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# Electron donor contributions to denitrification in the Elk Valley Aquifer, North Dakota

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*University of North Dakota*

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ELECTRON DONOR CONTRIBUTIONS TO DENITRIFICATION IN THE ELK  
VALLEY AQUIFER, NORTH DAKOTA

by

Amanda Marie Krieger

Bachelor of Science, University of North Dakota, 2012

A Thesis

Submitted to the Graduate Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Master of Science

Grand Forks, North Dakota

May  
2014

This thesis, submitted by Amanda Marie Krieger in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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Dr. Charles Moretti, Committee Member

This thesis is being submitted by the appointed advisory committee as having met all of the requirements of the School of Graduate Studies at the University of North Dakota and is hereby approved.

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Dr. Wayne Swisher  
Dean, School of Graduate Studies

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Date

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The UND Denitrification Team deserves recognition for the immense amount of work done prior to my time at UND. The data collected over the years was diligently documented and provided an excellent foundation for this thesis and perhaps several to come. I am also grateful for sample analyses by the Environmental Analytical Research Laboratory (EARL) at UND and by the North Dakota Department of Health (NDDH).

I would like to thank the North Dakota Water Resources Research Institute and the UND Graduate Program in Environmental Engineering for providing financial assistance for my graduate research.

## ABSTRACT

Six denitrification tracer tests were performed over eight and a half years in in-situ mesocosms (ISMs) in the Elk Valley Aquifer (EVA) in east-central North Dakota. Groundwater samples were analyzed to determine how much nitrate was lost beyond that explained by dilution of the bromide tracer. Additional losses were attributed to denitrification. The denitrification rates varied from 0.10 to 0.23 mg N/L/day for the six tests. In general, the major electron donors for denitrification are organic carbon (OC), pyrite ( $\text{FeS}_2$ ), and ferrous iron silicate minerals. In the EVA tracer tests, increases in sulfate indicated that the oxidation of pyrite explained a significant of the denitrification. The contributions of the three electron donors varied between tests and from test to test with pyrite, ferrous iron from silicate minerals, and OC apparently contributing 38-84%, 1-3%, and 14-59% to denitrification, respectively.

## CHAPTER I

### INTRODUCTION AND HYPOTHESIS

Nitrate ( $\text{NO}_3^-$ ) is associated with some important environmental issues of our time because of its widespread use and its mobility in soil. Nitrate is a significant threat to surface and subsurface waters, where it is costly to remediate, it elevates trophic levels, and it is related to hypoxic zones throughout the world, notably that in the Gulf of Mexico (e.g., Justic et al., 2002). Furthermore, 44% of the US population depends on groundwater for its drinking water supply — be it from either a public source or private well (National Groundwater Association, 2010). Rural regions in the US are especially susceptible to nitrate contamination of aquifers because of the predominance of agriculture and the associated use of fertilizers. Therefore, nitrate is considered one of the most common groundwater contaminants (Korom, 1992). Sustained ingestion through drinking water has been linked to several health problems, for example methemoglobinemia in infants, commonly referred to as blue baby syndrome (Comly, 1945).

Denitrification, the conversion of nitrate to nitrogen gas ( $\text{N}_2$ ), can remove nitrate from groundwater (Seitzinger et al., 2006). The four general requirements for denitrification are: (1) the presence of N oxides ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}$ , and  $\text{N}_2\text{O}$ ) as terminal electron acceptors, (2) the presence of bacteria possessing the metabolic capacity, (3) suitable electron donors, and (4) anaerobic conditions or restricted  $\text{O}_2$  ability (Firestone, 1982). Korom (1992) showed that the most important requirement for denitrification in

aquifers is the presence of suitable electron donors. The main three types of electron donors that contribute to aquifer denitrification are organic carbon, pyrite ( $\text{FeS}_2$ ), and ferrous iron (Korom, 1992). These electron donors have been shown to be relatively abundant in our region and particularly in aquifer sediments in eastern ND (Schuh et al., 2006 and Klapperich, 2008).

This research was apparently the first to study the variation in the contributions of electron donors in aquifer sediments for such a long period of time, nearly eight and a half years. This was yet another step in the UND research group's progress in predicting aquifer denitrification parameters based on the electron donors present in aquifer sediments.

### Hypothesis

This thesis hypothesizes that pyrite ( $\text{FeS}_2$ ) contributes to most of the denitrification in the EVA, although it might not explain it consistently. The rest of the denitrification will be attributed to organic carbon (OC) and ferrous iron silicate minerals.

## CHAPTER II

### BACKGROUND AND PRIOR WORK

Studying the geochemistry of a particular aquifer has its challenges. It is difficult and time consuming to recreate hydrogeological processes accurately in a laboratory; therefore in situ experiments may be appropriate. However, the configuration of a field setup could hinder the results of an experiment. Simply injecting amended water and sampling from a single well limits sampling time as the slug of water travels down gradient, lowering the sensitivity of the technique (Gilham et al., 1990). A balance between the level of control achieved in a laboratory and observing the behavior of the aquifer in nature is pertinent for a reliable experiment.

#### In Situ Mesocosms and Network

Korom et al. (2005) have developed a novel way to isolate aquifer sediments in stainless steel chambers called “in situ mesocosms” (ISMs). The US regional network of ISMs is shown on Fig 1. Two ISMs have also been installed near Lake Taupo on the north island of New Zealand.

The ISMs are large (186 L) stainless steel chambers installed in the saturated zone. The chambers are hammered into final position at the bottom of a bore hole such that the aquifer sediments remain relatively undisturbed, providing an in situ experimentation environment. The large size of the chambers allows for long-term monitoring of the geochemical evolution of the groundwater during denitrification so that insights into the electron donors that contributed to the denitrification may be gained.

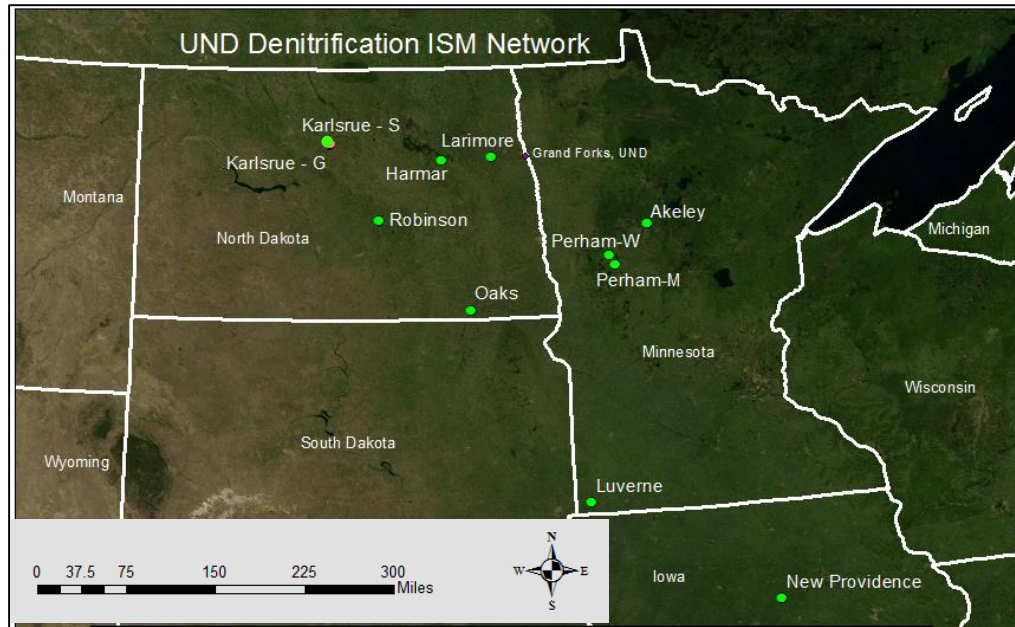


Figure 1. U.S. Network of Denitrification ISMs.

To date, there are 13 denitrification ISMs installed in which 21 denitrification tracer tests have been completed. Of the 13 ISM sites, eight ISMs have had several repeat tracer tests, with seven of these sites having had two tracer tests performed in them. This study focuses on the Elk Valley Aquifer ISM, at which six tracer tests have been performed. Groundwater denitrification rates measured at this site are among the fastest in the world (Green et al., 2008; Korom et al., 2010).

The construction, placement, and use of ISMs are described in detail in Korom et al. (2005), but a brief description of how denitrification tracer tests are performed follows. After installation each ISM was purged to make sure that natural formation water filled the ISMs. Groundwater was then pumped from each ISM into a reservoir on the ground surface with the tubing outlet placed on the bottom of the reservoir to avoid air contact for all but the earliest drawn water. Reservoir water was amended with either sodium nitrate ( $\text{NaNO}_3$ ) and sodium bromide ( $\text{NaBr}$ ), or potassium nitrate ( $\text{KNO}_3$ ) and



potassium bromide (KBr). Bromide was considered a tracer species because it does not naturally occur in the aquifer in high concentrations and it does not undergo oxidation-reduction reactions. The amended water was stirred and then siphoned back into the ISMs; the reservoir was periodically stirred gently to keep it well-mixed during the injection period. Several days after amendment an initial sample was taken from the ISM; it was then resampled every one or two months thereafter. Groundwater samples were filtered and analyzed using the standard methods listed on Table 1b in Korom et al. (2005).

### Geology of Elk Valley Aquifer

The Elk Valley Aquifer lies in east-central North Dakota and stretches across 500 square kilometers of Grand Forks County (Figure 2). The aquifer is unconfined and the water table is relatively shallow at an average of 3 m below the ground surface. Average thickness is approximately 10 m and maximum thickness is 19 m. The EVA consists of coarse, subangular, quartzose sand, detrital shale sand, and some gravel (Kelly and Paulson, 1970). There is a gradation in aquifer sediment texture from coarser sediments in the north to finer sediments in the south. The sandy, permeable soils coupled with the relatively small topographical relief of eastern ND allow a large percentage of precipitation to infiltrate to the groundwater system as measured by seasonal changes in the water table (Kelly and Paulson, 1970).

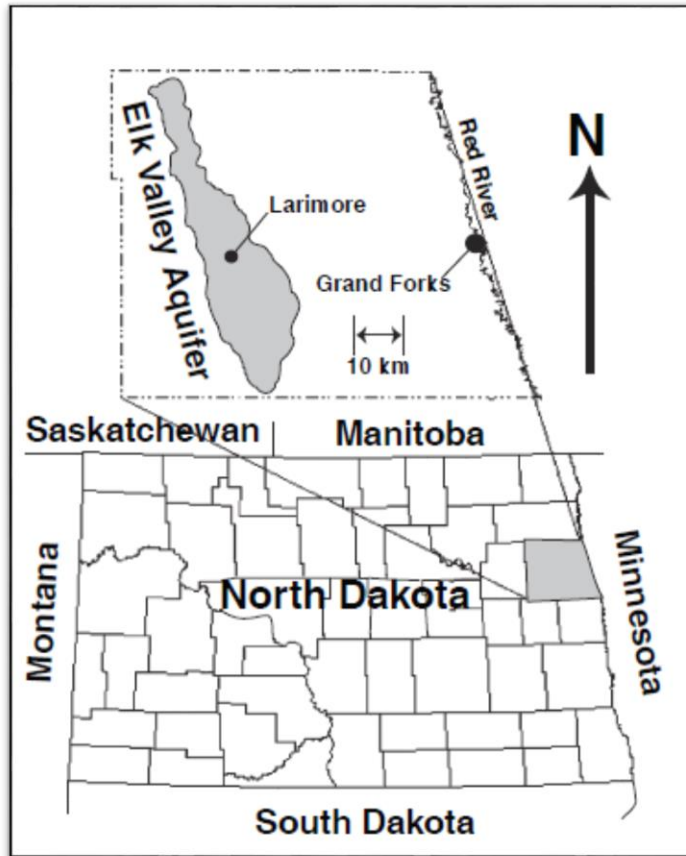


Figure 2. Location of Elk Valley Aquifer.

#### Vulnerability of Elk Valley Aquifer

In 1987 the US Environmental Protection Agency (EPA) developed DRASTIC, a standardized system for evaluating groundwater pollution potential of aquifers in the US. The acronym DRASTIC stands for *d*epth to water, net *r*echarge, *a*quifer media, soil media, *t*opography, *i*mpact of the vadose zone, and hydraulic *c*onductivity. These factors are compiled by rating each parameter and entering it into an equation, resulting in a numerical score (Aller, et al., 1987). Aquifers rated with the same physical parameters could then be compared and ranked. In 1996 the EVA was rated with a DRASTIC score of 167, ranking it the fifth most vulnerable aquifer out of 192 aquifers in the state (Radig, 1997).

In 1997 the ND Department of Health (NDDH) Division of Water Quality developed a system adapted from the EPA's DRASTIC model, known as a Geographic Targeting System (GTS) (Radig, 1997). The GTS not only prioritized aquifers throughout the state according to physical properties with DRASTIC, but also prioritized them according to permitted water use and susceptibility to agricultural chemical contamination per county. Total numerical monitoring scores of the GTS range between 3 and 9, with 9 being the most vulnerable. Figure 3 shows the results of the GTS study, with several aquifers, including EVA, ranked at a score of 9. The combined DRASTIC and GTS scores placed EVA as the first most vulnerable aquifer in the state (Radig, 1997).

Overall, the EVA is classified as one of the most vulnerable aquifers in North Dakota by both national and statewide standards. The most vulnerable aquifers receive the most funding in prevention and monitoring efforts. It is imperative that aquifer rankings are accurate so that funding is properly allocated.

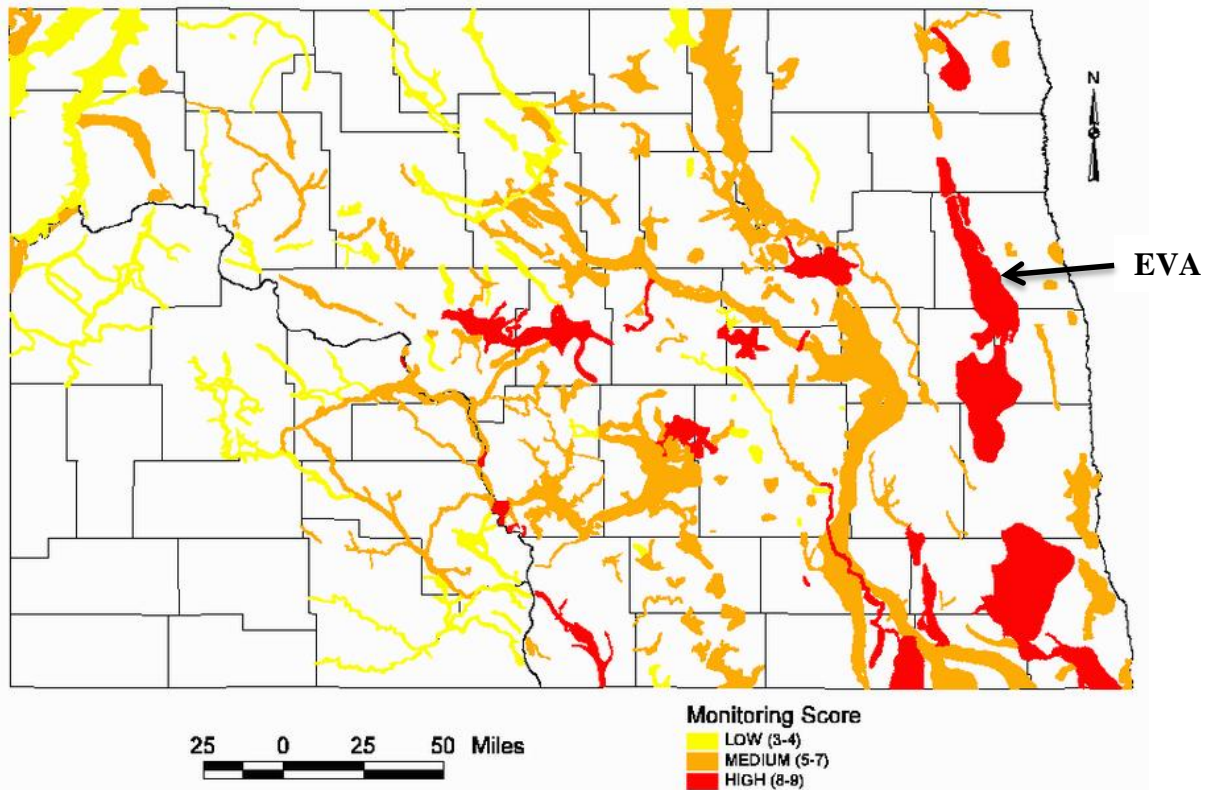


Figure 3. Classification of Aquifer Monitoring Prioritization in ND (Adapted from Radig, 1997).

