AN ABSTRACT OF THE THESIS OF

Danelle Bertrand for the degree of Master of Science in Civil Engineering presented
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Title: Fate of THMs in Columbia River Basalts During Aquifer Storage and Recovery

Abstract approved:

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Use of basalt aquifers for aquifer storage and recovery (ASR) systems is increasing in the

Pacific Northwest due to the large aerial extent of the Columbia River Basalt Group and

the suitability of basalts as ASR reservoirs. However, the degradation of

trihalomethanes (THMs), potentially carcinogenic disinfection by-products present in the

majority of treated ASR source water, has not been quantitatively studied directly in

basalt aquifers which have unique physical and geochemical characteristics. This study

uses data from three basalt ASR systems in Oregon to calculate THM degradation rates

corrected for dilution. Major ion concentration data was used to analyze dilution in the

absence of external tracers and reaction rates were calculated based on first-order kinetics

and residence times within the aquifer. Calculated total THM half-lives ranged over

three orders of magnitude from approximately 20 to 8,000d. Overall, THM reaction rate

trends were similar to those observed in non-basalt ASR systems with rates dependent on

ASR redox conditions and higher reaction rates observed under more reducing

conditions. Additionally, under anoxic and anaerobic conditions, higher reaction rates

were observed for ASR cycles with higher TOC concentrations. Contradictory to results

in non-basalt ASR systems, brominated THMs did not degrade more rapidly than

chloroform in anoxic basalt ASR cycles.

Fate of THMs in Columbia River Basalts During Aquifer Storage and Recovery

by
Danelle Bertrand

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Dean of the Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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Danelle Bertrand, Author

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CONTRIBUTION OF AUTHORS

GSI Water Solutions, Inc. provided all data and technical reports for the Tigard,

Beaverton, and McCarty Ranch ASR systems. Dr. Jack Istok assisted in developing the

ASR conceptual model illustrated in Figure 2 of Chapter 2 and the THM reaction rate

analysis method in Chapter 2 (Equations 2 through 6).

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<u>Introduction</u>:

Aquifer storage and recovery (ASR) is the temporary storage of water in aquifers; water is injected into the aquifer during the wet season when water supply is ample (injection phase), stored in the aquifer (storage phase), and recovered during the dry season to meet peak water demands (recovery phase). Interest in ASR is increasing in the United States due to population growth increasing water demands and the effects of climate change. Climate change in the Pacific Northwest in particular is predicted to cause earlier seasonal snow melt, and precipitation to fall as rain instead of snow, decreasing the availability of water in the dry summer months. The first ASR system in the United States began operating in 1968 in New Jersey, by 1992 there were 14 operational systems in seven states and by 2004 there were 69 operational ASR systems in 16 states, 20 of which are in Oregon, Washington, and California (Pyne 2004).

ASR aquifers in this study are within the Columbia River Basalt Group (CRBG), a geologic unit of thick Miocene basalt layers 6 to 17.5 million years old that extends across approximately 164,000 square kilometers of Oregon, Washington, and Idaho. Basalt aquifers are unique in that groundwater flow predominantly occurs in highly permeable horizontal interflow zones, representing basalt flow tops that now consist of layers of porous rock, bounded above and below by fairly impermeable dense basalt layers, representing original flow interiors. Additionally, basalts have unique geochemistry, tending to be anoxic with relatively high concentrations of dissolved iron

and manganese. High permeability interflow zones and extremely low permeability bounding layers cause basalts to have high horizontal transmissivities, creating high yields and storage capacities, making basalts well-suited as ASR reservoirs. Additionally, low vertical transmissivities limit natural recharge making basalts highly susceptible to net groundwater losses, and possible water table declines, when over pumping occurs. (Nelson 2009; USGS 2009; Golder & Associates et al. 2003)

United States federal law under the Safe Drinking Water Act Part C (underground injection control (UIC) regulations) paragraph 300h(d)(2) requires treatment of ASR source water to drinking water standards prior to injection, however, many states implement even more restrictive standards (Pyne 2005). Methods for meeting drinking water standards include disinfection with approved processes, the most prevalent of which is chlorination, which can result in the formation of trihalomethanes (THMs). THMs are formed when residual chlorine reacts with naturally occurring organic matter (NOM) during and subsequent to chlorine disinfection. The THM family consists of chloroform (CF) ($CHCl_3$), bromodichloromethane (BDCM) ($CHCl_2Br$), dibromochloromethane (DBCM) ($CHClBr_2$), and bromoform (BF) ($CHBr_3$). Suspected carcinogens, THMs are regulated by the EPA with a maximum contaminant level (MCL) for drinking water of 80μg/L (Dillon et al. 2005). There is particular concern over THMs in ASR systems since increases in THM concentrations after injection have been observed (Pavelic et al. 2005; Thomas et al. 2000; Dillon et al. 2005) due to in situ formation from the reaction of residual chlorine and aquifer organic matter, leading to possible violations of the MCL.

Fate of THMs in Columbia River Basalts During Aquifer Storage and Recovery

Danelle Bertrand

Literature Review:

A combination of field and laboratory studies has led to the current understanding of THM fate and transport in alluvial and limestone aquifer ASR systems (Dillon et al. 2005). However, quantitative studies of THM degradation for multiple ASR cycles have not been conducted for basalt aquifer ASR systems.

THMs are small, relatively soluble organic molecules with limited sorption and retardation in relatively low carbon content aquifers (National Research Council 2008). THMs are biologically degraded in ASR systems primarily due to cometabolism, transformation by microorganisms utilizing a different substrate as the primary source of energy or carbon, with degradation rates highly dependent on aquifer redox states and microbial community structure (Pyne 2005; Dillon et al. 2005; Pavelic et al. 2006; Wahman et al. 2005). Chloroform is the most persistent THM and does not significantly degrade until anaerobic conditions develop. Brominated THMs are degradable under anoxic and even oxic conditions in addition to anaerobic conditions (Dillon et al. 2005; Pavelic et al. 2005; Pyne 2005; Thomas et al. 2000).

More highly brominated THMs require less energy for biotransformation and tend to be degraded first in ASR systems under all redox conditions. As a result, THM removal tends to proceed in the following order: $CHBr_3 > CHClBr_2 > CHCl_2Br > CHCl_3$ (Dillon et al. 2005; Pyne 2005; Petkewich et al. 2004; Thomas et al. 2000).

Results from the 2005 American Water Works Association Research Foundation (AWWARF) Project 2618 indicate that THM degradation is more rapid under more

highly reducing conditions (Figure 1), and that total THM (TTHM) half-lives are highly

variable, ranging over three orders of magnitude (<1d to >120d). Under sulfate reducing

and methanogenic conditions, all THMs were readily degraded with half-lives of less

than 20 days. However, under aerobic conditions, THMs were fairly persistent with half-

lives greater than 50 days. The chloroform fraction of injectant water TTHMs is noted in

Figure 1 for the three aerobic sites, showing a clear trend of increasing TTHM half-lives

with increasing chloroform fractions due to its relative persistence compared to

brominated THMs. (Dillon et al. 2005; Pavelic et al. 2006)
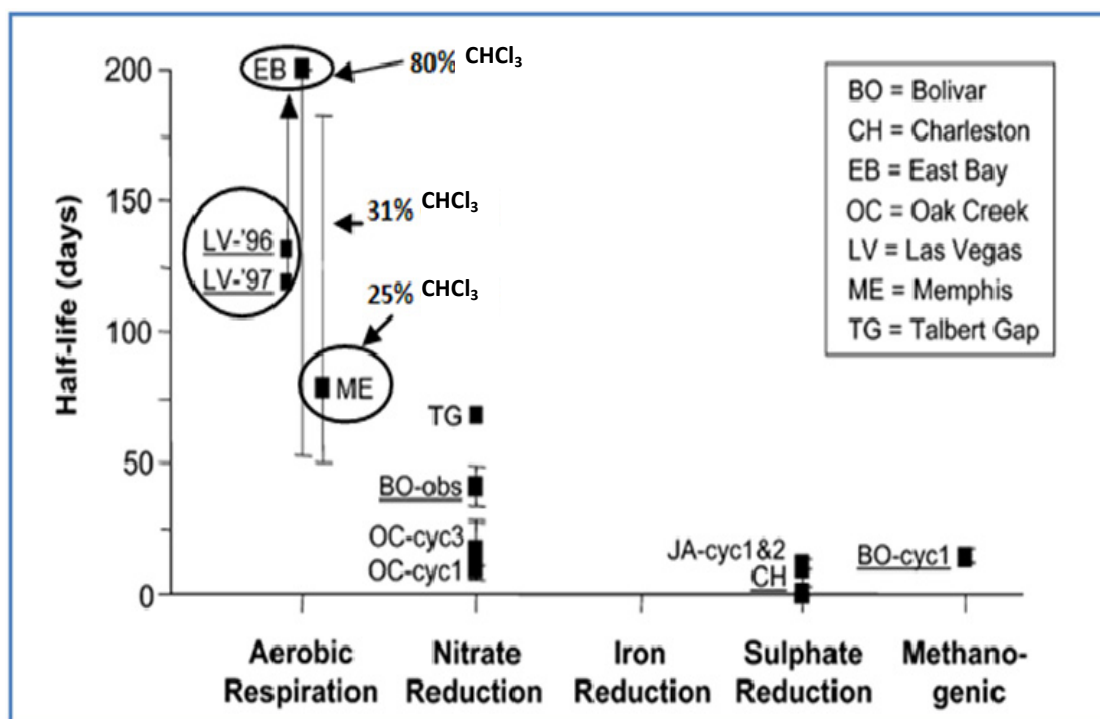
Figure 1: Total trihalomethane **(**TTHM) half-life vs. redox state for non-basalt ASR systems in a 2005 AWWARF study. The captions next to each half-life value represent the ASR site location with BO= Bolivar, South Australia; CH=Charleston, SC; EB= East Bay, CA; OC=Oak Creek, WI; LV=Las Vegas, NV; ME=Memphis, TN; TG=Talbert Gap, CA. Bars indicate the 95% probability limits for half-lives. (after Dillon et al. 2005)

In-situ formation of THMs due to the presence of residual chlorine in injectant water has been directly observed in ASR systems (Pavelic et al. 2005; Thomas et al. 2000; Dillon et al. 2005). In aerobic ASR aquifers, there can even be a net increase in THMs due to in-situ formation and negligible degradation (Thomas et al. 2000).

Based on lab studies with batch reactors, chemostat (CSTR) reactors, and biofilm columns with acetate as the primary substrate, likely biological THM transformation mechanisms include reductive dehalogenation and biological oxidation. Under methanogenic conditions, CF transformation has produced dichloromethane (DCM, CCl_2H_2), indicating reductive dechlorination (Gupta et al. 1996a; Egli et al. 1990), and carbon dioxide and methane, indicating biological oxidation (Bouwer et al. 1983). Bouwer and McCarty proposed the following equation to describe the methanogenic biological oxidation of CF:

$$CHCl_3 + 1.5H_2O = 0.75CO_2 + 0.25CH_4 + 3H^+ + 3Cl^-$$
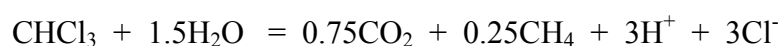
Under sulfate reducing conditions, CF transformation produced DCM in nearly equal molar concentrations as the input CF, suggesting almost exclusive reductive dechlorination as the transformation mechanism (Gupta et al. 1996b). Another study under anoxic denitrifying conditions, found dibromomethane (DBM, CBr_2H_2) to be the exclusive endproduct of BF transformation, confirming reductive debromination as a transformation mechanism (Bouwer et al. 1988).

Abiotic transformation mechanisms are possible, including hydrolysis and dehalogenation due to the oxidation of metallic iron, although biotransformation is

considered to be predominant (Dillon et al. 2005). Chemical hydrolysis can transform

THMs in alkaline conditions with hydroxide ions displacing the halogen ions (Shams El

Din 1998):

$$CHX_3 + 3H_2O = [CH(OH)_3] + 3HX$$
$$[CH(OH)_3] = 2H_2O + CO$$
$$[CH(OH)_3] = H_2O + HCOOH$$
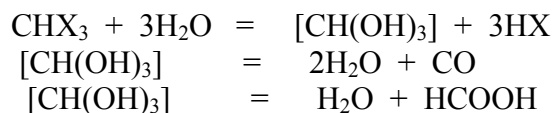
Although in highly alkaline conditions hydrolysis can be rapid, in the pH ranges typically

found in groundwater, hydrolysis of THMs is very slow with half-lives on the order of

years, and is not considered a dominant degradation mechanism (Dillon et al. 2005).

Aqueous reductive dehalogenation of chloroform can be caused by the presence of zero-

valent fine grained iron metal (Fe^0). The equation:

$$Fe^0 + CHCl_3 + H^+ \rightarrow Fe^{2+} + CH_2Cl_2 + Cl^-$$
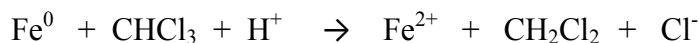
represents one simple mechanism for CF dehalogenation by iron metal due to dissolving

metal reduction (Matheson et al. 1994).

Previous studies have indicated that the majority of basalt aquifers are anoxic,

therefore THM reactivity in basalts would be expected to vary between conservative

behavior (similar to aerobic ASR systems) and rapid degradation (similar to anaerobic

ASR systems) as shown for the anoxic cycles in Figure 1. Shorter TTHM half-lives, i.e.

more rapid degradation, would be expected in more reducing conditions with

conservative behavior, i.e. longer half-lives, in aerobic conditions. Higher chloroform

fractions would be expected to result in longer TTHM half-lives and more highly

brominated THMs would be expected to degrade more rapidly under all redox conditions in basalt systems.

Objectives:

The objective of this study was to determine THM reaction rates and key factors affecting their reactivity in CRBG ASR systems. This involved:

(1) Developing a dilution analysis procedure to determine mixing fractions in the absence of added tracers, based on available concentrations of naturally occurring ions in ASR system injected water and groundwater

(2) Deriving an equation describing THM reaction during ASR cycles based on first order kinetics and plug flow transport within the aquifer

(3) Calculating THM reaction rates for selected ASR cycles using mixing fractions from the dilution analysis and a THM reaction equation developed for this study

(4) Identifying key factors with apparent correlations to TTHM half-lives in the basalt ASR systems investigated

Methods:

<u>ASR Setting</u>

ASR systems investigated in this study utilize CRBG aquifers in the Oregon cities of Echo (McCarty Ranch), Tigard, and Beaverton. The CRBG is divided into five formations, but only two, the Wanapum Basalt and the Grande Ronde Basalt, are present

at the sites investigated in this study. Tigard and Beaverton ASR systems are both for municipal drinking water use and the McCarty Ranch ASR system is used for irrigation purposes. Oregon law, under Oregon Water Resources Department (OWRD) rule 690-0350-0020 (5)(i)(C), allows injection of THMs at concentrations up to the state's drinking water standard of 80µg/L set by the Oregon Administrative Rule OAR 333-061-030.

The City of Tigard currently has two functioning ASR wells, ASR 1 and 2, operational since 2001 and 2006 respectively, utilizing the CRBG formation underlying Bull Mountain in the eastern end of the Tualatin Valley. Tigard's ASR source water is purchased from the City of Portland Water Bureau (water from the Bull Run System), the City of Lake Oswego (water from the Clackamas River), and the Joint Water Commission (JWC) which is owned jointly by the Cities of Hillsboro, Forest Grove, Beaverton and Tigard and the Tualatin Valley Water District. ASR 1 penetrates seven interflow zones over an uncased length from 300 to 606 ft below ground surface (bgs) with an intake at 470 ft bgs. ASR 2 contains five screened intervals over a length of steel casing from 559 to 1015 ft bgs accessing permeable fractured and pillow basalts with an intake at 584 ft bgs. Local CRGB yields exceed 1000 gpm and estimated transmissivities range from 300 gpd/ft to 80,000 gpd/ft with an average of 15,000 gpd/ft depending on the thickness and extent of each permeable zone. (Golder Associates et al. 2003; Golder Associates et al. 2001; GSI 2009)

The climate of the Tualatin Valley is typical of the Willamette Valley with cool wet winters and warm dry summers. Natural recharge to the Bull Mountain CRBG was

estimated between 1 and 3 in per year by Golder Associates in 2003. In the absence of pumping, CRBG groundwater migrates from the top of Bull Mountain towards Fanno Creek in the north and the Tualatin River in the south through an adjacent sedimentary aquifer. (Golder Associates et al. 2003; Golder Associates et al. 2001)

The City of Beaverton currently has three functioning ASR wells, only one of which is included in this study: the Hanson Rd. well, operational since 1999, which utilizes the Cooper Mountain CRBG formation in the eastern Tualatin Valley northwest of Bull Mountain (CH2MHill 1994; Eaton et al. 2008). Source water is treated Tualatin River water from the JWC (Eaton et al. 2008). Hanson Rd. well is a completely uncased open borehole accessing four distinct interflow zones with a combined thickness of 65ft over an uncased length from 210ft to 700ft bgs (Eaton et al. 2000). Local CRBG yields are similar to those of Tigard and transmissivities at the Hanson Rd. well range from 88,000 gpd/ft to 590,000gpd/ft, based on step-drawdown pumping tests with lower transmissivities encountered after about 1000 minutes of pumping, suggesting the presence of a hydraulic barrier such as a fault. Large variances in groundwater elevations further indicate the presence of several hydraulic barriers within the Cooper Mountain CRBG (Barry et al. 1999).

