ^{10}B (~19.9% relative abundance) and ^{11}B (80.1%). The lesser abundant boron stable isotope, ^{10}B, can be used as a tracer; however, DDW has determined the issues with retardation raise serious questions as to usefulness as predictive of travel time. Boric acid enriched in ^{10}B is available in large quantities at a relatively low cost (from Boron Product, LLC), because it is used in nuclear industries.

A significant change in isotope ratio can occur without a significant increase in the absolute B concentration. As a result, ^{10}B as a deliberate tracer requires less mass, by at least an order of magnitude, to tag an equivalent volume of water compared to concentration-based salt tracers such as bromide. This is because a shift in isotopic ratios (such as $^{11}B/^{10}B$) is much more pronounced than changes in concentration due to nonlinear mixing. Wells that pump small volumes (<10%) of the tagged plume still show a strong isotopic signal. Furthermore, we developed a new accurate boron analytical procedure using an inductively coupled plasma mass spectrometer (ICP-MS). Analytical costs on an ICP-MS (US$30/sample in 2013) are an order of magnitude lower than the thermal-ionization mass spectrometry (TIMS) system, one of the main reasons why boron is now realistic as a deliberate tracer. Analytical uncertainty, while greater on the ICP-MS (better than ±15‰), should not distort breakthrough curve interpretation if the tagged water is sufficiently enriched. The method also allows for a greater throughput of samples.

Isotopic compositions for boron are typically expressed in δ-units, as the deviation in parts per mil (‰) of the $^{11}B/^{10}B$ ratio from the sampled water relative to a standard. The standard ratio (NIST SRM 951; Coplen et al. 2002) is 4.0436. $\delta^{11}B$ of a sample is calculated by:

$$\delta^{11}B\ (‰) = \left(\frac{\left(^{11}B/^{10}B\right)_{sample} - \left(^{11}B/^{10}B\right)_{standard}}{\left(^{11}B/^{10}B\right)_{standard}}\right) x\ 1000 \qquad (1.1)$$

Natural waters range widely from −16‰ to +59‰ $\delta^{11}B$, with uncontaminated groundwater around +30‰ $\delta^{11}B$ (Vengosh et al., 1994). Treated municipal wastewater tends to be higher in ^{10}B, producing values around +1‰ to +10‰ $\delta^{11}B$ (Vengosh et al., 1994, Bassett et al., 1995; Leenhouts et al., 1998). Boron in wastewater generally originates from soaps and other detergents (Bassett et al., 1995). A tracer study at RHSG (Quast et al., 2006), nearby SGSG and receives similar source water, recorded untagged basin water of +2‰ and untagged groundwater of +5‰ and +8‰. California state drinking water notification level for absolute boron concentration is 1000 μg/L. Groundwater samples measured herein at SGSG, even with the tagged tracer plume present, were around 250 to 350 μg/L.

Boron species in natural water systems include boric acid ($B(OH)_3$) and borate ($B(OH)_4^-$), the portion of which depends on water pH. Boric acid is the dominant form and is a common micronutrient. Isotopic fractionation is controlled by the exchange reaction (Vengosh et al., 1994):

$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- = {}^{11}B(OH)_3 + {}^{10}B(OH)_4^- \qquad (1.2)$$

Adsorption-desorption reactions are the most significant mechanism influencing the ultimate fate of boron in water (Rai et al., 1984). Preferentially, $^{10}B(OH)_4^-$ is removed onto clay surfaces, which can retard the ion's transport relative to water flow and to conservative tracer migration (Vengosh et al., 1994).

Adsorption of B occurs through the anion's exchange with surface hydroxyl groups on aluminum (Al) and iron (Fe) oxide clay minerals, such as kaolinite, montmorillonite, and illite (Sims and Bingham, 1968; McPhail et al., 1972; Keren and Talpaz, 1984). Boron uptake is proportional to, among other factors, concentration in the solution, clay content, particle size, and pH. Preferential removal of ^{10}B increases with increasing pH, and as a result, is not always observed in groundwater systems. Field studies of boron transport have shown conservative movement in coarser sediments and retardation with high clay content (Leenhouts et al., 1998). The RHSG tracer study (Quast et al., 2006) determined that ^{10}B transport exhibited conservative movement, relative to the conservative xenon (^{136}Xe and ^{124}Xe) and water stable isotope tracers.

The present study served as the first objective comparison of Br^- and ^{10}B subsurface travel times in a field setting. Alkali halides, such as sodium bromide (NaBr) and potassium bromide (KBr), are the most commonly used salts for fluid tracing due to their conservative behavior (Davis et al., 1985; Chrysikopoulos, 1993; Prych, 1999). If sorption influences ^{10}B movement in the subsurface, Br^- will arrive consistently earlier to each well. Previous experiments conducted at SGSG employed Br^- as a groundwater tracer (Anders et al., 2004; Anders and Chrysikopoulos, 2005; Drewes et al., 2011) and were to document rapid flow beneath the basin.

The primary limitation of deliberate tracers is the substantial amount of mass needed to raise concentrations or isotope ratios in large volume settings. This escalates injection costs and the possibility for permitting conflict. An overabundant tracer also can induce density contrasts between the tagged and native groundwater (Istok and Humphrey, 1995).

1.2.3 Temperature as a Proxy for Heat

At the SGSG test basin, recycled water is warmed during treatment and after being transferred to a spreading pond, it acquires the diurnal heating/cooling trends. Hence, there is potential to use heat as a tracer at MAR sites, similar to how it has been used as a tracer near streams (Lapham, 1989; Stonestrom and Constantz, 2003; Constantz et al., 2003; Anderson, 2005). Recent studies have employed heat as a tracer at spreading basins to determine spatial and temporal variations of infiltration rates (Racz et al., 2012; Becker et al., 2013). Subsurface travel times in the near field can be estimated by peak matching of diurnal temperature changes (e.g., Laws et al., 2011; Becker et al., 2013).

Temperature sensors/loggers can record in less than 1-hour time steps with high precision (confidence to three decimal places). These time steps are more than two orders of magnitude quicker than the travel times of interest for permitting MAR operations. Heat flow is easy to measure (as temperature changes) and can be repeated numerous times to answer questions about seasonality or how changes in operations affect travel time. Like all intrinsic tracers, permitting is not required, because there is no artificial input.

Unfortunately heat flow is not conservative, because heat dissipates into the solid matrix during transport within the groundwater system (Constantz et al., 2003). A conservative tracer such as Br^- remains in the pore water solution and does not interact with sediment. Br^- is transported in the subsurface by (1) advective movement during water flow and (2) hydrodynamic dispersion. Heat flow occurs also through water advection and dispersion but includes one additional mechanism: thermal diffusion, or the capacity of solids to absorb and conduct energy. The influence of heat absorption/conduction by the solid matrix is inversely proportional to groundwater velocity (Constantz et al., 2003). With MAR sites engineered to maximize recharge rates, energy (heat) and chemical (Br^-, ^{10}B if conserved) transport should be similar near the spreading basins. Becker et al. (2013) found that heat dispersion under a spreading basin primarily was due to hydrodynamic mechanisms rather than thermal diffusion. If MAR sites are engineered to maximize recharge rates and if consistent maintenance procedures are adopted, heat may be applicable to GRRPs.

1.2.4 SF_6 Closed-System Injector

A closed-system injector for SF_6 will be necessary to comply with the research exemption for SF_6 by the California Air Resources Board. The closed-system injector should reduce SF_6 emissions to the atmosphere during injection by more than 90% compared to the current methodology that relies on the direct bubbling of the gas tracer into the spreading ponds. A membrane contactor that generates steep SF_6 concentration gradients through a gas permeable membrane was developed and evaluated as a potential new SF_6 injector for deliberate tracer studies. The injector was tested during an experiment initiated at the Yucaipa Valley Water District spreading pond in December 2012. This experiment was supported by the local water district and occurred independently from this WateReuse Research Foundation supported work. This study along with the laboratory tests demonstrate that an injection scheme based on the membrane contactor will work and will reduce the loss of SF_6 to the atmosphere at the time of tagging recharge water. Another approach used for charging rivers and other bodies of water with gas tracers is to submerge gas permeable tubing (silicone) directly in the water body that needs to be tagged (Cook et al., 2006; Visser et al. 2013; Benson et al., 2014).

Chapter 2

Experimental Approach

2.1 Field Locations

The new $^{35}S\text{-}SO_4$, ^{10}B, and heat tracer methods were evaluated at two MAR sites in Southern California that have well-characterized near-field travel times: (1) Montebello Forebay spreading grounds in Los Angeles County (^{10}B, heat, and ^{35}S) and (2) the OCWD Groundwater Recharge MAR facilities (^{35}S only). The MAR sites are located in recharge zones of a deep sedimentary basin bounded to the north by the San Gabriel Mountains and to the south by the Pacific Ocean (Figure 2.1).

Both MAR sites recharge an extensive network of freshwater-bearing aquifers that are found within 250 to <500 m thick unconsolidated basin fill. Primary aquifers are contained in Holocene alluvium and Pleistocene formations (CDWR, 1961, 2003; Yerkes et al., 1965). The unconsolidated sediments are largely nonmarine clastic deposits of interlayered gravels, sands, silts, and clays. Coarser sediments form the aquifers; finer deposits of silts and clays create semipermeable aquitards that allow for some hydraulic connection between aquifers (CDWR, 1961). Pliocene to upper Miocene marine sedimentary rocks (sandstone, siltstone, shale, and some conglomerate) underlie the unconsolidated Quaternary sediments as basement rock. However, these older units do not yield sufficient groundwater for pumping (Johnson, 2005).

Forebays are in the north and denote areas of unconfined aquifers where surface water percolates down to and replenishes deeper aquifers and are considered regional recharge areas for deep aquifers (Johnson, 2005). Pressure areas are in the south where confined aquifers receive minimal recharge from the surface area directly above. The spreading grounds at Montebello Forebay are situated within the principle recharge area for the Central Basin, a 717 km^2 sub-basin of the Los Angeles coastal plain (LACP) while the OCWD MAR facilities are located within the Santa Ana Forebay of the 906 km^2 Orange County coastal plain (OCCP). LACP and OCCP are both part of the same groundwater basin but are separated by a political divide along the Los Angeles County–Orange County line.

Artificial recharge occurs at surface-spreading basins as well as at direct injection wells. The latter are typically situated in a row along the coast to mitigate saltwater intrusion. Source waters to the MAR sites are composed of a mixture of seasonal runoff, imported high-quality surface water, and recycled wastewater. Deliberate tracer experiments and T/^{3}He groundwater dating surveys were conducted prior to this work at both the Montebello Forebay and OCWD MAR facilities (e.g., Gamlin et al., 2001; Clark et al., 2004; 2014; Quast et al., 2006; McDermott et al., 2008).

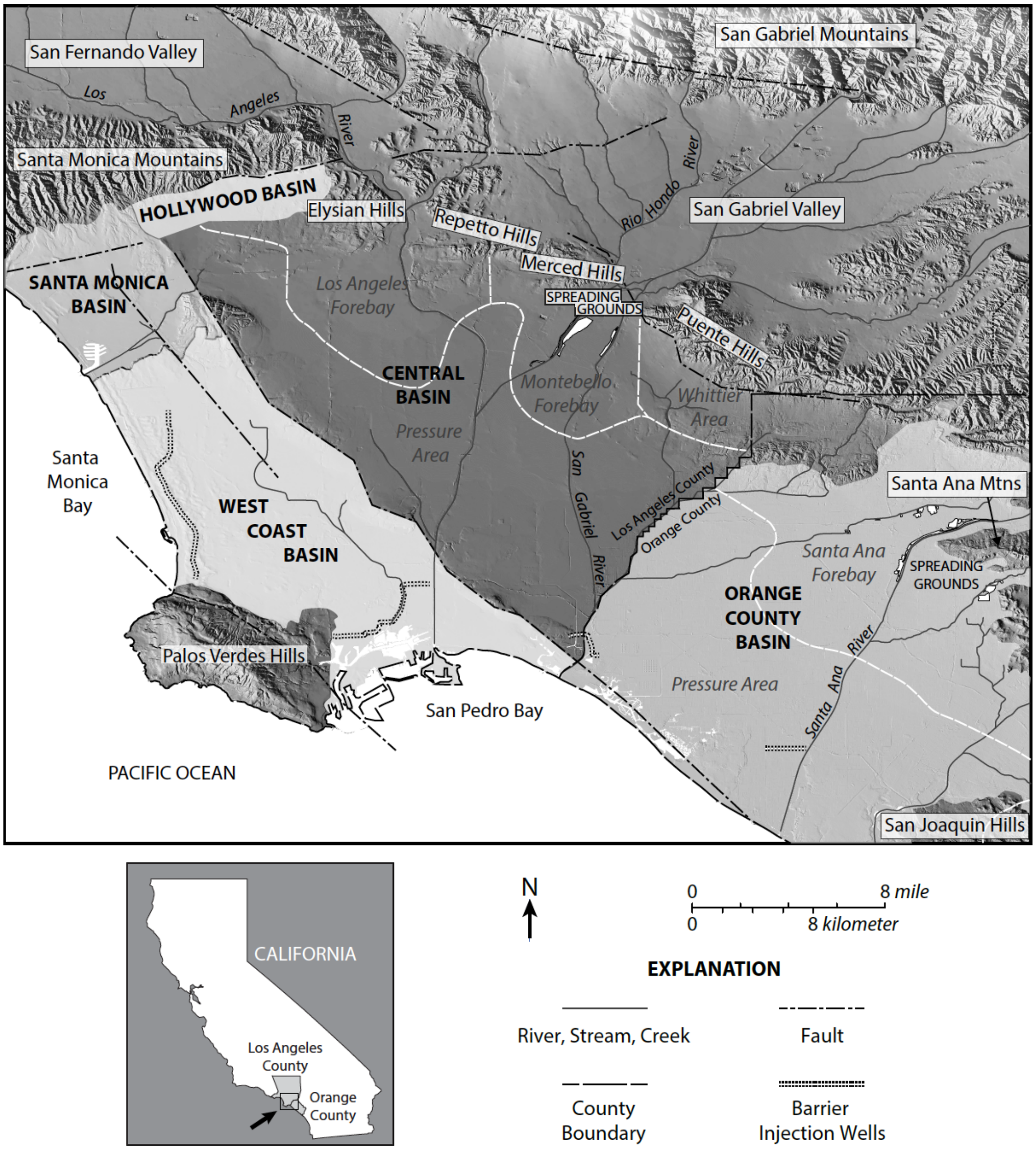

Figure 2.1. Shaded relief map of Los Angeles and Orange County coastal plains.

Note: Included on the map are the coastal plains sub-basins.

Source: Base map from the USGS 10-m National Elevation Dataset (Gesch, 2007); basin overlays from CDWR (2003), Yerkes and Campbell (2005), and Johnson (2005).

2.1.1 Montebello Forebay Spreading Grounds

Montebello Forebay (Figure 2.2) is operated by the Los Angeles County Department of Public Works (LACDPW) and the groundwater it recharges is managed by the Water Replenishment District of Southern California (WRD). The facility is composed of the Rio Hondo and San Gabriel spreading grounds (RHSG and SGSG, respectively). Artificial recharge at the Montebello Forebay started in 1938, and local water tables have risen by more than 25 m since then. In 1962 the Los Angeles County Sanitation Districts (LACSD) began providing tertiary-treated recycled wastewater for artificial recharge. Treatment occurs at the San Jose Creek, Whittier Narrows, and Pomona Water Reclamation Plants, and gravity flows through river channels or is piped directly to the basins.

The 30-year average of annual recharge at Montebello Forebay is 1.6×10^8 m^3 or 1.3×10^5 AF (WRD, 2012). The California Regional Water Quality Control Board, Los Angeles Region, establishes the limits for recycled water spreading at Montebello Forebay. Currently, about 30% of the water recharged at Montebello is derived from recycled water. In the near future, as part of its Water Independence Now program, WRD plans to bring this number to 55% ($>1.9 \times 10^4$ m^3/d or >15 AF/d) of the total supply. Stormwater capture will also escalate such that imported water can be completely phased out.

RHSG consists of 20 shallow (<4 m deep) infiltration basins that cover 3.1 km^2 (Figure 2.3a). SGSG has three spreading ponds of similar depth that cover 0.52 km^2, and at the northern extent of SGSG, there is a U.S. Geological Survey (USGS) research test basin (Figure 2.3b). Additional basins can be created in the San Gabriel River by inflating rubber dams; however, river recharge cannot be done in the Rio Hondo River, because it is concrete lined. An SF_6 tracer experiment and survey of $T/^3He$ ages were performed at these sites by McDermott et al. (2008). Their primary result was that depth not pumping or distance is the main factor controlling travel times near (within 150 m) the spreading basins. This finding led to changes in the CDPH draft groundwater recharge regulations resulting in the removal of the distance requirement.