#### Sampling

Groundwater sampling from the EVA ISM began in October, 1997 with the first tracer test and ended March, 2006 with the last sample of the sixth tracer test. Tracer tests were concluded when the  $\text{NO}_3\text{-N}$  concentrations were approximately less than 5 mg/L.

Groundwater samples were analyzed by both the NDDH laboratory and the Environmental Analytical Research Laboratory (EARL) at UND. Table 1 lists the important ions and species analyzed specifically from which laboratory. Field pH values were measured on-site.

Table 1. Major Species Analyzed by Laboratories.

Species	NDDH	EARL	In Field
Na <sup>+</sup>	X		
Mg <sup>2+</sup>	X		
K <sup>+</sup>	X		
Ca <sup>2+</sup>	X		
Mn <sup>2+</sup>	X		
Fe <sup>2+</sup>	X		
NH <sub>3</sub> -N (NH <sub>4</sub> <sup>+</sup> -N)	X		
F <sup>-</sup>	X		
Cl <sup>-</sup>	X		
HCO <sub>3</sub> <sup>-</sup>	X		
CO <sub>3</sub> <sup>2-</sup>	X		
SO <sub>4</sub> <sup>2-</sup>	X	X	
NO <sub>3</sub> -N	X	X	
Br <sup>-</sup>		X	
SiO <sub>2</sub>	X		
Inorganic C		X	
Organic C		X	
Total C		X	
pH			X*

\*NDDH laboratory pH used when field pH not available.

#### Prior Work

The UND Denitrification Team performed a similar assessment at the Karlsruhe-S ISM, at which two tracer tests were conducted. Those tracer tests indicated that contributions to denitrification from individual electron donors were about 4 – 18% from pyrite, 2 – 43% from non-pyrite Fe(II) in amphiboles, and 43 – 92% from organic carbon, depending on the sample date (Korom et al., 2012). The models showed that denitrification by some non-pyrite Fe(II) was essential to explain the evolution of the groundwater quality parameters observed at the sites in Karlsruhe. That was the first time the distribution of electron donors contributing to aquifer denitrification had ever

been reported. The current EVA study presented in this thesis differs from the Karlsruhe-S study in that it is a much longer study; over eight years at EVA compared to two years at Karlsruhe-S.

Tesoriero and Puckett (2011) reported on denitrification rates in shallow aquifers. Twelve areas across the US were studied by using monitoring well transects located along hypothesized groundwater flow paths. Tracers were utilized to provide an estimate of groundwater age. Air samples were taken downstream when the amended water was calculated to transect the downstream wells. Amounts of  $N_2$  were then calculated to determine the amount derived from denitrification. Their study suggested that denitrification tends to occur more quickly with sulfide oxidation rather than with carbon oxidation (Tesoriero et al., 2011). However, groundwater flow paths tend to cause physical mixing such as eddies as fluid flows around sediment particles. The physical mixing tends to create the appearance of lower reaction rates and fractionation parameters when measured at larger scales and longer flow paths (Green et al., 2010).

## CHAPTER III

### METHODOLOGY

The objective of this research was to study the geochemical evolution of the groundwater in the EVA ISM during each of the six denitrification tracer tests to estimate the contributions of electron donors to the denitrification. Before any determinations were made, the data were verified for analytical quality control. Two laboratories, EARL and NDDH, provided analyses for each sampling event. Duplicate samples provided for better discrepancy evaluation. Appendices A-E list the initial data and show the processes used to determine the final data set.

The next step was to estimate the denitrification rates in each of the six tracer tests. The percent contributions to denitrification by ferrous iron minerals, pyrite ( $\text{FeS}_2$ ), and organic carbon were then estimated.

#### Dilution

The process of pumping  $\text{NO}_3^-$ -amended water back into the ISM chamber caused some dilution with the native groundwater present in the chamber. The  $\text{NO}_3^-$ -amended water was also amended with  $\text{Br}^-$ , which is naturally in the aquifer, but only at low concentrations ( $< 1 \text{ mg/L}$ ). The  $\text{Br}^-$  tracer in the amended water was used to estimate the dilution rate with native groundwater. Loss of  $\text{NO}_3^-$  beyond that explained by dilution of the  $\text{Br}^-$  tracer was attributed to denitrification.

The ratios of the concentration of Br<sup>-</sup> at each sampling event to the concentration of Br<sup>-</sup> at the initial sampling event (day 0) was assumed to be equal to the ratios of the concentration of NO<sub>3</sub><sup>-</sup>N present by the process of dilution at each sampling event to the concentration of NO<sub>3</sub><sup>-</sup>N at the initial sampling event (day 0). The concentration of NO<sub>3</sub><sup>-</sup>N present by the process of dilution (NO<sub>3</sub><sup>-</sup>N by dilution) served as a starting point to estimate how much NO<sub>3</sub><sup>-</sup>N should have been measured had there been no denitrification. The results of Equation 1 are tabulated in Table 2-7.

$$(\text{NO}_3\text{-N by dilution}) = \left( \frac{\text{Br}_{t \neq 0}}{\text{Br}_{t=0}} \right) (\text{NO}_3\text{-N}_{t=0}) \quad (1)$$

#### Denitrification Rates

The concentration of NO<sub>3</sub><sup>-</sup>N attributed to denitrification was calculated by subtracting the concentration of NO<sub>3</sub><sup>-</sup>N measured from the concentration of NO<sub>3</sub><sup>-</sup>N calculated to be present by dilution only. The results of Equation 2, the concentration of NO<sub>3</sub><sup>-</sup>N assumed to have been denitrified, are tabulated in Table 2-7.

$$(\text{NO}_3\text{-N denitrified}) = (\text{NO}_3\text{-N by dilution}) - (\text{NO}_3\text{-N measured}) \quad (2)$$

Denitrification rates were calculated by assuming a linear relationship between sampling events. For each of the six tracer tests, concentrations of NO<sub>3</sub><sup>-</sup>N in mg/L denitrified were plotted versus time in days. The zero-order denitrification rate in mg/L/day was the slope of a linear fit line generated for each tracer test. For all tracer tests in the EVA, zero-order rates provided better fits for the data than first-order rates (Korom, 2005). The zero-order denitrification rate graphs of each tracer test are located in CHAPTER IV.



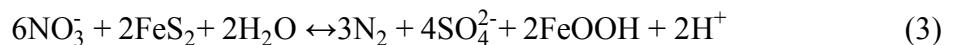
## Denitrification by Ferrous Iron Silicate Minerals

X-ray diffraction (XRD) analyses by Tefsay (2006) showed that the sediments in the EVA and Karlsruhe Aquifer have similarities. Both aquifers are composed of amphiboles, clinochlore, muscovite, biotite, plagioclase, alkali feldspar, quartz, calcite, dolomite, and pyrite. One amphibole identified in both aquifers was hornblende, a double chain silicate. Amphiboles are known to weather relatively slowly, as demonstrated by Bowen's reaction series (Faure, 1998).

It was assumed that hornblende will weather similarly and therefore contribute to denitrification similarly from aquifer to aquifer in ND. Korom et al. (2012) found denitrification by ferrous iron (Fe(II)) in hornblende to be between  $2.2 \times 10^{-5}$  M/year and  $1.3 \times 10^{-4}$  M/year in the Karlsruhe aquifer. The average of those two rates was assumed valid for EVA as well. The average denitrification rate of 0.003 mg/L/day was applied to all tracer tests to estimate the percent contribution by ferrous iron as hornblende.

## Denitrification by Pyrite

Some denitrification was explained by the increase of sulfate, which was attributed to the oxidation of pyrite ( $\text{FeS}_2$ ), the only sulfide mineral found by XRD in the EVA sediments (Tefsay, 2006). As  $\text{NO}_3^-$  is reduced to nitrogen gas, the sulfide in  $\text{FeS}_2$  is oxidized to sulfate, as shown in the redox reaction below (Equation 3). Unlike hornblende, pyrite has the ability to weather rapidly to goethite ( $\text{FeOOH}$ ), which is a well-documented observation during acid mine drainage (Larese-Casanova et al., 2012).



For every 2 moles of  $\text{FeS}_2$  and 6 moles of  $\text{NO}_3^-$  consumed, 4 moles of  $\text{SO}_4^{2-}$  are produced. The ratio of  $\text{SO}_4^{2-}$  produced to  $\text{NO}_3^-$  consumed allows for the estimation of the

increase in  $\text{SO}_4^{2-}$  in the water if all of the denitrification was due to the oxidation of pyrite.

Equation 3 also indicates potential Fe(II) contributions of one fifteenth of the denitrification by pyrite. No increase in Fe(II) was demonstrated in the groundwater samples during the tracer tests (Tables 46-51), indicating that the Fe(II) in pyrite had apparently been consumed. The apparent disappearance of Fe(II) from pyrite was also attributed to denitrification by pyrite.

The maximum increase of  $\text{SO}_4^{2-}$  ( $\max \Delta \text{SO}_4^{2-}$ ) by total denitrification with pyrite was calculated for each sampling event with Equation 4, where concentrations are in mg/L and molecular weights (MWs) are in g/mol. The results of Equation 4 are tabulated in Tables 14-19.

$$(\max \Delta \text{SO}_4^{2-}) = \frac{(\text{NO}_3\text{-N denitrified})}{\text{MW of NO}_3\text{-N}} * \frac{4 \text{ mol SO}_4^{2-}}{6 \text{ mol NO}_3^-} * \text{MW of SO}_4^{2-} \quad (4)$$

The fraction of  $\max \Delta \text{SO}_4^{2-}$  measured in a water sample was found using Equation 5. This was calculated for each sampling event subsequent to the initial one (Day 0) and is the estimate of denitrification by pyrite for each sampling event. The results of Equation 5 are tabulated in Tables 14-19.

$$\text{fraction of } \max \Delta \text{SO}_4^{2-} = \frac{(\text{SO}_4^{2-}{}_{t \neq 0} - \text{SO}_4^{2-}{}_{t=0})}{(\max \Delta \text{SO}_4^{2-})} \quad (5)$$

The average fraction of denitrification by  $\text{FeS}_2$  weighted by time was also calculated for each tracer test. The change in time was in days since the previous sample. The results of the Equation 6 are listed in Tables 14-19.

$$\text{average fraction of denitrification by FeS}_2 = \frac{\sum \text{fraction of } \max \Delta \text{SO}_4^{2-} * \Delta t}{t_{\text{total}}} \quad (6)$$

## Denitrification by Organic Carbon

The remainder of the denitrification not attributed to the oxidation of ferrous iron in amphibole or the oxidation of pyrite was attributed to organic carbon (OC). This assumption was made on the basis that the three major electron donors in aquifer denitrification are: OC, inorganic sulfide ( $\text{FeS}_2$ ), and ferrous iron (Korom, 1992).

CHAPTER IV  
RESULTS AND DISCUSSION

Denitrification Rates

The results of Equations 1 and 2 and were used to estimate the denitrification rates of each tracer test (Tables 2-7).

Table 2. Tracer Test 1 Denitrification Calculations.

Date	$\Delta$ time (days)	Br <sup>-</sup> (mg/L)	NO <sub>3</sub> -N Measured (mg/L)	NO <sub>3</sub> -N Dilution (mg/L)	NO <sub>3</sub> -N Denitrified (mg/L)
12/1/1997	0	76.4	135.2	135.20	0.00
12/27/1997	26	68.0	116.7	120.34	3.64
1/30/1998	60	62.1	106.6	109.89	3.29
2/27/1998	88	65.8	103.7	116.44	12.74
3/27/1998	116	44.5	69.4	78.75	9.35
4/30/1998	150	44.6	53.5	78.93	25.43
5/26/1998	176	40.0	36.3	70.79	34.49
6/23/1998	204	37.3	19.4	66.01	46.61
8/4/1998	246	32.1	6.4*	56.81	50.41
8/30/1998	272	33.1	0.81*	58.57	57.76

\* NDDH value.

Table 3. Tracer Test 2 Denitrification Calculations.

Date	$\Delta$ time (days)	Br <sup>-</sup> (mg/L)	NO <sub>3</sub> -N Measured (mg/L)	NO <sub>3</sub> -N Dilution (mg/L)	NO <sub>3</sub> -N Denitrified (mg/L)
10/27/1998	0	110.9	105.5	105.50	0.00
12/1/1998	34	111.0	100.6	105.60	5.00
1/16/1999	79	110.9	95.3	105.50	10.20
2/15/1999	108	110.3	89.3	104.93	15.63

Table 3. cont.

Date	$\Delta$ time (days)	Br <sup>-</sup> (mg/L)	NO <sub>3</sub> -N Measured (mg/L)	NO <sub>3</sub> -N Dilution (mg/L)	NO <sub>3</sub> -N Denitrified (mg/L)
3/12/1999	135	108.9	78.3	103.60	25.30
4/17/1999	170	95.7	70.6	91.04	20.44
5/25/1999	208	94.6	62.3	89.99	27.69
6/23/1999	236	83.5	50.0	79.43	29.43
7/20/1999	263	73.4	33.8	69.83	36.03
8/17/1999	290	63.5	23.2	60.41	37.21
10/26/1999	359	50.3	7.77	47.85	40.08
11/30/1999	393	47.9	1.86*	45.57	43.71
2/19/2000	472	39.0	0.02*	37.10	37.08
6/7/2000	580	33.1	0.02*	31.49	31.47

\*NDDH value

Table 4. Tracer Test 3 Denitrification Calculations.

Date	$\Delta$ time (days)	Br <sup>-</sup> (mg/L)	NO <sub>3</sub> -N Measured (mg/L)	NO <sub>3</sub> -N Dilution (mg/L)	NO <sub>3</sub> -N Denitrified (mg/L)
9/4/2000	0	66.8	109.0	109.0	0.0
10/2/2000	28	59.1	86.5*	96.4	9.9
11/15/2000	71	59.9	81.0	97.7	16.7
1/9/2001	125	66.2	69.5	108.0	38.5
3/22/2001	198	56.7	47.8	92.5	44.7
4/26/2001	232	55.9	37.0*	91.2	52.6
6/11/2001	277	52.6	25.0	85.7	60.7
7/31/2001	327	47.9	10.2	78.2	68.0
8/29/2001	355	40.9	2.83*	66.7	63.9

\*NDDH value

Table 5. Tracer Test 4 Denitrification Calculations.

Date	$\Delta$ time (days)	Br <sup>-</sup> (mg/L)	NO <sub>3</sub> -N Measured (mg/L)	NO <sub>3</sub> -N Dilution (mg/L)	NO <sub>3</sub> -N Denitrified (mg/L)
10/8/2001	0	58.4	95.615	95.62	0.00
11/20/2001	42	54.1	87.2	88.65	1.45
12/18/2001	70	54.3	81.8	88.98	7.18

Table 5. cont.

Date	$\Delta$ time (days)	Br <sup>-</sup> (mg/L)	NO <sub>3</sub> -N Measured (mg/L)	NO <sub>3</sub> -N Dilution (mg/L)	NO <sub>3</sub> -N Denitrified (mg/L)
2/5/2002	117	54.5	66.0	89.31	23.31
3/19/2002	161	53.2	53.4	87.18	33.78
5/14/2002	216	53.4	44.25	87.50	43.25
6/25/2002	257	52.1	30.7	85.37	54.67
8/14/2002	306	49.6	20.3	81.28	60.98
9/26/2002	348	47.1	11.3	77.18	65.88
10/21/2002	373	43.7	4.74*	71.61	66.87

\*NDDH value

Table 6. Tracer Test 5 Denitrification Calculations.

Date	$\Delta$ time (days)	Br <sup>-</sup> (mg/L)	NO <sub>3</sub> -N Measured (mg/L)	NO <sub>3</sub> -N Dilution (mg/L)	NO <sub>3</sub> -N Denitrified (mg/L)
11/13/2002	0	61.8	101	101.00	0.00
1/7/2003	54	63.6	94.6	103.94	9.34
3/12/2003	119	62.3	80.8	101.82	21.02
5/3/2003	170	62.9	72.8	102.80	30.00
7/15/2003	242	56.9	54.6	92.99	38.39
8/25/2003	282	60.8	46.0	99.37	53.37
10/20/2003	337	53.5	33.7	87.44	53.74
12/22/2003	399	51.2	20.3	83.68	63.38
2/18/2004	455	40.0	5.31	65.37	60.06
3/23/2004	490	34.2	0.58*	55.89	55.31

\*NDDH value

Table 7. Tracer Test 6 Denitrification Calculations.

