



Arsenic mobility and impact on recovered water quality during aquifer storage and recovery using reclaimed water in a carbonate aquifer

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ABSTRACT

Arsenic release from aquifers can be a major issue for aquifer storage and recovery (ASR) schemes and understanding the processes that release and attenuate As during ASR is the first step towards managing this issue. This study utilised the first and fourth cycles of a full scale field trial to examine the fate of As within the injectant plume during all stages of the ASR cycle, and the resultant water quality. The average recovered As concentration was greater than the source concentration; by 0.19 $\mu\text{mol/L}$ (14 $\mu\text{g As/L}$) in cycle 1 and by 0.34 $\mu\text{mol/L}$ (25 $\mu\text{g As/L}$) in cycle 4, indicating that As was being released from the aquifer sediments during ASR and the extent of As mobilisation did not decline with subsequent cycles. In the injection phase, As mobilisation due to oxidation of reduced minerals was limited to an oxic zone in close proximity to the ASR well, while desorption from Fe oxyhydroxide or oxide surfaces by injected P occurred further in the near well zone (0–4 m from the ASR well). With further aquifer passage during injection and greater availability of sorption sites there was evidence of attenuation via adsorption to Fe oxyhydroxides which reduced concentrations on the outer fringes of the injectant plume. During the period of aquifer storage, microbial activity resulting from the injection of organic matter resulted in increased As mobility due to reductive Fe oxyhydroxide dissolution and the subsequent loss of sorption sites and partial reduction of As(V) to the more mobile As(III). A reduced zone directly around the ASR well produced the greatest As concentration and illustrated the importance of Fe oxyhydroxides for controlling As concentrations. Given the small spatial extent of this zone, this process had little effect on the overall recovered water quality.

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1. Introduction

Arsenic release from sedimentary aquifers is a prevalent health issue affecting safe drinking water supplies (Chatterjee et al., 1995; Smedley and Kinniburgh, 2002; Bhattacharya et al., 2004; Duker et al., 2005). The processes postulated as leading to elevated concentrations of As in groundwater include oxidation of reduced As-bearing minerals, most commonly arsenian pyrite ($\text{FeAs}_x\text{S}_{2-x}$) or arsenopyrite (FeAsS) (Schreiber et al., 2003); reductive dissolution of Fe oxyhydroxide and the associated release of adsorbed As (Ahmed et al., 2004; Zheng et al., 2004; Keimowitz et al., 2005; Smedley et al., 2005; Postma et al., 2007); ligand exchange or displacement from sorption sites (Appelo et al., 2002; Smedley et al., 2003; Stollenwerk, 2003; Radu et al., 2005; Bauer and Blodau, 2006); and desorption following the reduction of As(V) to As(III) (Bose and Sharma, 2002; Oremland and Stolz, 2003). Conversely, As concentrations are reportedly controlled by attenuation mechanisms such as sorption, typically to amorphous $\text{Fe}(\text{OH})_3$,

goethite or hematite (Dixit and Hering, 2003; Foster, 2003; Stollenwerk, 2003; Giménez et al., 2007), but also carbonates (Charlet et al., 2007; Sørensen et al., 2008) under oxidising conditions and precipitation of sulfides (Kirk et al., 2004) under SO_4 reducing conditions.

Aquifer storage and recovery (ASR) is a technology for storing water in aquifers which utilises the same well for injection and recovery (Pyne, 2006). ASR provides storage to balance water resource availability with demand, without the evaporative losses or surface footprint associated with above ground storage systems. Arsenic release from aquifers can be a major issue for the water quality recovered from an ASR scheme and understanding the possible mechanisms that release and attenuate As in the aquifer aids in managing this issue. The recharge source, whether it is a surface water, groundwater, urban runoff or wastewater, is generally oxygenated. Well injection allows access to deeper confined anaerobic storage zones, often within variably confined carbonate and siliclastic aquifers that are not suited to infiltration. Thus by oxygenating the anoxic storage zone, injection can result in oxidation of reduced sulfide minerals (Herczeg et al., 2004) and the subsequent release of trace elements such as As from the aquifer (Stuyfzand, 1998; Arthur et al., 2001, 2005; Stuyfzand et al., 2002). Dissolution

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of carbonate minerals following injection of water not in equilibrium with the minerals in the storage zone (Mirecki et al., 1998; Le Gal La Salle et al., 2005) may also be considered as a pathway for As mobilisation in cases where arsenate is adsorbed to carbonate surfaces (Sø et al., 2008). Injection of organic matter in reclaimed water can also influence As mobility through abiotic and biotic processes such as competition between dissolved organic matter (DOM) and arsenate for sorption sites (Bauer and Blodau, 2006); loss of sorption sites through reductive dissolution of Fe(III); or increased mobility in the aqueous phase by reduction of As, from As(V) present at neutral pH in the charged species HAsO_4^{2-} to As(III) in the uncharged H_3AsO_3 species (Appelo and Postma, 1999). Once released, the mobility of these As species depends on the chemical environment within the aquifer, which can also result in subsequent removal prior to recovery, predominantly attributed to sorption under favourable conditions. In an ASR scheme the chemical environment can be quite transient, varying spatially within the plume of injected water and also temporally throughout the various stages of the cycle. In addition, the use of reclaimed wastewater containing organic matter in ASR can amplify the redox gradients that develop (Vanderzalm et al., 2006).

Despite being reported as a prevalent issue for the water recovered from an ASR scheme (Arthur et al., 2001, 2005; Price and Pichler, 2006; Vanderzalm et al., 2009), considerable uncertainty remains regarding the processes responsible for As mobilisation and immobilisation during the ASR cycle and the extent of their impact on the utility of the recovered water. Price and Pichler (2006) found As concentrated within pyrite framboids in Florida's Suwannee Limestone aquifer, where ASR operations have recovered As concentrations up to $130 \mu\text{g As/L}$ (Arthur et al., 2005). The likely mechanism of As mobilisation in this system was suggested to be through pyrite oxidation (Jones and Pichler, 2007). Following As release through pyrite oxidate, newly formed amorphous $\text{Fe}(\text{OH})_3$ can play an important role in controlling the mobility of As in the storage zone (Arthur et al., 2007; NRC, 2008). This paper uses the fate of a suite of environmental tracers, including As(III) and As(V) concentrations, to examine the processes impacting on the mobility of As during the injection, storage and recovery stages of the ASR cycle in a carbonate aquifer and their influence on the quality of water that is recovered.