2.1.1.1 Research Test Basin at San Gabriel Spreading Grounds

The multitracer experiment evaluating ^{10}B, Br^-, and heat (as measured by temperature) was conducted at the research test basin that marks the northern extent of SGSG (Figure 2.3b). The approximately 2000 m^2 basin was constructed and characterized by the USGS in the early 1990s (Schroeder et al., 2003). The basin was created to evaluate water quality changes during SAT when spreading recycled wastewater (Schroeder et al., 2003; Anders et al., 2004; Anders and Chryikopoulos, 2005), which can be pumped directly to this basin at controllable rates (about 2200 m^3/day during our experiment). More recent work at the test basin includes an investigation of the fate of trace organic chemicals contained in recycled water (Drewes et al., 2011; Laws et al., 2011).

Nine monitoring wells are situated in a line down gradient of the test basin (Figure 4). Each well is equipped with loggers that record hourly temperature and water level measurements. WRD installed the four most distant wells (as two well pairs) less than a month before the initiation of the multitracer injection. Well pairs monitor an upper unconfined aquifer and a lower semiconfined aquifer, separated by a low permeability clay deposit. Pre-experiment travels times were estimated to range from <1 day to 6 months, based on temperature peak matching by Laws et al. (2011) to the five wells available at that time and extrapolating out to the four newly installed wells. Hydrostratigraphy of the local area is known from detailed well logs and cone penetration tests (CPTs). SGSG is underlain by a typical California alluvial basin with a mix of high (sands and gravels) and low (silts and clays) hydraulic conductivity material. This creates the potential for preferential flow paths.

Schroeder et al. (2003) measured infiltration rates through the basin floor of 0.6 to 0.9 m/day, with 2 to 3 m of unsaturated flow between the floor and the recharge mound. Vertical hydraulic conductivities measured below the floor ranged from 0.24 to 26.5 m/day. The low value corresponds to ~15 cm thick clay-rich infiltration zone at the basin floor. This zone was likely still present to some places during the fall 2011 study (and is common on a spreading basin floor due to fine sediment deposition from the water and air blown dust). Horizontal conductivities ranged from 25.9 to 38.1 m/day and the mean porosity was 0.24.

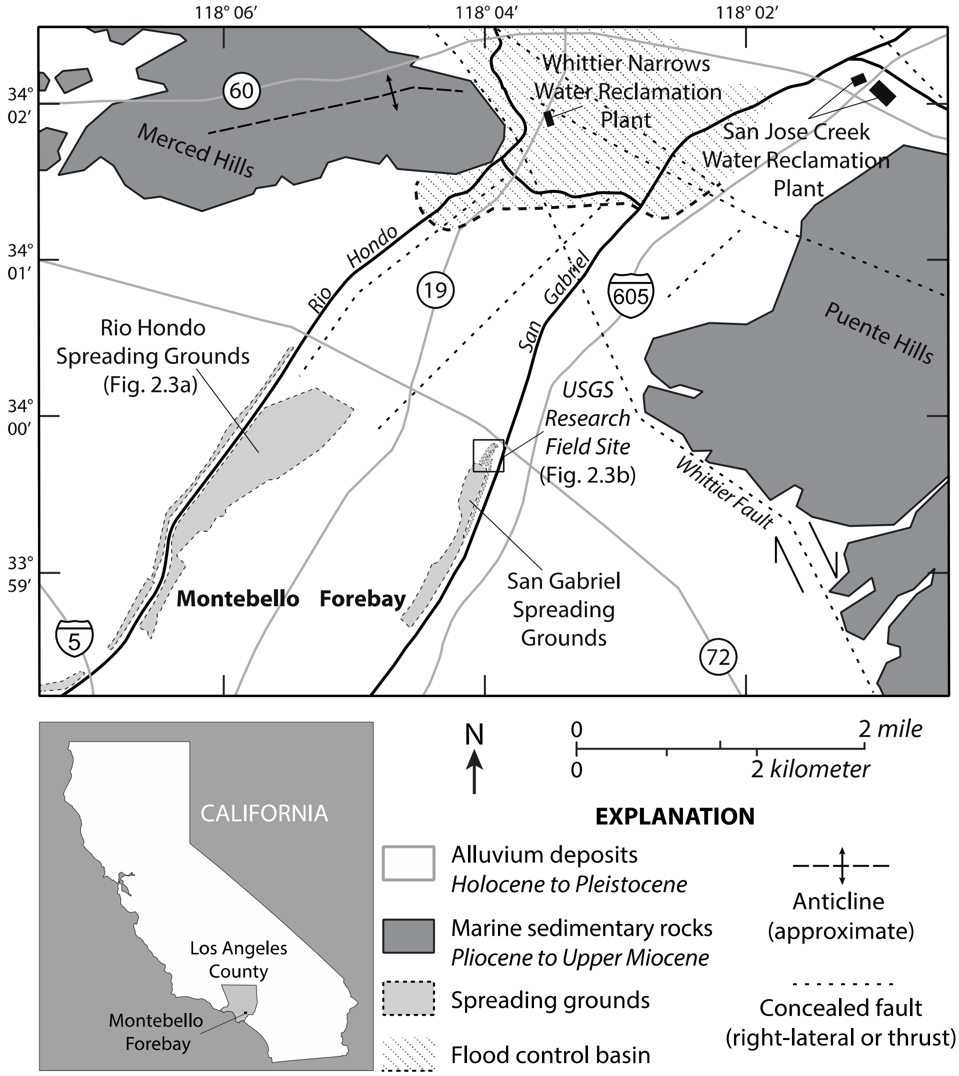

Figure 2.2. Location of Rio Hondo and San Gabriel spreading grounds.

Note: These spreading grounds are part of the Montebello Forebay MAR operation, Los Angeles County, CA.

Source: Base map modified from Schroeder et al. (2003); faults and folds from Yerkes and Campbell (2005).

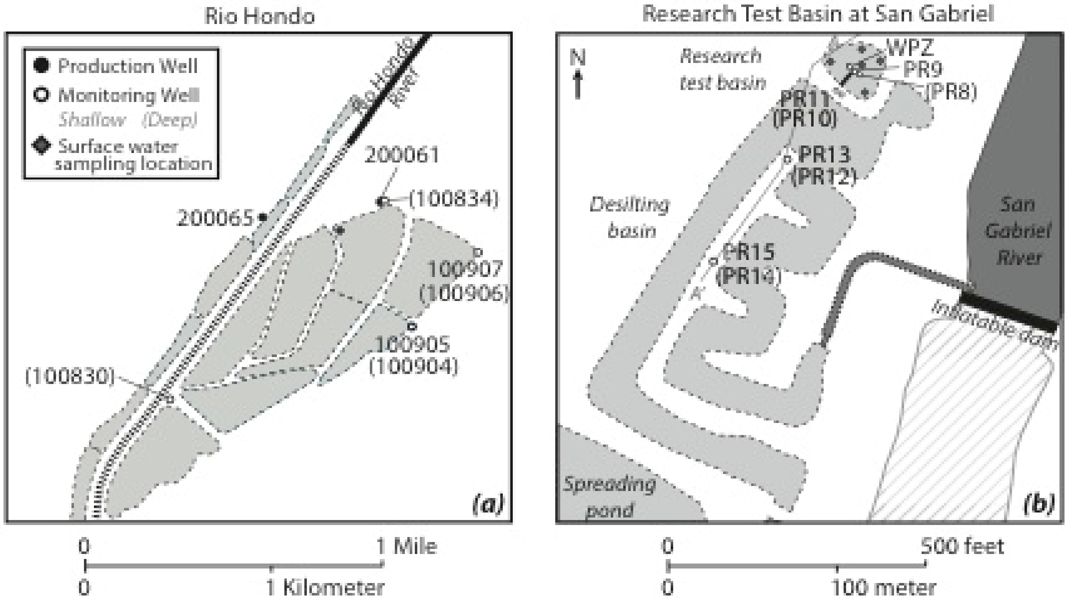

Figure 2.3. Wells sampled at the Montebello Forebay field locations.

Notes: (a) Instrumentation at RHSG field site includes two production wells (200061, 200065) and six monitoring wells (100830, 100834, 100904, 100905, 100906, 100907); (b) SGSG test basin includes nine monitoring wells (WPZ, PR8-15); see Figure 2.4 for A-A' cross section.

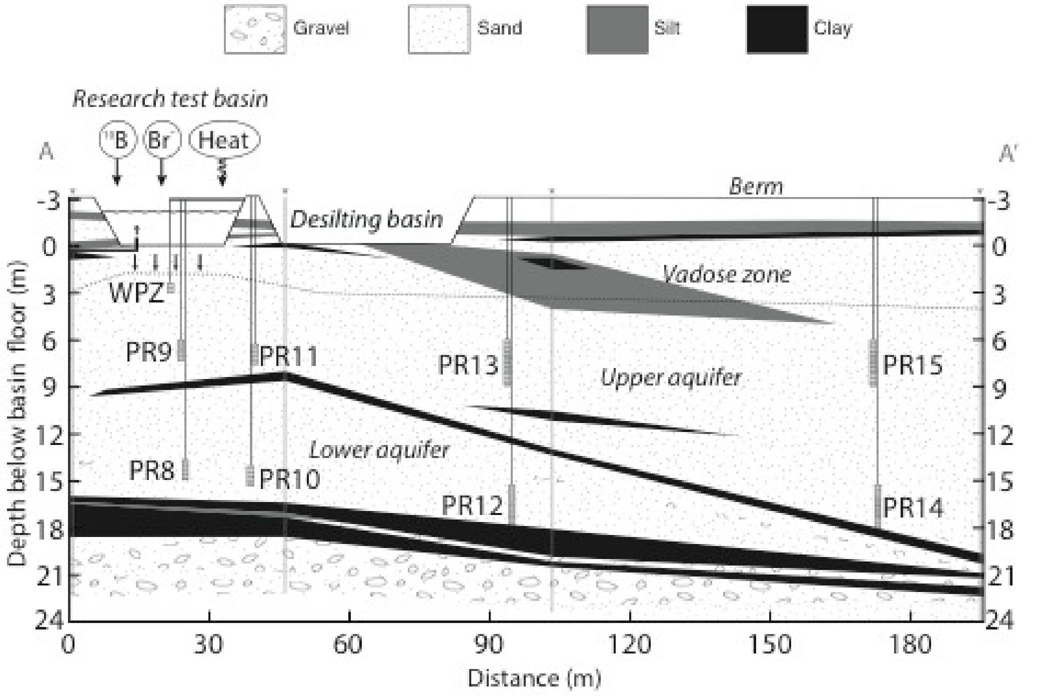

Figure 2.4. Simplified well location and stratigraphy underlying SGSG research test basin.

Notes: The stratigraphy is based on an array of cone penetration tests and detailed well logs. Aquifers are defined by sand- and gravel-dominated (>50%) horizons. Low permeability layers of silt and clay are shown in gray and black, respectively.

2.1.2 Orange County Groundwater Recharge Facilities

The OCWD MAR facilities are located in north-central Orange County within the Santa Ana Forebay, about 18 km downstream of Prado Dam (Figure 2.5). In the forebay region, natural recharge occurs primarily by direct percolation of Santa Ana River (SAR) water through highly permeable sands and gravels along the river. Since 1936 the OCWD has been artificially recharging various source waters along the SAR channel in Anaheim, CA, including imported water from the Colorado River Aqueduct and State Water Project, SAR base flow, and SAR storm flow. In addition to the SAR channel, OCWD currently operates two dozen surface spreading basins that cover 6 km^2 of wetted area and range in depth from 2 to 50 m.

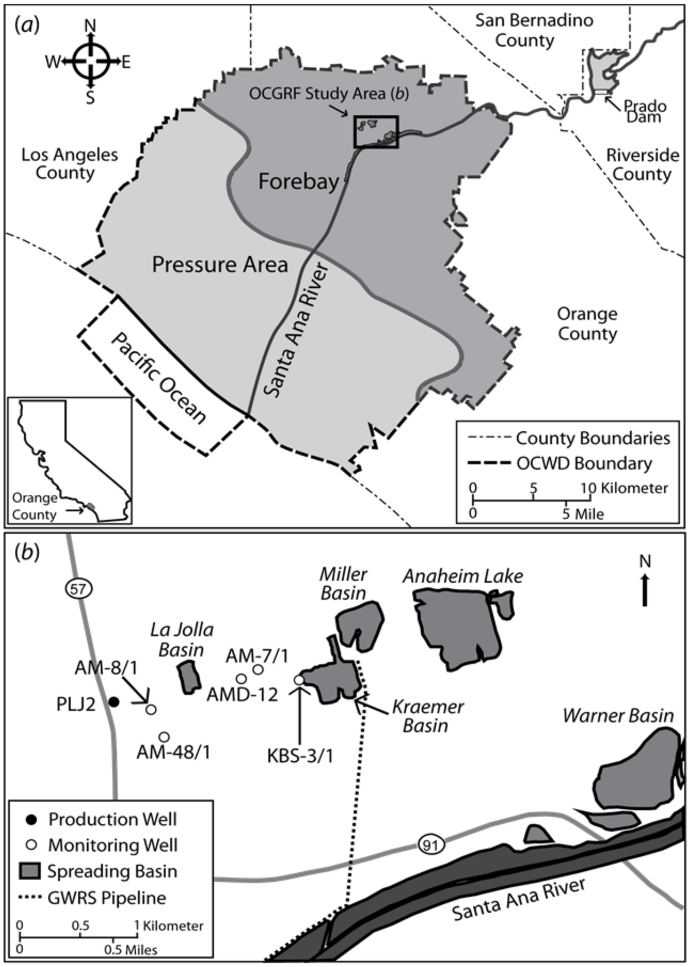

Figure 2.5. Map showing OCWD MAR study sites.

Notes: (a) OCWD MAR study area is located in Orange County, CA; (b) Location of recharge basins, Santa Ana River channel, and wells sampled in this study. Well PLJ2 is the only production well investigated in this study.

Recharge practices at the OCWD MAR facilities have been highly successful with 3.5×10^8 m^3 (2.8×10^5 AF) of water being recharged annually (Hutchinson, 2012). In 2008, OCWD began recharging recycled wastewater supplied by the OCWD groundwater replenishment system (GWRS), where the water is purified using a three-step advanced treatment process consisting of microfiltration, reverse osmosis, and ultraviolet light with hydrogen peroxide disinfection. Since 2008 recycled water from the GWRS provided 15% of the total surface water recharged by OCWD (Hutchinson, 2012). GWRS water is supplied to Miller and Kraemer Basins via a 21-km pipeline that transports water from the treatment plant in Fountain Valley to the basins in Anaheim.

2.2 Sulfur-35 Methods

2.2.1 Field Sampling

Surface water and groundwater samples of ^{35}S were collected from RHSG and OCWD MAR facilities periodically from 2010 to 2012 as part of routine monitoring at these sites. For each sample, 20 L of water were field or laboratory filtered into polyethylene containers using a 0.45 micron high-capacity filter. At RHSG, six monitoring wells and two production wells were sampled from January 2010 to February 2012 (Figure 2.3a). Four of the six monitoring wells were shallow and deep well pairs (100904 and 100906 are deeper with respect to 100905 and 100907). Surface water from the RHSG was collected from an infiltration basin on the northern end of the spreading grounds on two sampling events: January 31, 2010, and June 2, 2010. At the OCWD MAR study area (Figure 2.5), six monitoring wells, one production well, five infiltration basins, and SAR surface flows were sampled from December 2010 through December 2012. Multiple depths were sampled at well AMD-12. On April 6, 2012, GWRS water was collected from two points along the transmission pipeline: immediately posttreatment at the Fountain Valley treatment facility and the discharge into Miller Basin. A rainwater sample was collected on February 25, 2011, in Orange, CA, approximately 6 km south of the OCWD recharge facilities, and provides a measure of the ^{35}S-SO$_4$ activity of locally derived precipitation.

2.2.2 Sample Analysis

Sulfate concentrations for groundwater and surface waters at both study sites were determined by ion chromatography following EPA 300.0 method (Plaff, 1993). RHSG samples were analyzed on a Dionex model DX500 instrument at BC Laboratories, Inc., in Bakersfield, CA. The OCWD MAR samples were analyzed on a Dionex ICS 3000 instrument at the OCWD Water Quality Laboratory in Fountain Valley, CA.

Existing analytical methods for measuring ^{35}S were inadequate for MAR waters because of the high SO$_4$ concentrations (5−150 mg/L) typically found in these systems. We developed a novel method for handling the high sulfate loads of MAR waters so that sufficient volumes of water could be analyzed to detect ^{35}S.