Date	$\Delta$ time (days)	Br <sup>-</sup> (mg/L)	NO <sub>3</sub> -N Measured (mg/L)	NO <sub>3</sub> -N Dilution (mg/L)	NO <sub>3</sub> -N Denitrified (mg/L)
6/14/2004	0	75.55	107	107.00	0.00
7/19/2004	35	71.6	99.9	101.41	1.51
9/13/2004	91	72.7	97.3	102.89	5.59
10/26/2004	134	77.7	94.7	110.05	15.35
12/6/2004	175	69.1	79.0	97.83	18.83
2/3/2005	234	72.8	69.2	103.12	33.91

Table 7. cont.

Date	$\Delta$ time (days)	Br <sup>-</sup> (mg/L)	NO <sub>3</sub> -N Measured (mg/L)	NO <sub>3</sub> -N Dilution (mg/L)	NO <sub>3</sub> -N Denitrified (mg/L)
4/12/2005	302	62.8	54.5	88.87	34.37
6/14/2005	365	62.5	48.4	88.53	40.10
9/22/2005	465	49.8	27.7	70.57	42.83

\*NDDH value

Denitrification amounts from Tables 2-7 were plotted versus time to establish the denitrification rates of each tracer test (Figures 4-9). A linear trend was generated for each graph. In the upper right hand corner of each graph is the equation of the line with the slope representing the denitrification rate (mg/L/day) and the coefficient of determination,  $R^2$ .  $R^2$  values range between 0 and 1.0, with 1.0 representing a perfectly linear fit. Therefore, the closer the  $R^2$  value is to 1.0, the better the fit to the reported denitrification rate. All  $R^2$  values in Figures 4-9 were  $\geq 0.90$ .

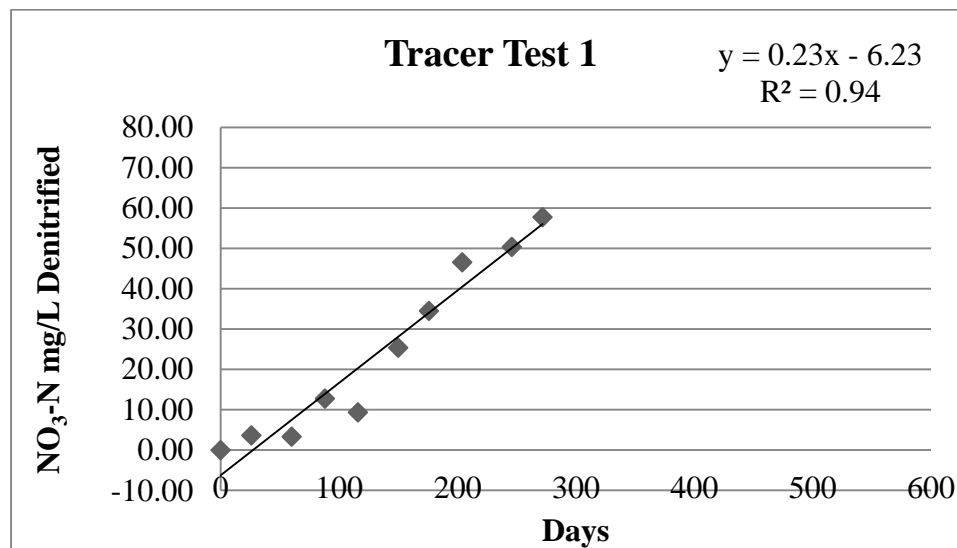


Figure 4. Tracer Test 1 Denitrification Rate.

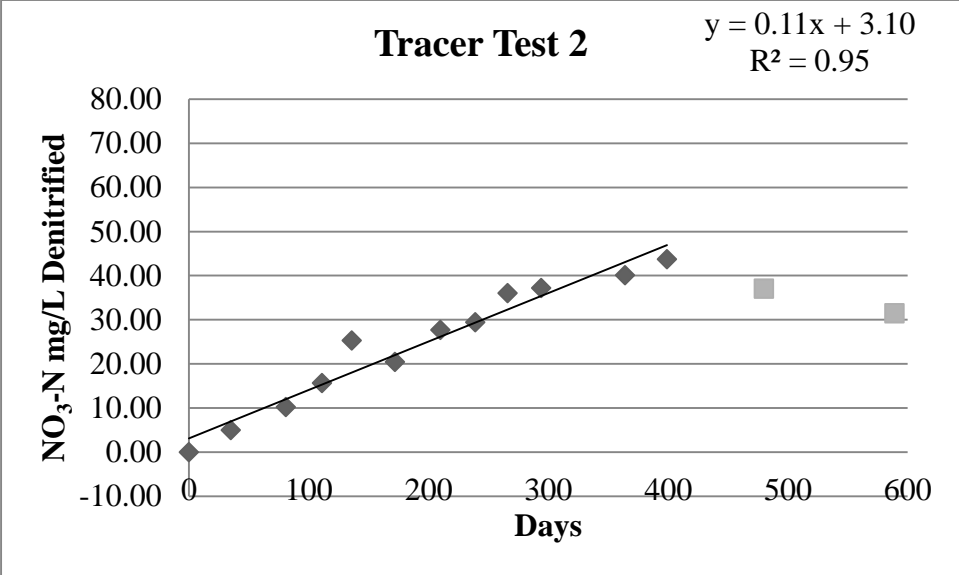


Figure 5. Tracer Test 2 Denitrification Rate.

The two gray squares in Figure 5 represent data with very low NO<sub>3</sub>-N concentrations (0.02 mg/L). Detectable denitrification had ceased at that point, and therefore those points were not included in the denitrification rate determination.

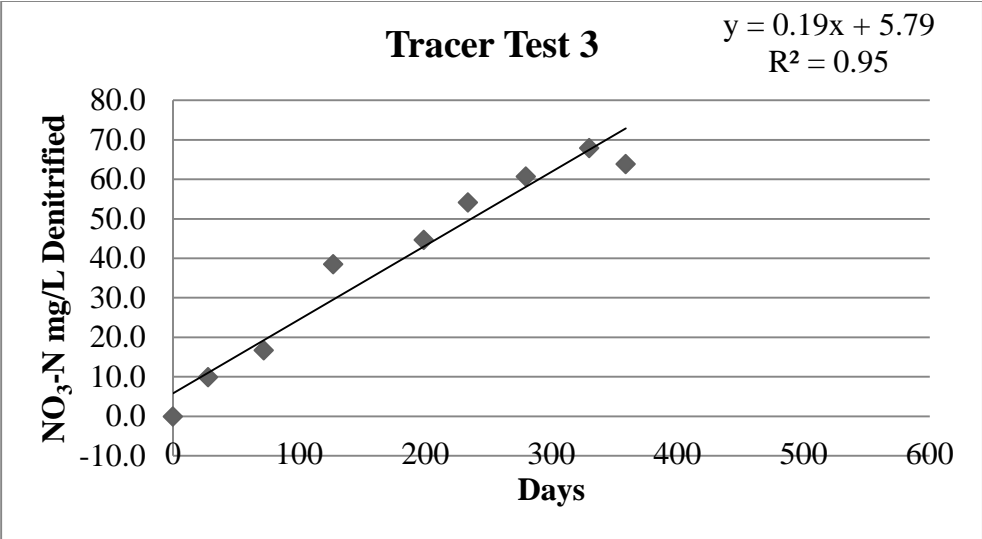


Figure 6. Tracer Test 3 Denitrification Rate.



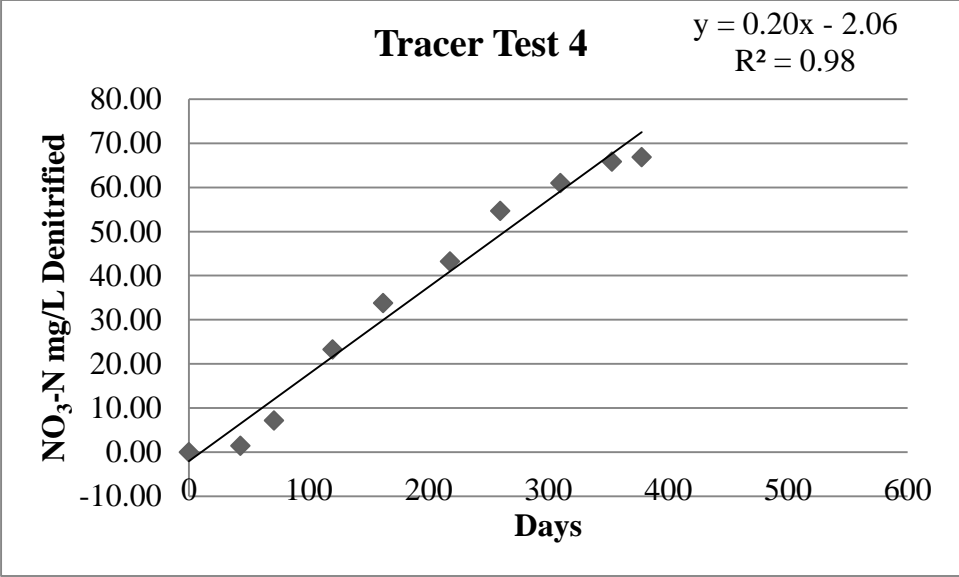


Figure 7. Tracer Test 4 Denitrification Rate.

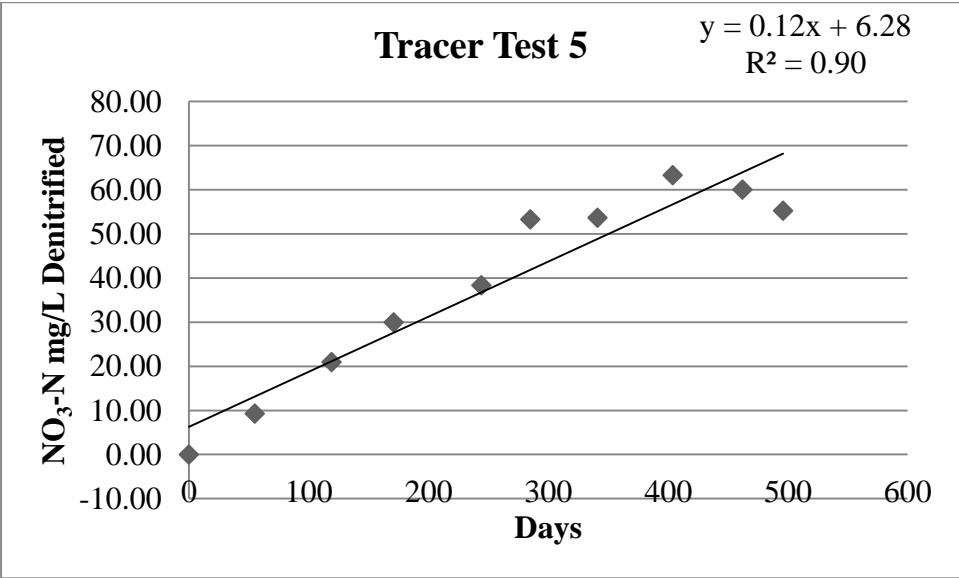


Figure 8. Tracer Test 5 Denitrification Rate.

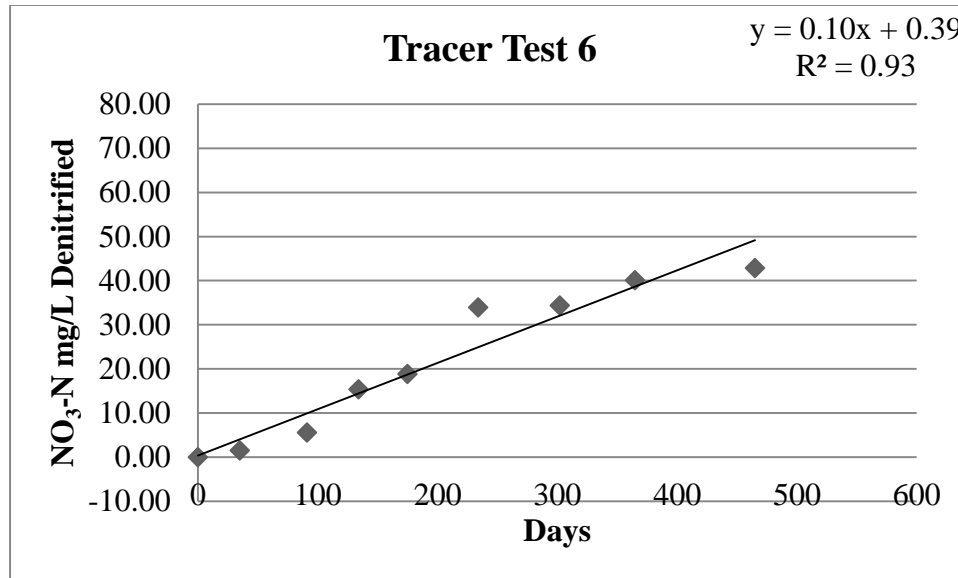


Figure 9. Tracer Test 6 Denitrification Rate.

Average denitrification rates in the EVA ranged from 0.10 to 0.23 mg/L/day for all six tracer tests (Table 8).

Table 8. Denitrification Rates of Elk Valley Aquifer.

Tracer Test	Denitrification Rate (mg/L/day)	Denitrification Rate (mg/L/year)
1	0.23	84.0
2	0.11	40.2
3	0.19	69.4
4	0.20	73.0
5	0.12	43.8
6	0.10	36.5

#### Contribution by Ferrous Iron Silicate Minerals

As previously stated, the EVA ISM is assumed to have the same ferrous iron denitrification rates from amphibole as hornblende as the Karlsruhe-S ISM. The rate of 0.003 mg/L/day was applied to all tracer tests to estimate the percent contribution by ferrous iron silicates (Tables 9-14).

Table 9. Tracer Test 1 Contribution from Fe(II) Silicate Minerals.

Date	$\Delta$ time days	NO <sub>3</sub> -N mg/L Measured	Denitrification by Fe(II) Minerals (mg/L)	Fraction Contribution by Fe(II) Minerals
12/1/1997	0	135.2	0.00	0.00
12/27/1997	26	116.7	0.08	0.02
1/30/1998	60	106.6	0.18	0.05
2/27/1998	88	103.7	0.26	0.02
3/27/1998	116	69.4	0.35	0.04
4/30/1998	150	53.5	0.45	0.02
5/26/1998	176	36.3	0.53	0.02
6/23/1998	204	19.4	0.61	0.01
8/4/1998	246	6.4	0.74	0.01
8/30/1998	272	0.81	0.82	0.01

Average fraction contribution to denitrification weighted by time by Fe(II) silicate minerals = 0.02.

Table 10. Tracer Test 2 Contribution from Fe(II) Silicate Minerals.

Date	$\Delta$ time days	NO <sub>3</sub> -N mg/L Measured	Denitrification by Fe(II) Minerals mg/L	Fraction Contribution by Fe(II) Minerals
10/27/1998	0	105.5	0.00	0.00
12/1/1998	34	100.6	0.11	0.02
1/16/1999	79	95.3	0.24	0.02
2/15/1999	108	89.3	0.33	0.02
3/12/1999	135	78.3	0.41	0.02
4/17/1999	170	70.6	0.52	0.03
5/25/1999	208	62.3	0.63	0.02
6/23/1999	236	50.0	0.72	0.02
7/20/1999	263	33.8	0.80	0.02
8/17/1999	290	23.2	0.88	0.02
10/26/1999	359	7.77	1.09	0.03
11/30/1999	393	1.86	1.20	0.03
2/19/2000	472	0.02	1.44	0.04
6/7/2000	580	0.02	1.77	0.06

Average fraction contribution to denitrification weighted by time by Fe(II) silicate minerals = 0.03.

Table 11. Tracer Test 3 Contribution from Fe(II) Silicate Minerals.