Primary aquifers in the vicinity of the Hanson Rd. ASR site include the Cooper Mountain basalt aquifer, which behaves as a leaky aquifer, and a sedimentary valley fill aquifer of unconsolidated gravel, sand, and silt overlying the CRBG formation at the base of the mountain and in the surrounding valleys. The CRBG formation contains an unconfined aquifer and underlying interflow zones within the basalt which become

confined when they are fully saturated. Precipitated recharge percolates down into the water table aquifer at Cooper Mountain and migrates downward, likely through faults, fractures, or uncased wells into interflow zones within the CRBG then travels downgradient becoming increasingly confined. CRBG groundwater eventually discharges to surface waters such as the Tualatin River. (CH2MHill 1994)

McCarty Ranch has a single ASR well, operational since 2006, located along Butter Creek in Echo, Oregon in the Echo Junction Subarea (EJS) within the Lower Umatilla Basin (CH2MHill 1993). The ASR well is 1294 ft deep with a 12 in diameter accessing five distinct CRBG interflow zones, from 476 ft to 975 ft bgs, ranging in thickness from 16 ft to 43 ft, with a combined thickness of 135 ft (OWRD 2009). Source water is chlorinated water from a collector well utilizing a seasonal alluvial aquifer along Butter Creek with water typically available in large quantities only from January to May, coinciding with the typical ASR injection period (Melady 2009). The ASR well utilizes the underlying CRBG formation with an estimated average transmissivity of 58,000 gpd/ft (GSI 2007).

Primary hydrogeologic units at the McCarty ASR well include a sedimentary aquifer overlying a CRBG aquifer. The climate is semiarid with a pan evaporation rate of approximately 39 in/yr and average precipitation of less than 10 in/yr, suggesting local precipitation contributes little to groundwater recharge. Principal recharge to the basalt aquifers is from infiltration into the Blue Mountains to the south which migrates north toward the Columbia River. (CH2MHill 1993)

Table 1: **ASR Source Water and Native Groundwater Characterization for Tigard, Beaverton, and McCarty Ranch**

Parameter	Tigard Native Groundwater (ASR1/ ASR2)	Tigard Source Water	Beaverton Native Ground-water	Beaverton Source Water	McCarty Native Ground-water	McCarty Source Water
Ions						
Ca^{2+} (mg/L)	25 / 22	2	40	9	21	46
Mg^{2+} (mg/L)	11 / 13	0.5	17	3	9	16
Na^+ (mg/L)	8 / 18	2	14	13	27	38
K^+ (mg/L)	3 / 5	<1	2	<1	6	4
Cl^- (mg/L)	4 / 23	3	42	5	32	9
SO_4^{2-} (mg/L)	4 / 1.4	<2	3	12	56	19
NO_3^- as N (mg/L)	1.7 / 0.5	<0.1	0.3	0.2 -1.5	<0.5	6
Silica as SiO_2 (mg/L)	66 / 54	9	66	18	31	38
HCO_3^- (mg/L)	95 / 132	10	117	43	149	267
Additional Parameters						
Temperature(^{o}C)	12 / 14	9	12	12	23	11
pH	6.8 / 6.9	7.8	6.8	7.5	7.5	7.0
ORP (mV)	183/38 - 111	656	330	606	-31	59 - 663
Conductivity (µS/cm)	145 / 345	32	356	139	321	515
Dissolved Oxygen (mg/L)	7 / 2	9	3	10	4	8
TOC (mg/L)	2.5 / <0.5	1.6	0.7	1.0	<1	3.2

Notes:
(1) Values in this table represent only typical values; actual values vary from cycle to cycle.
(2) "NM" denotes that the parameter was not measured.
(3) ORP is the oxidation reduction potential and TOC is the total organic carbon concentration.

Table 1 shows examples of typical ion concentrations and field parameters for the native groundwater and source water at Tigard, Beaverton, and McCarty Ranch. Native groundwater at the Tigard ASR 1 and 2 and Beaverton ASR wells can be characterized as slightly acidic with relatively high ion concentrations while typical ASR injectant water is slightly alkaline with fairly low ion concentrations (except for higher concentrations of

sulfate and sodium at Beaverton). At McCarty, source water has fairly high ion concentrations and neutral pH and native groundwater also has high ion concentrations but is slightly basic.   Nitrate concentrations in McCarty source water are fairly high likely due to fertilizer seepage upgradient of the source water well. Native groundwater at Tigard varies in dissolved oxygen (DO) from 2mg/L to 7 mg/L and in ORP from 38mV to 183mV, suggesting that redox conditions range from anoxic to aerobic. Source water at both Tigard and Beaverton is highly aerobic. At McCarty, source water DO concentrations and ORP are in the aerobic range, but native groundwater DO concentrations and ORP are low, suggesting that conditions may become less oxidizing as recovery progresses. (Golder Associates et al. 2003; GSI 2007)

Dilution Analysis

No external tracers were added to the injected source water at any of the ASR sites investigated. Lack of external tracers necessitated using naturally occurring ions in the source water and groundwater to determine the fraction of each water present in a given sample (i.e. the mixing fractions). In basalts, however, ion exchange and mineral dissolution may occur and many ions often do not behave conservatively (Dafny et al. 2006; Hinkle 1996). Furthermore, the data compiled in this study indicates that geochemical conditions driving ion exchange and mineral dissolution are highly variable spatially within the CRBG, causing ions that behave conservatively at one site to undergo water-rock reactions at other sites. Therefore, separate analyses were performed at each site to determine which ions behaved conservatively. A detailed description of the steps

used to perform the dilution analyses in this study is available in the supplementary material as Appendix A.

Additional complications arose due to the presence of water with three distinct geochemical compositions in many ASR cycles. Often, after the first cycle, the groundwater present at the ASR well prior to injection, "baseline" groundwater, consisted of a mix of previous ASR water (since most Oregon ASR permits allow extraction of only 95% of injected water by volume) and native groundwater. During such cycles, there are essentially three waters present: injected source water, baseline groundwater, and native groundwater. Figure 2 depicts a highly simplified conceptual model of the movement of the three waters as a typical ASR cycle progresses. It should also be noted that the baseline groundwater contains THMs, which may have undergone degradation during the time interval between cycles, adding another component to the THM degradation analysis.

Cl^- is naturally occurring in all ASR waters in this study and is widely considered to transport conservatively in basalts (Matter et al. 2007; Kranjc 1997). However, for many ASR cycles in this study, differences in Cl^- concentrations between injected source water and baseline groundwater were not large enough to use in a dilution analysis. For this study, tracers were required to have concentration differences greater than twice the minimum detection limit (MDL) between source water and baseline groundwater to ensure that observed concentration differences were greater than natural variations in each water. For cycles where chloride dilution analyses were not possible, it was necessary to identify other conservative ions to use as tracers.

(a) Prior to Injection (t₀ = 0)

C_{bl}=13mg/L

ASR Well

C_{nw}=23mg/L
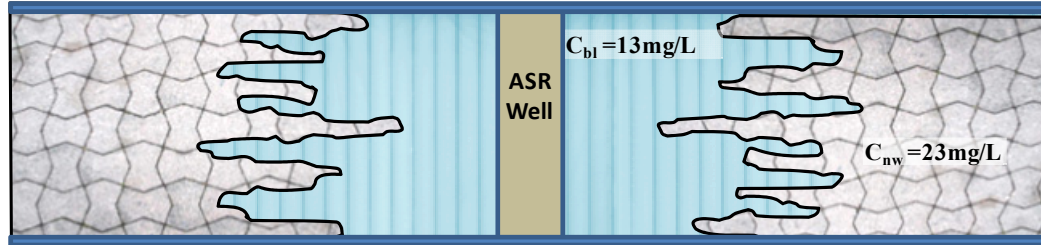
(b) End of Injection Period (t₁= 133d)

Sample: C = 3mg/L;   C/C_{bl} = 0.23

C_{sw}=3mg/L

C_{bl}=13mg/L

C_{nw}=23mg/L
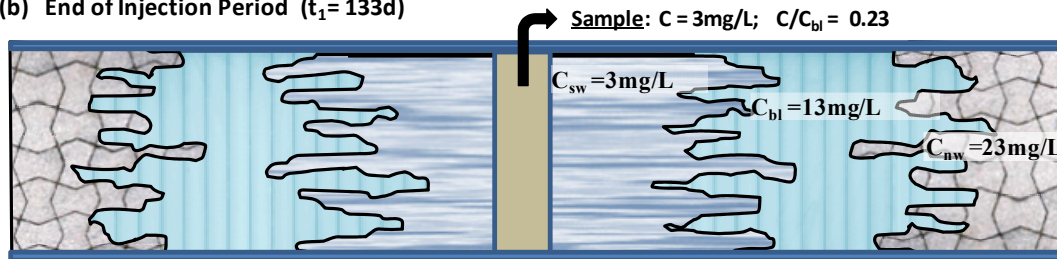
(c) During Recovery Phase (t₂= 315d)

Sample: C = 6mg/L;   C/C_{bl} = 0.46

C_{sw}=3mg/L

C_{nw}=23mg/L

C_{bl}=13mg/L
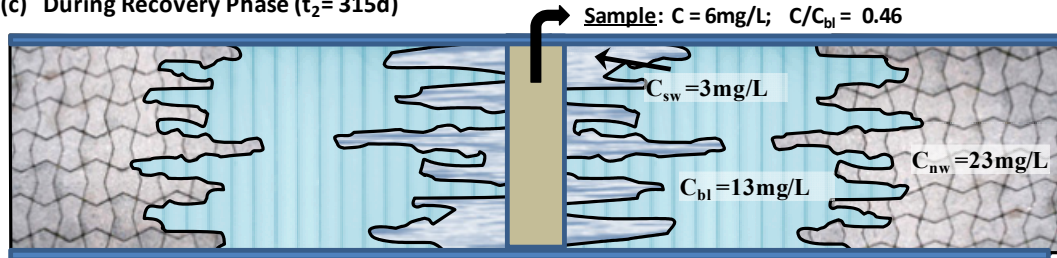
Native Groundwater (nw)   Baseline Groundwater (bl)   Injected Source Water (sw)

Figure 2: Simplified schematic showing the movement of source water (sw), baseline (bl) and native groundwater (nw) throughout a typical ASR cycle. Dilution analysis calculations are based on tracer concentrations in each water. C, C_{sw}, C_{bl}, and C_{nw} represent actual chloride concentrations in samples (taken at the ASR well), source water, baseline and native groundwater respectively at Tigard ASR 2, cycle 2 (2007), where it was possible to use Cl⁻ as a conservative tracer. Baseline normalized concentrations are denoted as C/C_{bl}.

Tigard ASR 1 will be used as an example of how ions other than Cl^- were chosen as conservative tracers. Chloride dilution analyses were possible at Tigard for ASR 2 cycles 1 and 2, but not at ASR 1. In order to identify other conservative ions in the Bull Mountain CRBG formation, recovery phase mixing fractions calculated with Cl^- were compared to those calculated with other ions for the two cycles at ASR 2 where chloride dilution analyses were possible. Ions investigated as possible alternative tracers were HCO_3^-, Ca^{2+}, Na^+, Mg^{2+}, NO_3^-, SO_4^{2-}, K^+, and SiO_2. Recovery phase time-series plots of fractions of injected source water (F_{sw}) calculated using each potential tracer were compared to the same plots for Cl^-. Based on a simple mass balance, in the absence of water-rock reactions, when only source water and baseline groundwater are present in a sample:

$$C = C_{sw} (F_{sw}) + C_{bl} (1-F_{sw})$$

$$F_{sw} = (C-C_{bl}) / (C_{sw}-C_{bl}) \quad \text{[Equation 1]}$$

where C=sample tracer concentration, C_{bl}=baseline tracer concentration, and C_{sw}=source water tracer concentration. For example in Figure 2(c), F_{sw} based on Cl^- is: $F_{sw} = (6 - 13)mg/L / (3 - 13)mg/L = 0.70$ (or the sample contains 70% source water). As shown in Figure 3 for ASR 2 cycle 1, HCO_3^-, Ca^{2+}, Mg^{2+}, and K^+ all exhibited F_{sw} trends similar to Cl^- and were identified as possible tracers.

F_{sw} calculations were performed assuming mixing between ASR source water and baseline groundwater only. This assumption was confirmed by comparing time-series plots of recovery phase ion concentrations normalized by baseline groundwater

concentrations, i.e. sample concentration divided by baseline groundwater concentration, for each of the possible tracers as shown in Figure 4 for ASR 1 cycle 4 and ASR 2 cycle 3. If baseline normalized concentrations (C/C_{bl} in Figures 2(b) and (c)) for all the potential tracers followed the same patterns and approached 1.0 as recovery progressed (Figure 4(a)), it was assumed that only baseline groundwater and injected source water were present in the recovered samples. However, if trends for selected ions were divergent and baseline normalized concentrations exceeded 1.0 (Figure 4(b)), it was assumed that native groundwater was present in the recovered sample in addition to source water and baseline groundwater. ASR cycles where data trends suggested that native groundwater was present in the recovery samples were not included in this study.
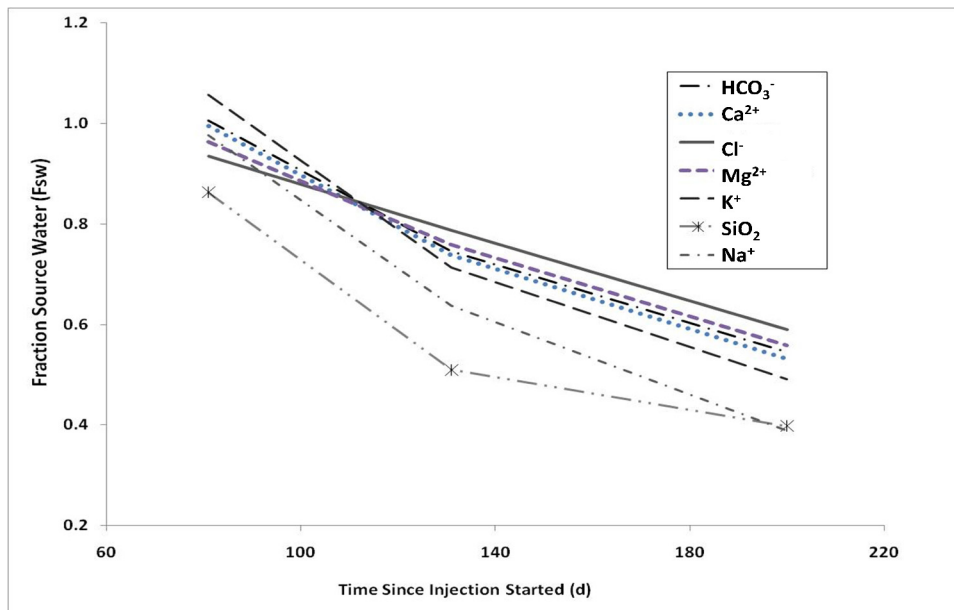
Figure 3: Plot of F_{sw} vs. time fot Tigard ASR 2 cycle 1. F_{sw} was calculated based on concentrations of the indicated ions using Equation 1. F_{sw} plots based on SiO_2 and Na^+ do not closely follow the plot based on Cl^-. SO_4^{2-} and NO_3^- were not included in this plot because they were not detected in any source water samples.

(a) Tigard ASR 1 Cycle 4

(b) Tigard ASR 2 Cycle 3
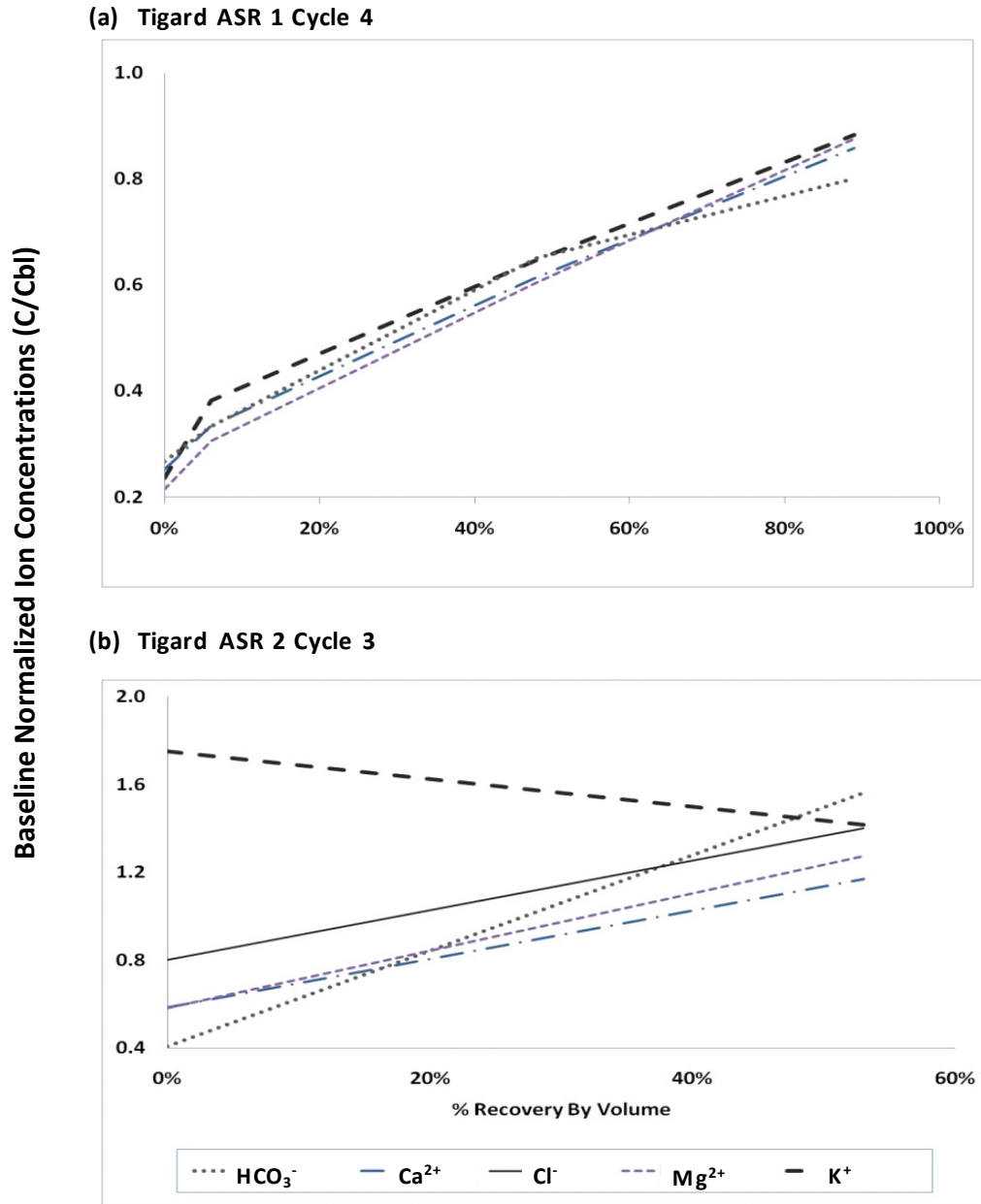
Figure 4: Baseline normalized tracer concentrations vs. percent injected water recovered by volume for Tigard ASR 1 cycle 4 and Tigard ASR 2 cycle 3. Percent recovery by volume = 100%*[Volume Recovered / Total volume injected]. In Figure (a), normalized tracer concentrations follow the same patterns and do not exceed 1.0, indicating that only baseline groundwater (GW) and source water are present. In Figure (b), normalized tracer concentrations exceed 1.0 and follow different patterns indicating that native GW is present in addition to baseline GW and source water.