Recovery of ^{35}S-SO$_4$ was achieved using a batch method technique modified from Michel et al. (2000). Between 3 and 20 L were processed for each sample to obtain a desired 500 to 1500 mg of SO$_4$. For the precipitation and GWRS sulfate samples (<1 mg/L SO$_4$), 26 ml of a 0.4M Na$_2$SO$_4$ carrier solution was added to achieve 1000 mg of SO$_4$. Samples were acidified to pH 3−4 using 5M HCl, and 15 g of Amberlite ion exchange resin was added and suspended by stirring each sample for 2 h. Dissolved ^{35}S-SO$_4$ was bound to the resin that was collected and transferred to ion exchange columns. To elute the ^{35}S-SO$_4$, 125 ml of a 5% NaCl solution was added. Samples were then passed through a column containing 2 g of activated carbon to remove colored impurities that could potentially interfere with liquid scintillation counting. The 30 mL addition of a 0.8M BaCl$_2$·2H$_2$O solution formed a ^{35}S-BaSO$_4$ precipitate that was rinsed with deionized water, dried, and suspended in a scintillation gel for liquid scintillation counting at Lawrence Livermore National Laboratory in Livermore, CA. ^{35}S-SO$_4$ activities are reported in mBq/L. The minimal detectable activity (MDA) and 1σ counting error are given by eqs 2.1 and 2.2:

$$MDA = \frac{2.71 + 3.29 * \sqrt{B * T}}{E * T * V} \tag{2.1}$$

$$1\sigma\ error = \frac{\sqrt{\frac{C}{T} + \frac{B}{T}}}{E * V} \tag{2.2}$$

where B = background ^{35}S-SO$_4$ activity (mBq), T = count time (min), E = counting efficiency, V = volume (L), and C = sample ^{35}S-SO$_4$ activity (mBq). Variation in the mass of SO$_4$ recovered per sample resulted in varying background count rates and counting efficiencies, with high-SO$_4$ samples having a higher background count rate and lower counting efficiency relative to low-SO$_4$ samples. Due to varying SO$_4$ yields, the MDA ranged between 0.5 and 3.4 mBq/L. One sigma counting errors were between 0.1 and 1.8 mBq/L.

2.2.3 Travel Time Calculation

Under a simplified piston flow model at an MAR surface spreading facility, a natural or deliberate tracer is incorporated into the source water above ground prior to recharge. Conservative tracers are recharged and transported through the aquifer at the mean velocity of the groundwater. Tracer input functions in this study were defined empirically using the ^{35}S-SO$_4$ activity of MAR surface water in the spreading ponds. The subsurface travel time of water was calculated using the following decay equation:

$$t = \frac{(^1/_\lambda)}{ln(^{N_o}/_N)} \tag{2.3}$$

where t is the subsurface travel time in years, λ is the decay constant for ^{35}S (2.894 yr^{-1}), and N$_o$/N is the activity ratio of the ^{35}S-SO$_4$ activity in the source water (N$_o$) and in the well (N) in mBq/L. Equation 2.3 does not account for subsurface dilution of young water (<1 year subsurface travel time) with older water (>1 year). Therefore, the calculated subsurface travel time represents a maximum travel time, because dilution of young recharge water with older groundwater would look like radioactive decay and lower the ^{35}S-SO$_4$ activity, resulting in an artificially long subsurface travel time. The assumption made in Equation 2.3 of negligible dilution of young with old water is appropriate for narrow screened shallow wells located near the infiltration basins; however, longer screened wells located farther down gradient of the infiltration basins are likely to be a mixture of groundwater of different ages (McDermott et al. 2008). Equation 2.3 also assumes conservative transport of sulfate with no sorption or sulfate reduction. The effect of sorption or sulfate reduction would be the same as mixing with older water in that the calculated subsurface travel time would be longer than the true subsurface travel time. Sulfate should behave as a conservative anionic complex and not experience significant sorption or reduction in these oxic, near-neutral groundwaters.

2.3 Boron-10, Bromide, and Temperature

Deliberate tracer experiments like the ^{10}B and Br^- experiment described herein require a physical injection event followed by episodic sampling of wells. Each well is sampled until breakthrough curves have been developed for all tracers, indicating that the tracer has passed the well. Breakthrough curves are a plot of relative tracer concentration (C) or normalized concentration (C/C_0) versus time. Groundwater travel times are calculated through breakthrough curve analysis.

2.3.1 Multitracer Injection at San Gabriel Research Test Basin

2.3.1.1 Geochemical Tracers

On September 6, 2011, the deliberate tracer experiment was initiated when two 57 L barrels of basin water (114 L total) spiked with Br^- and ^{10}B were released into the test basin at the SGSG. Three kg of powdered boric acid enriched to >92% ^{10}B and 36 kg of granular sodium NaBr were added in equal portions to the barrels. The tagged barrel water was pumped for 45 min through a 23 m soaker hose, which was dragged to cover the test basin in its entirety. After the barrels were emptied, inflow of recycled water was halted for 12 h to allow the tagged test basin water to mostly (~90%) drain and infiltrate as a single pulse. Inflow of recycled water then continued nonstop for 57 days, ending on November 2, 2011.

2.3.1.2 Temperature

Heat serves as an intrinsic tracer that does not require any artificial energy or chemical input (i.e., no physical injection). Recycled water began continuously entering the basin on September 2, 2011 (96 h prior to geochemical tracer injection) in order to build the recharge mound following a period of no recharge and basin maintenance. Temperatures were recorded hourly at loggers deployed in each well and in the middle of the test basin. Loggers are strategically suspended in the middle of each well screen. Infiltrating recycled water averaged 11.6 °C above native groundwater during early September and 8.3 °C by November. Ambient groundwater temperatures at the test basin rarely fluctuated more than 0.5 °C in the absence of artificial recharge.

Dilution of the recycled water plume with native groundwater can be estimated using temperature measurements. Following Drewes et al. (2011), the percent of recycled water pumped at each well is calculated as

$$\frac{T_b - T_w}{T_b - T_r} x\ 100\% \tag{2.4}$$

where T_b is temperature of background water, T_w is the highest temperature measured at the well, and T_r is the temperature of recycled water. Equation 2.4 is an oversimplification and does not take into account heat loss due to conductance by the aquifer solids. Therefore, calculated plume percentages are minimum values.

2.3.2 Field Sampling and Laboratory Analysis

Sampling occurred for 1 year following tracer injection. Immediately after injection, the tagged basin water was sampled every 4 h at five surface water locations (four corners and the center) until the basin drained. Once inflow of untagged water began again, basin water was collected once per day for the next 3 days. After injection, shallow, close wells (WPZ, PR9, PR11) were sampled every 4 to 8 h for ~6 days; thereafter, PR9 was sampled once per week for 2 weeks and PR11 for 3 weeks. Deeper or more distant wells (PR8, PR10, PR12–15) were sampled weekly for the first 3 months following injection; thereafter, sampling occurred approximately twice a month for the next 5 months, and finally once a month until September 2012. Once the tracer had passed a well, it was removed from the sampling schedule. As is common with deliberate tracer studies, a higher sampling resolution was limited by staff hours available.

Deep wells (PR8, 10, 12, 14) were sampled using dedicated Grundfos submersible pumps maintained by WRD. Shallow, close wells (WPZ, PR9, 11) were sampled using a Geotech peristaltic pump and shallow, distant wells (PR13, 15) were sampled using a Proactive Supernova-70 submersible pump. All wells were purged of three casing volumes of water prior to collection per standard protocols. Samples for Br^- and ^{10}B analyses were each collected through a 0.45 µm filter into125 mL Nalgene bottles.

Bromide concentrations were measured using a Dionex Model DX500 ion chromatograph at BC Laboratories, Bakersfield, CA, using the standard EPA method. BC lists a duplicate relative percent difference of 10% on the ion chromatograph; therefore, Br^- results are presented with uncertainty of ±10%. The practical quantification limit is 0.1 ppm.

Boron isotopic mass ratios were measured using a Finnigan MAT Element2 [sector] ICP-MS at University of California, Santa Barbara. Boron in the water samples was first ionized with inductively coupled plasma, then was isotopically separated and quantified using the mass spectrometer. Absolute and isotopic boron concentrations were calculated relative to two spiked gravimetric standards, one with natural boron isotope abundances and another enriched in ^{10}B. Groundwater samples typically were diluted by a factor of six to bring absolute concentrations down to the prepared standards. Samples collected directly from the test basin shortly after geochemical injection were diluted by a factor of 11 and, in one instance, for a sample collected directly next to the tagged barrels, by 189.

Instrumental mass bias (^{11}B, the larger ion, can deflect ^{10}B away from the detector) manifests as the offset of the measured values from the known concentrations of the standards. Reported isotopic ratios are all mass bias adjusted. Analytical uncertainty was measured from the drift of standard runs through an ICP-MS session. Both the natural abundance and enriched standards were run at the beginning, middle, and end of each session. At its worst, the standard deviation for measured isotopic ratios on the ICP-MS was ±15‰ $\delta^{11}B$ while at its best, the uncertainty was ±2‰ $\delta^{11}B$. Herein we will be reporting the worst-case errors.

Although one to two orders of magnitude worse than the precision capability of the thermal ionization mass spectrometry (TIMS) system, isotopic tracers such as boron still show a strong signature, even when sampling a relatively small portion (<10%) of the tagged plume. Cost savings and sample output (90–100 samples analyzed in a day) justify the decrease in analytical certainty using the ICP-MS.

Additional data for the desilting basin and for nearby production wells operated by Pico Water District (PWD) and San Gabriel Valley Water Company (SGVWC) were provided by WRD. Two production wells owned by PWD are located approximately 650 m due north (up gradient) of the test basin. These wells draw from deeper aquifers (35-118 m and 55-116 m screen depths). SGVWC operates one production well located 350 m southeast of the test basin that was active during the tracer experiment. This well also draws from deeper aquifers (93-141 m screen depth).

2.3.3 Travel Time Calculation

Breakthrough curves are characterized by the tracer first arrival (defined by the first detection and therefore the analytical method), tracer peak arrival (observed maximum concentration and therefore the frequency of sampling analytical method), and arrival of the tracer center of mass (COM), which is calculated using the entire breakthrough curve.

Chapter 3

Results and Discussion

3.1 Sulfur-35

3.1.1 Rio Hondo Spreading Grounds

RHSG surface water had ^{35}S-SO$_4$ activities of 26.9±1.8 mBq/L on January 31, 2010, and 7.5±1.4 mBq/L on June 2, 2010. The higher activity in January is likely due to an increase in the contribution of recent storm water runoff to the spreading basin following a series of precipitation events during winter 2009/2010. Because ^{35}S is produced in the upper atmosphere by cosmogenic rays, recent stormwater runoff is expected to have higher concentrations of ^{35}S relative to other source components (e.g., recycled or imported water). Furthermore, because the majority of the recharge at the RHSG typically occurs from late fall to early spring (Figure 3.1), the January 2010 ^{35}S-SO$_4$ activity (26.9±1.8 mBq/L) was assumed to be the input end member. This end member value was used to calculate the subsurface travel time using Equation 2.3.

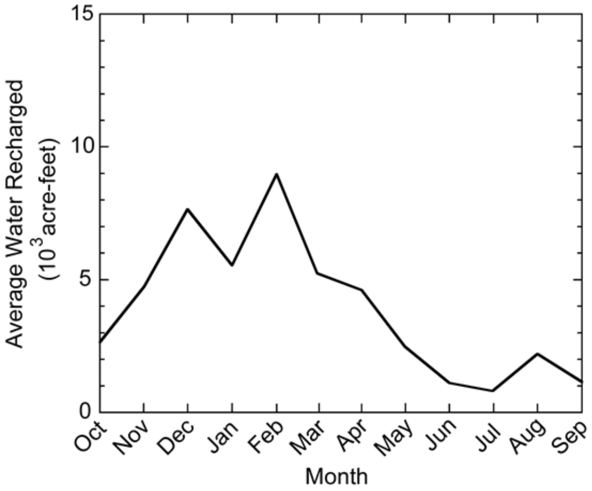

Figure 3.1. Five-year average monthly water recharged at the RHSG.

Notes: The majority (78%) of the recharge occurs from late fall to early spring (November to April) (LACDPW, 2013). The average for October to June include water year 2008–2009 to 2012–2013. July to September data include water year 2008–2009 to 2011–2012.

Time series measurements of ^{35}S-SO$_4$ activities in groundwater at monitoring and production wells ranged from <0.8 mBq/L to 12.0±1.0 mBq/L (Table 3.1). ^{35}S-SO$_4$ was not detected in six of the 29 groundwater samples, which included all three samples collected from production wells 200061 and 200065. The ^{35}S-SO$_4$ activities in RHGS groundwater imply subsurface travel times of 15±2 to >62 weeks (Table 3.1, Figure 3.2), which represent a range of maximum travel times, because no correction was made for mixing of young (<1 year old) recharge water with old (>1 year old) groundwater within the wells. Travel times could be shorter if mixing occurs between these two components, because dilution of young with old groundwater would appear as radioactive decay, resulting in an overestimation of groundwater travel time. We assumed negligible mixing for the monitoring wells, which were all located at shallow depths near the infiltration basins; however, dilution at production wells should be considered, because longer screened wells located farther down gradient of the infiltration basins are likely to be a mixture of groundwater of different ages (McDermott et al. 2008). For example, assuming no dilution at production well 200061, ^{35}S-SO$_4$ activities resulted in travel times of >43 weeks on March 29, 2011, and >49 weeks on February 23, 2012. Under a mixing scenario containing a 1:5 dilution of young with older groundwater, travel times to well 200061 are >14 and >20 weeks for March 29, 2011, and February 23, 2012, respectively.

Assuming an end member ^{35}S-SO$_4$ activity of 26.9±1.8 mBq/L for water recharged at the RHSG, seasonal differences in^{35}S-SO$_4$ travel times were observed for the monitoring wells, particularly for the two monitoring wells with the most robust data set: 100830 and 100834. For example, the three shortest ^{35}S-SO$_4$ travel times for well 100834 occurred during the main recharge period of late fall/early spring for each water year: 20±3 weeks on January 31, 2010; 17±2 weeks on March 28, 2011; and 15±2 weeks on February 23, 2012 (Figure 3.2). The steeper gradient due to enhanced recharge during periods of high recharge are likely driving shorter travel times to this well during this period. In the late spring/early summer, well 100834 had longer travel times (e.g., 43±7 weeks on May 23, 2010, and 34±2 weeks on May 23, 2011). These travel times imply that the late spring/early summer groundwater at well 100834 were approximately several months older than the samples collected in the winter/early spring, which is expected under a simplified piston flow model.

Fewer measurements were made at the other RHSG wells; however, a similar trend of shorter travel times during the main recharge period followed by longer travel times several months later was observed for wells where multiple measurements were made within the same water year (100830, 100906, 100907; Figure 3.2). For example, the ^{35}S-SO$_4$ travel time to well 100830 was 18±3 weeks on March 24, 2011, followed 27±2 weeks on July 13, 2011. Well 100906 had travels times of 34±4 weeks and 39±4 weeks on the May 23, 2011, and July 13, 2011 sampling events, respectively.

Table 3.1. Sulfate Concentration, ^{35}S-SO$_4$ Activity, and Subsurface Travel Time for Groundwater Collected at RHSG

Well ID and Collection Date	SO$_4$ (mg/L)	^{35}S-SO$_4$±1σ (mBq/L)[a]	^{35}S-SO$_4$ Travel Time±1σ (weeks)[b]
100830			
24 Mar 2011	30	9.7±1.1	18±2
24 Mar 2011[c]	30	9.7±1.4	18±3
13 Jul 2011	21	6.0±0.7	27± 2
15 Sep 2011	30	1.2±0.4	55±6
04 Jan 2012	30	1.8±0.4	48±4
23 Feb 2012	34	5.2±0.7	30±3
100834			
31 Jan 2010	21	8.9±1.6	20±3
22 Apr 2010	106	3.3±1.1	38±6
23 May 2010	146	2.5±1.0	43±7
28 Mar 2011	28	10.7±0.7	17±2
23 May 2011	146	4.1±0.4	34±2
13 Jul 2011	32	5.1±0.8	30±3
04 Jan 2012	25	3.7±0.4	35±2
23 Feb 2012	70	12.0±1.0	15±2
100904			
24-May-2011	22	7.9±0.4	22±2
23-Feb-2012	66	<1.6	>51
100905			
13 July 2011	36	5.1±0.8	30±3
23 Feb 2012	67	<1.7	>50
100906			
23 May 2011	NA	4.0±0.9	34±4
13 Jul 2011	25	3.1±0.7	39±4
07 Jan 2012	21	1.1±0.3	57±5
23 Feb 2012	44	1.8±0.7	49±7
100907			
24 Mar 2011	32	5.5±1.0	29±3
24 Mar 2011[c]	32	5.6±1.2	28±4
23 May 2011	22	3.4±0.4	37±2
07 Jan 2012	23	<0.8	>62
200061			
29 Mar 2011	77	<2.5	>43
23 Feb 2012	56	<1.8	>49
200065			
24 Mar 2011	83	<2.5	>42

Notes:

[a] Reported error is 1σ counting error.