2. Study site

A full-scale ASR trial at Bolivar, in the northern metropolitan area of Adelaide, South Australia (Dillon et al., 1999) between October 1999 and March 2010 investigated the mobilisation of As from a carbonate aquifer. Four ASR cycles were undertaken, injecting $704 \times 10^3 \text{ m}^3$ and recovering $501 \times 10^3 \text{ m}^3$, in total (Table 1). The period of storage undertaken in each ASR cycle varied considerably from 28 days (cycle 2) to 320 in cycle 3, with cycles

1 and 4 comparable at 111 and 178 days, respectively. The ASR field site was situated adjacent to a supply of reclaimed water for injection, from the Bolivar Water Reclamation Plant (WRP; located at the wastewater treatment plant), and in close proximity to a horticultural region utilising the reclaimed water for a seasonal irrigation source (Fig. 1). The reclaimed water had undergone secondary treatment, detention in wastewater stabilisation ponds, dissolved air flotation/filtration (DAFF) and chlorination. Biological nutrient removal (BNR) replaced trickle filters in January 2001 (cycle 1). Additional wellhead chlorination was operational intermittently through the ASR trial to control biological clogging (Pavelic et al., 2007).

The storage zone was the lower Tertiary sediments (T2) of the Port Willunga Formation, an approximately 60 m thick calcarenite aquifer. The ASR well was completed and open over most of the T2 aquifer thickness, approximately 100–160 m below ground surface (bgs) (Fig. 2) and separated from the overlying T1 limestone aquifer by a 7.5 m thick confining clay layer. Eleven sub-samples taken from intact cores of aquifer material collected between 104 and

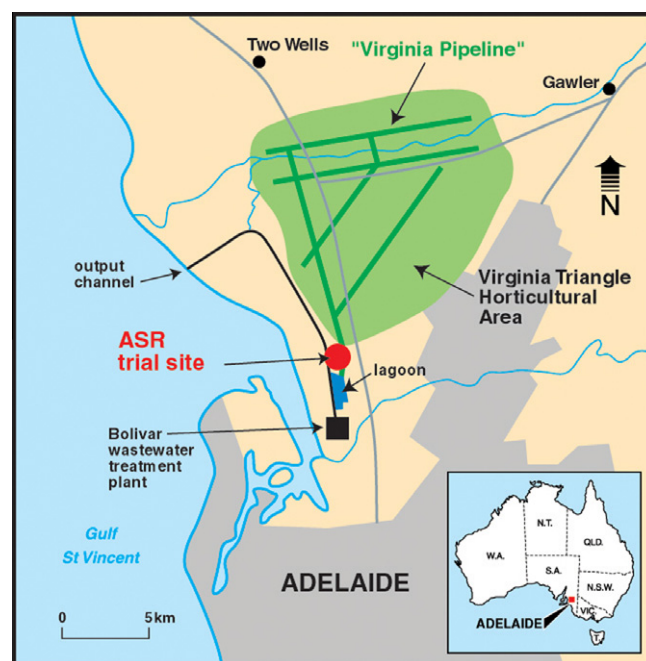


Fig. 1. Location of the Bolivar ASR site, situated adjacent to a supply of reclaimed water for injection, from the Bolivar wastewater treatment plant and in close proximity to a horticultural region utilising the reclaimed water for a seasonal irrigation source.

Table 1
Summary of ASR cycle testing for the Bolivar ASR scheme.

Within cycle no.	Period			Net volume ($\times 10^3 \text{ m}^3$)	Cum. net volume ($\times 10^3 \text{ m}^3$)	Avg. flow rate (L/s)
		Date	Days since start of trial			
Injection	1	11th Oct to 23rd Nov 1999	0–43	29	29	7.9
	1	4th to 21st Apr 2000	176–193	6	35	9.5
	1	4th Aug 2000 to 29th Mar 2001	298–535	215	250	11.5
	2	5th Mar to 27th Jun 2002	876–990	114	364	11.9
	3	11th Dec 2003 to 28th May 2004	1522–1691	155	519	11.2
	4	26th Aug 2008 to 16th Mar 2009	3242–3444	185	704	9.8
Recovery	1	18th Jul to 28th Nov 2001	646–779	152	152	15.0
	2	25th Jul to 8th Oct 2002	1018–1093	91	243	15.0
	3	22nd Apr to 21st Jul 2005	2020–2110	123	366	15.9
	4	10th Sep 2009 to 25th March 2010	3622–3816	135	501	8.7

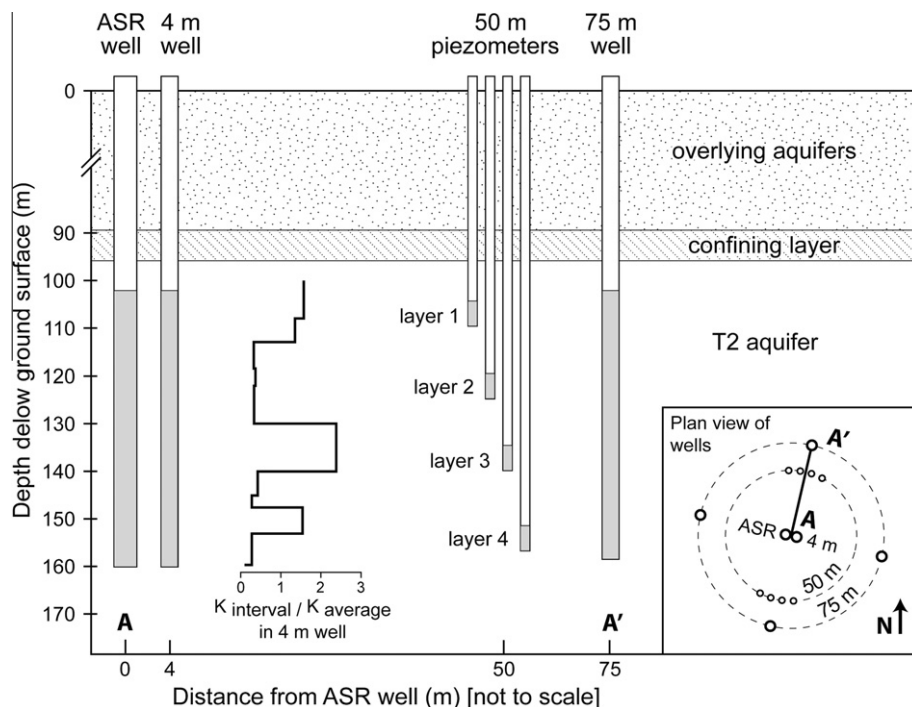


Fig. 2. Simplified vertical section (see inset) of the T2 aquifer showing the depth intervals intersected by the ASR well, 4 m fully penetrating well and the 50 m piezometers (Vanderzalm et al., 2006).

