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Publication Date

2016-12-01

DOI

10.1016/j.jhydrol.2016.04.036

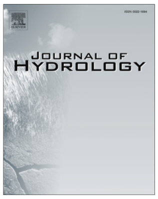
Peer reviewed

Journal of Hydrology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol



Research papers

Quantifying groundwater travel time near managed recharge operations using ^{35}S as an intrinsic tracer

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ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Hydrologic tracers
Travel time
Retention time
Sulfur-35
Montebello Forebay
Orange County Recharge Operation

SUMMARY

Identifying groundwater retention times near managed aquifer recharge (MAR) facilities is a high priority for managing water quality, especially for operations that incorporate recycled wastewater. To protect public health, California guidelines for Groundwater Replenishment Reuse Projects require a minimum 2–6 month subsurface retention time for recycled water depending on the level of disinfection, which highlights the importance of quantifying groundwater travel times on short time scales. This study developed and evaluated a new intrinsic tracer method using the naturally occurring radioisotope sulfur-35 (^{35}S). The 87.5 day half-life of ^{35}S is ideal for investigating groundwater travel times on the <1 year timescale of interest to MAR managers. Natural concentrations of ^{35}S found in water as dissolved sulfate ($^{35}SO_4$) were measured in source waters and groundwater at the Rio Hondo Spreading Grounds in Los Angeles County, CA, and Orange County Groundwater Recharge Facilities in Orange County, CA. $^{35}SO_4$ travel times are comparable to travel times determined by well-established deliberate tracer studies. The study also revealed that $^{35}SO_4$ in MAR source water can vary seasonally and therefore careful characterization of $^{35}SO_4$ is needed to accurately quantify groundwater travel time. More data is needed to fully assess whether or not this tracer could become a valuable tool for managers.

1. Introduction

Growing demands on groundwater resources makes the practice of artificially recharging underground aquifers increasingly important for supplementing water supply. In populated, semi-arid regions such as Southern California, the use of reclaimed water to replenish groundwater basins provides a safe and reliable (drought resistant) source for managed aquifer recharge (MAR). Water quality concerns are raised when recycled wastewater is a portion of MAR source waters. Understanding flow characteristics of recharged water near MAR operations is critical for protecting public and environmental health.

Water quality and numerical modeling studies near MAR operations have demonstrated that subsurface retention time is an important hydrologic parameter for the natural removal of potential contaminants (e.g., Fox and Makam, 2009; Laws et al., 2011). Based on the time dependent degradation and inactivation of many contaminants in the subsurface by natural attenuation processes (e.g. Yates and Yates, 1987; Fox et al., 2001; Drewes et al., 2002; Hiscock and Grischeck, 2002; Laws et al., 2011), collectively known as soil aquifer treatment (SAT), current California regulations for Groundwater Replenishment Reuse Projects (GRRP) require minimum subsurface retention times for recharge water prior to extraction for potable use (California Division of Drinking Water (DDW), 2014). For MAR facilities that apply recycled municipal wastewater, DDW requires tracer experiments to quantify minimum retention times of no less than 2 months for a response retention time, and between 2 and 6 months for pathogen removal credits depending on the amount of treatment above ground prior to recharge.

Many common deliberate (intentionally introduced) and intrinsic (existing in the environment) hydrologic tracers that are utilized to investigate subsurface flow characteristics are either unable to resolve subsurface travel times on <1 year timescales or require significant field and laboratory effort. For example, shallow groundwater dating techniques using well-established intrinsic tracers such as tritium/helium-3 ($T/^3He$), krypton-85 (^{85}K) and chlorofluorocarbon (CFC) dating methods typically have uncertainties of ±1–2 years (Ekwurzel et al., 1994; Cook and Herczeg, 2000), which is too large to effectively determine travel time on the <1 year timescale of interest to MAR managers and regulators. Deliberate (or intentionally introduced) tracer methods such as the non-reactive, synthetic sulfur hexafluoride (SF_6) gas and noble

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http://dx.doi.org/10.1016/j.jhydrol.2016.04.036
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Please cite this article in press as: Urióstegui, S.H., et al. Quantifying groundwater travel time near managed recharge operations using ^{35}S as an intrinsic tracer. J. Hydrol. (2016), http://dx.doi.org/10.1016/j.jhydrol.2016.04.036

gas isotopes of xenon (^{124}Xe and ^{136}Xe) have been used near MAR facilities (Moran and Halliwell, 2002; Clark et al., 2004; McDermott et al., 2008). A major disadvantage to the application of deliberate tracers is the significant field and laboratory effort necessary to develop sufficient data for robust breakthrough curves and to ensure that the tracer patch does not pass nearby monitoring wells without detection. Another significant limitation of deliberate hydrologic tracer experiments is that results are specific to hydrogeologic conditions and pumping regime at the time of the experiment and therefore may not represent minimum residence times, which is the management criteria. Furthermore, SF_6, which has been the principal deliberate tracer for determining groundwater retention times near MAR facilities in California (e.g., Gamlin et al., 2001; Clark et al., 2004, 2005; Avisar and Clark, 2005; McDermott et al., 2008) is now regulated because it is a strong greenhouse gas (IPPC, 1996). Current alternatives to SF_6, such as noble gas tracer studies are impractical due to high analytical costs and long analysis times despite progress being made on a new noble gas membrane inlet mass spectrometry (NG-MIMS) system (Visser et al., 2013). 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 retention times on timescales of <1 year, will improve MAR management and safe use of recycled water for augmenting local water supplies.

This study developed and evaluated a new groundwater tracer technique to quantify subsurface travel times near MAR facilities using the naturally-occuring radionuclide sulfur-35 (^{35}S), which is found in water as dissolved sulfate ($^{35}SO_4$). The new method was evaluated by comparing $^{35}SO_4$ travel times to those determined with deliberate tracer experiments at two southern California field sites: the Rio Hondo Spreading Grounds (RHSG) in Los Angeles County (McDermott et al., 2008; Clark, 2011), and the Orange County Water District (OCWD) Groundwater Recharge Facility in Orange County (e.g., Gamlin et al., 2001; Clark et al., 2004, 2014). This work is the first time $^{35}SO_4$ has been measured in these systems, and is intended as a feasibility study. Application of $^{35}SO_4$ for regulatory compliance would require additional studies beyond the scope presented here.

2. ^{35}S as a groundwater tracer

2.1. ^{35}S production and geochemistry

^{35}S is continually produced in the upper atmosphere by cosmic ray interaction with atmospheric argon. After its production, ^{35}S rapidly oxidizes to $^{35}SO_2$ and eventually to $^{35}SO_4$, and is transferred to groundwater as dissolved $^{35}SO_4$ mainly through recharge of precipitation (e.g., Tanaka and Turekian, 1991, 1995; Michel et al., 2000). Due to its short half-life of 87.5 days (Friedlander et al., 1981), ^{35}S is an ideal intrinsic radionuclide for investigating groundwater travel time up to 1.2 years (5 half-lives).

Dissolved $^{35}SO_4$ has been employed in hydrologic studies as an intrinsic tracer for SO_4 and groundwater for over two decades in high-elevation (mountain) basins where groundwater retention 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; Singleton et al., 2014). Although both wet and dry atmospheric deposition contributes $^{35}SO_4$ to rivers in low elevation regions of large river basins, dilution of atmospherically-derived $^{35}SO_4$ with anthropogenic SO_4 (i.e. that is SO_4 containing no detectable ^{35}S) is expected to lower the specific activity of $^{35}SO_4$ in SO_4. The ratio of ^{35}S to SO_4 may also decrease due to radioactive decay during transport downstream, or from input of ^{35}S-dead SO_4 from different reservoirs (soil zone, minerals, and biota).