[b] Travel times calculated using 26.9±1.8 mBq/L end member value based on RHSG. Reported error is the propagated 1σ counting error.

[c] Field duplicate

NA= Not available

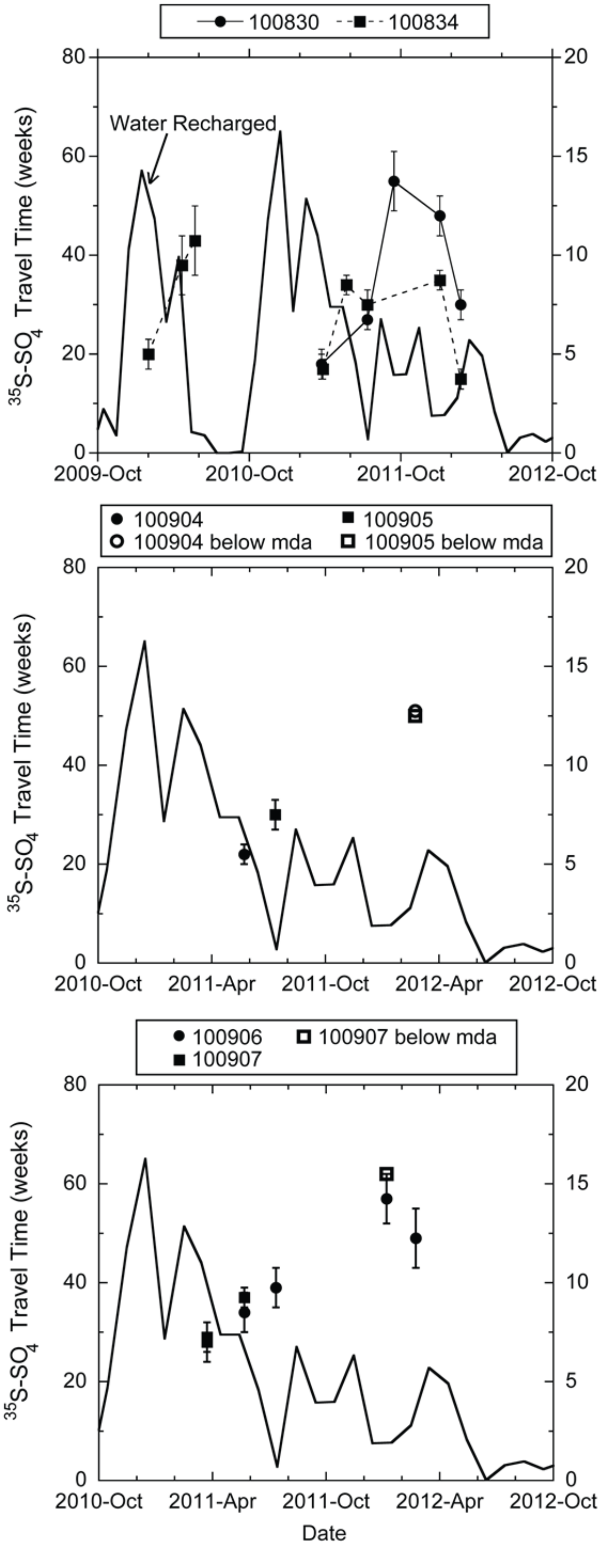

Figure 3.2. **Time series of ^{35}S-SO$_4$ travel times and monthly recharge at RHSG.**

Notes: Open symbols represent sampling events that were less than the MDA, and therefore these values are interpreted as a minimum travel time. For example, the monitoring well 100905 sampling event on February 23, 2012, was below MDA resulting in a travel time of >50 weeks.

A deliberate tracer study using SF_6 gas that was initiated at the RHSG in January 2010 (Clark et al., 2011) provides a valuable opportunity to evaluate the $^{35}S\text{-}SO_4$ method at this MAR site. From a DDW perspective, deliberate tracers like SF_6 are more conservative compared to intrinsic tracers like $^{35}S\text{-}SO_4$. Given the less conservative nature of intrinsic tracers, DDW requires a multiplier of 1.5 to estimate travel time (e.g., 6 months would require 9 months using an intrinsic tracer).

It is important to consider that deliberate and intrinsic tracer experiments may measure different hydrologic conditions and give different travel times. With deliberate tracer experiments, a conservative tracer is applied during a discrete wetting event, thus the mean groundwater travel times (defined as passage of 50% of the tracer patch) are dependent on the hydrologic conditions during the pulse release. In contrast, the naturally occurring $^{35}S\text{-}SO_4$ tracer is applied intermittently during recharge events when the source water contains a fraction of recent (<1 year old) runoff. Although these different source functions likely result in different groundwater travel times, the SF_6 experiment provides a useful comparison to identify trends in the subsurface travel times of recharged water to nearby wells.

The shortest $^{35}S\text{-}SO_4$ subsurface travel time was selected for comparison with the mean SF_6 travel because it represents the most conservative estimate that would be of interest to MAR managers. Travel times for $^{35}S\text{-}SO_4$ were within 6 weeks (1.5 months) of SF_6 travel times at four of the six monitoring wells: 100830, 100834, 100904, and 100906 (Table 3.2). Production wells 200061 and 200065 travel times were also in agreement for each tracer experiment indicating travel times of $\geq$38 weeks, suggesting that dilution of recent recharge with older groundwater is not a significant factor in the calculation of $^{35}S\text{-}SO_4$ travel time.

The largest discrepancy in subsurface travel time was observed at monitoring well 100907 (28±4 weeks for the $^{35}S\text{-}SO_4$ tracer and 6 weeks for the SF_6 tracer). It should be noted that the travel times for these two methods may have better agreement if more frequent sampling of $^{35}S\text{-}SO_4$ had been conducted for well 100907; as a result, we recommend monthly sampling of groundwater for future studies. Comparing the two methods, $^{35}S\text{-}SO_4$ as an intrinsic tracer provided reasonable estimates of subsurface travel times for some of the wells but overestimated travel time for other wells.

Table 3.2. Comparison of ^{35}S-SO$_4$ and SF$_6$ Subsurface Travel Times at RHSG

	Collection Month-Year		Travel time (weeks)	
Well ID	**^{35}S-SO$_4$**	**SF$_6$**	**^{35}S-SO$_4$[a]**	**SF$_6$[b]**
100830	Mar 2011	Jun 2010	18±3	19
100834	Feb 2012	Jun 2010	15±2	18
100904	May 2011	May 2010	22±2	16
100905	July 2011	Apr 2010	30±3	13
100906	May 2011	Aug 2010	34±4	28
100907	Mar 2011	Mar 2010	28±4	6
200061	Mar 2011	Oct 2010	>43	38
200065	Mar 2011	Jan 2012	>42	>104

Notes:

[a] ^{35}S-SO$_4$ travel times are the shortest travel times measured for each well. Reported errors are propagated 1σ counting error.

[b] SF$_6$ travel times are the mean travel times derived from the COM arrivals to wells reported by Clark et al. (2011).

3.1.2 Orange County Groundwater Recharge Facilities

At the OCWD MAR site, ^{35}S-SO$_4$ activity of surface waters from five infiltration basins and the SAR channel was <0.9 to 5.1±0.9 mBq/L, with 14 of the total 29 samples being below the minimal detectable activity (Table 3.3, Figure 3.3). With the exception of La Jolla Basin, all spreading basins had detectable ^{35}S-SO$_4$ for at least one sampling event. Post treatment GWRS water had relatively low ^{35}S-SO$_4$ activities, 0.6±0.1 and 0.7±0.1 mBq/L, at the inlet and outlet of the pipeline, respectively. The rain sample collected during a rain event on February 25, 2011, had a ^{35}S-SO$_4$ activity of 19.9±1.1 mBq/L, which was nearly four times that of the highest measured surface water activity (5.3±0.7 mBq/L for Warner Basin on March 21, 2012).

Low activity in the basins relative to local precipitation implies dilution of locally derived storm runoff at the OCWD MAR sites with ^{35}S-dead water (e.g. imported water), and/or storage of recent (<1 year old) runoff in surface reservoirs for over 1 year prior to its delivery to the spreading basins. In fiscal year (FY) 2011–2012 (July 2011 to June 2012), storm flow and local water made up less than 12% of the total source water to the groundwater basin (Hutchinson, 2012. Moreover, Hutchinson (2012) reported that the local average rainfall in FY 2011–2012 was 8.15 in., which was 43% below the 50-year average of 14.4 in. The largest contribution of direct rainfall to the basins during FY 2011–2012 occurred during March 2012 (79 AF of a total 338 AF for FY 2011–2012), which may help explain the relatively high ^{35}S-SO$_4$ activity in Kraemer Basin, Warner Basin, and the SAR Channel in March (Table 3.3, Figure 3.3). In this relatively dry water year, the low inputs of storm flow/local water combined with high inputs of imported water and SAR base flow resulted in lower ^{35}S-SO$_4$ activity in OCWD MAR surface waters relative to local precipitation.

Table 3.3. Sulfate Concentrations and $^{35}S\text{-}SO_4$ Activities for Surface Water and Precipitation at OCWD MAR Sites

Surface Water ID and Collection Date	SO_4 (mg/L)	$^{35}S\text{-}SO_4 \pm 1\sigma$ (mBq/L)[a]
Miller Basin		
25 Oct 2011	165	<1.4
20 Mar 2012	130	<2.7
06 Apr 2012	1.3	2.1±0.7
06 Apr 2012[b]	1.3	<1.5
05 Jun 2012[b]	1.3	<1.4
25 Sep 2012	0.5	1.4±0.3
25 Sep 2012[b]	0.5	1.2±0.3
04 Dec 2012	0.6	0.6±0.2
04 Dec 2012[b]	0.6	1.0±0.3
Kraemer Basin		
20 Mar 2012	2.3	5.1±0.9
05 Jun 2012	<0.5	<1.4
05 Jun 2012[b]	<0.5	<1.4
10 Dec 2012	72.7	<1.0
La Jolla Basin		
04 Dec 2012	73.4	<0.9
04 Dec 2012 [b]	73.4	<0.9
Rain[c]		
25 Feb 2012	NA	19.9 ±1.1
Anaheim Lake		
06 Mar 2012	132	<2.4
11 Sep 2012	28.4	0.9±0.4
01 Oct 2012	27.1	1.8±0.4
01 Oct 2012[b]	27.1	1.7±0.4
04 Dec 2012	71.1	<0.9
SAR Channel		
06-Mar 2012	154	5.1±1.1
06 Mar 2012[b]	154	2.8±1.0
05 Jun 2012	168	<1.4
04 Dec 2012	89.8	2.2±0.5
04 Dec 2012[b]	89.8	1.5±0.5
Warner Basin		
21 Mar 2012	122	5.3±0.7
10 Dec 2012	117	<1.0
10 Dec 2012[b]	117	2.3±0.5
GWRS TF[d]		
06 Apr 2012	1.1	0.6±0.1
GWRS MB[d]		
06 Apr 2012	0.6	0.7±0.1

Notes:

[a] Reported error is 1σ counting error.

[b] Field duplicate

[c] Rain sample was collected in the city of Orange, CA, from a location 6 km south of the OCWD MAR SITES.

[d] The groundwater replenishment system (GWRS) water was sampled from two locations along the transmission pipeline: (1) water immediately post treatment at the treatment facility in Fountain Valley (GWRS TF), and (2) GWRS discharge into Miller Basin (GWRS MB).

NA=Not Available

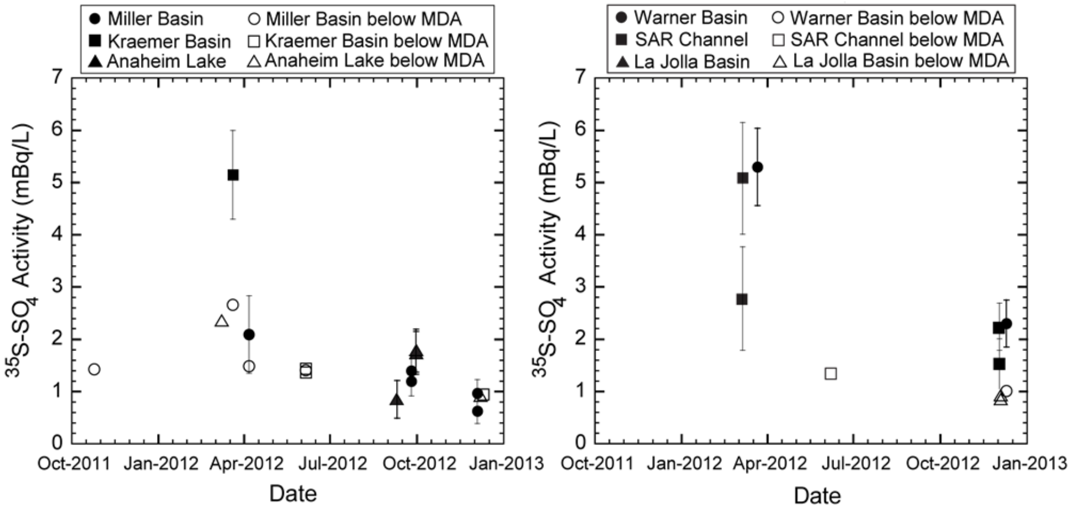

Figure 3.3. Activity in ^{35}S-SO$_4$ surface water collected from OCWD MAR sites.

Notes: Open symbols represent sampling events that were less than the MDA (see the text for an explanation of how the MDA was determined). Error bars represent 1σ counting errors.

The input end member at the OCWD MAR sites was defined as the ^{35}S-SO$_4$ activity of the nearest upgradient spreading basin to a given well. Based on groundwater contours, the general groundwater flow direction for the study area is in the west to southwest direction (Clark et al., 2004). Kraemer Basin is the nearest upgradient spreading basin for monitoring wells AM-7/1, AM-12/1, AM-12/2, and KBS-3/1, and La Jolla Basin is the nearest upgradient basin for wells AM-8/1, AM-48, and PLJ2. Deliberate tracer experiments by Clark et al. (2004, 2014) have shown that all of these wells are hydraulically connected to Kraemer Basin. Because average annual recharge at La Jolla Basin is less than 25% of the volume recharged at Kraemer Basin (Figure 3.4: 6.4×10^3 AF for La Jolla Basin and 2.9×10^4 AF for Kraemer Basin, Hutchinson, 2012), Kraemer Basin was assumed to be the main input end member for all wells sampled in this study.

Two of the three Kraemer Basin sampling events were below detectable ^{35}S-SO$_4$ activities. The ^{35}S-SO$_4$ activity on March 20, 2012, was 5.1±0.9 mBq/L. Based on the Kraemer Basin end member value of 5.1±0.9 mBq/L, the groundwater ^{35}S-SO$_4$ activities of <0.7 to 3.9±0.6 mBq/L imply subsurface travel times of 5±4 to >35 weeks (Table 3.4, Figure 3.5).

The shortest ^{35}S-SO$_4$ travel times are in poor agreement with the mean SF$_6$ travel times reported by Clark (2014), because several wells have travel times that vary by 10 or more weeks (Table 3.5); however, a couple of trends were similar between the two experiments. For example, monitoring well AM-7/1, which had the shortest mean SF$_6$ travel time (24 weeks), was the only well with ^{35}S-SO$_4$ activity consistently above the detection limit, implying that groundwater from well AM-7/1 consistently had a component of recent recharge. The mean SF$_6$ travel times to wells AMD-12/1 and AM-8/1 were 31 and 37 weeks, respectively. Travel times for ^{35}S-SO$_4$ followed a similar pattern of a shorter travel time to well AMD-12/1 (21±6 weeks) compared to well AM-8/1 (29±8 weeks).

