TRACING ARTIFICIALLY RECHARGED GROUNDWATER USING WATER AND CARBON ISOTOPES

Junior G Mazariegos • Jennifer C Walker[*] • Xiaomei Xu • Claudia I Czimczik

Department of Earth System Science & W. M. Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory, University of California, Irvine, CA, 92697-3100, USA.

ABSTRACT. We conducted an isotopic analysis of groundwater in Orange County, California, USA, around the Talbert Seawater Injection Barrier to determine if recycled water, used to artificially recharge local aquifers, carries a unique isotopic signature that can be used as a tracer. From September 2014 to April 2015, we collected groundwater from six privately owned wells within the coastal groundwater basin, along with various surface waters. All water samples were analyzed for their stable isotopic composition ($\delta^{18}O$, δD), the $\delta^{13}C$ and ^{14}C signature of the dissolved inorganic carbon (DIC) pool, DIC concentration, pH, and salinity. The DIC of groundwater mixing with recycled water is enriched in ^{14}C above natural background levels, with varying signal strength through time, depleted in $\delta^{13}C$, and low in DIC concentration. Water isotopes further suggest that recycled water is a mixture of Colorado River water and regional groundwater. In contrast, groundwater found further away from the injection barrier has carbon and water isotope composition consistent with regional groundwater and Santa Ana River water. Our findings imply that recycled water injected through the Talbert Barrier is isotopically unique, and that ^{14}C enrichment may be used as an intrinsic tracer of artificial recharge within the basin.

KEYWORDS: aquifer, recycled water, replenished water, radiocarbon.

INTRODUCTION

California has long faced water supply challenges (Hundley 2001). Currently, the state is in the midst of an unprecedented water crisis caused by recent environmental changes in the Bay-Delta ecosystem, severe drought, and unsustainable groundwater withdrawal to supply agriculture and a rising population (Frederiksen 1996; Famiglietti 2014). As a result, many water districts are incorporating artificial recharge and the use of treated wastewater ("recycled water") into their management plans (Gleick 2000). Recycled water gives water agencies a reliable local water source that can be used to increase artificial recharge, while reducing cost and dependence on imported water supplies.

Artificial recharge is an engineered process that uses surface infiltration or direct injection to replenish groundwater supplies, allowing excess water to be stored in an aquifer for future use. Typically, surface infiltration is enhanced through the use of percolation ponds, diversion basins, ditches, dry streambeds, and other retention structures. These features increase the amount of time surface water is in contact with the unsaturated zone, allowing for increased infiltration. However, in areas where the surface is not permeable enough for percolation, or withdrawal far exceeds recharge, it may be necessary to use direct injection, i.e. using injection wells to directly pump water into the aquifer. This has been a common replenishment strategy for management agencies combating seawater intrusion (Hudson et al. 1995; Johnson and Whitaker 2003; Herndon and Markus 2014).

Understanding the spatial and temporal mixing of this water within the aquifer system is difficult due to the complexity of the underground geological setting. Therefore, the use of tracers is crucial in determining the heterogeneity of hydraulic conductivity, which is needed for predicting residence times and mixing of injected water. Traditional pulse-and-chase methods require adding a tracer to a recharge supply, followed by close monitoring of nearby wells to detect the tracer. While this strategy is effective, it requires adding chemicals such as ionized

*Corresponding author. Email: jclehman@uci.edu.

substances (e.g. common salt), organic dyes, gases (^{133}Xe and [85]Kr), or fluorocarbons (CCl$_3$F and CCl$_2$F) to aquifers that often serve as drinking water supply (Davis et al. 1980; Clark et al. 2014). This requires careful planning and permitting.

Using the *intrinsic* isotopic signatures of the water itself, and its constituents, allows for an alternative tracer method that does not require the addition of artificial substances. In this study, we analyzed the stable isotope composition (^{18}O/^{16}O, ^{2}H/^{1}H) of groundwater, the stable and radioactive isotope compositions (^{13}C/^{12}C and ^{14}C/^{12}C, respectively) of dissolved inorganic carbon (DIC), and chemical properties (DIC concentration, pH, and salinity) to trace artificial recharge with the ultimate goal of improving the understanding of the recharge dynamics of an aquifer experiencing both natural and artificial recharge.

Hydrological Setting

Our study was conducted in Orange County, California, a densely populated urbanized region with a Mediterranean climate (Figure 1a). The Orange County Groundwater Basin (basin) consists of a dynamic coastal aquifer system that covers a surface area of approximately 906 km^2 with the capacity to hold about 81 km^3 (66 million acre feet) of fresh groundwater (OCWD 2015). However, the local groundwater agency manages the basin within an operating range of approximately 0.62 km^3 (500,000 acre feet) of usable storage, which supplies about 70% of the local water supply (OCWD 2015). The basin is vertically subdivided into three aquifer systems: the Shallow, Principal, and Deep aquifers. Geographically, the basin is partitioned into two regions: the Forebay Area and the Pressure Area (Figure 1a).

The Forebay Area is largely composed of unconfined aquifers compromised of relatively coarse-grained unconsolidated sediments (sands and gravels) that allow for surficial groundwater recharge through percolation basins and within the Santa Ana River (SAR) channel. Forebay recharge sources include SAR base and storm flows, imported water, and purified recycled water from Orange County Water District's Groundwater Replenishment System (GWRS) (Santa Ana River Watermaster 2014). In contrast, the Pressure Area is a region in which the aquifers are less connected to surface waters due to the presence of intervening aquitards comprised of fine-grained sediments (silts and clays), resulting in a more confined aquifer condition (Figure 1b). The coastal edge of the Pressure Area is bounded by the Newport–Inglewood Fault Zone, which acts as a groundwater barrier protecting the Principal and Deep aquifer systems from seawater intrusion. However, due to the meandering of the ancestral SAR over the last 40,000 yr, a 4-km-wide geological gap was eroded and permeable sediments were subsequently deposited, forming a low lying region known as the Talbert Gap. Portions of the Talbert Gap are connected to the Pacific Ocean and also merged with the uppermost Principal aquifer zones (OCWD 2015).

