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Case Study

Heat, ^{10}B-Enriched Boric Acid, and Bromide as Recycled Groundwater Tracers for Managed Aquifer Recharge: Case Study

Timothy E. Becker[1]; Jordan F. Clark[2]; and Theodore A. Johnson[3]

Abstract: California guidelines for indirect potable recycled wastewater reuse projects currently require groundwater tracers to demonstrate subsurface residence time for pathogenic microorganism control. Residence times over 6 months from infiltration to drinking water extraction are required. Two prospective tracers were evaluated in this case study: boron-10 (as ^{10}B-enriched boric acid) and heat (with recharging water ~10°C warmer than native groundwater). Bromide (Br$^-$) was also released as a control. ^{10}B is attractive as a deliberate tracer because (1) reasonably accurate and affordable measurements can be made on an inductively coupled plasma mass spectrometer (ICP-MS) system, and (2) isotopic tracers require significantly less mass to tag an equivalent water volume than concentration-based salt tracers like Br$^-$. ^{10}B and Br$^-$ tracer breakthroughs were observed at seven of nine monitoring wells, although at one well the detection of ^{10}B was barely observable and may have resulted from a slight change in source water composition. ^{10}B arrived 25% later than Br$^-$ on average, showing retardation through exchange with clay surfaces. Heat flow, requiring no artificial input, was interpreted from temperature changes recorded hourly at well loggers. Residence times to all wells were successfully determined from temperature changes with the longest flow path of 6 months. This implies that dilution of Br$^-$ and ^{10}B is a limitation the geochemical tracer experiment. **DOI: 10.1061/(ASCE)HE.1943-5584 .0001070.** © *2014 American Society of Civil Engineers.*

Author keywords: Groundwater; Travel time; Water flow; Heat flow; Recharge basin; Water reclamation.

Introduction

Water quality concerns are raised when recycled wastewater is a part of managed aquifer recharge (MAR) source waters. Understanding the fate and transport of potential contaminants 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 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). Many potential contaminants, such as most infective microorganisms (pathogens), persist in recycled water even after tertiary treatment at above-ground facilities; however, contaminants 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. 2003; Hiscock and Grischeck 2002; Laws et al. 2011). These natural attenuation processes are collectively known as soil aquifer treatment (SAT) and further improve the quality of recharged water for subsequent potable and nonpotable reuse.

Current California draft regulations for groundwater replenishment reuse require specific subsurface residence times prior to

extraction for potable use to demonstrate acceptable pathogen control [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 above-ground treatment technologies before recharge and the method used to determine subsurface travel times. Minimum time for tertiary-treated recycled water is 6 months when a deliberate (or artificial or added) tracer experiment is used.

DDW recommends deliberate tracer experiments for establishing retention times underground from MAR facilities using recycled wastewater. Deliberate tracers are introduced into the water system and therefore are distinguished from intrinsic (or environmental) tracers that already exist in the water (Davis et al. 1980; 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 time scales at minimum cost that 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; McDermott et al. 2008). However, SF$_6$ emission is being regulated in California because it is a strong greenhouse gas (~24,000 times stronger than CO$_2$ on a per molecule basis over a 100-year period) [Intergovernmental Panel on Climate Change (IPCC) 1996]. Significantly less SF$_6$ [2013 mixing ratio: ~8 parts per trillion by volume (pptv)] has been released to the atmosphere than CO$_2$ [2013 mixing ratio: ~400 parts per million by volume (ppmv)], so its contribution to global warming is small. Nonetheless, the future of SF$_6$ as a tracer remains in doubt.

Standard groundwater dating techniques using intrinsic tracers, such as tritium/helium-3 (T/^{3}He) and chlorofluorocarbon (CFC)

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methods, have uncertainties of typically ±2 years, too large to be effective at determining most MAR travel times. Furthermore, these techniques are often difficult to interpret at long-screened production wells where mixing of multiple flow lines (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; 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 has recently developed a more cost-effective analytical system, the noble gas membrane inlet mass spectrometry (NG-MIMS) system (Visser et al. 2013).

A major disadvantage to the application of deliberate tracers is the significant field and laboratory effort that is necessary in order to develop sufficient data for robust breakthrough curves. These experiments also work best in areas with a large number of 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 hydrologic conditions change in response to variable recharge or pumping that change local hydraulic gradients, a second tracer experiment may be needed to reevaluate groundwater travel times. Budgets may constrain the ability to tag large spreading ponds with both ^{10}B-enriched boric acid and granular bromide. Finally, dilution caused by both hydrodynamic dispersion and long screens can limit the application of these experiments.

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, which requires a deliberate tracer (Johnson 2009; DDW 2013).

This case study simultaneously evaluated two deliberate tracers (^{10}B, Br$^-$) and one intrinsic tracer (heat) at the San Gabriel Spreading Grounds (SGSG) research test basin, part of the Montebello Forebay MAR operation in Los Angeles County, California. The goals were to evaluate: (1) the possible retardation of the now more affordable boron isotopic deliberate tracer relative to conservative flow, and (2) the potential for heat flow to interpret residence time through temperature time series collected hourly with high-quality well loggers. While ^{10}B and heat are established hydrogeologic tracers, their application to satisfy MAR residence time requirements is still limited. The study of Quast et al. (2006) is very similar to this one but differs in a few important ways. This study was conducted at a test basin that has (1) better well control, (2) better known hydrostratigraphy, and (3) better control over the recharge rate of recycled wastewater. The latter is important when considering the unfortunate drying of the tagged basin midway through the Quast et al. (2006) experiment.

Boron-10 and Bromide Tracers

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). Boron occurs naturally as two stable isotopes, ^{10}B (~19.9% relative abundance) and ^{11}B (80.1%). ^{10}B, the lesser abundant boron stable isotope, is preferred as a deliberate tracer. 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.