Since water in MAR facilities using recycled water is likely to have high SO_4 concentrations and low ^{35}S activity, a new analytical method (Urióstegui et al., 2015) for liquid scintillation counting of $^{35}SO_4$ was used. The method increased the signal to noise ratio of ^{35}S to SO_4 by processing a larger masses of $^{35}SO_4$ compared to previous methods, which allowed for accurate measurements of $^{35}SO_4$ in these high SO_4 waters.

2.2. Travel time calculation

Under a simplified plug flow model at an MAR surface spreading facility, a deliberate or intrinsic tracer is incorporated into the source water above ground prior to recharge. Based on ideal tracers being non-reactive and not sorbing readily to the aquifer material, they are recharged and transported through the aquifer at the mean groundwater velocity. Tracer input functions in this study were empirically defined using the $^{35}SO_4$ activity of MAR surface water in spreading ponds. The subsurface travel time of water was calculated using the following decay equation:

$$t = \frac{1}{\lambda}\ln\left(\frac{N}{N_o}\right) \tag{1}$$

where t is the subsurface travel time in years, λ is the decay constant for ^{35}S (2.894 yr^{-1}), and N/N_o is the activity ratio of the $^{35}SO_4$ activity in the well (N) and in the source water (N_o) in mBq/L. In Eq. (1), dilution of young water (<1.2 year subsurface travel time) with older water (>1.2 year subsurface travel time) would mimic radioactive decay and lower the $^{35}SO_4$ activity, resulting in an artificially long calculated subsurface travel time if a correction is not made for dilution is unaccounted. Minimal dilution of young with old water is likely for narrow screened, shallow wells located near the infiltration basins; however, longer screened productions wells located further down gradient are likely mix groundwater of different ages (Manning et al., 2005; McDermott et al., 2008).

Eq. (1) assumes conservative transport of $^{35}SO_4$ with no sorption or sulfate reduction. When considering $^{35}SO_4$ activity alone (i.e. not normalized to sulfate concentration), 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. Based on measured neutral pH conditions and dissolved oxygen concentrations of >3 mg/L in source waters and groundwater at both sites investigated in this study, $^{35}SO_4$ should behave as a conservative anionic complex and not experience significant sorption or reduction in oxic, near-neutral groundwaters.

3. Study sites

The RHSG and OCWD MAR sites are located in southern California, with the RHSG being situated in the Montebello Forebay of the Central Basin and the OCWD MAR facilities are located in the Santa Ana Forebay of the Orange County Coastal Plain (Fig. 1). Both MAR sites have been artificial recharging water since the 1930s.

3.1. Montebello Forebay Recharge Facilities

The Montebello Forebay is composed of the RHSG and San Gabriel Spreading Grounds (SGSG), with the RHSG consisting of 20 shallow (<4 m deep) infiltration basins that cover 3.1 km^2 (Fig. 1). Additional basins are created in the San Gabriel River by inflating rubber dams; however, river recharge does not occur in the concrete-lined Rio Hondo River.

The facility is operated by the Los Angeles County Department of Public Works (LACDPW) and managed by the Water

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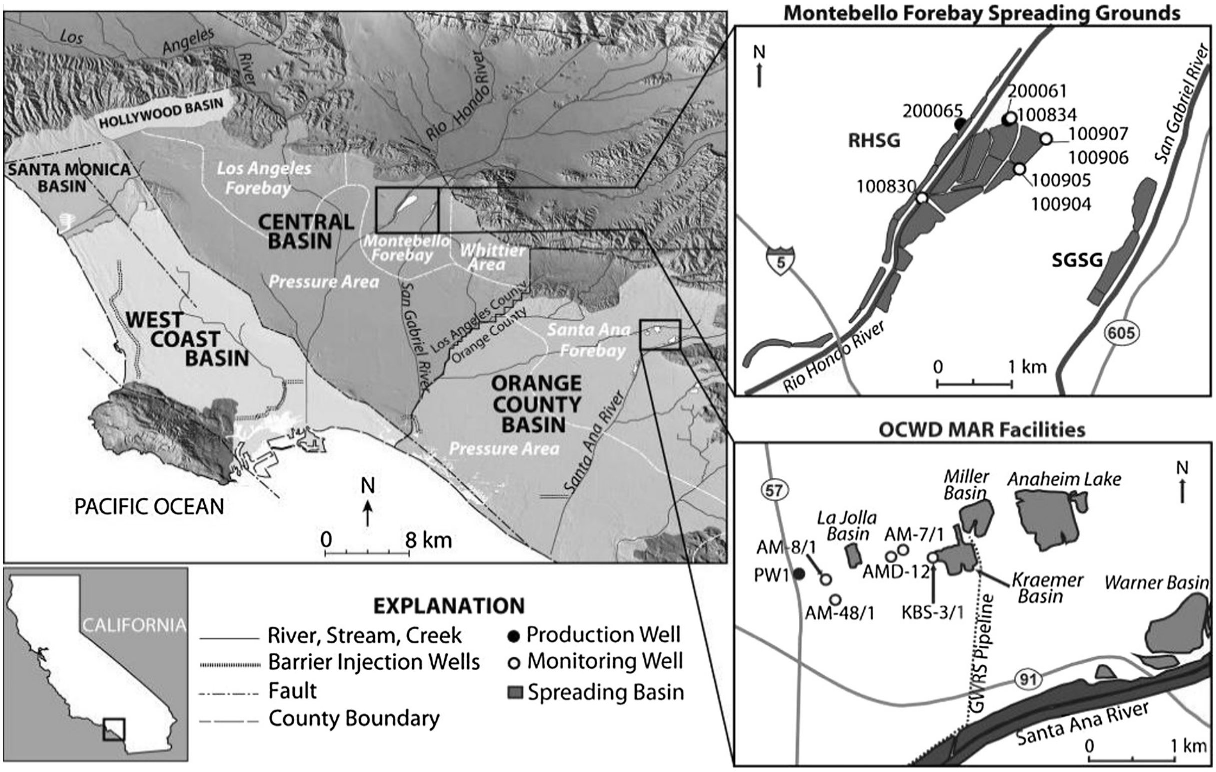

Fig. 1. Location of RHSG and OCWD MAR facilities in southern California and maps showing spreading basins and wells sampled in this study.

Replenishment District of Southern California (WRD). In 1962, the Los Angeles County Sanitation Districts (LACSD) began providing treated recycled wastewater for artificial recharge via gravity flow through river channels or pipes to the spreading basins. The 30-year average annual recharge at Montebello Forebay Spreading Grounds is 1.5×10^8 m^3 (1.2×10^5 AF), which includes local water, imported water, and recycled water (WRD, 2015).

3.2. Orange County Groundwater Recharge Facilities

In the Santa Ana Forebay, 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 operates two dozen surface spreading basins at the OCWD MAR facilities that cover 6 km^2 of wetted area and range in depth from 2 m to 50 m (Fig. 1). In 2008, OCWD began recharging recycled wastewater supplied by the OCWD Groundwater Replenishment System (GWRS) via a 21-km pipeline to Miller and Kraemer Basins. GWRS water is purified using a three-step advanced treatment process consisting of microfiltration, reverse osmosis and ultraviolet light with hydrogen peroxide disinfection. Annual recharge at the OCWD MAR facilities is 3.5×10^8 m^3 (2.8×10^5 AF) (Hutchinson, 2013), with GWRS supplying 15% of the total source water recharged by OCWD.

