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Fate of disinfection by-products in groundwater during aquifer storage and recovery with reclaimed water

Paul Pavelic[a,*], Brenton C. Nicholson[b], Peter J. Dillon[a], Karen E. Barry[a]

[a]*CSIRO Land and Water, PMB 2, Glen Osmond, SA 5064, Australia*
[b]*Australian Water Quality Centre, PMB 3, Salisbury 5108, Australia*

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Abstract

Knowledge on the behaviour of disinfection by-products (DBPs) during aquifer storage and recovery (ASR) is limited even though this can be an important consideration where recovered waters are used for potable purposes. A reclaimed water ASR trial in an anoxic aquifer in South Australia has provided some of the first quantitative information at field-scale on the fate and transport of trihalomethanes (THMs) and haloacetic acids (HAAs). The results revealed that THM half-lives varied from <1 to 65 days, with persistence of chloroform being highest and bromoform lowest. HAA attenuation was rapid (<1 day). Rates of THM attenuation were shown to be highly dependent on the geochemical environment as evidenced by the 2–5 fold reduction in half-lives at the ASR well which became methanogenic during the storage phase of the trial, as compared to an observation well situated 4 m away, which remained nitrate-reducing. These findings agree with previous laboratory-based studies which also show persistence declining with increased bromination of THMs and reducing redox conditions.

Modelling suggests that the chlorinated injectant has sufficient residual chlorine and natural organic matter for substantial increases in THMs to occur within the aquifer, however this is masked in some of the field observations due to concurrent attenuation, particularly for the more rapidly attenuated brominated compounds. The model is based on data taken from water distribution systems and may not be representative for ASR since bromide and ammonia concentrations in the injected

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* Corresponding author. Tel.: +61 8 8303 8742; fax: +61 8 8303 8750.
E-mail address: Paul.Pavelic@csiro.au (P. Pavelic).

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water and the possible role of organic carbon in the aquifer were not taken into consideration. During the storage phase DBP formation potentials were reduced as a result of the removal of precursor material despite an increase in the THM formation potential per unit weight of total organic carbon. This suggests that water quality improvements with respect to THMs and HAAs can be achieved through ASR in anoxic aquifers.

Keywords: Aquifer storage and recovery; Trihalomethanes; Haloacetic acids; Biodegradation; Groundwater

1. Introduction

Disinfection of water is carried out to protect public health from risks associated with microbial pathogens. Although the most commonly used disinfectant for treatment of potable water supplies is chlorine because it is both cheap and effective, it is well-known that chemical disinfection produces disinfection by-products (DBPs) through their reaction with the natural organic matter (NOM) found in the water, of which, the trihalomethanes (THMs) and haloacetic acids (HAAs) tend to predominate (Rook, 1974; Nicholson and Ying, 2005). Some of the disinfection by-products produced are carcinogenic in animals and are therefore possible human carcinogens. Nicholson and Ying (2005) offer examples of the maximum permissible drinking water guideline levels for total trihalomethanes (TTHMs): 250 μg/L in Australia, 80 μg/L in the USA, and 10 μg/L in Germany. The stricter guidelines can be difficult to meet, even in waters with low levels of NOM.

Aquifer storage and recovery (ASR) is the intentional recharge of aquifers using a well to inject and later recover water from that same well. Chlorination is sometimes used in the pretreatment of source water for ASR where it may assist in controlling microbial fouling around the injection/recovery well. Although much is known about the disinfection processes and the factors controlling DBP formation, much less is known about the behaviour of DBPs in aquifers during ASR. The few studies that have been conducted include those by Roberts et al. (1982), Singer et al. (1993), Miller et al. (1993), Mirecki et al. (1998), Thomas et al. (2000), and Fram et al. (2003). With the exceptions of Roberts et al. (1982) and Fram et al. (2003), they have been qualitative in nature, and the level of analysis generally extending no further than to examine whether attenuation does or does not occur. From these studies it has also been shown that formation of DBPs may continue to occur following injection (Singer et al., 1993; Fram et al., 2003), leading to concentrations in recovered water that may exceed that of the injectant.

The primary aim of this study was to evaluate the fate and transport of THMs and HAAs that are present in the injected chlorinated reclaimed water during ASR at a field site during the first 2 years of a research trial. The specific objectives of the study were to: (i) quantify rates of attenuation of DBPs having accounted for the effects of adsorption and mixing, (ii) examine the association between DBP persistence and redox conditions in the aquifer; (iii) assess the potential for formation of DBPs in the aquifer; and (iv) evaluate the change in DBP precursors and DBP yield due to ASR.

This research has been conducted as part of a wider ASR trial to evaluate the viability of storing surplus reclaimed water in a carbonaceous aquifer for irrigation supplies during dry periods (Dillon et al., 1999). A number of other research activities that are being undertaken at the site include work on aquifer characterisation and conservative solute transport (Pavelic et al., 2001), isotopic tracer studies (Le Gal La Salle et al., 2002), geochemical transformations (Vanderzalm et al., 2002) and multi-species reactive transport modelling (Greskowiak et al., 2005), well clogging (Rinck-Pfeiffer et al., 2000), fate of injected natural organic matter (Skjemstad et al., 2002) and microbial ecology/fate of pathogens (Toze and Hanna, 2002).

2. Site description and experimental methods

2.1. Description of field site

The reclaimed water ASR trial was conducted at the Bolivar site, situated 25 km north of the centre of Adelaide in South Australia on farmland north of the Bolivar sewage treatment plant (STP) (Fig. 1). The aquifer targeted for study is known locally as the "T2" aquifer, the second of several Tertiary marine-deposited limestone formations continuous across the Adelaide Plains (Gerges, 1999). Locally, the T2 is encountered between the depths of around 100–160 m below ground surface and is

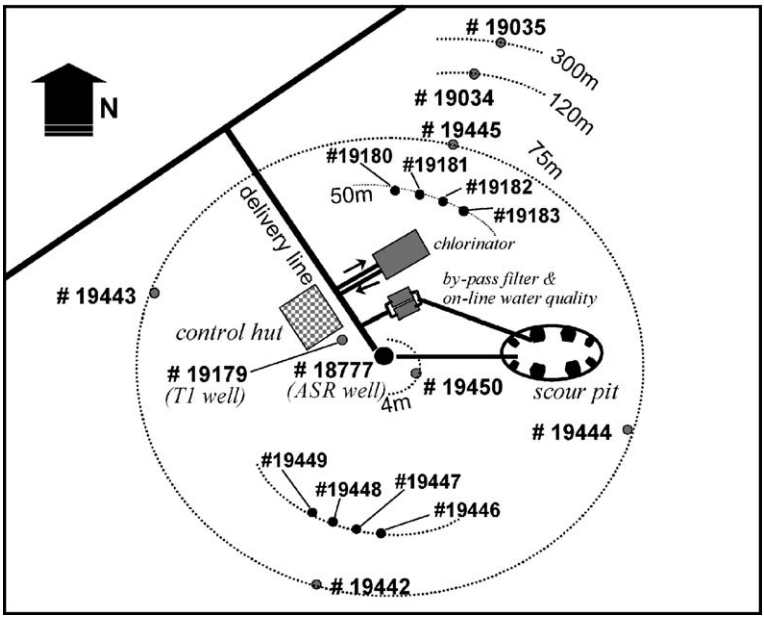

Fig. 1. Bolivar ASR trial site layout (not drawn to scale).

