Process Modeling of Trihalomethanes During Aquifer Storage and Recovery

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Hydrogeology

By

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entitled

Process Modeling of Trihalomethanes During Aquifer Storage and Recovery

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ABSTRACT

Aquifer storage and recovery has been used to meet consumer demand, particularly in the southwestern United States, by injecting treated water underground during wet periods and recovering water during dry periods. Trihalomethanes are the most common disinfection by-products found in chlorinated water, a result of chlorine reacting with dissolved organic matter, and are linked to adverse human health effects. The study objective is to examine processes associated with the attenuation of trihalomethanes surrounding a dual-use well using a numerical model with data and physical and chemical processes pertinent to the Las Vegas Springs aquifer. Thirty-one well data sets provided by the Southern Nevada Water Authority, a chloride mass balance to adjust for dilution, calculated parameters such as liquid diffusion coefficient, and estimated parameters such as longitudinal dispersivity were used to build a single layer, confined, homogeneous, and isotropic model to simulate trihalomethane attenuation. Trihalomethane concentrations at the well during recovery were moderately sensitive to flow rates and porosity, and highly sensitive to a high reaction rate and a low longitudinal dispersivity. The chemical reaction between trihalomethanes and aquifer material was slow with a reaction rate of -0.0032 1/day. A numerical model of trihalomethane attenuation during aquifer storage and recovery may provide water utilities with a tool to monitor trihalomethane transport as it concerns public drinking water.
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1 INTRODUCTION

1.1 OVERVIEW AND SIGNIFICANCE

Population increase puts a high demand on fresh water resources, particularly in the southwest United States. The Las Vegas metropolitan area is experiencing a population boom, and its lack of water resources has led to an innovative way to conserve and distribute water. The Southern Nevada Water Authority (SNWA) has used an aquifer storage and recovery program to meet consumer demand where water from Lake Mead, the largest man-made reservoir in the U.S. (SNWA, 2015), is injected in the aquifer through injection wells during wet periods and pumped out or recovered during dry periods. There were about 95 aquifer storage and recovery sites in the U.S., as of April 2009 (Pyne, 2009).

Along with meeting demand comes concern about clean water. Chlorination is the most common method to remove bacteria from drinking water. Disinfection by-products are formed when chlorine reacts with dissolved organic matter, in the form of humic or fulvic acids (Elshorbagy, 2000) and naturally occurring bromine in an aquifer (Figure 1). Trihalomethanes are the most common disinfection by-products; other major classes include haloacetic acids and haloacetonitriles (Sadiq and Rodriguez, 2004). Water treatment facilities can remove disinfection by-product components such as organic matter, but are not designed to remove disinfection by-products themselves. The United States Environmental Protection Agency established a Maximum Contaminant Level (MCL) for total trihalomethanes at 0.08 mg/L in drinking water. Long-term consumption of drinking water containing total trihalomethane concentrations greater than the MCL is
linked with liver, kidney, and central nervous system problems as well as increased risk of cancer (USEPA, 2013). Trihalomethane fate in aquifers is significant because it relates to public health.

Thousands of disinfection by-product studies have been conducted, but fewer than a dozen involve disinfection by-product fate and transport in conjunction with aquifer storage and recovery. Most disinfection by-product studies focus on those formed at water treatment facilities, as opposed to tracking the by-products in an aquifer.

1.2 BACKGROUND

In 1974, Congress passed the Safe Drinking Water Act to protect the U.S. drinking water supply. Trihalomethanes were first reported in drinking water that same year. In 1979, the U.S. Environmental Protection Agency established an MCL for total trihalomethanes at 0.10 mg/L (‘total’ refers to the combination of four compounds – see Figure 1). In 1998, the total trihalomethane MCL was lowered to 0.08 mg/L (USEPA, 2013).

Trihalomethanes are compounds found in liquid form through indirect anthropogenic influence. Chlorination typically occurs at the end of the water treatment process (Abdullah et al., 2003). Hypochlorous acid is the product of residual chlorine reacting with water, which can dissociate to hypochlorite. Trihalomethanes and haloacetic acids form instantaneously when hypochlorite comes in contact with dissolved organic matter in the form of humic or fulvic acid (Figure 1). Although haloacetic acids are the second most common disinfection by-products, they are rarely recovered in water samples from the pumping stage using an instrument detection limit of $5.0 \times 10^{-4}$ mg/L, due to mixing of injectate with native groundwater and microbial activity (Thomas et al.,
Figure 1. Conceptualization of the chemical mechanisms of trihalomethane formation (modified from Sun et al., 2009). Total trihalomethanes are comprised of four halogenated hydrocarbons which are trichloromethane (chloroform), bromodichloromethane, dibromochloromethane, and tribromomethane (bromoform) (Elshorbagy, 2000).

2000). Trihalomethane formation occurs rapidly and is ~80% complete after about five days (Leising, 2009). On the other hand, the time it takes an initial trihalomethane concentration to reduce by half is on the order of tens of days (Leising, 2009).

The SNWA has not used aquifer storage and recovery for the last few years. In Las Vegas, the aquifer storage and recovery process started with pumping water from the Colorado River at Lake Mead. The water is disinfected at a treatment facility and travels through a distribution pipeline for two to three days to a dual-use well (Figure 2). A dual-use well is used for both injection and pumping. In this research the term “pumping” refers to the recovery or extraction of groundwater. In general, injection occurred from October to April and pumping occurred from late May to October (SNWA-WRD, 2009). Total trihalomethane (TTHM) concentrations leaving the Alfred Merritt Smith Water Treatment Facility (~ 600 meters from Lake Mead’s central west area) or the River Mountains Water Treatment Facility (east Henderson, ~ 34 km from Lake Mead’s central west area) ranged from 0.015 to 0.025 mg/L, while concentrations at aquifer storage and recovery wells averaged between 0.04 and 0.05 mg/L (SNWA-WRD, 2009). Maximum
Figure 2. Simplified representation of a dual-use well (modified from Leising, 2004) where injection occurs first, followed by pumping (recovery). The TTHMs enter the aquifer through the well and spread radially.

trihalomethane concentrations in dual-use wells were approximately 0.1 mg/L (SNWA-WRD, 2009). Injection occurred at an average rate of $2.34 \times 10^7$ m$^3$/year ($1.90 \times 10^4$ acre-feet/year) and pumping was an average rate of $4.81 \times 10^7$ m$^3$/year ($3.90 \times 10^4$ acre-feet/year) (SNWA-WRD, 2009). Monitoring wells ~1.6–3.2 km down-gradient (~1–2 miles) from dual-use wells had low trihalomethane concentrations of less than 0.028 mg/L (SNWA-WRD, 2009). From 2002 to 2009, all end-of-season trihalomethane well samples in the Las Vegas Valley Water District had concentrations of less than 0.03 mg/L (SNWA-WRD, 2009). Dilution alone cannot account for the low down gradient trihalomethane concentrations (SNWA-WRD, 2009), suggesting that additional processes occur. Attenuation of trihalomethane concentrations occur with
increasing distance from the dual-use well because of dispersion (which leads to
dilution), advection, and chemical reactions.