As a result of agricultural pumping during the first half of the 20th century, and municipal pumping due to urbanization and population increase in the second half, declining groundwater levels led to seawater intrusion into the Shallow aquifer system (Johnson and Whitaker 2003). In response, the local groundwater management agency built a seawater intrusion barrier (Talbert Seawater Injection Barrier, Figure 1) in 1975. The barrier comprises a series of injection wells drilled along the Talbert Gap that pump water directly into the Shallow and Principal aquifer systems, maintaining a hydraulic mound or pressure ridge that prevents seawater intrusion (OCWD 2015).
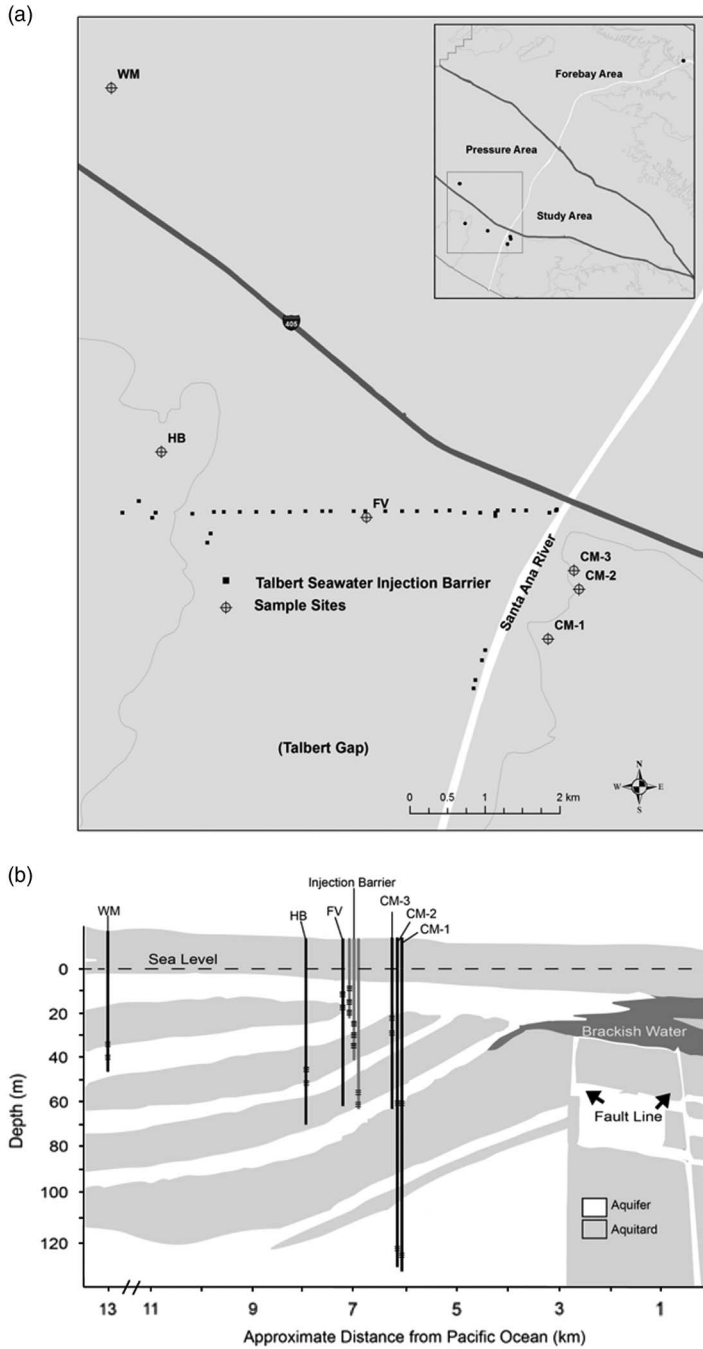
(a)

(b)

Figure 1 (a) Sampling sites (open circles) in Orange County, California. Filled squares indicate the location of the Talbert Injection Barrier wells. The shaded lines delineate topographical formations. (b) Cross-section view of the aquifer system in the Pressure Area, modified from OCWD (2014). The hash marks on the wells indicate the depth of the well screenings (i.e. the depth interval from which the wells draw groundwater).

The source water for the injection barrier has varied over the years. In the past, a mixture of local groundwater, recycled water, and imported waters (from both the Colorado River Project and California State Water Project) were used in a mixed blend (OCWD 2015). However, since December 2009, injection water has consisted of nearly 100% recycled water. Currently, about 0.04 km^3 (32,950 acre feet) of high-quality recycled water is allocated to the injection barrier annually (OCWD 2014). This recycled water is thoroughly treated wastewater that, after secondary treatment, has undergone three additional advanced treatment processes: microfiltration, reverse osmosis, and ultraviolet light with hydrogen peroxide addition (OCWD 2014). The source of water to the wastewater treatment system is mainly from the local drinking water supply, which is a mixture of the local groundwater and imported water.

Although investigations on water and carbon isotopes had been carried out in this groundwater aquifer system before (Hudson et al. 1995; Davisson et al. 1996, 1998, 1999), no systematic studies were conducted in the last 20 yr. However, many changes have occurred, such as the construction of a new and advanced recycled water treatment plant (operational since 2008) that utilizes improved treatment processes and has much higher treatment capacity, as well as changes in water sources and proportions for injection. Here, we revisit wells at different distances from the injection barrier, and show that measuring water isotopes together with both the stable and the long-lived radioactive carbon (with a half-life of 5730 yr) isotopes provides a powerful means to track recycled water through the aquifer system over decades.