156 m below ground revealed that the mineralogy is dominated by calcite (74%) and quartz (18%), with minor contributions from ankerite (4.8%), microcline (1.9%), albite (<1%) and hematite (<0.5%). The intact cores of aquifer material were stored in N-filled sealed tubes and refrigerated immediately after sampling to minimise the potential for oxidation after sampling. Furthermore, sub-samples were taken after removal of the outer surface of the core material that may have been contaminated by drilling fluids or oxidation. Hematite was identified in all samples of T2 core material ($n = 11$) but reported at less than the XRD detection limit of 0.5%. The average sediment organic C and cation exchange capacity are 0.2% and 20 meq/kg, respectively. Pyrite framboids were identified with scanning electron microscopy (Rinck-Pfeiffer et al., 2000), but have not been quantified, within the samples of T2 aquifer material from this site. However, the pyrite content of the T2 aquifer has previously been reported as $1 \pm 0.8\%$ at a site approximately 11 km to the NE (Herczeg et al., 2004) with an average As content within the T2 aquifer of 50 ppm (6–144 ppm) at a site 9 km to the SE (Vanderzalm et al., 2010).

Horizontal hydraulic conductivity varies over almost 3 orders of magnitude (10^{-1} to 10^2 m/day) when measured on core samples over a 10 cm scale (Wright et al., 2002), and the storage zone can be represented by four horizontal layers, alternating between high and low permeability (Pavelic et al., 2006). The average hydraulic conductivity derived from a pumping test over the whole aquifer thickness is 3 m/day (Martin et al., 1998). This work reports hydrogeochemical data from the ASR well, a fully penetrating observation well 4 m from the ASR well and one piezometer 50 m (50 m n-3) from the ASR well, intersecting a high permeability layer from 134 to 139 m bgs (layer 3). Travel time to the 4 m radius is approximately 1–2 days (Pavelic et al., 2006), representing changes soon after injection, while travel time to the 50 m radius is of the order of 100 days and is close to the outer fringe of the injectant plume. This examination focuses on As mobility during two full ASR cycles; the first and fourth ASR cycles, to compare the response of the carbonate aquifer to reclaimed water injection over time.

The dominant geochemical processes and water quality changes during reclaimed water ASR at Bolivar have been examined previously in: a quantitative reactive transport model of the first ASR cycle (Greskowiak et al., 2005); an isotopic assessment of the organic and inorganic C cycles in cycle 1 (Le Gal La Salle et al., 2005); an understanding of redox processes and the fate of organic matter in cycle 1 and 2 (Vanderzalm et al., 2006); and an evaluation of the association between source water quality and clogging processes over 3 ASR cycles (Pavelic et al., 2007). A summary of the major geochemical reactions is presented as background prior to examining the mobility of As under varying conditions during the ASR cycles. The water recovered after ASR was anoxic, with a lower nutrient content but higher Ca concentration than the source water, as a result of removal through redox reactions induced by the injection of organic C and dissolution of calcite (Greskowiak et al., 2005; Le Gal La Salle et al., 2005; Vanderzalm et al., 2006). These processes were observed within the first 4 m of aquifer passage during the injection phase in water quality changes at the 4 m observation well and the zone immediately surrounding the ASR well was reported as one of high microbial activity (Greskowiak et al., 2005; Pavelic et al., 2007). The redox state of the ambient groundwater prior to ASR and of the groundwater in the storage zone during most of the ASR cycles was predominantly denitrifying with some Fe reduction (both Fe(II) and Fe(III) are present) (Vanderzalm et al., 2006). Oxidic conditions were evident at 4 m during the initial stages of injection prior to acclimation of the indigenous microbial population to the source water, and NO_3^- was detected in the groundwater at 4 m when the source water concentration was above 0.1 mmol/L with complete removal prior to the 50 m radius. With cessation of flow during aquifer storage, the most notable change in redox state was evident with a more reduced condition developing around the ASR well, progressing to methanogenesis in the first ASR cycle and to SO_4 reduction in three subsequent cycles. In contrast at the 4 m radius, only a marginal increase in dissolved Fe was evident with storage, SO_4^{2-} remained stable and CH_4 was not detected. Calcite dissolution was rapid, largely complete within 4 m resulting in neutral pH and serving as an important relief to

biological clogging (Pavelic et al., 2007). Dissolution was induced by the undersaturation of the injectant with respect to carbonate minerals and to buffer the production of biogenic CO₂ (Le Gal La Salle et al., 2005).

3. Methods

Sampling, preservation and analysis methodology was based on the Standard Methods for the Examination of Water and Wastewater (APHA, 1998). Ground water samples were collected after stabilisation of pH, temperature, DO, EC and Eh, in accordance with appropriate well purging (approximately 3 well volumes). These physical parameters were measured *in situ* using a TPS-FL90[®] probe in a flow-through cell, directly from the pump discharge to prevent atmospheric exposure. Eh values were measured with a TPS Ag/AgCl electrode and were reported relative to the standard H electrode (SHE) after calibration against Zobell's solution. Alkalinity was determined by potentiometric titration to an end-point pH of 4.5 and reported as HCO₃⁻; Cl⁻, N and P were determined by colorimetric flow analysis; major ions, metals and metalloids were determined by inductively coupled plasma-optical emission spectroscopy (ICP-ES; Spector); organic C (OC) concentrations were measured by potassium persulfate/ultra-violet oxidation with detection by flame ionisation; and δ³⁴S of dissolved SO₄²⁻ was measured using elemental analysis isotope ratio mass spectrometry (Carmody et al., 1998) and expressed in comparison to the triolite phase of the Canyon Diablo meteorite (CDT). The molar percentages of dissolved gas present in groundwater were determined by head-space gas chromatography, with a detection limit of 0.01%. Metal and metalloid samples were acidified immediately after sampling with HNO₃ to pH < 2. Dissolved metal and metalloid samples were filtered through a 0.45 µm filter immediately after sampling and prior to acidification. Analysis of total As in samples filtered through a 0.45 and 0.20 µm filter was undertaken for eight samples to evaluate the importance of colloidal As in the size fraction 0.20–0.45 µm in water samples. Samples were maintained below 4 °C and transported to the Australian Water Quality Centre (AWQC), Bolivar, South Australia for analysis within 24 h of sampling. Analysis of dissolved As(III) and As(V) in waters was undertaken in the fourth cycle only and all samples were filtered through 0.45 µm filters, preserved with ultrapure HCl and maintained below 4 °C in the dark (McCleskey et al., 2004) prior to As speciation analysis at the CSIRO Land and Water, Adelaide. The total As(III) concentrations in solutions were determined by hydride generation-inductively coupled plasma-mass spectrometry (HG-ICP-MS) (Maher et al., 2003; Kirby et al., 2004). The As(III) concentrations in samples were determined following the formation of As(III)H₃ volatile hydrides through the addition of 2 M HCl and 1% sodium tetrahydroborate, the volatile As(III)H₃ species were directly analysed by ICP-MS by measuring the As intensity at m/z 75. Total As(V) concentrations were determined through the difference between total As concentrations determined by ICP-MS and total As(III) concentrations by HG-ICP-MS. Arsenic concentrations (intensities) were determined by ICP-MS using an Agilent 7500ce with He as a collision gas at a flow rate of 2 mL/min. The quantification limit (QL) for As(III) by HG-ICP-MS was 0.1 µg/L and for total As by ICP-MS was 0.4 µg/L.