Isotopic tracers can be favorable for evaluating groundwater recharge due to low analytic detection limits (e.g., Quast et al. 2006). 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 with concentration-based salt tracers like Br$^-$. This is because a shift in isotopic ratios (^{11}B/^{10}B) is much more pronounced than changes in concentration due to nonlinear mixing (Fig. 1). Wells that pump small volumes (<10%) of the tagged plume still show a strong isotopic signal.

Furthermore, as will be shown subsequently, accurate boron measurements can be made on an inductively coupled plasma mass spectrometer (ICP-MS) reducing analytical costs ($30/sample in 2013) by an order of magnitude compared with the traditional thermal-ionization mass spectrometry (TIMS). This is one of the main reasons boron is being considered as a deliberate tracer. Analytical uncertainty, while greater on the ICP-MS, should not distort breakthrough curve interpretation if the tagged water is sufficiently enriched.

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

$$\delta^{11}B = \left[\frac{(^{11}B/^{10}B)sample - (^{11}B/^{10}B)standard}{(^{11}B/^{10}B)standard} \right] \times 1,000 \quad (1)$$

Natural waters range widely from −16 to +59‰ δ^{11}B, with uncontaminated groundwater around +30‰ δ^{11}B (Vengosh et al. 1994). Treated municipal wastewater tends to be higher in ^{10}B, producing values around +1‰ to +10‰ δ^{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 Rio Hondo Spreading Grounds (RHSG) (Quast et al. 2006), nearby the test basin that receives similar source waters, reported untagged basin water of +2‰ and untagged groundwater of +5‰ and +8‰.
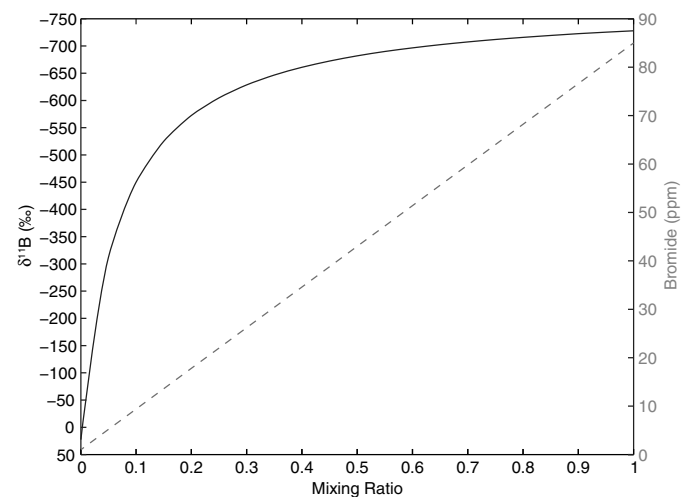

Fig. 1. Mixing ratios of the tagged recycled plume and native groundwater for boron-10 (solid black) and bromide (dashed gray) tracers; a ratio of 1 corresponds to 100% tagged water; plume end-member concentrations are derived from the average test basin water 4 h after initial tracer release; groundwater end-member is a typical background value

California state drinking water notification level for absolute boron concentration is 1,000 μg/L. Groundwater samples measured herein, even with the tagged tracer plume present, were between 250 and 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, with boric acid the dominant form. Adsorption–desorption reactions are the most significant mechanism influencing the fate of boron in water (Rai et al. 1986). $B(OH)_4^-$ is preferentially removed onto clay surfaces, which can retard the ion's transport relative to water flow and to conservative tracer migration (Vengosh et al. 1994).

B adsorption occurs through the anion's exchange with surface hydroxyl groups on Al and 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, pH, concentration in the solution, and clay content and particle size. Preferential removal of ^{10}B increases with increasing pH, and is not always observed in groundwater systems as a result. Field studies of boron transport have shown conservative movement in coarser sediments and retardation in aquifers with high clay content (Leenhouts et al. 1998).

The Rio Hondo tracer study (Quast et al. 2006) determined that ^{10}B transport was conservative relative to the conservative xenon (^{136}Xe and ^{124}Xe) and wastewater intrinsic tracers (primarily the boron to chloride ratio and sulfate concentration). However, the Quast et al. (2006) study had (1) a smaller well network (only five wells) compared with this case study (nine wells), (2) very few basin samples collected post injection, and (3) two distinct wetting periods separated by 1.5 months of a dry basin, compared with a single continuous recharge event. Quast et al. (2006) shows two tracer peaks for both B and Xe isotopes, one prior to and one after the drying, suggesting that further ^{10}B tracer experiments were needed to resolve this potential experimental flaw. It is unclear why these two tracers behaved so similarly considering one is a noble gas and the other is a speciated solute.

The present case study also served as the first objective comparison of ^{10}B to Br$^-$ subsurface travel times. Alkali halides such as NaBr and KBr are the most commonly used salts for fluid tracing due to their conservative behavior (Davis et al. 1980; 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 established travel times to a subset of the wells sampled herein.

Limitations for deliberate tracers are primarily 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 can also induce density contrasts between the tagged and native groundwater (Istok and Humphrey 1995; Quast et al. 2006). The authors cannot rule out density flow problems here; however, 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.

Intrinsic Heat Tracer

Recycled wastewater is warmed at treatment plants and after being transferred to a spreading pond, it can acquire the diurnal heating–cooling trends. Therefore heat as a tracer at MAR sites has a great potential because it has been used near streams (Lapham 1989; Stonestrom and Constantz 2003; Constantz et al. 2003; Anderson 2005). A few 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 changes (e.g., Laws et al. 2011; Becker et al. 2013).

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. Permitting is also not required because there is no artificial input and temperature sensors and loggers can record in better than 1-h time steps with high precision.