1.3 Problem Statement

The study objective is to examine processes associated with the attenuation of
trihalomethanes surrounding a dual-use well using a numerical model with data and
physical and chemical processes pertinent to the Las Vegas Springs aquifer. The
reactions that form trihalomethanes continue to occur after injection for approximately
two weeks of which the reactions are ~80% complete after five days (SNWA-WRD,
2009). Since the formation reaction can occur over a relatively short time period,
trihalomethane concentrations may increase during pumping as a result of dissolved
organic matter in the aquifer before degradation occurs (Nicholson and Ying, 2005).
Degradation refers to the removal of TTHMs from the system due to chemical reactions
or microbial activity. Although TTHMs are volatile, volatilization does not occur in the
aquifer because this process occurs mostly above ground or in the vadose zone
(Nicholson and Ying, 2005). TTHMs consist mainly of chloroform (Izbicki et al., 2010)
which has a water solubility of 7500 to 9300 mg/L at 25°C (World Health Organization,
2004).

A potential mechanism for TTHM removal is biodegradation (Thomas et al.,
Chloroform biodegradation by native microbes in both aerobic and anaerobic conditions
is not a significant removal process for chloroform in aquifer storage and recovery based
on the lack of methane, ammonia, and organic carbon present in the Las Vegas Valley
aquifer necessary for microbial metabolism (Landmeyer et al., 2000). Biodegradation causes a decrease in the maximum solute concentration (Fetter, 1993, Ch. 3, p. 115-162).

Additional mechanisms for TTHM removal may include adsorption (Landmeyer et al., 2000), chemical hydrolysis (Nicholson and Ying, 2005) and chemical reactions with aquifer material. Adsorption occurs when a solute adheres to the surface of the aquifer material and is dependent on the organic carbon present (Karickhoff, 1984), especially when the organic carbon fraction is ≥1% of aquifer material based on weight (Karickhoff et al., 1979). The fraction of organic carbon refers to the organic matter that can adsorb the organic contaminant (Causarano et al., 2008). Adsorption onto grains is unlikely in Las Vegas Valley because this process involves more than the extremely small (<0.01%) fraction of organic carbon present (Katzer and Brothers, 1989; Landmeyer et al., 2000). Chemical hydrolysis refers to the hydroxide ion (OH⁻) breaking the bond between the carbon and a functional group containing a bromine or chlorine atom (Fetter, 1993, Ch. 7, p. 295-337). A functional group is the reactive part of the molecule (Bruice, 2007, Ch. 2, p. 71-122). Chemical hydrolysis is not a large component of trihalomethane attenuation because it is a slow process with chemical hydrolysis TTHM half-lives of 1 to 3500 years (Nicholson and Ying, 2005). Biodegradation, adsorption, and chemical hydrolysis were not considered in this research, while chemical reactions with aquifer material were considered.

The processes controlling TTHM fate during aquifer storage and recovery in Las Vegas Valley have not been extensively studied. The premise of this research is to investigate what controls TTHM distribution in an aquifer during aquifer storage and
recovery in which only advection, dispersion, diffusion, and chemical reactions are occurring.

1.4 Study Area

Las Vegas Valley (Figure 3) was selected for the model based on available data from Joseph F. Leising, Ph.D. (formerly of the SNWA). The data provided by Leising includes 15 dual-use (injection and pumping), 19 artificial recharge (injection only) and 24 production (pumping only) wells. The time frame is approximately from 1989 to 2013, but this varies based on parameter and well. Data before 2000 are sparse, so data only from 2000 to 2013 were considered in calculations. Important data of the study area include the following: sample date, TTHM (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) concentration, chloride (Cl) concentration, and

**Figure 3.** Map of Las Vegas Valley and well field (modified from Google Earth). Las Vegas Valley is in southern Nevada and lies to the west of Lake Mead. The Las Vegas Valley Well Field is in the northwest area.
**Figure 4.** Monthly pumping (production) rates at one well over three pumping seasons (Nevada Division of Water Resources, 2013). Pumping rates can vary from season to season.

**Figure 5.** Relationships among producing hydrostratigraphic units in Las Vegas Valley (modified from Leising, 2004). The Las Vegas Springs aquifer is bordered by aquitards which are zones of low permeability where water can pass through and be stored (Schwartz and Zhang, 2003). Both municipal and domestic wells primarily draw water from the Las Vegas Springs aquifer. Municipal wells are typically deeper than domestic wells.
Figure 6. Hydrostratigraphic units in Las Vegas Valley (Modified from Leising, 2004; Donovan, 1996). The Las Vegas Springs aquifer is named because most of the source rock material coming from the Spring Mountains to the west. Additional material originates from the Red Rock Canyon area to the west and the McCullough Mountains to the southeast.

Flow rates of injection and pumping. The injection (October to April) rate averaged 64,000 m$^3$/d (~52 acre-feet/day) across 34 injection wells, while the pumping (May to October) rate averaged 132,000 m$^3$/d (~107 acre-feet/day) across 39 pumping wells (Leising, 2009). An example of fluctuating monthly pumping rates for a single well is found in Figure 4.

The depth of the wells range from 150-300 meters (Figure 5; Leising, 2004). These wells are found in mostly cemented alluvial fan gravel and some unconsolidated fan gravel and sand (Figure 6; Leising, 2004; Donovan, 1996). As of the year 2000, the aquifer recharge portion of the Las Vegas Springs aquifer comprises about 67 square kilometers (~26 square miles) (Leising, 2004).
1.5 Previous Studies

A previous Las Vegas Valley study (Thomas et al., 2000) took a three end-member approach to evaluate trihalomethane (THM) decline during aquifer storage and recovery. The three-end members included injectate, residual treated water from the previous season, and native water (groundwater containing no THMs and having a chloride concentration of 4–5 mg/L) (Thomas et al., 2000). A representative selection of injection and recovery water chemistry data from 36 wells, collected from 1990 to 1996, were used in numerical models (Thomas et al., 2000). With dilution alone and using chloride as a conservative tracer, one would expect THM-chloride ratios to decline during recovery. The study concluded that predicted THM concentrations did not equal measured values, inferring dilution is not the only process affecting THM concentrations (Thomas et al., 2000). An estimated 10% to 23% of TTHM concentration decline is due to additional processes (Thomas et al., 2000) such as biodegradation.

A study conducted in South Australia (Pavelic et al., 2005) examined disinfection by-product fate during aquifer storage and recovery considering THM adsorption, mixing, and redox conditions. An anoxic aquifer comprised mostly of calcite and quartz, with a carbon content of 0.1 to 0.3 % and a transmissivity of 150 m²/d was studied (Pavelic et al., 2005). Four fully penetrating wells, including one aquifer storage and recovery and three observation wells, were sampled from October 1999 to November 2001. Samples of injectate, groundwater, and recovered water were analyzed for THMs approximately every two weeks. Travel time through the distribution system to the well was approximately one to two days. The average injection rate ranged from 900 m³/d (0.73 acre-feet/day) to 1300 m³/d (1.05 acre-feet/day), while pumping was more
consistent at about 1300 m$^3$/d (Pavelic et al., 2005). In the experimental method, THM concentration was assumed to exponentially decay during injection instead of being introduced as an instantaneous pulse (Pavelic et al., 2005). The study concluded that THM adsorption was not a significant factor (Pavelic et al., 2005). In terms of biodegradation, half-lives in order of longest to shortest were chloroform (65 days), bromodichloromethane (31 days), dibromochloromethane (27 days), and bromoform (<1 day) based on a mass balance and reaction rate constant (Pavelic et al., 2005).