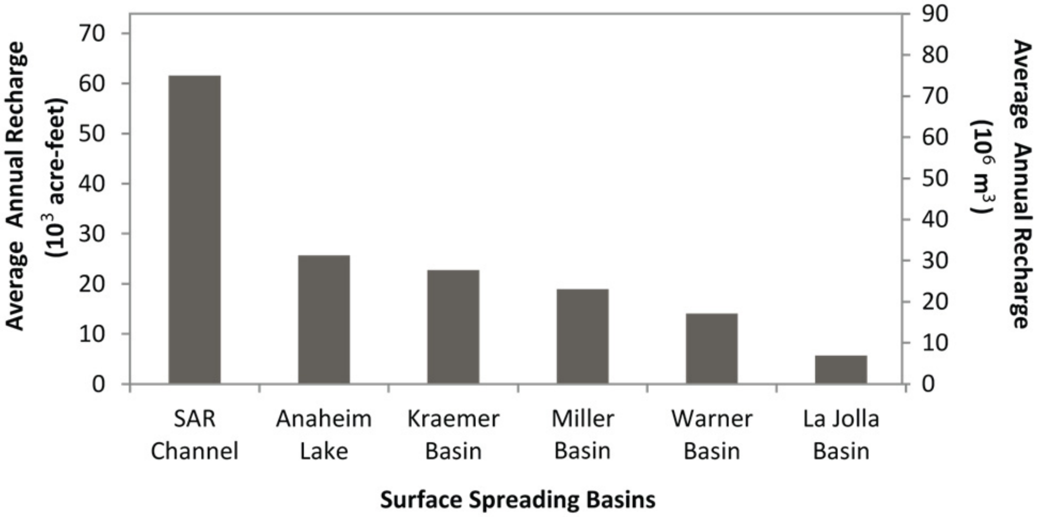

Figure 3.4. Average annual recharge for selected OCWD MAR spreading ponds.

Notes: Reported values for SAR Channel, Anaheim Lake, Kraemer Basin, and Miller Basin are the 5-year average for July to June, 2007–2008 to 2011–2012. Since La Jolla Basin was put into service in December 2007, the reported value for this basin is the 4-year average for July to June, 2008–2009 to 2011–2012 (Hutchinson, 2012). GWRS water is delivered to Miller Basin and Kraemer Basin.

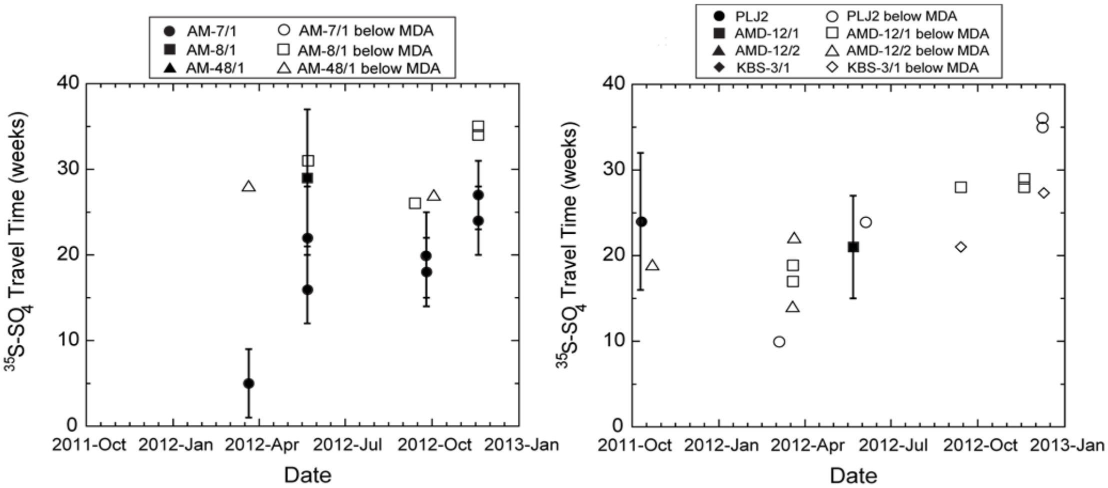

Figure 3.5. Travel times for ^{35}S-SO$_4$ groundwater from Kraemer Basin to downgradient wells.

Note: Open symbols represent sampling events that were less than the MDA; therefore, these values are interpreted as a minimum travel time.

Table 3.4. Summary of Sulfate Concentrations, $^{35}S-SO_4$ Activities, and Subsurface Travel Times at OCWD MAR Sites

Well ID and Collection Date	SO_4 (mg/L)	$^{35}S-SO_4\pm1\sigma$ (mBq/L)[a]	^{35}S Travel Time (weeks)[c]
AM-7/1			
21 Mar 2012	6.4	3.9±0.6	5±4
22 May 2012	3.1	1.5±0.4	22±6
22 May 2012[b]	3.1	2.1±0.3	16±4
25 Sep 2012	4.3	1.9±0.3	18±4
25 Sep 2012[b]	4.3	1.7±0.3	20±5
19 Nov 2012	2.4	1.2±0.2	27±4
19 Nov 2012[b]	2.4	1.3±0.2	24±4
AM-8/1			
22 May 2012	58.9	1.0±0.4	29±8
22 May 2012[b]	58.9	<0.9	>31
13 Sep 2012	34.2	<1.2	>26
19 Nov 2012	26.1	<0.8	>34
19 Nov 2012[b]	26.1	<0.7	>35
AMD-12/1			
21 Mar 2012	36.7	<1.8	>19
21 Mar 2012[b]	36.7	<2.0	>17
22 May 2012	51.4	1.6±0.4	21±6
13 Sep 2012	46.8	<1.1	>28
19 Nov 2012	52.5	<1.0	>29
19 Nov 2012[b]	52.5	<1.1	>28
AMD-12/2			
26 Oct 2011	35.5	<1.8	>19
21 Mar 2012	74	<1.5	>22
21 Mar 2012[b]	74	<2.3	>14
AM-48/1			
21 Mar 2012	86.3	<1.1	>28
03 Oct 2012	36.8	<1.2	>27
03 Oct 2012[b]	36.8	<1.2	>27
KBS-3/1			
13 Sep 2012	2.3	<1.6	>21
10 Dec 2012	99.5	<1.2	>27
PLJ2			
10 Oct 2011	62.3	1.3±0.5	24±8
05 Mar 2012	79.8	<2.9	>10
04 Jun 2012	83.7	<1.3	>24
10 Dec 2012	29.9	<0.7	>36
10 Dec 2012[b]	29.9	<0.7	>35

Notes:

[a] Reported error is 1σ counting error.

[b] Field duplicate

[c] Travel times calculated using 5.1±0.9 mBq/L end member value based on Kraemer Basin. Reported error is the propagated 1σ counting error.

Table 3.5. Comparison of Subsurface Travel Times at OCWD MAR Sites Determined by $^{35}S\text{-}SO_4$ and SF_6 Tracers

	Collection Month-Year		Travel Time (weeks)	
Well ID	**$^{35}S\text{-}SO_4$**	**SF_6**	**$^{35}S\text{-}SO_4$[a]**	**SF_6[b]**
AM-7/1	Mar 2012	Jul 2008	5±4	24
AM-8/1	May 2012	Sep 2008	29±8	37
AMD-12/1	May 2012	Aug 2008	21±6	31
AMD-12/2	Mar 2012	>Jan 2009	>14	>50
AM-48	Oct 2012	Jul 2008	>27	26
KBS-3/1	Sep 2012	–	>21	*
PLJ2	Oct 2011	–	24±8	*

Notes:

[a] $^{35}S\text{-}SO_4$ travel times are the shortest travel times measured for each well. Reported error is the propagated 1σ counting error.

[b] SF_6 travel times are the mean travel times to wells reported by Clark (2014).

*Incomplete breakthrough: center mass travel time is a minimum or could not be calculated.

3.2 San Gabriel Spreading Grounds Research Test Basin

3.2.1 Boron-10 and Bromide

To define the input conditions, water samples were collected from the test basin about 4 h after injection. They averaged about 85 ppm (mg/L) Br^- and −725‰ $\delta^{11}B$; however, the pond was not well mixed ([Br^-] range: 4 ppm to 380 ppm, median: 10 ppm; $\delta^{11}B$ range: −521‰ to −976‰ $\delta^{11}B$, median: −741‰; total [B]: 0.36 ppm to 6.7 ppm, median: 0.46 ppm). The high-end samples for both Br^- and $\delta^{11}B$ (total boron and most negative $\delta^{11}B$) occurred at the surface sampling location closest to the barrels. The test basin was closer to being well mixed by the next sampling event, 8 h following injection ([Br^-] range: 2.5 ppm to 23 ppm, median: 8.5 ppm; $\delta^{11}B$ range: −438‰ to −851‰ $\delta^{11}B$, median: −696‰; total [B]: 0.34 ppm to 0.68 ppm, median: 0.43 ppm). The basin was nearly emptied by infiltration about 12 h following injection. The two sampling sites remaining measured 8.3 ppm and 13.0 ppm for [Br^-], −696‰ and −804‰ $\delta^{11}B$ for the ^{10}B tracer (total [B]: 0.46 ppm and 0.55 ppm).

Untagged recycled water began recharging the test basin again shortly thereafter. Br^- fell to background levels by the next sampling event 24 h following injection. $\delta^{11}B$ water samples collected at 24 and 48 h were still slightly enriched in ^{10}B (−43‰ and −10‰, respectively) and total [B] (0.45 and 0.29 ppm). ^{10}B levels finally fell to background (+24‰ in $\delta^{11}B$; total [B]: 0.27 ppm) by the 72-h sampling event. As discussed in the method section, boron isotope measurements have a standard error of ±15‰ $\delta^{11}B$, and bromide concentrations have an uncertainty of ±10%.

Boron and bromide tracer breakthroughs were observed at six and seven of the nine monitoring wells, respectively (Figures 3.6 and 3.7; Appendix A for raw data). No breakthrough was observed at the two deep, distant wells (PR12, PR14) after 1 year of sample collection, presumably due to dilution of both deliberate tracers. The ^{10}B plume was also too dilute at PR15 (shallow but most distant); its breakthrough was only within the range of analytical uncertainty on the ICP-MS, but a breakthrough curve is still apparent if it is assumed that the composition of the recycled wastewater source is invariant and the investigator is willing to accept that the observed maximum value contained less than 2% of the tagged water.

Peak tracer values at the wells, if compared to average tagged basin concentration, suggest the maximum of the break through curves contained a small fraction (10–40%) of the plume at the distant and deep wells. Sampling bias or a poorly mixed tagged basin heavily influences plume faction calculations. Tracer plumes unevenly distributed across the basin, coupled with the presence of any preferential infiltration zones, explain peak values significantly less than an averaged basin.

Arrival of Br^- was always coincident or preceded the ^{10}B arrival. Travel time ratios for $^{10}B/Br^-$ COM range from 1.0 to 1.4, indicating that boron arrives, on average, ~25% later than bromide. The lag between Br^- and ^{10}B arrivals in general increases with both increasing distance and arrival time from the spreading pond. Because of this issue, ^{10}B is not a conservative tracer as is desirable for compliance determinations, and DDW has recommended it not be used in California.

Table 3.6. Summary of Geochemical Tracer First Arrival, Peak Arrival, Center of Mass (COM) Arrival, and Travel Time Ratios

Well	First Arrival				Peak Arrival				COM[b] Arrival		$\delta^{11}B/Br^-$ COM Travel Time Ratio
	$\delta^{11}B$		Br^-		$\delta^{11}B$		Br^-		$\delta^{11}B$	Br^-	
	Time[a]	‰	Time	ppm	Time	‰	Time	ppm	Time	Time	
WPZ	0.2	−207	0.2	3.4	0.7	−549	0.7	6.2	0.7	0.7	1.0
PR8	14.7	−165	7.7	0.4	14.7	−165	14.7	0.6	17.9	13.6	1.3
PR9	1.9	−50	1.6	0.4	2.4	−237	2.1	3.5	2.4	2.1	1.1
PR10	19.8	−15	14.7	0.7	33.8	−112	26.8	1.2	32.7	23.3	1.4
PR11	1.9	−189	1.6	0.4	2.4	−296	1.9	4.0	2.4	1.9	1.3
PR12	–	–	–	–	–	–	–	–	–	–	–
PR13	14.8	-392	7.8	1.6	14.8	−391	14.8	1.9	16.2	11.8	1.4
PR14	–	–	–	–	–	–	–	–	–	–	–
PR15[c]	–	+5	19.8	0.2	–	−3	–	2.3	–	38.9	–

Notes:

[a] Days following end of tracer injection (approximately 6:00 p.m. on Sep 6, 2011)

[b] COM for nearby wells (WPZ, PR9, PR11) is inferred as the tracer peak arrival; COM for more distant wells (PR8, PR10, PR13, PR15), where sampling events did not necessarily capture peak, is calculated by integrating area under breakthrough curve and dividing by time that tracer was detectable above background levels.

[c] For PR15, if interpreted as a breakthrough curve, the times of the first arrival, peak, and COM for ^{10}B were, respectively 26.9 days, 33.8 days, and 39.7 days. Analytical uncertainty for $\delta^{11}B$ and Br^- measurements are ±15‰ and ±10%, respectively.

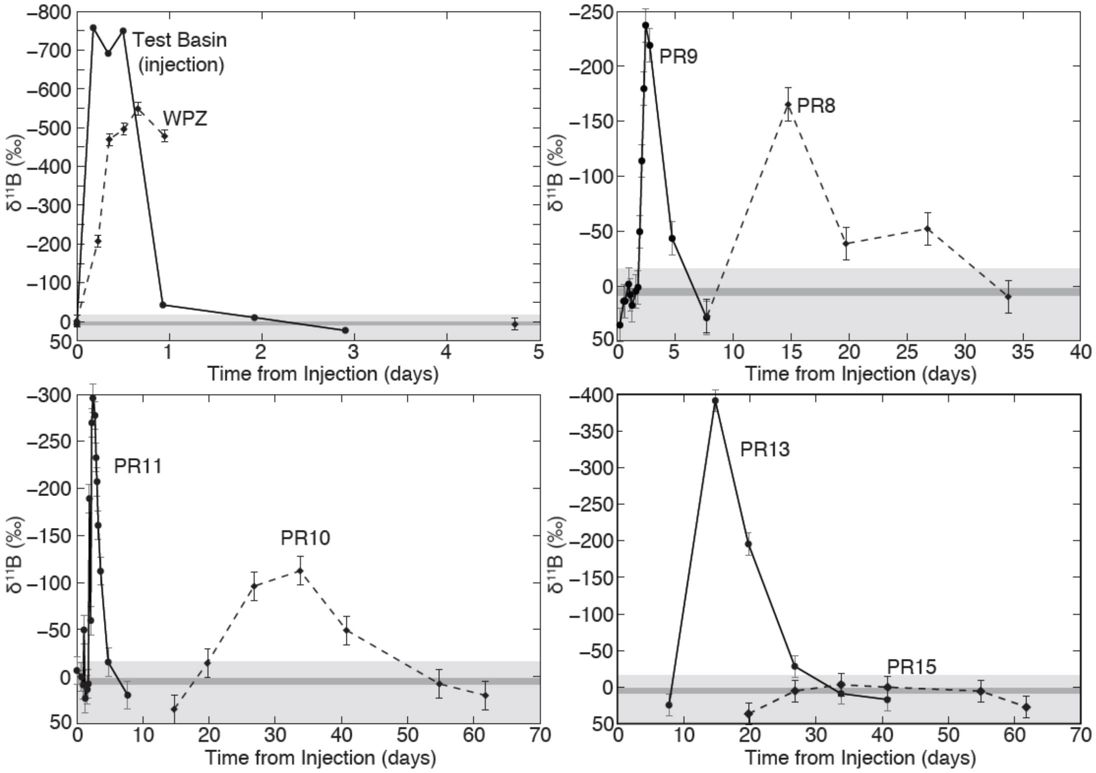

Figure 3.6. Boron-10 breakthrough curves.

Notes: Initial test basin concentration (at t_0) is average of samples taken directly from San Jose Creek treatment plants. Values are shown with analytical uncertainty of ±15‰ δ^{11}B except for test basin samples, which are an average of multiple sites. Light gray box: range of δ^{11}B found in natural waters (-16‰ to +59‰); dark gray box: range of untagged basin and groundwater reported for the nearby RHSG. Please note: The y-axes are inverted.

Source: Light gray box reported by Vengosh et al. (1994); dark gray box reported by Quast et al. (2006).