separated from the overlying fresh aquifer, known as T1, by a 7.5 m thick confining layer of Munno Para Clay. Its lithology ranges from fossiliferous and marly limestones through to siliceous calcarenite (Martin et al., 1998) (Fig. 2). The mineralogical composition of the aquifer is dominated by calcite and quartz, but small quantities of ankerite, mica, albite and pyrite are typically present. The organic carbon content of the aquifer matrix varies from 0.1% to 0.3%. The aquifer has a moderate transmissivity of 150 m^2/day (Martin et al., 1998) and is distinctly heterogeneous with depth but relatively uniform in lateral extent. Flowmeter profiles and solute breakthroughs at observation wells during injection suggests the aquifer is composed of four main layers of different permeability (Pavelic et al., 2001). Ambient groundwater flow is generally in a N–NW direction at an estimated velocity of 2 m/year.

A network of 16 observation wells was established within a 600 m radius of the ASR well (Fig. 1). All of the wells are fully penetrating with 'open hole' completions except for the two clusters at the 50 m radius, where each cluster is comprised of four wells with a short interval (4–5 m) completion in each of four layers that exhibit different permeabilities. Only data from the ASR well (#18777), along with the 4 m observation well (#19450) and two of the 50 m wells where breakthrough of injected water occurred (#19181 and #19449) will be considered here.

Source water for ASR was derived from the Bolivar STP, where the tertiary treated effluent was aerated in stabilisation lagoons, followed by dissolved air flotation and filtration (DAFF) treatment and chlorine dosing which was supplemented by additional dosing at the well head during the latter part of the trial.

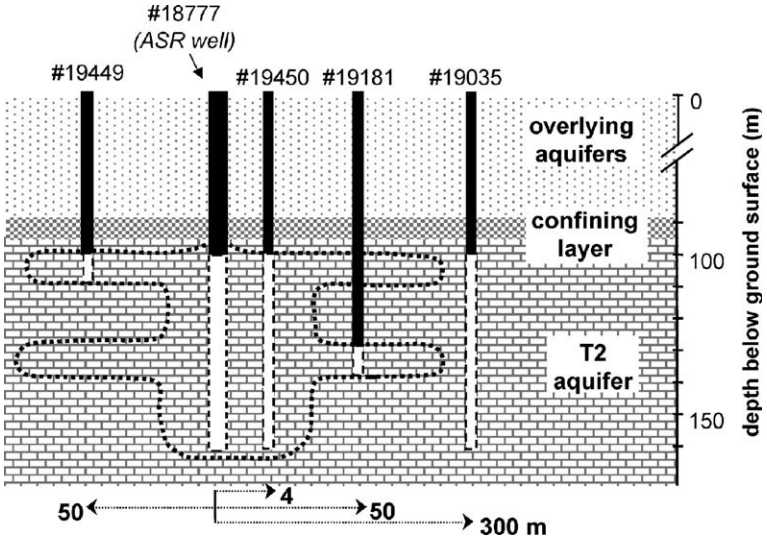

Fig. 2. Simplified vertical section along approximate N–S transect showing the wells where data is presented in this study. Inferred distribution of injectant in the aquifer at the end of the injection phase is indicated by the dashed curve. (Note that horizontal axis is not drawn to scale).

2.2. ASR test schedule

The first ASR cycle, between October 1999 and November 2001, was monitored for THMs and HAAs. Chloride, which is a conservative tracer of the injected water, was monitored at the ASR well and at a number of observation wells.

The operating schedule for the first ASR cycle is presented in Fig. 3. The injection phase occurred between October 1999 and March 2001 and was divided into three distinct test periods (tests 1–3). The largest volume was for test 3, which contributed around 85% of the total volume injected. Average injection rates ranged from 10 to 15 L/s. The position of the injected water front at the end of injection was estimated to be approximately 60 m assuming homogenous piston flow (neglecting dispersion), however the layered stratigraphy of the aquifer resulted in greater migration of injectant along the two more permeable layers (to >120 m but <300 m in both cases). Fig. 2 also shows the inferred cross-sectional distribution of injected water at the end of the injection phase when the maximum spatial extent of the injected water plume was reached. The recovery phase occurred between July and November 2001, where approximately 60% of the total volume injected was withdrawn at a pumping rate of 15 L/s.

2.3. Sample collection and analysis

THMs were monitored approximately fortnightly in the injectant, stored groundwater and recovered water. HAAs were monitored on a less frequent basis. Samples to be analysed for DBPs were collected by filling (without headspace) 500 mL plastic polyethylene terephthalate (PET) bottles containing ascorbic acid (THMs) or ammonium chloride (HAAs), stored on ice, and submitted to the Australian Water Quality Centre laboratories within 8 h of collection. THMs were analysed using an in-house headspace gas chromatographic method with electron capture detection.

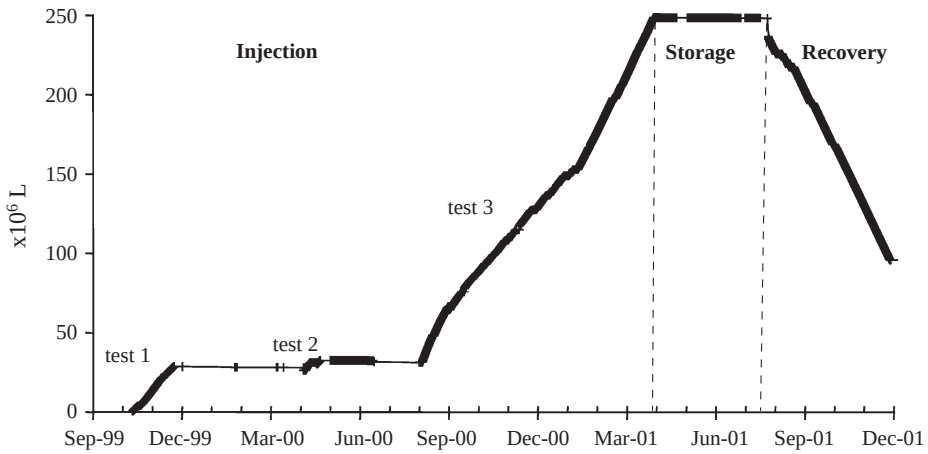

Fig. 3. Cumulative volume of injected water stored (October 1999 to November 2001).

Reporting limits were 1 μg/L with a precision (relative standard deviation) of 3.8–6.9%. Haloacetic acids were analysed by an in-house method (solvent extraction followed by methylation and gas chromatographic analysis with electron capture detection) based on US EPA method 552. Reporting limits were 1 μg/L with a relative standard deviation of 1.9–18.4%. Both methods, including the use of PET bottles, are fully accredited by the Australian National Association of Testing Authorities (NATA) and are used widely in monitoring programs.