MATERIALS AND METHODS

Water Sampling

Groundwater samples ($n = 50$) were collected every 2 weeks from six routinely producing, privately owned wells from September 2014 to April 2015 in the basin's Pressure Area. Surface water samples were collected from recharge sources: SAR ($n = 2$) and the California State Water Project (SWP) ($n = 1$). Additionally, municipal tap water ($n = 1$) and local precipitation ($n = 1$) were also collected.

All water samples for carbon (^{14}C, δ^{13}C) and water (δ^{18}O, δD) isotope analyses were collected in 60-mL clear borosilicate glass vials with 0.125 silicone/PTFE and black Viton septa (Sigma-Aldrich, St. Louis, MO, USA). To avoid contamination, vials and septa were acid-washed in a 10% HCl solution, rinsed three times with 18.2 MΩcm (Milli-Q) water, and vials were then baked at 550°C for 2 hr. During sampling, all vials were filled and allowed to overflow three times their volume. Vials were filled, capped with no headspace, and analyzed within 1 week to minimize the exchange of DIC with atmospheric CO$_2$. The following is sampling information for specific wells/locations:

- At production wells (WM, FV, and CM-1 to -3), groundwater was collected from wellhead spigots. To flush possibly stagnant water, each well was allowed to run through the open spigot uninterrupted for 5 min prior to collection.

- At sampling site HB, groundwater samples were collected in two different locations due to well site access issues. At the start of the study, samples were collected at an irrigation spigot supplied by a tank that is fed by the well. Later, water samples were taken directly from the well spigot. These data are reported as averages for the site.

- Surface water samples from the SAR were collected near Featherly Regional Park, in Yorba Linda. In addition, the SWP was sampled in Palmdale on an exposed part of the aqueduct. All surface water samples were sampled using a 10-L bucket with a piece of

silicone tubing permanently attached to the base. The bucket was lowered into the water and rinsed three times before sample vials were filled through the silicone tubing.

- Local municipal tap water was collected in a residence within the study area. In addition, local precipitation was captured on a balcony of a building at UC Irvine.

pH and Salinity Measurements

The pH was measured in the laboratory using 40 mL of water with a portable pH meter (Eco Tester pH 2, Oakton, Vernon Hills, IL, USA). Salinity was measured using a hand-held salinity refractometer with automatic temperature correction (RHS-10ATC, Westover Scientific, Bothell, WA, USA).

Water Stable Isotope Measurements

$\delta^{18}O$ and δD were analyzed using 1-mL aliquots of water on a High Temperature Conversion Elemental Analyzer (TC/EA) coupled to an isotope ratio mass spectrometer (IRMS, Delta Plus XL, Thermo Fisher Scientific, Waltham, MA, USA). All measurements were performed at the Center for Isotope Tracers in Earth Science (CITIES) at UC Irvine using a series of NIST certified and internal lab calibrated standards. The δ notation is a per mill (‰) expression relative to the V-SMOW standard. The analytical precision of the analysis is 0.1‰ for $\delta^{18}O$ and 1‰ for δD, based on long-term measurements of secondary standards.

Dissolved Inorganic Carbon (DIC) Extraction and Carbon Isotope Measurements

For ^{14}C and $\delta^{13}C$ analyses, the DIC of each water sample was extracted using a rapid headspace-extraction approach (Gao et al. 2014). The method was modified by injecting 20 mL of ultra-high-purity (UHP) N_2 gas into the vials through the septa using a gas-tight syringe while the vial was inverted. Simultaneously, a second needle was pierced into the septa. The pressure from the injection of N_2 gas pushed 20 mL of water out of the vial through the second needle, creating the headspace required for the extraction. Samples were acidified with 0.5 mL of 85% H_3PO_4 and heated at 75°C for 2 hr. Afterwards, the headspace volume (about 23 mL) was extracted using an air-tight 60-mL syringe and injected into a vacuum line through a septa port. The CO_2 was cryogenically purified and quantified manometrically, and then converted to graphite via closed-tube zinc reduction (Xu et al. 2007). All ^{14}C measurements were performed alongside processing standards and blanks at the W M Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory (KCCAMS). ^{14}C results are expressed as percent modern carbon (pMC) relative to the primary ^{14}C oxalic acid I standard (HOxI), following Stuiver and Polach (1977). The analytical precision is 2–3‰ for modern samples, based on long-term measurements of secondary standards.

For $\delta^{13}C$ analysis, the purified DIC-CO_2 was subsampled on the vacuum line, injected into a UHP He-filled Exetainer® (Labco, Lempeter, UK) vial using a gas-tight syringe, and analyzed via a Gas Bench II linked to an IRMS (Delta plus XP, Thermo Fisher Scientific). The fractionation introduced by the headspace extraction method is relatively small ($< \sim 0.2‰$, Gao et al. 2014). The δ notation is a per mill (‰) expression relative to the V-PDB standard. The precision is ~0.2‰ based on long-term measurements of secondary standards.

DIC concentration was calculated from the CO_2 extraction yield on the vacuum line, headspace extraction efficiency (Gao et al. 2014), and Henry's law (CO_2 solubility in water) (Diamond and Akinfiev 2003).

RESULTS AND DISCUSSION

pH and Salinity

The pH of all groundwater samples ranged from 7.0 to 8.5, whereas that of surface waters (SAR & SWP) ranged from 7.9 to 8.8 (Table 1). On average, groundwater samples had a pH of 7.8 ± 0.4, which is consistent with values reported by an earlier study (Hudson et al. 1995). All groundwater samples (as well as the SAR and SWP) had a salinity of ≤1 ppt, indicating there is likely no influence of seawater intrusion affecting our sample sites.