Unfortunately, heat flow is not conservative because it dissipates into the solid matrix during transport within the groundwater system (Constantz et al. 2003). Conservative tracers like Br$^-$ remains in the pore water solution and do 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, which is the capacity of solids to absorb or conduct energy. The influence of heat absorption and 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. Becker et al. (2013) found that heat dispersion under a spreading basin was due primarily to hydrodynamic mechanisms rather than thermal diffusion.

Materials and Methods

Description of Study Area

The multitracer experiment evaluating ^{10}B, Br$^-$, and heat was conducted at the research test basin that marks the northern extent of SGSG (Figs. 2, and 3). The approximately 2,000-m^2 basin was constructed and characterized by the U.S. Geological Survey (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). Recycled wastewater can be pumped directly to this basin at a controllable rate (approximately 2,200 m^3/day). More recent work at the test basin includes an investigation of the fate of trace organic chemicals contained in recycled wastewater (Drewes et al. 2011; Laws et al. 2011).

Nine monitoring wells are situated in a line down gradient of the test basin (Fig. 4). The wells are equipped with loggers that record hourly temperature and water level measurements. The Water Replenishment District (WRD) of southern California, which manages the supply to SGSG and the neighboring RHSG, installed the four most distant wells (as two well pairs) less than a month before the multitracer injection. Well pairs monitor an upper unconfined aquifer and a lower semiconfined aquifer, separated by a low permeability clay deposit. Preexperiment travel 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.
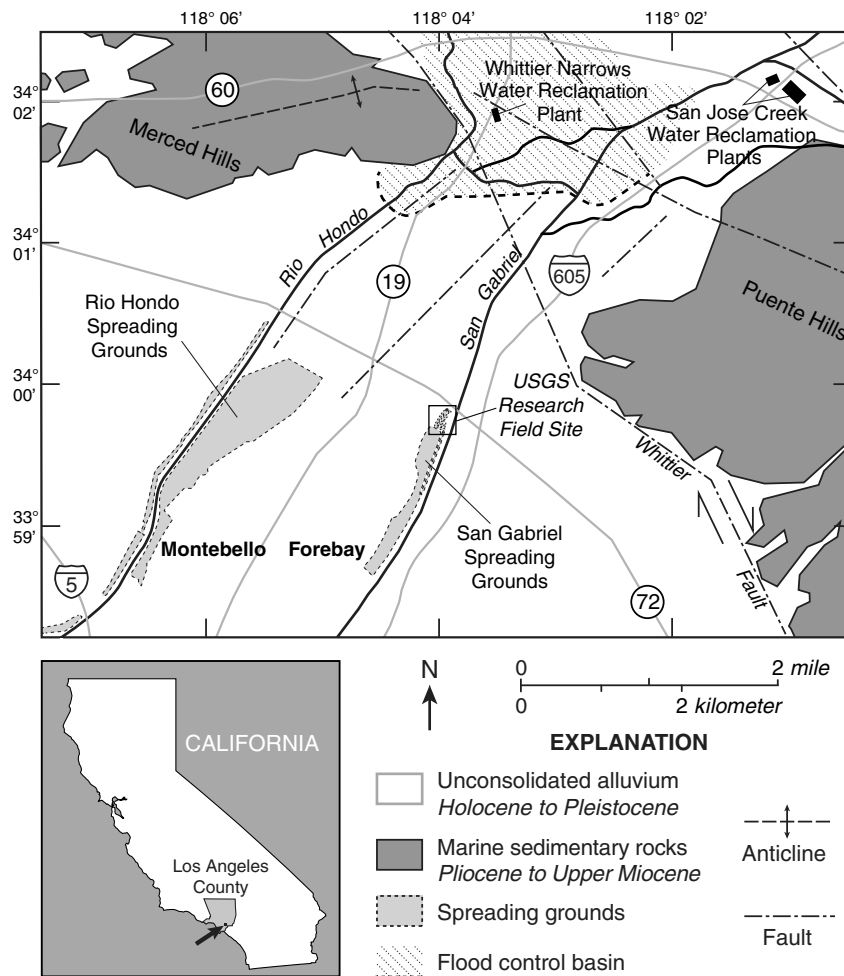
Fig. 2. Location of Rio Hondo and San Gabriel Spreading Grounds, part of the Montebello Forebay MAR operation, Los Angeles County, CA (adapted from Schroeder et al. 2003; faults and folds data from Yerkes and Campbell 2005)
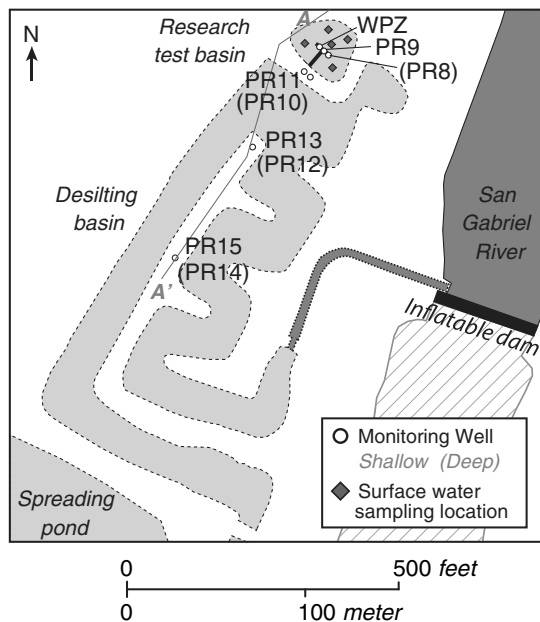

Fig. 3. USGS research field site at SGSG includes nine monitoring wells (WPZ, PR8–15); see Fig. 1 for site location, Fig. 4 for A–A' cross section

Schroeder et al. (2003) measured infiltration rates through the basin floor of 0.6 to 0.9 m/day, with unsaturated flow between the floor and the recharge mound typically for 2 to 3 m. Vertical hydraulic conductivities measured below the floor ranged from 0.24 (the ~15-cm-thick clay-rich infiltration zone at the basin floor) to 26.5 m/day (the ~2 m of the percolation zone below the clay). The low conductivity clay-rich zone is common on a spreading basin floor due to the deposition of fine sediment carried by the recharge water to the basin and was still present to some degree during this fall 2011 study. Horizontal conductivities ranged from 25.9 to 38.1 m/day.