A study out of Roseville, California (Izbicki et al., 2010) examined the effect of aquifer material heterogeneity on the fate and transport of THMs using a numerical groundwater flow model with particle tracking. Flow rate (tracer test), THM concentration, and chloride concentration data were sampled from the study area. The alluvial aquifer contained an upper section of silt and clay and a lower section of black sands and gravel (Izbicki et al., 2010). The 2-dimensional MODFLOW model had an injection rate of 1.80 x 10$^4$ m$^3$/d (14.59 acre-feet/day) and pumping rate of 1.40 x 10$^4$ m$^3$/d (11.35 acre-feet/day), while the MODPATH particle tracker near an aquifer storage and recovery well had an injection rate of 7.35 x 10$^3$ m$^3$/d (5.96 acre-feet/day) (Izbicki et al., 2010). Samples were collected from four fully penetrating wells, including one aquifer storage and recovery and three observation wells, on a weekly to monthly basis from May 2004 to February 2008. Injection occurred from December 2005 to April 2006, storage for 438 days, and recovery from July 2007 to February 2008 (Izbicki et al., 2010). Transmissivity in the lower aquifer was 2.8 x 10$^3$ m$^2$/d (Izbicki et al., 2010).
Continuing with the Roseville, California study, adsorption and biodegradation may be significant at the study site. For comparison, based on Las Vegas Valley research (Landmeyer et al., 2010), adsorption and biodegradation is not significant. Unexpectedly low THM concentrations with chloride as a conservative tracer were found in the upper 9 m of the aquifer storage and recovery well screen near the end of the pumping phase (Izbicki et al., 2010). The THMs in the injectate consisted of 94% chloroform and 6% bromodichloromethane based on weight (Izbicki et al., 2010). During the storage phase, free chlorine which consists of hypochlorous acid (the product of residual chlorine reacting with water) and hypochlorite ranged from 0.2 mg/L to <0.05 mg/L (detection limit) (Izbicki et al., 2010). Based on the chloride mass balance, 35% of the injectate was recovered, while 65% was unrecovered (Izbicki et al., 2010). Dilution was the governing process during the early stages of injection. Adsorption and degradation may have occurred during the latter stages of the aquifer test based on a lack of brominated THMs (bromodichloromethane, dibromochloromethane, bromoform) present which degrade quicker than chloroform (Izbicki et al., 2010). Chloroform degrades slowly in strongly reducing or methanogenic conditions (Nicholson et al, 2002). The aquifer was not strongly reducing which implies adsorption may be the main reason for chloroform removal (Izbicki et al., 2010). THM concentrations were 45% greater during post-injection compared with injectate concentrations (Izbicki et al., 2010). Heterogeneity in the form of thin highly permeable layers allowed for THMs to move further away from the well and for attenuation through adsorption as oxygenated injectate mixed with reducing native water (Izbicki et al., 2010).
2 METHODS

2.1 APPROACH

A numerical model is used to examine the processes that control TTHM attenuation during aquifer storage and recovery. The single layer computational domain and boundary conditions of the foundation simulation (details in Section 2.6) are found in Figures 7. and Table 1. The lengths of the x- and y- directions were determined based on trial and error and were large enough to not interfere with the cone of depression.

Figures 7. A.) Computational domain. The top figure represents the computational domain. Blue lines illustrate the concept of cell bias where cells get larger further from the well. B.) Boundary conditions. The bottom figure represents the boundary conditions where specified head is defined as a function of space.
Table 1. Parameters defining domain. The datum is at the base of the well. There is no initial hydraulic gradient.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>aquifer thickness</td>
<td>300</td>
<td>m</td>
</tr>
<tr>
<td>starting hydraulic head</td>
<td>300</td>
<td>m</td>
</tr>
<tr>
<td>top elevation</td>
<td>300</td>
<td>m</td>
</tr>
<tr>
<td>bottom elevation</td>
<td>0</td>
<td>m</td>
</tr>
<tr>
<td>dual use well</td>
<td>in southwest corner</td>
<td>[-]</td>
</tr>
</tbody>
</table>

The z axis length of 300 meters was determined based on Las Vegas Valley municipal dual-use (aquifer storage and recovery) well depth (Figure 5, Leising, 2004). While some parameter values (i.e. injection, pumping, TTHM concentration, reaction rate constant) were determined using SNWA data, other parameters (i.e. specific storage, liquid diffusion coefficient) were calculated. Several parameters were estimated due to lack of available data.

While the information found in Figure 7 and Table 1 contain the basis for the computer modeling, raw TTHM and chloride concentration data had to be analyzed to determine a selection of wells for further analysis.

2.2 WELL SELECTION

To determine which dual-use well time frames to analyze, criteria included the following: start of pumping season, pumping rates, sample date, and sample time. Dual-use well flow rates in Las Vegas Valley were found online (Nevada Division of Water Resources, 2013) in the State Engineer’s reports from 2000 to 2013. The time frame of 2000 to 2013 was selected based on sparse data before 2000. Time frames with high pumping rates greater than $1.24 \times 10^4$ m$^3$/d (100 million gallons/month) had first priority during the analysis process because a higher rate translates to more TTHM movement.
Figure 8. Las Vegas Valley Water District (LVVWD) wells and geographic groupings (from Leising, 2009). There are 43 dual-use wells. The 11 dual-use wells of interest are circled in black. Geographic groupings include far northwest, water resource center, gowan, near northwest, west charleston, and LVVWD main well field. Wells in the water resource center group are used by a separate entity and supply golf courses, not homes (J. Leising, personal communication, November 3, 2013).
Pumping seasons with at least seven TTHM samples were considered for further analysis. After studying several time frames for different dual-use wells, one to five pumping seasons for each of the 11 wells were selected and resulted in 32 plots containing raw TTHM and chloride concentrations (Appendix A). Most of the 11 dual-use well data sets were selected based on recommendation by Joseph F. Leising, Ph.D. (supplier of SNWA data). The Las Vegas Valley Water District wells used in analysis came from the geographic groupings of the near northwest, water resource center, and gowan geographic areas (Figure 8).

TTHM samples from the 11 wells were adjusted for dilution. Since the injectate mixes with naturally occurring groundwater, accounting for dilution allows the other attenuation processes to be highlighted.

2.3 Chloride Mass Balance

The chloride mass balance was important to consider because the injectate is diluted when it comes in contact with the native groundwater. The chloride mass balance was used to determine what proportion of the sample is due to dilution and what percentage is based on chemical reactions with aquifer material. Chloride was used because it is a conservative compound. The proportion of aquifer recharge water was determined through a chloride mass balance, which is composed of chloride concentration in the (a) naturally occurring groundwater, (b) sample and (c) injectate at the wellhead. The following process explains how the proportion of aquifer recharge water ($X_{inj}$) was calculated using chloride as the conservative tracer

$$C_{inj}X_{inj} + C_{gw}X_{gw} = C_sX_s$$

where
\[ C_{\text{inj}} = \text{injectate chloride concentration, [M/L}^3] \]
\[ C_{\text{gw}} = \text{naturally occurring groundwater chloride concentration, [M/L}^3] \]
\[ C_s = \text{sample chloride concentration, [M/L}^3] \]
\[ X_{\text{inj}} = \text{fraction of injectate in sample collected at wellhead} \]
\[ X_{\text{gw}} = \text{fraction of naturally occurring groundwater in sample} \]
\[ X_s = \text{fraction of sample in sample (i.e., 1)} \]

If \( X_s = 1 \), then \( X_{\text{inj}} + X_{\text{gw}} = 1 \). Rearranging this relationship and substituting into Equation (1)

\[ C_{\text{inj}}X_{\text{inj}} + C_{\text{gw}} (1-X_{\text{inj}}) = C_s (1) \]

By rearranging and solving for \( X_{\text{inj}} \)

\[ X_{\text{inj}} = \frac{C_s - C_{\text{gw}}}{C_{\text{inj}} - C_{\text{gw}}} \]

The chloride in the sample, \( C_s \), was determined using the data provided by SNWA (Appendix A). A groundwater chloride concentration, \( C_{\text{gw}} \), of 3 mg/L was determined based on native groundwater averaging between 2 to 5 mg/L of chloride (Leising, 2009, Thomas et al., 2000; Katzer and Brothers, 1989). An injectate chloride concentration, \( C_{\text{inj}} \), of 50 mg/L was used in calculations based on Lake Mead water (Thomas et al., 2000).