In addition to exhibiting mixing fraction trends similar to Cl^-, potential tracers were required to demonstrate conservative behaviors for all ASR cycles to which they were applied. If an ion's concentration considerably increased or decreased during the storage phase, it was excluded as a tracer. Large changes in concentration during storage are likely due to reaction and not mixing since only source water is likely to be present at the ASR well, where samples are taken. At Tigard ASR 1, HCO_3^-, Ca^{2+}, Mg^{2+}, and K^+ met this criteria, whereas NO_3^-, SiO_2 and Na^+ tended to significantly increase in concentration prior to the recovery phase (Figures 5(a) and (b) show trends for K^+ and SiO_2 as examples).

For ASR cycles in which baseline groundwater was determined to contain previous ASR water, ions were excluded as tracers if baseline concentrations reached native groundwater concentrations prior to the start of injection. It was assumed that baseline groundwater contained previous cycle ASR water if the recovered volume was less than the injected volume for the previous ASR cycle, if major ion concentrations for baseline water were significantly different from native groundwater concentrations, or if baseline water contained THMs. A change in baseline ion concentrations toward native groundwater concentrations between the end of the previous cycle and the beginning of the successive cycle suggests reaction during the ASR rest period when minimal mixing is occurring. Baseline groundwater concentrations for NO_3^-, SiO_2 (Figure 5(b)), and Na^+ tended to either reach or exceed native groundwater levels indicating reaction during the ASR rest period between cycles. However Ca^{2+}, HCO_3^-, K^+ (Figure 5(a)), and Mg^{2+} once

again exhibited conservative behavior with baseline concentrations lower than native

groundwater concentrations.

(a)

(b)
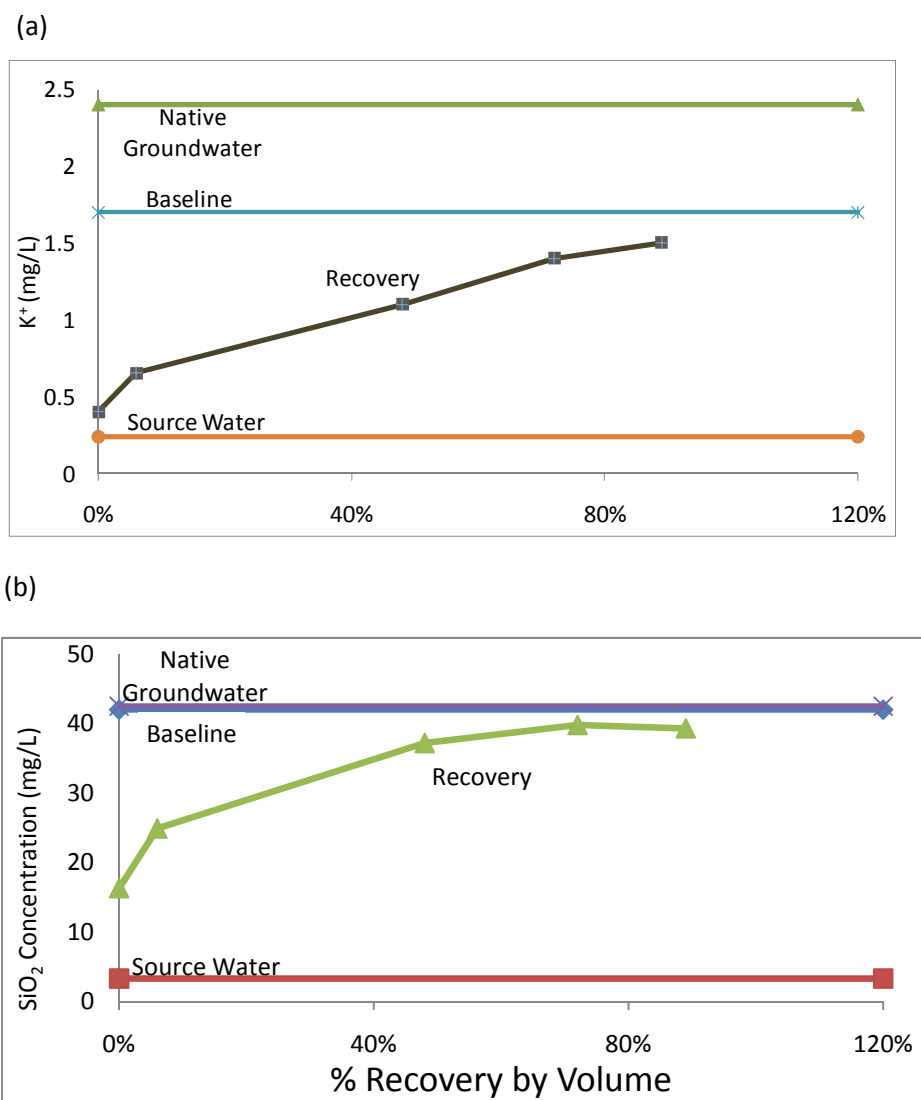
Figure 5: Concentrations of K^+ and SiO_2 in source water, native and baseline groundwater and throughout recovery for Tigard ASR 1 cycle 4 (2005). K^+ exhibits conservative behavior whereas silica does not. Percent recovery by volume = 100%*(Volume Recovered)/(Total Volume Injected).

Ions used as tracers were required to have fairly consistent concentrations in both baseline groundwater and source water during the ASR cycle being analyzed. In addition, tracers were required to have similar concentrations for multiple samples of native groundwater since baseline groundwater contains a mixture of previous cycles' source water and native groundwater. Highly variable tracer concentrations in source water, baseline or native groundwater can cause concentration increases or decreases in addition to those caused by mixing, effectively skewing dilution analysis results. For instance, SO_4^{2-} and NO_3^- concentrations tended to be highly variable in the native groundwater (where data was available) causing trends during recovery to be highly erratic, increasing above and then decreasing below baseline concentrations during recovery.

Meaningful concentration data must be present for all tracers for each ASR cycle where they are utilized. As with the chloride analysis, differences in concentration between baseline groundwater and source water were required to be at least twice the minimum detection limit (MDL) to ensure actual differences in concentration existed in addition to variances due to measurement method analyses and natural fluctuation in each water present. When MDLs were greater than or equal to 1.0 mg/L, tracer concentrations were required to be higher than detection limits for all recovered and source water samples to ensure that adequate information was present in the data to calculate accurate dilution fractions.

When chloride analyses were possible, F_{sw} in recovered samples was calculated with Cl^- only. In cycles where a chloride dilution analysis was not possible due to nearly

equal concentrations of Cl^- in baseline groundwater and source water, F_{sw} was calculated

for all suitable tracers and the average was taken as the final value. For Tigard ASR 1,

Ca^{2+}, Mg^{2+}, HCO_3^-, and K^+ were chosen as tracers and used to calculate all mixing

fractions. At Tigard ASR 2 and Beaverton, Cl^- was used as the sole tracer for dilution

analyses. At McCarty Ranch, Cl^- was used as the sole tracer for cycle 4.

THM Reaction Rate Analysis

First-order in-situ reaction rates were estimated for each THM present above the

MDL for one or more cycles at all four ASR sites investigated. Data sets for each ASR

cycle consisted of measured concentrations of the four THMs and the additional

parameters in Table 1 for baseline groundwater, source water, and recovered water.

Additionally, metals, radionuclides, synthetic organic compounds, and volatile organic

compounds were measured, but were undetected in almost all samples. Source water was

sampled one to three times during the injection period and recovered water was sampled

two to four times during the recovery period. The same data is available for one to three

samplings during the storage period for some cycles at Beaverton and Tigard ASR 1. All

storage and recovery samples are taken at the ASR well and represent conditions at the

well only as illustrated in Figure 2. Appendix B shows the full data set for Tigard ASR 1

cycle 4 as an example and Table 2 shows a limited portion of this data set to illustrate the

THM reaction rate analysis.

Table 2: **Tigard ASR 1 Cycle 4 TTHM Reaction Rate Analysis Parameters**

	Baseline Groundwater	Injection Period	Storage Period	Recovery Period	
Sampling Date	12/6/2004	12/6/2004	5/23/2005	6/27/2005	8/16/2005
t (time since injection started, d)		0	168	203	253
Average Pumping Rate (GPM)		604.3	0	652.1	
F_{sw} [Eqtn 1]			1.00	0.98	0.49
% Recovery (FR *100%) [Eqtn 5]				6%	35%
t_a (residence time of source water in aquifer, d) [Eqtn 4]			34	76	166
TTHM (total THMs, µg/L)	13.5	28.6	88.3	40.8	21.6
k (calculated first-order TTHM reaction rate constant, 1/d)	0.014				

Notes:
  (1) The calculated TTHM reaction rate constant, k, is based on highlighted
       concentrations during storage and recovery and baseline groundwater
       concentration only.
  (2) The injection period was from December 6, 2004 to April 19, 2005 (134 days)
       with a total injected volume of 116.6 million gallons (MG) and the recovery
       period was from June 20 to October 16, 2005 (118 days) with a total recovered
       volume of 110.8MG.

     In situ THM formation was observed (as an increase in THM concentration) after

ASR injection, due to reaction of organic matter and residual chlorine, in all cycles

analyzed except for Tigard ASR 1 cycle 5 (2006) and ASR 2 cycle 1 (2006). However,

THM formation was not modeled in this study because inadequate data was available.

Therefore, THM degradation rates were calculated based on data collected beginning at

the highest measured THM concentration (88.3µg/L for TTHM in Table 2) during

storage and recovery. After the occurrence of the highest THM concentration, it was

assumed that all residual chlorine had been utilized and formation was no longer

occurring. If formation was in fact still occurring, THM degradation rates would be

underestimated, therefore the assumption is conservative.

The equation describing THM degradation was developed based on first-order

kinetics assuming that only baseline groundwater and source water were present in

recovery period samples and that the different waters present did not mix within the

aquifer as depicted in Figure 2. Although recovery period samples contained a mixture

of source water and baseline groundwater making the dilution analysis necessary, the

waters were assumed to mix within the well shaft and not within the aquifer. This is

based on an ideal plug flow assumption that the two waters follow separate preferential

flow paths within the aquifer. For each sample, the THM concentration can be calculated

as:

$$C(t) = F_{sw}(t) \ (C_{sw}(t)) + (1 - F_{sw}(t)) \ (C_{bl}(t)) \quad \text{[Equation 2]}$$

where t = time since injection started, $C(t)$ = sample THM concentration, $F_{sw}(t)$ = fraction

of source water in the sample, $C_{sw}(t)$ = source water THM concentration, and $C_{bl}(t)$ =

baseline groundwater THM concentration.

Baseline groundwater is sampled just prior to injection and has a subsequent

residence time, or time within the aquifer, of t for each sample. Therefore, an equation

for $C_{bl}(t)$ can be derived as follows:

$$\frac{dC_{bl}(t)}{dt} = -k \ (C_{bl}(t))$$

$$\int_{C_{blo}}^{C_{bl}(t)} \frac{dC_{bl}(t)}{C_{bl}(t)} = -k \int_{0}^{t} dt$$

$$C_{bl}(t) = (C_{blo})e^{(-kt)} \qquad \text{[Equation 3]}$$

where k = the THM first-order reaction rate constant and C_{blo} = the baseline groundwater THM concentration at time $t = 0$ (start of injection).

In order to calculate $Csw(t)$, it is necessary to find the residence time of the source water in the sample within the aquifer, t_a. This can be estimated as:

$$t_a = t - t_{inj}(1 - FR(t)) \qquad \text{[Equation 4]}$$

where t_{inj} = the total duration of the injection period and $FR(t)$ = the fraction of source water recovered based on the total volume of water injected and the volume of source water recovered at time t. The product $t_{inj}(1\text{-}FR(t))$ is an estimate of the time the source water in the sample was injected into the aquifer. Therefore, $t - t_{inj}(1\text{-}FR(t))$ is the difference between the time the sample was taken and the time the source water was injected into the aquifer. $FR(t)$ can be calculated as follows:

$$FR(t) = \frac{Volume \ of \ Source \ Water \ Recovered \ at \ time, t}{V_{inj}}$$

$$FR(t) = \frac{\int_{t_{ro}}^{t} Fsw(t) \ Q_r \ dt}{Vinj} = \frac{Q_r}{Vinj} \sum_{i=1}^{n} [\left(\tfrac{1}{2}\right) \left(F_{sw\,i} - F_{sw\,(i-1)}\right) (t_i - t_{(i-1)})] \qquad \text{[Equation 5]}$$

where V_{inj} = the total volume of source water injected, t_{ro} = the time at the start of the

recovery period (since the beginning of injection), and Q_r = the average recovery

pumping rate. For the summation lower bound, $t_{(i=0)} = t_{ro}$ and $F_{sw(i=0)} = F_{sw}(t_{ro})$ (F_{sw} at the

start of recovery, usually equal to 1.0) and for the upper bound, $t_{(i=n)} = t$ and $F_{sw(i=n)} = F_{sw}$

(t).

$C_{sw}(t)$ for a recovered sample can be calculated by integrating the first-order rate

equation from the highest measured THM concentration, $C_{sw}(t_{a*})$ (88.3µg/L in Table 2),

to the sample source water concentration, $C_{sw}(t_a)$. The time t_{a*} is the residence time of

the source water for the sample containing the highest THM concentration (t_a calculated

for the sample with the maximum THM concentration, 34 days in Table 2).

$$\int_{C_{sw}(t_{a*})}^{C_{sw}(t_a)} \frac{dC_{sw}(t_a)}{C_{sw}(t_a)} = -k \int_{t_{a*}}^{t_a} dt$$

$$C_{sw}(t_a) = C_{sw}(t_{a*})e^{\left(-k(t_a - t_{a*})\right)} \quad \text{[Equation 6]}$$

The combined equation describing THM reaction can be found by substituting

Equations 3 and 6 into Equation 2:

$$C(t) = F_{sw}(t)\left(C_{sw}(t_{a*})\right) e^{-k(t_a - t_{a*})} + \left(1 - F_{sw}(t)\right)(C_{blo}) e^{-kt} \quad \text{[Equation 7]}$$

First-order rate constants, k, were found by fitting Equation 7 to the sample THM data

(the highlighted points for TTHM in Table 2) using Solver in Excel by varying k and

minimizing the squared error between measured and predicted concentrations.

Results:

Calculated first-order TTHM (total THMs), CF (CHCl$_3$), and BDCM (CHCl$_2$Br)

reaction rate constants and half-lives are shown in Table 3 for each ASR cycle analyzed.

Recovery phase redox conditions are also noted for each ASR cycle. Reaction rates for

BF (CHBr$_3$) and DBCM (CHClBr$_2$) could not be calculated because their concentrations

were below detection limits for most baseline, source water, and recovery phase samples.

BDCM reaction rates could not be calculated at McCarty or for Tigard ASR 2 cycle 2

(2007) because BDCM concentrations were below detection limits in all recovery phase

samples.

Table 3: Calculated THM Reaction Rates and Statistics

		k (1/d)	$t_{1/2}$ (d)	n	r	P
Beaverton						
Cycle 2 (1999)	TTHM	$5.5(10^{-4})$	1300	3	0.99998	0.004
(Aerobic)	CF	$-2.8(10^{-5})$	NA	3	0.99995	0.007
	BDCM	$2.3(10^{-3})$	300	3	0.997	0.047
Cycle 9 (2006)	TTHM	$5.4(10^{-4})$	1300	2	--	--
(Aerobic)	CF	$5.6(10^{-4})$	1200	2	--	--
	BDCM	$8.8(10^{-4})$	790	2	--	--
Tigard ASR 1						
Cycle 3 (2004)	TTHM	$1.8(10^{-4})$	3,800	3	0.390	0.745
(Aerobic)	CF	$3.2(10^{-5})$	22,000	3	0.591	0.598
	BDCM	$1.7(10^{-3})$	410	3	0.952	0.198
Cycle 4 (2005)	TTHM	$1.4(10^{-2})$	50	3	0.944	0.215
(Anoxic)	CF	$1.4(10^{-2})$	49	3	0.947	0.207
	BDCM	$5.5(10^{-3})$	130	3	0.562	0.620
Cycle 5 (2006)	TTHM	$2.2(10^{-3})$	310	3	0.846	0.358
(Anoxic)	CF	$2.2(10^{-3})$	310	3	0.836	0.370
	BDCM	$2.0(10^{-3})$	360	3	0.999	0.029
Tigard ASR 2						
Cycle 1 (2006)	TTHM	$2.5(10^{-4})$	2,700	3	0.988	0.098
(Anoxic)	CF	$2.5(10^{-6})$	280,000	3	0.991	0.084
	BDCM	$6.7(10^{-3})$	100	3	0.865	0.334
Cycle 2 (2007)	TTHM	$8.8(10^{-5})$	7,900	2	--	--
(Aerobic)	CF	$6.7(10^{-5})$	10,000	2	--	--
	BDCM	--	--	--	--	--
McCarty						
Cycle 3 (2007) [1]	TTHM	$3.7(10^{-2})$	19	2	--	--
(Anaerobic)	CF	$3.7(10^{-2})$	19	2	--	--
Cycle 4 (2008)	TTHM	$2.4(10^{-2})$	28	2	--	--
(Anaerobic)	CF	$2.4(10^{-2})$	28	2	--	--

Notes:
1) Reaction rates for McCarty cycle 3 were calculated based on simple first-order kinetics ($C(t) = C_o e^{(-kt)}$) based on two recorded recovery sample concentrations as an order of magnitude check for the calculated cycle 4 reaction rate. Insufficient data was available to perform a full analysis for cycle 3.
2) k is the calculated first-order reaction rate coefficient, $t_{1/2}$ is the calculated half-life, n is the number of data points used to calculate k, r is the correlation coefficient, and P is the probability that the correlation is not significant.
3) Listed redox conditions are for the recovery phase for each ASR cycle

The regression correlation coefficient, r, and the probability of error, P, for the reaction rate regression analysis for each ASR cycle where $n>2$ (more than two data points was used in the regression) is also in Table 3. P is the probability that the correlation is not significant and is random based on the fit of Equation 7 to the actual data, indicated by r, and the number of data points, n, with higher r and n resulting in lower P.