^{10}B *and Bromide Injection*

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. Three kilograms of powdered boric acid enriched to $>92\%^{10}$B and 36 kg of granular sodium bromide (NaBr) were added in total to the barrels. After the salts had dissolved, 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 wastewater 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 wastewater then continued nonstop for 57 days, ending on November 2, 2011. The basin was wet and infiltrating the
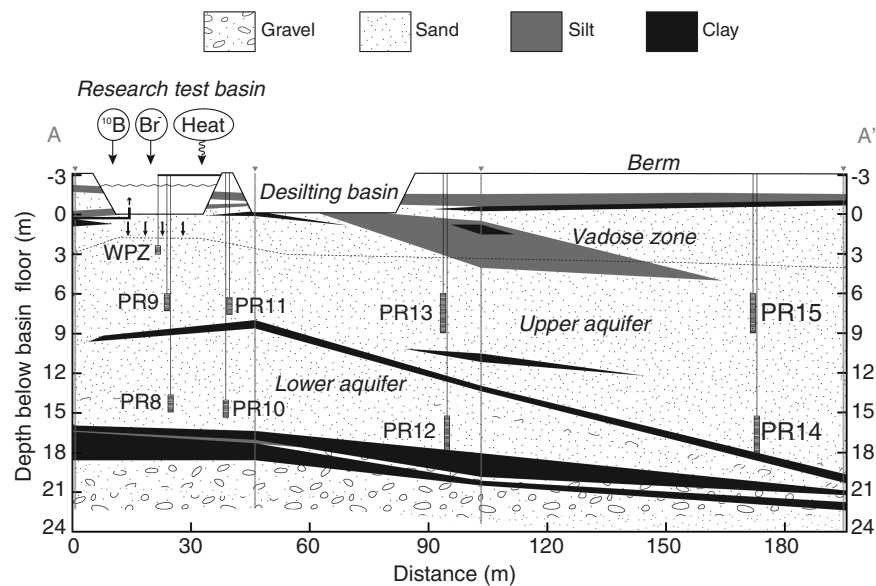
Fig. 4. Monitoring well location and idealized stratigraphy underlying the research field site at SGSG; aquifers are defined by sand- and gravel-dominated (containing >50% specified grain size) layers; low-permeability layers of silt and clay are shown in gray and black, respectively; stratigraphy interpreted from well logs and cone penetration tests (gray triangles); see Fig. 3 for section location

subsurface continuously for 61 days unlike the basin during the Quast et al. (1996) experiment.

Heat Tracer

Heat serves as an intrinsic tracer that does not require any artificial energy or chemical input (i.e., no physical injection). Recycled wastewater began continuously entering the basin on September 2, 2011 (96 h prior to geochemical tracer injection) in order to build the recharge mound. 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 wastewater averaged 11.6°C above native groundwater during early September and 8.3°C by November.

Field Sampling, Laboratory Analysis, and Additional Data

Sampling occurred for 1 year following tracer injection. Immediately after injection, the tagged basin water was sampled every 4 h at five locations (four corners and the center) until the basin volume was reduced by approximately 90%. 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 hours 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.

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 into new 125-mL Nalgene bottles. Br^- concentrations were measured using a Dionex Model DX500 ion chromatograph at BC Laboratories, Bakersfield, California, with 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 parts per million (ppm).

Boron isotope 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 were typically 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 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. The standard deviation for measured isotopic ratios on the ICP-MS was ±15‰ $\delta^{11}B$.

While one to two orders of magnitude worse than the precision of the TIMS system, isotopic tracers like boron still show a strong signature even when sampling a relatively small portion (2–10%) of the tagged plume (Fig. 1). Cost savings and sample output (90–100 samples analyzed in a day) justify the decrease in analytical certainty using the ICP-MS. The more difficult and larger uncertainty is the untagged groundwater end member. As described subsequently, this can make interpretation of breakthrough uncertain when the dilution is large.

Results and Discussion

^{10}B and Bromide Transport

Water collected at the test basin approximately 4 h after the injection averaged about 85 ppm (mg/L) Br^- and −725‰ $\delta^{11}B$;

however, the pond was not well mixed ([Br$^-$] range: 4 to 380 ppm, median: 10 ppm; δ^{11}B range: -521 to $-976‰$ δ^{11}B, median: $-741‰$; total [B]: 0.36 to 6.7 ppm, median: 0.46 ppm). The high-end samples for both Br$^-$ and δ^{11}B (total boron and most negative δ^{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 to 23 ppm, median: 8.5 ppm; δ^{11}B range: -438 to $-851‰$ δ^{11}B, median: $-696‰$; total [B]: 0.34 to 0.68 ppm, median: 0.43 ppm). The basin was nearly drained 12 h following injection. The only two sampling sites remaining measured 8.3 and 13.0 ppm for [Br$^-$], $-696‰$ and $-804‰$ δ^{11}B for the ^{10}B tracer (total [B]: 0.46 and 0.55 ppm).

