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Clark, Jordan F
Urióstegui, Stephanie H
Bibby, Richard K
et al.

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Quantifying Apparent Groundwater Ages near Managed Aquifer Recharge Operations Using Radio-Sulfur (^{35}S) as an Intrinsic Tracer

Jordan F. Clark [1,*], Stephanie H. Urióstegui [1,2,3], Richard K. Bibby [3], Bradley K. Esser [3] and Gideon Tredoux [4]

1. Department of Earth Science, University of California, Santa Barbara, CA 93106, USA
2. Environmental Support and Programmatic Outreach, Lawrence Livermore National Laboratory, Livermore, CA 94551, USA; uriostegui1@llnl.gov
3. Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory, Livermore, CA 94551, USA; bibby1@llnl.gov (R.K.B.); esser1@llnl.gov (B.K.E.)
4. CSIR Natural Resources and the Environment (retired), Stellenbosch 7559, ZA, South Africa; gideon.tredoux@gmail.com

* Correspondence: jfclark@geol.ucsb.edu; Tel.: +1-805-893-7838; Fax: +1-805-893-2314

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Abstract: The application of the cosmogenic radioisotope sulfur-35 (^{35}S) as a chronometer near spreading basins is evaluated at two well-established Managed Aquifer Recharge (MAR) sites: the Atlantis facility (South Africa) and Orange County Water District's (OCWD's) Kraemer Basin (Northern Orange County, CA, USA). Source water for both of these sites includes recycled wastewater. Despite lying nearer to the outlet end of their respective watersheds than to the headwaters, ^{35}S was detected in most of the water sampled, including from wells found close to the spreading ponds and in the source water. Dilution with ^{35}S-dead continental SO_4 was minimal, a surprising finding given its short ~3 month half-life. The initial work at the Atlantis MAR site demonstrated that remote laboratories could be set up and that small volume samples—saline solutions collected after the resin elution step from the recently developed batch method described below—can be stored and transported to the counting laboratory. This study also showed that the batch method needed to be altered to remove unknown compounds eluted from the resin along with SO_4. Using the improved batch method, times series measurements of both source and well water from OCWD's MAR site showed significant temporal variations. This result indicates that during future studies, monthly to semi-monthly sampling should be conducted. Nevertheless, both of these initial studies suggest the ^{35}S chronometer may become a valuable tool for managing MAR sites where regulations require minimum retention times.

Keywords: hydrologic tracers; travel time; retention time; radio-sulfur (^{35}S); Atlantis MAR Facility (South Africa); Orange County Water District MAR Facility (California; USA)

1. Introduction

An increasingly important water supply option is Managed Aquifer Recharge (MAR) combined with wastewater reuse. While many MAR facilities are currently in development, a number of them have been in operation for more than a half a century. These sites include the well-established dune replenishment systems of the Netherlands [1–3], numerous Riverbank Filtration sites along European rivers such as the Rhine, (e.g., [4]) and the Elbe, (e.g., [5,6]), the Montebello Forebay Spreading Grounds of Los Angeles County, CA, USA [7], and the Orange County Forebay, located in Northern Orange County, CA, USA [8,9].

Indirect potable reuse with MAR has a number of advantages. Firstly, many urban groundwater basins are heavily utilized for water supply and are often in overdraft. Therefore, much of the infrastructure, such as production wells and aquifer storage space, already exists. Secondly, water quality generally improves with distance and travel time (e.g., [10,11]). Many potential contaminants, such as most infective microorganisms (pathogens) and some trace organic compounds, may persist in recycled water even after tertiary treatment at above ground facilities; however, many contaminants are naturally removed or become inactive with time in the subsurface (e.g., [12–16]). These natural attenuation processes are collectively known as soil aquifer treatment (SAT) and further improve the quality of recharged water for subsequent potable and non-potable reuse. These water quality improvements are considered an additional benefit of MAR (e.g., [17]).

Despite numerous examples of the success of indirect potable reuse with MAR, often the public raises concerns during the permitting process [18,19]. As a result, numerous governmental agencies have developed guidelines (e.g., [17,20–23]). The state of California, which has a long history of indirect potable reuse, first proposed regulating these operations in 1978 as part of the Wastewater Reclamation Criteria (Title 22, Division 4, Chapter 3) of the California Code of Regulations and Environmental Health [20]. By the early 1990s, draft rules were established that required numerous pre-infiltration criteria and both a subsurface retention time (for pathogen inactivation) and a travel distance. Also at this time, techniques were developed to formally evaluate the subsurface retention criteria. The results from deliberate (added) tracer experiments using dissolved gases such as noble gas isotopes and sulfur hexafluoride (SF_6) at the Orange County Water District (OCWD) MAR operations [9] and the Water Replenishment District of Southern California spreading ground [24] showed that the travel distance criteria between recharge operation and potable supply wells made little sense. Not too surprisingly given the local alluvial geology, these deliberate tracer experiment results showed that depth, not distance was a better predictor of travel time near spreading ponds. Subsequently, the travel distance rule was removed in favor of tracer travel time as the sole criterion for subsurface residence time of recycled water [7].