A conceptual understanding of the processes controlling As mobility was developed by examining time series water quality data and using Cl⁻ as a conservative tracer to quantify the change in the concentration of non-conservative species (e.g. As) via mass balance calculation. The calculation of As excess, or release from the aquifer, was based on the mass balance or difference between the measured concentration and the concentration expected from conservative mixing alone, using Cl⁻ as a conservative tracer.

$$[M]_{mb} = [M]_{meas} - (f[M]_{inj} + (1-f)[M]_{gw}) \quad (1)$$

and

$$f = \frac{[Cl]_{meas} - [Cl]_{gw}}{[Cl]_{inj} - [Cl]_{gw}} \quad (2)$$

where [M]_{meas} = species concentration measured in sample (mmol/L), [M]_{gw} = species concentration in ambient groundwater (mmol/L), [M]_{inj} = species concentration in injectant (mmol/L), [M]_{mb} = species mass balance (mmol/L).

4. Results

The Bolivar ASR scheme injected an oxygenated source water rich in N, P and organic C into a carbonate storage zone containing brackish anaerobic water (Table 2). The pH of the carbonate storage zone remained neutral with any acidity within the injectant or produced *in situ* buffered by carbonate dissolution soon after injection (Vanderzalm et al., 2006). Prior to the commencement of the ASR trial, the As concentration in the undisturbed groundwater of the T2 aquifer was on average 0.07 µmol/L, and largely dissolved (0.05 µmol/L). The concentrations of soluble As(III) and As(V) were measured in the ambient groundwater of the T2 aquifer before the start of the fourth ASR cycle, from a well 300 m from the ASR well and not affected by previous ASR cycles which indicated that soluble As in the ambient groundwater was dominated by

Table 2

Comparison of average water quality for the Bolivar ASR scheme (average ± std deviation).^a

mmol/L unless stated	Ambient ⁽²²⁾	Injected ⁽⁴⁰⁾	Recovered ⁽³⁴⁾
Temp (°C)	26 ± 1	19 ± 5 ⁽³⁷⁾	21 ± 3 ⁽²¹⁾
pH (pH units)	7.3 ± 0.1	7.1 ± 0.5	7.3 ± 0.2 ⁽²¹⁾
Eh (mV SHE)	50 ± 60	450 ± 290 ⁽³⁸⁾	40 ± 40 ⁽²¹⁾
O ₂	<0.02	0.17 ± 0.11	<0.02 ⁽²⁹⁾
EC (ms/cm)	3.5 ± 0.4	2.1 ± 0.2	2.2 ± 0.2 ⁽²⁹⁾
Cl ⁻	26 ± 3 ⁽³²⁾	12 ± 1	13 ± 2
SO ₄ ²⁻	2.8 ± 0.4	2.0 ± 0.2	2.2 ± 0.2
HCO ₃ ⁻	4.5 ± 0.9	4.0 ± 1.3	4.7 ± 0.5
Ca ²⁺	3.8 ± 0.4	1.1 ± 0.2	1.7 ± 0.2
Na ⁺	21 ± 3 ⁽³²⁾	13 ± 1	13 ± 1
Mg ²⁺	3.2 ± 0.4	1.5 ± 0.1	1.6 ± 0.3
K ⁺	0.4 ± 0.1	1.2 ± 0.2	1.1 ± 0.1
TOC	0.05 ± 0.05	1.4 ± 0.4	1.0 ± 0.4
DOC	0.05 ± 0.05	1.3 ± 0.3	1.0 ± 0.5
TKN	0.006 ± 0.003	0.82 ± 0.81	0.3 ± 0.2
NH ₄ ⁺ -N	0.005 ± 0.002	0.63 ± 0.78	0.2 ± 0.2
NO ₃ ⁻ -N	<0.0004	0.20 ± 0.21	0.009 ± 0.02
TP	0.0009 ± 0.0006	0.046 ± 0.044	0.024 ± 0.017
Filterable reactive P (FRP)	<0.0002	0.035 ± 0.043	0.020 ± 0.015
Fe total	0.02 ± 0.01	0.004 ± 0.009 ⁽³⁶⁾	0.012 ± 0.009
Fe soluble	0.01 ± 0.01	0.002 ± 0.005 ⁽²⁴⁾	0.009 ± 0.004 ⁽¹⁹⁾
Mn total	0.0005 ± 0.0002	0.001 ± 0.001 ⁽²⁹⁾	0.001 ± 0.001 ⁽¹⁹⁾
Mn soluble	0.0005 ± 0.0002	0.0009 ± 0.0007 ⁽²⁹⁾	0.001 ± 0.002 ⁽¹⁹⁾
As total (µmol/L)	0.07 ± 0.04	0.04 ± 0.03 ⁽³²⁾	0.30 ± 0.16 ⁽²²⁾
As soluble (µmol/L)	0.05 ± 0.01	0.03 ± 0.01 ⁽²⁷⁾	0.27 ± 0.13 ⁽²⁰⁾
As(III) soluble (µmol/L) ^b	<0.001 ^c	<0.001 ⁽⁵⁾	0.34 ± 0.14 ⁽²⁾
As(V) soluble (µmol/L) ^b	0.02 ^c	0.037 ± 0.009 ⁽⁵⁾	0.09 ± 0.09 ⁽²⁾

Number of samples are shown in superscript in parenthesis.

^a half detection limit was substituted for measurements reported as < detection limit.

^b As(III) and As(V) only measured in cycle 4 and therefore the sum does not equal the average soluble As concentration.

^c 1 sample taken prior to cycle 4 from a background well 300 m from the ASR well.

As(V) alone. The soluble As in groundwater within the storage zone (ASR, 4 m, 50 m wells) in between cycle 3 and 4 also showed the predominance of As(V). Arsenic within the reclaimed water injectant was also predominantly in the soluble fraction, present as As(V) and with an average concentration of $0.04 \mu\text{mol/L}$. The concentrations of As(III) and As(V) in samples filtered through $0.2 \mu\text{m}$ and $0.45 \mu\text{m}$ were comparable, indicating that soluble As was not associated with the colloidal fraction of $0.2\text{--}0.45 \mu\text{m}$.