For Beaverton cycle 2, the negative CF reaction rate of $k = -0.00003/d$ may be due to slight errors in F_{sw} values caused by small fluctuations in tracer concentrations within baseline groundwater and source water. CF is likely conservative for this cycle with $k \approx 0$.

Discussion:

Calculated TTHM half-lives were strongly dependent on recovery phase redox conditions (Figure 6), with more reducing conditions resulting in shorter TTHM half-lives (higher reaction rates), similar to results from previous studies in non-basalt aquifers. Grey data points in Figure 6 are the average TTHM half-lives from the AWWARF study in non-basalt aquifers (see Figure 1) and are included for comparison. Additionally, anoxic and anaerobic reaction rates seemed to be dependent on recovery phase TOC concentrations, a trend that was not investigated in the AWWARF study, with higher reaction rates for higher TOC concentrations. This would be reasonable for THM degradation due to cometabolism with TOC as a substrate. Average recovery

phase TOC concentrations are noted for anoxic and anaerobic cycles in Figure 6, showing

decreasing half-lives for increased TOC concentrations. This trend was not observed for

aerobic ASR cycles in this study.
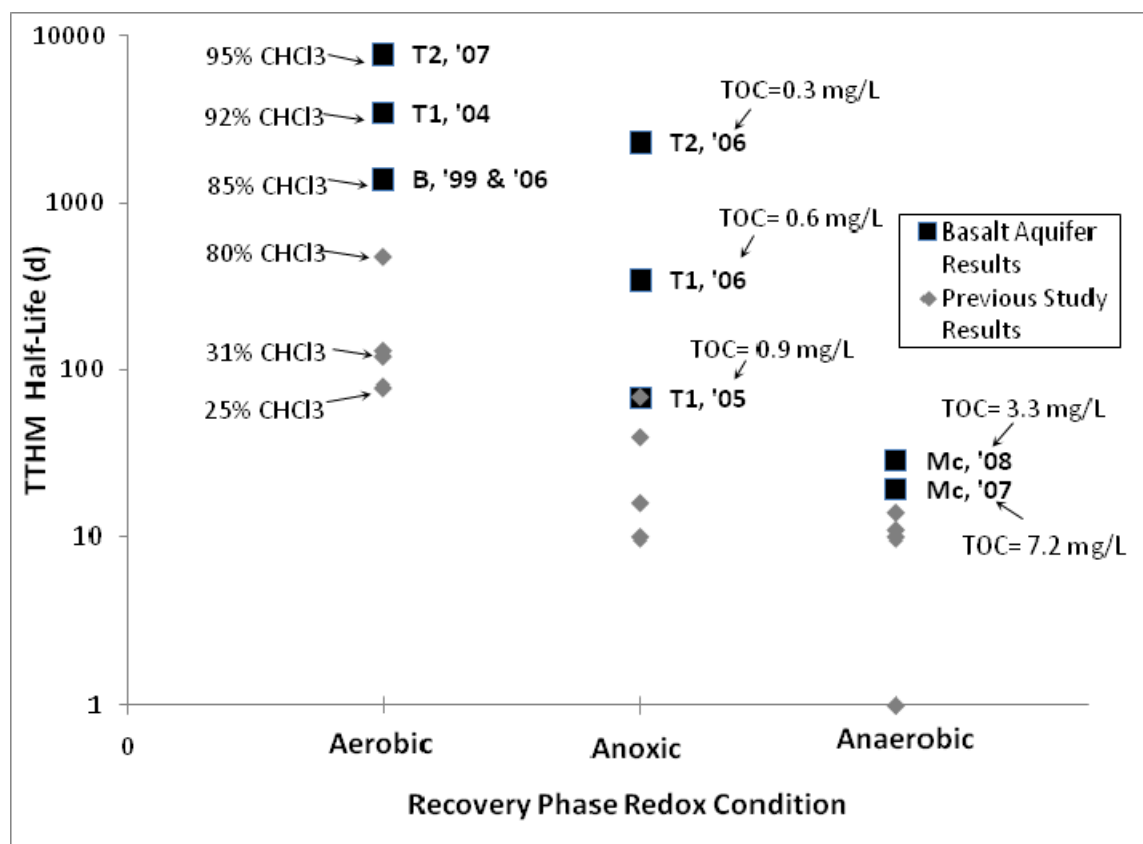
Figure 6: Basalt aquifer ASR system total trihalomethane (TTHM) half-lives vs. recovery phase redox conditions for all ASR cycles in this study, showing decreasing half-lives for more reducing recovery phase conditions. Data points in grey are results from previous studies from Figure 1. Average recovery CF (CHCl3) fractions are noted for the aerobic cycles and average recovery TOC concentrations are noted for the anoxic and anaerobic cycles from this study. T1 = Tigard ASR 1, T2 = Tigard ASR 2, B = Beaverton, and Mc = McCarty.

Redox conditions at McCarty were ambiguous with nitrate, sulfate, and

manganese reduction possible for cycles 3 and 4. Recovery phase DO concentrations

were less than 1mg/L and average ORP was 4 mV for both cycles, indicating anoxic or anaerobic conditions. Both nitrate and nitrite were undetected in all recovery phase samples. Although no manganese was detected in any source water samples, dissolved manganese concentrations increased from 9.5µg/L to 24µg/L during the 2007 cycle and increased from 6.5µg/L to 13.6µg/L during the 2008 cycle between baseline groundwater sampling prior to the start of injection and recovery phase sampling, indicating possible manganese reduction. High concentrations of sulfate were measured during both cycles with recovery phase concentrations of 15 mg/L to 48 mg/L, similar to source water and baseline groundwater concentrations. Dissolved iron was detected in only one recovery phase sample during the 2008 cycle at 0.23 mg/L (comparable to source water concentrations) but was not detected during the 2007 cycle, making iron reduction unlikely.

For all aerobic ASR cycles in this study, CF was essentially conservative with calculated half-lives ranging from 1200 to 22,000d, while BDCM was more reactive with half-lives ranging from 300 to 800d and k_{CF}/k_{BDCM} ranging from 1.8 (Beaverton cycle 9) to 67 (Tigard ASR 1 cycle 3). This is consistent with the observation in non-basalt aquifers that more highly brominated THMs tend to be degraded first in ASR systems. However, contrary to the results from previous studies, this pattern was not observed for the anoxic cycles where BDCM reaction rates were on the same order as or lower than CF reaction rates for Tigard ASR 1 cycles 4 and 5.

CF fractions (CF conc. / TTHM conc.) were very high for all cycles investigated, ranging from 0.82 to 0.89 at Beaverton, 0.87 to 0.98 at Tigard ASR 1, 0.89 to 1.0 at

Tigard ASR 2, and equal to 1.0 for all McCarty samples. High CF fractions are likely

responsible for the long or large half-lives calculated in this study compared to the half-

lives calculated in the AWWARF study (Figure 1 and grey data points in Figure 6)

where CF fractions were much lower. Remaining THMs were comprised primarily of

BDCM. In aerobic recovery phase conditions, shorter or smaller half-lives were

observed for cycles with lower CF fractions. As shown in Figure 6, calculated TTHM

half-lives for aerobic cycles at Tigard ASR 1 and 2 were higher than for the two aerobic

Beaverton cycles where CF fractions were lower. It should be noted that this trend is

based on only four data points and warrants further investigation, however it follows the

same trend observed in non-basalt aquifers (Figure 1).

Small data sets and lack of external tracers introduced significant error to the

results of this study. Error due to small data sets and lack of fit between measured and

predicted THM concentrations are quantified by P (Table 3). Although calculated

correlation coefficients generally indicated significant fit with $r > 0.8$ for all cycles except

Tigard ASR 1 cycles 3 and 4, calculated P values are relatively high due to error

introduced by using very limited data sets. Additional error introduced by the dilution

analysis is less quantifiable and is primarily due to tracer concentration fluctuations

within baseline groundwater and source water due to aquifer heterogeneity and multiple

sources of injected water. For dilution analyses with multiple tracers, errors associated

with baseline and source water concentration fluctuations are possible for each tracer

utilized as well as error related to calculating F_{sw} based on the average for all tracers.

There are also several possible sources of error in the THM reaction model. First-order reaction kinetics were assumed and reaction rates in baseline groundwater and source water were assumed to be equal. However, actual reaction kinetics could have deviated from first-order behavior and reaction rates in baseline groundwater may not have been equal to reaction rates in source water since THM concentrations are generally much higher in source water than baseline groundwater. Degradation rates may be underestimated if THM formation continued after the occurrence of the highest recorded THM concentration. In addition, estimates for $FR(t)$ are calculated by trapezoidal integration of $F_{sw}(t)$ during the recovery phase based on only two to four data points which may not adequately define the actual $F_{sw}(t)$ curve.

Conclusion:

Although the method presented in this paper results in significant uncertainty in calculated reaction rates, it is valuable because it allows for reaction rate estimation using data that is readily available for most ASR sites due to permitting requirements. It does not require any additional sampling or lab testing, or the associated costs of each, and the requisite data has already been collected for previous ASR cycles for many ASR sites. At a minimum, this method results in reaction rate estimates that indicate whether THMs are generally conservative (as at Beaverton and Tigard ASR 2), mildly reactive (as at Tigard ASR 1) or readily degradable (as at McCarty) within a given ASR system.

Calculation of mixing fractions as outlined in this study can also help operators understand how their ASR systems behave. Figure 7 shows the graph of F_{sw} vs. percent ASR water recovered by volume for Beaverton's Hanson Rd. ASR well during cycle 2 (1999). This graph demonstrates that F_{sw} drops fairly rapidly after the start of recovery, indicating that significant amounts of groundwater are pumped out during the recovery phase even when much less than 100% of injected water is recovered by volume, likely due to Beaverton's leaky CRBG aquifer and uncased well. This also helps to explain why major ion concentrations at Beaverton quickly exceeded baseline groundwater concentrations early in recovery during several cycles and began to increase toward native groundwater concentrations: likely extraction of native groundwater, in addition to baseline groundwater and source water, began soon after the start of recovery.
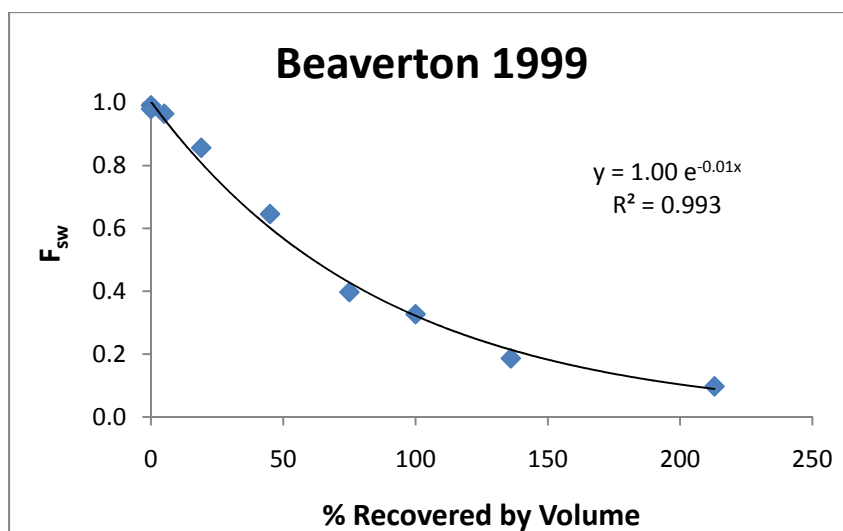
Figure 7: Source water fractions (F_{sw} based on Cl^-) vs. percent water recovered by volume for Beaverton's Hanson Rd. ASR well during cycle 2 (1999). Percent recovered by volume = 100%*[Volume Recovered / Total volume injected]. Only native groundwater and source water were present during this cycle.

Additional sampling, testing, but most importantly the addition of an external tracer could significantly improve the accuracy of the reaction rates calculated using this method. The simplest way to decrease uncertainty would be to analyze both major ions and THMs in all recovery phase samples. In five of the nine cycles listed in Table 3, data for one to three recovery phase samples could not be used in the reaction rate calculation because although major ions were measured, THMs were not. Use of these additional data could have greatly decreased calculated P values. Taking additional recovery phase samples, particularly early in recovery when the mixing of all three waters is less likely, would also increase the number of usable data points for calculating k and increase confidence in calculated values. Although it would clearly impose a supplementary expense, adding a tracer such as chloride or fluoride at concentrations much higher than

those of baseline and native groundwater to the ASR source water would remove much of the uncertainty associated with the dilution analysis.

Further research is warranted to study THM reaction rate trends in basalt aquifers and to develop a three water mixing dilution analysis method. In this study, reaction rates were calculated for only four aerobic cycles, three anoxic cycles, and two anaerobic cycles providing very small data sets for trend analysis in each redox condition. It would be particularly helpful to calculate THM reaction rates for additional anoxic basalt ASR cycles, since THM half-lives were found to range from low (in the mildly reactive range) to fairly high (in the conservative range) in anoxic cycles. Development of a working method for three water mixing dilution analysis would allow reaction rates to be calculated for cycles where native groundwater is present in recovery phase samples in addition to baseline groundwater and source water. In this study, three cycles at Beaverton could not be analyzed due to three water mixing, reducing the number of aerobic cycles that could be analyzed by almost half.

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APPENDICES

Appendix A—Dilution Analysis Procedure

Steps for Dilution Analysis:

(1) Use chloride as a tracer when data are available and when concentration differences between baseline groundwater, source water, and native groundwater are greater than twice the detection limit (i.e. significant differences in chloride concentration must exist between the waters in question to provide a meaningful estimate of dilution)

(2) When it is not possible to use chloride data for a dilution analysis for a particular ASR cycle:

   a) At the sites where chloride data exists in accordance with step (1), compare normalized (by baseline or native groundwater concentrations) time-series concentrations during storage and recovery for each ion to the same plots for chloride. Visually identify ions with plots that closely follow the plots for chloride as possible tracers.

   b) For the ions identified as possible tracers in step a), eliminate any ion as a possible tracer that does not satisfy the following conditions:
      i. Differences in concentrations between baseline groundwater and source water are at least twice the minimum detection limit to ensure actual concentration differences exist in addition to natural variations in each water and analysis accuracy
      ii. When detection limits are greater than or equal to 1mg/L, ion concentrations should be higher than detection limits for all recovered and source water samples to ensure adequate information is available to calculate accurate dilution fractions
      iii. Concentrations do not significantly change during storage (where storage data is available) suggesting reaction in addition to mixing
      iv. For ASR cycles in which baseline groundwater consists of previous ASR water (according to the water balance), baseline concentrations do not reach native groundwater concentrations prior to ASR injection
         --Convergence of ion concentrations to native groundwater concentrations between the end of the previous cycle and the beginning of the current cycle suggests reaction in addition to mixing

v. Native groundwater concentrations are not highly variable (for cases when data is available for several native groundwater samples)

--e.g. sulfate and nitrate concentrations are highly variable at the Beaverton ASR site making them unsuitable as tracers

c) For ASR Cycles where chloride cannot be used for dilution analysis, compare normalized ion trends for ions identified in a) and b) to each other. If an ion displays significantly different trends than the other ions chosen as tracers (more than 10% and 0.04 deviance in F_{sw} from the average of the other tracers), discard it as a possible tracer for that cycle.

(3) <u>Determination of Mixing Regime</u>: After tracers are chosen using steps 1) and 2), determine which waters are mixing during each ASR cycle at each time point analyzed throughout recovery

a) Compare time-series plots of ion concentrations during recovery normalized by baseline concentrations for the chosen tracers.

i. If baseline normalized concentrations for all tracers follow the same patterns and approach 1.0 as recovery progresses, assume that only injected source water and baseline groundwater is present in the recovered samples.

ii. If the different tracers exhibit dissimilar patterns for baseline normalized concentrations, and if normalized concentrations exceed 1.0 (recovery concentrations are greater than baseline concentrations), assume source water, baseline, and native groundwater are present in the recovered samples.

(4) Determine final mixing fractions using chloride alone when suitable data is available and using an average of the mixing fractions for all identified tracers when suitable chloride data is not available.