Current California regulations for Groundwater Replenishment Reuse Projects (GRRP) require specific subsurface residence times prior to extraction for potable use wells [7,25]. Minimum residence times, from infiltration at spreading ponds to extraction at drinking water wells, are based on the degree of aboveground treatment before recharge. Minimum time for tertiary-treated recycled water is typically six months, whereas minimum travel time for advanced treated recycled water (microfiltration, reverse osmosis, advanced oxidation) could be as little as two months. The California regulations consider deliberate tracer experiments as the best method for establishing retention times for surface spreading projects. Travel times determined with intrinsic tracers such as radio-sulfur (^{35}S) discussed herein, are considered less reliable and the GRRP rules only allow 0.67 virus log reduction credit per month of residence time underground versus 1 log per month for a deliberate tracer [25]. Therefore, the minimum travel time is nine months for tertiary-treated recycled water if determined using an intrinsic tracer.

Here we discuss, evaluate, and recommend improvements for using ^{35}S as an intrinsic tracer near MAR facilities at the Atlantis site in South Africa and the OCWD operations in Northern Orange County, CA, USA.

1.1. Geochemistry of ^{35}S

^{35}S is a cosmogenic radioisotope produced in the upper atmosphere from nuclear reactions between cosmic rays and argon (^{40}Ar) gas. It has a relatively short half-life of 0.240 years or 87.5 days (λ = 2.89 year^{-1} or 0.00792 day^{-1}) [26]. Much like ^{14}C and tritium, which are also produced by cosmic rays in the upper atmosphere, it rapidly oxidizes (for ^{35}S to $^{35}SO_4$) and eventually enters the tropospheric water cycle. It is delivered to surface water via both wet and dry deposition [27,28]. Because its activity becomes undetectable after about five half-lives (1.2 years), most SO_4 in the environment is ^{35}S-dead. As a result, very few measurements have been made downstream from mountain watersheds.

Most of the literature on the use of ^{35}S as a hydrologic tracer discusses studies where the applications of ^{35}S has been restricted to high-elevation basins that have short groundwater residence times (<1 year), weak biogeochemical cycling, and little water/rock interactions. In these settings, stream and snow [SO_4] are low, and the hydrologic SO_4 budget is dominated by atmospheric inputs that have relatively high ^{35}S activities [29–32]. In contrast, recharge water and groundwater associated with MAR operations will have higher sulfate concentrations, low to intermediate ^{35}S activities, and the potential for biogeochemical cycling.

Another reason that ^{35}S-dating has rarely been attempted near MAR operations is because the traditional method (e.g., [31]) for analyzing ^{35}S with liquid scintillation counting (LSC) is difficult in high [SO_4] waters, as is typically found near MAR sites. Only recently has a new batch method been developed for these types of samples [33].

Here, we will discuss using ^{35}S as a groundwater chronometer. Assuming simple piston flow, the groundwater apparent age, t, can be estimated with:

$$t = -\frac{1}{\lambda} ln\left(\frac{A}{A_0}\right) \tag{1}$$

where λ is the decay constant (see above), A is the observed activity in the well sample, and A_0 is the initial activity in the source (recharge) water.