TTHM samples for the 11 wells were adjusted for dilution by dividing TTHM concentrations by the proportion of aquifer recharge water and then multiplying by 100. The calculated percentage of aquifer recharge water ranged from 1.5% to 2.1%. Dilution-adjusted TTHM and chloride plots are found in Appendix B.

SNWA data were also used to calculate a chemical reaction rate for TTHM attenuation.
2.4 Reaction Rate

The reaction rate is a vital component of the advection-dispersion-reaction equation (explained in depth in Section 2.5) which is used for solute transport. TTHM concentrations depend on the amount of hypochlorite, bromide, and dissolved organic matter present (Elshorbagy, 2000; Leising, 2004) which affects the reaction rate. No adsorption was assumed to occur (Leising, 2009; Miller et al., 1993) and a sorbed reaction rate was not taken into consideration. A reaction rate was calculated based on the first-order ordinary differential equation

$$\frac{dC}{dt} = -kC \quad (4)$$

where

- $C$ = TTHM concentration, [M/L$^3$]
- $k$ = chemical reaction rate constant or source attenuation rate, [1/T]
- $t$ = time, [T]

By separating variables and integrating

$$\ln(C) = -kt + B \quad (5)$$

Then taking the exponent of both sides, simplifying and applying the initial condition where $C_0$ = initial concentration at $t = 0$, the solution is

$$C = C_0e^{-kt} \quad (6)$$

By plotting dilution-adjusted TTHM concentrations of 31 data sets from 11 dual-use wells (Figures 9a and 9b), a rate constant range was calculated using different groundwater and injectate chloride concentrations. One data set (well 24, year 2004) was excluded from the original 32 data sets because a TTHM concentration lacked a paired chloride concentration which was necessary for dilution adjustment. Figure 9(a) includes TTHM data from day 0 to day 152 since the start of pumping, while Figure 9(b) includes
Figure 9.  A.) Days since start of pumping (day 0 to 152) versus normalized adjusted TTHM concentration. Each symbol and color combination represents one of 31 data sets from 11 dual-use wells. The black line is the exponential trendline, $C/C_0 = 2.2434e^{-0.0055t}$. Within each data set, three samples were typically taken within the first hour of pumping resulting in approximately half the data points occurring within the first two days of pumping. This early time data inflates the reaction rate.

B.) Days since start of pumping (day 3 to 152) versus normalized adjusted TTHM concentration. With data from the first two days excluded, this plot is more representative of the reaction rate. The black line is the exponential trendline, $C/C_0 = 1.8482e^{-0.0032t}$. 


data from day 3 to day 152. The rate constant was estimated based on an exponential trendline fit from day 3 to day 152 since the start of pumping. Samples taken within two days after the start of pumping, which accounted for ~53% of the data points, have less evidence of dilution and degradation reactions. The reason is that the first water pumped out was the last water injected and therefore had less time to mix and react. The first two days were excluded from the analysis due to noisy data after examining a plot of all 152 days since the start of pumping (Figure 9a). The reaction rate constant, k, for input in the computer model was -0.0032 1/d (Figure 9b).

TTHM half-life is a function of the reaction rate constant. The first-order reaction rate for the dissolved (liquid) phase is typically given in terms of half-life, where rate constant, \( k = \ln 2 / t_{1/2} \) (Zheng and Wang, 1999). The time frame for each half-life remains constant. Looking at all 31 data sets, an exponential trendline of day 3 to day 152 since start of pumping versus dilution-adjusted TTHM concentration yielded a half-life, \( t_{1/2} = \ln 2 / k = \ln 2 / (-0.0032 \text{ 1/d}) = 217 \text{ days} \). For comparison, Nicholson and Ying (2005) reported TTHM half-life > 120 days (1995-1996 ASR cycle) and > 130 days (1996-1997 ASR cycle) in the Las Vegas Valley.

2.5 MODFLOW and MT3DMS Governing Equations

A numerical model with similar properties to those in Las Vegas Valley was used to simulate subsurface flow and TTHM transport through an aquifer. The Groundwater Modeling System (GMS) is a graphical user interface which houses three-dimensional numerical modeling programs widely used in groundwater research including MODFLOW and MT3DMS. Groundwater flow was simulated using the MODFLOW model, and TTHM transport was simulated using the MT3DMS model. Each model runs
on a governing equation, the groundwater flow equation for MODFLOW and the advection-dispersion-reaction equation for MT3DMS. This research uses the 2-dimensional versions of these equations.

2.5.1 Flow Model

The MODFLOW numerical model solves the groundwater flow equation (Equation 8). The 2-dimensional groundwater flow equation (Zheng and Wang, 1999) is

\[ \frac{\partial}{\partial x_i} (K \frac{\partial h}{\partial x_i}) + q_s = S_s \frac{\partial h}{\partial t} \]  

where

- \( K \) = hydraulic conductivity [L/T]
- \( S_s \) = specific storage of aquifer [1/L], (Fetter, 2001)
- \( S \) = storage coefficient [dimensionless]
- \( b \) = aquifer thickness [L]
- \( q_s \) = fluid sink/source term, volumetric flow rate per unit volume of aquifer representing fluid sources (positive) and sinks (negative), [1/T]
- \( h \) = hydraulic head [L]
- \( x_i \) = distance along the respective Cartesian coordinate axis, [L]

where subscript “i” ranges from 1 to 2 which correspond to the x-axis and y-axis, respectively.

Using substitution and rearranging, the 2-dimensional groundwater flow equation, Equation (7), becomes

\[ K \left( \frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \right) + q_s = \frac{S}{b} \frac{\partial h}{\partial t} \]  

The model domain, boundary conditions and grid sizes remain the same for MODFLOW and MT3DMS (Figure 7, Table 1). The model consists of a single confined aquifer. The grid covers 115 columns and 115 rows (13,225 cells total) and a bias of 1.04 in the x- and y-directions. A cell bias of 1.04 means that an adjacent cell is 4% larger than
its predecessor, moving away from the well. The area of the smallest cell is 0.31 m$^2$ and is larger than the typical diameter of a municipal well which is 0.15 – 0.20 m (Donovan, 1996). The area of the largest cell is 2,362.93 m$^2$.