The As concentration in water recovered from the ASR well following each cycle was greater than that injected ($0.04 \mu\text{mol/L}$) or within the ambient groundwater ($0.05 \mu\text{mol/L}$) (day 0) (Fig. 3), indicating release due to water–rock interactions in the ASR cycle. The magnitude of the net increase in As was, on average, $0.19 \mu\text{mol/L}$ ($14 \mu\text{g As/L}$) and $0.34 \mu\text{mol/L}$ ($25 \mu\text{g As/L}$) in cycles 1 and 4, respectively (Fig. 4). For comparison, the recovered water in cycle 3 was approximately $0.22 \mu\text{mol/L}$ ($16 \mu\text{g As/L}$) greater than that expected from conservative behaviour and the behaviour in cycle 2 is unknown as As concentrations were not measured. Thus the extent of As mobilisation did not diminish over 4 full ASR cycles, where a total volume of $704 \times 10^3 \text{ m}^3$ of reclaimed water injection had been undertaken. The As present in the recovered water was present as both As(III) and As(V), but predominantly as As(III).

The processes that lead to increased As in the recovered water at Bolivar can be examined by considering the temporal and spatial fate of As during the injection and storage phases. During the injection phase, an increase in As of approximately $0.11 \mu\text{mol/L}$ was evident in the 4 m observation well within only 1–2 days residence time in the aquifer. The soluble As fraction between injection and the 4 m well was present mainly as As(V). In contrast the As concentration at the 50 m radius, the edge of the injectant plume, remained similar to the ambient condition without any evidence of mobilisation from the aquifer matrix. While the net As concentration did not increase at 50 m, the relative contribution of As species varied during the ASR cycle. Prior to ASR and during injection, soluble As at the 50 m radius was comprised of As(V) alone, while during storage and recovery both As(III) and As(V) were present.

There was evidence of As release at both the ASR and 4 m wells during the storage phase. Arsenic concentrations increased consid-

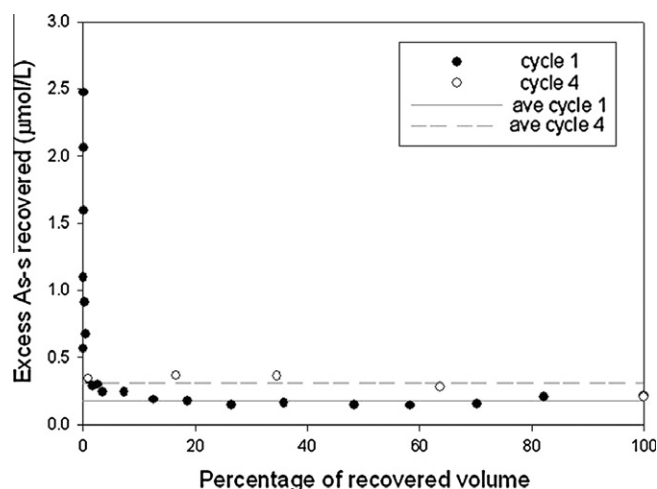


Fig. 4. Excess As in water recovered from the ASR well during the first and fourth cycles at Bolivar. Excess As was calculated from the difference between the measured concentration and the concentration expected from conservative mixing alone, using Cl^- as a conservative tracer.

erably under the more reducing redox state that developed around the ASR well during aquifer storage reaching $1.4 \mu\text{mol/L}$ after 69 days of storage in cycle 1 and $1.3 \mu\text{mol/L}$ after 175 days in storage in cycle 4. The maximum As concentration reached at 4 m, $0.19 \mu\text{mol/L}$ cycle 1 and $0.28 \mu\text{mol/L}$ cycle 4, at the end of the storage phase remained an order of magnitude lower than in the ASR well, and similar to the concentrations observed in the injection phase. The peak concentration (and excess), of $2.5 \mu\text{mol/L}$, occurred with 80 m^3 of recovery in cycle 1, but rapidly declined within around $1 \times 10^3 \text{ m}^3$ ($<0.5\%$) of recovery to plateau to a reasonably constant concentration during each recovery phase (Fig. 4). The As gain during the fourth storage cycle was contributed by both As species but the As(III) component remained consistent at around $0.3 \mu\text{mol/L}$ and the As(V) component was variable reaching $1 \mu\text{mol/L}$ (coinciding with the peak in soluble As of $1.3 \mu\text{mol/L}$).

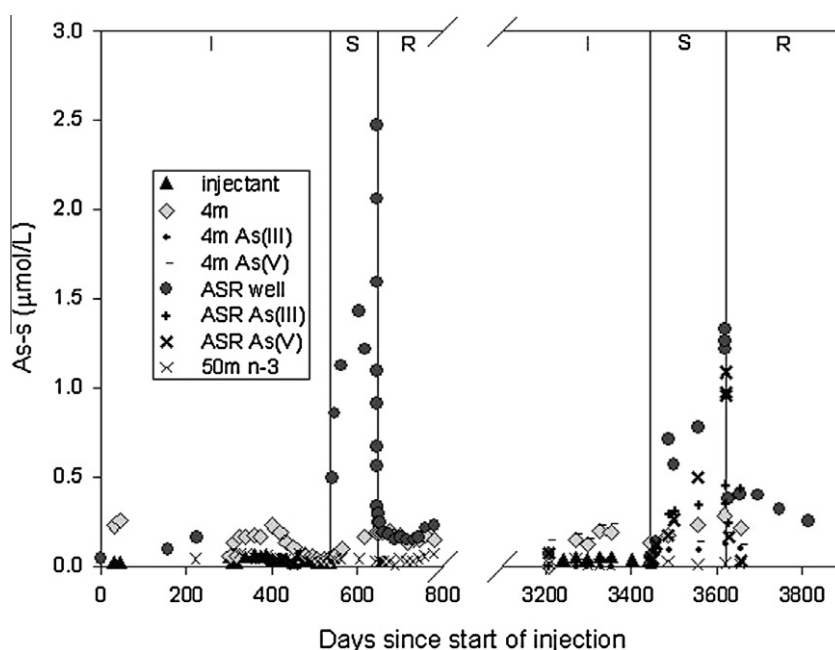


Fig. 3. Soluble As behaviour during the first (days 0–779) and fourth (days 3242–3816) ASR cycles at Bolivar. As(III) and As(V) concentrations in the ASR and 4 m wells are shown for the fourth cycle. I = injection; S = storage; R = recovery.

5. Discussion

Arsenic mobilisation was apparent through the ASR cycle with an average gain of approximately 0.23 $\mu\text{mol/L}$ (17 $\mu\text{g As/L}$) in the recovered water based on cycles 1, 3 and 4. A small portion ($\sim 0.01 \mu\text{mol/L}$) of insoluble As was injected but accumulation and dissolution of particulate bound As does not account for the observed gain in soluble As concentrations. While the As concentrations found in recovered water were below the long-term trigger value for As in water used for irrigation, 100 $\mu\text{g/L}$ (ANZECC and ARMCANZ, 2000), the Bolivar ASR trial provides an opportunity to investigate the dominant mechanisms behind the As mobilisation.