Water Isotope Composition (δD and δ^{18}O)

The isotopic composition of the SAR water was -49 ± 4‰ for δD and -7.3 ± 0.7‰ for δ^{18}O ($n = 2$, Table 1). This is typical for river systems in regions that are fed by both local and distant precipitation (Williams and Rodoni 1997). The SWP water had relatively light isotopic values of -74‰ for δD, and -11.0‰ for δ^{18}O ($n = 1$, Table 1). Municipal tap water had the most negative values, with a δD of -100‰ and δ^{18}O of -12.2‰, indicating it was likely sourced from the Colorado River Water Project (Coplen and Kendall 2000). In addition, coastal rainwater isotopes collected on March 10, 2015 had values of -41‰ for δD and -7.3‰ for δ^{18}O ($n = 1$). However, the groundwater sampling region is typically recharged by precipitation falling further inland than our rainwater sample collection site. Therefore, the recharge is likely isotopically enriched compared to our precipitation sample.

Groundwater showed a variable range in water isotope values ranging from -50 to -64‰ for δD and from -7.1 to -9.1‰ for δ^{18}O (Figure 3a-b, Table 1). This agrees with a previous study (Williams 1997), which found that groundwater in the basin is a mixture of water from four sources: "local" recharge from coastal precipitation (isotopic range: δD = -58 to -40‰, δ^{18}O = -8.3 to -5.7‰), referred to here as "precipitation"; "native" recharge from the SAR drainage (isotopic range: δD = -63 to -56‰, δ^{18}O = -9.3 to -8.3‰), referred to here as "SAR"; "recent" recharge from SAR water that has experienced increased evaporation due to diversion of SAR flow into retention structures and percolation basins (isotopic range: δD = -61 to -59‰, δ^{18}O = -8.3 to -8.1‰), referred to here as "modern SAR"; and "Colorado" recharge which is a mixture of native water and water imported from Colorado State Project water (isotopic range: δD = -82 to -60‰, δ^{18}O = -10.5 to -8.6‰). The isotopic ranges of these four source waters are illustrated in Figure 2.

The groundwater isotopes from sample wells generally fell within two groups. At well WM, which is further inland and more distant from the injection barrier than the other wells, groundwater was generally heavier, with a δD of -53 ± 1‰ and δ^{18}O of -7.6 ± 0.3‰ ($n = 9$). All other wells displayed lighter water isotope ratios, with the lightest values measured at well HB (δD of -61 ± 2‰ and δ^{18}O of -8.5 ± 0.3‰, $n = 10$). This suggests that groundwater produced by WM was mainly recharged by local precipitation (Figure 2). Wells within 1.5 km of the injection barrier generally had δD values < -52‰ and δ^{18}O values < -8‰, suggesting the water came from mixtures of the lower SAR recharge and was possibly influenced by isotopically light, imported Colorado water (Figure 2). Our water isotope data agrees with the salinity measurements in that no detectable influence of seawater intrusion was found.

DIC Isotope Composition (^{14}C-DIC and δ^{13}C-DIC)

The ^{14}C-DIC signature of the surface waters was similar to that of the current atmospheric ^{14}CO$_2$ (102 pMC; X Xu, unpublished data), with 98.7 ± 0.2 pMC (average $\pm$ SD, $n = 2$) for SAR and 84.6 pMC for SWP water ($n = 1$). Groundwater ^{14}C-DIC ranged from

Table 1 Overview of isotopic compositions, pH and DIC concentration of analyzed water samples. Value in bracket next to the well label is the well depth at where water was drawn.

KCCAMS	Date MM/DD/YYYY	$\delta^{18}O$ ‰	δD ‰	^{14}C[a] pMC	$\delta^{13}C$ ‰	pH	DIC mmol/L
WM [45.4 m]							
150072	11/07/2014	–7.6	–54.6	93.34 (0.21)	n.m.	7.8	n.m.
150073	11/07/2014	–7.5	–54.0	94.03 (0.22)	n.m.	8.1	n.m.
150082	11/21/2014	–7.8	–54.4	93.30 (0.21)	–13.9	7.7	5.7
151619	12/05/2014	–7.6	–54.5	92.47 (0.21)	–15.0	7.4	5.0
151625	12/22/2014	–7.1	–51.8	93.42 (0.19)	–13.8	7.4	5.9
152498	01/09/2015	–7.4	–52.6	92.79 (0.15)	–13.7	7.5	5.0
153050	01/26/2015	–7.2	–51.9	92.90 (0.00)	–13.4	7.2	6.7
156062	02/06/2015	–8.1	–53.3	92.82 (0.16)	–13.5	7.3	7.0
156072	02/20/2015	–7.5	–52.2	93.05 (0.13)	–13.7	7.3	6.7
156085	03/06/2015	–8.0	–50.1	92.92 (0.14)	–13.5	7.3	5.8
HB [74.4 m]							
144319	09/01/2014	–8.7	–63.5	326.77 (0.98)	n.m.	7.8	n.m.
144320	09/01/2014	–8.7	–64.7	330.24 (0.83)	n.m.	8.1	n.m.
148334	10/22/2014	–8.3	–61.6	259.09 (0.70)	n.m.	n.m.	n.m.
148335	10/22/2014	–8.3	–63.4	258.79 (0.68)	n.m.	8.5	n.m.
150074	11/07/2014	–8.7	–62.9	215.45 (0.58)	n.m.	7.7	n.m.
151621	11/21/2014	–8.6	–63.4	284.11 (1.01)	–16.5	8.0	1.2
151620	12/05/2014	–8.4	–60.6	292.14 (0.84)	–16.1	8.4	1.1
152500	01/09/2015	–8.3	–58.3	135.86 (0.23)	–16.4	7.4	2.9
153048	01/26/2015	–7.7	–57.3	124.00 (0.19)	–16.1	7.1	3.2
153049	01/26/2015	–8.2	–60.3	161.00 (0.26)	–16.1	6.8	2.3
156059	02/06/2015	–8.5	–57.7	144.88 (0.24)	–16.2	7.4	3.4
156057	02/06/2015	–8.1	–57.2	154.54 (0.23)	–16.3	7.5	3.1
156058	02/06/2015	–8.4	–58.4	154.37 (0.23)	–16.3	7.5	2.6
156070	02/20/2015	–8.1	–60.0	270.75 (0.60)	–16.4	7.6	1.2
156068	02/20/2015	–8.6	–60.2	198.75 (0.41)	–16.6	7.3	1.9
156069	02/20/2015	–10.2	–61.5	197.84 (0.37)	–16.5	7.3	1.7
156081	03/06/2015	–8.2	–57.9	142.65 (0.22)	–16.4	7.3	2.9
156084		–9.1	–58.7	182.97 (0.34)	–16.6	7.0	2.0
CM-1 [140.8 m]							
151621	12/08/2014	–8.5	–59.1	123.27 (0.23)	–14.1	8.2	3.3
151626	12/22/2014	–8.5	–59.8	120.79 (0.23)	–14.8	7.9	4.3
152501	01/12/2015	–8.3	–58.5	118.47 (0.23)	–14.2	7.8	3.5
156063	02/09/2015	–8.6	–57.6	117.86 (0.17)	–14.4	7.8	3.8
156075	03/02/2015	–8.1	–57.2	119.74 (0.17)	–14.4	n.m	3.5
156096	03/23/2015	–9.0	–59.7	119.63 (0.18)	–15.0	7.9	4.1
156101	04/13/2015	n.m.	n.m.	120.93 (0.18)	–14.5	7.9	4.1
CM-2[140.2 m]							
151623	12/08/2014	–8.5	–57.8	96.95 (0.18)	–14.1	8.1	3.4
151627	12/22/2014	–7.6	–54.0	95.06 (0.18)	–14.5	8.0	3.1
152502	01/12/2015	–8.6	–59.2	97.10 (0.16)	–13.8	8.1	2.6
156065	02/09/2015	–7.7	–51.6	97.96 (0.14)	–14.1	8.0	3.2
156076	03/02/2015	–8.4	–57.8	94.09 (0.13)	–14.2	8.4	2.7
156097	03/23/2015	–9.1	–59.9	102.02 (0.15)	–14.4	8.2	3.1