4. Methods

4.1. Field sampling

Surface water and groundwater from RHSG and OCWD MAR facilities were collected from 2010 to 2012 as part of routine monitoring at these sites. For each $^{35}SO_4$ sample, 20 L of water were field or laboratory filtered into polyethylene containers using a 0.45 μm high-capacity filter. At RHSG, six monitoring wells (100830, 100834, and 100904 to 100907) and two production wells (200061 and 200065) were sampled from January 2010 to February 2012 (Fig. 1). Four of the six monitoring wells in Fig. 1 occur in pairs; wells 100904 and 100906 are deep relative to 100905 and 100907 (Table 1). 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, six monitoring wells, one production well, five infiltration basins, and SAR surface flows were

Table 1
Summary of well information. The distance was measured from the shoreline of the nearest up gradient basin directly to the well.

Well ID	Well type	Distance from pond (m)	Depth to top of screen (m bgs)	Depth to bottom of screen (m bgs)
RHSG				
100830	Monitoring	43	16	28
100834	Monitoring	31	18	35
100904	Monitoring	3	24	27
100905	Monitoring	3	8	18
100906	Monitoring	5	23	26
100907	Monitoring	5	7	15
200061	Production	18	67	122
200065	Production	77	73	107
OCWD				
AM-7/1	Monitoring	130	64	69
AM-8/1	Monitoring	1250	82	87
AM-48/1	Monitoring	1250	82	91
AMD-12/1	Monitoring	525	101	107
AMD-12/2	Monitoring	525	149	158
KBS-3/1	Monitoring	<100	24	27
PW1	Production	1670	123	150

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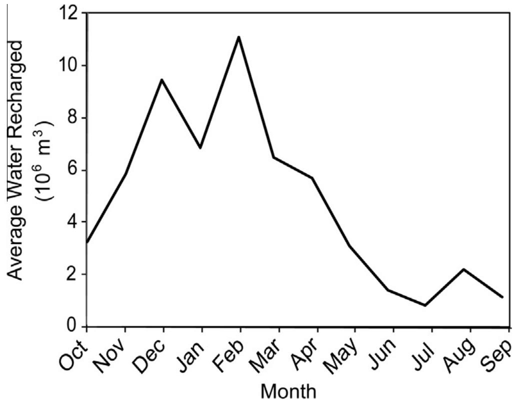

Fig. 2. Average monthly water recharged at the RHSG from water year 2008–2009 to 2012–2013. The majority (79%) of the recharge occurs from late fall to early spring (November to April) (LACDPW, 2013).

sampled from December 2010 through December 2012 (Fig. 1). Multiple depths were sampled at well AMD-12, with well AMD-12/1 screened at a shallower depth relative to AMD 12/2 (Table 1). On April 6, 2012, GWRS water was collected from two points along the transmission pipeline: immediately post-treatment at the Fountain Valley treatment facility and the discharge into Miller Basin. A rainwater sample collected on February 25, 2011 in Orange, CA, approximately 6 km south of the OCWD MAR facilities, provides a measure of the $^{35}SO_4$ activity of locally-derived precipitation.

4.2. Laboratory analysis

Recovery of $^{35}SO_4$ was achieved using a batch method technique (Urióstegui et al., 2015). Between 3 and 20 L were processed for each sample to obtain a desired 500–1500 mg of SO_4. For low-SO_4 samples containing $\leqslant$5 mg/L, a carrier (100 mg of ^{35}S-dead SO_4 as dissolved Na_2SO_4) was added to ensure effective recovery of sulfate in the sample. Samples were acidified to pH 3–4 using 5 M HCl and an anion exchange resin (Amberlite, IRA-400) was suspended in the sample for 2 h. The bound $^{35}SO_4$ was eluted from the resin with 5% NaCl aqueous solution. Samples were then passed through a column containing at least 2 g of activated carbon to remove colored impurities that could potentially interfere with liquid scintillation counting. A 0.8 M $BaCl_2{\cdot}2H_2O$ solution was added in excess to form a $BaSO_4$ precipitate that was rinsed with deionized water, dried, and suspended in Insta-Gel Plus scintillation cocktail for liquid scintillation counting at Lawrence Livermore National Laboratory in Livermore, California.

The $^{35}SO_4$ activities are reported in mBq/L. Results were yield-corrected based on the gravimetric recovery of $BaSO_4$, decay-corrected to the sample collection date, and background-corrected based on mass-dependent background rates provided in Urióstegui et al. (2015). In order to quantify $^{35}SO_4$ subsurface travel times up to 9 months (3 half-lives) for plug flow transport of recharge water to nearby wells, $^{35}SO_4$ activity in source waters should ideally be 8 times above background count rates. Samples with non detectable $^{35}SO_4$ activity are reported as less than the two sigma (2σ) counting error, which is sample specific due to varying counting parameters and sample properties. The average 1σ counting error was 1.2 mBq/L and percent relative 1σ counting error was 30%. The uncertainty reported for the calculated $^{35}SO_4$ travel times are the average propagated 1σ counting errors.

The SO_4 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, California. The OCWD MAR samples were analyzed on a Dionex ICS 3000 instrument at the OCWD Water Quality Laboratory in Fountain Valley, California.

5. Results and discussion

5.1. Rio Hondo Spreading Grounds

RHSG surface water had $^{35}SO_4$ activities of 26.9 ± 1.8 mBq/L on January 31, 2010 and 7.5 ± 1.4 mBq/L on June 02, 2010. The higher activity in January compared to June is likely due to an increase in

Table 2
Sulfate concentration, $^{35}SO_4$ activity, and subsurface travel time for groundwater collected at RHSG.

Well ID and collection date	SO_4 (mg/L)	$^{35}SO_4 \pm 1\sigma$ (mBq/L)[a]	$^{35}SO_4$ travel time ± 1σ (weeks)[b]	Well ID and collection date	SO_4 (mg/L)	$^{35}SO_4 \pm 1\sigma$ (mBq/L)[a]	$^{35}SO_4$ travel time ± 1σ (weeks)[b]
100830				*100905*			
24-Mar-2011	30	12.6 ± 1.4	14 + 3/−2	13-July-2011	36	7.1 ± 1.1	24 ± 3
24-Mar-2011[c]	30	10.7 ± 1.6	17 ± 3	23-Feb-2012	67	<2.7	>41[e]
13-Jul-2011	21	6.9 ± 0.8	25 + 3/−2	*100906*			
15-Sep-2011	30	1.7 ± 0.6	50 + 8/−5	23-May-2011	NA	4.0 ± 0.9[d]	34 + 5/−4
04-Jan-2012	30	2.8 ± 0.6	40 ± 4	13-Jul-2011	25	3.8 ± 0.8	35 ± 4
23-Feb-2012	34	6.0 ± 0.8	27 ± 3	07-Jan-2012	21	1.6 ± 0.5	51 + 7/−5
100834				23-Feb-2012	44	2.4 ± 1.0	44 + 9/−6
31-Jan-2010	21	8.9 ± 1.6[d]	20 + 4/−3	*100907*			
22-Apr-2010	106	3.3 ± 1.1[d]	38 + 8/−5	24-Mar-2011	32	7.9 ± 1.5	22 + 4/−3
23-May-2010	146	2.5 ± 1.0[d]	43 + 10/−6	24-Mar-2011[c]	32	8.3 ± 1.8	21 + 5/−4
28-Mar-2011	28	15.0 ± 1.0	10 ± 2	23-May-2011	22	4.1 ± 0.5	34 + 3/−2
13-Jul-2011	32	6.5 ± 1.0	25 ± 3	07-Jan-2012	23	0.7 ± 0.5	66 + 24/−10
04-Jan-2012	25	5.4 ± 0.6	29 ± 2	*200061*			
23-Feb-2012	70	21.1 ± 1.7	4 ± 2	29-Mar-2011	77	3.7 ± 1.7	36 + 11/−7
100904				23-Feb-2012	56	2.0 ± 1.2	47 + 16/−8
28-Mar-2011	29	12.0 ± 1.3	15 ± 2	*200065*			
28-Mar-2011[c]	29	13.0 ± 1.7	13 + 3/−2	24-Mar-2011	83	2.0 ± 2.4	44 + 32/−11
24-May-2011	22	10.3 ± 0.6	17 ± 2				
23-Feb-2012	66	2.5 ± 1.5	42 + 16/−8				

NA = Not available.
[a] Reported error is 1σ counting error.
[b] Travel times are calculated using 26.9 ± 1.8 mBq/L end-member value. Travel time error is the propagated 1σ counting error based on decay of ^{35}S.
[c] Field duplicate.
[d] No yield correction performed for samples with greater than 100% recovery.
[e] Sample with non detectable $^{35}SO_4$ activity is calculated using the 2σ counting error.