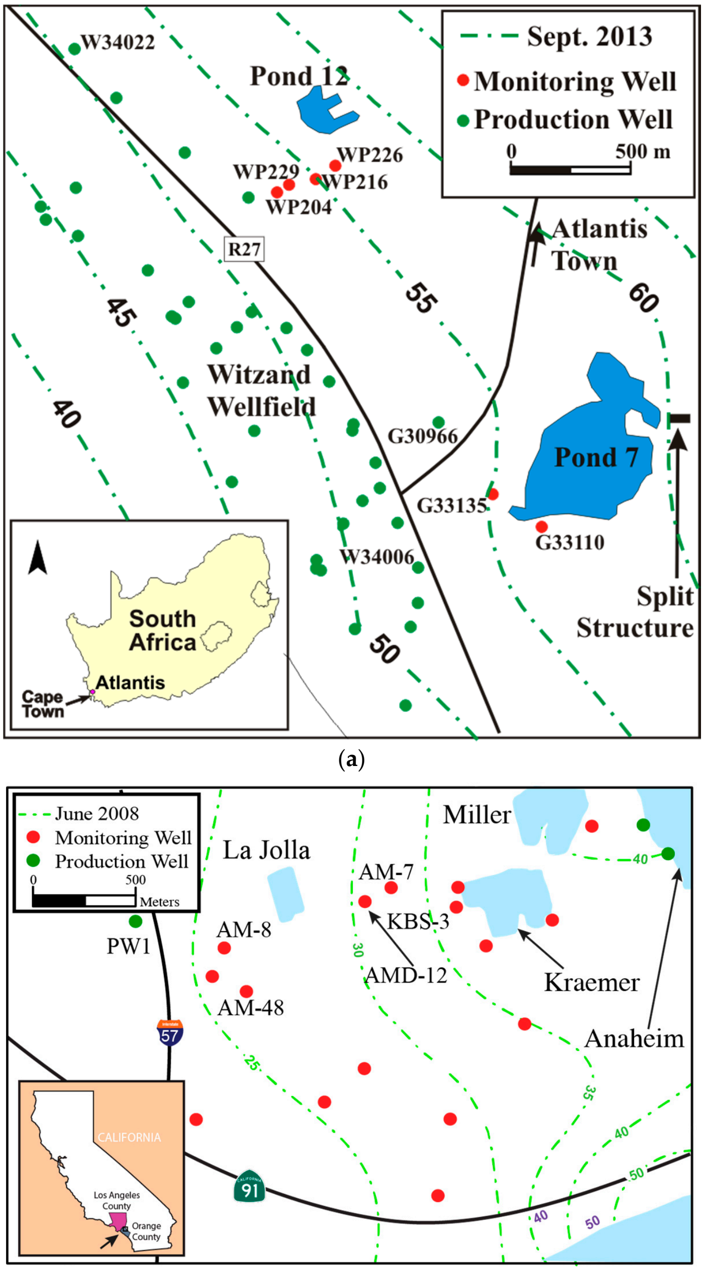
In order to use ^{35}S as an intrinsic tracer near MAR operations, a number of simplifying assumptions are made. As mentioned above, we will be using the piston flow model to interpret the apparent ages. This model assumes no mixing between flow paths, which typically have different ages. Furthermore, Equation (1) requires that A_0 is known and invariant. These assumptions will be examined as part of this paper.

1.2. Field Locations

The application of ^{35}S as a groundwater dating tool near MAR operations was tested at (1) the Atlantis MAR site in South Africa and (2) the OCWD MAR site near the Kraemer Spreading Basin in Orange County, CA, USA.

1.2.1. The Atlantis MAR System

The Atlantis MAR facility was constructed during the late 1970s [34,35]. It consists of an urban storm water collection system, to which treated domestic wastewater is added, and three recharge facilities. Two infiltration basins—Pond 7 and 12—recharge the potable aquifer and are 400 to 700 m up gradient from the large Witzand well field (Figure 1a); a third basin is located near the coast and maintains a seawater intrusion barrier. The blend of reclaimed (recycled) domestic wastewater and storm water is used as source water for the MAR operation. Lower quality runoff and reclaimed water from industrial areas are diverted by separate drainage and transferred only to the lower basin that maintains the seawater barrier. This flow separation is the primary means for minimizing the water quality impacts to the local water supply. Natural attenuation of contaminants within the soil/aquifer systems provides the final treatment. Approximately 2 × 10^6 m^3 of water are recharged annually to the underlying Witzand aquifer, supporting at a maximum one-third of the total water demand for the town of Atlantis [35].



(a)

(b)

Figure 1. Maps of the field areas including locations of infiltration basins, production and monitoring wells, and local piezometric surface. (**a**) The Atlantis Managed Aquifer Recharge (MAR) site with an insert of South Africa and (**b**) the Orange County Water District (OCWD) MAR site down gradient from Kraemer Basin with an insert of California, USA. Please note that the approximate area of the OCWD MAR site is located on the California map with an arrow pointing at a small black rectangle.

1.2.2. The OCWD MAR System

The Kraemer Spreading Basin is one of the northern spreading ponds maintained by the OCWD (Figure 1b). It is located in the Santa Ana Forebay Region of the Orange County Coastal Plain, which overlies the Orange County Groundwater Basin. For more than 75 years, OCWD has been actively replenishing and managing this groundwater basin that supplies ~70% of the total water demand for approximately 2.5 million inhabitants. In 2008, OCWD began recharging recycled wastewater supplied by the OCWD's Groundwater Replenishment System (GWRS). The cleaned wastewater is pumped via a 21-km pipeline to Kraemer and Miller Basins for groundwater replenishment. GWRS water is purified using a three-step advanced treatment process consisting of microfiltration, reverse osmosis and ultraviolet light with hydrogen peroxide disinfection. Currently, OCWD operates more than 400 hectares of surface spreading facilities and recharges annually approximately 3.0×10^8 m^3 [36], with GWRS supplying 40% of the total source water. In addition to the Kraemer and Miller basins, OCWD MAR operations include Anaheim Lake, Burris Pit, La Jolla and Warner Basins, and a 9 km section of the Santa Ana River (SAR).