<u>Notes for Dilution Fraction Calculations:</u>

(1) When calculated source water fractions (F_{sw}) for early recovery samples are greater than 1.0 and less than 1.05, use F_{sw}=1.0.

a. Likely due to minor fluctuations in source water concentrations

(2) When data for storage concentrations prior to recovery are given, use these concentrations as source water concentrations (which are often variable)

Appendix B – Tigard ASR 1 Cycle 4 Complete Data Set

Tigard ASR 1 Cycle 4 (2005):   Volume ASR Water Injected:= 116.6 MG
Volume ASR Water Recovered = 110.8 MG

Injection Start Date: 12/6/2004   Recovery Start Date: 6/20/2005
Injection End Date: 4/19/2005   Recovery End Date: 10/16/2005
Average Injection Pumping Rate: 604.3 GPM   Average Recovery Pumping Rate: 652.1 GPM

Category	Analyte	Regulatory Standard	Regulatory Criteria	Units	Baseline Groundwater ASR1-C4GW 12/6/2004	Injection Period ASR1-C4SW1 12/6/2004	ASR1-C4SW2 2/25/2005	ASR1-C4SW3 4/19/2005	Stored Water ASR1-C4T1 5/23/2005	Recovered Water ASR1-C4R1 6/27/2005	ASR1-C4R2 6/27/2005	ASR1-C4R3 8/16/2005	ASR1-C4R4 9/13/2005	ASR1-C4R5 10/3/2005
Disinfection by-Products	Bromodichloromethane	None	None	mg/L	0.0011	0.0024			0.002	0.001		0.001		
	Bromoform	None	URC	mg/L	0.0005 U	0.0005 U			0.0005 U	0.0005 U		0.0005 U		
	Chlorodibromomethane	None	None	mg/L	0.0005 U	0.0005 U			0.0005 U	0.0005 U		0.0005 U		
	Chloroform	None	URC	mg/L	0.0124	0.0262			0.0863	0.398		0.0206		
	Dibromoacetic Acid	None	None	mg/L	0.003 U	0.003 U			0.003 U	0.003 U		0.003 U		
	Dichloroacetic Acid	None	None	mg/L	0.003 U	0.02			0.0021	0.003 U		0.003 U		
	Monobromoacetic Acid	None	None	mg/L	0.003 U	0.003 U			0.003 U	0.003 U		0.003 U		
	Monochloroacetic Acid	None	None	mg/L	0.003 U	0.003 U			0.003 U	0.003 U		0.003 U		
	Total Haloacetic Acids	0.06	MCL	mg/L	0.003 U	0.0558			0.0156	0.003 U		0.003 U		
	Total Trihalomethanes	0.08	MCL	mg/L	0.0135	0.0286			0.0883	0.0408		0.0216		
	Trichloroacetic Acid	None	None	mg/L	0.003 U	0.0358			0.0135	0.003 U		0.003 U		
Field Parameters	Dissolved Oxygen	None	None	mg/L	7.4	9.5	10.1	10.5	10.2	8.7	9.8	9.1	9.2	5.4
	ORP	None	None	mV	131	226		268	119	31	45	108	117	124
	pH	6 - 8.5 standard units	SMCL	pH	6.77	6.78	6.9	7.26	6.76	6.92	6.92	6.36	6.74	6.05
	Specific Conductance	None	None	us/cm	116	59	18	26	45	38	61	84	103	127
	Temperature	None	None	degC	10.9	11.1	8	9.6	9.7	9.3	9.5	10.1	10.5	10.2
	Total Dissolved Solids	500	SMCL	mg/L								42	53.0	
Geochemical	Bicarbonate	None	None	mg/L	60	22	10	10	16	15	25	39	39	48
	Calcium	None	None	mg/L	12.7	5.7	1.6	2.8	3.2	3.4	5.1	7.8	9.8	10.9
	Carbonate	None	None	mg/L	2 U	2 U	2 U	2 U	2 U	2 U	2 U	2 U	2 U	2 U
	Chloride	250	SMCL	mg/L	3	4	3	3	3	8	3	3	3	3
	Hardness (as CaCO3)	250	SMCL	mg/L	60	24	8	8	16	16	24	32	44	48
	Magnesium	None	None	mg/L	6.01	1.71	0.65	0.62	1.29	1.39	2.28	3.63	4.64	5.26
	Nitrate as N	10	MML	mg/L	1.5	0.5 U	0.5 U	0.5 U	0.6	0.6	0.7	0.5 U	0.5 U	1.6
	Nitrate+Nitrite	10	MCL	mg/L	1.5	0.01 U	0.01 U	0.01 U	0.66	0.6	0.7	0.01 U	0.01 U	1.6
	Nitrite as N	1	MCL	mg/L	0.01 U	0.01 U	0.01 U	0.01 U	0.06	0.01 U	0.01 U	0.01 U	0.01 U	0.01 U
	Potassium	None	None	mg/L	1.7	0.4	0.2	0.1	0.4	0.5	0.8	1.1	1.4	1.5
	Silica	None	None	mg/L	42	13.3	8.6	9.2	16.3	19.6	30.2	37.2	39.8	39.3
	Sodium	20	URC, SMCL	mg/L	6.97	7.3	2.85	2.98	4.18	4.01	4.56	5.44	5.65	6.02
	Sulfate	250	URC, SMCL	mg/L	5	8	5 U	1.4	1.6	1	2.1	2.6	3.4	2.7
	Total Alkalinity	None	SMCL	mg/L	60	22	10	10	16	15	25	39	48	48
	Total Dissolved Solids	500	SMCL	mg/L	120	60	20	20	40	49	68	90	100	110
	Total Organic Carbon	None	None	mg/L	0.58	1.33	1.63			0.9				
	Total Suspended Solids	None	None	mg/L	2 U	2 U	2 U	8	2	2	2 U	2 U	2 U	2 U

Appendix B Cont.--Tigard ASR 1 Cycle 4 (page 2 of 4)

Category	Analyte	Regulatory Standard	Regulatory Criteria	Units	Baseline Groundwater ASR1-C4GW 12/6/2004	Injection Period ASR1-C4SW1 12/6/2004	ASR1-C4SW2 2/25/2005	ASR1-C4SW3 4/19/2005	Stored Water ASR1-C4T1 5/23/2005	Recovered Water ASR1-C4R1 6/27/2005	ASR1-C4R2 6/27/2005	ASR1-C4R3 8/16/2005	ASR1-C4R4 9/13/2005	ASR1-C4R5 10/3/2005
Metals	Aluminum	0.05	SMCL	mg/L		0.05 U				0.05 U				
	Antimony	0.006	MCL	mg/L		0.001 U				0.001 U				
	Arsenic	0.05	MCL, MML	mg/L		0.002 U				0.002 U				
	Barium	1	MCL, MML	mg/L		0.002 U				0.05 U				
	Beryllium	0.004	MCL	mg/L		0.0005 U				0.0005 U				
	Cadmium	0.005	MCL, MML	mg/L		0.001 U				0.001 U				
	Chromium	0.05	MCL, MML	mg/L		0.002 U				0.002 U				
	Copper	1.3	MCL	mg/L		0.005 U				0.005 U				
	Iron, Dissolved	0.3	SMCL	mg/L		0.05 U				0.05 U				
	Iron, Total	0.3	None	mg/L		0.05 U				0.05 U				
	Lead	0.015	MCL, MML	mg/L		0.001 U				0.001 U				
	Manganese, Dissolved	0.05	SMCL	mg/L		0.002 U				0.002 U				
	Manganese, Total	0.05	None	mg/L		0.004				0.002 U				
	Mercury	0.002	MCL, MML	mg/L		0.0002 U				0.0002 U				
	Nickel	0.1	MCL	mg/L		0.004 U				0.004 U				
	Selenium	0.01	MCL, MML	mg/L		0.002 U				0.002 U				
	Silver	0.05	MML, SMCL	mg/L		0.005 U				0.005 U				
	Thallium	0.002	MCL	mg/L		0.0006 U				0.0006 U				
	Zinc	5	SMCL	mg/L		0.01 U				0.01 U				
Miscellaneous	Color	15 standard units	SMCL	cu	5 U	5				5 U				
	Corrosivity	Non-Corrosive	SMCL	mg/L	-1.75	-2.54	-3.21	-2.85	-2.87	-2.75	-2.37	-2.61	-2.01	-2.67
	Cyanide	0.2	MCL, MML	mg/L	0.02 U	0.02 U				0.02 U				
	Fluoride	2	MCL, MML, SMCL	mg/L	0.5 U	0.5 U				0.5 U				
	Methylene Blue Active Substance	0.5	SMCL	mg/L	0.05 U	0.05 U				0.05 U				
	Odor	3 threshold #s	SMCL	ton	2	1				1 U				
Radionuclides	Gross Alpha	15 pCi/L	MML	pCi/L		1 U				3 U				
	Gross Beta	50 pCi/L	MML	pCi/L		2 U				2 U				
	Radium 226/228			pCi/L		0.2 U				1 U				
	Radon			pci/L	329					412				392
	Uranium			mg/L		0.001 U				0.001 U				
Synthetic Organic Compounds	2,4,5-TP	0.01	MCL, MML	mg/L		0.0004 U				0.0004 U				
	2,4-D	0.07	MCL, MML	mg/L		0.0002 U				0.0002 U				
	3-Hydroxycarbofuran	None	None	mg/L		0.004 U				0.004 U				
	Alachlor (Lasso)	0.002	MCL, MML	mg/L		0.0004 U				0.0004 U				
	Aldicarb	None	None	mg/L		0.002 U				0.002 U				
	Aldicarb Sulfone	None	None	mg/L		0.001 U				0.001 U				
	Aldicarb Sulfoxide	None	None	mg/L		0.003 U				0.003 U				
	Aldrin	None	None	mg/L		0.0001 U				0.0001 U				
	Atrazine	0.003	MCL, MML	mg/L		0.0002 UX				0.0002 U				
	Benzo (a) pyrene	0.0002	MCL	mg/L		0.00004 U				0.00004 U				
	BHC-gamma (Lindane)	0.0002	MCL, MML	mg/L		0.00002 UX				0.00002 U				
	Butachlor	None	None	mg/L		0.001 U				0.001 U				
	Carbaryl	None	None	mg/L		0.004 U				0.004 U				
	Carbofuran	0.04	None	mg/L		0.001 U				0.001 U				
	Chlordane	0.002	MCL	mg/L		0.0004 UX				0.0004 U				
	Dalapon	0.2	MCL	mg/L		0.002 U				0.002 U				

Appendix B Cont.--Tigard ASR 1 Cycle 4 (Page 3 of 4)

Category	Analyte	Regulatory Standard	Regulatory Criteria	Units	Baseline Groundwater ASR1-C4GW 12/6/2004	Injection Period ASR1-C4SW1 12/6/2004	ASR1-C4SW2 2/25/2005	ASR1-C4SW3 4/19/2005	Stored Water ASR1-C4T1 5/23/2005	Recovered Water ASR1-C4R1 6/27/2005	ASR1-C4R2 6/27/2005	ASR1-C4R3 8/16/2005	ASR1-C4R4 9/13/2005	ASR1-C4R5 10/3/2005
Synthetic Organics cont.	Di-(2-Ethylhexyl)adipate	0.4	MCL	mg/L		0.001 U				0.001 U				
	Di-(2-Ethylhexyl)phthalate	0.006	MCL	mg/L		0.0013 U				0.0013 U				
	Dibromochloropropane (DBCP)	0.0002	MCL	mg/L		0.00002 U				0.00002 U				
	Dicamba	None	None	mg/L		0.0005 U				0.0005 U				
	Dieldrin	None	None	mg/L		0.0001 U				0.0001 U				
	Dinoseb	0.007	MCL	mg/L		0.0004 U				0.0004 U				
	Diquat	0.02	MCL	mg/L		0.0004 U				0.0004 U				
	Endothall	0.1	MCL	mg/L		0.01 U				0.01 U				
	Endrin	0.0002	MCL, MML	mg/L		0.00002 U				0.00002 U				
	Ethylene Dibromide (EDB)	5e-005	MCL, MML	mg/L		0.00001 U				0.00001 U				
	Glyphosate	0.7	MCL, MML	mg/L		0.01 U				0.01 U				
	Heptachlor	0.0004	MCL, MML	mg/L		0.00004 U				0.00004 U				
	Heptachlor Epoxide	0.0002	MCL, MML	mg/L		0.00002 U				0.00002 U				
	Hexachlorobenzene	0.001	MCL, MML	mg/L		0.0001 UX				0.0001 U				
	Hexachlorocyclopentadiene	0.05	MCL, MML	mg/L		0.0002 UX				0.0002 U				
	Methomyl	None	None	mg/L		0.004 U				0.004 U				
	Methoxychlor	.04	MCL, MML	mg/L		0.0002 U				0.0002 U				
	Metolachlor	None	None	mg/L		0.002 U				0.002 U				
	Metribuzin	None	None	mg/L		0.001 U				0.001 U				
	Pentachlorophenol	0.001	MCL, MML	mg/L		0.00008 U				0.00008 U				
	Picloram	0.5	MCL, MML	mg/L		0.0002 U				0.0002 U				
	Polychlorinated Biphenyls (PCBs)	0.0005	MCL, MML	mg/L		0.0002 UX				0.0002 U				
	Propachlor	None	None	mg/L		0.001 UX				0.001 U				
	Simazine	0.004	MCL, MML	mg/L		0.0001 UX				0.0001 U				
	Toxaphene	None	MCL, MML	mg/L		0.001 UX				0.001 U				
	Vydate	0.2	MCL	mg/L		0.002 U				0.002 U				
Volatile Organics	1,1,1-Trichloroethane	0.2	MCL, MML	mg/L		0.2 U				0.2 U				
	1,1,2-Trichloroethane	0.005	MCL, MML	mg/L		0.005 U				0.005 U				
	1,1-Dichloroethene	0.007	MCL, MML	mg/L		0.007 U				0.007 U				
	1,2,4-Trichlorobenzene	0.07	MCL, MML	mg/L		0.07 U				0.07 U				
	1,2-Dichloroethane	0.005	MCL, MML	mg/L		0.005 U				0.005 U				
	1,2-Dichloroethene (Cis)			mg/L		0.07 U				0.07 U				
	1,2-Dichloropropane	0.005	MCL, MML	mg/L		0.005 U				0.005 U				
	Benzene	0.005	MCL, MML	mg/L		0.005 U				0.005 U				
	Carbon Tetrachloride	0.005	MCL, MML	mg/L		0.005 U				0.005 U				
	Dichloromethane	0.005	MCL, MML	mg/L		0.005 U				0.005 U				
	Ethylbenzene	0.7	MCL, MML	mg/L		0.7 U				0.7 U				
	Monochlorobenzene	0.1	MCL, MML	mg/L		0.1 U				0.1 U				
	O-Dichlorobenzene	0.6	MCL, MML	mg/L		0.6 U				0.6 U				
	P-Dichlorobenzene	0.075	MCL, MML	mg/L		0.075 U				0.075 U				
	Styrene	0.1	MCL, MML	mg/L		0.1 U				0.1 U				
	Tetrachloroethylene	0.005	MCL, MML	mg/L		0.005 U				0.005 U				
	Toluene	1	MCL, MML	mg/L		1 U				1 U				
	Trans-1,2-Dichloroethene	0.1	MCL, MML	mg/L		0.1 U				0.1 U				
	Trichloroethene	0.005	MCL, MML	mg/L		0.005 U				0.005 U				
	Vinyl Chloride	0.002	MCL, MML	mg/L		0.002 U				0.002 U				
	Xylenes, Total	10	MCL, MML	mg/L		10 U				10 U				

Appendix B Cont. –Tigard ASR 1 Cycle 4 (Page 4 of 4)

Table Notes:

(1) Blank cell indicates analyte not tested
(2) U = Analyte not detected at indicated detection limit
(3) X = During the extraction, a water bath went out of specified temperature limits. The percent recovery of the laboratory fortified blank showed that certain analytes and a surrogate were not within our specified control limits. Consequently, the batch QA/QC criteria were not met and the flagged analytes cannot be validated. All individual sample surrogate recoveries were well within acceptable QA/QC requirements at approximately 90%. The reported results are believed to be accurate and representative of the sample.

APPENDIX C: DETAILED DILUTION ANALYSIS

No external tracers were added to the injected source water at any of the ASR sites investigated, complicating the dilution analysis. Lack of external tracers necessitated using naturally occurring ions in the source water and groundwater to determine the fraction of each water present in a given sample (i.e. the mixing fractions). In basalts, however, ion exchange and mineral dissolution may occur and many ions often do not behave conservatively (Dafny et al. 2006; Hinkle 1996). Furthermore, the data compiled in this study indicates that geochemical conditions driving ion exchange and mineral dissolution are highly variable spatially within the CRBG, causing ions that behave conservatively at one site to undergo water-rock reactions at other sites. Therefore, separate analyses were performed at each site to determine which ions behaved conservatively.

Additional complications arose due to the presence of three waters in many ASR cycles. Often, after the first cycle, the groundwater present at the ASR well prior to injection, "baseline" groundwater, consisted of a mix of previous ASR water (since most Oregon ASR permits allow extraction of only 95% of injected water by volume) and native groundwater, effectively adding a third water to the dilution analysis. During such cycles, there are essentially three waters present: injected source water, baseline groundwater, and native groundwater. Figure 1 depicts a highly simplified conceptual model of the movement of the three waters as a typical ASR cycle progresses. It should also be noted that the baseline groundwater contains THMs, which may have undergone

degradation during the time interval between cycles, adding another component to the THM degradation analysis.