2.4. Analysis of the data

2.4.1. Sorption

If sorption of a DBP compound is assumed to follow a linear isotherm, then it can be shown that the movement of that species is retarded (or travel time increased) with respect to the movement of water by a scalar known as the retardation factor, R and defined by Domenico and Schwartz (1998) as:

$$R = 1 + ((1-n)/n)\rho_s K_d \tag{1}$$

where $K_d = f_{oc} K_{oc}$ and K_d is the distribution coefficient for a linear isotherm, ρ_s, n and f_{oc} are the particle density, porosity and weight fraction of organic carbon of the porous media, and K_{oc} is the adsorption coefficient related to the organic carbon content.

2.4.2. Attenuation

Two classes of solute are considered; the conservative tracer, C_1 (i.e. Cl) and the reactant, C_2 (i.e. DBP). It is assumed that the concentration of tracer in the injectant, $C_{1\ inj}$ and in the ambient groundwater, $C_{1\ amb}$ are constant, and that these concentrations are sufficiently different such that the proportion of injectant present in any sampled mixture at any time, otherwise known as the "mixing fraction", f_1 (t) can be estimated from the following simple mass balance equation:

$$f_1(t) = \frac{C_1(t)_{mix} - C_{1\ amb}}{C_{1\ inj} - C_{1\ amb}} \tag{2}$$

where $C_{1\ inj}$ and $C_{1\ amb}$ have been defined and $C_1(t)_{mix}$ is the tracer concentration in the mixture at any particular time during the storage or recovery phases of the ASR cycle.

Although conservative behaviour is not presumed for the reactant, the corresponding mixing fraction, $f_2(t)$ is:

$$f_2(t) = \frac{C_2(t)_{mix} - C_{2\ amb}}{C_{2\ inj} - C_{2\ amb}} \tag{3}$$

where $C_{2\ inj}$, $C_{2\ amb}$ and $C_2(t)_{mix}$ are the concentrations of the reactive solute in the injectant, ambient groundwater and mixture, respectively.

The general principles behind two methodologies for evaluating attenuation are described below.

Method 1. The attenuation of DBPs can generally be described by a first-order reaction. That is, the rate of attenuation at any time, t is linearly proportional to the

concentration of the reactant, C_2. This may be described by the following kinetic equation:

$$\frac{\partial C_2}{\partial t} = -kC_2 \tag{4}$$

where k is the attenuation rate coefficient [time^{-1}]. Eq. (4) may be solved to yield the following exponential relationship which relates the concentration at any sampled time, $C_2(t)$ to the initial concentration, $C_2(0)$.

$$C_2(t) = C_2(0)\mathrm{e}^{-kt} \tag{5}$$

and can then be rearranged for the only unknown term, k as:

$$k = \frac{-\ln\left[\frac{C_2(t)}{C_2(0)}\right]}{t} \tag{6}$$

Generally Eq. (6) can be applied to batch-reactor types of experiments, but cannot be directly applied to ASR studies because waters withdrawn during the recovery phase are a blend of the injected and ambient end-members, due to the dispersion and dilution process.

To compensate for the effects of mixing in the aquifer Eqs. (2) and (5) are combined, such that:

$$C_2(t) = \frac{f_1(t)}{f_1(0)}C_2(0)\mathrm{e}^{-kt} \tag{7}$$

hence

$$k = \frac{-\ln\left[\frac{C_2(t)f_1(0)}{C_2(0)f_1(t)}\right]}{t} \tag{8}$$

Eq. (8) can be used to describe the rate of attenuation of DBPs in an aquifer during the storage or recovery phase at either the ASR well or an observation well.

Method 2. An approach similar to the above was developed by Haggerty et al. (1998) for analysing the rate coefficients for microbially induced reactions (e.g. denitrification) from "push–pull" tests (which are essentially a scaled-down version of ASR). Haggerty et al. (1998) has shown that at the end of injection at a constant rate with constant concentrations C_1 and C_2 for a period t_{inj} that:

$$\ln\left[\frac{f_2\left(t-t_{\mathrm{inj}}\right)}{f_1\left(t-t_{\mathrm{inj}}\right)}\right] = \ln\left[\frac{\left(1-\mathrm{e}^{-k\left(t-t_{\mathrm{inj}}\right)}\right)}{k\left(t-t_{\mathrm{inj}}\right)}\right] - k\left(t-t_{\mathrm{inj}}\right) \tag{9}$$

where f_1 and f_2 are defined as per Eqs. (2) and (3).

The attenuation rate can be estimated from the best-fit of the slope of the plot of the LHS of Eq. (9) versus the time since injection ceased ($t-t_{\mathrm{inj}}$).

It is generally more intuitive to express attenuation in terms of the so-called "half-life" ($t_{1/2}$):

$$t_{1/2} = -\frac{\ln(0.5)}{k} = \frac{0.693}{k} \tag{10}$$

The principal difference between the two methodologies is that Method 1 assumes the injectant is introduced as an instantaneous (Dirac) pulse, whilst Method 2 accounts for the extended nature of injection by considering exponential decay of the reactant over the course of injection phase.

Despite differences between the two methods, numerically equivalent rates are derived, since in practice, Eqs. (8) and (9) are differentiated by the inclusion of two constants in the logarithmic term on the RHS of Eq. (8), and which affects only the absolute value but has no influence on the slope (i.e. k). Method 2 was chosen and so plotting the log-transformed concentrations of the relative DBP and Cl ratios as a function of time since the end of injection allows k to be determined from the regression slope and therefore $t_{1/2}$.

The main assumptions associated with both of the methods are:

a) *End-member concentrations are constant*: temporal variability in the injected concentrations of either the tracer or reactant, or spatial variability in ambient concentrations lead to errors in the calculated attenuation rate. Neither method allows for the effects of spatially variable tracer concentrations, which, after the first ASR cycle, can be problematic. Non-zero background DBP concentrations are to some extent accounted for through the use of the mixing fraction rather than the measured concentrations (Eq. (3)).
b) *No formation of DBPs in the aquifer*: this is most problematic where formation is ongoing over the period where attenuation is evaluated. However, when formation occurs, it is generally rapid (as will be demonstrated later) and has typically reached completion before groundwater monitoring commences. In this case, concentrations from the first groundwater sampling (day 7) was used as initial conditions since concentrations at $t-t_{inj}=0$ would not have been representative of input concentrations. Therefore using data from day 7 onwards is preferable to commencing at day 0 as the formation that had previously occurred should have no affect on the determination of k.
c) *Spatially uniform attenuation rates*: this assumption may not always be met since, for instance, there is the potential for multiple redox zones to occur in the storage zone. Analysis of the data from a number of wells gives some indication of the significance of this phenomenon.
d) *Losses due to adsorption are small*: it is assumed that removal by biodegradation is the dominant removal mechanism, and this is supported by data presented later.

Overall, the errors associated with both methods are mainly attributed to the uncertainty in the mixing fractions due to spatial and temporal variability effects. The uncertainty in half-lives was estimated by calculating the upper and lower 95% confidence limits about the mean half-life by adding for the lower-limit and subtracting for the upper-limit, twice

the standard error of the inactivation rate (note that this produces results which are non-symmetric about $t_{1/2}$).