Date	$\Delta$ time days	NO <sub>3</sub> -N mg/L Measured	Denitrification by Fe(II) Minerals mg/L	Fraction Contribution by Fe(II) Minerals
9/4/2000	0	109.0	0.00	0.00
10/2/2000	28	86.5	0.08	0.01
11/15/2000	71	81.0	0.22	0.01
1/9/2001	125	69.5	0.38	0.01
3/22/2001	198	47.8	0.60	0.01
4/26/2001	232	37.0	0.70	0.01
6/11/2001	277	25.0	0.84	0.01
7/31/2001	327	10.2	0.99	0.01
8/29/2001	355	2.83	1.08	0.02

Average fraction contribution to denitrification weighted by time by Fe(II) silicate minerals = 0.01.

Table 12. Tracer Test 4 Contribution from Fe(II) Silicate Minerals.

Date	$\Delta$ time days	NO <sub>3</sub> -N mg/L Measured	NO <sub>3</sub> -N mg/L Denitrified	Denitrification by Fe(II) Minerals mg/L	Fraction Contribution by Fe(II) Minerals
10/8/2001	0	95.615	0.00	0.00	0.00
11/20/2001	42	87.2	1.45	0.13	0.09
12/18/2001	70	81.8	7.18	0.21	0.03
2/5/2002	117	66.0	23.31	0.36	0.02
3/19/2002	161	53.4	33.78	0.49	0.01
5/14/2002	216	44.25	43.25	0.65	0.02
6/25/2002	257	30.7	54.67	0.78	0.01
8/14/2002	306	20.3	60.98	0.93	0.02
9/26/2002	348	11.3	65.88	1.06	0.02
10/21/2002	373	4.74	66.87	1.13	0.02

Average fraction contribution to denitrification weighted by time by Fe(II) silicate minerals = 0.02.

Table 13. Tracer Test 5 Contribution from Fe(II) Silicate Minerals.

Date	$\Delta$ time days	NO <sub>3</sub> -N mg/L Measured	NO <sub>3</sub> -N mg/L Denitrified	Denitrification by Fe(II) Minerals mg/L	Fraction Contribution by Fe(II) Minerals
11/13/2002	0	101	0.00	0.00	0.00
1/7/2003	54	94.6	9.34	0.17	0.02
3/12/2003	119	80.8	21.02	0.36	0.02
5/3/2003	170	72.8	30.00	0.51	0.02
7/15/2003	242	54.6	38.39	0.73	0.02
8/25/2003	282	46.0	53.37	0.86	0.02
10/20/2003	337	33.7	53.74	1.02	0.02
12/22/2003	399	20.3	63.38	1.21	0.02
2/18/2004	455	5.31	60.06	1.39	0.02
3/23/2004	490	0.58	55.31	1.49	0.03

Average fraction contribution to denitrification weighted by time by Fe(II) silicate minerals = 0.02.

Table 14. Tracer Test 6 Contribution from Fe(II) Silicate Minerals.

Date	$\Delta$ time days	NO <sub>3</sub> -N mg/L Measured	NO <sub>3</sub> -N mg/L Denitrified	Denitrification by Fe(II) Minerals mg/L	Fraction Contribution by Fe(II) Minerals
6/14/2004	0	107	0.00	0.00	0.00
7/19/2004	35	99.9	1.51	0.11	0.07
9/13/2004	91	97.3	5.59	0.27	0.05
10/26/2004	134	94.7	15.35	0.40	0.03
12/6/2004	175	79.0	18.83	0.53	0.03
2/3/2005	234	69.2	33.91	0.70	0.02
4/12/2005	302	54.5	34.37	0.91	0.03
6/14/2005	365	48.4	40.10	1.10	0.03
9/22/2005	465	27.7	42.83	1.40	0.03

Average fraction contribution to denitrification weighted by time by Fe(II) silicate minerals = 0.03.

The contributions to denitrification weighted by time from ferrous iron as hornblende varied from 1 to 3% at the EVA ISM.

### Contribution by Pyrite

The fraction of denitrification by pyrite was estimated by the increase of  $\text{SO}_4^{2-}$ .

Tables 15-20 tabulate the results of Equations 4-6. The weighted averages of the fraction of increase of  $\text{SO}_4^{2-}$  by  $\text{FeS}_2$  are listed at the bottom of the tables. That value is the average fraction  $\text{FeS}_2$  contributed to denitrification for each tracer test.

Table 15. Tracer Test 1 Contribution from Pyrite.

Date	$\Delta$ time (days)	$\text{SO}_4^{2-}$ mg/L Measured	Max $\Delta$ $\text{SO}_4^{2-}$	Fraction of Max $\Delta$ $\text{SO}_4^{2-}$	Fraction of Max $\Delta$ $\text{SO}_4^{2-}$ * $\Delta$ t
12/1/1997	0	64.6	0.00		
12/27/1997	26	66.7	16.62	0.13	3.29
1/30/1998	60	70.0	15.06	0.36	12.19
2/27/1998	88	83.2	58.26	0.32	8.94
3/27/1998	116	99.5	42.74	0.82	22.86
4/30/1998	150	124.9	116.25	0.52	17.64
5/26/1998	176	154.0	157.68	0.57	14.74
6/23/1998	204	190.5	213.10	0.59	16.54
8/4/1998	246	202.6	230.47	0.60	25.15
8/30/1998	272	227.7	264.12	0.62	16.06

Weighted average fraction of denitrification by  $\text{FeS}_2 = 0.51$ .

Table 16. Tracer Test 2 Contribution from Pyrite.

Date	$\Delta$ time (days)	$\text{SO}_4^{2-}$ mg/L Measured	Max $\Delta$ $\text{SO}_4^{2-}$	Fraction of Max $\Delta$ $\text{SO}_4^{2-}$	Fraction of Max $\Delta$ $\text{SO}_4^{2-}$ * $\Delta$ t
10/27/1998	0	59.30	0.00		
12/1/1998	34	65.30	22.84	0.26	9.19
1/16/1999	79	81.60	46.64	0.48	22.00
2/15/1999	108	79.10	71.46	0.28	8.31
3/12/1999	135	88.80	115.67	0.26	6.38
4/17/1999	170	91.30	93.46	0.34	12.33
5/25/1999	208	89.60	126.62	0.24	9.09
6/23/1999	236	107.50	134.58	0.36	10.39
7/20/1999	263	127.80	164.72	0.42	11.23
8/17/1999	290	134.50	170.12	0.44	12.38

Table 16. cont.

Date	$\Delta$ time (days)	SO <sub>4</sub> <sup>2-</sup> mg/L Measured	Max $\Delta$ SO <sub>4</sub> <sup>2-</sup>	Fraction of Max $\Delta$ SO <sub>4</sub> <sup>2-</sup>	Fraction of Max $\Delta$ SO <sub>4</sub> <sup>2-</sup> * $\Delta$ t
10/26/1999	359	146.00	183.26	0.47	33.12
11/30/1999	393	156.40	199.84	0.49	17.01
2/19/2000	472	158.20	169.54	0.58	47.25
6/7/2000	580	133.10	143.88	0.51	55.91

Weighted average fraction of denitrification by FeS<sub>2</sub> = 0.38.

Table 17. Tracer Test 3 Contribution from Pyrite.

Date	$\Delta$ time (days)	SO <sub>4</sub> <sup>2-</sup> mg/L Measured	Max $\Delta$ SO <sub>4</sub> <sup>2-</sup>	Fraction of Max $\Delta$ SO <sub>4</sub> <sup>2-</sup>	Fraction of Max $\Delta$ SO <sub>4</sub> <sup>2-</sup> * $\Delta$ t
9/4/2000	0	40.2	0.00		
10/2/2000	28	49.0	45.43	0.19	5.42
11/15/2000	71	80.1	76.54	0.52	22.94
1/9/2001	125	130	176.13	0.51	28.04
3/22/2001	198	186	204.47	0.71	51.34
4/26/2001	232	212	247.88	0.69	24.26
6/11/2001	277	240	277.75	0.72	33.09
7/31/2001	327	256	310.73	0.69	34.72
8/29/2001	355	259	292.20	0.75	21.71

Weighted average fraction of denitrification by FeS<sub>2</sub> = 0.62.

Table 18. Tracer Test 4 Contribution from Pyrite.

Date	$\Delta$ time (days)	SO <sub>4</sub> <sup>2-</sup> mg/L Measured	Max $\Delta$ SO <sub>4</sub> <sup>2-</sup>	Fraction of Max $\Delta$ SO <sub>4</sub> <sup>2-</sup>	Fraction of Max $\Delta$ SO <sub>4</sub> <sup>2-</sup> * $\Delta$ t
10/8/2001	0	42.05	0.00		
11/20/2001	42	71.3	6.63	4.41*	189.61*
12/18/2001	70	99	32.82	1.74*	48.58*
2/5/2002	117	136.5	106.56	0.89	106.36
3/19/2002	161	176	154.43	0.87	36.43
5/14/2002	216	215	197.77	0.87	48.97
6/25/2002	257	236.1	249.98	0.78	32.60
8/14/2002	306	260	278.80	0.78	39.09
9/26/2002	348	276	301.22	0.78	33.40
10/21/2002	373	297	305.74	0.83	20.85

\*Unrealistic. Weighted average fraction of denitrification by FeS<sub>2</sub> = 0.84.

Fractions of max increase of  $\text{SO}_4^{2-}$  greater than 1.00 are apparent errors. The two sampling events from Tracer Test 4 with unrealistic values were not included in the weighted average fraction calculation.

Table 19. Tracer Test 5 Contribution from Pyrite.

Date	$\Delta$ time (days)	$\text{SO}_4^{2-}$ mg/L Measured	Max $\Delta$ $\text{SO}_4^{2-}$	Fraction of Max $\Delta$ $\text{SO}_4^{2-}$	Fraction of Max $\Delta$ $\text{SO}_4^{2-}$ * $\Delta$ t
11/13/2002	0	64.6	0.00		
1/7/2003	54	104	42.71	0.92	50.73
3/12/2003	119	148.5	96.10	0.87	55.88
5/3/2003	170	191	137.16	0.92	47.92
7/15/2003	242	195	175.54	0.74	54.23
8/25/2003	282	232	244.00	0.69	28.13
10/20/2003	337	252	245.69	0.76	42.71
12/22/2003	399	297	289.77	0.80	50.53
2/18/2004	455	291	274.62	0.82	47.82
3/23/2004	490	265	252.91	0.79	26.94

Weighted average fraction of denitrification by  $\text{FeS}_2 = 0.82$ .

Table 20. Tracer Test 6 Contribution from Pyrite.

Date	$\Delta$ time (days)	$\text{SO}_4^{2-}$ mg/L Measured	Max $\Delta$ $\text{SO}_4^{2-}$	Fraction of Max $\Delta$ $\text{SO}_4^{2-}$	Fraction of Max $\Delta$ $\text{SO}_4^{2-}$ * $\Delta$ t
6/14/2004	0	62.7	0.00		
7/19/2004	35	69.6	6.88	1.00	35.08
9/13/2004	91	88.1	25.57	0.99	55.62
10/26/2004	134	112	70.16	0.70	30.21
12/6/2004	175	121	86.09	0.67	27.64
2/3/2005	234	148	155.07	0.55	32.61
4/12/2005	302	164	157.16	0.64	43.83
6/14/2005	365	190	183.36	0.70	43.85
9/22/2005	465	187	195.84	0.63	63.21

Weighted average fraction of denitrification by  $\text{FeS}_2 = 0.71$ .



The average contributions to denitrification from pyrite varied from 38 to 84% at the Elk Valley Aquifer ISM. The average denitrification rates from each tracer test were plotted with the average percent contribution of pyrite to denitrification in Figure 10.

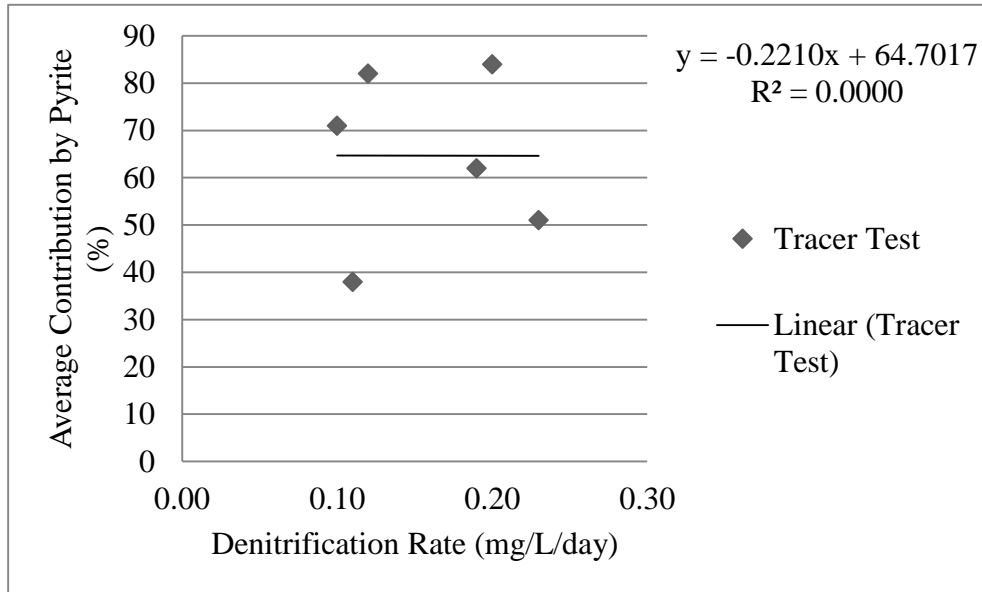


Figure 10. Pyrite Contribution and Denitrification Rate.

One hypothesis suggests that denitrification rates increase with the increase of denitrification by  $S^-$  (Tesoriero et al., 2011; references therein). Denitrification did not increase as contribution from pyrite increases in the EVA ISM, as indicated by the  $R^2$  value of essentially zero. Pyrite nonetheless contributed significantly to denitrification in the EVA, up to 84% as indicated in Tracer Test 4. Schuh et al. (2006) determined that with the current loading rate of  $NO_3^-$  in the EVA there is sufficient pyrite to support lithotrophic denitrification for 11,000 to 175,000 years depending on specific location.

#### Contribution by Organic Carbon

The remainder of  $NO_3^-$ -N denitrified not by ferrous iron silicate minerals or by pyrite was assumed to be by OC. The contributions of OC to denitrification were

tabulated in Tables 21-26 along with the contributions from pyrite and ferrous iron as hornblende.

Table 21. Tracer Test 1 Estimated Contributions from Electron Donors.

Date	$\Delta$ time (days)	Fraction Contribution by FeS <sub>2</sub>	Fraction Contribution by Fe(II) Minerals	Fraction Contribution by OC
12/1/1997	0			
12/27/1997	26	0.13	0.02	0.85
1/30/1998	60	0.36	0.05	0.59
2/27/1998	88	0.32	0.02	0.66
3/27/1998	116	0.82	0.04	0.15
4/30/1998	150	0.52	0.02	0.46
5/26/1998	176	0.57	0.02	0.42
6/23/1998	204	0.59	0.01	0.40
8/4/1998	246	0.60	0.01	0.39
8/30/1998	272	0.62	0.01	0.37

Table 22. Tracer Test 2 Estimated Contributions from Electron Donors.

Date	$\Delta$ time (days)	Fraction Contribution by FeS <sub>2</sub>	Fraction Contribution by Fe(II) Minerals	Fraction Contribution by OC
10/27/1998	0			
12/1/1998	34	0.26	0.02	0.72
1/16/1999	79	0.48	0.02	0.50
2/15/1999	108	0.28	0.02	0.70
3/12/1999	135	0.26	0.02	0.73
4/17/1999	170	0.34	0.03	0.63
5/25/1999	208	0.24	0.02	0.74
6/23/1999	236	0.36	0.02	0.62
7/20/1999	263	0.42	0.02	0.56
8/17/1999	290	0.44	0.02	0.53
10/26/1999	359	0.47	0.03	0.50
11/30/1999	393	0.49	0.03	0.49
2/19/2000	472	0.58	0.04	0.38
6/7/2000	580	0.51	0.06	0.43

Table 23. Tracer Test 3 Estimated Contributions from Electron Donors.