During the mixing process if only baseline groundwater and source water are present, the concentration of any given ion in the mix is controlled by the following equation:

$$C = C_{sw}(F_{sw}) + C_{bl}(1-F_{sw}) \text{ +/- water-rock reactions} \quad (0)$$

where C is the concentration of the ion in the mixed water, C_{sw} is the concentration of the ion in the injected source water, C_{bl} is the baseline ion concentration in the ambient groundwater, and F_{sw} represents of fraction of injected water in the mixture. If there are no water-rock reactions, e.g., dissolution-precipitation, ion exchange, etc., the concentration of a given ion in the hybrid water results from simple mixing only. We can further manipulate the equation above in order to express F_{sw} in terms of the relative concentrations of the waters in question.

$$C = C_{sw}(F_{sw}) + C_{bl} - C_{bl}(F_{sw})$$

$$C - C_{bl} = F_{sw}(C_{sw} - C_{bl})$$

$$F_{sw} = (C-C_{bl})/(C_{sw}-C_{bl}) \quad \text{[Equation 1]}$$

Chloride is naturally occurring in all ASR waters of interest in this study and is widely considered to be conservative in basalts (Matter et al., 2007; Kranjc, 1997).

However, for many ASR cycles in this study, differences in chloride concentrations between injected source water and baseline groundwater were not large enough for meaningful use in a dilution analysis. For this study, tracers were required to have concentration differences greater than twice the minimum detection limit (MDL) between source water and baseline groundwater to ensure that observed concentration differences were greater than natural variations in each water. For cycles where chloride dilution analyses were not possible, it was necessary to identify other conservative ions to use as tracers.

Tigard ASR 1 and 2 Dilution Analysis:

Tigard's ASR 1 and 2 dilution analysis were far more complicated than the dilution analyses for Beaverton and McCarty and will be discussed in detail to illustrate the process used in this study.

Chloride dilution analyses were possible at Tigard for ASR 2 cycles 1 and 2, but not at ASR 1. In order to identify other conservative ions in the Bull Mountain CRBG formation, recovery phase mixing fractions calculated with Cl^- were compared to those calculated with other ions for the two cycles at ASR 2 where chloride dilution analyses were possible. Ions investigated as possible alternative tracers were bicarbonate, calcium, sodium, magnesium, nitrate, sulfate, potassium, and silica. Recovery phase time-series plots of fractions of injected source water (Fsw) calculated using each potential tracer were compared to the same plots for chloride. As previously derived,

when only source water and baseline groundwater are present and no rock-water

reactions are occurring:

$$Fsw = (C-Cbl) / (Csw-Cbl) \quad [\text{Equation 1}]$$

where C=sample tracer concentration, Cbl=baseline tracer concentration, and

Csw=source water tracer concentration. As shown in Figure 2 for ASR 2, magnesium,

calcium, potassium, and bicarbonate all exhibited Fsw trends similar to chloride for both

cycles 1 and 2 and were identified as possible tracers.

In addition to exhibiting mixing fraction trends similar to chloride, potential

tracers were required to demonstrate conservative behaviors for all ASR cycles to which

they were applied. If an ion's concentration considerably increased or decreased during

the storage phase, it was excluded as a tracer. Large changes in concentration during

storage are likely due to reaction and not mixing since only source water is likely to be

present at the ASR well, where samples are taken. As shown in Figures 3, 4, 5, and 6 at

Tigard ASR1 calcium, bicarbonate, magnesium, and potassium ions did not tend to

increase in concentration above source water levels during storage whereas nitrate and

silica tended to significantly increase in concentration prior to the recovery phase as

shown in Figures 7 and 8.

For ASR cycles in which baseline groundwater was determined to contain

previous ASR water, ions were excluded as tracers if baseline concentrations reached

native groundwater concentrations prior to the start of injection. It was assumed that

baseline groundwater contained previous cycle ASR water if the recovered volume was

less than the injected volume for the previous ASR cycle, if major ion concentrations for baseline water were significantly different from native groundwater concentrations, or if baseline water contained THMs. A change in baseline ion concentrations toward native groundwater concentrations between the end of the previous cycle and the beginning of the successive cycle suggests reaction during the ASR rest period when minimal mixing is occurring. Baseline groundwater concentrations for nitrate, silica, and sodium tended to either reach or exceed native groundwater levels as shown in Figures 7, 8, and 9 respectively indicating reaction during the ASR rest period between cycles. However calcium, bicarbonate, magnesium, and potassium (Figures 3, 4, 5, and 6) once again exhibited conservative behavior with baseline concentrations lower than native groundwater concentrations.

Ions used as tracers were required to have fairly consistent concentrations in both baseline groundwater and source water during the ASR cycle being analyzed. In addition, tracers were required to have similar concentrations for multiple samples of native groundwater since baseline groundwater contains a mixture of previous cycles' source water and native groundwater. Highly variable tracer concentrations in source water, baseline or native groundwater can cause concentration increases or decreases in addition to those caused by mixing, effectively skewing dilution analysis results. For instance, sulfate and nitrate concentrations tend to be highly variable in native groundwater (where data is provided) causing trends during recovery to be highly erratic as shown in Figures 7 and 10.

Meaningful concentration data must be present for all tracers for each ASR cycle where they are utilized. As with the chloride analysis, differences in concentration between baseline groundwater and source water were required to be at least twice the minimum detection limit (MDL) to ensure actual differences in concentration existed in addition to variances due to measurement method analyses and natural fluctuation in each water present. When MDLs were greater than or equal to 1.0 mg/L, tracer concentrations were required to be higher than detection limits for all recovered and source water samples to ensure that adequate information was present in the data to calculate accurate dilution fractions.

Fsw calculations were performed assuming mixing between ASR source water and baseline groundwater only. This assumption was confirmed by comparing time-series plots of recovery phase ion concentrations normalized by baseline groundwater concentrations, i.e. sample concentration divided by baseline groundwater concentration, for each of the possible tracers as shown in Figure 11 for all three cycles at ASR 2. If baseline normalized concentrations (C/Cbl in Figures 1 (b) and (c)) for all the potential tracers followed the same patterns and approached 1.0 as recovery progressed (as in Tigard ASR 2 cycles 1 and 2 in Figure 11), it was assumed that only baseline groundwater and injected source water were present in the recovered samples. However, if trends for selected ions were divergent and baseline normalized concentrations exceeded 1.0 as in Tigard ASR 2 cycle 3 (Figure 11), it was assumed that native groundwater was present in the recovered sample in addition to source water and baseline groundwater. Plots of baseline normalized ion concentrations vs. time or percent

recovery (volume recovered / total volume injected *(100%)) are shown for cycles 3, 4, and 5 at Tigard ASR 1 (Figure 12). Tigard ASR 1 cycles 4 and 5 exhibited trends consistent with mixing between baseline groundwater and source water only. However, for the last sampling in cycle 3, C/Cbl > 1.0 for all tracers, likely due to the presence of native groundwater in the sample as in addition to baseline groundwater and source water, therefore the last sample point was excluded from the analysis. The first two samplings in cycle 3 exhibited trends consistent with mixing between baseline groundwater and source water only and were used for the THM reaction rate analysis.

Discussion of Beaverton Dilution Analysis:

During Beaverton's cycle 2 (1999) only native groundwater and source water were present (i.e. baseline water did not contain previous cycle ASR water). Figure 13 shows the graph of Fsw (based on chloride, calcium, magnesium, and chloroform) vs. percent recovered by volume (volume recovered / total volume injected *(100%)) for Beaverton cycle 2. The Fsw plots for both calcium and magnesium followed the same trend as for chloride and were used to investigate mixing during other Beaverton cycles. Fsw based on chloroform also followed approximately the same trend as Fsw based on chloride indicating that chloroform was fairly conservative during this cycle. Figure 14 shows the dilution corrected concentrations ($C_{\text{dilution corrected}} = C/Fsw$ where Fsw was based on chloride), or the concentration in the source water only, for total trihalomethanes (TTHM), chloroform (CF), and bromodichloromethane (BDCM). It was possible to calculate dilution corrected concentrations for this cycle because only native groundwater, which contains no THMs, and source water were present. As shown in

Figure 14, the dilution corrected concentrations for the third and fourth samplings

(circled data points in Figure 14) exhibited a trend that was inconsistent with the rest of

the data points, significantly dipping in concentration. After the dip in concentration, the

dilution corrected concentrations then significantly increased to concentrations similar to

the first and second samplings. Since it is unlikely that formation would have been

occurring during this period based on residual chlorine concentrations of 0 to 0.05mg/L,

it would not make sense for the concentrations to significantly dip, and then increase.

Therefore, the circled data points in Figure 14 were not used for the THM reaction rate

analysis. The dip in dilution corrected concentrations may have been caused by a

decreased residual chlorine concentration during part of the injection period, leading to

less overall THM formation (which would occur soon after injection) and therefore lower

initial THM concentrations, in a portion of the injected source water.

Figure 15 shows the baseline normalized concentrations vs. time for chloride,

calcium, and magnesium for Beaverton cycle 9 (2006). As shown, although baseline

normalized concentrations followed the same pattern and approached 1.0, indicating two

water mixing, the plot for chloride was offset from the plots for calcium and magnesium.

This could be due to an inaccurate recorded baseline concentration for chloride. Due to

the possible inaccuracy in Fsw based on chloride, the THM reaction rate analysis was

performed with Fsw based on chloride only and with Fsw based on the average from

calcium and magnesium. Both analyses gave reaction rates for TTHM, CF, and BDCM

on the same order of magnitude and the reaction rates based on chloride were chosen as

the final reported values.

Discussion of McCarty Dilution Analysis:

Very little data was available for the McCarty analysis. Cycle 4 (2008) was the

only cycle with enough data to perform both a dilution analysis and THM reaction rate

analysis. Only two recovery samplings were taken during this cycle and no storage

samples were taken.   Figure 16 shows the plot of Fsw vs. time based on chloride,

calcium, and magnesium for McCarty cycle 4 showing that the plots for calcium and

magnesium approximately follow the same pattern as the plot for chloride. However,

since the source water concentrations for calcium and magnesium were greater than the

baseline groundwater concentrations, baseline normalized concentrations (C/Cbl) for

these ions were initially greater than 1.0, then approached 1.0 as recovery progressed.

Source water concentrations were greater than baseline concentrations for some ions at

McCarty because source water was groundwater from a seasonal alluvial aquifer and not

surface water that was treated in a water treatment plant as was the case for Tigard and

Beaverton. However, since baseline normalized trends for calcium and magnesium

followed the same patterns and since baseline normalized trends for all three ions

(calcium, magnesium, and chloride) tended toward 1.0 as recovery progressed, it was

assumed that only source water and baseline groundwater were present in the samples.

Concluding Dilution Analysis Remarks:

When chloride analyses were possible, Fsw in recovered samples was calculated

with chloride only. In cycles where a chloride dilution analysis was not possible due to

nearly equal concentrations of chloride in baseline groundwater and source water, Fsw

was calculated for all suitable tracers and the average was taken as the final value. For

Tigard ASR 1, calcium, magnesium, bicarbonate, and potassium were chosen as tracers

and used to calculate all mixing fractions. For Tigard ASR 2, Beaverton, and McCarty,

chloride was used as the sole tracer.

Figure 1: Simplified schematic showing the movement of source water (sw), baseline (bl) and native groundwater (nw) throughout a typical ASR cycle. Dilution analysis calculations are based on tracer concentrations in each water. C, C_{sw}, C_{bl}, and C_{nw} represent actual chloride concentrations in samples (taken at the ASR well), source water, baseline and native groundwater respectively at Tigard ASR 2, cycle 2 (2007), where it was possible to use Cl^- as a conservative tracer. Baseline normalized concentrations are denoted as C/C_{bl}.