5.1. Injection phases processes

One possible explanation for the As mobilisation is the oxidation of pyrite in an oxic environment around the site of injection. Pyrite oxidation (Eq. (3)) was previously documented during a nearby stormwater ASR operation also targeting the T2 aquifer but the impact on As concentrations was not reported. The extent of pyrite oxidation was limited by the availability of reactive pyrite and thus affected only the initial $1.2 \times 10^3 \text{ m}^3$ of a total $2.6 \times 10^3 \text{ m}^3$ injection (Herczeg et al., 2004).



Some penetration of O_2 to the 4 m radius was observed during the early stage of injection only, with a dissolved O_2 concentration of 0.17 mmol/L in groundwater from the 4 m well after only 2 days of injection. Assuming an As to Fe molar ratio of 0.0054 (Stuyfzand, 1998), a gain of 0.11 $\mu\text{mol/L}$ As between injection and the 4 m observation equates to gains in Fe and SO_4^{2-} of 0.02 mmol/L and 0.04 mmol/L, respectively (Eq. (3)). However, aside from an early peak in Fe (also Ni and Zn) the concomitant increases in Fe expected from pyrite oxidation following injection were not observed (Fig. 5). In an oxic environment the Fe(II) released from pyrite oxidation may be oxidised to Fe(III) oxyhydroxides such as goethite (FeOOH) and amorphous $\text{Fe}(\text{OH})_3$, depending on pH. These newly formed amorphous Fe oxyhydroxides, along with resident oxide minerals such as hematite, can then immobilise any As that is released during pyrite oxidation via adsorption (Stollenwerk, 2003). If Fe oxyhydroxide effectively scavenges As, the net effect of this process may not be obvious through a change in the aqueous concentrations of As and Fe. However, it does alter the contributions of As associated with sulfide minerals and Fe oxides within the sediments, which in turn impacts on the mobility of As during the storage and recovery phases of an aquifer storage and recovery cycle.

The magnitude of the SO_4^{2-} addition was not significant enough to be distinguished from the large pools of native and injected SO_4^{2-} at 2.8 mmol/L and 2.3 mmol/L, respectively. Sulfur isotopes can be useful in identifying pyrite oxidation as this process introduces light SO_4^{2-} with a negative $\delta^{34}\text{S}$ signature (Herczeg et al., 2004) which is quite distinct from the enriched $\delta^{34}\text{S}$ signatures of the ambient groundwater (11.3‰ CDT) and the reclaimed water injectant (10.2‰ CDT). However, in this case, the amount of SO_4^{2-} addition from pyrite oxidation was not great enough to influence the $\delta^{34}\text{S}$ signature of SO_4^{2-} sampled from the fully penetrating 4 m observation well, aside from targeted sampling in discrete intervals soon after injection commenced. The highest ambient As concentrations, 0.09–0.19 $\mu\text{mol/L}$, were found in less permeable layers of the aquifer, from approximately 119–124 m bgs and 151–156 m bgs (layers 2 and 4 in Fig. 2). Groundwater samples taken from layer 2 using packer sampling after $20 \times 10^3 \text{ m}^3$ of injection and full penetration of the injectant, indicated elevated total Fe

(0.59 mmol/L) and total As (5.8 $\mu\text{mol/L}$) concentrations and a ^{34}S signature depleted by 2‰ when compared with the other intervals.

The second mechanism to be considered for As mobilisation in this reclaimed water ASR scheme is displacement from surface complexation sites. Initially As(V) was the dominant As species present in the ambient groundwater, likely to be present as HAsO_4^{2-} under the Eh and pH of the storage zone (Stollenwerk, 2003) suggesting that aquifer surface complexation sites would also contain As(V), as this charged species is prone to adsorption. Injection of nutrient-rich reclaimed water can lead to displacement of As due to competition for surface complexation sites, often attributed to HPO_4^{2-} (Smedley et al., 2003; Stollenwerk, 2003). The average P concentration injected was 0.046 mmol/L, but this varied considerably with P concentrations in the injectant an order of magnitude higher in the fourth cycle (average 0.08 mmol/L) than in the first (average 0.009 mmol/L) (Fig. 6). While the extent of As mobilisation did not increase proportionally, based on the recovered water quality it was greater in the fourth cycle (0.34 $\mu\text{mol/L}$) than in the first (0.19 $\mu\text{mol/L}$).

Overall there was a weak positive correlation between the excess in As measured at the 4 m well during the injection cycle and the ratio of total P to soluble As for cycle 1 (Fig. 7) where a low injectant TP/As-s ratio tended to coincide with low As release ($< 0.05 \mu\text{mol/L}$ excess As). However, this was not evident during the fourth cycle injection phase (Fig. 7), suggesting that the impact of displacement in the near well zone (0–4 m) reduced with time. The variability in the concentration of P in the injected source water equates to a minimum in the ratio of total P to soluble As (TP/As-s) of 78. This is expected to have a significant impact on the adsorption of As given that a PO_4^{3-} to As (V) ratio of 10:1 has previously been reported to cause a 50% reduction in the adsorption of As(V) at neutral pH (Stollenwerk, 2003). Neither of these two mechanisms for As release, pyrite oxidation and desorption by injected P, altered the As species present and As (V) remained dominant during the injection phase.

The elevated As concentrations observed in the near well zone were not evident on the outer fringe of the injected plume at the 50 m radius, suggesting As attenuation occurs with further aquifer passage between 4 m and 50 m. Attenuation of As with aquifer passage has previously been documented in dual well schemes via adsorption to newly formed amorphous Fe oxyhydroxide surfaces (Stuyfzand et al., 2002). This behaviour was also illustrated for P, which forms similar surface associations to As(V) (Stollenwerk, 2003), indicating the importance of sorption in controlling the aqueous concentrations of anions during migration of the injected front in the aquifer.

Given that calcite can also provide sorption sites for As, calcite dissolution could also provide a mechanism for As release (Stollenwerk, 2003). However, in this case no correlation was observed between the calculated excess for As and Ca. Also, the period of greatest calcite dissolution during the latter stage of injection cycle 1 coincided with low As concentrations, suggesting that calcite dissolution was not responsible for As mobilisation.