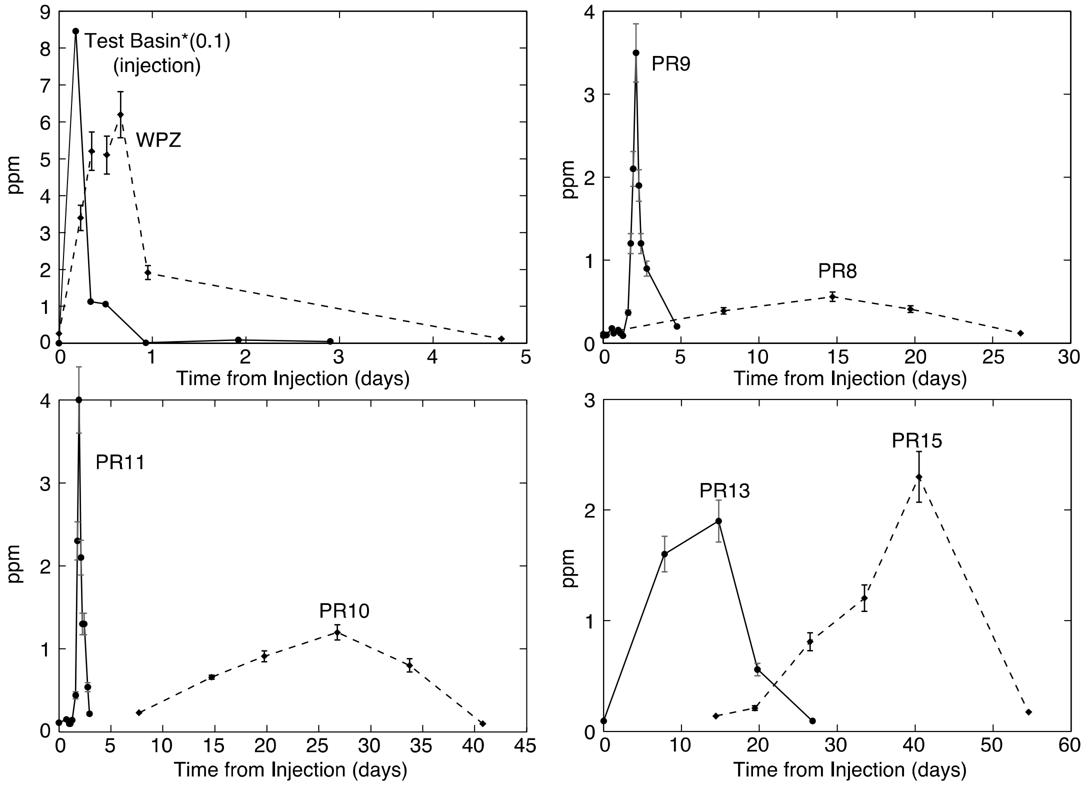

Figure 3.7. Bromide breakthrough curves.

Notes: Native groundwater contained bromide concentrations from typically <0.1 ppm. Note test basin is scaled down by an order of magnitude to fit display window. Initial test basin concentration (at t_0) is based on average background, not sampled directly, and is therefore shown in gray. Values are shown with analytical uncertainty of ±10% except for test basin samples, which are an average of multiple sites.

3.2.2 Retardation of Boron-10

Nonconservative transport in a neutral pH (Schroeder et al. 2003) groundwater system, albeit with clay layers present, is a considerable problem for the boron tracer. Later arrivals would suggest a slower flow path and overestimate the retention time. As a consequence, wells on the border of not meeting DDW minimum residence times would require different tracer. It is possible, however, that the relatively poor sample collection resolution (common for deliberate tracer studies) and laboratory uncertainty created a sampling bias. The potential range of COM calculations about common sampling events is discussed in Appendix B. At SGSG's near-field monitoring network, with observed travel times to six wells within a month or less, the spread is relatively minor (likely ±3 days at worst). It is unfortunate that the geochemical tracers were never detectable above background at the two wells whose travel times are closer to the CDPH desired time of 6 months (for spreading projects) showing how dilution affects the interpretation of deliberate tracer experiments.

As a MAR tracer, ^{10}B-enriched boric acid is not without advantages. Salt tracers such as NaBr require more mass by an order of magnitude to tag an equal volume. This is because a shift in isotopic ratios (such as ^{11}B/^{10}B) is much more pronounced than changes in concentration (Figure 3.8). Wells that pump even small volumes (5–10%) of the tagged plume show a strong isotopic signal (>50‰).

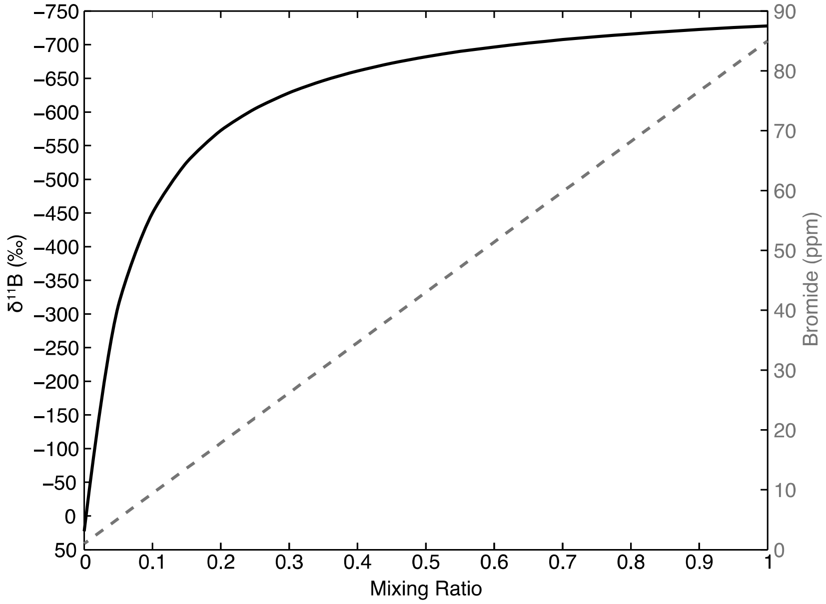

Figure 3.8. Theoretical mixing lines of the tagged recycled water and native groundwater for ^{10}B and Br^- tracers.

Notes: The solid black line show the mixing line for ^{10}B whereas a dashed gray line shows the linear mixing of Br^-. A ratio of 1 corresponds to 100% plume. Plume end member concentrations are derived from the average test basin water 4 h after initial tracer release; groundwater end member is the typical background value determined for the field area.

3.2.3 Temperature

Native groundwater not influenced by MAR operations averaged between 17.9° C and 25.0° C (Table 3.7) and rarely fluctuated more than 0.5° C over a period of a day. Infiltrating recycled water averaged 28.9° C during early September 2011 and 25.6° C by November 2011. A 37 mm rain event on October 5, 2011 (approximately 33 days after continuous recharge at the test basin) briefly lowered infiltrating water by about 2° C. It is important to note that solar radiation is not the only warming mechanism: recycled water arrives warm to the basin from the wastewater treatment plants. Only one well, PR10, was logging temperature for months prior to the experiment (Figure 3.9). That well showed a steadily falling temperature signal, with little perturbation, as the groundwater dropped to ambient levels following the earlier season's warm recharge plume.

Travel time estimation through peak matching of diurnal signals was only possible at one monitoring well (WPZ, logger located 2.7 m below basin floor; Figure 3.10). Peak matching is ideal as it allows for precise travel times that can be calculated many times during the recharge event (e.g., Drewes et al. 2011; Becker et al. 2013). This is helpful to establish any temporal or spatial changes in infiltration rates (e.g., Racz et al., 2012). Most wells, however, recorded a warming period that spanned days (PR9, PR11) to weeks (PR8, PR10, PR13, PR15) to months (PR12, PR14) as the warm recharge plume arrived at each well (Figure 3.11). The warming period is defined here to begin when a well logger recorded temperatures 0.5 °C above that of background (17.9° to 25.0° C). The period ends as temperatures plateau at closer wells, indicating steady-state conditions between the continuously recharging recycled wastewater plume and local groundwater or when temperatures peak at the more distant wells that record the long recharge event as a single pulse.

Even without a diurnal signal, heat flow interpretations provide travel times to all wells within the same range as the geochemical tracers. Moreover, whereas the added tracers became too dilute to detect above background at wells PR12 and PR14, a temperature change was successfully measured. Well loggers at PR12 and PR14, the deepest and farthest wells from the basin, recorded the >2 month recharge event as a large, single pulse, creating profiles akin to breakthrough curves that yield definitive peaks. Temperatures rose then fell as the recharge plume passed the wells; travel times are estimated from the peak. Despite being 76 m farther down gradient from the test basin, temperature changes at PR14 occurred nearly 50 days earlier than PR12. This is attributed to the semiconfining unit that lies above PR12 but below PR14, allowing for faster transport to the latter (Figure 2.4).

Travel times to PR8, PR9, PR10, and PR11 were also estimated through peak matching of the October 5, 2011, rain event. Travel time was calculated as the offset between the test basin signal and each well's response. The slowest response was ~1 month to PR10. Data from distant wells (PR12-15) either did not record a temperature response to the rain event or were too noisy to distinctly show the event. In addition to cooling down the test basin recharge water, the rain presumably caused some ponding within the adjacent desilting basin (although no water was observed in the channel following the rain event on October 10, 2011). This volume was minor compared to that infiltrating the test basin, and its impact on groundwater movement is assumed to be negligible.

Table 3.7. Summary of Well Logger Temperature Measurements and Estimated Percentage of Recycled Water Pumped

WELL	Warming Period				Peak[a]		Percent Recycled[b]
	Begin		End				
	Time (days)	Temp (°C)	Time (days)	Temp (°C)	Time (days)	Temp (°C)	%
WPZ	–	–	–	–	0.15 – 0.90	–	99
PR8	14.6	17.9	33.3	27.2	13.3	–	85
PR9	2.1	17.9	8.3	28.7	2.2	–	98
PR10	25.7	17.9	49.1	25.6	29.5	–	72
PR11	3.3	17.9	8.5	28.8	2.0	–	99
PR12[c]	–	–	–	–	181	21.5	36
PR13	13.8	20.0	35.8	27.5	–	–	88
PR14[c]	–	–	–	–	133	23.9	57
PR15	50.0	25.0	60.5	26.7	–	–	81

Notes:

[a] Peak matching at WPZ from diurnal signal and at PR8-11 from October 5, 2011, rain event; PR12 and PR14 are peak temperature arrivals.

[b] Estimated using Equation 2.4, which assumes heat is transported conservatively.

[c] As explained in the text, at the most distant wells, temperature changes are interpreted as a simple pulse injection and the maxiumun is used rather than the warming period.

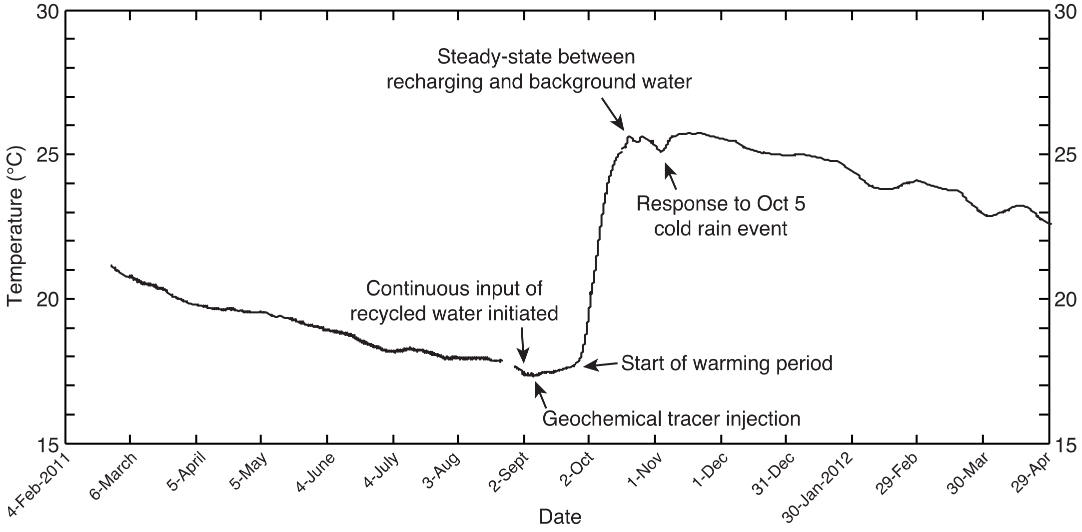

Figure 3.9. Extended temperature measurements for monitoring well PR10.

Notes: Water temperatures steadily declined following the 2010–2011 recharge season. The arrival of the warm recharge plume following continuous input to the test basin beginning in early September 2011 is clear.

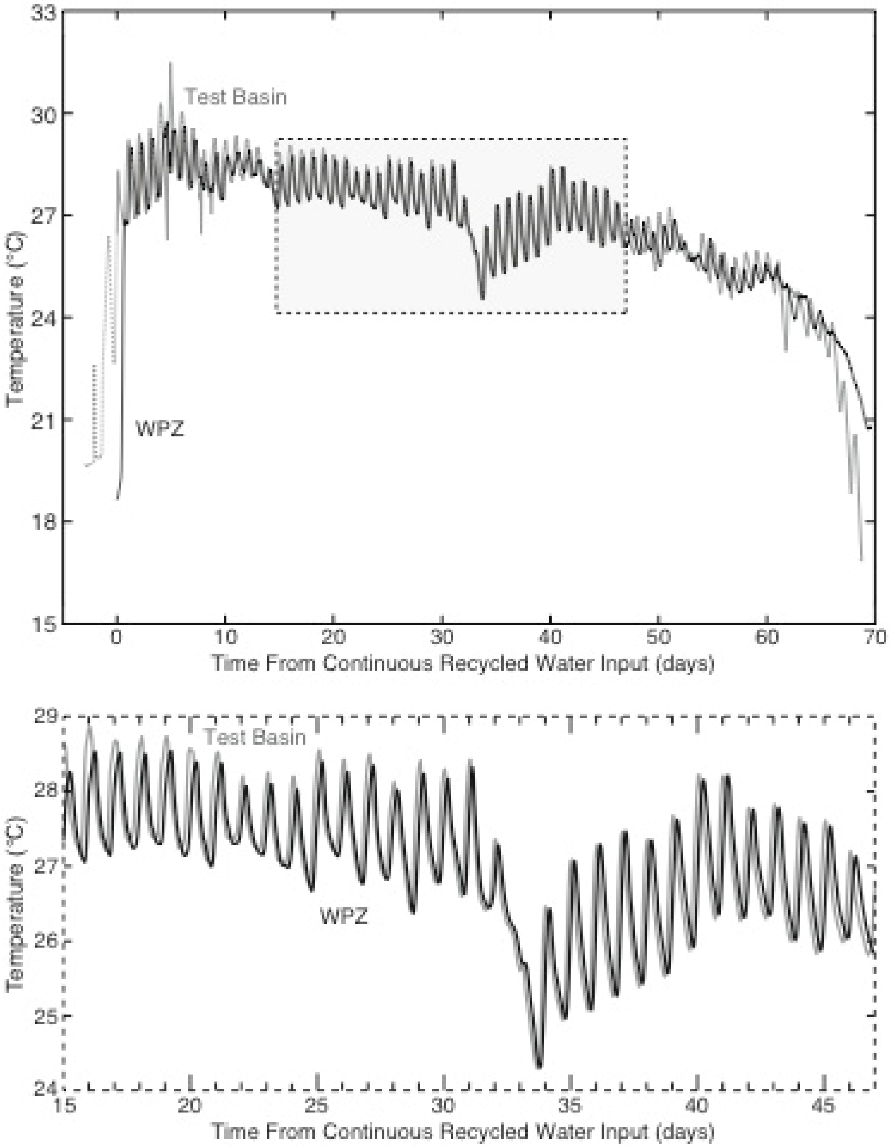

Figure 3.10. Test basin and WPZ temperature measurements.

Notes: Start of inflow (t_0) occurred 4 days prior to tracer injection. Native groundwater not influenced by recharge events averaged about 17.3 °C, WPZ was a little warmer at t_0 due to the preceding wettings that built the recharge mound. A strong diurnal temperature signal was recorded in the basin, with a general decreasing trend associated with seasonal changes from late summer to fall. Diurnal peak matching records a >20 days period (bottom panel) of very rapid travel from the basin to WPZ. The test basin and WPZ records are plotted respectively, as a gray dashed and solid black lines.