Figure 2: Fsw vs. time based for Tigard ASR 2 cycles 1 and 2. Fsw (fraction of injected source water) was calculated based on concentrations of each ion listed. Fsw based on calcium, magnesium, potassium, and bicarbonate closely follow the trends for Fsw based on chloride and were chosen as potential tracers.
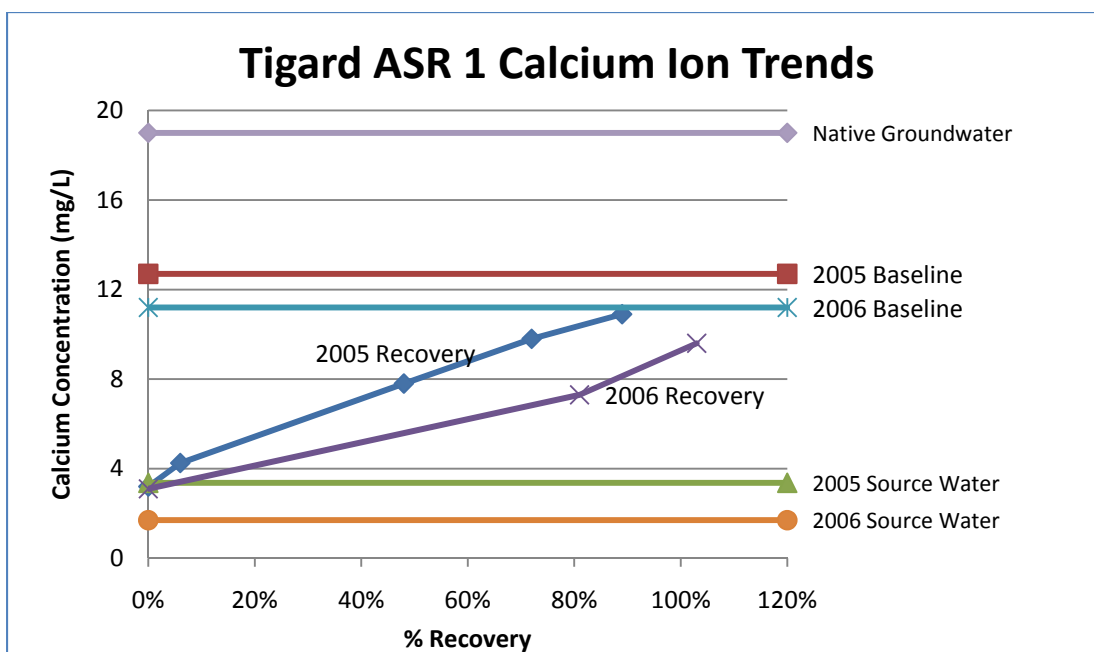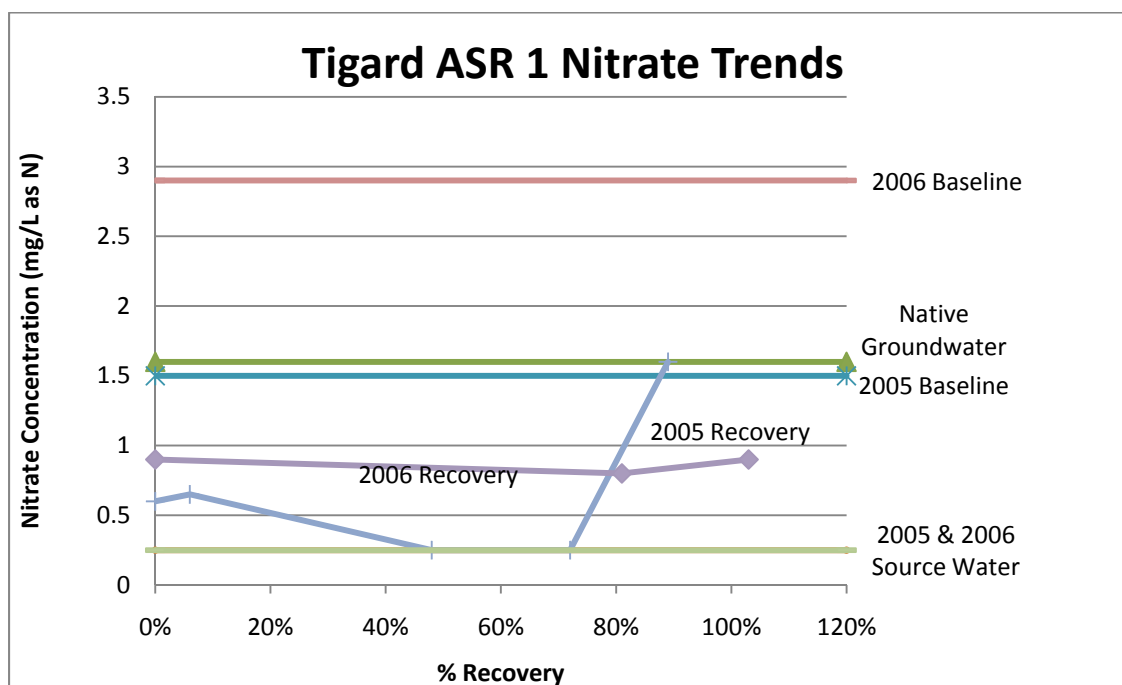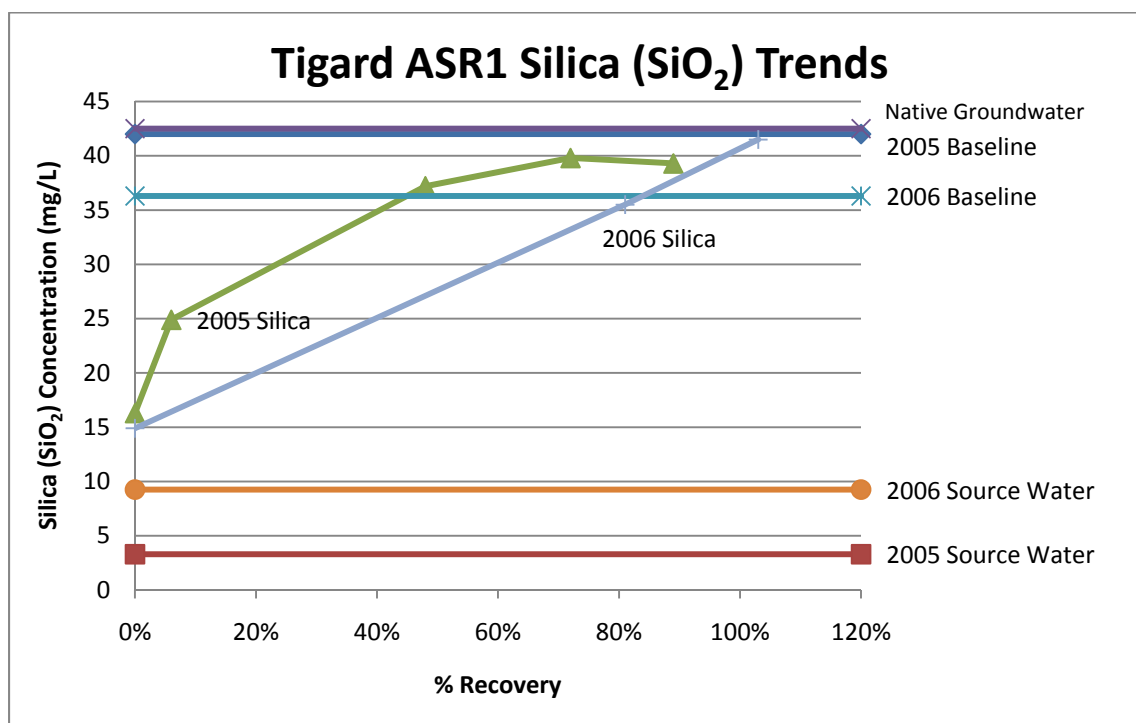
Figure 3: Tigard ASR 1 calcium ion trends during recovery. Calcium ions exhibit conservative behavior with baseline concentrations lower than native groundwater concentrations and no significant changes in concentration from source water levels during storage prior to the start of recovery. Recovery fractions calculated based on volume assuming a constant pumping rate.
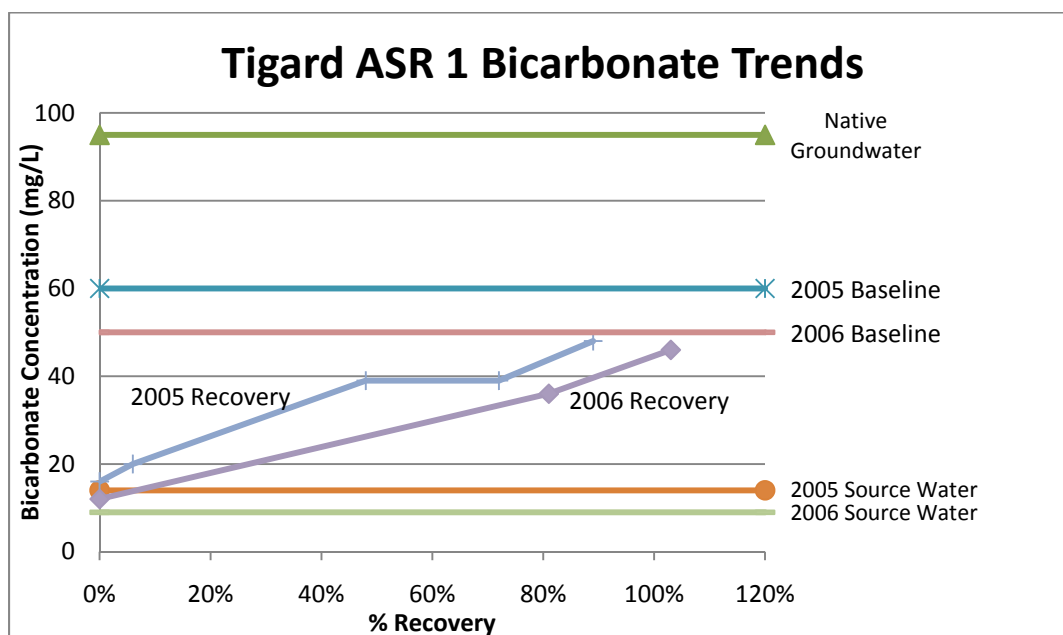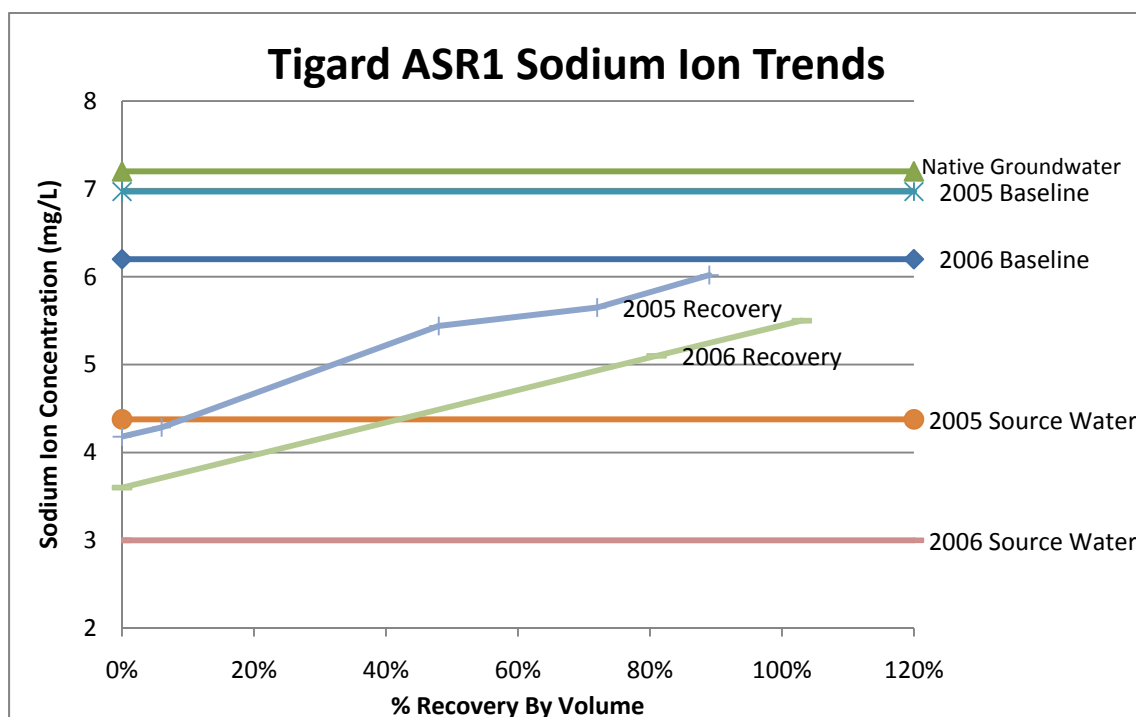
Figure 4: Tigard ASR 1 bicarbonate trends during recovery. Bicarbonate exhibits conservative behavior with baseline concentrations lower than native groundwater concentrations and no significant changes in concentration from source water levels during storage prior to the start of recovery. Recovery fractions calculated based on volume assuming constant pumping rate.
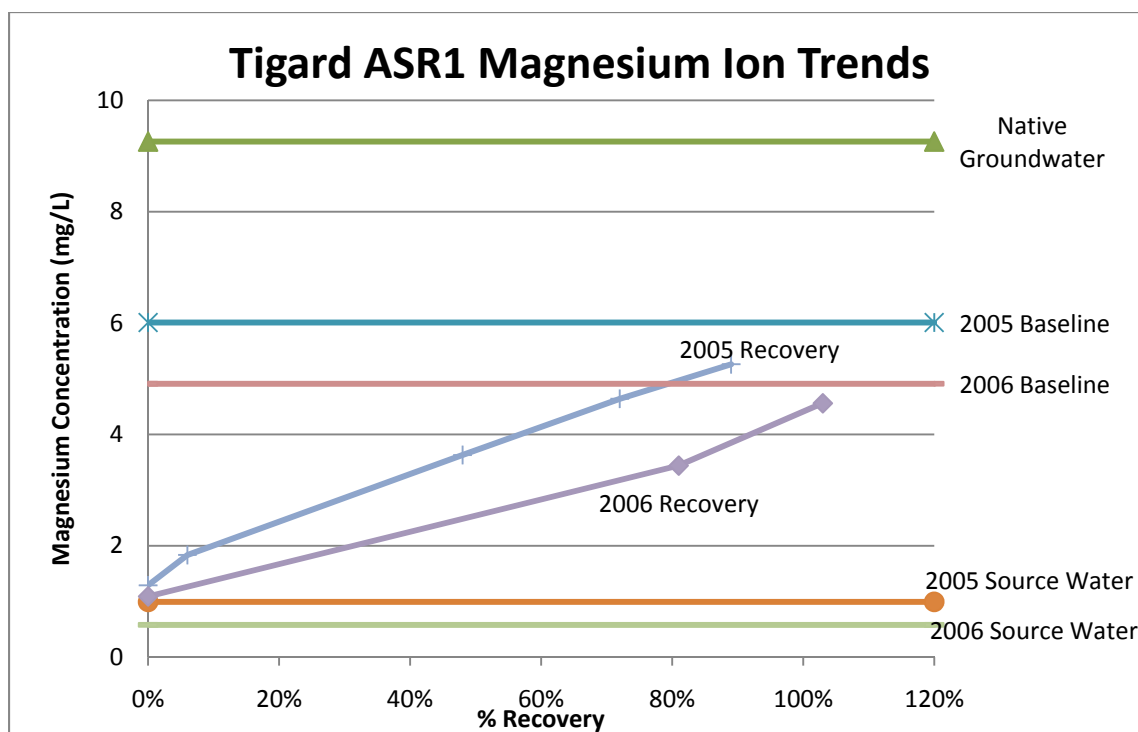
Figure 5: Tigard ASR 1 magnesium ion trends during recovery. Magnesium ions exhibit conservative behavior with baseline concentrations lower than native groundwater concentrations and no significant changes in concentration from source water levels during storage prior to the start of recovery. Recovery fractions calculated based on volume assuming a constant pumping rate.
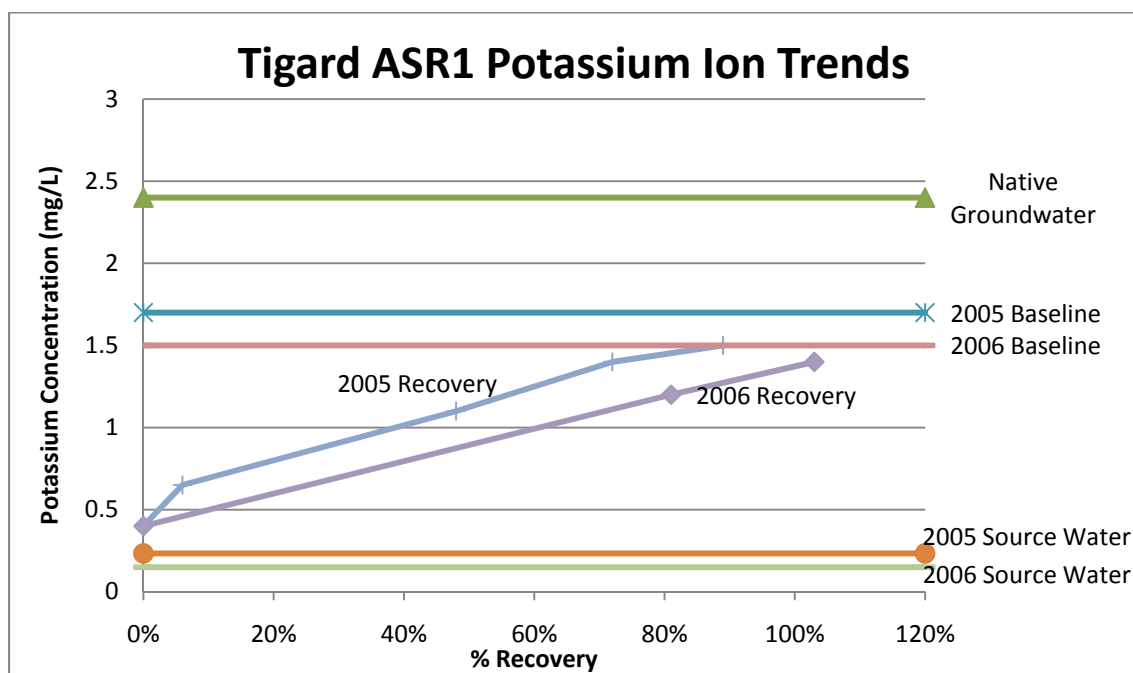
Figure 6: Tigard ASR 1 potassium ion trends during recovery. Potassium ions exhibit conservative behavior with baseline concentrations lower than native groundwater concentrations and no significant changes in concentration from source water levels during storage prior to the start of recovery. Recovery fractions calculated based on volume and constant pumping rates.

Figure 7: Tigard ASR 1 nitrate trends during recovery. Nitrate exhibits non-conservative behavior with baseline concentrations exceeding native groundwater concentrations, erratic recovery patterns, and significant changes from source water concentrations prior to the start of recovery. Recovery fractions calculated based on volume assuming constant pumping rates.

Figure 8: Tigard ASR 1 silica (SiO_2) trends during recovery. Silica exhibits non-conservative behavior with baseline concentrations reaching native groundwater concentrations and significant increases in concentrations from source water concentrations prior to the start of recovery. Recovery fractions calculated based on volume assuming constant pumping rates.