5.2. Storage phase processes

The magnitude of As release increased during aquifer storage with the onset of a reduced redox state where a third mobilisation mechanism, reductive dissolution of As-containing Fe oxyhydroxide surfaces is indicated by a concomitant increase in Fe (Fig. 5). It is possible that some of the Fe and As release is due to recycling of microbial biofilm, where trace amounts of elements may be concentrated (Sonzogni et al., 2004). Reductive dissolution of Fe oxyhydroxide surfaces and the loss of sorption sites provides the potential to exceed guideline values for irrigation (cycle 1), but this can be managed by discarding the initial volume of recovered

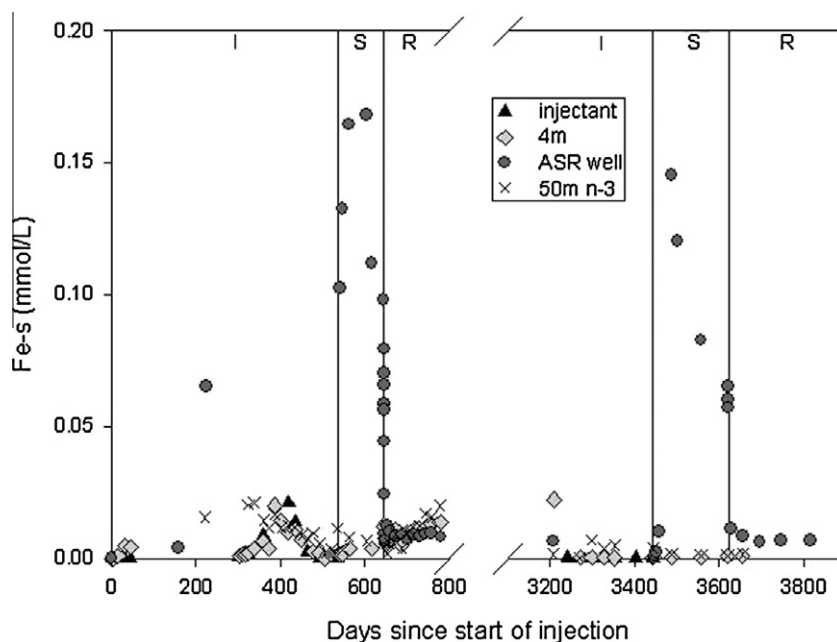


Fig. 5. Soluble Fe behaviour during the first and fourth ASR cycles at Bolivar. I = injection; S = storage; R = recovery.

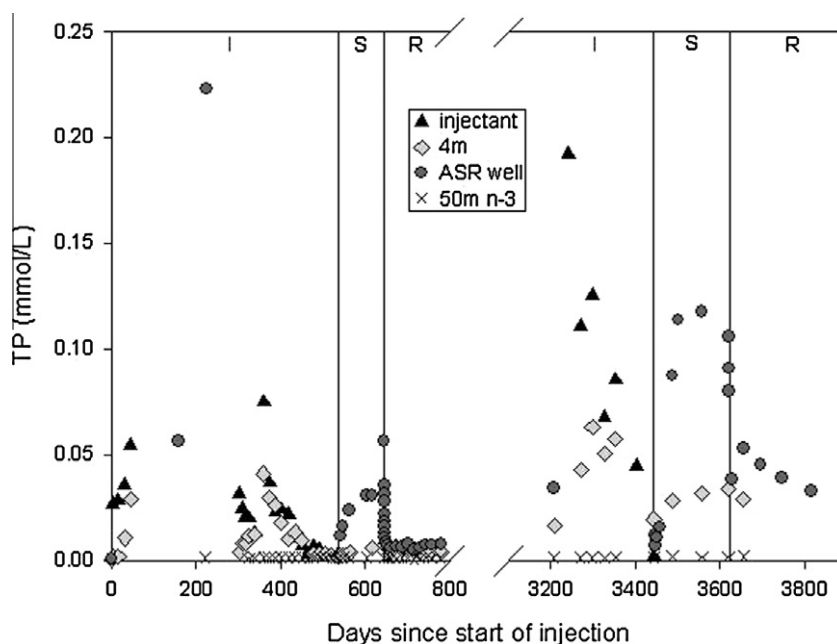


Fig. 6. Phosphorus behaviour during the first and fourth ASR cycles at Bolivar. I = injection; S = storage; R = recovery.

water. The elevated concentrations of elements such as As, Fe and organic C (OC), at the start of recovery were found to be mainly present in the soluble fraction and thus not caused by the physical removal of biofilm encrustations. The magnitude of this As increase indicates that a significant amount of As was immobilised by newly-formed Fe oxyhydroxides that form in the vicinity of the ASR well due to pyrite oxidation during injection. Increases in As and Fe concentrations due to microbially mediated reductive Fe oxyhydroxide dissolution under the reduced conditions that develop under low or no-flow has previously been reported in domestic supply wells in a confined sandstone aquifer despite there being a low organic C content ($\text{DOC} < 1 \text{ mg/L}$) (Gotkowitz et al., 2004; Sonzogni et al., 2004). In the T2 aquifer reductive Fe dissolution

and subsequent As mobilisation under no-flow (storage) are most evident around the ASR well but also further out in the storage zone (e.g. 4 m but not seen at 50 m) suggesting that mobilisation, then immobilisation occurs near to injection. There is also a partial reduction of As(V) to As(III) during storage which may enhance the desorption process in the zone around the injection well, but was not evident at the 50 m radius.

The influence of changes driven by redox reactions induced by the injection of organic C in reclaimed water on As concentrations and mobility was most evident during the storage phase of each ASR cycle. Greskowiak et al. (2005) reported that injected particulate organic C (POC) accumulates around the point of injection (ASR well) where it is subsequently solubilised, in conjunction

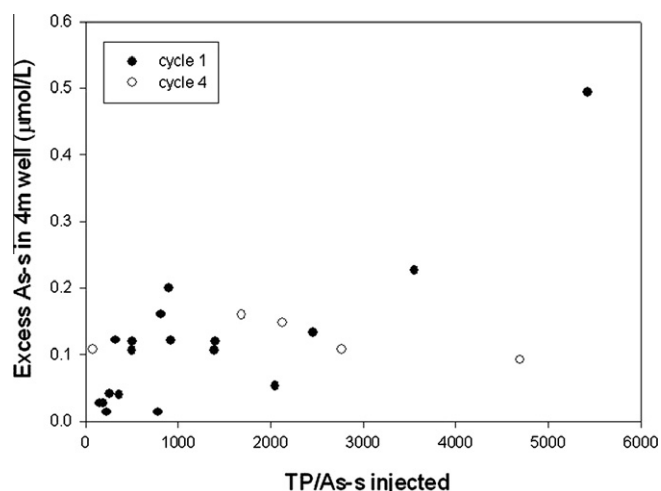


Fig. 7. Relationship between the excess As at 4 m during injection and the total P to soluble As ratio in the injected reclaimed water during the first and fourth ASR cycles at Bolivar.