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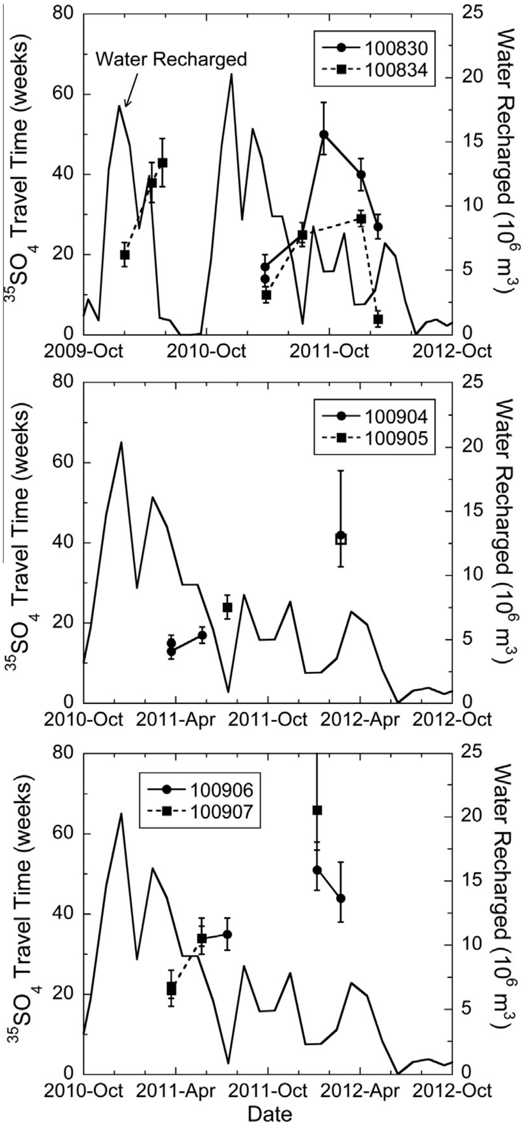

Fig. 3. Time series of $^{35}SO_4$ travel times for monitoring wells and monthly recharge at RHSG. Errors are propagated 1σ counting errors. The February 23, 2012 sample collected from well 100905 had $^{35}SO_4$ activity below detection limit, therefore the open symbol represents a minimum travel time.

Table 3
Comparison of mean $^{35}SO_4$ and SF_6 subsurface travel times at RHSG.

Well ID	Travel time (weeks)		
	Shortest $^{35}SO_4$[a]	Mean $^{35}SO_4$[b]	Mean SF_6[c]
100830	14 + 3/−2	29 ± 14	19
100834	4 ± 2	24 ± 14	18
100904	13 + 3/−2	22 ± 14	16
100905	24 ± 3	24 ± 3	13
100906	34 + 5/−4	41 ± 8	28
100907	21 + 5/−4	36 ± 21	6
200061	36 + 11/−7	42 ± 8	38
200065	44 + 32/−11	44 + 32/−11	>104

[a] Reported errors are the propagated 1σ counting error.

[b] Reported errors are the standard deviation of calculated $^{35}SO_4$ travel times to each well.

[c] SF_6 travel times are the mean travel times derived from the center of mass (COM) arrivals to wells reported by Clark (2011).

Table 4
Summary of dilution at RHSG. Measured $^{35}SO_4$ activity is the average activity measured at each well, and expected activity is the activity expected based on the mean SF_6 travel times reported in Clark (2011).

Well ID	Calculated initial source water $^{35}SO_4$ (mBq/L)[a]	Well $^{35}SO_4$ (mBq/L)		Fraction young recharge
		Measured	Expected	
100830	19.5	6.8	9.4	0.7
100834	24.4	9.0	9.9	0.9
100904	23.1	9.5	11.1	0.9
100905	14.6	7.1	13.1	0.5
100906	14.2	3.0	5.7	0.5
100907	7.4	5.3	19.3	0.3
200061	23.8	2.9	3.3	0.9
200065	NA	2.0	–[*]	–[*]

[a] Initial $^{35}SO_4$ activity for recharge source water based on the SF_6 travel times and measured $^{35}SO_4$ activity at each well assuming no dilution and plug flow.

[*] Expected activity for well could not be calculated because the mean travel time was >104 weeks.

the contribution of recent storm water runoff to the spreading basin following a series of precipitation events during winter 2009/2010. Since ^{35}S is atmospherically produced, recent storm water 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 (Fig. 2), the January 2010 $^{35}SO_4$ 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 Eq. (1). It is also important to note that the June 2010 activity is only slightly lower than the January 2010 activity after correcting for radioactive decay (10.2 ± 0.7 mBq/L vs. 7.4 ± 1.4 mBq/L).

Time series measurements of $^{35}SO_4$ activities in groundwater ranged from 0.7 ± 0.5 mBq/L to 21.1 ± 1.7 mBq/L with the exception of the sample collected from 100905 on February 23, 2012, which had a $^{35}SO_4$ activity of <2.7 mBq/L (Table 2). For the samples having measurable $^{35}SO_4$ activity, calculated subsurface travel times were between 4 ± 2 and 66 + 24/−10 weeks (Table 2, Fig. 3). Seasonal differences in $^{35}SO_4$ 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 $^{35}SO_4$ travel time for well 100830 was 14 ± 3/−2 and 17 ± 3 weeks on March 24, 2011, which increased to 25 + 3/−2 weeks on July 13, 2011. For well 100834, the three shortest $^{35}SO_4$ travel times occurred during the main recharge period of late fall to early spring for each water year: 20 + 4/−3 weeks on January 31, 2010; 10 ± 2 weeks on March 28, 2011; and 4 ± 2 weeks on February 23, 2012 (Fig. 3). The groundwater at well 100834 is approximately several months older in the late spring to early summer than groundwater sampled in the winter to early spring, which is expected under a simplified piston flow model. The steeper gradient due to enhanced recharge during periods of high recharge are likely driving shorter travel times to this well during the late fall to early spring period. Seasonal variability in the input end member may also explain the seasonal variation in groundwater travel time. The simplified assumption that the $^{35}SO_4$ activity in the surface spreading pond in January is representative of the average water recharged at the RHSG may not capture the variability in the input end-member throughout the high recharge period. To constrain the influence of seasonal variability on $^{35}SO_4$ travel times, we recommend monthly sampling of $^{35}SO_4$ in surface water and groundwater for future studies.

A deliberate tracer study using SF_6 gas (Clark, 2011) provides a valuable opportunity to evaluate the $^{35}SO_4$ method at the RHSG. The SF_6 experiment was initiated January 28, 2010 by injecting SF_6 gas into five spreading basins at the RHSG over the course of two weeks. Surface water samples were collected from a small boat during that time to empirically determine the tracer input function. After the injection period, well samples were collected

Table 5
Sulfate concentrations and $^{35}SO_4$ activities for surface water and precipitation at the OCWD MAR sites.