Earlier deliberate tracer experiments demonstrated that a zone of highly transmissive material extends down gradient of Kraemer Basin for more than 3 km [9,37]. Within this zone, linear groundwater velocities are approximately 2000 m/year. It is possible that this preferential flow zone is a buried river channel given its proximity to the SAR and the alluvial geology of this MAR site.

2. Materials and Methods

Field campaigns were conducted at the Atlantis and OCWD MAR operations, respectively, during August 2010 and 2012–2013. Twenty-liter water samples were collected using submersible pumps after flushing with three well volumes following standard procedures. Before processing, samples were filtered using 0.45 µm high capacity cartridge filters. During the Atlantis field campaign, a temporary laboratory was set up in a garage. With a small kitchen scale and house drill purchased locally, the batch method of Urióstegui et al. [33]—acidification to a pH of 2–4 followed by a 2 h spin with ~20 g of Amberlite™ IRA-400 ion exchange resin—was used to process samples through the 125 mL NaCl elution step. By pausing here, the volume of water for each sample transferred from South Africa to the USA was reduced from 20 L containers to 125 mL Nalgene bottles. After returning to the USA, the samples were sent to Lawrence Livermore National Laboratory (LLNL) where the final steps of the batch method were completed (e.g., $BaSO_4$ precipitation, mixing with scintillant gel, LSC, and $[SO_4]$ measurements on an ion chromatograph using standard methods). The chemical yields were determined by analyzing raw and post batch spin water for $[SO_4]$ and performing mass balance calculations.

It is important to note that some of the Atlantis samples were yellowish after the 125 mL NaCl elution step. This was especially true for the Pond 12 and Split Structure samples. Apparently, other compounds contained in some of these samples were being collected by the Amberlite™ resin and eluted with the salt solution. A modification was made to the batch method prior to starting to process samples collected near Kraemer Basin in Orange County, CA USA. The salt solution was passed through a column containing at least 2 g of activated carbon to remove colored impurities that could potentially interfere with LSC prior to the $BaSO_4$ precipitation.

3. Results

Despite their geographical locations away from the headwater streams of their respective hydrologic basins, ^{35}S was detected at both field sites. Groundwater activities were not always lower than the presumed source surface water activities, and time series measurements (at Kraemer Basin) indicate that both ground and surface waters vary temporally.

3.1. The Atlantis MAR System

Three surface waters, which feed into the potable aquifer spreading basins, three production wells, and six monitoring wells were sampled (Tables 1 and 2). While the two spreading basins had nearly identical ^{35}S activities (Pond 7: 13.7 ± 0.8 mBq/L and Pond 12: 16.2 ± 0.9 mBq/L) the water entering the ponds was slightly lower (Spilt Structure: 12.8 ± 0.8 mBq/L). The well water samples ranged between 5.9 ± 0.7 mBq/L and 15.5 ± 3.8 mBq/L. Assuming a mean initial activity based on the ponds of 15.0 mBq/L and the simple piston flow model, the apparent ages of the groundwater ranged between 0 and 17 wks (Table 2). The apparent ages do not vary systematically with distance from the pond edge (Figure 2).

Table 1. [SO_4] and $^{35}SO_4$ activities for source water and precipitation at the Atlantis and OCWD MAR sites.

Sample ID	Collection Date	SO_4 (mg/L)	$^{35}SO_4 \pm 1\sigma$ (mBq/L) [a]		
			Sample	Field Duplicate	Reported [b]
Atlantis MAR					
Pond 7	02-Aug-2010	46.3	13.7 ± 0.8	NA	13.7 ± 0.8
Pond 12	04-Aug-2010	57.1	16.2 ± 0.9	NA	16.2 ± 0.9
Split Structure	04-Aug-2010	58.2	12.8 ± 0.8	NA	12.8 ± 0.8
OCWD MAR (Data from [38])					
Kraemer Basin	20-Mar-2012	2.3	<2.7 [c]	NA	<2.7 [c]
Kraemer Basin	05-Jun-2012	<0.5	0.3 ± 0.6 [d]	0.5 ± 0.6 [d]	0.4 ± 0.4
Kraemer Basin	10-Dec-2012	72.7	<1.4 [c]	NA	<1.4 [c]
Kraemer Basin	05-Feb-2013	109	17.1 ± 1.7	19.4 ± 1.9	18.3±1.3
La Jolla Basin	10-Dec-2012	73.4	ND	0.3 ± 0.8	0.3 ± 0.8
La Jolla Basin	04-Feb-2013	117	13.6 ± 1.8	16.0 ± 2.0	14.8 ± 1.3
La Jolla Basin	01-Apr-2013	215	16.0 ± 2.3	15.0 ± 2.3	15.5 ± 1.6
Precipitation [e]	25-Feb-2011	NA	19.9 ± 1.1	21.4 ± 1.2	20.7 ± 0.8
GWRS TF [f]	06-Apr-2012	1.1	0.6 ± 0.1 [d]	NA	0.6 ± 0.1 [d]
GWRS MB [f]	06-Apr-2012	0.6	0.7 ± 0.1 [d]	NA	0.7 ± 0.1 [d]