2.4.3. Formation

Models to describe the formation of THMs following chlorination in water distribution systems have recently begun to emerge (Clark and Sivaganesan, 1998; Westerhoff et al., 2000; Gallard and von Gunten, 2002). Of those, the model of Clark and Sivaganesan (1998) was chosen for use in this study since its development was based on a substantial set of water quality data (42 waters), and the data needed to derive the coefficients in the model were readily available. The ultimate equation given by Clark and Sivaganesan, derived from second-order kinetics for coupled TTHM formation and chlorine decay is given as:

$$C_2(t) = D\left[C_3(0) - \left(\frac{C_3(0)(1-R)}{1-R\mathrm{e}^{-k_c t}}\right)\right] + C_2(0) \tag{11}$$

where R and D are dimensionless parameters defined below, $C_3(0)$ is the initial chlorine residual, and k_c is the rate constant for chlorine decay [time^{-1}]. The equation describing changes in chlorine residual with time may be found in Clark and Sivaganesan.

Best-fit equations were deduced from empirical data by Clark and Sivaganesan to predict the three unknowns: D, k_c, and M, which are functions of the chlorine dosage, pH, temperature and total organic carbon.

2.5. Determination of DBP formation potential

The DBP formation potential (FP) is used to evaluate the propensity for NOM to form DBPs by exposing the water sample to excess chlorine under standardised test conditions and measuring the peak concentration of DBPs formed. In this case the specific test conditions were: waters buffered at pH 7.4, dosed with 20 mg/L chlorine and incubated at 35 °C for 4 h after which residual chlorine is quenched and DBP concentrations determined.

2.6. Composition of injected water and ambient groundwater

The compositions of injected water and ambient groundwater for the Bolivar site are substantially different (Table 1). The anoxic ambient groundwater is brackish and only the high concentration of dissolved solutes prevents its use for irrigation or drinking. The source water has a lower temperature, has higher levels of particulate matter, dissolved oxygen, dissolved organic carbon, nutrients, and bacteria, but has lower salinity than the ambient groundwater. The quality of the injectant (i.e. reclaimed water) exhibits significant temporal variability as reflected in the relatively high values of standard deviations given in Table 1. Chloride is a useful conservative tracer in this system due to the contrast between the two end members. The effect that the chlorine residual (average concentration of 0.7 mg/L) would have on the injected chloride

Table 1
Composition of the injected water and ambient groundwater (means and standard deviations reported)

Parameter (mg/L)	Injectant	Ambient groundwater
Temperature (°C)	20.4±4.5	25.9±1.0
pH	7.1±0.4	7.3±0.1
Dissolved oxygen	4.4±3.4	0.1±0.1
Redox potential (mV SHE)	300±260	42±32
Electrical conductivity (μS/cm)	2270±90	3590±330
Chloride	433±40	932±92
Bromide	1.2±1.1	3.3±0.4
Sulphate	208±13	274±39
Ammonia-N	15.5±11.3	0.08±0.06
Nitrate-N	1.4±1.5	<0.005
Dissolved organic carbon	16.7±2.1	0.3
Total organic carbon	18.2±2.3	0.3
Chlorine residual (total)	0.7±0.4	0
Heterotrophic plate count (cells/mL)	$1.7\times10^5\pm2.3\times10^5$	120±130

concentration (average concentration of 433 mg/L) due to chemical hydrolysis is insignificant (Nicholson and Ying, 2005).

3. Results and discussion

3.1. Variability in injected DBP concentration and composition

DBPs concentrations in the injectant were highly variable, with TTHM concentrations ranging from 5 to 157 μg/L (Fig. 4). Similar trends were evident for individual THMs and HAAs. Over the period from October 2000 to March 2001 ammonia levels declined from around 28 mg/L during winter to <0.1 mg/L in summer (January to March). Most of this variability can be related to changes in ammonia levels in the source water. During winter most of the added chlorine was consumed by the ammonia and TTHM levels were very

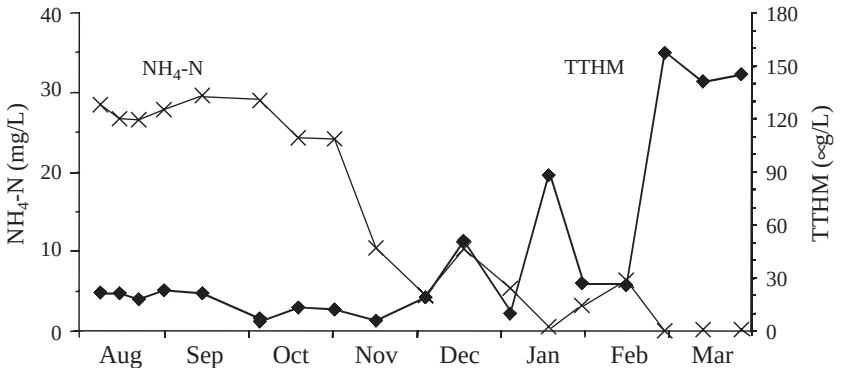

Fig. 4. TTHM and ammonia concentrations in the injected water during test 3, August 2000 to March 2001.

low (<30 μg/L). During summer TTHM levels were much higher (>140 μg/L). Although seasonal changes in THMs did occur, concentrations were relatively stable, at least over the 1–2-day time-scale for transport of injected water to the 4 m well. For monitoring purposes, it was fortuitous that the final injection phase concluded at a time when injected concentrations of TTHM were high, allowing a strong signature in the groundwater at the ASR and 4 m wells over the storage phase. Vanderzalm et al. (2002) identified that changes in ammonia concentration in the injectant are driven by nitrification and denitrification processes within the lagoon detention step in the Bolivar STP. It is well known that when chlorine is added to ammonia-containing waters, the ammonia competes with NOM to form chloroamines and which produce less DBPs. Other factors such as temperature and chlorine residual appear to have been of secondary importance.

The THM constituents in the injected water were dominated by chloroform and bromoform, which on average comprised over 80% of the TTHMs. Bromodichloromethane and dibromochloromethane become relatively more significant only when ammonia concentrations were low.

3.2. Adsorption

As water moves through the aquifer, DBP compounds will be adsorbed onto particulate matter until equilibrium, as determined by the compound's partition coefficient between the water and the organic component of the solid phase (K_{oc}), is reached. The overall effect of adsorption on movement of injectant away from the ASR well will be the retardation of components relative to the movement of injected water as traced by chloride.

Table 2 lists the DBPs for which K_{oc} has been estimated from the literature and the calculated retardation factors based on parameter estimates for the T2 aquifer at Bolivar. The very low retardation factors suggest that adsorption is of minor consequence.