The injection and pumping rates were calculated to be approximately 2000 m$^3$/d and -3500 m$^3$/d, respectively, based on average yearly rates (+19,000 acre-feet/year, -39,000 acre-feet/year) that were converted to daily rates (m$^3$/d) and then divided by the number of wells receiving injection (34) or pumping (39) (Leising, 2009). The pumping rate was rounded up to the nearest thousandth to become -4000 m$^3$/d. These flow rates were divided by four to simulate flow in one Cartesian coordinate quadrant which is acceptable under homogeneous and isotropic conditions.

The simulations were broken down into stress periods which are subdivided into time steps. Each stress period covered 30 days. Injection and pumping were represented by three stress periods each or 90 days. The six stress periods were divided into 1, 1, 1, 40, 4 and 4 time steps respectively. The first stress period started at injection, while the fourth stress period started at pumping. There were more time steps during the pumping phase to account for daily and weekly changes. Simulation time covered 180 days.

To account for water stored in the confined aquifer, a specific storage term was needed which requires a storage coefficient and aquifer thickness. The storage coefficient ranges from 0.0045 to 0.0375 (Zikmund, 1996; Donovan, 2000; Donovan, 2010) based on averages of different Las Vegas Valley regions. An average storage coefficient of 0.02 was selected within the literature range. Using a storage coefficient of 0.02 and an aquifer thickness of 300 m, specific storage equals $6.67 \times 10^{-5}$ l/m.
Figure 10. Hydraulic conductivity distribution of the Las Vegas Spring aquifer (Donovan, 1996). Hydraulic conductivity was estimated by dividing transmissivity by thickness.
Hydraulic conductivity in the simulations covered one layer and was isotropic. Estimated hydraulic conductivity for the Las Vegas Springs aquifer ranges from $< 1.5 \text{ m/d}$ to $> 25 \text{ m/d}$ (Figure 10, Donovan, 1996). A value of 25 m/d was selected from the high end range because the majority of the dual-use well data sets came from the area where 25 m/d was an estimated hydraulic conductivity. A high rate would also simulate a more permeable aquifer material.

MODFLOW calculations resulted in a head distribution that was then used in MT3DMS in the form of a velocity field to calculate the TTHM concentration distribution.

### 2.5.2 Solute Transport Model

MT3DMS is a three-dimensional solute transport model based on the advection-dispersion-reaction equation (Zheng and Wang, 1999). The 2-dimensional advection-dispersion-reaction equation (Zheng and Wang, 1999) is

$$\frac{\partial (\theta C)}{\partial t} = \frac{\partial}{\partial x_i} \left( \theta D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} \left( \theta v_i C \right) + q_s C_s + R_n$$  \hspace{1cm} (9)

- **Accumulation**
- **Dispersion**
- **Advection**
- **Source/sink**
- **Reaction**

where

- $\theta$ = porosity [dimensionless]
- $C$ = dissolved concentration of TTHMs, [M/L$^3$]
- $D_{ij}$ = hydrodynamic dispersion coefficient, [L$^2$/T]; double subscript where $i = 1$ and $j = 2$ represent three components ($D_{11}, D_{12} = D_{21}, D_{22}$) for the 2-D field (Bear, 1988)
- $v_i = \frac{q_i}{\theta}$ = average linear water velocity, [L/T]
- $q_i$ = the specific discharge or Darcy flux, [L/T]
- $C_s$ = concentration of the source or sink flux for TTHMs, [M/L$^3$]
- $R_n$ = chemical reaction term, [M/L$^4$T]
Expanding the left side of the equation and writing the chemical reaction term as a first-order reaction of dissolved phase

\[
\frac{\partial C}{\partial t} + \frac{\partial \theta}{\partial t} C = \frac{\partial}{\partial x_i} \left( \theta D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} \left( \theta v_i C \right) + q_s C_s - k \theta C
\]

where \( k = \) first-order reaction rate for dissolved phase, \([1/T]\)

Rearranging

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left( \theta D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} \left( \theta v_i C \right) + q_s C_s - \frac{\partial \theta}{\partial t} C - k \theta C
\]

Equation (11) represents the change in the TTHM concentration equal to the change in mass flow due to dispersion, advection, source/sink and chemical reactions. Dispersion mixes dissolved mass with the fluid causing the contaminant to spread (Schwartz & Zhang, 2003). Advection transports dissolved mass by fluid flow (Schwartz & Zhang, 2003). The source/sink is the dual-use well where TTHMs are introduced and fluid enters or exits the domain. Reactions with aquifer material reduce TTHM concentration as represented by a negative reaction rate.

MT3DMS contains several subpackage options including advection, dispersion, source/sink mixing and chemical reaction. Each simulation had 3 to 4 of these packages running. The model domain, boundary conditions, and grid sizes were the same for MODFLOW and MT3DMS (Figure 7, Table 1). Flow rates, stress periods and time steps were also unchanged. While details on the foundation simulation are provided in Section 2.6, the differences in the solute transport model compared with the groundwater flow model is that the TTHMs enter the aquifer during the first three stress periods (90 days).
using the source/sink mixing package and a diffusion coefficient value is used in the dispersion package taking into account transport by concentration gradient.

The reaction rate was simulated using MT3DMS, and it should be noted that the reaction package can only model one species and is not intended for modeling chemical reactions between species (ex. chloroform and bromoform) (Zheng and Wang, 1999). Since the diffusion coefficients for chloroform, bromodichloromethane, dibromochloromethane, and bromoform are similar ($8.9 \times 10^{-3} \text{ m}^2/\text{d}$ to $9.2 \times 10^{-3} \text{ m}^2/\text{d}$, USEPA, 2011), TTHMs were assumed to act as one species.

### 2.5.2.1 Liquid Diffusion Coefficient of Chloroform

To determine the dispersion term of the advection-dispersion-reaction equation (Equation 11), a liquid diffusion coefficient is needed. Since the majority of a TTHM concentration is comprised of chloroform (Izbicki et al., 2010; Leising, 2009), the assumption was made that the diffusion coefficient of chloroform and TTHMs are very similar. The liquid diffusion coefficient was calculated using the Wilke-Chang estimation method (Wilke and Chang, 1955)

\[
D = \frac{7.4 \times 10^{-8} (\varphi M_B)^{1/2} T}{n_B V_A^{0.6}}
\]  

(12)

where

- $D$ = free solution diffusion coefficient of chloroform (solute A) at very low concentrations in water, [cm$^2$/s]
- $M_B$ = molecular weight of water (solvent B), [g/mol]
- $T$ = temperature, [K]
- $n_B$ = viscosity of water (solvent B), [centipoise]
- $V_A$ = molar volume of chloroform at its normal boiling temperature, [cm$^3$/mol]
- $\varphi$ = association factor of water as it relates to the solute, [dimensionless]
Table 2. Parameters used to calculate chloroform diffusion coefficient using the Wilke-Chang estimation method

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>molecular weight (water)</td>
<td>18.02</td>
<td>g/mol</td>
</tr>
<tr>
<td>temperature</td>
<td>293.15†</td>
<td>K</td>
</tr>
<tr>
<td>viscosity (water)</td>
<td>1.002†</td>
<td>centipoise</td>
</tr>
<tr>
<td>association factor (water)</td>
<td>2.6*</td>
<td>[-]</td>
</tr>
<tr>
<td>molar volume (chloroform)</td>
<td>85.64‡</td>
<td>cm³/mol</td>
</tr>
<tr>
<td>diffusion coefficient</td>
<td>1.03E-05</td>
<td>cm²/s</td>
</tr>
</tbody>
</table>

* recommended value when water is solvent (Reid et al., 1987, Ch. 11, p. 577-631)
† at room temperature, 20°C
‡ molar volume (chloroform) calculated using molecular weight (119.38 g/mol) divided by chloroform density at boiling point, 60°C (1.394 g/cm³)
§ centimeters were used because the Wilke-Chang method also used centimeters

The estimated Wilke-Chang free solution diffusion coefficient value of chloroform is 8.89 x 10⁻⁵ m²/d (1.03 x 10⁻⁵ cm²/s) using the parameters found in Table 2.