Notes: NA = Not Available; ND = Not Detectable; [a] Reported error is 1σ counting error; [b] For field duplicates samples, the reported $^{35}SO_4$ activity is the average activity for the two samples; [c] For samples with non-detectable $^{35}SO_4$ activity, reported uncertainty is 2σ counting error which is sample-specific (see [38] for details); [d] No yield correction performed for samples with greater than 100% recovery; [e] Rain sample was collected in the city of Orange, CA, from a location 6 km south of the OCWD MAR sites; [f] Groundwater Replenishment System (GWRS) water was sampled from two locations along the transmission pipeline: (TF) water immediately post-treatment at the treatment facility in Fountain Valley and (MB) GWRS discharge into Miller Basin.

Table 2. Well type, downgradient distance, [SO_4], $^{35}SO_4$ activities, and ^{35}S apparent ages for groundwater at the Atlantis MAR sites. The apparent ages were calculated assuming the A_0 is average activity of Pond 7 and 12 and the error is the 1σ propagated counting error.

Well ID	Sample Date	Well Type [a]	Distance (m)	[SO_4] (mg/L)	$^{35}SO_4 \pm 1\sigma$ [b] (mBq/L)	Age ± σ [c] (wk)
G30966	01-Aug-2010	PW	420	34.3	15.5 ± 3.8	−1 ± 4
G33110	04-Aug-2010	MW	65	50.1	14.1 ± 0.8	1 ± 1
G33135	04-Aug-2010	MW	140	42.4	9.6 ± 0.7	8 ± 1
W34006	04-Aug-2010	PW	510	52.2	9.5 ± 0.8	8 ± 2
W34022	04-Aug-2010	PW	1000	28.0	9.9 ± 0.8	7 ± 1
WP204	02-Aug-2010	MW	265	29.3	6.3 ± 0.6	16 ± 2
WP216	02-Aug-2010	MW	190	35.7	9.6 ± 0.7	8 ± 1
WP226	02-Aug-2010	MW	130	38.0	5.9 ± 0.7	17 ± 2
WP229	02-Aug-2010	MW	220	45.7	12.5 ± 0.8	3 ± 1

Notes: [a] PW = Production Well; MW = Monitoring Well; [b] Reported error is 1σ counting error; [c] Propagated counting error.

3.2. The Kraemer Spreading Basin

Over the period of two years, time series measurements were collected from six of the principal recharge locations of which only two—Kraemer and La Jolla Basins—are discussed in this paper. A total of 29 source water plus one precipitation and two GWRS samples were collected (see [38], and Table 1). Many of these samples were collected in duplicate. Five of the 29 source samples were below the analytical detection limit. These ^{35}S-free samples were collected either during dry periods (late spring through early winter; $n = 3$) or contained a significant fraction of GWRS water ($n = 2$). However it is important to note that the GWRS samples were not below the detection limit; rather they were very close to it (0.6 ± 0.1 mBq/L) and had very low [SO_4] (Table 1).

Groundwater samples (Table 3) were collected from seven monitoring wells (AM-7/1, AM-8/1, AM-48/1, AM-12/1, AM-12/2, and KBS-3/1) and one production well (PW1), all of which were shown to be hydraulically connected with Kraemer Basin using earlier deliberate tracer experiments [9,37]. AM-12/1 and AM-12/2 are at the same location but screened at different depths with AM-12/2 at the deeper interval. The ^{35}S activities in these well samples ranged from below detection limit to 13.6 ± 1.3 mBq/L. Groundwater apparent ^{35}S ages varied with both season [38] and distance from Kraemer Basin (Figure 2; Table 3).

Table 3. Well type, downgradient distance, [SO_4], $^{35}SO_4$ activity, and ^{35}S apparent age for groundwater at OCWD MAR sites. The apparent ages were calculated assuming the A_0 of the source water using Equation (2) and the error is the 1σ propagated counting error. Data from [38].