Retardation factors can also be calculated from the breakthrough curves at observation wells, although in this case, only data for chloroform is valid (as it is the only DBP not substantively affected by biodegradation and the average injected concentration was 8 μg/L). The fractional breakthrough for chloride and chloroform (as defined in Eqs. (2) and (3)) at the 4 m well during test 1 is given in Fig. 5. Since there was no dosing of chlorine at the wellhead during this test (only at the DAFF treatment plant situated approximately 2 km upstream), there was minimal opportunity for additional THM formation in the aquifer to confound breakthrough. The travel time to this well varied from 1 to 2 days, depending

Table 2
Retardation factors for selected DBPs based on K_{oc} data from Nicholson et al. (2002), density of aquifer solids of 2.65 g/cm^3, porosity of 0.45 (Pavelic et al., 2001) and organic carbon content of 0.2%

DBP compound	Formula	K_{oc}	Retardation factor
Chloroform	$CHCl_3$	59	1.4
Bromodichloromethane	$CHCl_2Br$	48	1.3
Dibromochloromethane	$CHClBr_2$	77	1.5
Bromoform	$CHBr_3$	151	2.0
Dichloroacetic acid	$CHCl_2CO_2H$	5.2	1.0
Trichloroacetic acid	CCl_3CO_2H	32	1.2

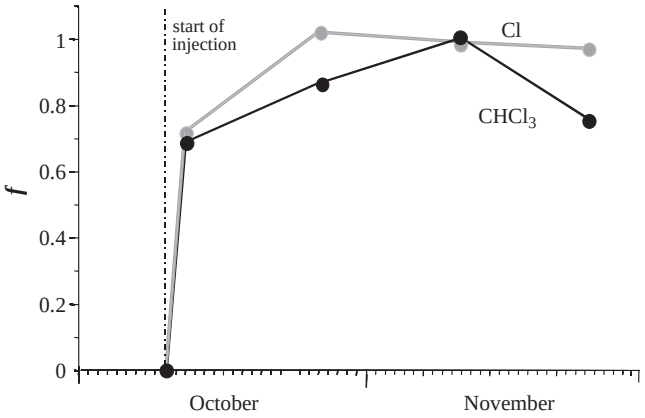

Fig. 5. Mixing fractions (f) for chloroform and chloride at the 4 m observation well (#19450) during injection test 1 in October and November 1999 (travel time to this well is 1–2 days).

on the injection rate, with complete breakthrough of injected water within 7 to 14 days. Thus the estimated retardation factor for chloroform of approximately 1.0 is in good agreement with previous data suggesting sorptive capacity of the T2 aquifer is low. Roberts et al. (1982) and Fram et al. (2003) have drawn similar conclusions at field studies in California, as have Rivett et al. (2001) in Canada.

3.3. Hydrolysis

THMs and HAAs can potentially be degraded by chemical hydrolysis which involves attack by hydroxide ion at the carbon bearing the halogen substituent. However extremely long hydrolysis half-lives for THMs have been reported (e.g. in Buszka et al., 1994). Although no specific hydrolysis data for HAAs are available, it would appear that rates are also very slow (Nicholson and Ying, 2005). Thus chemical hydrolysis is not considered to be important in the biodegradation of THMs or HAAs. Removal of HAAs by other abiotic processes may occur by decarboxylation to form the corresponding THM compound, however, this also occurs at an insignificant rate (Nicholson and Ying, 2005). Therefore since chemical processes are insignificant, microbial processes must be primarily responsible for any degradation occurring.

3.4. HAAs attenuation from 4 m observation well data

The available HAA data was less extensive than for THMs (sampling only occurred on three occasions during the injection phase). The injectant contained a range of HAAs, with a relatively high proportion of brominated compounds, as was the case for the THMs (Table 3). Only dichloroacetic acid at a concentration of 1 μg/L was detected at the 4 m observation well. Thus all HAAs apart from dichloroacetic acid were effectively removed during the 1–2-day travel time to that well. Sampling during the recovery phase failed to detect any HAAs in the recovered water. Given that retardation factors are low and hydrolysis is negligible reaffirms the ready removal of these compounds by microbial

Table 3
HAA levels in injectant and the 4 m observation well on 1 March 2001 (end of test 3)

HAA	Concentration (μg/L)	
	Injectant	4 m well
CH_2ClCO_2H	<5	<5
$CHCl_2CO_2H$	3	1
CCl_3CO_2H	18	<1
CH_2BrCO_2H	<1	<1
$CHBr_2CO_2H$	<1	<1
$CHBrClCO_2H$	2	<1
$CBrCl_2CO_2H$	35	ND[a]

[a] ND=not determined.

processes as noted in previous studies (Singer et al., 1993; Landmeyer et al., 2000; Thomas et al., 2000).

3.5. THM changes during storage and recovery

Complete breakthrough of injectant occurred at the 4 m and 50 m wells during the 248×10^6 L injection phase such that the total number of pore flushes was in excess of 100 at 4 m and 2–3 flushes at 50 m.

The most useful monitoring period was during the storage phase from April to July 2000 (0–110 days after injection ceased). Virtually all DBPs were removed at the ASR well during storage (Fig. 6a). As there was no significant change in the chloride concentration from mixing with ambient groundwater during this period, this loss can only be attributed to biodegradation. There appears to be a significant difference in attenuation rates between the ASR and the 4 m well, with greater persistence associated with the 4 m well (Fig. 6b). A brief pulse of some of the chlorinated THMs in the recovered water at the commencement of pumping appears to be the result of residual THMs in the vicinity of the 4 m well. Continued pumping over a 4-month period detected no subsequent THMs in the recovered water or at the 4 m well.

No THM breakthroughs were detected at either of the next-closest observation wells at the 50 m radius where complete breakthrough of injected water had occurred by the end of the injection phase. Fig. 6c presents the data for one of these wells (#19181). Note that although complete chloride breakthrough had occurred by the start of the storage phase at this well from the initial value of around 900 mg/L, the concentration exceeded the average injected value by around 100 mg/L because this reflected the higher than average concentration of the injectant during the first half of test 1. Given that the travel time to the 50 wells during the injection phase is in the order of 100 days, the non-detection of THMs was as expected from the half-life estimates at the 4 m observation well.

3.6. Biodegradation of DBPs

Table 4 presents attenuation rate data, expressed as half-lives, for total and individual THM compounds and HAAs using Method 2. An example plot for the TTHM data at the