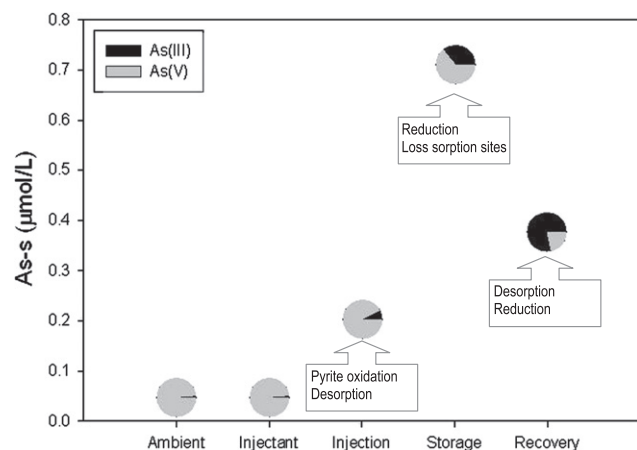


Fig. 8. Conceptual understanding of the fate of soluble As and contributions from As(III) and As(V) during an ASR cycle (based on the fourth cycle at Bolivar).

with dynamic processes of microbial mass production and biomass decay. While this microbial cycling occurs during injection, it becomes apparent during the storage phase where the DOC concentration increases significantly without any flow to flush it away. Also in the absence of injection there is no longer a supply of O_2 or NO_3^- and alternative electron acceptors, hematite, SO_4^{2-} and inorganic C, are utilised during storage (Greskowiak et al., 2005; Vanderzalm et al., 2006). To illustrate the significance of the OC accumulation around the ASR well, Pavelic et al. (2007) reported a reduction in hydraulic conductivity in the near well zone by one order of magnitude due to this largely organic clogging layer. An increase in As mobility due to redox processes has previously been reported in the presence of an organic C supply in regional scale investigations of elevated As concentrations in groundwater used for drinking water supply (Smedley et al., 2003; Charlet et al., 2007; Postma et al., 2007; Sthiannopkao et al., 2008); beneath landfill sites (Keimowitz et al., 2005); and also associated with biofilm development in domestic supply wells in the absence of a significant organic C source (Gotkowitz et al., 2004; Sonzogni et al., 2004).

Further evaluation of the role injected OC has in As mobility can be examined through the redox zones that develop around the ASR

well in subsequent cycles. While the increase in dissolved Fe was more rapid in the fourth cycle than in the first (Fig. 5), the extent of SO_4 reduction and methanogenesis was most significant in the first ASR cycle, illustrated by detection of only 1–2 vol.% dissolved CH_4 after > 100 days of storage in cycle 4 as compared to 67 vol.% after 80 days storage in cycle 1. It is expected that microbial activity in the vicinity of the ASR declined after cycle 1 due to improved nutrient removal in the Bolivar WRP in conjunction with efforts to minimise clogging through well backwashing techniques. All fractions of OC in the source water declined with subsequent cycles, average DOC and POC in cycle 4 were 60% and 20% of that in cycle 1, which may explain a reduction in microbial activity in the zone around the ASR well in latter cycles. The increase in the magnitude of P released during the fourth cycle storage is likely to be due to accumulation of higher injected concentrations in this cycle in the near well zone during the injection phase.

When Fe(III) reduction was evident in the ASR well during the storage phase, As was present as both As(III) and As(V) despite the shift to more reducing conditions. Reduction of Fe(III) in hematite released As(V) and then under the more reducing conditions with an increase in soluble Fe concentrations, As(V) was partially reduced to As(III). However As(III) contributed a maximum of 60% of the soluble As during the storage phase, slightly less significant than reported by Smedley et al. (2003) and Sthiannopkao et al. (2008) where highly reducing groundwater was coincident with greater than 60% and 80% As(III), respectively.

In addition, the soluble As species were altered from As(V) alone to a mixture of As(V) and As(III) within the entire storage zone regardless of the magnitude of the As increase during the storage phase, as gleaned from the ASR well and the 4 m and 50 m observation wells. Presumably, the increased concentration of DOC within the entire storage zone induced a shift to slightly more reducing conditions during the period of aquifer storage and resulted in partial reduction of As(V) and possibly some loss of sorption sites on solid surfaces.

6. Conclusions

The injection of reclaimed water into a carbonate aquifer mobilised a source of As from the aquifer sediments, and the magnitude of this As release did not decline during 4 ASR cycles, or injection of $704 \times 10^3 \text{ m}^3$. With the introduction of oxygenated source water, it is expected that traces of pyrite within the sediments are oxidised soon after injection, evident in the initial stages of the first cycle when elevated Fe concentrations and dissolved O_2 were measured in groundwater in the 4 m observation well. However As release through pyrite oxidation appears to be short lived in the near well zone (0–4 m), possibly limited by the availability of reactive pyrite within the sediments. Following this, injection of P in the reclaimed water leads to As release due to displacement from Fe oxyhydroxides which is expected to continue until all surface complexation sites are exhausted. The source of As for desorption includes As present under ambient conditions, but also that released by pyrite oxidation and subsequently adsorbed to Fe oxyhydroxide surfaces.

During the injection phase the mobility of As in the storage zone was largely dependent on sorption to Fe oxyhydroxide surfaces. The importance of Fe oxyhydroxides for control of As concentrations was illustrated by the dramatic increase of As and Fe coincident with reductive Fe dissolution in the ASR well during storage when a more reduced redox condition developed. The effect of storage was not only an increase in As concentration but also a change in the contribution of As species as As(V) was partially reduced to As(III). The high As concentrations associated with the loss of sorption sites during storage was limited to a zone immedi-

ately around the injection well and thus had a minimal impact on the recovered water quality (<0.5% volume recovered). However the change in As redox state due to the presence of organic matter was evident throughout the entire storage zone, even at the 50 m radius where concentrations remained unchanged.

The water recovered from the Bolivar ASR scheme was higher in As concentration than that injected or in the ambient groundwater. The behaviour of As within the storage zone was consistent with release during pyrite oxidation and competitive desorption by injected P in the injection phase. Reduction during storage resulted in a change in As species in the recovered water when compared with that of the injectant, with both As(V) and As(III) present (Fig. 8).

While this example is not utilised for drinking water supply, it exemplifies the processes that are likely to impact on ASR schemes in carbonate aquifers. Despite ambient and injected water quality that complies with guideline values, there is potential to exceed drinking water quality standards when As is released from the sediments during ASR. These As mobilisation processes lead to far greater concern when the ASR scheme is a supply of drinking water and more stringent As guideline values apply. In a reclaimed water ASR scheme it may be possible to manage the extent of As mobilisation by minimising the amount of organic matter introduced within the source water which is available to induce reduction of Fe(III) surfaces and also to achieve some net removal of As adsorbed to Fe oxyhydroxide through regular backwashing to remediate clogging of the ASR well.

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