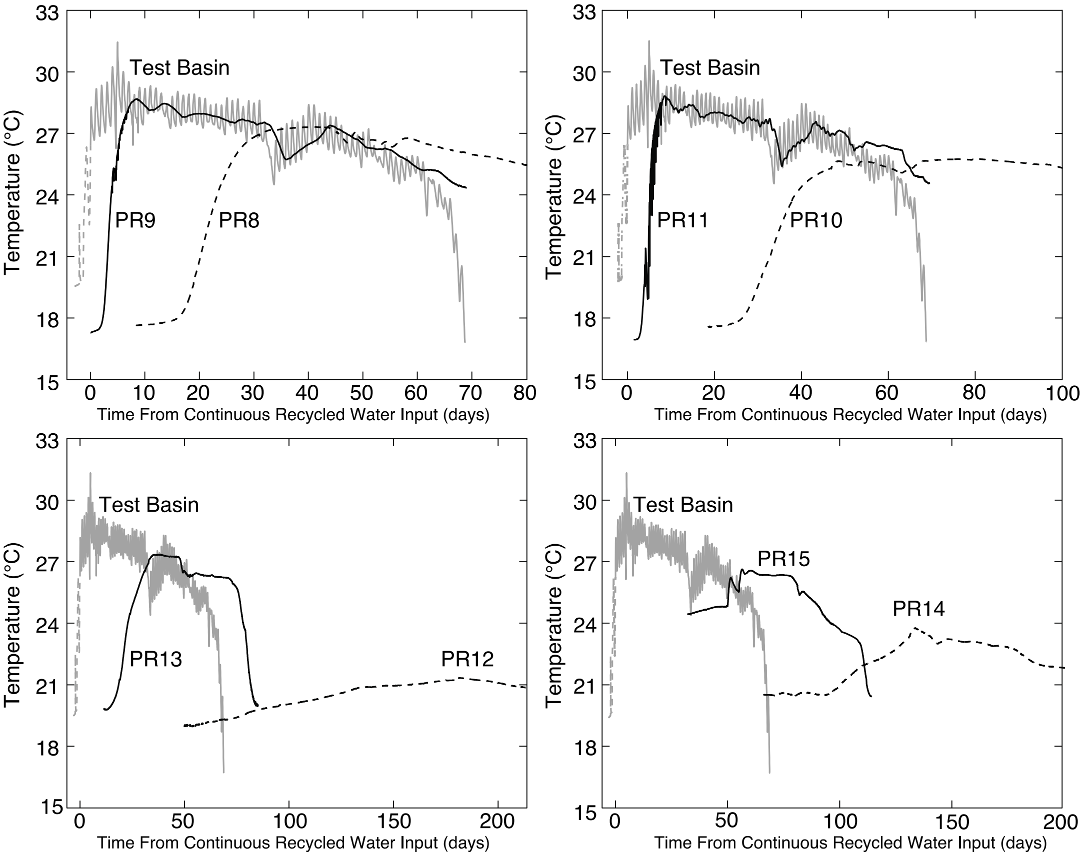

Figure 3.11. PR8-15 temperature measurements, with test basin for reference.

Note: Distant wells (PR12-15) have higher background temperatures because of earlier recharge events that already passed all other wells.

3.2.4 Travel Time Comparison

Heat transport coincides most closely with chemical COM arrival. First arrival of ^{10}B and Br$^-$ is often days to weeks prior to the 0.5° C response recorded by the well loggers. Heat is not a conservative tracer. Conservative tracers such as Br$^-$ remains dissolves in pore water, whereas heat will, to a certain degree, dissipate into the solid matrix. The bulk recharge plume is clearly detected at the loggers. Small preferential flow paths in the aquifer are harder to resolve. Nevertheless, temperature measurements are still useful for identifying the majority of the plume despite this weakness.

Table 3.8 summarizes geochemical and heat flow travel times to all wells, compared to those estimated by Laws et al. (2011) at wells WPZ and PR8–11. Laws et al. used temperature measurements from summer 2008 and spring 2009. Diurnal peak matching was possible at WPZ, PR9, and PR11. Estimated travel times to those wells are very similar to the present study, although no diurnal signal was measured at PR9 or PR11 herein.

Travel times to PR8 and PR10 differ between the two studies. Laws et al. (2011) used apparent peak temperature arrivals to estimate a 60 day travel time to both PR8 and PR10. If the data were interpreted as a warming period and subsurface residence times were interpreted from its start, these times would be cut in half. During their 2008 experiment, the warming period began around 28 days at PR8 and around 40 days at PR10. These travel times are still greater than those determined here, likely due to different hydrologic conditions between the 2008/09 and 2011 data collection periods. During both studies recharge water was continuously entering the test basin over multiple months, but the earlier study occurred closer in time to the winter recharge season.

Table 3.8. Travel Times Derived from ^{10}B COM, Br$^-$ COM, Heat Flow, and the October Rain Event Compared to Laws et al. (2011)

Well	THIS STUDY				Laws et al. (2011)
	Boron-10	Bromide	Heat[a]	Rain Event[b]	
	Time (days)	Time (days)	Time (days)	Time (days)	Time (days)
WPZ	0.7	0.7	0.15–0.9	0.20–0.25	0.5
PR8	17.9	13.6	14.6	13.3	60
PR9	2.4	2.1	2.1	2.2	2.1
PR10	32.7	23.3	25.7	29.5	60
PR11	2.4	1.9	3.3	2.0	3.0
PR12	–	–	181.1	–	–
PR13	16.2	11.8	13.8	–	–
PR14	–	–	133.8	–	–
PR15[c]	–	38.9	50.0	–	–

Notes: Travel time estimates were based on diurnal peak matching when possible.

[a] Heat flow travel times from diurnal peak matching (WPZ), start of the warming period (PR8-11, PR13, PR15), or peak temperature arrival (PR12, PR14).

[b] Travel time determined by the migration of the short-term cooling caused by the October rain event. The transient temperature change was not observed at PR12-15.

[c] For PR15, if interpreted as a breakthrough curve, the COM arrival for ^{10}B was 39.7 days

The travel times determined during the October rain event that lowered the basin temperature by gives the opportunity to objectively examine if the flow was affected by a change in density after the tracers were added. The offset of diurnal temperature peaks between the test basin and the nearest well (as recorded by the well loggers) remained consistent during the injection event and untagged recharge plume infiltration around that time, suggesting that the tagged plume did not significantly alter flow. This is also true for the rain event that occurred about one month after the injection of tracers. The travel time of the temperature offset agrees very well with the Br$^-$ COM travel time at four of the five wells where it was observed (Table 3.8). The one exception is PR10, which had the longest flow time (23.3 days for Br$^-$ and 29.5 for heat). This indicates that a better interpretation scheme than peak matching is needed, presumably due to non-ideal transport due to water rock heat exchange.

3.2.5 Well Water Levels

Data loggers recorded water table elevation (total head) above mean sea level at each well (Figure 3.12). The test basin sensor recorded height of ponded water, with a dry basin floor located about 49 m above mean sea level (MSL). Water levels at the test basin sensor and closer wells (WPZ, PR8-11) jumped on September 2, 2011, as the basin filled, before dropping sharply on September 6, 2011, as the basin emptied following geochemical tracer injection. Levels rebounded briefly when recycled water input continued. The general trend, however, was a steadily falling water table during the next 25+ days of continuous input to the test basin.

Multiple factors influence water levels around SGSG. Groundwater always flows down and away from spreading basins to replenish down gradient aquifers. For water levels to remain stable near spreading basins, recharge water must enter at the same rate as it drains to deeper aquifers where it is produced. Artificial recharge generally exceeds natural discharge during the winter months when water demand is lower and the larger basins are active, causing the water table to rise. Regional drainage occurs during the summer months. Regional water levels fell during the length of the tracer experiment because no recharge water entered the spreading grounds. SGSG monitoring well levels dropped 3 to 4 m by the end of September.

Groundwater levels rebounded in response to local phenomena (precipitation and recharge water entering the test basin and adjacent desilting basin). Local precipitation is recorded as the cumulative daily total so exact times are not known. The 37 mm event on October 5, 2011, was the only to occur during the first 60 days. Four more rain events in November averaged 8 mm per event. Despite a low-resolution record, well water levels clearly increased in response to precipitation and subsequent recharge in all wells (Figure 3.12). Groundwater typically rebounded ~0.5 m following each rain event (Figure 3.12), before slowly falling back to previous levels. This rise and fall spanned multiple days.

Well water levels most dramatically increased (about 3 m) during the two periods of recharge in the desilting basin and surrounding SGSG basins. The first period occurred between October 19 and October 21, 2011, where 0.22×10^5 m^3 of recycled water was recharged. The second occurred between October 25 and November 2, 2011, when 1.0×10^6 m^3 of recycled water was recharged. Although the two periods collectively recharged 10 times the volume that entered the test basin, desilting basin recharge did not affect the multitracer experiment, because tracer breakthroughs at the seven wells (WPZ, PR8-11, PR13, PR15) all preceded October 19 when the desilting basin was dry. This stronger recharge may have affected the last stage of our experiments and travel to the most distant wells.

Because of deep well screens and relatively light pumping, local production wells had little to no influence. Collectively, local active wells pumped 2.1×10^5 m^3 of water from September 2 to November 2, 2011, or about 7×10^4 m^3 more than the volume that infiltrated the test basin. Ninety percent of production occurred at a single PWD well, which averaged 4100 m^3/day over 48 days of activity. Pumping is typically considered heavy if it exceeds 7500 m^3/day.

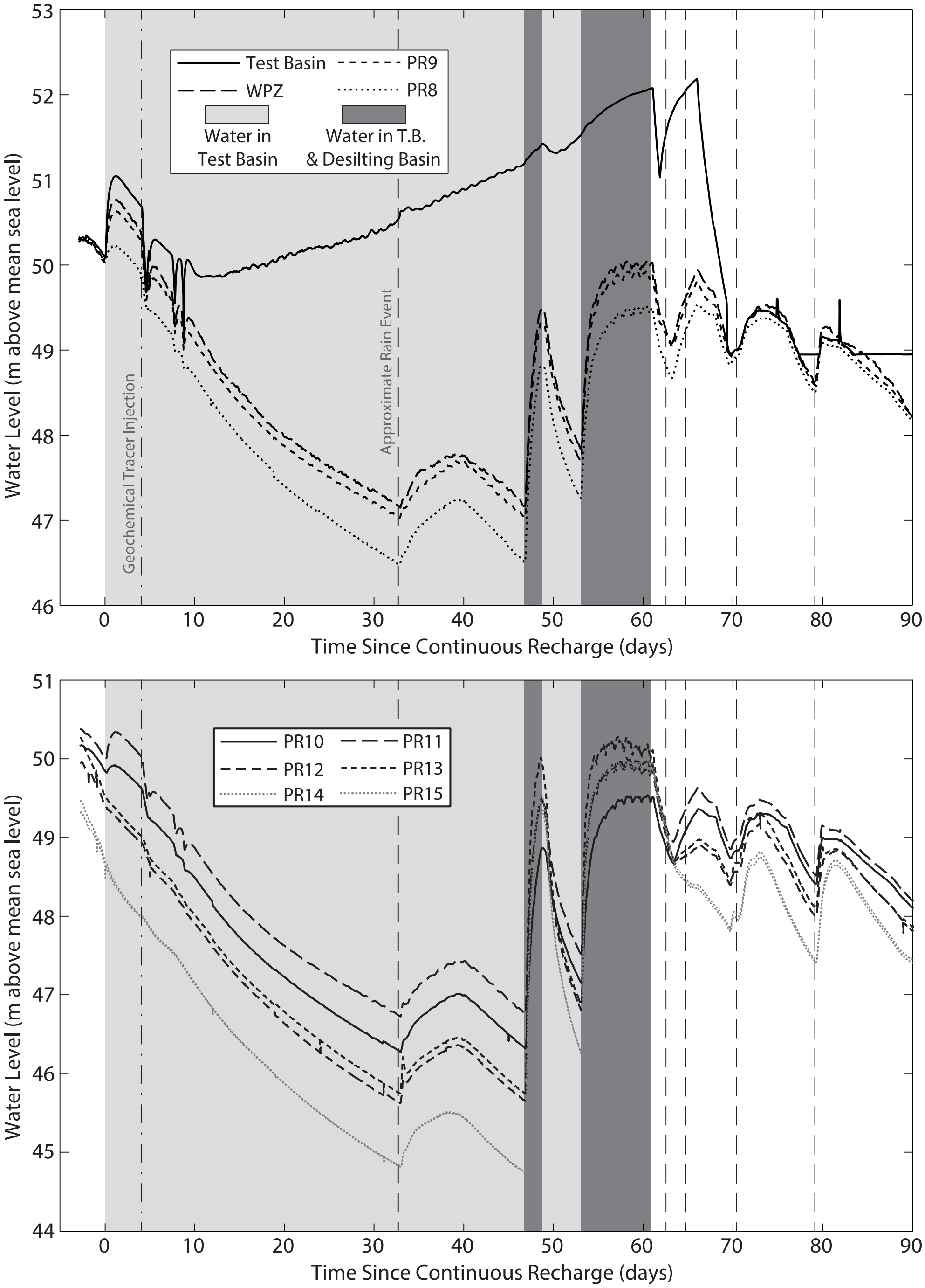

Figure 3.12. Well water levels above mean sea level (MSL).

Note: A dry basin floor is ~49 m above MSL. Time duration of artificial recharge at the test basin is shown in light gray; duration of recharge at both test basin and desilting basin in dark gray**.**

3.2.6 Vertical Velocity and Recharge Rate

A simplifying assumption can be made that vertical flow velocities dominate near the water table directly under the test basin if the recharge mound acts as a local groundwater divide. Vertical flow velocity is recharge rate divided by sediment porosity that was measured to be

0.24 by Schroeder et al. (2003). Velocities are estimated through multiple approaches. Darcy's Law describing fluid flow through a porous media can be written as

$$Q = K\,A\left(\frac{dh}{dl}\right) \tag{3.1}$$

where *Q* is discharge (in volume per time), *K* is hydraulic conductivity (length per time), *A* is cross-sectional area (length^2), and *dh/dl* is the dimensionless hydraulic gradient. Recharge rate (darcian flux) is discharge per unit area (*Q/A*) or hydraulic conductivity multiplied by the gradient (*K dh/d*l).

Recycled water was delivered to the test basin at about 2200 m^3/d (Q). The surface area of the basin is approximately 2000 m^2 (A). Therefore, the recharge rate of recycled water was 1.1 m/day based on a simple mass balance approach assuming no loss to evaporation. This is equivalent to a vertical velocity (adjusted for 0.24 porosity) of 4.5 m/day.

Vertical hydraulic gradients are accurately measured using the well water levels. The gradient between WPZ to PR9 averaged 0.034 during the two month recharge event. Assuming a vertical hydraulic conductivity of 26.5 m/day based on Schroeder et al. (2003), the estimated recharge rate in the upper aquifer is 0.9 m/day. This is equivalent to a vertical velocity of 3.8 m/day.

Finally, vertical flow can be estimated from average tracer travel times. A flow line from the test basin to WPZ to PR9 has an average vertical velocity of 3.3 m/day, equivalent to a recharge rate of 0.8 m/day. The aquitard that separates upper and lower aquifers dramatically slows vertical movement. A flow line from PR9 to PR8 has an average vertical velocity of 0.5 m/day, or a lower aquifer recharge rate of 0.1 m/day.

Chapter 4

Conclusions

4.1 Sulfur-35

This study successfully developed a new analytically technique for measuring natural ^{35}S-SO$_4$ activity in high sulfate waters typical of MAR facilities. From 2010 to 2012, groundwater and surface waters collected from RHSG and OCWD MAR facilities were successfully analyzed for ^{35}S-SO$_4$ activities. Calculated travel times were reasonable estimates in some cases compared to those determined by the well-established SF$_6$ deliberate tracer method at these sites. However, in some cases travel times were significantly overestimated.

The usefulness of this ^{35}S-SO$_4$ technique at each MAR site is dependent on characterization of the ^{35}S-SO$_4$ activities in MAR source waters and evaluation of mixing scenarios. MAR facilities using recycled water are likely to have high SO$_4$ concentrations and low ^{35}S activity. The ^{35}S-SO$_4$ method was successfully applied at RHSG; however, its application was limited at OCWD MAR facilities due to consistently low ^{35}S-SO$_4$ activity in recharge surface waters. To quantify ^{35}S-SO$_4$ subsurface travel times of 9 months (three half-lives) for piston flow transport of recharge water to nearby wells, natural surface water ^{35}S-SO$_4$ activity should ideally be eight times above the MDA determined by the counting conditions. Based on the MDA range of 0.5 to 3.4 mBq/L determined for natural samples in this study, recharge surface waters should be between 3.9 and 27.3 mBq/L in order to track recharged water for 9 months. Another factor affecting the application of the ^{35}S-SO$_4$ method is potential dilution of recharge water with older groundwater. While considered at these study sites, the travel time comparisons between SF$_6$ and ^{35}S-SO$_4$ suggests that mixing of recharge water with older groundwater was not a significant factor; however, mixing scenarios should be investigated at other MAR sites as it will affect calculated travel times.