Date	$\Delta$ time (days)	Fraction Contribution by FeS <sub>2</sub>	Fraction Contribution by Fe(II) Minerals	Fraction Contribution by OC
9/4/2000	0			
10/2/2000	28	0.19	0.01	0.80
11/15/2000	71	0.52	0.01	0.47
1/9/2001	125	0.51	0.01	0.48
3/22/2001	198	0.71	0.01	0.27
4/26/2001	232	0.69	0.01	0.29
6/11/2001	277	0.72	0.01	0.27
7/31/2001	327	0.69	0.01	0.29
8/29/2001	355	0.75	0.02	0.23

Table 24. Tracer Test 4 Estimated Contributions from Electron Donors.

Date	$\Delta$ time (days)	Fraction Contribution by FeS <sub>2</sub>	Fraction Contribution by Fe(II) Minerals	Fraction Contribution by OC
10/8/2001	0			
11/20/2001	42	4.41*	0.09	-3.50*
12/18/2001	70	1.74*	0.03	-0.77*
2/5/2002	117	0.89	0.02	0.10
3/19/2002	161	0.87	0.01	0.12
5/14/2002	216	0.87	0.02	0.11
6/25/2002	257	0.78	0.01	0.21
8/14/2002	306	0.78	0.02	0.20
9/26/2002	348	0.78	0.02	0.21
10/21/2002	373	0.83	0.02	0.15

\*Unrealistic.

Negative fractional values and fractional values greater than 1.00 are unrealistic.

The two sampling events from Tracer Test 4 with negative contributions attributed by OC were not included in average contribution calculations.

Table 25. Tracer Test 5 Estimated Contributions from Electron Donors.

Date	$\Delta$ time (days)	Fraction Contribution by FeS <sub>2</sub>	Fraction Contribution by Fe(II) Minerals	Fraction Contribution by OC
11/13/2002	0			
1/7/2003	54	0.92	0.02	0.06
3/12/2003	119	0.87	0.02	0.11
5/3/2003	170	0.92	0.02	0.06
7/15/2003	242	0.74	0.02	0.24
8/25/2003	282	0.69	0.02	0.30
10/20/2003	337	0.76	0.02	0.22
12/22/2003	399	0.80	0.02	0.18
2/18/2004	455	0.82	0.02	0.15
3/23/2004	490	0.79	0.03	0.18

Table 26. Tracer Test 6 Estimated Contributions from Electron Donors.

Date	$\Delta$ time (days)	Fraction Contribution by FeS <sub>2</sub>	Fraction Contribution by Fe(II) Minerals	Fraction Contribution by OC
6/14/2004	0			
7/19/2004	35	1.00	0.07	-0.07*
9/13/2004	91	0.99	0.05	-0.04*
10/26/2004	134	0.70	0.03	0.27
12/6/2004	175	0.67	0.03	0.30
2/3/2005	234	0.55	0.02	0.43
4/12/2005	302	0.64	0.03	0.33
6/14/2005	365	0.70	0.03	0.28
9/22/2005	465	0.63	0.03	0.34

\*Inaccurate.

Negative fractional values are unrealistic. The two sampling events from tracer test 6 with negative contributions attributed by OC were not included in average contribution calculations.

A summary of the average contributions by pyrite, ferrous iron silicate minerals, and OC from test to test is in Table 27 and plotted in Figure 12.

Table 27. Average Contributions to Denitrification Weighted by Time.

Tracer Test	FeS <sub>2</sub>	Fe(II) Minerals	OC	Total
1	0.51	0.02	0.47	1.00
2	0.38	0.03	0.59	1.00
3	0.62	0.01	0.37	1.00
4	0.84	0.02	0.14	1.00
5	0.82	0.02	0.16	1.00
6	0.71	0.03	0.26	1.00

A plot of the OC contributions to denitrification rates (Figure 11) was utilized to identify possible trends from test to test. The low R<sup>2</sup> value signifies that there was no correlation between denitrification rates and OC contributions.

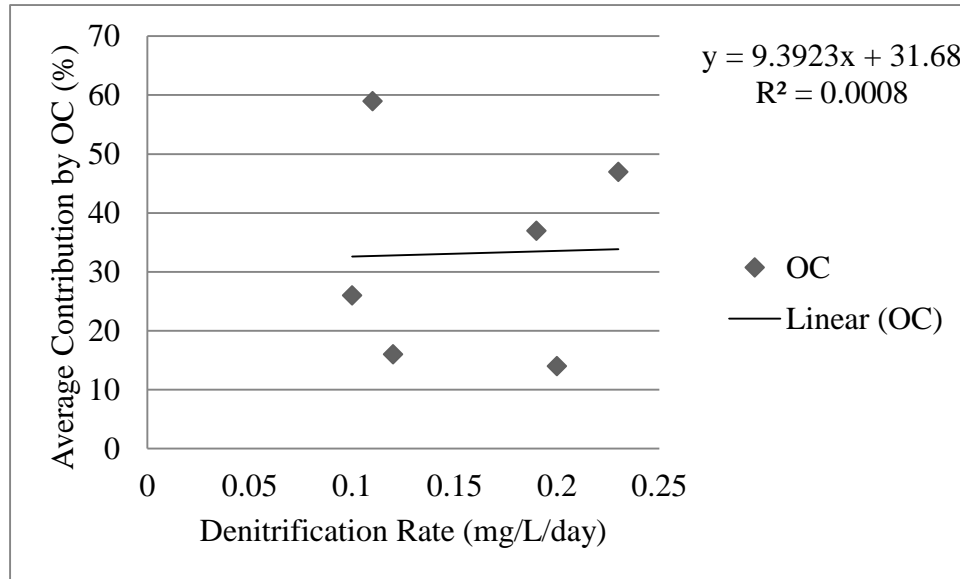


Figure 11. OC Contribution and Denitrification Rate.

The results in Figures 10 and 11 show that there is no correlation between the amount of denitrification contributed by the two largest electron donors (pyrite and OC) to denitrification rates, respectively, at the Elk Valley ISM. The data in Table 27 (shown

on Figure 12) show that the contributions of electron donors at the site were variable, with no apparent pattern.

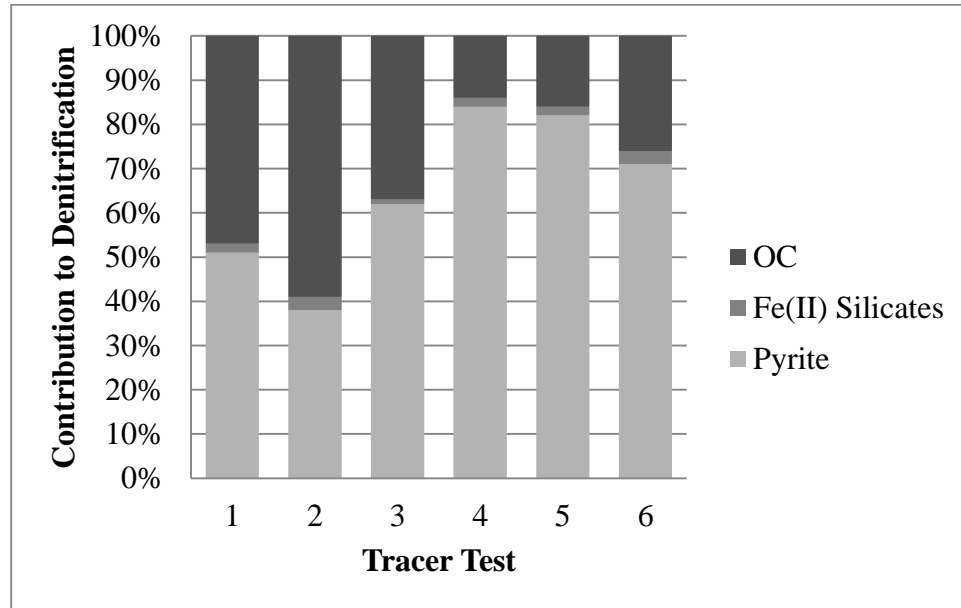


Figure 12. Percent Contributions to Denitrification.

The source(s) of the organic electron donor (OC) have not yet been positively identified. One possible source is OC in the native groundwater. However, OC concentrations did not decrease during tracer tests. In some cases the OC concentrations had increased as the tracer tests progressed (Appendix B). Other prospective sources are OC from glacial outwash derived from Cretaceous shale and likely to have low reactivity because of its age, which is relatively common (Korom et al., 2012; and references therein), other organic matter deposited during the formation of the aquifer, and decayed bacterial bodies (biofilm).

The sources of the electron donors, whether organic (OC) or inorganic (pyrite and ferrous iron silicate minerals), remain fixed in the ISM chamber once installed. The results suggest that the noted variability in denitrification rates was not caused by the

source of electron donors so much as the consumers of the electron donors, the bacterial population.

Chapelle (2001) noted that the bacterial populations in soils are dynamic when there is a constant flux of nutrients, but commented that it is less clear what happens in deeper groundwater systems. More recently Williamson et al. (2012) showed that biofilm dynamics in an alluvial aquifer is also dynamic along a nutrient gradient; however, the conditions were generally aerobic, not denitrifying. The results reported herein suggest that the bacterial population involved with denitrification in aquifers may also be dynamic and this is apparently the first study to do so.

Microorganisms obtain energy during denitrification by transferring electrons from electron donors, such as pyrite, OC, and ferrous iron minerals, to nitrate, which is a compound that accepts electrons (Chapelle, 2001). Based on the electron donors used there are two types of bacteria involved with denitrification at the EVA site: lithotrophic and heterotrophic. Bacteria using inorganic electron donors, such as pyrite and ferrous iron, are lithotrophic, “rock-eaters,” and use inorganic carbon (derived from CO<sub>2</sub>) in groundwater to provide carbon for cell growth and maintenance. Sulfur-oxidizing bacteria are specific lithotrophic bacteria that are able to use pyrite to denitrify (Friedrich, et al., 2001). Bacteria using organic carbon are heterotrophic, “self-feeders,” and use their energy source, OC, also as a source of carbon for cell growth and maintenance.

The type of electron donor consumed at a higher rate during denitrification is theorized to be a result of the type of bacteria forming the majority of the biofilm population. When the lithotrophic bacteria population increases in response to the increase in nitrate concentrations during a tracer test, the resulting biofilm produced

could be used as an energy source by heterotrophic bacteria. Organic carbon consumption by heterotrophs could at times surpass pyrite consumption by lithotrophs. Once the biofilm source of organic carbon becomes limiting, lithotrophic bacteria may then be able to outcompete heterotrophic bacteria for nitrate supplies. Such a relationship in population dynamics between the lithotrophic and heterotrophic bacteria is postulated to explain the variability observed in the contributions of electron donors during denitrification at the EVA site.



## CHAPTER V

### CONCLUSIONS AND FUTURE STUDY

Based on physical parameters, EVA is highly susceptible to pollution, including that from agricultural activities. Tracer tests showed that the EVA ISM responded rapidly to  $\text{NO}_3^-$  pollution with the ability to denitrify between 37 and 84 mg  $\text{NO}_3\text{-N}$  per liter of aquifer over the course of a year. Although this study only analyzed  $\text{NO}_3^-$  contamination, it brought to light the importance of aquifer geochemistry. This aquifer, albeit physically susceptible to contamination, has exhibited the ability to cleanse itself of nitrates with no addition of outside energy sources.

Contributions to denitrification from ferrous iron silicate minerals, pyrite, and OC in the EVA ISM ranged from 1-3%, 38-84%, and 14-59%, respectively. Pyrite contributed the most to denitrification overall. However, no trends were implied by the comparison of denitrification rates and pyrite or OC contributions. Denitrification will continue to be vital to the overall quality of EVA, as long as  $\text{NO}_3^-$  contamination continues in the area, e.g. via agricultural practices. At the current loading rate of  $\text{NO}_3^-$  in the EVA there is sufficient pyrite to support autotrophic denitrification for 11,000 to 175,000 years depending on specific location (Schuh et al., 2006).

#### Future Study

Recommendations for future study include biofilm sampling of the EVA before and after nitrate amendment. Positive identification of bacterial populations could lead to more insight as to why the EVA is able to denitrify so quickly. Categorization of the

bacterial population as more heterotrophic or more lithotrophic during greater contributions to denitrification from OC or pyrite as electron donors, respectively, could verify the influence of bacterial dynamics in denitrifying groundwater systems.

Perhaps the denitrification rates exhibited at EVA are common in similar aquifers. ISM experiments on other highly susceptible aquifers could be performed to determine if vulnerability to  $\text{NO}_3^-$  is truly an issue. Such experiments could augment the ranking systems used for prioritizing aquifer monitoring and consequently ensure money is spent appropriately using the most up-to-date scientifically-based methods.

## APPENDICES

## Appendix A

### PHREEQC Example

PHREEQC (Parkhurst and Apello, 1999), a computer program developed by the U.S. Geological Survey for simulating geochemical reactions, was used to speculate inorganic C (IC) in the forms of bicarbonate and carbonate in groundwater quality during the denitrification tracer tests in the ISMs. A temperature of 10 degrees Celsius was considered constant. The values for  $\text{SO}_4^-$  entered into PHREEQC were an average of the NDDH and EARL concentrations. Lab pH was used when field pH was not available. EARL values were used for  $\text{NO}_3\text{-N}$ , except when  $\text{NO}_3\text{-N}$  values were under 5 mg/L, and then NDDH values were used due to their increased accuracy at low concentrations.

A typical PHREEQC entry is shown below:

```
Solution Larimore Dataset1 12-01-97
temp 10
pH 7.4
units ppm
Na 12.7
Mg 41
K 349
Ca 119
Mn .678
Fe .112
F .67
Cl 9.8
S(6) 64.3
N(5) 135.2
Br 76.4
C(4) 69.7 as C
End
```

After the calculations were run, the output was analyzed for bicarbonate and carbonate concentrations. The  $\text{HCO}_3^-$ ,  $\text{CaHCO}_3^+$ ,  $\text{MgHCO}_3^+$ ,  $\text{MnHCO}_3^+$ ,  $\text{FeHCO}_3$ , and  $\text{NaHCO}_3$  values in molality were given by PHREEQC and then converted to mg/L and

summed to provide the value in the PHREEQC  $\text{HCO}_3^-$  column. Similarly, the  $\text{CO}_3^{2-}$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{MnCO}_3$ ,  $\text{FeCO}_3$ , and  $\text{NaCO}_3^-$  were converted to mg/L and summed to provide the value in the PHREEQC  $\text{CO}_3^{2-}$  column.

The following is the output reading from the input example, Larimore Dataset1 12-01-97.

-----  
Reading data base.  
-----

SOLUTION\_MASTER\_SPECIES  
SOLUTION\_SPECIES  
PHASES  
EXCHANGE\_MASTER\_SPECIES  
EXCHANGE\_SPECIES  
SURFACE\_MASTER\_SPECIES  
SURFACE\_SPECIES  
RATES  
END

-----  
Reading input data for simulation 1.  
-----

Solution Larimore Dataset1 12-01-97  
temp 10  
pH 7.4  
units ppm  
Na 12.7  
Mg 41  
K 349  
Ca 119  
Mn .678  
Fe .112  
F .67  
Cl 9.8  
S(6) 64.3  
N(5) 135.2  
Br 76.4  
C(4) 69.7 as C  
End

-----  
Beginning of initial solution calculations.