The Wilke-Chang estimation method was selected based on the solute having a low concentration.

To account for tortuosity of flow paths, the liquid diffusion coefficient of chloroform was calculated using the following equation (Gilham et al., 1984)

\[
D^* = D \cdot \tau
\]  

(13)

where

\[
D^* = \text{liquid diffusion coefficient [L}^2/\text{T]}
\]

\[
D = \text{free solution diffusion coefficient [L}^2/\text{T]}
\]

\[
\tau = \frac{\theta^{10/3}}{\varphi^2} = \text{liquid tortuosity factor (Jury et al., 1999) [dimensionless]}
\]

\[
\theta = \text{water content [dimensionless]}
\]

\[
\varphi = \text{porosity [dimensionless]}
\]
Using 0.3 for water content and for porosity, the calculated liquid diffusion coefficient of chloroform was $1.78 \times 10^{-5} \text{ m}^2/\text{d}$ which is similar to the diffusion coefficient of chloroform in water $8.64 \times 10^{-5} \text{ m}^2/\text{d}$ (Schwartz and Zhang, 2003).

With detailed information on why certain parameters were selected and how parameters were calculated, a full description of the foundation simulation follows.

### 2.6 Foundation Simulation

The simulations started out simple and subsequently grew in complexity. One confined aquifer was used throughout the modeling process based on the Las Vegas Springs aquifer. Most simulations covered one quadrant with the dual-use well in the corner, as opposed to four quadrants with the dual-use well in the center. Under homogeneous and isotropic conditions (i.e. symmetric), simulating one quadrant is equivalent to understanding the overall flow and solute transport. For simplicity and to differentiate between injectate and native groundwater, TTHMs were not present before injection.

Several simulations were carried out, some of which were part of a sensitivity analysis (Section 2.7). Although the parameters in Figures 7 and Table 1 were used in all simulations, Table 3 contains a more detailed explanation of the foundation simulation.

### 2.7 Sensitivity Analysis

Once the foundation simulation was established, a sensitivity analysis was used to identify model parameters that affect the variation of the output (Saltelli, 2004). In the advection-dispersion-reaction equation, the TTHM concentration is effected by the average linear water velocity, the hydrodynamic dispersion, the porosity and the reaction rate. A sensitivity analysis was conducted to determine the effects of changes in
Table 3. Parameters used in foundation simulation. For additional details on computational domain, well location and boundary conditions, see Figure 7.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>x-direction, Number of cells, Bias</td>
<td>1250 m, 115, 1.04</td>
</tr>
<tr>
<td>y-direction, Number of cells, Bias</td>
<td>1250 m, 115, 1.04</td>
</tr>
<tr>
<td>z-direction, Number of cells, Bias</td>
<td>300 m, 1, 1</td>
</tr>
<tr>
<td>Stress Periods</td>
<td>6 Stress Periods, 30 Days Each (180 Days Total)</td>
</tr>
<tr>
<td>Hydraulic Conductivity</td>
<td>25 m/d</td>
</tr>
<tr>
<td>Specific Storage</td>
<td>6.67E-05  l/m</td>
</tr>
<tr>
<td>Flow Rate (injection, pumping)*</td>
<td>500 m³/d, -1000 m³/d</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.3</td>
</tr>
<tr>
<td>Packages</td>
<td>Advection, Dispersion, Source/Sink mixing, Chemical reaction</td>
</tr>
<tr>
<td>Stress Periods (Source/Sink Mixing Package)</td>
<td>Stress Period 1,2,3 (90 Days Injection)</td>
</tr>
<tr>
<td>Effective Molecular Diffusion Coefficient</td>
<td>1.78E-05  m/d</td>
</tr>
<tr>
<td>Longitudinal Dispersivity**</td>
<td>20 m</td>
</tr>
<tr>
<td>Initial TTHM Concentration</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>TTHM Reaction Rate</td>
<td>-0.0032  1/d</td>
</tr>
</tbody>
</table>

* These rates are a result of dividing by four to account for the flow in one quadrant. The original injection and pumping rates were 2000 m³/d and -4000 m³/d, respectively.

** Longitudinal dispersivity was based on literature plots of scale versus longitudinal dispersivity (Xu and Eckstein, 1995; Gelhar et al., 1992). The ratio of horizontal transverse dispersivity to longitudinal dispersivity (TRPT) and the ratio of vertical transverse dispersivity to longitudinal dispersivity (TRVT) were equal to one another.

Table 4. Parameters for sensitivity analysis. The parameter values for low, medium and high may not constitute a low, medium or high value outside the context of this analysis. Flow rates are for flow in one quadrant and are a result of dividing by four.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (injection, pumping), m³/d</td>
<td>250, -500</td>
<td>500, -1000</td>
<td>1000, -2000</td>
</tr>
<tr>
<td>Longitudinal dispersivity, m</td>
<td>2</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.15</td>
<td>0.2, 0.25</td>
<td>0.3, 0.35</td>
</tr>
<tr>
<td>Reaction rate, 1/d</td>
<td>-0.00032</td>
<td>-0.0032</td>
<td>-0.032</td>
</tr>
</tbody>
</table>
estimated injection and pumping rates, longitudinal dispersivity, porosity, and reaction rate (Table 4). Sensitivity analysis parameters were categorized into low, medium and high groupings. Parameter ranges were selected based on those in the foundation simulation which included the medium flow rate, medium longitudinal dispersivity, medium reaction rate, and high porosity (0.3) value. Values for each group were determined using estimated values, some of which came from reviewing SNWA data and literature (Donovan, 1996).
3 RESULTS AND DISCUSSION

Model results from the pumping stage of aquifer storage and recovery were used to improve the understanding of the influential TTHM attenuation processes. Analyses of advection, hydrodynamic dispersion, and chemical reactions with TTHMs were used to interpret the processes controlling TTHM attenuation in the aquifer near the dual-use well. Results of these analyses are found in the following sections of simulated TTHM movement and sensitivity analysis.

3.1 SIMULATED TTHM MOVEMENT

Physical and chemical mass transport processes include advection, dispersion and reactions with aquifer material. Results of these physical and chemical mass transport processes are found in Figures 11 and 12. Foundation simulation parameters were used in observing TTHM concentrations over six months of pumping (Figure 11) and by distance from the dual-use well (Figure 12). The contaminant entered through the well and spread radially under the homogeneous and isotropic conditions. In Figure 11, the TTHM concentration at the well during the first day of pumping is 0.0751 mg/L which is less than the injectate TTHM concentration of 0.1 mg/L.