Well ID and Collection Date	Well Type [a]	Dist. (m) [b]	[SO_4] (mg/L)	$^{35}SO_4$ ± 1 σ (mBq/L) [c]	$^{35}SO_4$ ± 1σ (mBq/L) [c]	Reported [d]	Appt. Age Time ± 1 σ (wk) [e]
KBS-3/1	MW	25					
13-Sep-2012			2.3	7.3 ± 0.7 [f]	NA	7.3 ± 0.7 [f]	*
10-Dec-2012			99.5	ND	NA	ND	>53 [g]
05-Feb-2013			112	15.9 ± 1.8	11.3 ± 1.8	13.6 ± 1.3	6 ± 2
02-Apr-2013			177	5.4 ± 1.8	NA	5.4 ± 1.8	30 ± 6
AM-7/1	MW	350					
21-Mar-2012			6.4	4.2 ± 0.6	NA	4.2 ± 0.6	*
22-May-2012			3.1	2.0 ± 0.2 [f]	2.2 ± 0.6	2.1 ± 0.3	*
25-Sep-2012			4.3	2.5 ± 0.3	2.3 ± 0.3	2.4 ± 0.2	*
19-Nov-2012			2.4	1.4 ± 0.2 [f]	1.6 ± 0.2 [f]	1.5 ± 0.1	*
27-Feb-2013			17.3	4.5 ± 0.4	3.4 ± 0.5	4.0 ± 0.3	*
16-Apr-2013			46.3	3.1 ± 0.4	2.4 ± 0.5	2.8 ± 0.3	20 ± 2
11-Jun-2013			53	1.7 ± 1.4	1.5 ± 1.4	1.6 ± 1.0	23 ± 13
AM-8/1	MW	1220					
22-May-2012			58.9	1.7 ± 0.6	1.0 ± 0.6	1.4 ± 0.4	36 ± 5
13-Sep-2012			34.2	7.0 ± 0.7	NA	7.0 ± 0.7	*
19-Nov-2012			26.1	ND	ND	ND	>36 [g]
27-Feb-2013			15.7	3.0 ± 0.4	2.8 ± 0.3	2.9 ± 0.3	4 ± 2
16-Apr-2013			20.7	2.4 ± 0.3	2.1 ± 0.3	2.3 ± 0.2	15 ± 2
11-Jun-2013			21	2.6 ± 0.8	2.5 ± 0.8	2.6 ± 0.6	7 ± 4
AM-48/1	MW	1200					
21-Mar-2012			86.3	ND	NA	ND	>26 [g]
03-Oct-2012			36.8	ND	ND	ND	>31 [g]
05-Feb-2013			25.2	3.9 ± 0.5	4.2 ± 0.6	4.1 ± 0.4	4 ± 2
04-Apr-2013			44.3	2.7 ± 0.4	4.3 ± 0.6	3.5 ± 0.4	13 ± 4
AMD-12/1	MW	470					
21-Mar-2012			36.7	ND	ND	ND	>24 [g]
22-May-2012			51.4	2.6 ± 0.6	NA	2.6 ± 0.6	19 ± 4
19-Nov-2012			52.5	ND	ND	ND	>37 [f]
05-Feb-2013			17.9	2.9 ± 0.3	3.8 ± 0.5	3.4 ± 0.3	1 ± 2
16-Apr-2013			9.1	1.7 ± 0.2	2.6 ± 0.3	2.2 ± 0.2	0 ± 2
11-Jun-2013			4	1.6 ± 0.5	1.9 ± 0.6	1.8 ± 0.4	*
AMD-12/2	MW	500					
21-Mar-2012			74	2.5 ± 2.1	1.2 ± 1.6	1.9 ± 1.3	34 ± 15
26-Feb-2013			136	4.8 ± 1.6	10.3 ± 1.8	7.6 ± 1.2	20 ± 3
16-Apr-2013			142	ND	NA	ND	>41 [g]
11-Jun-2013			108	3.2 ± 2.7	10.1 ± 3.2	6.7 ± 2.1	18 ± 6
PW1	PW	1650					
04-Jun-2012			83.7	ND	NA	ND	>35 [g]
10-Dec-2012			29.9	ND	ND	ND	>38 [g]
04-Feb-2013			27.8	4.3 ± 0.5	4.4 ± 0.6	4.4 ± 0.4	4 ± 2
03-Jun-2013			26	2.7 ± 0.9	NA	2.7 ± 0.9	11 ± 4

Notes: [a] PW = Production Well; MW = Monitoring Well; [b] Dist. = distance from Kraemer Basin; for KBS-3/1 and AMD-12/2 distance is based on both distance and depth; [c] Reported error is 1σ counting error; [d] For field duplicates, the reported $^{35}SO_4$ activity is the average activity for the two samples; [e] Propagated counting error; [f] No yield correction performed for samples with greater than 100% recovery; [g] Apparent ^{35}S ages for samples with non-detectable activity are calculated using the 2σ counting error; * Apparent ^{35}S ages undetermined due to a higher $^{35}SO_4$ activity for groundwater relative to the source water end-member; ND = Non-detectable; NA = Not Available.