-----  
Initial solution 1. Larimore Dataset1 12-01-97

-----Solution composition-----

Elements	Molality	Moles
Br	9.570e-04	9.570e-04
C(4)	5.808e-03	5.808e-03
Ca	2.972e-03	2.972e-03
Cl	2.767e-04	2.767e-04
F	3.530e-05	3.530e-05
Fe	2.007e-06	2.007e-06
K	8.933e-03	8.933e-03
Mg	1.688e-03	1.688e-03
Mn	1.235e-05	1.235e-05
N(5)	9.661e-03	9.661e-03
Na	5.529e-04	5.529e-04
S(6)	6.699e-04	6.699e-04

-----Description of solution-----

pH = 7.400  
pe = 4.000  
Specific Conductance (uS/cm, 10 oC) = 1383  
Density (g/cm3) = 1.00043 (Millero)  
Activity of water = 0.999  
Ionic strength = 2.271e-02  
Mass of water (kg) = 1.000e+00  
Total alkalinity (eq/kg) = 5.311e-03  
Total CO2 (mol/kg) = 5.808e-03  
Temperature (deg C) = 10.000  
Electrical balance (eq) = 1.253e-03  
Percent error, 100\*(Cat-|An|)/(Cat+|An|) = 3.53  
Iterations = 8  
Total H = 1.110177e+02  
Total O = 5.555479e+01

-----Distribution of species-----

Species	Molality	Log Activity	Log Molality	Log Activity	Gamma
OH-	8.510e-08	7.344e-08	-7.070	-7.134	-0.064
H+	4.487e-08	3.981e-08	-7.348	-7.400	-0.052

H2O	5.551e+01	9.995e-01	1.744	-0.000	0.000
Br	9.570e-04				
Br-	9.570e-04	8.233e-04	-3.019	-3.084	-0.065
C(4)	5.808e-03				
HCO3-	5.138e-03	4.483e-03	-2.289	-2.348	-0.059
CO2	5.162e-04	5.189e-04	-3.287	-3.285	0.002
CaHCO3+	7.750e-05	6.762e-05	-4.111	-4.170	-0.059
MgHCO3+	5.397e-05	4.681e-05	-4.268	-4.330	-0.062
CaCO3	8.081e-06	8.123e-06	-5.093	-5.090	0.002
CO3-2	6.319e-06	3.662e-06	-5.199	-5.436	-0.237
MgCO3	2.569e-06	2.583e-06	-5.590	-5.588	0.002
MnHCO3+	2.279e-06	1.977e-06	-5.642	-5.704	-0.062
MnCO3	1.432e-06	1.439e-06	-5.844	-5.842	0.002
NaHCO3	1.201e-06	1.207e-06	-5.921	-5.918	0.002
FeHCO3+	3.870e-07	3.357e-07	-6.412	-6.474	-0.062
FeCO3	6.544e-08	6.578e-08	-7.184	-7.182	0.002
NaCO3-	1.697e-08	1.472e-08	-7.770	-7.832	-0.062
Ca	2.972e-03				
Ca+2	2.802e-03	1.623e-03	-2.553	-2.790	-0.237
CaSO4	8.399e-05	8.443e-05	-4.076	-4.073	0.002
CaHCO3+	7.750e-05	6.762e-05	-4.111	-4.170	-0.059
CaCO3	8.081e-06	8.123e-06	-5.093	-5.090	0.002
CaF+	3.253e-07	2.822e-07	-6.488	-6.549	-0.062
CaOH+	7.798e-09	6.764e-09	-8.108	-8.170	-0.062
CaHSO4+	1.938e-11	1.681e-11	-10.713	-10.774	-0.062
Cl	2.767e-04				
Cl-	2.767e-04	2.390e-04	-3.558	-3.622	-0.064
MnCl+	5.554e-09	4.818e-09	-8.255	-8.317	-0.062
FeCl+	2.848e-10	2.470e-10	-9.545	-9.607	-0.062
MnCl2	4.999e-13	5.025e-13	-12.301	-12.299	0.002
MnCl3-	3.813e-17	3.307e-17	-16.419	-16.481	-0.062
FeCl+2	2.325e-18	1.317e-18	-17.634	-17.881	-0.247
FeCl2+	2.673e-21	2.319e-21	-20.573	-20.635	-0.062
FeCl3	5.511e-26	5.540e-26	-25.259	-25.256	0.002
F	3.530e-05				
F-	3.343e-05	2.885e-05	-4.476	-4.540	-0.064
MgF+	1.536e-06	1.332e-06	-5.814	-5.875	-0.062
CaF+	3.253e-07	2.822e-07	-6.488	-6.549	-0.062
NaF	7.906e-09	7.948e-09	-8.102	-8.100	0.002
HF	1.319e-09	1.326e-09	-8.880	-8.877	0.002
MnF+	1.139e-09	9.877e-10	-8.944	-9.005	-0.062
FeF+	2.491e-10	2.161e-10	-9.604	-9.665	-0.062
HF2-	1.463e-13	1.269e-13	-12.835	-12.896	-0.062
FeF+2	1.909e-14	1.081e-14	-13.719	-13.966	-0.247
FeF2+	1.186e-14	1.029e-14	-13.926	-13.988	-0.062
FeF3	4.435e-16	4.459e-16	-15.353	-15.351	0.002

Fe(2)	1.762e-06					
Fe+2	1.277e-06	7.490e-07	-5.894	-6.126	-0.232	
FeHCO3+	3.870e-07	3.357e-07	-6.412	-6.474	-0.062	
FeCO3	6.544e-08	6.578e-08	-7.184	-7.182	0.002	
FeSO4	2.999e-08	3.014e-08	-7.523	-7.521	0.002	
FeOH+	2.106e-09	1.827e-09	-8.677	-8.738	-0.062	
FeCl+	2.848e-10	2.470e-10	-9.545	-9.607	-0.062	
FeF+	2.491e-10	2.161e-10	-9.604	-9.665	-0.062	
FeHSO4+	8.940e-15	7.754e-15	-14.049	-14.110	-0.062	
Fe(3)	2.455e-07					
Fe(OH)3	1.421e-07	1.429e-07	-6.847	-6.845	0.002	
Fe(OH)2+	1.014e-07	8.793e-08	-6.994	-7.056	-0.062	
Fe(OH)4-	1.999e-09	1.734e-09	-8.699	-8.761	-0.062	
FeOH+2	3.401e-11	1.925e-11	-10.468	-10.715	-0.247	
FeF+2	1.909e-14	1.081e-14	-13.719	-13.966	-0.247	
FeF2+	1.186e-14	1.029e-14	-13.926	-13.988	-0.062	
Fe+3	8.840e-16	3.010e-16	-15.054	-15.521	-0.468	
FeSO4+	8.103e-16	7.029e-16	-15.091	-15.153	-0.062	
FeF3	4.435e-16	4.459e-16	-15.353	-15.351	0.002	
Fe(SO4)2-	5.035e-18	4.368e-18	-17.298	-17.360	-0.062	
FeCl+2	2.325e-18	1.317e-18	-17.634	-17.881	-0.247	
Fe2(OH)2+4	1.865e-19	1.916e-20	-18.729	-19.718	-0.988	
FeCl2+	2.673e-21	2.319e-21	-20.573	-20.635	-0.062	
FeHSO4+2	1.383e-22	7.828e-23	-21.859	-22.106	-0.247	
Fe3(OH)4+5	5.292e-23	1.512e-24	-22.276	-23.820	-1.544	
FeCl3	5.511e-26	5.540e-26	-25.259	-25.256	0.002	
H(0)	2.318e-26					
H2	1.159e-26	1.165e-26	-25.936	-25.934	0.002	
K	8.933e-03					
K+	8.919e-03	7.703e-03	-2.050	-2.113	-0.064	
KSO4-	1.431e-05	1.241e-05	-4.844	-4.906	-0.062	
KOH	6.671e-10	6.706e-10	-9.176	-9.174	0.002	
Mg	1.688e-03					
Mg+2	1.586e-03	9.307e-04	-2.800	-3.031	-0.232	
MgHCO3+	5.397e-05	4.681e-05	-4.268	-4.330	-0.062	
MgSO4	4.365e-05	4.388e-05	-4.360	-4.358	0.002	
MgCO3	2.569e-06	2.583e-06	-5.590	-5.588	0.002	
MgF+	1.536e-06	1.332e-06	-5.814	-5.875	-0.062	
MgOH+	2.349e-08	2.038e-08	-7.629	-7.691	-0.062	
Mn(2)	1.235e-05					
Mn+2	8.436e-06	4.949e-06	-5.074	-5.305	-0.232	
MnHCO3+	2.279e-06	1.977e-06	-5.642	-5.704	-0.062	
MnCO3	1.432e-06	1.439e-06	-5.844	-5.842	0.002	
MnSO4	1.957e-07	1.967e-07	-6.708	-6.706	0.002	
MnCl+	5.554e-09	4.818e-09	-8.255	-8.317	-0.062	
Mn(NO3)2	1.403e-09	1.410e-09	-8.853	-8.851	0.002	



MnF+	1.139e-09	9.877e-10	-8.944	-9.005	-0.062
MnOH+	1.016e-09	8.813e-10	-8.993	-9.055	-0.062
MnCl2	4.999e-13	5.025e-13	-12.301	-12.299	0.002
MnCl3-	3.813e-17	3.307e-17	-16.419	-16.481	-0.062
Mn(3)	5.477e-28				
Mn+3	5.477e-28	1.523e-28	-27.261	-27.817	-0.556
N(5)	9.661e-03				
NO3-	9.661e-03	8.312e-03	-2.015	-2.080	-0.065
Mn(NO3)2	1.403e-09	1.410e-09	-8.853	-8.851	0.002
Na	5.529e-04				
Na+	5.509e-04	4.788e-04	-3.259	-3.320	-0.061
NaHCO3	1.201e-06	1.207e-06	-5.921	-5.918	0.002
NaSO4-	7.561e-07	6.558e-07	-6.121	-6.183	-0.062
NaCO3-	1.697e-08	1.472e-08	-7.770	-7.832	-0.062
NaF	7.906e-09	7.948e-09	-8.102	-8.100	0.002
NaOH	7.900e-11	7.942e-11	-10.102	-10.100	0.002
O(0)	0.000e+00				
O2	0.000e+00	0.000e+00	-45.717	-45.714	0.002
S(6)	6.699e-04				
SO4-2	5.270e-04	3.021e-04	-3.278	-3.520	-0.242
CaSO4	8.399e-05	8.443e-05	-4.076	-4.073	0.002
MgSO4	4.365e-05	4.388e-05	-4.360	-4.358	0.002
KSO4-	1.431e-05	1.241e-05	-4.844	-4.906	-0.062
NaSO4-	7.561e-07	6.558e-07	-6.121	-6.183	-0.062
MnSO4	1.957e-07	1.967e-07	-6.708	-6.706	0.002
FeSO4	2.999e-08	3.014e-08	-7.523	-7.521	0.002
HSO4-	9.928e-10	8.612e-10	-9.003	-9.065	-0.062
CaHSO4+	1.938e-11	1.681e-11	-10.713	-10.774	-0.062
FeHSO4+	8.940e-15	7.754e-15	-14.049	-14.110	-0.062
FeSO4+	8.103e-16	7.029e-16	-15.091	-15.153	-0.062
Fe(SO4)2-	5.035e-18	4.368e-18	-17.298	-17.360	-0.062
FeHSO4+2	1.383e-22	7.828e-23	-21.859	-22.106	-0.247

-----Saturation indices-----

Phase	SI	log IAP	log KT	
Anhydrite	-1.97	-6.31	-4.34	CaSO4
Aragonite	0.03	-8.23	-8.26	CaCO3
Calcite	0.18	-8.23	-8.41	CaCO3
CO2(g)	-2.02	-3.28	-1.27	CO2
Dolomite	0.03	-16.69	-16.72	CaMg(CO3)2
Fe(OH)3(a)	1.79	6.68	4.89	Fe(OH)3
Fluorite	-1.07	-11.87	-10.80	CaF2
Goethite	7.12	6.68	-0.44	FeOOH
Gypsum	-1.72	-6.31	-4.59	CaSO4:2H2O

H2(g)	-22.85	-25.93	-3.08	H2
H2O(g)	-1.92	-0.00	1.92	H2O
Halite	-8.49	-6.94	1.55	NaCl
Hausmannite	-13.66	51.28	64.94	Mn3O4
Hematite	16.17	13.36	-2.81	Fe2O3
Jarosite-K	-3.32	-11.32	-8.00	KFe3(SO4)2(OH)6
Manganite	-4.45	20.89	25.34	MnOOH
Melanterite	-7.24	-9.65	-2.41	FeSO4:7H2O
O2(g)	-42.95	-45.71	-2.77	O2
Pyrochroite	-5.71	9.49	15.20	Mn(OH)2
Pyrolusite	-11.61	32.29	43.91	MnO2:H2O
Rhodochrosite	0.33	-10.74	-11.07	MnCO3
Siderite	-0.77	-11.56	-10.79	FeCO3

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 End of simulation.  
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 Reading input data for simulation 2.  
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 End of run.  
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## Appendix B

### Initial Tracer Test Data

Tables 28-33 list the initial data analyzed for each tracer test. Subsequent winnowing of data involved removing data that was either not pertinent to the study or data that did not accurately represent the aquifer, such as the following cases.

Several sampling events were at the ground surface, before injection into the chamber. Denitrification occurring before the amended water was introduced back into the aquifer was not considered for this study. Such events precede “Day 0”. They are: 10/30/1997 (Tracer Test 1), 10/8/1998 (Tracer Test 2), 8/17/2000 (Tracer Test 3), and 6/8/2004 (Tracer Test 6), including any duplicates.

Two sampling events only included analyses done by EARL, which provided very incomplete data sets. They are: 12/13/2005 and 3/8/2006, both from Tracer Test 6. The two samples were not considered further.

One sampling event had an apparently erroneous  $\text{Br}^-$  measurement which was twice the expected concentration, based on samples taken before and afterwards. The sampling date is 8/2/2005 from Tracer Test 6. The analyses from this date were not considered further.

Another sampling event had an apparently erroneous EARL  $\text{NO}_3\text{-N}$  value, and was subsequently replaced by the respective NDDH measurement. The sampling event took place 10/2/2000 during Tracer Test 3.

Table 28. Tracer Test 1 Initial Data.

atm/wk wt	Date	NDDH			Field pH	NDDH			PHREEQC			NDDH			EARL			NDDH			EARL			NDDH			OC mg/L	TC mg/L
		Na <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	K <sup>+</sup> mg/L		Cd <sup>2+</sup> mg/L	Mn <sup>2+</sup> mg/L	Fe <sup>2+</sup> mg/L	NH <sub>3</sub> -N mg/L	F <sup>-</sup> mg/L	Cl <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	CO <sub>3</sub> <sup>2-</sup> mg/L	CO <sub>3</sub> <sup>2-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	NO <sub>3</sub> -N mg/L	NO <sub>3</sub> -N mg/L	NO <sub>3</sub> -N mg/L	NO <sub>3</sub> -N mg/L	Br <sup>-</sup> mg/L	SiO <sub>2</sub> mg/L	IC mg/L	IC mg/L	OC mg/L		
22.989768	10/30/1997	1.1	27.5	258	79.8	0.449	0.039	<0.010	7.44	0.490	9.2	379	293.0	<1	0.90	41	44.9	95.5	89.8	83.0	25.6	25.6	63.1	1.75	64.9			
	12/1/1997	12.7	41.0	349	119	0.678	0.112	0.012	7.40*	0.670	9.80	358	321.8	<1	1.11	64.0	64.6	140	135.2	76.4	25.6	25.6	69.7	7.29	77.0			
	1/20/1998	8.1	32.9	279	97.6	0.546	0.047	0.067	7.42*	0.670	9.17	346	329.2	<1	1.06	69.5	66.7	115	116.7	68.0	23.5	23.5	71.1	2.78	73.9			
	2/27/1998	59	31.7	289	93.7	0.561	<0.007	not done	7.30*	0.640	9.63	357	312.4	<1	0.75	74.3	70.0	3.55	106.6	62.1	23.8	69.3	2.91	72.2				
	3/27/1998	86	13.2	291	237	0.547	<0.007	<0.010	7.29*	0.690	9.10	337	329.2	<1	1.32	82.4	83.2	90.7	103.7	65.8	18.8	65.9	8.08	74.0				
	4/30/1998	116	11.4	24.0	189	0.464	<0.007	0.060	7.48	0.690	9.46	301	282.8	<1	0.90	109	99.5	73.6	69.4	44.5	21.6	60.5	2.90	63.4				
	5/26/1998	149	13.4	24.3	179	0.487	0.035	0.024	7.58	0.726	8.65	280	262.9	<1	1.05	134	124.9	53.3	53.5	44.6	23.7	55.4	3.55	59.0				
	6/23/1998	202	11.1	22.7	155	0.462	<0.007	<0.007	7.54	0.690	7.65	279	243.0	<1	0.84	156	150.0	37.9	36.3	40.0	23.3	51.5	3.23	54.8				
	8/4/1998	243	6.4	19.1	129	0.453	<0.007	<0.010	7.66	0.860	8.36	252	231.0	<1	1.08	206	190.5	21.5	19.4	37.3	24.9	48.2	17.3	65.5				
	8/30/1998	269	10.4	20.8	130	0.384	<0.007	<0.010	7.64	0.990	8.19	245	224.3	<1	0.89	227	202.6	6.4	4.9	32.1	22.3	46.9	27.1	74.0				

\* Lab pH used  
nd = not detected

Table 29. Tracer Test 2 Initial Data.