Table 1 (*Continued*)

KCCAMS	Date MM/DD/YYYY	$\delta^{18}O$ ‰	δD ‰	$^{14}C^a$ pMC	$\delta^{13}C$ ‰	pH	DIC mmol/L
156102	04/13/2015	n.m.	n.m.	139.50 (0.15)	–14.5	8.2	3.5
CM-3 [61.0 m]							
151624	12/08/2014	–8.6	–60.6	174.36 (0.36)	–13.6	8.2	2.4
152503	01/12/2015	–8.4	–59.7	153.43 (0.26)	–14.0	7.9	3.2
156066	02/09/2015	–8.3	–58.3	165.68 (0.26)	–13.9	7.5	3.0
156077	03/02/2015	–8.4	–59.7	179.10 (0.29)	–13.9	8.0	2.9
156098	03/23/2015	–9.1	–63.0	167.57 (0.30)	–14.2	7.9	3.0
156103	04/13/2015			169.43 (0.31)	–14.0	8.1	3.5
FV [65.2 m]							
150078	11/13/2014	–8.4	–62.5	128.85 (0.31)	–15.3	7.9	1.0
152504	12/30/2014	–8.3	–58.1	118.14 (0.19)	n.m.	8.0	1.0
Santa Ana River (SAR)							
156079	03/05/2015	–6.8	–45.9	98.89 (0.15)	–11.9	8.0	3.5
156095	03/22/2015	–7.9	–51.2	98.54 (0.19)	–13.1	7.9	4.4
CA State Water Project (SWP)							
156093	03/22/2015	–11.0	–73.5	84.62 (0.13)	–10.5	8.8	1.4
Municipal Tap Water							
144313	07/14/2014	–12.2	–100.3	85.62 (0.20)	n.m.	n.m.	n.m.
Local Precipitation							
n.a.	03/10/2011	–7.3	–41.4	n.m.	n.m.	n.m.	n.m.

Notes: n.m. = not measured, n.a. = none assigned, [a] values in brackets are the analytical errors (1σ) for the ^{14}C analyses, which were mainly calculated from the counting statistics, fluctuations during measurement, and background corrections.

92.5 to 328.5 pMC. With the exception of two wells (HB and CM-2), ^{14}C-DIC values were generally stable over the study duration (Figure 3c).

Groundwater production well WM had the lowest abundance of ^{14}C-DIC, with an average of 93.0 ± 0.4 pMC ($n = 9$, Figure 3c, Table 1). This, in addition to the water isotopes, suggests that WM represents the unaltered background signature of native groundwater in the Shallow aquifer within the Pressure Area of the basin. Based on the water isotopes, the dominant source of groundwater to this well is natural recharge (local precipitation), as it does not appear to be influenced by the injection barrier that is about 6 km away.

Production wells FV and CM-1 also displayed stable, although slightly elevated, ^{14}C-DIC values of 123.5 ± 7.6 ($n = 2$) and 120.1 ± 1.8 pMC ($n = 7$), respectively. In contrast, the DIC in production wells HB and CM-3 was found to be significantly enriched in ^{14}C at all times, averaging 219.4 ± 69.7 pMC ($n = 10$) and 168.3 ± 8.8 pMC ($n = 6$), respectively (Figure 3c). Although groundwater at some sites was significantly enriched in ^{14}C, exceeding contemporary atmospheric $^{14}CO_2$ values, all measured levels are well below drinking water standards.