Untagged recycled wastewater began recharging the test basin again shortly thereafter. [Br$^-$] fell to background levels by the next sampling event 24 h following injection. The δ^{11}B water samples collected at 24 and 48 h were still slightly enriched in ^{10}B and total [B] (respectively, 0.45 and 0.29 ppm and $-43‰$ and $-10‰$). ^{10}B levels finally fell to background ($+24‰$ in δ^{11}B; total [B]: 0.27 ppm) by the 72-h sampling event. Boron isotope and [Br$^-$] measurements are assigned standard deviation of $\pm15‰$ δ^{11}B and $\pm10\%$, respectively.

^{10}B and Br$^-$ tracer breakthroughs were observed at seven of the nine monitoring wells (Figs. 5 and 6), although the breakthrough at PR-15 was barely detectable [breakthrough data can be found in Becker (2013)]. No breakthrough was observed at the two deep, distant wells (PR12, PR14) after 1 year of sample collection, presumably due to dilution of both tracers. Breakthrough curves, summarized in Table 1, are characterized by the tracer first arrival (defined by the first detection and therefore the analytical method), tracer peak arrival (observed maximum and therefore the frequency of sampling), and arrival of the tracer center of mass (COM).

^{10}B at PR15 (shallow but most distant) was 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 one is willing to accept that the observed values contained less than 2% of the tagged water. Its breakthrough could also be explained by a transient change in the wastewater that has migrated through the system. Unfortunately, the authors did not continue monitoring the source water composition after the brief injection period. However, Quast et al. (2006) reported δ^{11}B values between $+2‰$ and $+8‰$ in untagged water during their tracer experiment at the nearby RHSG. These values are within the analytical uncertainty of the peak value observed during this experiment (δ^{11}B $= -3‰$) and make the interpretation that there was no breakthrough at PR15 plausible. Additional support for this interpretation comes from the general range of δ^{11}B ($-16‰$ to $+59‰$) in groundwater reported by Vengosh et al. (1994).

Peak tracer values to the wells, if compared to a well-mixed average tagged basin concentration, suggest a small sampled fraction (5–10%) of the plume. 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 the averaged basin.

Arrival of Br$^-$ was always coincident or preceded the ^{10}B arrival. ^{10}B/Br$^-$ COM travel time ratios range from 1 to 1.4, indicating that ^{10}B arrives ~25% later than Br$^-$ on average. The lag between bromide and boron arrivals generally increases with increasing distance and arrival time from the spreading pond, with PR15 as the exception, if it is assumed that the breakthrough is due to the tracer addition and not a change to the source water.
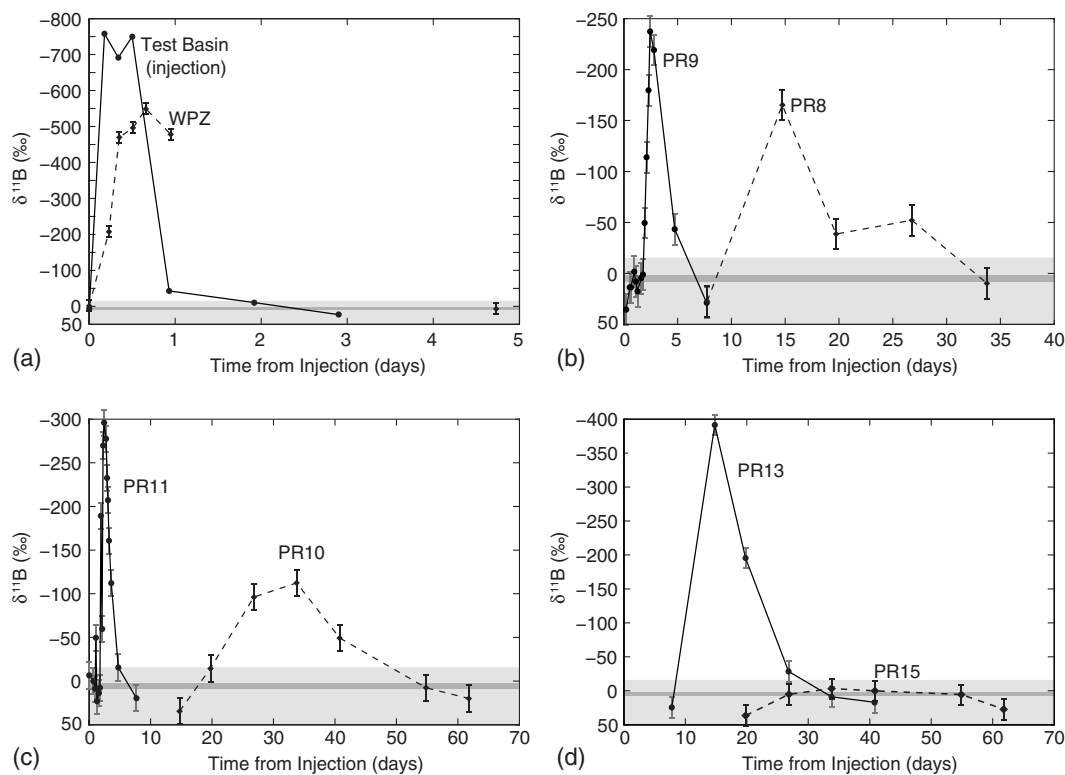