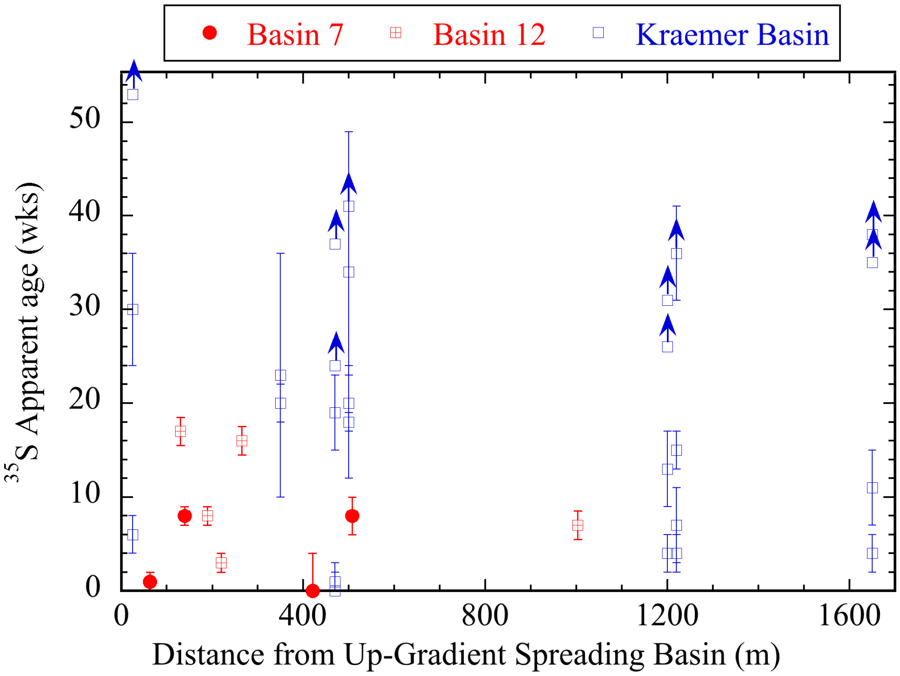


Figure 2. Apparent ^{35}S age plotted against distance down gradient for the nearest spreading basin. The two transects near the Atlantis MAR site are in red and the transect near the OCWD's Kraemer Basin is in blue. Samples with no detectable ^{35}S are indicated with arrows rather than error bars. See Tables 2 and 3 for the data.

4. Discussion

One of the significant findings of these two field experiments is that ^{35}S is detectable near MAR facilities and in MAR source water that contains a significant fraction of reuse water. Therefore, it may prove to be a valuable intrinsic tracer. However, there are a number of lessons to be learned from these initial studies.

4.1. The Atlantis MAR System

The lack of a systematic apparent age trend with distance downgradient from the spreading ponds is puzzling. The Atlantis MAR system was sampled at the end of the austral winter precipitation season when the groundwater basin was at its highest historic levels. In fact, ponding was observed in many of the topographic lows near the basins (Figure 3). It is also likely (based on screen depth) that the wells were sampling different aquifer zones along different flow paths. In fact, some of the well water may not have originated at the spreading ponds. Therefore, short-circuiting of the flow system is likely to have occurred. Finally, the color of many of the samples implies that there may be additional uncertainty in the analytical results due to potential interference with LSC. This result led to an improved methodology that was developed prior to the second study that took place in Southern California, USA.

The Atlantis study demonstrated that the ^{35}S method could be used in a relatively remote location with commonly available supplies such as a kitchen scale and a house drill. In fact, with a bit more prepping, the kitchen scale is not necessary (i.e., Amberlite™ and NaCl could be pre-weighed into small sample bottles or plastic bags). There does not appear to be any problem with storing the ^{35}S extracted into the saline solution for a few weeks prior to its precipitation as $BaSO_4$. This facilitates the transport and shipping of samples to the counting laboratory.

Figure 3. Photograph of WP226 at the Atlantis MAR system. The water level in the well was approximately equal to the surface of the small puddle.

4.2. The OCWD MAR System

Significantly more data was available at the OCWD MAR site than at the Atlantis site, most importantly the collection of time series measurements, better information about well distance and depths, MAR recharge rates, and additional information about travel time from earlier deliberate tracer experiments [9,37]. The OCWD MAR study focused on Kraemer basin and down gradient hydraulically connected wells. It shows that ^{35}S activity in both the source water and groundwater varies significantly. Therefore, it is necessary to collect time series measurements. Much of the uncertainty is most likely due to variations with the source water activity and the simplified piston flow model. As discussed by Urióstegui et al. [38], monthly to semi-monthly samples for the source water should be collected along with additional general chemistry to improve mixing models that could help improve the apparent age calculations.