Our results confirm those of a previous study (Hudson et al. 1995), which found the presence of high ^{14}C-DIC near the injection barrier. The ^{14}C enrichment had been attributed to transient pulses of elevated ^{14}C in the recycled water supply, which entered the groundwater through the injection barrier (Hudson et al. 1995). Remineralized carbonate scale from pipes within the recarbonation pond of the previous recycled water treatment plant had a ^{14}C signature of 402 pMC, further supporting this hypothesis (Hudson et al. 1995). The ultimate source of the
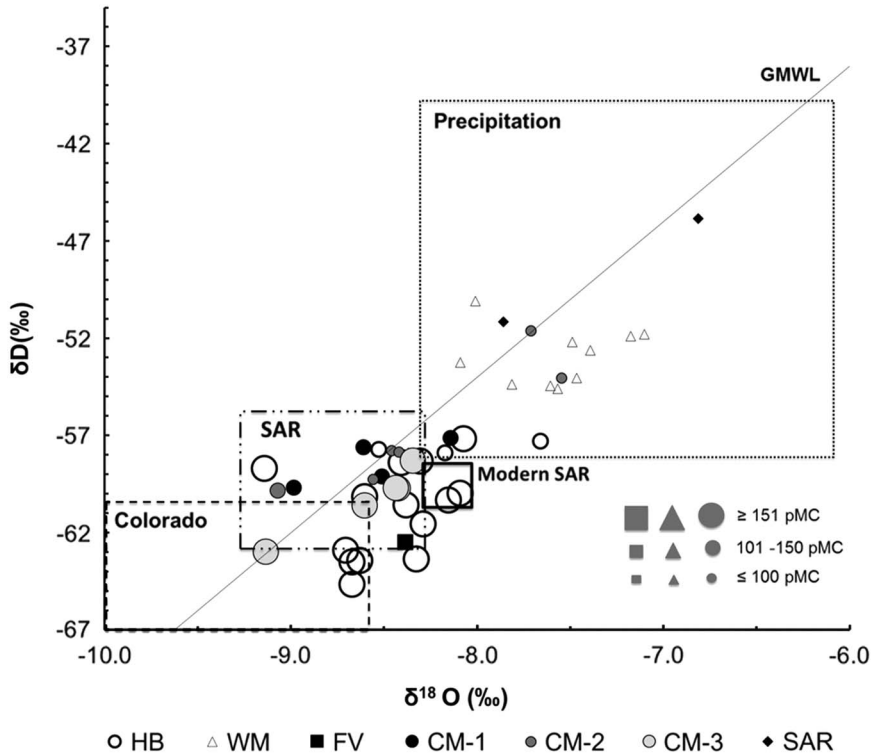
Figure 2 δD vs. δ^{18}O of groundwater samples collected for this study. The line represents the global meteoric water line.[14]C signatures are indicated by symbol size. Sources of recharge and their isotopic ranges are interpreted according to Williams (1997). "Precipitation" represents recharge from local coastal precipitation, "SAR" refers to recharge along the lower river watershed, "modern SAR" is recharge from SAR water that has experienced evaporation caused by recent human interference with the river flow, and "Colorado" refers to recharge water that is a mixture of both Colorado River water and natural groundwater.

elevated ^{14}C has not been fully determined. However, there are known ^{14}C tracer manufacturers located within the service area of the sanitation district supplying source water to the treatment plant. In addition, recent studies have found that both secondary treatment effluent and sludge are enriched in [14]C (165–251 pMC; Tseng et al. 2015).

The δ^{13}C-DIC signature of all groundwaters ranged from –13.3 to –16.5‰ (Table 1). In contrast, the δ^{13}C-DIC signature of surface waters was enriched (SAR and SWP: –10.4 to –13.1‰), likely due to exchange with regional atmospheric CO_2, which typically has enriched δ^{13}C signatures between –8.5 and –10.5‰ (X Xu, unpublished data). During the study, the δ^{13}C signature for each groundwater production well was relatively stable and somewhat distinct (Figure 3d). The DIC at both HB and FV wells was significantly depleted in δ^{13}C (–16.3 ± 0.2‰ and –15.3‰, respectively) when compared to the average δ^{13}C of –14.1 ± 0.4‰ of the other wells. This indicates that the wells HB and FV have a higher input of organic-matter-sourced C. Additional factors that can impact the δ^{13}C in groundwater are the exchange between DIC and CO_2 gas (atmospheric and soil gas) and carbonate dissolution (Hudson et al. 1995).
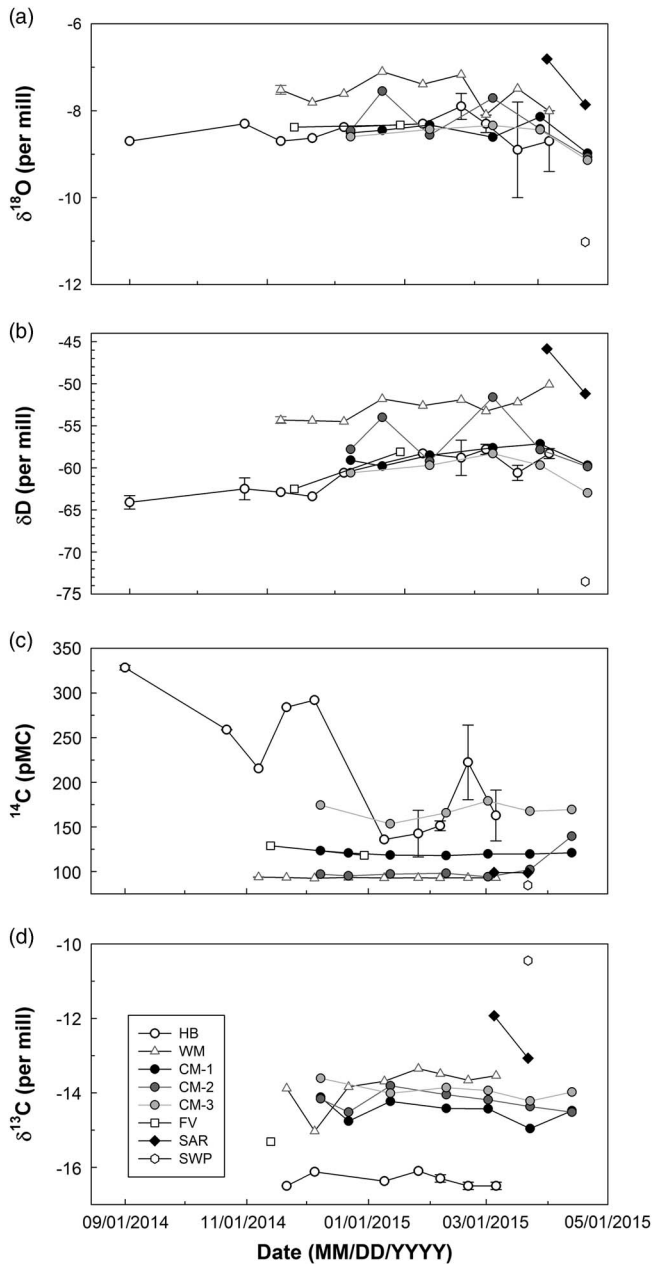
Figure 3 Time series of water isotopes (a) $\delta^{18}O$ and (b) δD, and of (c) ^{14}C-DIC and (d) $\delta^{13}C$-DIC from September 2014 to April 2015 for groundwater production wells (HB, WM, CM-1, CM-2, CM-3, FV) and surface waters (SAR, SWP).