Fig. 5. Boron-10 breakthrough curves with inverted y-axis; initial test basin concentration (at t_0) is average of samples taken directly from San Jose Creek treatment plants; values are shown with analytical uncertainty of $\pm15‰$ δ^{11}B except for test basin samples, which are an average of multiple sites; the gray box is the range of δ^{11}B found in natural waters ($-16‰$ to $+59‰$) reported by Vengosh et al. (1994); the black box is the range of untagged basin and groundwater reported at the nearby RHSG by Quast et al. (2006)
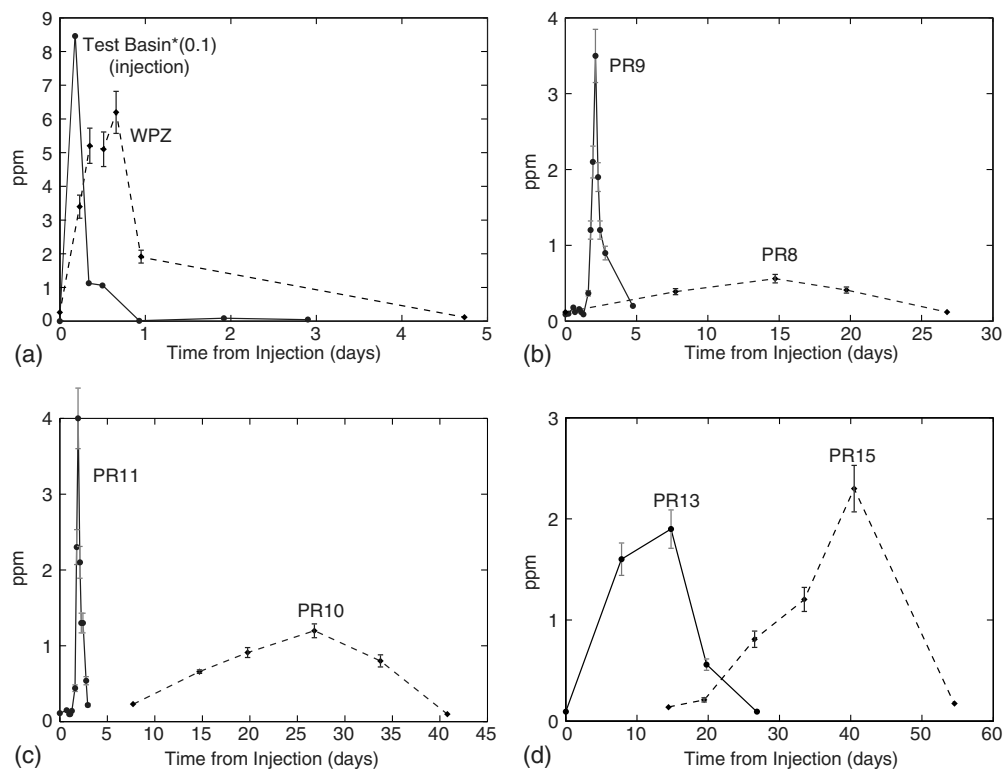
Fig. 6. Bromide breakthrough curves; native groundwater contained bromide concentrations typically below 0.1 ppm; test basin is scaled down by an order of magnitude to fit display window; initial test basin concentration (at t_0) is based on average background, not sampled directly, and is therefore shown in gray; values are shown with analytical uncertainty of $\pm 10\%$ except for test basin samples, which are an average of multiple sites

Table 1. ^{10}B and Br$^-$ Tracer Breakthrough Summary

Well	First arrival δ^{11}B Time[b]	First arrival δ^{11}B ‰	First arrival Br$^-$ Time	First arrival Br$^-$ ppm	Peak arrival δ^{11}B Time	Peak arrival δ^{11}B ‰	Peak arrival Br$^-$ Time	Peak arrival Br$^-$ ppm	COM[a] arrival δ^{11}B Time	COM[a] arrival Br$^-$ Time	^{10}B/Br$^-$ COM travel time ratio
WPZ	0.2	−207	0.2	3.4	0.7	−549	0.7	6.2	0.7	0.7	1
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	2.4	1.9	1.3
PR12	—	—	—	—	—	—	—	—	—	—	—
PR13	14.8	−392	7.8	1.6	14.8	−392	14.8	1.9	16.2	11.8	1.4
PR14	—	—	—	—	—	—	—	—	—	—	—
PR15[c]	—	+5	19.8	0.2	—	−3	40.8	2.3	—	38.9	—

Note: Analytical uncertainty for δ^{11}B and Br$^-$ measurements is ± 15‰ and $\pm 10\%$, respectively.
[a]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 the time that tracer was detectable above background levels.
[b]Days following tracer injection (approximately 18:00 on September 6, 2011).
[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, 33.8, and 39.7 days; the travel time ratio of the center of mass is 1.02.

Heat Flow

Native groundwater not influenced by MAR operations averaged 17.3°C at the start of the tracer experiment and rarely fluctuated more than 0.5°C. Infiltrating recycled wastewater averaged 28.9°C during early September and 25.6°C by November. Solar radiation is not the only warming mechanism: recycled wastewater arrives warm to the basin from the treatment plants. Only one well, PR10, was logging temperature for months prior to the experiment (Fig. 7). That well shows 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) (Fig. 8). Peak matching is ideal because it allows for precise travel times that can be calculated many times during the recharge event (e.g., Drewes et al. 2011; Racz et al. 2012; Becker et al. 2013). This is helpful to establish any temporal changes in infiltration rates. Most wells, however, recorded a
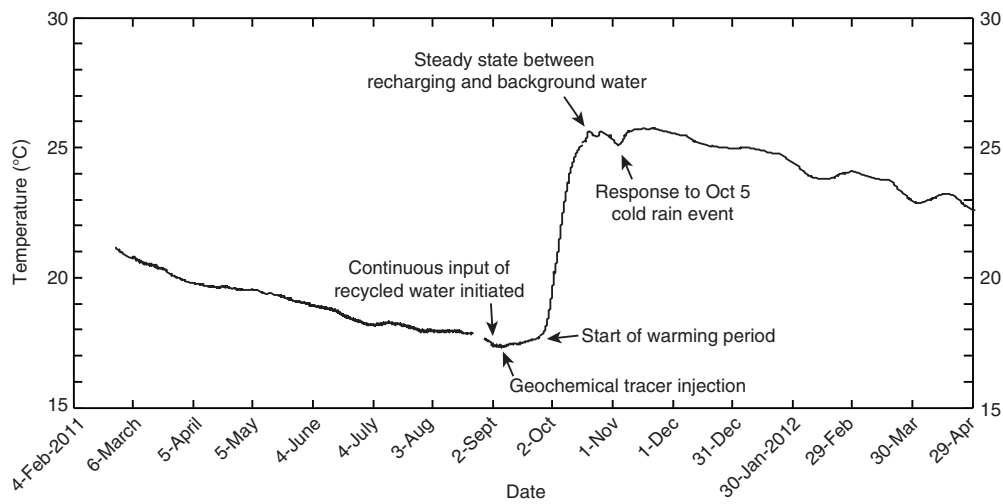
Fig. 7. Extended temperature measurements for monitoring well PR10; water temperatures steadily declined following the 2010–2011 recharge season; the arrival of the warm recharge plume, following continuous input to the test basin beginning in early September 2011, is clear