Sample ID and collection date	SO_4 (mg/L)	$^{35}SO_4$ ± 1σ (mBq/L)[a]			Sample ID and collection date	SO_4 (mg/L)	$^{35}SO_4$ ± 1σ (mBq/L)[a]		
		Sample	Field duplicate	Reported[c]			Sample	Field duplicate	Reported[c]
SAR					*Miller Basin*				
06-Mar-2012	154	18.9 ± 4.0	11.0 ± 3.9	15.0 ± 2.8	20-Mar-2012	130	<5.4[e]	NA	<5.4[e]
05-Jun-2012	168	<3.90[e]	NA	<3.90[e]	06-Apr-2012	1.3	2.0 ± 0.7[b]	0.8 ± 0.6[b]	1.4 ± 0.5
04-Dec-2012	89.8	5.3 ± 1.1	3.2 ± 1.0	4.3 ± 0.7	05-Jun-2012	1.3	0.4 ± 0.7	0.2 ± 0.7	0.3 ± 0.5
05-Feb-2013	137	8.3 ± 1.9	19.0 ± 2.4	13.7 ± 1.5	25-Sep-2012	0.5	1.9 ± 0.3[b]	1.7 ± 0.3[b]	1.8 ± 0.2
02-Apr-2013	133	16.2 ± 1.7	NA	16.2 ± 1.7	04-Dec-2012	0.6	0.6 ± 0.2[b]	1.0 ± 0.3[b]	0.8 ± 0.2
Warner Basin					02-Apr-2013	0.8	1.5 ± 0.2	1.2 ± 0.2	1.4 ± 0.1
20-Mar-2012	122	15.4 ± 2.1	NA	15.4 ± 2.1	04-Jun-2013	4.4	1.7 ± 0.6	2.2 ± 0.6	2.0 ± 0.4
10-Dec-2012	117	1.5 ± 1.2	6.6 ± 1.3	4.1 ± 0.9	*Kraemer Basin*				
04-Feb-2013	110	14.9 ± 1.7	20.6 ± 2.0	17.8 ± 1.3	20-Mar-2012	2.3	<2.7[e]	NA	<2.7[e]
01-Apr-2013	125	22.0 ± 1.8	NA	22.0 ± 1.8	05-Jun-2012	<0.5	0.3 ± 0.6[b]	0.5 ± 0.6[b]	0.4 ± 0.4
18-Jun-2013	142	6.9 ± 3.6	5.0 ± 4.1	6.0 ± 2.7	10-Dec-2012	72.7	<1.4[e]	NA	<1.4[e]
La Jolla Basin					05-Feb-2013	109	17.1 ± 1.7	19.4 ± 1.9	18.3 ± 1.3
10-Dec-2012	73.4	<1.5[e]	0.3 ± 0.8	0.3 ± 0.8	01-Apr-2013	188	28.4 ± 2.5	11.1 ± 2.0	19.8 ± 1.6
04-Feb-2013	117	13.6 ± 1.8	16.0 ± 2.0	14.8 ± 1.3	*Rain*[d]				
01-Apr-2013	215	16.0 ± 2.3	15.0 ± 2.3	15.5 ± 1.6	25-Feb-2011	NA	19.9 ± 1.1	21.4 ± 1.2	20.7 ± 0.8
Anaheim Lake					*GWRS TF*[f]				
01-Oct-2012	27.1	6.0 ± 0.6	5.9 ± 0.6	6.0 ± 0.4	06-Apr-2012	1.1	0.6 ± 0.1[b]	NA	0.6 ± 0.1[b]
05-Feb-2013	119	8.6 ± 1.6	18.5 ± 2.1	13.6 ± 1.3	*GWRS MB*[f]				
04-Jun-2013	160	3.9 ± 4.1	8.3 ± 4.5	6.1 ± 3.0	06-Apr-2012	0.6	0.7 ± 0.1[b]	NA	0.7 ± 0.1[b]

NA = Not available.
ND = Not detectable.

[a] Reported error is 1σ counting error.

[b] No yield correction performed for samples with greater than 100% recovery.

[c] For field duplicates samples, the reported $^{35}SO_4$ activity is the average activity for the two samples.

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

[e] For samples with non detectable $^{35}SO_4$ activity, reported activity is <2σ counting error which is sample specific.

[f] 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).

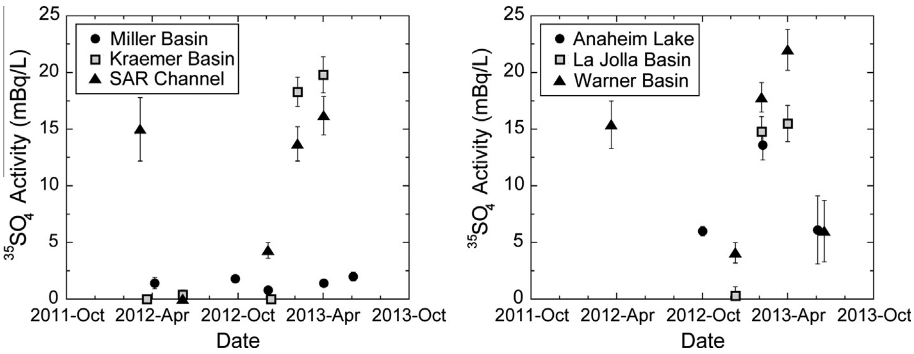

Fig. 4. $^{35}SO_4$ activities in surface water collected from OCWD MAR sites. Samples with non detectable activity are plotted as 0 mBq/L. Error bars represent 1σ counting errors.

for 1 year, and SF_6 breakthrough curves were used to determine groundwater travel times. These methods employed are described in earlier experiments at RHSG and discussed in detail in McDermott et al. (2008).

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 $^{35}SO_4$ tracer is introduced intermittently during recharge events when the source water contains a fraction of recent (<1.2 year old) runoff. Given the less conservative nature of intrinsic tracers like $^{35}SO_4$ compared to deliberate tracers like SF_6, DDW requires a multiplier of 1.5 to estimate travel time (California DDW, 2014); whereas a travel time of 6 months using deliberate tracer methods would satisfy regulations for the use of recycled water in managed aquifer recharge, a travel time of 9 months would be required using intrinsic tracers. Although different source functions for the two methods 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 mean travel times determined by the $^{35}SO_4$ method were within six weeks (1.5 months) of SF_6 travel times at four of the six monitoring wells: 100830, 100834, 100904, and 100906 (Table 3). Each experiment indicated travel times of ⩾38 weeks to production wells 200061 and 200065; however, the $^{35}SO_4$ method overestimated travel time to wells 100905 and 100907. The discrepencies between travel times may be due to an oversimplified end-member source term, mixing or dilution of young (<1.2 year old) recharge water with old (>1.2 year old) groundwater in the subsurface, or to different responses of each tracer to the

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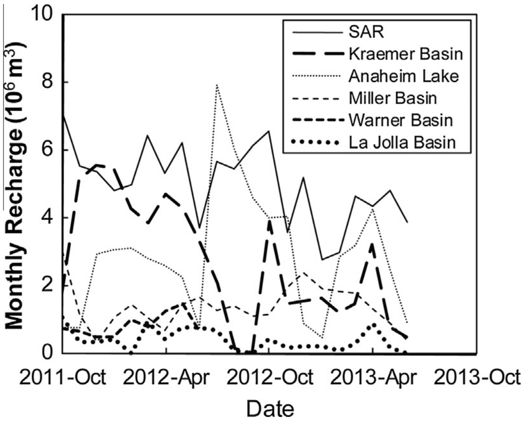

Fig. 5. Total monthly recharge from October 2011 to June 2013 for the OCWD MAR spreading basins (Hutchinson, 2013). For Warner Basin, monthly recharge was available from October 2011 to June 2012.

effects of mixing of multiple age components across screen intervals (McCallum et al., 2015). Hydrological processes such as mixing, dispersion, or dilution would appear as radioactive decay of $^{35}SO_4$, resulting in an overestimation of groundwater travel time. Determining an end member value for native groundwater in MAR systems is challenging due to the difficulty in accurately identifying native groundwater.