When comparing $\delta^{13}C$ vs. ^{14}C-DIC signatures (Figure 4), the groundwater samples generally fall along a mixing line of the elevated ^{14}C carbonate scale found in treatment plant pipes ($\delta^{13}C \approx -29.5‰$, $^{14}C \approx 402$ pMC; Hudson et al. 1995), air ($\delta^{13}C \approx -8‰$, $^{14}C \approx 102$ pMC), and carbonate ($\delta^{13}C \approx 2‰$, $^{14}C \approx 0$ pMC). We hypothesize that the ^{14}C and ^{13}C signatures of
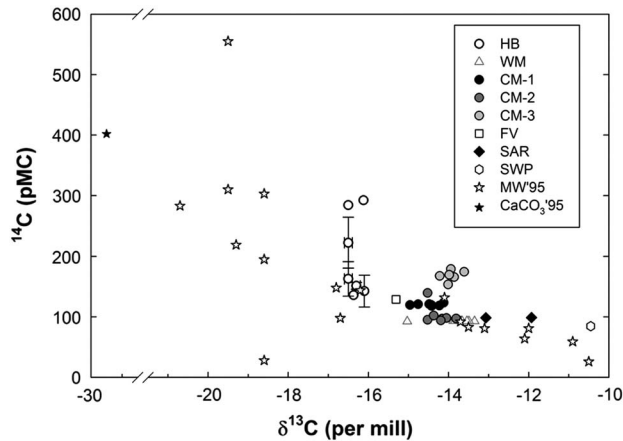
Figure 4 $\delta^{13}C$ vs. ^{14}C of DIC in groundwater samples collected in this study, and of DIC in groundwater (open stars) and carbonate scale from the previous recycled water treatment plant (closed star) reported by Hudson et al. (1995).

organic material are imparted onto the DIC of the recycled water during the treatment processes. In the past, CO_2 gas produced from lime regeneration was used to adjust the pH of recycled water during the recarbonation process (Davisson et al. 1999). This would imply that groundwater with depleted ^{13}C would more likely have an enriched ^{14}C content, as was observed in well HB.

Temporal Variations

Several wells showed significant temporal variations in their ^{14}C-DIC, most notably in HB. The ^{14}C-DIC content reached a maximum of 330.2 pMC in September 2014, before falling to a minimum of 124.2 pMC in January 2015, after which it increased to 270.8 pMC in February (Figure 3c). Several factors may control these dynamics: (1) changes in recycled water injection rates at the injection barrier, (2) changes in basin-wide water withdrawal and recharge together affecting the hydrostatic balance and the groundwater flow paths, and thereby changing the proportions of source waters to wells near the injection barrier, and (3) fluctuations in the ^{14}C signature of waters coming into the wastewater treatment plant.

During 2014, there were two major shutdowns of injection in the barrier, a 26-day shutdown from June 7 through July 2, 2014 and a 9-day shutdown from October 18 to 26, 2014 (OCWD 2014). However, water isotopes did not covary with the ^{14}C-DIC signature, suggesting no significant changes in water sources. Thus, the more likely explanation for the variation of ^{14}C-DIC is changes in the ^{14}C end-member of the injection water with time. Unfortunately, we did not have access to monitor the injection water directly. Nonetheless, the ability to detect such significant changes demonstrates the sensitivity of the ^{14}C measurement and its potential utility as a tracer for the injected recycled water, in conjunction with the stable isotopes.

Mixing of Recycled Water with Local Groundwater (^{14}C Keeling Plot)

A Keeling plot is a two-end-member linear mixing model. It was originally applied to model isotopic mass balance in atmospheric studies (Keeling 1958, 1961); however, it is now commonly used in many other fields, such as ecosystem (Pataki et al. 2003) and oceanography

studies (Walker et al. 2014). The model is based on the conservation of mass and isotopes when mixing occurs between two end-members, specifically a low concentration background C component (C_{bg}) and a high concentration source C component (C_s) (Equations 1–2):

$$C_t = C_{bg} + C_s \tag{1}$$

$$\delta_t C_t = \delta_{bg} C_{bg} + \delta_s C_s \tag{2}$$

where C_t, C_{bg}, and C_s, and δ_t, δ_{bg} and δ_s, are the concentrations and carbon isotopic ratios of the total, background, and source, respectively. If δ_{bg} and δ_s remain constant during the sampling period, the isotopic composition of the source C can be obtained from the intercept δ_s (Equation 3):

$$\delta_t = C_{bg}\left(\delta_{bg} - \delta_s\right)\left(1 / C_t\right) + \delta_s \tag{3}$$