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 (Fig. 9). The warming period is defined here to begin when a well logger recorded temperatures 0.5°C

Fig. 8. Test basin and WPZ temperature measurements: (a) start of inflow (T_0) occurred 4 days prior to tracer injection, a strong diurnal temperature signal was recorded in the basin, with average temperatures declining as late summer transitioned into fall; (b) at the shallowest screen below the test basin, diurnal fluctuations were observed for >20-day period showing very rapid travel from the basin to WPZ

above that of background. The period ends as temperatures plateau at closer wells, indicating steady-state conditions between the continuously recharging recycled plume and native groundwater, or peak at the more distant wells that record the long recharge event as a single pulse.

Even without a diurnal signal, heat flow interpretations yielded 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, temperature changes were 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 with 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, PR14 arrived nearly 50 days earlier than PR12. This is attributed to the clay aquitard that lies above PR12 but below PR14, allowing for faster transport to the latter (Fig. 3).

Travel times to WPZ, PR8, PR9, PR10, and PR11 were also estimated through peak matching of the October 5, 2011, rain event (Table 2). This event occurred approximately 33 days after the wetting of the test basin (day 30 of the tracer experiment). Travel time was calculated as the offset between the test basin signal and each well's response. The furthest well to show a response was PR10, which recorded the transient cooling ~1 month later. More 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 collecting in and cooling down the test basin recharge water, the rain presumably caused some ponding within the adjacent desilting basin, though no ponding was noticed during the October 10, 2011, sampling event. This volume was minor in comparison to that infiltrating the test basin, and its impact on groundwater movement is assumed to be negligible.
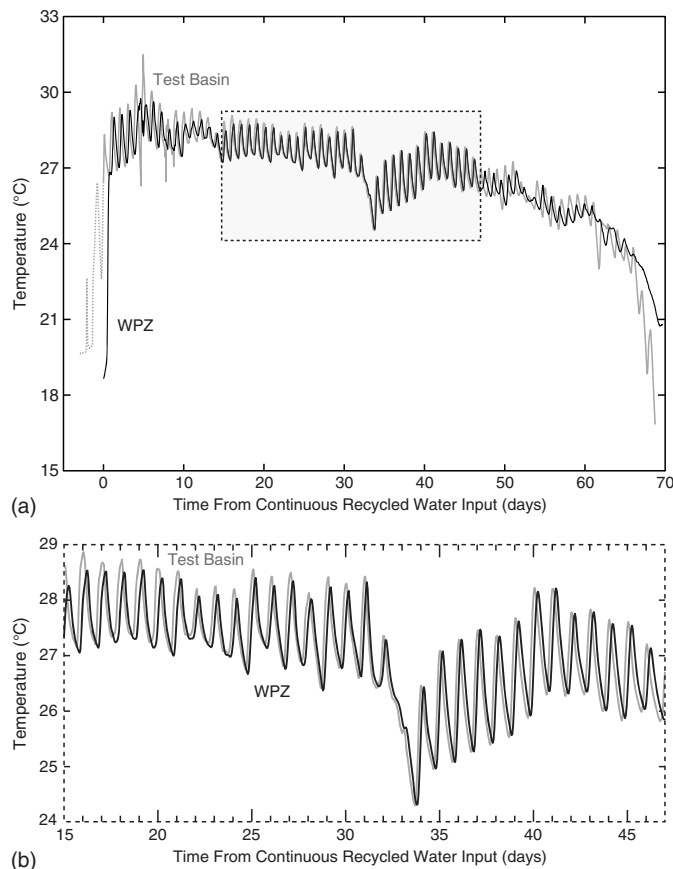
Retardation of ¹⁰B