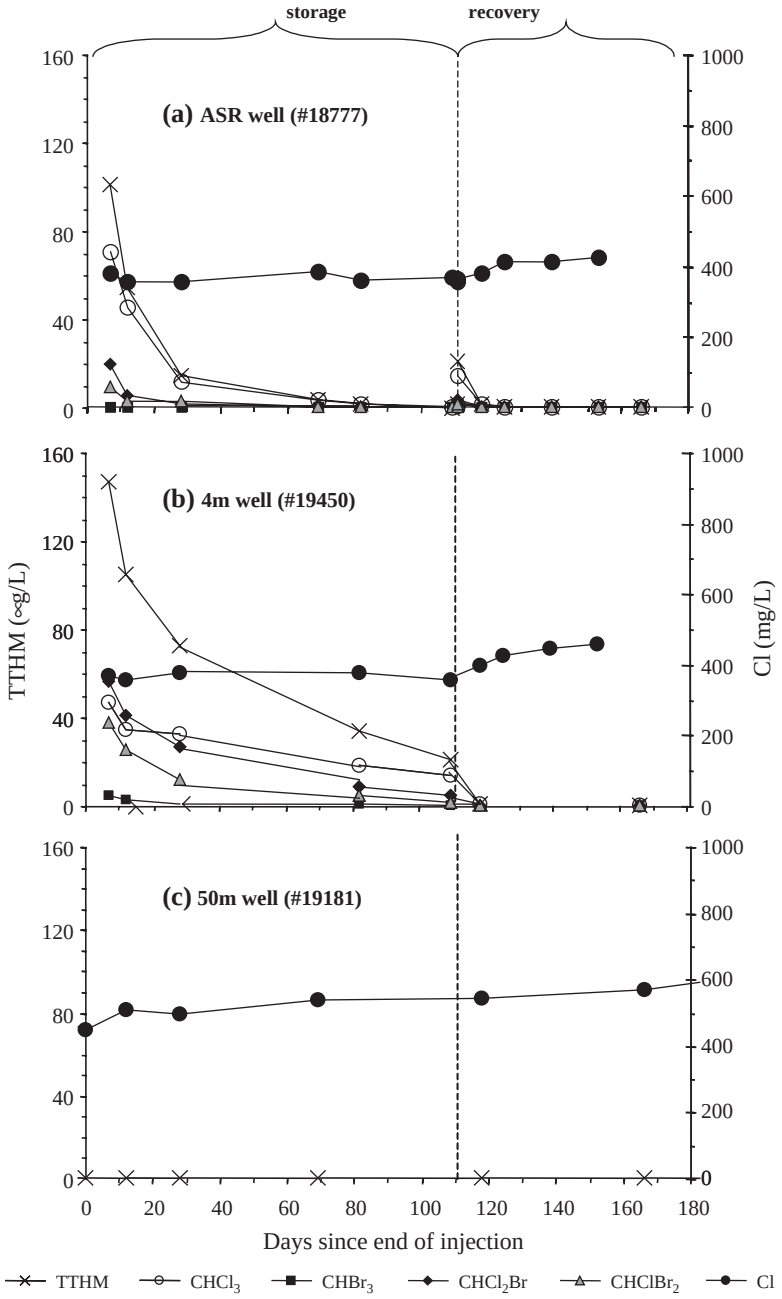

Fig. 6. THM and Cl data for storage period following test 3 and earliest recovery at the ASR, 4 m and 50 m wells.

Table 4
DBP attenuation rate data, expressed as half-lives based on the monitoring data during the storage phase following test 3 (95% confidence limits shown in brackets alongside the 'best-fit' value)

Well	Half-life (days)					
	TTHMs	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	HAAs
ASR	14 [12–17]	15 [13–18]	13 [9–29]	17 [11–36]	<1[a]	
4 m obs	40 [36–49]	65 [53–84]	31 [27–35]	27 [22–35]	9 [8–12]	<1[a] [na]

[a] Based on concentration changes between ASR and 4 m well during injection phase since insufficient data above detection limit to make reliable estimate during storage.

ASR and 4 m wells is given in Fig. 7. Half-lives for chloroform are generally higher than other THMs (15–65 days cf. <1–39 days). Bromoform is the most rapidly attenuated THM. HAAs are readily removed during passage to the nearest observation well at the 4 m radius, indicating the half-life is <1 day.

Roberts et al. (1982) report on the injection of chlorinated reclaimed water at the Palo Alto Baylands site in the San Francisco Bay area. In this aquifer, where the dissolved oxygen data suggests the redox state was probably anaerobic, half-lives of 23 days were reported for each of the THM compounds, which is within the range of values reported here. Singer et al. (1993) observed that THMs and HAAs removal occurred beyond that which could be accounted for by mixing, and HAA removal was found to be most rapid. Rates of attenuation were not reported.

3.7. Relationship between half-lives and redox conditions

One of the most pronounced features of the data given in Table 4 is the 2–5 fold contrast in DBP attenuation over a 4 m distance between the ASR and nearest observation wells. An explanation for this was sought by examining the geochemical environment within the zone occupied by the injected water mass, since previous studies have highlighted the dependence of redox conditions on DBP attenuation.

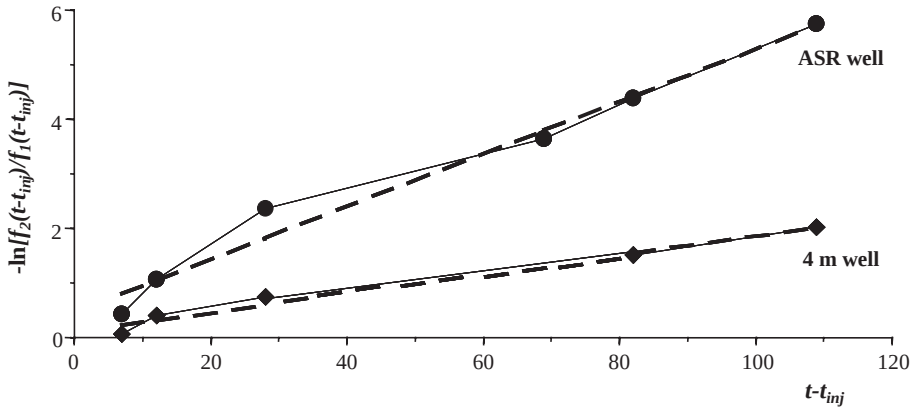

Fig. 7. Log-transformed TTHM data for ASR and 4 m wells showing lines of best-fit used to calculate k and $t_{1/2}$ for storage period following test 3 (definition of terms used on x and y axes given in Section 2.4.2).

In related studies at the research site, Vanderzalm et al. (2002) and Greskowiak et al. (2005) have shown that mineralization of DOC by microbial metabolism is the major link between the organic and inorganic hydrochemistry, which strongly influences carbon and nitrogen cycling. Microbial activity is most pronounced immediately around the ASR well since a proportion of the injected particulate organic matter accumulates around the ASR well. Growth of reaction-mediating microbial populations derive energy from oxidation of organic substrate which leads to a sequential consumption of available electron acceptors (O_2, NO_3^-, etc.) and therefore to the formation of distinct redox zones that vary as a function of spatial distance from the ASR well and with time. Biofilm development is common to ASR with reclaimed water, and laboratory column studies using aquifer materials and source water from this site have demonstrated this (Rinck-Pfeiffer et al., 2000).

During the injection phase, the contrast in the quality between that of the injectant and at the 4 m well was relatively subdued, however a strong geochemical gradient developed over this 4 m distance during the storage phase (Vanderzalm et al., 2002), which as Fig. 6 shows, can not be attributed to mixing. Decreases in redox potential (Eh) at the ASR well were consistent with increased microbial activity (Fig. 8). Eh values at the 4 m well were typically higher. Depletion of nitrate in the groundwater around the ASR well in the initial stages of the storage phase then led to a reduction in the sulphate concentration of up to 1.5 mmol L^{-1}, whilst no sulphate reduction occurred at the 4 m well. This indicates that this near-well redox zone is highly localized. Methane gas and hydrogen sulphide were also present at the ASR well at the end of the storage period but not in the 4 m well. Methane, the dominant gas, peaked at concentrations in excess of the solubility limit (>2 mmol L^{-1}), whilst dissolved sulphide peaked at 0.02 mmol L^{-1} (Vanderzalm et al., 2002). The mean temperature of the groundwater during this period was approximately 20 °C, with the mean temperature difference between the two wells of less than 1 °C.