at/mple wt	Date	NDDH			Field pH	NDDH			PHREEQC			NDDH			EARL			NDDH			EARL			NDDH			OC mg/L	TC mg/L
		Na <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	K <sup>+</sup> mg/L		Ca <sup>2+</sup> mg/L	Mn <sup>2+</sup> mg/L	Fe <sup>2+</sup> mg/L	NH <sub>3</sub> -N mg/L	F <sup>-</sup> mg/L	Cl <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	CO <sub>3</sub> <sup>2-</sup> mg/L	CO <sub>3</sub> <sup>2-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	NO <sub>3</sub> -N mg/L	NO <sub>3</sub> -N mg/L	NO <sub>3</sub> -N mg/L	NO <sub>3</sub> -N mg/L	Br <sup>-</sup> mg/L	SiO <sub>2</sub> mg/L	IC mg/L	IC mg/L	OC mg/L		
22.9898	10/8/1998	3.6	29.8	9.9	82.6	0.565	<0.007	<0.010	7.58	0.490	5.89	368	338.3	<1	1.54	26.9	24.80	0.02	<0.01	<0.1	28.6	71.4	12.0	83.4				
	10/8/1998	4.4	29.0	369	79.8	0.544	<0.007	0.052	7.69	0.500	5.96	379	not done	<1	not done	25.5	21.90	101	105.4	106.6	28.4	not done	not done	not done				
	10/27/1998	6.6	32.4	328	91.3	0.622	<0.007	<0.010	7.6	0.460	6.00	362	343.4	<1	1.62	61	59.30	108	105.5	110.9	25.8	72.1	0.6	72.7				
	12/1/1998	34	31.4	290	88.6	0.603	<0.007	<0.010	7.07	0.460	6.03	353	291.8	<1	0.41	66	65.30	101	100.6	111.0	25.5	69.7	0	69.5				
	1/16/1999	79	8.5	32.0	356	0.590	<0.007	0.051	7.04	0.490	5.78	356	305.7	<1	0.40	78.15	81.60	94.0	95.3	110.9	26.3	73.9	8.2	82.1				
	2/15/1999	108	9.0	29.5	302	0.535	<0.007	0.030	7.44	0.530	5.96	357	316.9	<1	0.99	79.2	79.10	81.7	89.3	110.3	23.8	68.2	4.2	72.3				
	3/12/1999	135	7.6	29.0	264	0.535	<0.007	<0.010	7.78	0.550	6.10	364	348.1	<1	2.33	89.15	88.80	78.6	78.3	108.9	21.6	71.8	6.2	78.0				
	4/17/1999	170	9.1	28.1	268	0.508	<0.007	0.046	7.47	0.580	6.48	351	306.4	<1	1.00	91.35	91.30	63.4	70.6	95.7	23.7	65.6	9.1	74.7				
	5/25/1999	208	9.2	27.0	231	0.486	<0.007	0.140	7.66	0.580	6.05	352	312.6	<1	1.55	92.75	89.60	61.0	62.3	94.6	21.7	65.2	0.6	65.8				
	6/23/1999	236	9.5	27.1	226	0.494	<0.007	0.121	7.56	0.560	5.61	349	296.8	<1	1.17	109.75	107.50	44.3	50.0	83.5	24.4	62.7	1.9	64.6				
	7/20/1999	263	9.2	23.7	196	0.432	<0.007	<0.010	7.72	0.580	5.57	351	307.2	<1	1.61	127.9	127.80	27.5	33.8	73.4	19.4	63.7	1.8	65.5				
	8/17/1999	290	9.7	23.0	177	0.414	<0.007	0.027	7.56	0.650	5.93	340	302.5	<1	1.08	137.25	134.50	21.5	23.2	63.5	22.9	63.9	1.8	65.7				
	10/26/1999	359	9.9	20.3	172	0.291	<0.010	<0.010	7.62	0.790	5.87	310	292.9	<1	1.11	148.5	146.00	7.38	7.77	50.3	21.4	61.4	7.2	68.6				
	11/30/1999	393	9.7	19.6	178	0.297	<0.010	0.016	7.39	0.770	5.91	284	284.6	<1	0.63	160.2	156.40	1.86	1.86	47.9	20.5	62.0	8.5	70.5				
	2/19/2000	472	9.4	20.8	154	0.378	<0.010	<0.010	7.53	0.710	6.00	302	291.1	<1	0.92	157.1	158.20	0.02	<0.01	39.0	25.9	61.8	0.5	62.3				
	6/7/2000	580	8.0	20.0	131	0.402	<0.010	<0.010	7.60	0.560	7.77	315	297.7	<1	1.10	135.05	133.10	0.02	<0.01	33.1	23.7	62.6	2.2	64.8				

\* Lab pH used  
nd = not detected

Table 30. Tracer Test 3 Initial Data.

Date	at/mole wt	Δtime days	NDDH		NDDH		NDDH		NDDH		NDDH		NDDH		NDDH		NDDH		NDDH		NDDH													
			Na <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	K <sup>+</sup> mg/L	Ca <sup>2+</sup> mg/L	Mn <sup>2+</sup> mg/L	Fe <sup>2+</sup> mg/L	NH <sub>4</sub> -N mg/L	pH	Field	F <sup>-</sup> mg/L	Cl <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	PHREEQC CO <sub>3</sub> <sup>2-</sup> mg/L	NDDH CO <sub>3</sub> <sup>2-</sup> mg/L	PHREEQC SO <sub>4</sub> <sup>2-</sup> mg/L	NDDH SO <sub>4</sub> <sup>2-</sup> mg/L	EARL SO <sub>4</sub> <sup>2-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	NO <sub>3</sub> -NO <sub>2</sub> -N mg/L	NDDH NO <sub>3</sub> -NO <sub>2</sub> -N mg/L	EARL NO <sub>3</sub> -NO <sub>2</sub> -N mg/L	NO <sub>3</sub> -NO <sub>2</sub> -N mg/L	Br <sup>-</sup> mg/L	EARL Br <sup>-</sup> mg/L	SiO <sub>2</sub> mg/L	NDDH SiO <sub>2</sub> mg/L	IC mg/L	NDDH IC mg/L	OC mg/l	NDDH OC mg/l	TC mg/L
8/17/2000	nd	32.9	8.9	86.2	0.511	0.165	<0.010	7.25	0.480	5.13	394	not done	<1	not done	28.7	27.60	0.02	<0.01	<0.1	28.0	not done	not done	not done	not done	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7
9/4/2000	177	33.8	11.5	88.8	0.550	<0.010	<0.010	7.34	0.500	5.20	407	363.80	<1	0.96	35.7	40.2	98.1	109.0	66.8	27.4	79.9	4.8	84.7	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
10/2/2000	28	32.9	12.0	86.9	0.558	<0.010	<0.010	7.54	0.510	5.08	382	385.01	<1	1.57	49.0	49.0	86.5	106	59.1	25.5	79.9	4.8	84.7	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
11/15/2000	71	179	13.4	91.6	0.572	<0.010	<0.010	7.95	0.560	5.54	397	391.09	<1	4.08	79.2	80.1	83.7	81.0	59.9	28.6	79.9	4.8	84.7	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
1/9/2001	125	155.5	30.5	81.35	0.5325	<0.010	<0.010	7.68	0.520	4.84	393	377.26	<1	2.00	122	130	64.2	69.5	66.2	24.85	78.5	0.7	79.2	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
3/22/2001	198	174	33.7	92.4	0.604	<0.010	<0.010	7.71	0.620	4.55	396	369.18	<1	2.21	169	186	50.4	47.8	56.7	27.4	76.6	6.3	82.9	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
4/26/2001	232	160	32.4	89.7	0.5888	<0.010	<0.010	7.63	0.650	5.40	368	306.52	<1	1.81	212	206	37.0	38.7	55.9	26.3	63.6	4.0	67.6	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
6/11/2001	277	150	31.5	87.0	0.578	<0.010	<0.010	7.67	0.660	5.22	348	342.67	<1	1.64	240	240	23.5	25.0	52.6	25.6	71.7	1.7	73.4	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
7/31/2001	327	141	30.5	83.5	0.564	0.029	<0.010	7.68	0.560	4.61	432	352.75	<1	1.84	259	256	10.8	10.2	47.9	25.8	73.4	2.8	76.2	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
8/29/2001	355	131	28.5	77.1	0.523	<0.010	<0.010	7.81	0.660	5.30	373	300.82	<1	2.02	299	259	2.83	2.9	40.9	24.9	61.9	20.9	82.8	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	

\* Lab pH used  
nd = not detected

Table 31. Tracer Test 4 Initial Data.

Date	at/mole wt	Δtime days	NDDH		NDDH		NDDH		NDDH		NDDH		NDDH		NDDH		NDDH		NDDH		NDDH		NDDH												
			Na <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	K <sup>+</sup> mg/L	Ca <sup>2+</sup> mg/L	Mn <sup>2+</sup> mg/L	Fe <sup>2+</sup> mg/L	NH <sub>4</sub> -N mg/L	pH	Field	F <sup>-</sup> mg/L	Cl <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	PHREEQC CO <sub>3</sub> <sup>2-</sup> mg/L	NDDH CO <sub>3</sub> <sup>2-</sup> mg/L	PHREEQC SO <sub>4</sub> <sup>2-</sup> mg/L	NDDH SO <sub>4</sub> <sup>2-</sup> mg/L	EARL SO <sub>4</sub> <sup>2-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	NO <sub>3</sub> -NO <sub>2</sub> -N mg/L	NDDH NO <sub>3</sub> -NO <sub>2</sub> -N mg/L	EARL NO <sub>3</sub> -NO <sub>2</sub> -N mg/L	NO <sub>3</sub> -NO <sub>2</sub> -N mg/L	Br <sup>-</sup> mg/L	EARL Br <sup>-</sup> mg/L	SiO <sub>2</sub> mg/L	NDDH SiO <sub>2</sub> mg/L	IC mg/L	NDDH IC mg/L	OC mg/l	NDDH OC mg/l	TC mg/L	NDDH TC mg/L
10/8/2001	0	184	33.0	88.2	4.7	88.2	<0.010	7.23	0.520	5.41	358	343.31	<1	0.70	39.4	42.05	91.8	95.6	58.4	27.3	77.6	2.3	79.9	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7		
11/20/2001	42	176	32.2	85.3	5.8	85.3	<0.010	6.84	0.500	5.18	357	342.09	<1	0.96	72.0	71.3	88.6	87.2	54.1	26.6	74.5	2.6	77.1	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7		
12/18/2001	70	173	32.5	87.4	6.4	87.4	<0.010	7.26*	0.490	2.60	366	352.82	<1	0.76	101	99	78.7	81.8	54.3	27.9	74.6	3.8	78.4	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7		
2/5/2002	117	174	33.4	88.6	6.7	88.6	0.025	<0.010	7.48	0.500	5.22	366	348.60	<1	1.24	131	136.5	64.4	66.0	54.5	26.1	74.5	3.1	77.6	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
3/19/2002	161	169	33.6	89.5	6.8	89.5	<0.010	<0.010	7.17	0.570	5.60	366	324.36	<1	0.57	179	176	53.4	53.4	25.3	74.7	0.1	74.7	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7		
5/14/2002	216	176	34.7	91.5	7.4	91.5	<0.010	0.243	7.42	0.48	5.19	360	346.33	<1	1.08	205	215	43.1	44.3	53.4	25.8	74.8	1.1	75.9	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
6/25/2002	257	155	32.6	86.2	6.7	86.2	<0.010	0.189	7.42	0.76	3.86	356	345.80	<1	1.04	224	236.1	31.6	30.7	52.1	23.9	74.7	0.0	74.5	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
8/14/2002	306	141	30.5	80.0	6.7	80.0	<0.010	<0.010	7.59	0.520	5.34	355	350.04	<1	1.47	263	260	20.3	20.3	49.6	22.5	73.6	1.1	74.7	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
9/26/2002	348	130	29.0	76.1	6.6	76.1	0.580	0.134	7.53	0.560	5.60	351	350.39	<1	1.25	297	276	11.0	11.3	47.1	22.9	74.3	0.7	75.6	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
10/21/2002	373	120	27.5	6.4	73.9	0.525	0.026	<0.010	7.67	0.550	5.03	339	350.47	<1	1.67	283	297	4.74	4.76	43.7	24.4	73.0	2.6	75.6	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7	
10/21/2002	373	131	29.9	80.3	6.9	80.3	0.607	0.040	<0.010	7.67	0.550	5.03	339	350.44	<1	1.76	283	297	4.74	4.76	43.7	24.4	73.0	2.6	75.6	<0.1	66.8	<0.1	66.8	27.4	25.0	not done	not done	4.8	84.7

\* Lab pH used  
nd = not detected

Table 32. Tracer Test 5 Initial Data.

Date	NDDH											
	Na <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	K <sup>+</sup> mg/L	Ca <sup>2+</sup> mg/L	Mn <sup>2+</sup> mg/L	Fe <sup>2+</sup> mg/L	NH <sub>3</sub> -N mg/L	pH	F <sup>-</sup> mg/L	Cl <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L
11/13/2002	183	30.5	4.0	80.3	0.553	0.083	0.028	7.51	0.513	5.24	5.41	340
1/7/2003	191	33.2	5.2	85.4	0.637	0.028	<0.010	7.56	0.487	4.94	5.52	330
3/12/2003	119	186	33.1	87.2	0.656	0.023	<0.010	7.67	0.490	5.50	5.355	344
5/3/2003	170	186	34.0	89.4	0.697	0.029	<0.010	7.58	0.519	5.18	5.12	346
7/15/2003	242	177	33.9	89.5	0.710	<0.010	<0.010	7.42	0.474	4.89	not done	346
8/25/2003	282	175	33.2	88.0	0.707	<0.010	<0.010	7.46	0.516	5.52	not done	342
10/20/2003	337	163	31.9	84.5	0.685	0.049	<0.010	7.49	0.529	4.96	5.57	349
12/22/2003	399	158	31.8	85.2	0.769	0.570	<0.010	7.57	0.521	5.31	5.37	349
2/18/2004	455	144	29.0	76.7	0.651	0.019	<0.010	7.64	0.524	5.06	not done	364
3/23/2004	490	142	27.6	72.8	0.620	0.019	<0.010	7.69	0.535	5.08	4.57	362

\*Lab pH used

nd = not detected

Table 33. Tracer Test 6 Initial Data.

Date	NDDH											
	Na <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	K <sup>+</sup> mg/L	Ca <sup>2+</sup> mg/L	Mn <sup>2+</sup> mg/L	Fe <sup>2+</sup> mg/L	NH <sub>3</sub> -N mg/L	pH	F <sup>-</sup> mg/L	Cl <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L
6/8/2004	202	30.1	1.9	77.8	0.617	<0.010	<0.010	7.24	0.506	3.39	348	not done
6/14/2004	0	202	32.0	83.3	0.666	<0.010	<0.010	7.52	0.464	3.61	341	325.46
7/19/2004	35	182	31.0	2.7	81.2	0.664	<0.010	7.53	0.472	3.61	345	318.34
9/13/2004	89	174	30.3	3.3	78.7	0.660	<0.010	7.44	0.470	3.70	336	289.88
10/26/2004	132	182	31.8	4.1	82.9	0.700	<0.010	7.31	0.461	3.66	327	316.85
12/6/2004	172	171	30.8	4.2	80.8	0.688	<0.010	7.46	0.441	3.62	347	330.15
2/3/2005	229	171	30.5	4.6	81.6	0.700	<0.010	7.41	0.433	3.59	331	323.35
4/12/2005	298	165	30.9	4.6	83.9	0.733	<0.010	7.46	0.451	3.60	327	324.96
6/14/2005	360	163	30.0	4.6	81.0	0.726	<0.010	7.48	0.430	3.60	328	331.23
8/2/2005	408	155	31.2	5.0	87.0	0.752	<0.010	7.53	0.448	3.79	338	331.57
9/22/2005	458	142	28.9	4.6	77.6	0.704	<0.010	7.50	0.452	3.66	332	331.27
12/13/2005	539	not done	not done	not done	not done	not done	not done	7.46	not done	not done	not done	not done
3/8/2006	624	not done	not done	not done	not done	not done	not done	7.63	not done	not done	not done	not done

\*Lab pH used

nd = not detected

## Appendix C

### Charge Balance Error

One common criterion for verifying the accuracy of laboratory analyses is charge balance error (CBE). CBEs provide a comparison of the summations of cations and anions in an aqueous solution, whereas significant deviation from electroneutrality indicates a possible error in sampling, handling, or analytical procedures. Freeze and Cherry (1979) suggest an acceptable absolute CBE is less than 5%. CBEs for all EVA samples were calculated using the following equation, where ion concentrations were in meq/L.

$$\text{CBE} = \frac{(\sum \text{Cations} - \sum \text{Anions})}{(\sum \text{Cations} + \sum \text{Anions})} \times 100\%$$

Since two separate laboratories were utilized in the detection of some major anions, a system for calculating CBEs from each laboratory was established. Tables 34 and 35 list the major cations and anions used in the calculations and which laboratory detected their presence. All cations identified were results from the NDDH laboratory, therefore the summation of cations was the same for both NDDH and EARL CBEs. The summation of anions was different due to the duplication of analyses from both laboratories. The summation of anions for the NDDH were simply the major anions detected plus the bromide ion reported by the EARL. The summation of anions for the EARL CBE consisted of all anions reported by the EARL, plus carbonate and bicarbonate concentrations calculated by PHREEQC, as well as chloride and fluoride concentrations reported by the NDDH laboratory.