Nonconservative transport in a neutral pH (Schroeder et al. 2003) groundwater system, albeit with clay layers present, is a weakness for the boron tracer. Later arrivals suggest a slower flow path, overestimating the subsurface retention time. As a consequence, wells on the border of violating DDW minimum residence times would likely require more testing. It is possible, however, that
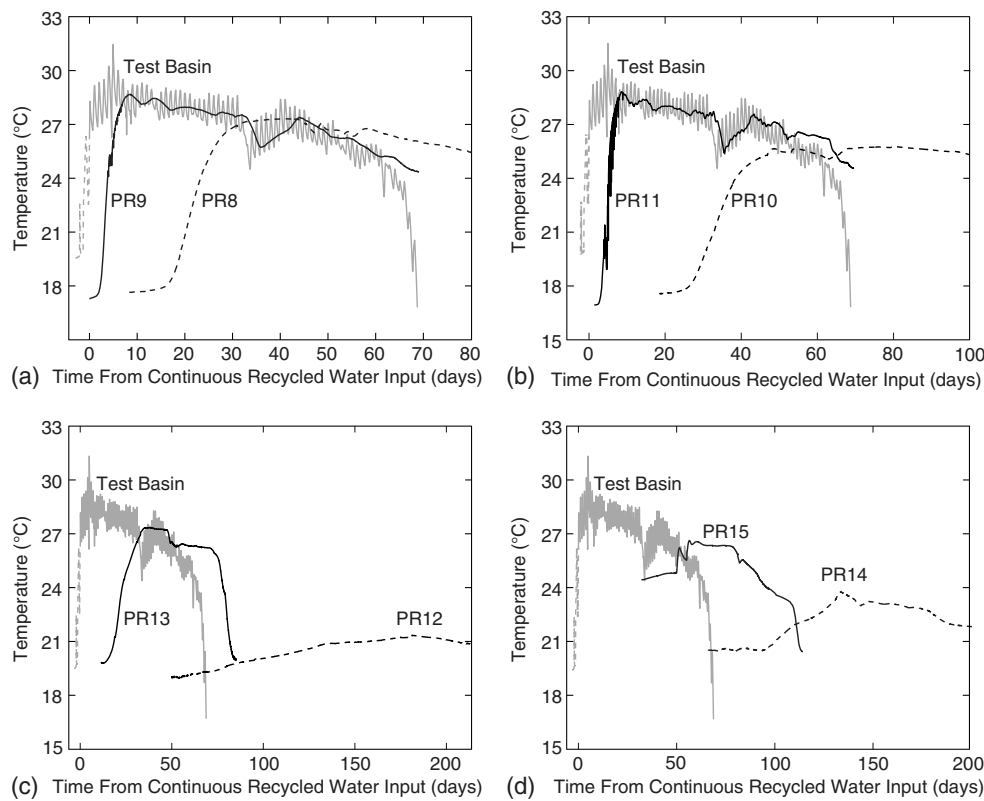
Fig. 9. PR8–15 temperature measurements, with test basin for reference; distant wells (PR12–15) have higher background temperatures because of earlier recharge events that already passed all other wells

the relatively poor sample collection resolution (common for most deliberate tracer studies) and laboratory uncertainty created a sampling bias. The potential range of COM arrivals are discussed in Appendix S1 and Fig. S1. At San Gabriel'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 DDW target of 6 months. Tracer dilution is an issue for deliberate tracer experiments and limit their application.

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 like Br$^-$ remain dissolved 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, though small preferential flow paths in the aquifer are harder to resolve. Temperature measurements are still useful for describing the majority of the plume despite this weakness.

Table 2 summarizes geochemical and heat flow travel times to all wells compared with those estimated by Laws et al. (2011) at wells WPZ and PR8–11. Laws et al. used temperature measurements from the 2008 summer and 2009 spring. Diurnal peak matching was possible at three (WPZ, PR9, and PR11) of the five wells they examined. 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. This interpretation is still an overestimate of the travel times determined here, likely due to different hydrologic conditions between the 2008 and

Table 2. ^{10}B and Br$^-$ COM and Heat Flow Travel Times Compared to Laws et al. (2011)

	This study				Laws et al. (2011)[a]
	Boron-10	Bromide	Heat[b]	Rain event[a]	
Well	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	—	—

[a]Travel time determined by the migration of the short-term cooling caused by the October 5, 2011, rain event.
[b]Heat flow travel times from diurnal peak matching (WPZ), start of the warming period (PR8-11, PR13, PR15), or peak temperature arrival (PR12, PR14).
[c]For PR15, if interpreted as a breakthrough curve, the COM arrival for ^{10}B was 39.7 days.

2011 data collection. Recharge water was continuously entering the test basin over multiple months for both experiments, but the earlier study occurred closer in time to the winter recharge season.

Conclusions

This case study indicates that the transport of boric acid enriched in ^{10}B is not ideal. The tracer is retarded presumably due to exchange on clay surfaces in the subsurface. As a result, travel times overestimate actual groundwater flow time, especially in wells far (in depth and lateral distance) from the injection point. Unless a relic of sampling resolution, this is a weakness for the boron tracer. The advantages of isotopic tracers are that (1) significantly less mass is needed for the same volume of water, and (2) detection is easier because of nonlinear mixing. ^{10}B breakthroughs, despite an injection mass an order of magnitude lower than Br^-, were observed at six of the seven wells where Br^- breakthrough occurred. ^{10}B measurements were also made on the more affordable ICP-MS system, with analytical uncertainty better than $\pm 15‰$ δ^{11}B.

Deliberate tracer studies are commonly hindered by (1) mass needed, with large projects approaching unrealistic costs, raising mixing concerns in the tagged basin and the potential to affect flow, and (2) poor sampling resolution, limited largely by staff hours and analytical expenses. Nevertheless, boric acid enriched in ^{10}B may be the best option when deep unsaturated zones may limit the effectiveness of gas tracers. However, dilution, budget, and retardation must be considered when using enriched boric acid.

Heat has great potential as an intrinsic tracer at MAR facilities. Temperature measurements are inexpensive and easy to collect with modern well loggers that offer high sensitivity, vastly higher sampling resolution compared to deliberate tracers, and no artificial energy or chemical inputs are added to potable aquifers.

Diurnal peak matching, when available in the near field, is ideal and provides a precise travel time estimate. Here, offset of a cold rain event also provided a reliable estimate of travel time to four wells very close to the basin. Further 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 that 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 and mixing concerns are drastically reduced. While 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. Intrinsic tracers should be considered a viable test method to satisfy California permit requirements for recycled wastewater recharge projects.

Acknowledgments

Supplemental Data

Appendix S1 and Fig. S1 are available online in the ASCE Library (http://www.ascelibrary.org).

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