Figure 9: Tigard ASR 1 sodium ion trends during recovery. Sodium ions exhibit non-conservative behavior with baseline concentrations approaching native groundwater concentrations. Additionally, native groundwater sodium concentrations tend to be highly variable. Recovery fractions calculated based on volume assuming constant pumping rates.
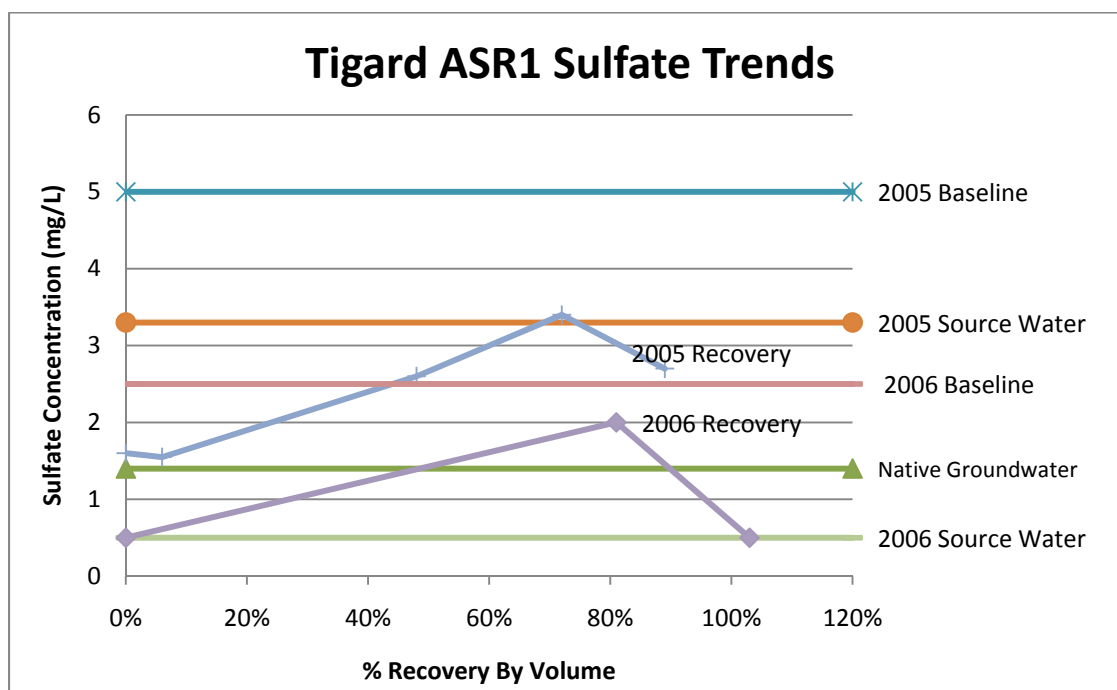
Figure 10: Tigard ASR 1 sulfate trends during recovery. Sulfate exhibits non-conservative behavior with erratic recovery trends where concentrations during recovery exceed both native and baseline groundwater concentrations, indicating high variability in sulfate concentrations within all three waters. Recovery fractions calculated based on volume assuming constant pumping rates.
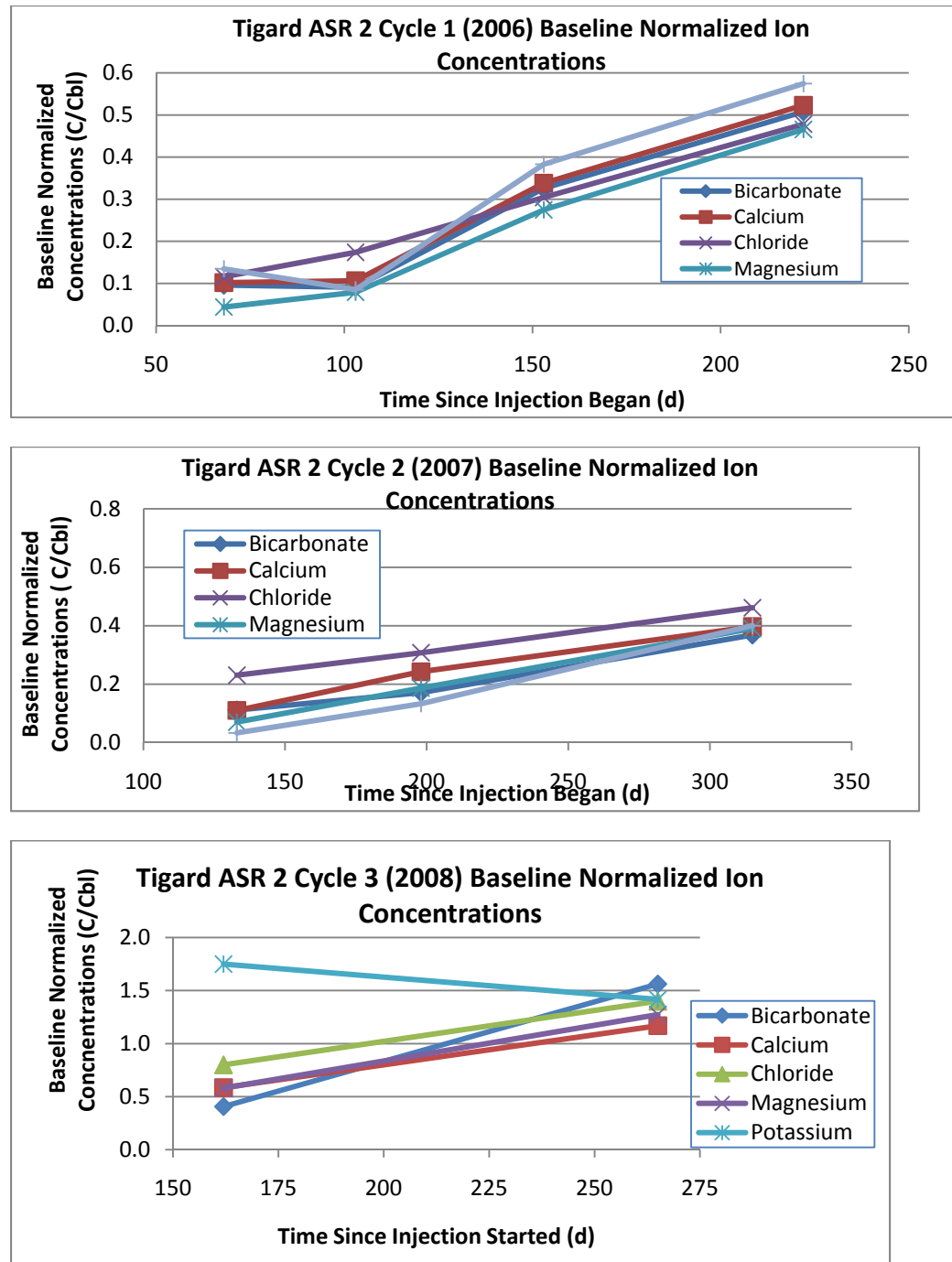
Figure 11: Recovery phase baseline normalized ion concentrations (C/Cbl) for cycles 1, 2, and 3 at ASR 2. For cycles 1 and 2 baseline normalized concentrations follow approximately the same patterns and approach 1.0, consistent with mixing between baseline groundwater and source water only. However, cycle 3 baseline normalized concentrations exceed 1.0 and do follow divergent patterns, indicating that native groundwater is likely present in addition to baseline groundwater and source water.
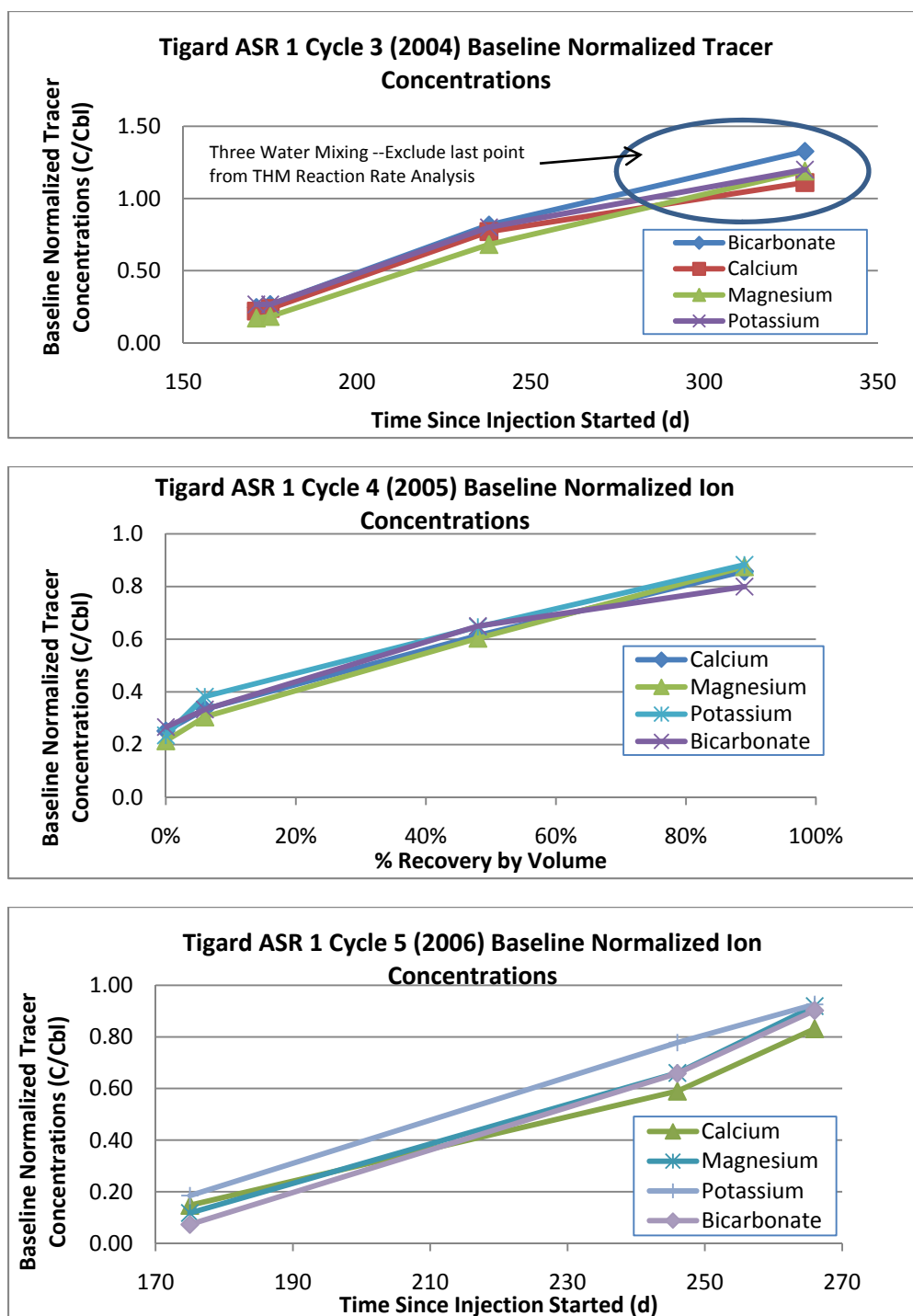
Figure 12: Baseline normalized (C/Cbl) tracer concentrations for all cycles analyzed at Tigard ASR 1. These plots show mixing between source water and baseline groundwater only for cycles 4 and 5 and for the first two sample points during cycle 3. However, for the last point in the cycle 3 plot, C/Cbl > 1.0 and therefore, some native groundwater is likely present in the sample.
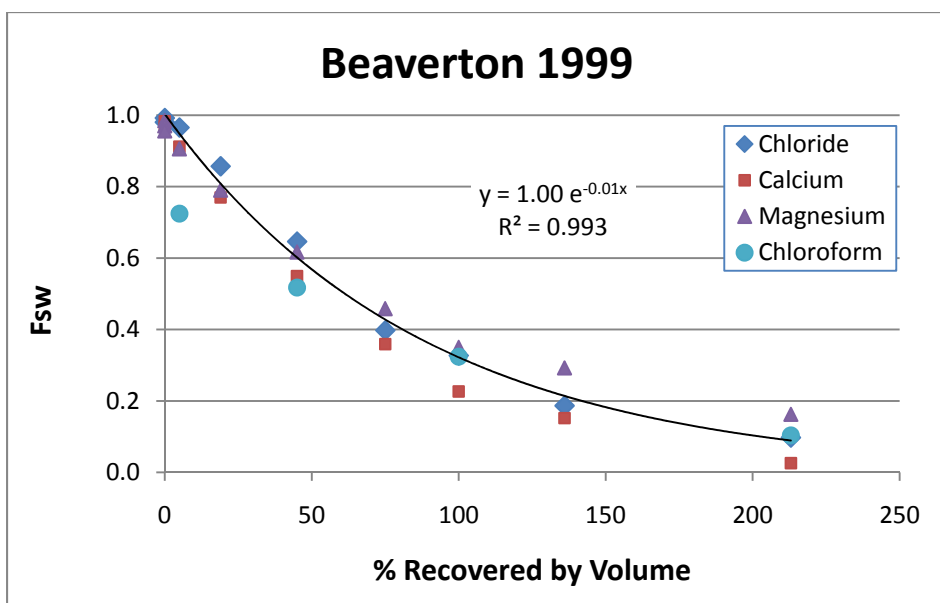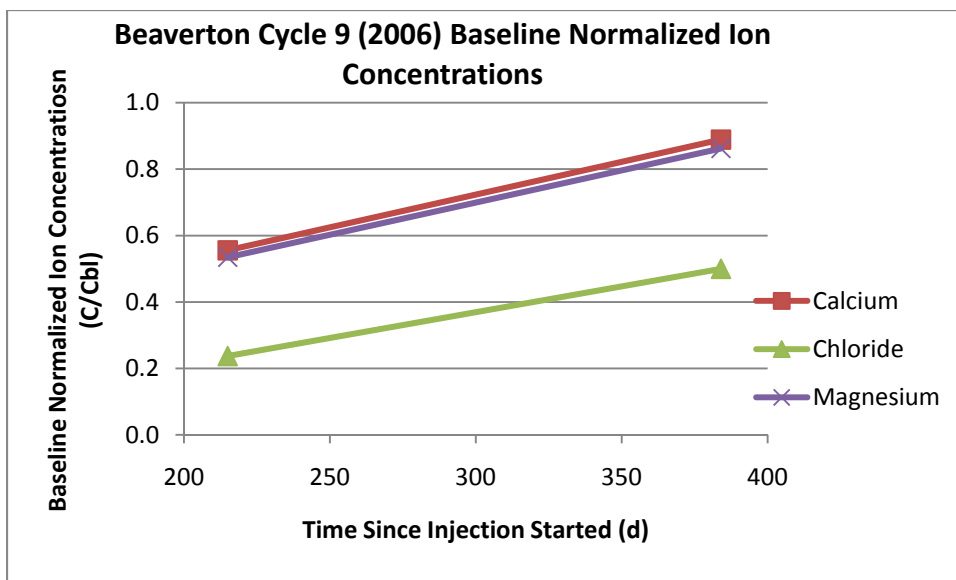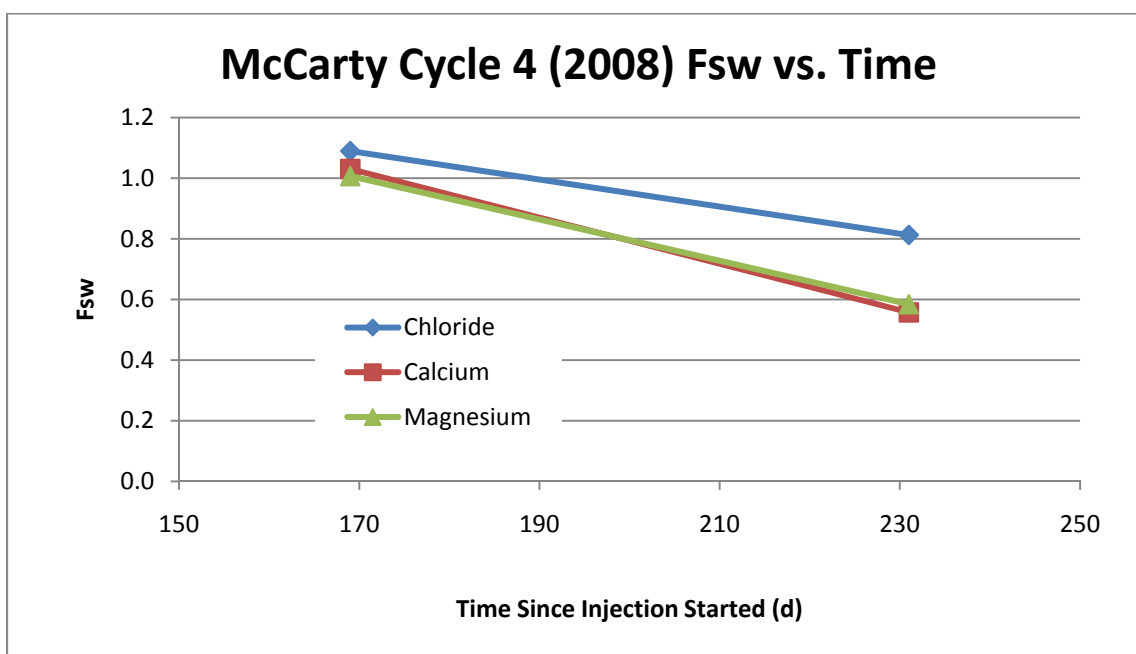
Figure 13: Fraction source water (Fsw) vs. time for Beaverton cycle 2 (1999). Fsw calculations were based on chloride, calcium, magnesium, and chloroform concentrations. Only native groundwater and source water were present during this cycle.
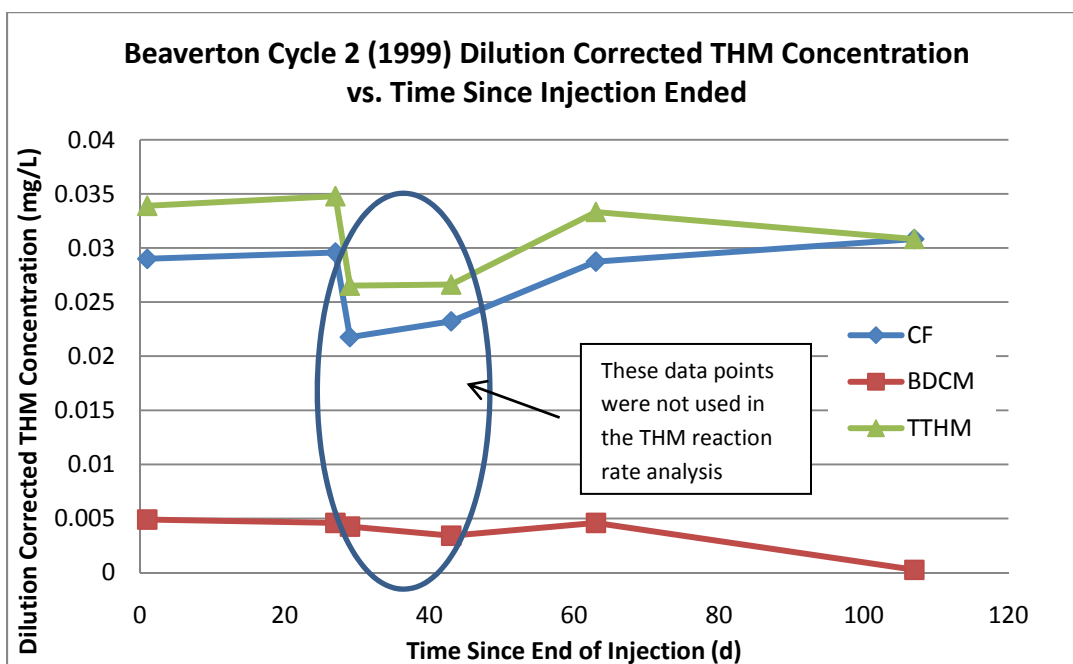

Figure 14: Dilution corrected THM concentrations for Beaverton cycle 2 (1999). The circled data points were not used in the THM reaction rate analysis because they exhibited a trend that was inconsistent with the other data points.

Figure 15: Baseline normalized ion concentrations for Beaverton cycle 9 (2006). The plot for chloride is significantly offset from the plots for calcium and magnesium. All three plots followed approximately the same patterns and approached 1.0, indicative of two water mixing.

Figure 16: Fraction source water (Fsw) vs. time for McCarty cycle 4 (2008). Fsw calculations were based on chloride, calcium and magnesium ion concentrations.
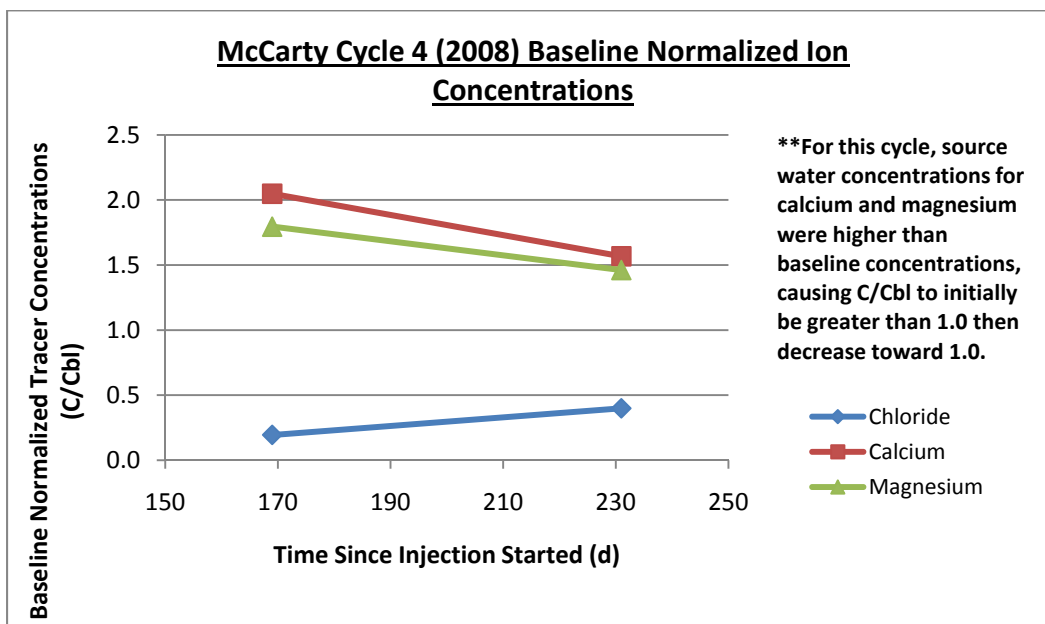
Figure 17: McCarty cycle 4 (2008) baseline normalized ion concentrations. For this cycle, source water concentrations for calcium and magnesium were higher than baseline concentrations, causing C/Cbl to initially be greater than 1.0, then decrease toward 1.0. This is not indicative of three water mixing, it is only due to the source water concentrations being higher than the baseline groundwater concentrations.