The most reducing redox condition of the groundwater during the storage phase was nitrate-reducing at the 4 m observation well, and methanogenic at the ASR well. The more rapid removal of THMs under methanogenic conditions observed in this study is consistent with the literature (Nicholson and Ying, 2005). Previous studies have suggested that HAAs are readily microbially degraded under both aerobic and anaerobic conditions (Singer et al., 1993; Thomas et al., 2000). For example, Thomas et al. (2000) reports complete degradation of HAAs within 1 month of storage in an aerobic aquifer. However reducing conditions are usually required for effective biodegradation of THMs, and highly reduced conditions are needed to degrade chloroform. Under aerobic conditions, THMs have been observed to behave conservatively over monitoring periods extending up to several years (Miller et al., 1993; Fram et al., 2003).

3.8. Formation of DBPs in aquifers

The concentrations of DBPs produced through chlorination is dependant on a number of factors. For each THM the ultimate concentration is a function of chlorine dosage and contact time, the type and concentration of NOM present, water temperature, pH, ammonia and bromide concentrations (Symons et al., 1982). Higher precursor levels,

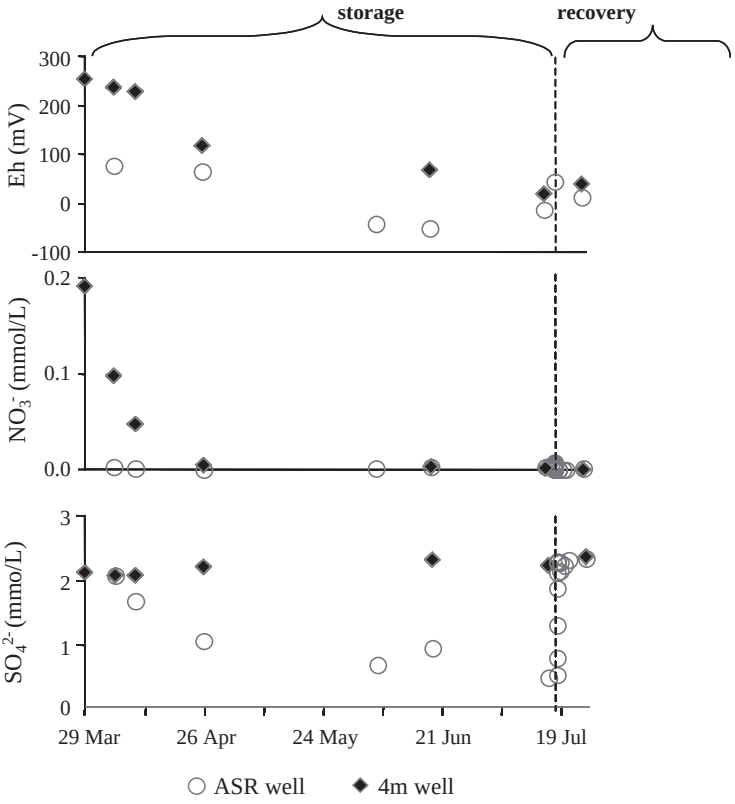

Fig. 8. Eh, NO_3^- and SO_4^{2-} changes at the ASR and 4 m wells during the storage phase and on the commencement of recovery (source: Vanderzalm et al., 2002).

chlorine dose rates, pH, temperature and longer reaction times all lead to higher THM levels, all other factors being equal.

A number of previous studies on disinfection in the water treatment field have shown that the reaction-chain that leads to DBP formation (e.g. $Cl_2 \rightarrow$HOCl/HOBr$\rightarrow$THMs) is not instantaneous, but typically occurs over time scales of tens to hundreds of hours (e.g. Clark and Sivaganesan, 1998). Further, it has been recognised that in some circumstances, largely depending on chlorine dose and demand, that DBP concentrations may continue to increase during transport through the distribution system as residual chlorine reacts with NOM (Chen and Weisel, 1998). Continued formation of DBPs in aquifers is likely in light of the common practice of chlorinating the injectant at the well-head. If the chlorine dose exceeds demand then chlorine will not be totally consumed leading to incomplete DBP formation before injection occurs. Subsequent sampling may reveal a DBP concentration increase in the aquifer.

Application of the Clark and Sivaganesan (1998) model to the “typical” injectant, presented in Fig. 9 shows that the asymptotic formation of TTHMs is associated with a corresponding decline in residual chlorine. Seventy-one percent of the final concentration

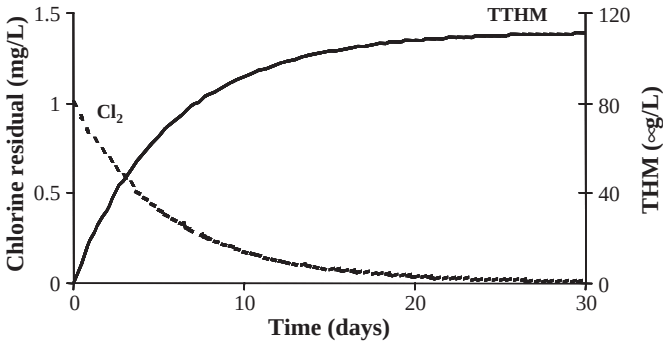

Fig. 9. Predicted THM formation and chlorine decay for Bolivar injectant (temperature=20 °C, pH=7.0, TOC=18 mg/L and chlorine residual=1 mg/L, giving D=112, k_c=7.36, M=0.001).

is reached within the first 7 days (the period before the first groundwater sampling takes place), but formation may continue for up to 30 days. The maximum predicted TTHM concentration increase would be 110 μg/L, and the actual predicted concentration needs to consider the level present in the water prior to dosing.

To assess whether or not THM formation occurred at the Bolivar site, THM concentrations in the injectant, as measured at the well-head, were compared with concentrations measured in the groundwater at the 4 m observation well on 17 occasions during the injection test 3. The results, presented in Fig. 10, show consistent evidence for increased concentrations of some THMs in the aquifer. At the start and at the end of the period concentrations of chloroform and bromodichloromethane increased in the aquifer. In the case of dibromochloromethane generally there was no substantial concentration change during 4 m of aquifer passage, whilst for bromoform, concentrations in groundwater were significantly depressed, and only measurable when input concentrations

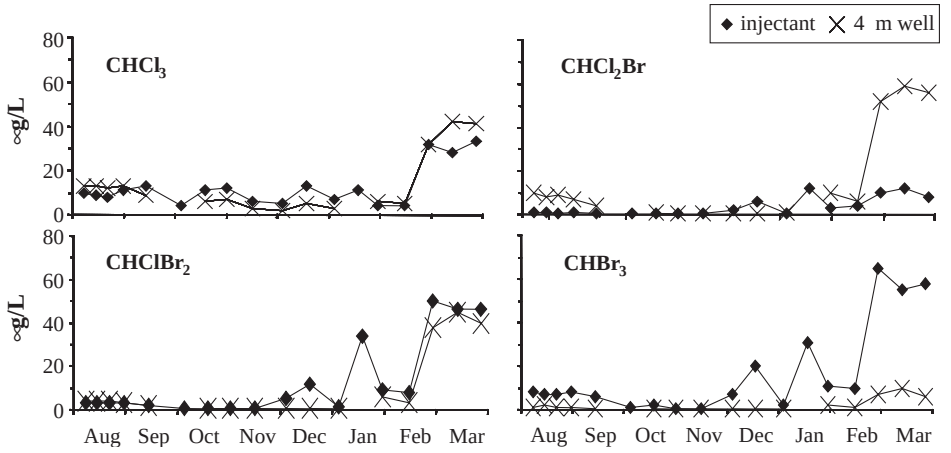

Fig. 10. THM concentrations in injectant and in groundwater at the 4 m observation well during injection test 3 (travel time to this observation well is 1–2 days).

were high due to rapid biodegradation. Similarly, it can be presumed that HAA concentrations would have also increased were it not for their rapid attenuation.