As a simplistic calculation of dilution, where the ambient groundwater is assumed to contain no $^{35}SO_4$ activity, the fraction of young recharge water at each well was estimated by calculating the ratio between the measured mean $^{35}SO_4$ activity and expected activity based on the mean SF_6 travel times. By decay-correcting the intial source water $^{35}SO_4$ activity of 26.9 mBq/L to the groundwater activity that would be expected based on the mean SF_6 travel times to each well, the fraction of groundwater that initially had an activity of 26.9 mBq/L can be calculated. This fraction of recent recharge ranged from 0.3 to 0.9 with four of the seven wells having young recharge fractions $\geqslant 0.7$ (Table 4). These results suggests dilution of young recharge water with older groundwater is between 10% and 70% for wells sampled at the RHSG, which results in an overestimation of $^{35}SO_4$ travel times under this simplified scenario.

The discrepancy between the deliberate and intrinsic tracer travel times could also result from assuming that the source-water activity of $^{35}SO_4$ was constant at 26.9 mBq/L during the experiment when it was actually variable. The initial source water activity would need to be between 7.4 and 24.4 mBq/L (Table 4), which is reasonable based on the activities measured in source waters at two study sites. A more rigourous analysis of dilution factors would be necessary to constrain dilution and mixing of different ages.

5.2. Orange County Groundwater Recharge Facilities

At the OCWD MAR site, $^{35}SO_4$ activity of surface waters from five infiltration basins and the SAR channel was 0.2 ± 0.7 to 28.4 ± 2.5 mBq/L, with the exception of five of the total 53 samples that had non detectable $^{35}SO_4$ activity (Table 5, Fig. 4). Low $^{35}SO_4$ activity in post-treatment GWRS water (0.6 ± 0.1 and 0.7 ± 0.1 mBq/L) indicates that a recent (<1.2 year old) water

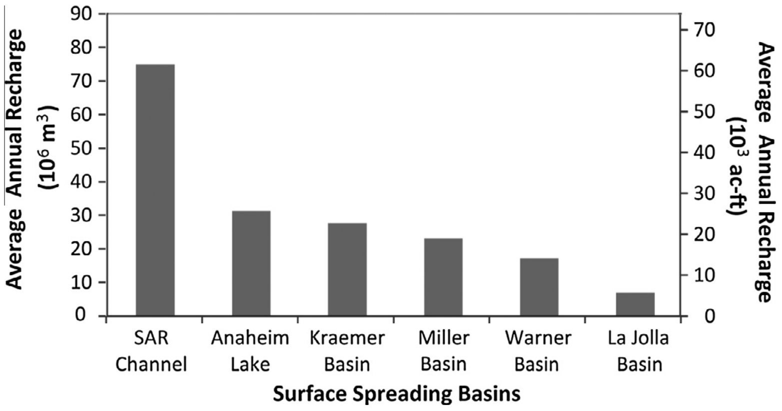

Fig. 6. Average annual recharge for selected OCWD MAR spreading ponds. Reported values for SAR Channel, Anaheim Lake, Kraemer, and Miller are the 5-year average for July to June, 2007–2008 to 2011–2012. Since La Jolla Basin was put into service in December 2007, the reported value for this basin is the 4-year average for July to June, 2008–2009 to 2011–2012 (Hutchinson, 2013). GWRS water is delivered to Miller Basin and Kraemer Basin.

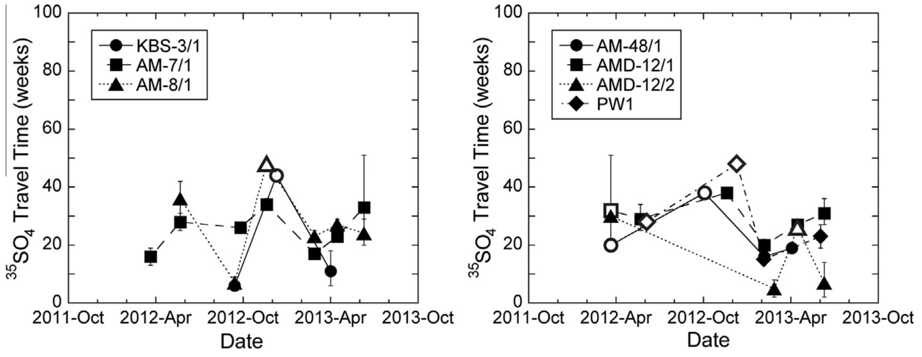

Fig. 7. $^{35}SO_4$ groundwater travel times from Kraemer Basin to down gradient wells. Open symbols represent sampling events that were below detection.

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Table 6
Summary of sulfate concentrations, $^{35}SO_4$ activities, and subsurface travel times for groundwater at the OCWD MAR sites.

Well ID and collection date	SO_4 (mg/L)	$^{35}SO_4 \pm 1\sigma$ (mBq/L)[a]			$^{35}SO_4$ travel time ± 1σ (weeks)[d]
		Sample	Field duplicate	Reported[c]	
KBS-3/1					
13-Sep-2012	2.3	7.3 ± 0.7[b]	NA	7.3 ± 0.7[b]	6 ± 2
10-Dec-2012	99.5	<0.9[e]	NA	<0.9[e]	>44
05-Feb-2013	112	15.9 ± 1.8	11.3 ± 1.8	13.6 ± 1.3	–[*]
02-Apr-2013	177	5.4 ± 1.8	NA	5.4 ± 1.8	11 + 7/−5
AM-7/1					
21-Mar-2012	6.4	4.2 ± 0.6	NA	4.2 ± 0.6	16 ± 3
22-May-2012	3.1	2.0 ± 0.2[b]	2.2 ± 0.6	2.1 ± 0.3	28 ± 3
25-Sep-2012	4.3	2.5 ± 0.3	2.3 ± 0.3	2.4 ± 0.2	26 ± 2
19-Nov-2012	2.4	1.4 ± 0.2[b]	1.6 ± 0.2[b]	1.5 ± 0.1	34 ± 2
27-Feb-2013	17.3	4.5 ± 0.4	3.4 ± 0.5	4.0 ± 0.3	17 ± 2
16-Apr-2013	46.3	3.1 ± 0.4	2.4 ± 0.5	2.8 ± 0.3	23 ± 2
11-Jun-2013	53	1.7 ± 1.4	1.5 ± 1.4	1.6 ± 1.0	33 + 18/−9
AM-8/1					
22-May-2012	58.9	1.7 ± 0.6	1.0 ± 0.6	1.4 ± 0.4	36 + 6/−5
13-Sep-2012	34.2	7.0 ± 0.7	NA	7.0 ± 0.7	7 ± 2
19-Nov-2012	26.1	<0.7[e]	<0.7[e]	<0.7	>48
27-Feb-2013	15.7	3.0 ± 0.4	2.8 ± 0.3	2.9 ± 0.3	23 ± 2
16-Apr-2013	20.7	2.4 ± 0.3	2.1 ± 0.3	2.3 ± 0.2	27 ± 2
11-Jun-2013	21	2.6 ± 0.8	2.5 ± 0.8	2.6 ± 0.6	24 + 5/−4
AM-48/1					
21-Mar-2012	86.3	<3.4[e]	NA	<3.4	>20
03-Oct-2012	36.8	<1.2[e]	<1.2[e]	<1.2	>38
05-Feb-2013	25.2	3.9 ± 0.5	4.2 ± 0.6	4.1 ± 0.4	16 ± 2
04-Apr-2013	44.3	2.7 ± 0.4	4.3 ± 0.6	3.5 ± 0.4	19 ± 2
AMD-12/1					
21-Mar-2012	36.7	<1.8[e]	<1.8[e]	<1.8	>32
22-May-2012	51.4	2.6 ± 0.6	NA	2.6 ± 0.6	29 + 5/−4
19-Nov-2012	52.5	<1.2[e]	<1.2[e]	<1.2	>38
05-Feb-2013	17.9	2.9 ± 0.3	3.8 ± 0.5	3.4 ± 0.3	20 ± 2
16-Apr-2013	9.1	1.7 ± 0.2	2.6 ± 0.3	2.2 ± 0.2	27 ± 2
11-Jun-2013	4	1.6 ± 0.5	1.9 ± 0.6	1.8 ± 0.4	31 + 5/−4
AMD-12/2					
21-Mar-2012	74	2.5 ± 2.1	1.2 ± 1.6	1.9 ± 1.3	30 + 21/−9
26-Feb-2013	136	4.8 ± 1.6	10.3 ± 1.8	7.6 ± 1.2	5 ± 3
16-Apr-2013	142	<2.4[e]	NA	<2.4	>26
11-June-2013	108	3.2 ± 2.7	10.1 ± 3.2	6.7 ± 2.1	7 + 7/−5
PW1					
04-Jun-2012	83.7	<2.1[e]	NA	<2.1	>28
10-Dec-2012	29.9	<0.7[e]	<0.7[e]	<0.7	>48
04-Feb-2013	27.8	4.3 ± 0.5	4.4 ± 0.6	4.4 ± 0.4	15 ± 2
03-Jun-2013	26	2.7 ± 0.9	2.8 ± 0.8[b]	2.8 ± 0.6	23 + 5/−4