To define the source water initial ^{35}S activity, A_0, the [SO_4] concentration of the well samples was used. Variations in Kraemer Basin ^{35}S activity can be partial explained by the mixing between GWRS and other source waters such as the SAR and MET water, which is composed of California State Water Project and Colorado River waters. GWRS is distinguished from these other sources by its low [SO_4]. To estimate the A_0, [SO_4] and ^{35}S activity of all of the source water measurements (many of which are from [38]) were used. Furthermore, it was assumed that high [SO_4] waters with low activities had undergone significant decay in addition to dilution with GWRS water (Figure 4). The liner fit through the cloud of remaining data, which we assume had little decay, was used to estimate A_0:

$$A_0 = 1.4 + 0.12\,[SO_4],\ R^2 = 0.92 \tag{2}$$

The resulting ^{35}S apparent ages range between <1 wk to >53 wks. In fact, in seven samples (from three wells) ages could not be calculated because the groundwater activity exceeded the source water value calculated with Equation (2). This shows that the source water initial activity is more complicated than simple mixing between low [SO_4] GWRS and other higher [SO_4] waters. Urióstegui et al. [38] used a different approach and estimated different ^{35}S apparent ages down gradient from Kraemer Basin.

As was observed from the Atlantis MAR study, the groundwater ^{35}S apparent ages did not systematically vary down gradient from the spreading pond at the OCWD MAR site (Figure 2); they did however vary with season [38]. One of the more interesting observations is the significant decrease in the ^{35}S apparent ages that occurred at both AM-8 and PW1 after January 2013 (Table 2). These wells are located down gradient from the La Jolla Spreading Basin. Although La Jolla Basin was recharging the underlying aquifer during the entire study period, its rate of recharge was significantly lower than Kraemer Basin (typically more than 5 times lower), except for a two-month period when neither basin recharged much due to the lack of water caused by the recent Californian drought (OCWD unpublished data). This intermittent suspension of recharge may have led to a change of groundwater flow near these two basins. The young ^{35}S apparent ages at these two wells suggest a different source water beginning with the February 2013 samples. Assuming that the other source was La Jolla Basin (mean 2013 ^{35}S activity = 15.2 mBq/L) and that it accounts for 100% of the groundwater, the mean ^{35}S apparent ages are, respectively, 22 wks and 26 wks for AM-8 and PW1. The assumption that, for these two wells, 100% of the groundwater originated at La Jolla Basin is clearly wrong based on the [SO_4] data. Once again this interpretation highlights the need for a better age dating model than the assumed piston flow model used in this paper.

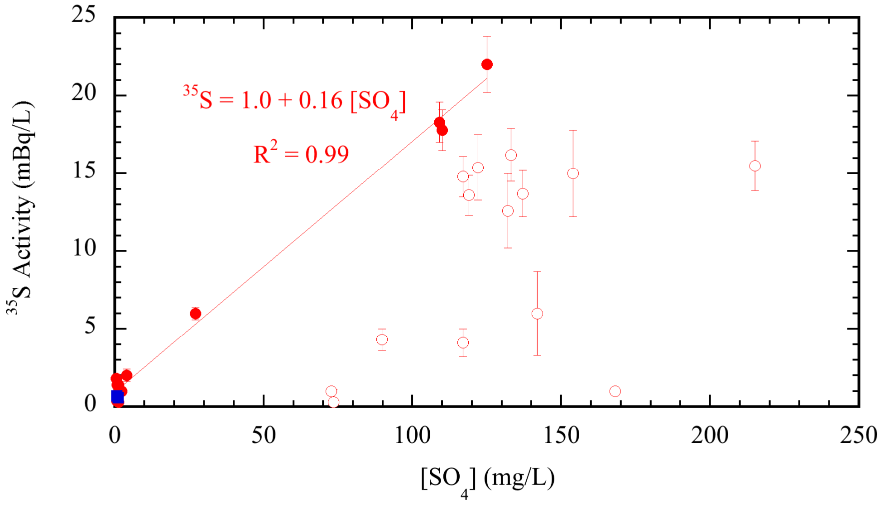


Figure 4. ^{35}S activities and [SO_4] from source water samples at the OCWD MAR site. The data is from either Table 1 or Urióstegui et al. [38]. The linear fit is for the data we believe have not undergone significant radioactive decay (filled red dots). The open red dots represent samples we interpret as having experienced significant radioactive decay and the blue squares are samples of GWRS water. The resulting line is used to calculate initial ^{35}S activities, A_0, for down gradient wells from Kraemer Basin (see Table 3).

5. Conclusions and Implications

These two initial ^{35}S studies demonstrate that this intrinsic tracer may be a new tool for investigating subsurface retention time near MAR sites. In particular, the ^{35}S method might become a valuable management tool for satisfying travel time requirements for GRRP in California USA. However, prior to its acceptance, additional work needs to be done. Assessing the frequency of sampling and developing improved models of apparent age are necessary. The Atlantis MAR study demonstrated that the ^{35}S method can be used in remote areas and partially processed small volume samples can be transport back the laboratory.

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