Measurements of the total chlorine residual at the well-head, although sparse, reveal that where formation occurred there was a residual, ranging between 0.3 and 1.1 mg/L. Where THM formation did not occur, chlorine residuals were less than the detectable limit of 0.1 mg/L. The absence of ammonia during the latter period was clearly a contributing factor in allowing chlorine concentrations to persist and thus formation of some THMs to occur. It is worthwhile to note that often the apparent lack of TTHM increase is actually due to chloroform and bromodichloromethane formation being insufficient to offset the collective decreases of dibromochloromethane and bromoform due to biodegradation. The maximum measured formation for TTHMs was substantially less than that predicted by the model which was due in part to concurrent attenuation. The prediction of formation in the aquifer does not consider bromide or ammonia concentrations, which are also known to play a role, nor the OC in the aquifer, whose effect is unknown.

3.9. Changes in DBP formation potential

Only in the final phase of injection when ammonia concentrations had reduced to sub-mg/L levels were valid comparisons of formation potential (FP) possible. A portion of the data from the 4 and 50 m observation wells was also suitable for similar reasons.

Table 5 shows that DBP FPs in the source water are relatively high due to high precursor levels. However in relative terms, as per unit weight of TOC, they are quite low compared to other ASR sites (Pavelic et al., 2005). The data from 1st March 2001 shows clear evidence of declines in both THM- and HAA-FPs at the 4 and 50 m observation wells with increased radial distance and residence time. This decline is attributable to the effect of a removal of OC in the groundwater (Le Gal La Salle et al., 2002; Skjemstad et al., 2002; Vanderzalm et al., 2002; Greskowiak et al., 2005). Further evidence for precursor removal from a mass balance calculation of TOC and Cl inputs and outputs

Table 5
DBP formation potential data

Sample	Date	Time[a] (days)	Percent injectant	TOC (mg/L)	TTHM-FP (μg/L)	μg TTHM-FP/mg TOC	HAA-FP (μg/L)	μg HAA-FP/mg TOC
Ambient g/w (#19035)	–	NA	0	0.3	ND	–	ND	–
Injectant	1 Mar 2001	0	100	15.4	293	19.0	154	10.0
4 m well (#19450)	1 Mar 2001	~1	100	13.6	281	20.7	106	7.8
50 m well (#19449)	1 Mar 2001	~100	91[b]	8.8	247	28.1	90	10.2
50 m well (#19449)	11 Sep 2001	~300	86	8.8	231	26.3	79	9.0
50 m well (#19449)	28 Sep 2001	~400	41	4.6	102	22.2	28	6.1

NA=not applicable; GW=groundwater; ND=not determined.
[a] Residence time of inject water in aquifer.
[b] Mixing fraction underestimated due to variability in chloride concentration of the injectant.

recovered over the course of pumping showed that at the end of the test only 46% of the TOC was withdrawn compared with 55% of the injectant (Pavelic et al., 2005). This suggests the net a loss of ~16% of the injected TOC within the aquifer is the result of the net TOC formed by microbial activity less that removed by adsorption or chemical and microbial degradation.

Skjemstad et al. (2002) identified the low DBP yield to be due to the relatively low molecular weight and aromaticity of the NOM in the reclaimed water, and demonstrated that higher molecular weight material in the injectant is preferentially sorbed to the aquifer matrix. Thus it was proposed that an overall reduction in the DBP-FP could be expected, but that there would be an increase per unit weight of DOC since the remaining NOM would produce more DBPs. The data presented here offers some support for this claim. Although FPs were reduced through ASR, it appears that THM-FP/TOC ratios in groundwater at the 4 and 50 m observation wells are significantly higher than in the injectant, indicating an increase as a result of aquifer storage and/or passage (Table 5). There is also some evidence for declining THM and HAA ratios at the 50 m well during the recovery phase due to mixing with ambient groundwater that would appear to have a lower ratio. Interestingly, in a study of a similar nature involving tertiary treated reclaimed water at Montebello Forebay in Los Angeles County, Leenheer et al. (2001) showed that the ambient groundwater, and not the injectant, was the major contributor to the THM-FP. Their structural characterisation of the NOM in the reclaimed water showed that the predominance of aromatic sulphonates and fulvic acids produced minimal THMs. THM-FP(μg)/TOC(mg) ratios of 40–90 were measured in their groundwater, which appears to be higher than at the Bolivar site.

4. Conclusions

This field trial involving reclaimed water ASR for irrigation usage has provided some of the first quantitative information on THM and HAA fate and transport in an anoxic aquifer. Attenuation data from this study are very much as expected from our knowledge of degradation processes determined experimentally in the laboratory and in the field. These data also conform with the theory that attenuation is highly dependent on the type of DBP compound and on the geochemical conditions in the aquifer.

THM half-lives, which take into account mixing effects with ambient groundwater, varied by two orders of magnitude for different DBP compounds (<1 to 65 days). Chloroform was found to be the most persistent compound; bromoform the least. HAA attenuation was more rapid than for THMs (<1 day). Spatial variations in THM attenuation within the injected water plume could be explained from the geochemical data. Half-lives were 2–5 times lower at the ASR well where the redox state became methanogenic during the storage phase as compared to an observation well 4 m away which remained nitrate-reducing. To our knowledge, this could be the first field study to demonstrate how contrasting, and highly localised redox environments affect THM persistence.

Modelling suggests that the source waters have sufficient residual chlorine and NOM for substantial increases in THMs to occur in the aquifer, however this is masked in some of the field observations due to concurrent attenuation, particularly for the more rapidly

attenuated brominated compounds. Formation was only directly evidenced for chloroform and bromodichloromethane. Data for the model was based on literature values for water distribution systems that may not be representative for ASR since bromide and ammonia concentrations in the injected water, and the possible role of OC in the aquifer are not taken into account. The potential for in-situ formation of DBPs in the aquifer warrants further research.

DBP formation potentials (FP) were reduced as a result of the removal of DBP precursor material. This is offset by an increase in the FP per unit weight of TOC for the THMs, whilst FP/TOC values are the same or lower for the HAAs following storage in the aquifer. A reduction in precursors could be expected to yield lower DBPs following post-chlorination of recovered water.

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