NA = Not available.
ND = Not detectable.
[a] Reported error is 1σ counting error.
[b] No yield correction performed for samples with greater than 100% recovery.
[c] For field duplicates, the reported $^{35}SO_4$ activity is the average activity for the two samples.
[d] Travel times calculated assuming 10.1 ± 0.6 mBq/L as the $^{35}SO_4$ input end-member. Reported error is 1σ counting error based on the decay of ^{35}S.
[e] For samples with non detectable $^{35}SO_4$ activity, the reported activity is the <2σ counting error which is sample specific.
[*] Travel time undetermined due to a higher $^{35}SO_4$ activity for groundwater relative to the source water end-member.

component is minimal in GWRS water. A trend of low $^{35}SO_4$ activity was also observed for Miller and Kraemer Basins during the months in which the basins were receiving mainly GWRS inflow. For example, inflow to Kraemer in March 2012 and June 2012 was from GWRS water (Hutchinson, 2013), and $^{35}SO_4$ activity was non detectable in March and 0.4 ± 0.4 mBq/L in June. In February 2013, the inflow to Kraemer Basin consisted entirely of SAR water, which resulted in a significantly higher $^{35}SO_4$ activity of 18.3 ± 1.3 mBq/L indicating a larger fraction of recent (<1.2 year old) water in SAR water compared to GWRS water.

The $^{35}SO_4$ activity in local precipitation near the OCWD site was 20.7 ± 0.8 mBq/L in February 2011, which is lower than the activity in the January 2010 recharge source waters at RHSG. Although direct precipitation is expected to have the highest $^{35}SO_4$ activity due to $^{35}SO_4$ being produced in the atmosphere, seasonal and annual variation in the $^{35}SO_4$ activity in precipitation have been observed for central Sierra Nevada basins (Singleton et al., 2014). Variability in $^{35}SO_4$ deposition in precipitation may explain the lower activity in the OCWD precipitation relative to the RHSG water.

Compared to the high $^{35}SO_4$ activity observed in local precipitation, the lower $^{35}SO_4$ activity in the majority of OCWD MAR surface waters implies dilution of locally derived storm runoff with ^{35}S-dead water. The source of ^{35}S-dead water may be imported water and/or storage of recent runoff in upstream surface reservoirs such as the Prado Wetlands 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, 2013). Moreover, local average rainfall was 20.8 cm for FY 2011–2012 and 14.7 cm in in FY 2012–2013, which was more than 40% below the 50-yr average of 36.6 cm (Hutchinson, 2013; Hutchinson, pers.

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Table 7
Comparison of groundwater travel times at OCWD MAR sites determined by $^{35}SO_4$ and SF_6 tracers.

Well ID	Travel time (weeks)			
	Shortest $^{35}SO_4$[a]	Mean $^{35}SO_4$[b]	Mean SF_6[c]	Mean Xe[c]
AM-7/1	16 ± 3	25 ± 7	25	15.3
AM-8/1	7 ± 2	23 ± 11	>37[*]	38.3
AMD-12/1	20 ± 2	27 ± 5	31	NA
AMD-12/2	5 ± 3	14 ± 14	NA	NA
AM-48/1	16 ± 2	18 ± 2	26	NA
KBS-3/1	6 ± 2	9 ± 4	6	–[*]
PW1	15 ± 2	19 ± 6	NA	NA

NA = Not available.

[a] Reported error is the propagated 1σ counting error.

[b] Reported errors are the standard deviation of calculated $^{35}SO_4$ travel times to each well.

[c] SF_6 and Xe travel times are the mean travel times to wells reported by Clark et al. (2014).

[*] Incomplete breakthrough; mean travel time is a minimum or could not be calculated.

Table 8
Summary of dilution at OCWD MAR site. Measured $^{35}SO_4$ activity is the average activity measured at each well, and expected activity is the activity expected based on the mean SF_6 travel times reported in Clark et al. (2014).

Well ID	Calculated initial source water $^{35}SO_4$ (mBq/L)[a]	$^{35}SO_4$ (mBq/L)		Fraction young recharge
		Measured	Expected	
AM-7/1	10.0	2.5	2.5	1.0
AM-8/1	21.8	2.8	1.3	1.0[*]
AMD-12/1	2.2	0.4	1.8	0.2
AMD-12/2	NA	5.4	NA	NA
AM-48/1	16.1	3.8	2.4	1.0[*]
KBS-3/1	13.9	10.0	7.2	1.0[*]
PW1	NA	3.6	NA	NA

NA = Not available.

[a] Initial $^{35}SO_4$ activity for recharge source water based on the SF_6 travel times and measured $^{35}SO_4$ activity at each well assuming no dilution and plug flow.

[*] For wells with calculated fraction of young recharge >1.0, a fraction of 1.0 is reported.

comm.). During these relatively dry water years, the low inputs of storm flow/local water combined with high inputs of imported water and SAR base flow resulted in lower $^{35}SO_4$ activity in OCWD MAR surface waters relative to local precipitation.

The $^{35}SO_4$ activity in OCWD MAR surface water varies significantly by season (Fig. 4) due to seasonal differences in recharge source water, with the exception of La Jolla Basin which had the lowest volume recharged during the study period (Fig. 5). Higher $^{35}SO_4$ activity was generally observed in the early spring, likely due to a larger component or recent storm runoff in the spring months. For example, $^{35}SO_4$ activity in Warner Basin increased from 4.1 ± 0.9 mBq/L on December 10, 2012 to more than 15 mBq/L in February and April 2013 (Table 5, Fig. 4).