The spatial TTHM distribution at several snapshots during pumping is shown in Figure 12. With a porosity of 0.3, the injectate represented 0.03% of the computational domain after 90 days of injection and the amount pumped represented 0.06% of the computation domain after 90 days of pumping. Early stages of pumping show a rapid TTHM decline because the last water injected is the first water removed therefore having little exposure to attenuation effects. Latter stages show a more gradual decline because dispersion, advection, and chemical reactions with aquifer material have occurred.
Figure 11. TTHM concentration at dual-use well during six months of pumping (recovery). TTHMs were introduced into the aquifer for 90 days at a concentration of 0.1 mg/L before pumping occurred.

Figure 12 shows TTHM concentrations along a horizontal transect from the well for various times. Distance values were affected by cell bias and cells are aligned with the x-axis. Had the distance been calculated at a 45° angle to the x-axis there would be an error (overestimation) up to 25 meters because with a cell bias cells grow incrementally moving away from the well.

The Péclet number is the ratio of the advective and diffusive transport. Péclet number, $Pe = \frac{\text{transport by advection}}{\text{transport by diffusion}}$ (Zheng and Bennett, 1995) or $Pe = \frac{vL}{D_d}$ (Domenico and Schwartz, 1998) where $v =$ advective velocity [L/T], $L =$ characteristic pore length [L], and $D_d =$ diffusion coefficient [L^2/T]. The Péclet number is related to the Damköhler number which is used to determine whether the chemical reaction or diffusion dominates (Domenico and Schwartz, 1998). If $Pe \ll 1$, then
Figure 12. Distance from well versus TTHM concentration at 12 pumping (recovery) phases. This is one simulation. TTHM concentrations approach zero at ~90 meters from the dual-use well. The x-axis originally extended to 300 meters, but was cropped since TTHM concentrations remain zero > 100 meters from the well.

Damköhler number II applies where \( \text{Da}_{\text{II}} = \frac{k L^2}{D_d} \) and \( k = \text{reaction constant [1/T]} \) (Domenico and Schwartz, 1998).

The cells along the x-axis of the computational domain were examined to calculate the Péclet and Damköhler numbers. The Péclet number ranged from 0.03 (85 meters from well along x-axis) to 2.56 (~1 meter from well along x-axis) with the majority of the numbers less than one. The \( \text{Da}_{\text{II}} \) number was calculated since the \( \text{Pe} \ll 1 \) which means diffusion occurs much faster than the reaction (Domenico and Schwartz, 1998). The \( \text{Da}_{\text{II}} \) number ranged from \( 4.2 \times 10^{-9} \) (85 meters from well along x-axis) to \( 2.4 \times 10^{-10} \) (~1 meter from well along x-axis).
With an understanding of the simulated TTHM movement, the analysis continued with changes to different parameters and the subsequent TTHM concentrations near the dual-use well.

3.2 Sensitivity Analysis

There are four sensitivity analysis scenarios, one for each parameter. Comparisons of low, medium, and high values of flow rate, porosity, longitudinal dispersivity and reaction rate (Table 4) were used to observe effects on TTHM concentrations. The following scenarios are based on the foundation simulation with the aforementioned parameter values changing between simulations.

3.2.1 Flow Rates at the Well

Three simulations were run to see the effect of flow rates on TTHM concentration at the well head. Flow rates at the well include injection and pumping represented by low (+250 m$^3$/d, -500 m$^3$/d), medium (+500 m$^3$/d, -1000 m$^3$/d) and high rates (+1000 m$^3$/d, -2000 m$^3$/d). These rates were considered constant and represented flow in one quadrant. At the start of pumping, TTHM concentrations at the well varied by ~0.01 mg/L depending on flow rate (Figure 13). Higher flow rates correspond to more advection and dispersion occurring because the contaminant plume extends further than in the medium or low flow rate situations. Over 90 days the effect of flow rate lessened and TTHM concentrations converged because all the water injectate was pumped out. For the three flow rates, TTHM concentrations at the well were nearly independent of flow rate after 90 days of pumping.
Figure 13. Effect of flow rates on TTHM concentration at dual-use well during three months of pumping. TTHMs were introduced into the aquifer for 90 days before pumping occurred. Faster flow rates resulted in a higher concentration of TTHMs reaching the dual-use well.

3.2.2 Porosity

Five simulations were run to see the effect of porosity on TTHM concentration at the well head. Porosity was represented by low (0.15), medium (0.20, 0.25) and high (0.30, 0.35) values. Five values were chosen instead of three because porosity is estimated to range from 0.15 to 0.25 in Las Vegas Valley (Donovan, 1996), 0.30 was used in the foundation simulation, and 0.35 was greater than the porosity used in the foundation simulation.

Porosity relates the specific discharge and average linear velocity by the relationship \( v = \frac{q}{\theta_e} \) (Schwartz and Zhang, 2003), where \( v = \) average linear velocity \([L/T]\), \( q = \) specific discharge or Darcy flux \([L/T]\) and \( \theta_e = \) effective porosity. Volumetric
Figure 14. Effect of porosity on TTHM concentration at dual-use well during three months of pumping. TTHM concentrations varied more during the first month and gradually converged after three months.

discharge is held constant in the five simulations (Figure 14). As porosity decreases, average linear velocity increases. The largest variation in TTHM concentration at the well head occurred during the first few days of pumping. TTHM concentrations converged to 0.01 mg/L after 90 days. For the porosity range 0.15–0.35, TTHM concentrations at the well were nearly independent of porosity after 80 days of pumping because the TTHM concentrations were so low, there was no room for fluctuation.

Porosity was used to calculate the liquid tortuosity factor, $\tau = \theta^{10/5} / \varphi^2$ (Jury et al., 1999) where $\theta =$ water content and $\varphi =$ porosity, as explained in Section 2.5.2.1 (Liquid Diffusion Coefficient of Chloroform). The liquid diffusion coefficient, $D^*$, is a function of the liquid tortuosity factor. While there are five simulations in Figure 14 each with a
different porosity value, the liquid diffusion coefficient remained constant for all
simulations. This may have led to a bias in the simulated TTHM concentrations.

3.2.3 Longitudinal Dispersivity

Three simulations were run to see the effect of longitudinal dispersivity on TTHM
congestion at the well head. Longitudinal dispersivity was represented by low (2 m),
medium (20 m) and high (50 m) values. While 20 m was used in the foundation
simulation, the low value was selected simply as an order of magnitude smaller and the
high value was selected as slightly more than double the medium value. It is difficult to
estimate a realistic dispersivity value that describes contaminant spreading accurately
because it is scale dependent.

A low longitudinal dispersivity corresponds to a small zone of mixing. A high
longitudinal dispersivity corresponds to a larger zone of mixing resulting in a smaller
TTHM concentration at the well. Longitudinal dispersivity, \( \alpha_L \), affects the dispersion of
the TTHMs, particularly if the value is low. When \( \alpha_L = 2 \) meters, initial TTHM
concentrations at the well are nearly the same as the 0.1 mg/L TTHM injectate
concentration (Figure 15). The low longitudinal dispersivity results in a higher initial
TTHM concentration while the medium or high values represent more dispersion taking
place and result in a lower initial TTHM concentration. A higher longitudinal dispersivity
value represents more variation in path length, and more exposure to variation in pore
size (Fetter, 1993, Ch.2, p. 43-114).
Figure 15. Effect of longitudinal dispersivity on TTHM concentration at dual-use well during three months of pumping. A small longitudinal dispersivity resulted in a steep TTHM decrease during the first two months of pumping. After three months of pumping, the TTHM concentration is approximately the same in all three cases.