The ^{14}C-DIC signature vs. 1/DIC concentration (1/[DIC]) is shown as a Keeling plot in (Figure 5). With the exception of the FV well, all sites generally fall on the same mixing line, showing that as [DIC] decreases, ^{14}C-DIC generally increases. A model II linear regression (excluding the FV well) indicates that the high [DIC] source water (the *y* intercept), a close representative of the unaltered groundwater for the aquifer, has a ^{14}C-DIC signature of 45.8 ± 8.6 pMC (equivalent to a mean ^{14}C age of 6300 ± 1500 yr BP). The Keeling plot further implies that the other end-member could have come from the injection water, which is inferred to have a low [DIC] and high ^{14}C signature. This is evident when comparing well HB, which showed the highest ^{14}C-DIC signature and lowest average [DIC] of 2.2 ± 0.8 mmol/L ($n = 10$), to WM, which had the lowest ^{14}C-DIC signature and a higher average [DIC] of 6.0 ± 0.8 mmol/L ($n = 8$, Table 1).

Davisson et al. (1999) also found evidence that the injection water is undersaturated in calcite and likely causes carbonate dissolution within the aquifer. This matches well with the observation that all groundwater samples fall on a mixing line of the elevated ^{14}C precipitate and carbonates (Figure 4). Addition of calcite CO_3^{-2} to the DIC pool would cause a decrease in the ^{14}C signature, suggesting that the ^{14}C signature of the injection water is likely higher than is
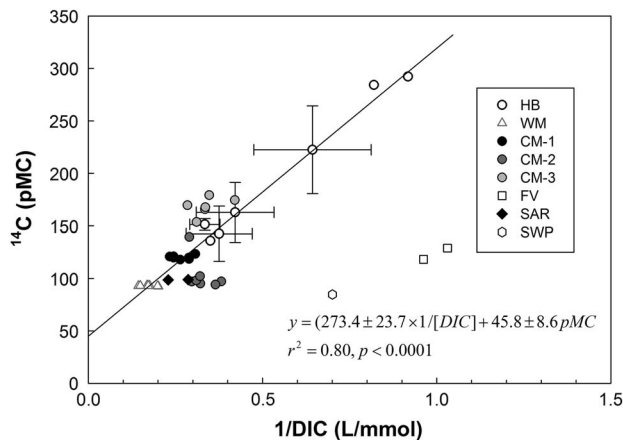

Figure 5 ^{14}C-DIC Keeling plot constructed for groundwater production wells.

measured in the groundwater, or could be estimated from a two-end-member system. Carbonate dissolution would also cause an increase in δ^{13}C-DIC. This matches well with the observation from Figure 4, that as ^{14}C signatures decrease, δ^{13}C generally increase.

The exception of well FV may be explained by its much shallower screened depth interval and close proximity to the injection barrier. Chloride concentration data from water district monitoring wells suggest that shallow wells in the vicinity of the injection barrier are extremely sensitive to seasonal fluctuations in groundwater levels, causing groundwater flow to occasionally shift between landward and seaward (OCWD 2014), thereby possibly changing source waters to the wells. Although the ^{14}C-DIC signature at FV was still enriched, it was probably influenced by more recent injection water from the expanded and upgraded treatment facility that does not feature recarbonation or a separate pulse event with a different ^{14}C signature.

Tracing Recycled Water by Coupling Water and C Isotopes

Coupled water and ^{14}C isotope mixing models further corroborate the relation of enriched ^{14}C-DIC to the injection barrier (Figure 2). Enriched levels of ^{14}C-DIC (denoted by symbol size) are associated with water recharged from "Colorado," "SAR," or "modern SAR," yet never local "precipitation." This is likely a result of local groundwater mixing with injection water. Prior to 2009, the injection water itself was a mixture of local groundwater, treated wastewater, and Colorado River water; however, since then it has been comprised solely of recycled water produced at the new facility.

In summary, both the previous studies (Hudson et al. 1995; Davisson et al. 1996, 1999) and our observations indicate that the recycled water is generally characterized by relatively light δ^{13}C-DIC and elevated ^{14}C-DIC signatures. This ^{14}C-enriched DIC likely originates from CO_2 oxidized from organic materials in the treatment plant, even though some of this CO_2 had likely been removed during the post-treatment degassing used in the newer treatment facility. Some CO_2 can remain and be equilibrated into DIC when the pH is adjusted to approximately 8.5 in the end product. Also, because of the advanced treatment processes and partial degassing procedure, the current recycled water (produced since 2008) has low DIC content compared to the local groundwater.

We expect that the level of elevated ^{14}C in this recycled water can vary greatly due to the change in the amount of ^{14}C in the waste stream and its mixing with other carbon sources within the aquifer system, such as other water sources and the underlying geological substrate. The recycled water is generally depleted in both ^{18}O and D, because its source waters are blended with isotopically light Colorado River and SAR waters. The water isotopes could be decoupled from the carbon isotope signatures depending on the sources and relative proportions of blended waters.

CONCLUSION

Our study shows that the isotopic analysis of water and DIC may be an effective and noninvasive approach for tracing the fate and long-term (years to decades) temporal dynamics of recycled water and thus provides an additional tool for groundwater management. Particularly in the Orange County coastal aquifer system, the existence of long-lived ^{14}C enrichment provides an additional intrinsic tracer that allows following the interactions of recycled water for decades.

The challenge remains to establish the isotopic end-member signatures of recycled water used at the injection barrier and to investigate its variability. Future studies are also needed to investigate whether ^{14}C enrichment is a typical occurrence in recycled water from metropolitan areas.

Alternatively, non-^{14}C-enriched recycled water may also be used to understand the mixing of recycled water with older groundwater found at greater depth. We hope that this approach of coupling ^{14}C with ^{13}C and water stable isotopes as an environmental intrinsic tracer will improve the capability and efficiency of using ^{14}C in water related studies for more than just apparent age of groundwater.

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