Groundwater contours suggest that the general groundwater flow direction for the study area is in the west to southwest direction (Clark et al., 2004, 2014), with Kraemer Basin being the nearest up-gradient spreading basin for monitoring wells AM-7/1, AM-12/1, AM-12/2, and KBS-3/1, and La Jolla Basin being the nearest up-gradient basin for wells AM-8/1, AM-48/1, and PW1. Deliberate tracer experiments conducted by Clark et al. (2004, 2014) demonstrated that all of the wells sampled in this study were hydraulically connected to Kraemer Basin. Although La Jolla Basin was put into operation in December 2007, the west–southwest hydraulic gradient from Kraemer Basin did not change significantly between 1998 and 2008. The average annual recharge at La Jolla Basin is 75% less than the volume recharged at Kraemer Basin (Fig. 6: $7.0 \times 10^6\ m^3$ for La Jolla Basin and $2.8 \times 10^7\ m^3$ for Kraemer Basin) providing further evidence that Kraemer Basin is the nearest up gradient input source for the wells samples in this study.

Based on the strong hydrologic connection between Kraemer Basin and the wells sampled for $^{35}SO_4$ activity, the average Kraemer Basin $^{35}SO_4$ activity of 10.1 ± 0.6 mBq/L was assumed to be the input end-member. The two surface water samples that were below detection were incoporated into the end-member value by assuming that the 2σ counting error was the $^{35}SO_4$ activity for each sampling event. Based on the average end-member value of 10.1 ± 0.6 mBq/L, $^{35}SO_4$ groundwater travel times at OCWD were between 5 ± 3 and >48 weeks (Table 6, Fig. 7). A travel time could not be calculated for KBS-3/1 on February 05, 2013 because the groundwater $^{35}SO_4$ activity was larger than the input end-member, showing the need for more work in characterizing the source water activity.

Time series measurements of groundwater travel times were seasonally variable, which may be due to high variability in the source water end-member. For example, the $^{35}SO_4$ travel times for well AM-8/1 were between 7 ± 2 and >48 weeks based on the input end-member of 10.1 ± 0.6 mBq/L; however, assuming an end-member value of 19.8 ± 1.6 mBq/L, which was the highest $^{35}SO_4$ activity observed for Kraemer Basin, the range of $^{35}SO_4$ travel times for well AM-8/1 increases to between 19 ± 2 and >59 weeks. The increase in travel time of approximately 12 weeks (3 months) may explain some of the variability observed for the time series measurements of groundwater travel times at the OCWD MAR site and the oversimplified plug flow model. These results highlight the need for careful characterization of the input endmember at MAR sites where $^{35}SO_4$ activity in recharge source water varies significantly by season.

The mean $^{35}SO_4$ groundwater travel times at OCWD were compared to those determined by previous deliberate tracer experiments that used SF_6 (2008) and ^{136}Xe (1998). In calculating the mean $^{35}SO_4$ travel time to each well, only the $^{35}SO_4$ activities that were above detection were considered. The mean $^{35}SO_4$ travel times were within six weeks of the mean SF_6 travel times for all five wells sampled in both experiments (Table 7). Similar to the travel time comparison for the RHSG experiment, discrepencies in the comparison of $^{35}SO_4$ and SF_6 travel times may be due to an oversimplification of the end-member, dilution and/or mixing of groundwater ages, or differences in hydrologic conditions for the intrinsic and deliberate tracer experiments employed at the OCWD MAR site. Using the same approach for calculating the fraction of young recharge described for the RHSG, the calculated young fraction for OCWD wells was 1.0 with the exception of a young fraction of 0.2 calculated for well AMD-12/1 (Table 8).

Alternatively, the small discrepancy between the deliberate and intrinsic tracer travel times may result from assuming that the source-water activity of $^{35}SO_4$ was constant during the experiment when it was actually variable. The calculated initial source water $^{35}SO_4$ activities under this scenario would have to be between 2.2 and 21.8 mBq/L, which is within the range observed for OCWD source waters. Under this alternative scenario, the dilution of young recharge water with old groundwater may be minimal for the majority of the wells with the exception of well AMD-12/1.

6. Conclusions

This study successfully measured $^{35}SO_4$ in MAR waters, which has not been previously attempted since it was not possible to detect $^{35}SO_4$ in these high SO_4 systems prior to the development of a new analytical method (Urióstegui et al., 2015). A key finding of this study was the high seasonal variability in $^{35}SO_4$ activity in recharge source waters and groundwaters. Seasonal differences in recharge and well production can significantly affect $^{35}SO_4$ activity in MAR waters, therefore we recommend determination of time

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series of source waters and groundwater with a frequency of at least 1 month.

At the RHSG and OCWD MAR sites, $^{35}SO_4$ groundwater travel times were similar to those determined by earlier deliberate tracer experiments when considering the difference in input functions of the two approaches such as sampling dates and varying hydrologic conditions. However, some wells at the RHSG had travel times that were significantly different, which is possibly due to an oversimplified input end-member activity and plug-flow model interpreation. These results highlight the need for constraining the input-end member to accurately quantify $^{35}SO_4$ groundwater travel times and also determining robust methods for estimating dilution of recently recharged groundwater.

Dilution of young recharge water with old groundwater or mixing of groundwater of different ages complicates the interpretation of $^{35}SO_4$ travel times. Given the difficulty in accurately identifying an end-member for native groundwater at the RHSG and OCWD MAR sites, a simplistic mixing calculation was performed to estimate dilution in the groundwater basins. The fractions of young recharge of 0.2–1.0 indicate that dilution may significantly affect $^{35}SO_4$ travel times for some wells. Mixing across screened intervals in addition to a well-constrained end-member is necessary to successful apply $^{35}SO_4$ as a tracer for regulatory compliance.

$^{35}SO_4$ is currently underutilized as an intrinsic tracer technique in groundwater studies. This work demonstrates that it can be a valuable tool in investigating the subsurface travel times on less than one year timescales at MAR sites. In future studies, the effect of varying recharge and pumping conditions on groundwater travel time can be quantified more easily by the $^{35}SO_4$ method than by conducting multiple deliberate tracer experiments. For many MAR sites, the method would be a valuable survey tool to indicate the presence/absence of >1.2 year old water, with groundwater from wells lacking $^{35}SO_4$ despite high activities in recharge source water indicating that the water must be older than 1.2 years.

Acknowledgements

This work was supported by the WateReuse Research Foundation (WRRF-09-11) in cooperation with the Water Replenishment District of Southern California, the Orange County Water District, the State of California Groundwater Ambient Monitoring & Assessment (GAMA) Special Studies Program, and the Lawrence Graduate Scholarship Program at the Lawrence Livermore National Laboratory.

We thank Theodore Johnson, Peter Piestrzeniewicz, and Benny Chong from WRD for their assistance at the Montebello Forebay Spreading Grounds. We would also like to thank Jason Dadakis, Roy Herndon, Nira Yamchika, Adam Hutchinson, Greg Woodside, Patrick Versluis, and Mike Wehner from OCWD for their encouragement and project support. Alex Cruz and Bronson Cabalitasan from UCSB assisted in ^{35}S analyses. The original idea for using ^{35}S as an intrinsic tracer near MAR came from a conservation between JFC and Dr. Andrew L. Herczeg (CSIRO, Land and Water, Adelaide, South Australia) while both were visiting the Water Resources Programme, International Atomic Energy Agency. Contributions by Stephanie Urióstegui, Richard Bibby, and Brad Esser were performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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Please cite this article in press as: Urióstegui, S.H., et al. Quantifying groundwater travel time near managed recharge operations using ^{35}S as an intrinsic tracer. J. Hydrol. (2016), http://dx.doi.org/10.1016/j.jhydrol.2016.04.036