3.2.4 Reaction Rate

Three simulations were run with reaction rate changing by an order of magnitude between simulations. The reaction rate was represented by low (-0.00032 1/d), medium (-0.0032 1/d) and high (-0.032 1/d) values. TTHMs were introduced into the aquifer for 90 days before pumping occurred. Since reaction rate determines how fast TTHMs are removed from fluid flow, a faster rate would have a steeper slope and a slower rate would have a more gradual slope. A smaller reaction rate means TTHMs will persist in the aquifer longer due to the reaction occurring over a longer time frame. The low and medium reaction rates resulted in similar TTHM concentrations throughout the pumping period, although the low rate resulted in a slightly higher TTHM concentration reaching
Figure 16. Effect of reaction rate on TTHM concentration at dual-use well during three months of pumping. The faster reaction rate resulted in the quick decay of TTHMs so that fewer TTHMs reached the dual-use well. The slower reaction rate constants resulted in a greater initial TTHM concentration reaching the well.

The well (Figure 16) because TTHMs underwent less decay in that case. The high reaction rate resulted in a steeper initial decline of TTHM concentrations within the first week of pumping.

The initial TTHM concentration, during the first day of pumping, of the medium (yellow diamonds in Figure 16) and low (green diamonds) reaction rate simulations are similar at approximately 0.08 mg/L. The reaction rates may be small enough allowing the pumping rate to dominate the TTHM concentration reaching the well and ties in with the small Da,II number (range from 4.2 x 10^9 (85 meters from well along x-axis) to 2.4 x 10^10 (~1 meter from well along x-axis)) which signifies diffusion occurs much faster than the low and medium reaction rates. With the high (blue diamonds) reaction
rate, the decay occurs fast enough to result in a 0.02 mg/L drop in initial TTHM concentration over the medium and slow rates. Advection and dispersion are also taking place and have a greater influence at the high reaction rate. A faster reaction rate causes more TTHMs to react with the aquifer material, therefore removing TTHMs that would have otherwise reached the well during pumping.

3.3 Conclusion

TTHM concentration data and dual-use well characteristics were combined with a numerical model to understand the processes and influential factors of TTHM attenuation during aquifer storage and recovery. The pumping or recovery stage was examined as a representation of the TTHMs in drinking water that could be delivered to residents. The physical and chemical mass transport processes of advection, dispersion and reactions with aquifer material all affected TTHM concentrations at the dual-use well. The largest change in TTHM concentration occurred during the first few days, regardless of sensitivity analysis parameter ranges. TTHM concentrations were one-tenth the injectate concentration (0.1 mg/L) after 90 days of pumping. Under the confines of the foundation simulation and sensitivity analysis, TTHM concentrations were moderately sensitive to flow rates and porosity, and highly sensitive to a high reaction rate and a low longitudinal dispersivity.

This research was based on a single layer, homogeneous and isotropic aquifer which was an idealized version of reality. Parameters like hydraulic conductivity are complex and may vary over several meters. The numerical model produces approximate results. A more in depth sensitivity analysis may reveal interactions between parameters
(Saltelli, 2004). It is possible that the grid size was larger than it needed to be and the number of grid points may have influenced the output.

Suggestions for future work are focused on adding complexity which might include adding more layers, conducting a sensitivity analysis of the ratio of horizontal transverse dispersivity to longitudinal dispersivity (which is taken into account when 2 or more layers are present), adding spatial heterogeneities of hydraulic parameters (i.e. Monte Carlo simulations for hydraulic conductivity), and solving the advection-dispersion-reaction equation using an analytical approach. The Las Vegas Springs aquifer could also be considered semi-confined. In reality, the LVVWD main well field has springs, well interference, infrastructure, and faults in the area (J. Leising, personal communication, November 3, 2013) that could be included in a future model.

The benefits of modeling THM attenuation may include the ability to identify operational strategies by water utility operators that minimize THM formation, to evaluate technical feasibility of establishing more stringent THM regulation, and to improve decision making for management of public health risks associated with THMs (Semerjian et al., 2009). However, there are also limitations to modeling THM attenuation. The limitations include that the model may not always be easily reproduced and may have modeling errors that are difficult to find. Additional limitations may include application to only a specific water source, inadequate model validation, and occasional lack of terms to simulate important parameters (Semerjian et al., 2009). A numerical model will never be the same as reality, but can be used, in this case, as a tool to monitor contaminant transport concerning public drinking water.
4 REFERENCES


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APPENDIX A: 32 RAW TTHM AND CL DATA SETS OF DUAL-USE WELLS DURING PUMPING

The following plots include raw TTHM (Appendix A), dilution-adjusted TTHM (Appendix B) and chloride data sets (Appendices A and B). Each plot is labeled with a well name which starts with the letter “W” followed by four characters containing numbers and/or letters. The well name is followed by the year in parentheses when the samples were taken and analyzed.

The 32 data sets represent a selection of dual-use wells operated in the Las Vegas Valley. Raw data of days since start of pumping (x-axis) versus TTHM concentration (primary y-axis, blue diamonds) and chloride concentration (secondary y-axis, green circles) were plotted. Chloride is the conservative tracer. The primary y-axis (TTHM concentration) ranges from 0 to 0.18 mg/L. The secondary y-axis (Cl concentration) ranges from 0 to 120 mg/L, except for W073 (2005) which ranges from 0 to 140 mg/L. Raw TTHM concentrations ranged from 0.0023 (W033) to 0.1731 mg/L (W024). Chloride concentrations ranged from 10.663 (W033) to 140 mg/L (W073).

Even though the plots represent the pumping phase only, it is helpful to know when injection and pumping occurred. In general, injection occurred from October to April and pumping occurred from May to October. The average pumping length is approximately 105 days of which the maximum is 152 days and the minimum is 59 days.

Interference from another dual-use well was possible considering proximity to other wells (Figure 8, LVVWD wells and geographic groupings). In plot W005A (2009), for example, TTHM concentrations were virtually non-detected. This may have been caused by well interference.
W085 (2004)

W120 (2005)

W120 (2006)

W120 (2007)
APPENDIX B: 31 DILUTION-ADJUSTED TTHM DATA SETS OF DUAL-USE WELLS DURING PUMPING

The 31 data sets represent a selection of dual-use wells operated in the Las Vegas Valley. The W024 (2004) data set was removed from further analysis because a TTHM sample lacked a paired chloride concentration, therefore causing a break in the data. Dilution-adjusted data of days since start of pumping (x-axis) versus TTHM concentration (primary y-axis, blue diamonds) and chloride concentration (secondary y-axis, green circles) were plotted. Chloride is the conservative tracer. The primary y-axis (dilution-adjusted TTHM concentration) ranges from 0 to 10 mg/L. The secondary y-axis (Cl concentration) ranges from 0 to 120 mg/L, except for W073 (2005) which ranges from 0 to 140 mg/L. The proportion of aquifer recharge water, used to determine dilution-adjusted TTHM concentrations, ranged from 1.5% (W033) to 2.1% (W073). Dilution-adjusted TTHM concentrations ranged from 0.2838 (W023A) to 8.7481 mg/L (W024). Chloride concentrations ranged from 10.663 (W033) to 140 mg/L (W073). Dilution-adjusted TTHM values are greater than raw TTHM values. Dilution is accounted for by using a chloride mass balance (Section 2.3) and thus makes the dilution-adjusted TTHM values more concentrated.