Deliberate tracer experiments using a ^{35}S-SO$_4$ standard are not currently recommended by the DDW and are not economical feasible for large-scale surface spreading facilities. For example, the average size of the five OCWD MAR facilities spreading basins sampled in this study is 1275 AF, (1.6×10^6 m^3). At least 170 ml of a 1 µCi/ml ^{35}S-SO$_4$ standard (NIST-traceable from Eckert and Ziegler) would be necessary to achieve a 3.9 mBq/L in a basin approximately 1275 AF, at a cost of USD $44,000 for the standard alone. Both the RHSG and OCWD MAR sites had surface water activities > 3.9 mBq/L; however, due to varying MDA values that result from varying ^{35}S-SO$_4$ background count rates, an input end member of >20 mBq/L is recommended for application of the intrinsic ^{35}S-SO$_4$ tracer method at other MAR facilities. Careful characterization of the input function is important when determining the feasibility of using ^{35}S-SO$_4$ as a natural tracer, especially for sites that incorporate significant fractions of recycled water. Therefore, we recommend that time series with a frequency of at least 1 month are collected from the source water.

Unlike deliberate tracer studies that are dependent on the hydrologic conditions during the injection period (typically a few days to a few weeks), the ^{35}S-SO$_4$ intrinsic tracer method is applied over a longer time period during each recharge season. If the ^{35}S-SO$_4$ end member is constrained for each season, the effect of varying recharge and pumping conditions on subsurface travel time can be quantified more easily by the ^{35}S-SO$_4$ method than by conducting multiple deliberate tracer experiments. The ^{35}S-SO$_4$ intrinsic tracer technique can be a valuable tool in investigating the subsurface travel times on <1 year timescales at MAR sites where $^{35}S\text{-}SO_4$ activity is significantly above the detection limit.

4.2 Boron-10

Boric acid enriched in ^{10}B is not a conservative tracer as non-ideal transport behavior in response to clay exchange retards its movement in the subsurface; therefore, DDW has already required the use of a different tracer instead of ^{10}B. As a result of retardation, travel times may overestimate actual groundwater flow time, especially in wells far (in depth and lateral distance) from the injection point. Unless a relict of sampling resolution, this is a weakness for the boron isotope tracer. The advantage of isotopic tracers is that (1) significantly less mass is needed for the same volume of water and (2) detection is easier because of nonlinear mixing. Breakthroughs of ^{10}B, despite injection mass an order of magnitude lower than Br^-, were observed at six of the seven wells near the test basin at SGSG where Br^- breakthrough occurred. We also demonstrated that ^{10}B measurements can be on the more-affordable high throughput ICP-MS system, with analytical uncertainty better than ±15‰ $\delta^{11}B$.

Deliberate tracer studies are commonly hindered by (1) mass needed, with large projects approaching unrealistic costs, mixing concerns in the tagged basin, and the potential buoyancy affect to flow and (2) poor sampling resolution, limited largely by staff hours and analytical expenses. In cases where unsaturated flow concerns outweigh budgetary restrictions, boric acid enriched in ^{10}B may be the best option. However, dilution limits the application of both added tracers, and budgets limit the mass of boric acid available.

4.3 Temperature

This study showed that heat has great potential as an intrinsic tracer at MAR facilities. It has a relative long history of use in riverine systems. Temperature measurements are inexpensive and easy to collect with modern well loggers that offer high sensitivity, vastly higher sampling resolution compared to deliberate tracers. In addition no artificial energy or chemical inputs are added to potable aquifers.

Temperature and pressure sensors with data loggers can be used to estimate the bulk recharge volume. Diurnal peak matching, when available in the near field, is ideal and provides a precise travel time estimate very near the recharge basin. Here, a temperature offset of a cold rain event also provided a reliable estimate of travel time to four wells very close to the basin. The rain event was observed at a fifth well (PR10) after ~1 month, suggesting that non-ideal transport occurred, presumably due to exchange of heat with the aquifer material. Farther away from the infiltration area, where short-term surficial events may not penetrate, a proper interpretation of the warming period is essential for estimating accurate travel times. The biggest drawback is the small preferential flow paths can go undetected, presumably by dissipation to the aquifer sediment.

Intrinsic tracer experiments, such as heat, can be just as reliable as deliberate tracers to determine subsurface residence times at MAR facilities, even though heat can be lost from the infiltrating water. Such studies can also be repeated if recharge conditions change and dilution/mixing concerns are drastically reduced. Intrinsic tracers should be considered a viable test method to satisfy regulatory requirements for recycled water recharge projects.

4.4 Summary

Heat and ^{35}S should be considered as new intrinsic tracer methods near MAR facilities with some pivotal considerations. The ^{35}S method requires tests during all four seasons, because the results vary by season reflecting seasonal differences in recharge and well production. The ^{35}S method did overestimate travel time for some wells. Successful application of the ^{35}S method at other MAR sites depends on quantification of source waters and preferably ^{35}S activities being above 20 mBq/L. Although the heat method shows promise, in order to take full advantage of heat as a tracer, advancements in the modeling of temperature need to be made. Boric acid enriched in ^{10}B showed retardation relative to the conservative Br^- tracer and is, therefore, not recommended for use as a deliberate tracer near MAR facilities.

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Appendix A

^{10}B and Br$^-$ Well Data

	Sampling Time	Time from Injection (days)[a]	δ^{11}B (‰)[b]	Bromide (ppm)[b]
Barrel 1	9/6/11 16:15	0	−983.98	260,000
Barrel 2	9/6/11 16:15	0	−984.60	260,000
Basin (average)	9/6/11 22:45	0.18	−757.43	84.6
Basin	9/7/11 2:30	0.34	−691.61	11.24
Basin	9/7/11 5:15	0.50	−749.98	10.65
Basin	9/7/11 16:30	0.93	−42.77	0.16
Basin	9/8/11 16:09	1.92	−10.45	0.88
Basin	9/9/11 16:08	2.90	+23.13	0.44
Basin	10/31/11 14:05	54.82	+31.75	0.083

[a] T_0 is when injection ended (barrels pumped dry) 18:00 on September 6, 2011.
[b] Mean concentrations of surface sampling sites

Well	Sampling Time	Time from Injection (days)	δ^{11}B (‰)	Bromide (ppm)
WPZ	9/6/11 16:34	0	−1.21	0.26
WPZ	9/6/11 23:48	0.23	−207.30	3.4
WPZ	9/7/11 2:48	0.35	−469.95	5.2
WPZ	9/7/11 6:41	0.51	−495.85	5.1
WPZ	9/7/11 10:13	0.66	−549.23	6.2
WPZ	9/7/11 17:07	0.95	−477.88	1.9
WPZ	9/11/11 11:55	4.73	+7.17	0.12
WPZ	9/14/11 10:49	7.69	+20.62	<0.1

Note: WPZ screen depth below basin floor: 2.4–3.0 m; distance down gradient from center of test basin: 0 m

Well	Sampling Time	Time from Injection (days)	δ^{11}B (‰)	Bromide (ppm)
PR8	9/6/11 15:38	0.00	+23.74	0.12
PR8	9/14/11 12:12	7.74	+27.52	0.39
PR8	9/21/11 11:45	14.73	−165.25	0.56
PR8	9/26/11 11:55	19.73	−38.53	0.41
PR8	10/3/11 13:00	26.78	−52.18	0.12
PR8	10/10/11 12:07	33.74	+9.65	0.13
PR8	10/17/11 12:41	40.76	+17.36	<0.1
PR8	10/31/11 14:02	54.82	+25.98	<0.1
PR8	11/7/11 12:28	61.76	–	<0.1

Note: PR8 screen depth below basin floor: 13.4-14.9 m; distance down gradient from center of test basin: 1.5 m

Well	Sampling Time	Time from Injection (days)	δ^{11}B (‰)	Bromide (ppm)
PR9	9/6/11 15:41	0	+31.96	<0.1
PR9	9/6/11 23:20	0.21	+35.47	<0.1
PR9	9/7/11 7:43	0.56	+13.65	0.18
PR9	9/7/11 10:28	0.67	+13.60	0.12
PR9	9/7/11 17:17	0.96	−1.65	0.16
PR9	9/7/11 20:56	1.11	+8.12	0.12
PR9	9/8/11 0:55	1.27	+17.61	0.09
PR9	9/8/11 8:57	1.61	+4.65	0.37
PR9	9/8/11 13:01	1.78	+1.23	1.2
PR9	9/8/11 16:53	1.94	−49.58	2.1
PR9	9/8/11 21:00	2.11	−113.99	3.5
PR9	9/9/11 1:25	2.3	−179.52	1.9
PR9	9/9/11 4:53	2.44	−237.49	1.2
PR9	9/9/11 13:13	2.79	−218.94	0.9
PR9	9/11/11 11:45	4.73	−43.30	0.2
PR9	9/14/11 11:00	7.69	+28.78	0.14
PR9	9/21/11 11:42	14.72	+24.33	--

Note: Monitoring well PR9 screen depth: 6.1–7.6 m; distance down gradient from center of test basin: 1.5 m

Well	Sampling Time	Time from Injection (days)	δ^{11}B (‰)	Bromide (ppm)
PR10	9/6/11 16:42	0	+26.52	0.15
PR10	9/14/11 11:40	7.72	+33.68	0.23
PR10	9/21/11 11:19	14.71	+34.57	0.66
PR10	9/26/11 12:18	19.75	−14.51	0.91
PR10	10/3/11 13:17	26.79	−96.11	1.2
PR10	10/10/11 12:25	33.75	−112.43	0.8
PR10	10/17/11 12:56	40.78	−49.37	<0.1
PR10	10/31/11 14:17	54.83	+7.72	<0.1
PR10	11/7/11 12:44	61.77	+19.88	<0.1

Note: Monitoring well PR10 screen depth: 13.7-15.2 m; distance down gradient from center of test basin: 15 m

Well	Sampling Time	Time from Injection (days)	δ^{11}B (‰)	Bromide (ppm)
PR11	9/6/11 17:31	0	−6.58	0.11
PR11	9/7/11 11:20	0.71	+0.09	0.15
PR11	9/7/11 17:50	0.98	+8.81	0.1
PR11	9/7/11 20:38	1.1	−49.68	<0.1
PR11	9/8/11 0:45	1.27	+22.91	0.14

PR11	9/8/11 8:46	1.6	+13.55	0.44
PR11	9/8/11 12:50	1.77	+7.74	2.3
PR11	9/8/11 16:46	1.93	−189.02	4.0
PR11	9/8/11 21:04	2.11	−59.73	2.1
PR11	9/9/11 0:48	2.27	−269.68	1.3
PR11	9/9/11 4:49	2.44	−295.82	1.3
PR11	9/9/11 12:51	2.77	−277.60	0.54
PR11	9/9/11 16:44	2.93	−232.54	0.22
PR11	9/9/11 19:51	3.06	−207.22	0.22
PR11	9/10/11 0:44	3.27	−160.56	0.16
PR11	9/10/11 8:49	3.6	−112.25	0.15
PR11	9/11/11 12:30	4.76	−15.39	<0.1
PR11	9/14/11 11:35	7.72	+19.74	0.15
PR11	9/21/11 11:36	14.72	+22.44	0.15
PR11	9/26/11 0:08	19.24	+22.55	0.17

Note: Monitoring well PR11 screen depth: 6.4–7.9 m; distance down gradient from center of test basin: 15 m

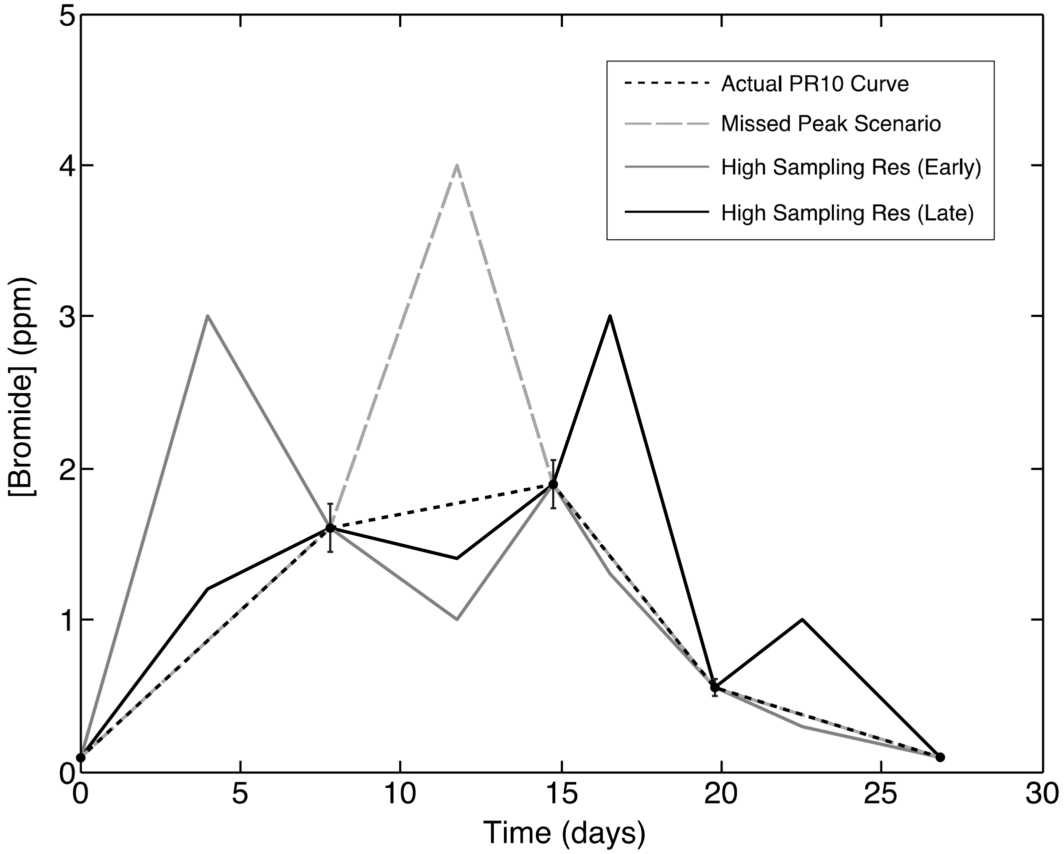
Well	**Sampling Time**	**Time from Injection (days)**	**δ^{11}B (‰)**	**Bromide (ppm)**
PR13	9/7/11 12:26	0	+18.48	<0.1
PR13	9/14/11 14:05	7.82	+24.52	1.6
PR13	9/21/11 12:52	14.77	−391.61	1.9
PR13	9/26/11 13:10	19.78	−195.72	0.56
PR13	10/3/11 14:08	26.82	−28.70	<0.1
PR13	10/10/11 13:05	33.78	+8.75	<0.1
PR13	10/17/11 13:40	40.81	+17.01	<0.1
PR13	10/31/11 14:52	54.86	+18.11	<0.1
PR13	11/7/11 13:16	61.79	+21.86	<0.1

Note: Monitoring well PR13 screen depth: 6.1–9.1 m; distance down gradient from center of test basin: 76 m.

Well	**Sampling Time**	**Time from Injection (days)**	**δ^{11}B (‰)**	**Bromide (ppm)**
PR15	9/7/11 13:22	0	+30.44	0.12
PR15	9/14/11 13:51	7.81	+30.37	0.13
PR15	9/21/11 13:31	14.8	+34.37	0.14
PR15	9/26/11 13:50	19.81	+36.48	0.21
PR15	10/3/11 15:02	26.86	+5.12	0.81
PR15	10/10/11 13:43	33.81	−3.27	1.2
PR15	10/17/11 14:14	40.83	+0.08	2.3
PR15	10/31/11 15:20	54.88	+5.43	0.17
PR15	11/7/11 13:49	61.81	+27.24	<0.1
PR15	11/14/11 13:45	68.81	+22.02	<0.1

Note: Monitoring well PR15 screen depth: 6.1–9.1 m; distance down gradient from center of test basin: 152 m

Appendix B
Breakthrough Curve Scatter



Four scenarios are presented, demonstrating the potential range in center of mass calculations about common sampling points. The five PR13 bromide sampling points that constitute its breakthrough curve are shown. COM is relative to the area under the curve. The actual curve (dashed) yields a COM estimate of 11.9 days. The "missed peak" scenario (light gray), in which the actual center of the tracer plume passed between weekly sampling events, yields a COM of 11.8 days. The final two scenarios present a sampling resolution twice that of the actual, one (dark gray) showing higher concentrations with earlier samples, the other (black) has higher concentrations later. The "early" scenario yields a COM of 9.8 days, the "later" of 13.1 days. Another possibility for drift is due to analytical uncertainty of the instrument. As with a higher sampling resolution, COM estimations do fluctuate but not drastically. Compounding both likely generates uncertainty on the order of ± 2 to 3 days for COM arrival, with uncertainty increasing in the far field.

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