In the case of 3/23/2004 in Tracer Test 5, PHREEQC was not able to speciate  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$  due to the lack of IC data evaluated at that date. Final  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  values were from NDDH laboratory.

Table 34. List of Major Cations.

<b>Cations</b>	<b>NDDH</b>	<b>EARL</b>
$\text{Na}^+$	X	
$\text{Mg}^{2+}$	X	
$\text{K}^+$	X	
$\text{Ca}^{2+}$	X	
$\text{Mn}^{2+}$	X	
$\text{Fe}^{2+}$	X	
$\text{NH}_3\text{-N (NH}_4^+)$	X	

Table 35. List of Major Anions.

<b>Anions</b>	<b>NDDH</b>	<b>EARL</b>
$\text{F}^-$	X	
$\text{Cl}^-$	X	
$\text{HCO}_3^-$	X	X*
$\text{CO}_3^{2-}$	X	X*
$\text{SO}_4^{2-}$	X	X
$\text{NO}_3\text{-N}$	X	X
$\text{Br}^-$		X

\*As inorganic C speciated by PHREEQC.

CBEs for the NDDH values and EARL values are listed in Tables 36-41. A higher concentration of anions results in a negative CBE, while a higher concentration of cations produces a positive CBE. The average absolute CBEs for the laboratories are tabulated at the bottom of the respective absolute CBE columns as a tool for comparison as a whole between the two laboratories.



Table 36. Tracer Test 1 Charge Balance Error.

Date	Δtime days	Sum	NDDH Sum	NDDH	NDDH	EARL Sum	EARL	EARL
		Cations meq/L	Anions meq/L	CBE %	CBE   %	Anions meq/L	CBE %	CBE   %
12/1/1997	0	18.820	18.463	0.96	0.96	17.576	3.42	3.42
12/27/1997	26	15.092	16.473	-4.37	4.37	16.296	-3.83	3.83
1/30/1998	60	15.271	8.734	27.23	27.23	15.296	-0.08	0.08
2/27/1998	88	13.262	14.830	-5.58	5.58	15.691	-8.39	8.39
3/27/1998	116	10.999	13.317	-9.53	9.53	12.551	-6.59	6.59
4/30/1998	150	10.829	12.024	-5.23	5.23	11.605	-3.46	3.46
5/26/1998	176	9.664	11.279	-7.71	7.71	10.561	-4.43	4.43
6/23/1998	204	10.053	10.702	-3.13	3.13	9.921	0.66	0.66
8/4/1998	246	8.092	9.883	-9.97	9.97	8.958	-5.08	5.08
8/30/1998	272	8.637	9.817	-6.39	6.39	9.210	-3.21	3.21
Average CBE:					8.01			3.92

Table 37. Tracer Test 2 Charge Balance Error.

Date	Δtime days	Sum	NDDH Sum	NDDH	NDDH	EARL Sum	EARL	EARL
		Cations meq/L	Anions meq/L	CBE %	CBE   %	Anions meq/L	CBE %	CBE   %
10/27/1998	0	15.921	16.530	-1.88	1.88	16.00	-0.26	0.26
12/1/1998	34	14.836	15.968	-3.68	3.68	14.91	-0.26	0.26
1/16/1999	79	16.654	15.677	3.02	3.02	15.10	4.91	4.91
2/15/1999	108	14.781	14.911	-0.44	0.44	14.81	-0.09	0.09
3/12/1999	135	13.636	15.004	-4.78	4.78	14.75	-3.92	3.92
4/17/1999	170	13.639	13.593	0.17	0.17	13.39	0.92	0.92
5/25/1999	208	12.540	13.506	-3.71	3.71	12.85	-1.21	1.21
6/23/1999	236	12.358	12.447	-0.36	0.36	11.92	1.78	1.78
7/20/1999	263	10.748	11.487	-3.33	3.33	11.24	-2.25	2.25
8/17/1999	290	10.475	11.018	-2.53	2.53	10.43	0.23	0.23
10/26/1999	359	9.493	9.588	-0.50	0.50	9.25	1.30	1.30
11/30/1999	393	9.384	9.008	2.04	2.04	8.87	2.81	2.81
2/19/2000	472	9.052	8.893	0.88	0.88	8.78	1.55	1.55
6/7/2000	580	8.223	8.679	-2.70	2.70	8.33	-0.66	0.66
Average CBE:					2.14			1.58

Table 38. Tracer Test 3 Charge Balance Error.

Date	$\Delta$ time days	Sum Cations meq/L	NDDH Sum Anions meq/L	NDDH CBE %	NDDH  CBE   %	EARL Sum Anions meq/L	EARL CBE %	EARL  CBE   %
9/4/2000	0	15.226	15.426	-0.654	0.654	15.606	-1.233	1.233
10/2/2000	28	14.853	14.366	1.665	1.665	14.442	1.403	1.403
11/15/2000	71	15.469	15.066	1.319	1.319	14.864	1.996	1.996
1/9/2001	125	13.723	14.557	-2.946	2.946	14.877	-4.033	4.033
3/22/2001	198	15.374	14.477	3.003	3.003	14.243	3.818	3.818
4/26/2001	232	14.505	13.973	1.868	1.868	12.988	5.516	5.516
6/11/2001	277	13.863	13.217	2.384	2.384	13.264	2.206	2.206
7/31/2001	327	13.212	14.002	-2.902	2.902	12.629	2.258	2.258
8/29/2001	355	12.286	13.236	-3.724	3.724	11.259	4.360	4.360
Average CBE:					2.274			2.980

Table 39. Tracer Test 4 Charge Balance Error.

Date	$\Delta$ time days	Sum Cations meq/L	NDDH Sum Anions meq/L	NDDH CBE %	NDDH  CBE   %	EARL Sum Anions meq/L	EARL CBE %	EARL  CBE   %
10/8/2001	0	15.261	6.887	37.807	37.807	14.250	3.424	3.424
11/20/2001	42	14.731	7.543	32.272	32.272	14.182	1.898	1.898
12/18/2001	70	14.786	8.218	28.550	28.550	14.147	2.209	2.209
2/5/2002	117	14.933	8.848	25.585	25.585	14.143	2.715	2.715
3/19/2002	161	14.779	9.927	19.641	19.641	13.656	3.950	3.950
5/14/2002	216	15.290	10.350	19.268	19.268	14.169	3.804	3.804
6/25/2002	257	13.921	10.654	13.291	13.291	13.593	1.192	1.192
8/14/2002	306	12.828	11.477	5.559	5.559	13.422	-2.265	2.265
9/26/2002	348	12.030	12.126	-0.400	0.400	13.093	-4.233	4.233
10/21/2002	373	11.354	11.620	-1.157	1.157*	13.013	-6.806	6.806*
10/21/2002	373	12.366	11.620	3.110	3.110	13.014	-2.552	2.552
*Not used in final tabulation. Average CBE:					18.548			2.824

CBE proved to be a successful way to compare the duplicate sample analyses of 10/21/2002 in Tracer Test 4. The second set of analyses had much better CBE and consequently it was the data set utilized.

Table 40. Tracer Test 5 Charge Balance Error.

Date	$\Delta$ time days	Sum	NDDH Sum	NDDH	NDDH	EARL Sum	EARL	EARL
		Cations meq/L	Anions meq/L	CBE %	CBE   %	Anions meq/L	CBE %	CBE   %
11/13/2002	0	14.603	14.730	-0.43	0.43	15.02	-1.40	1.40
1/7/2003	54	15.459	14.462	3.33	3.33	15.59	-0.42	0.42
3/12/2003	119	15.331	14.933	1.32	1.32	15.43	-0.34	0.34
5/3/2003	170	15.527	15.526	0.00	0.00	15.83	-0.96	0.96
7/15/2003	242	15.121	14.808	1.05	1.05	14.25	2.98	2.98
8/25/2003	282	14.917	14.803	0.38	0.38	14.49	1.46	1.46
10/20/2003	337	14.117	14.219	-0.36	0.36	14.02	0.34	0.34
12/22/2003	399	13.956	13.878	0.28	0.28	14.07	-0.40	0.40
2/18/2004	455	12.660	12.785	-0.49	0.49	12.80	-0.57	0.57
3/23/2004	490	12.260	12.132	0.52	0.52			
Average CBE:					0.82			0.98

Table 41. Tracer Test 6 Charge Balance Error.

Date	$\Delta$ time days	Sum	NDDH Sum	NDDH	NDDH	EARL Sum	EARL	EARL
		Cations meq/L	Anions meq/L	CBE %	CBE   %	Anions meq/L	CBE %	CBE   %
6/14/2004	0	15.66	15.13	1.71	1.71	15.39	0.87	0.87
7/19/2004	35	14.61	14.58	0.13	0.13	14.86	-0.85	0.85
9/13/2004	89	14.10	15.26	-3.94	3.94	14.60	-1.75	1.75
10/26/2004	132	14.80	14.81	-0.02	0.02	15.41	-2.02	2.02
12/6/2004	172	14.14	14.71	-1.98	1.98	14.59	-1.58	1.58
2/3/2005	229	14.16	14.15	0.06	0.06	14.40	-0.82	0.82
4/12/2005	298	14.05	13.82	0.83	0.83	13.58	1.71	1.71
6/14/2005	360	13.74	13.72	0.09	0.09	13.79	-0.17	0.17
9/22/2005	458	12.57	13.20	-2.43	2.43	12.08	1.98	1.98
Average CBE:					1.24			1.31

An effort to keep ion analyses consistent from one laboratory or the other was made, versus mixing and matching data. Since Br<sup>-</sup> was analyzed by EARL only, the EARL CBEs were reviewed for deviation of more than  $\pm 5.0\%$ . Three EARL CBEs from Tracer Test 1 were beyond  $-5.0\%$ : 2/27/1998, 3/27/1998, 8/4/1998. The corresponding

NDDH CBEs were also beyond -5.0%. Sorting by CBEs was rejected for these cases due to the lack of improvement from using CBE from either laboratory. However the NDDH CBE on 4/26/2001 of Tracer Test 3 was a great improvement from the EARL CBE values.  $\text{NO}_3\text{-N}$  and  $\text{SO}_4^{2-}$  values for this sampling event will be from NDDH analyses.

In all sampling events, EARL  $\text{NO}_3\text{-N}$  values under 5.0 mg/L were replaced with NDDH  $\text{NO}_3\text{-N}$  values. The NDDH was believed to be more accurate at lesser concentrations than the EARL was. All other data are results from EARL, with the exception of NDDH substitutions which were noted in the final data sets, Tables 46-51.

## Appendix D

### Cation Exchange Capacity

Soils tend to have a general negative charge due to the presence of colloids, which are the most active part of the soil. The soil colloids retain cations on their surfaces, which can be exchanged for other cations. Cation exchange capacity (CEC) is the quantity of cations the soil can hold for exchange with groundwater system. In order to establish if CEC was a factor in EVA tracer tests, the actual concentrations of cations was compared to the relative concentrations of cations due to dilution. The distribution of major exchangeable cations in productive soils is  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ \sim \text{NH}_4^+ \sim \text{Na}^+$ . (Bohn et al., 1985)

The cation considered for CEC in this study was sodium ( $\text{Na}^+$ ) due to its addition as  $\text{NaNO}_3$  and  $\text{NaBr}$  in the amended water for Tracer Tests 3-6.  $\text{Na}^+$  was assumed to undergo dilution similar to the  $\text{Br}^-$  tracer. However,  $\text{Na}^+$  was already present in the native groundwater, as shown in the initial data of Tracer Tests 1 and 2 (Tables 28 and 29). An average  $\text{Na}^+$  concentration was extrapolated from the initial data, as opposed to back-calculation from the  $\text{Br}^-$  tracers. The average  $\text{Na}^+$  concentrations from Tracer Tests 1 and 2 were 10.3 mg/L and 8.3 mg/L, respectively. An initial concentration of 9.3 mg/L was assumed for the native groundwater.

The first steps of determining the CEC of the EVA were to determine the relative concentrations of  $\text{Na}^+$  measured ( $\text{Na}^+$  actual rel. conc.), the concentration of  $\text{Na}^+$  due to dilution, and the relative concentrations of  $\text{Na}^+$  due to dilution ( $\text{Na}^+$  dilution rel. conc.). The difference between the actual relative concentrations and the relative concentrations

by dilution can then be calculated. These values were calculated using the following equations and are tabulated in Tables 42-45.

$$(\text{Na}^+ \text{ actual rel. conc.}) = \frac{(\text{Na}^+_{t \neq 0})}{(\text{Na}^+_{t=0})}$$

$$(\text{Na}^+ \text{ dilution}) = \frac{\text{Br}^-_{t \neq 0} * \text{Na}^+_{t=0}}{\text{Br}^-_{t=0}} + \left(1 - \frac{\text{Br}^-_{t \neq 0}}{\text{Br}^-_{t=0}}\right) * \text{Na}^+_{\text{initial}}$$

$$(\text{Na}^+ \text{ dilution rel. conc.}) = \frac{(\text{Na}^+ \text{ dilution}_{t \neq 0})}{(\text{Na}^+ \text{ dilution}_{t=0})}$$

$$\Delta \text{relative conc.} = (\text{Na}^+ \text{ actual rel. conc.}) - (\text{Na}^+ \text{ dilution rel. conc.})$$

Table 42. Tracer Test 3 Cation Exchange Capacity.

			Na <sup>+</sup>	Na <sup>+</sup>	Na <sup>+</sup>	Na <sup>+</sup>	
	Δtime	Br <sup>-</sup>	Actual	Actual	Dilution	Dilution	Δ Rel Conc.
Date	days	mg/L	mg/L	Rel Conc.	mg/L	Rel Conc.	Act - Dil
9/4/2000	0	66.80	177.00	1.00	177.00	1.00	0.00
10/2/2000	28	59.10	172.00	0.97	157.67	0.89	0.08
11/15/2000	71	59.90	179.00	1.01	159.68	0.90	0.11
1/9/2001	125	66.20	155.50	0.88	175.49	0.99	-0.11
3/22/2001	198	56.70	174.00	0.98	151.64	0.86	0.13
4/26/2001	232	55.90	160.00	0.90	149.64	0.85	0.06
6/11/2001	277	52.55	150.00	0.85	141.23	0.80	0.05
7/31/2001	327	47.90	141.00	0.80	129.55	0.73	0.06
8/29/2001	355	40.90	131.00	0.74	111.98	0.63	0.11

Table 43. Tracer Test 4 Cation Exchange Capacity.

			Na <sup>+</sup>	Na <sup>+</sup>	Na <sup>+</sup>	Na <sup>+</sup>	
	Δtime	Br <sup>-</sup>	Actual	Actual	Dilution	Dilution	Δ Rel Conc.
Date	days	mg/L	mg/L	Rel Conc.	mg/L	Rel Conc.	Act - Dil
10/8/2001	0	58.35	184.00	1.00	184.00	1.00	0.00
11/20/2001	42	54.10	176.00	0.96	171.28	0.93	0.03
12/18/2001	70	54.30	173.00	0.94	171.87	0.93	0.01
2/5/2002	117	54.50	174.00	0.95	172.47	0.94	0.01
3/19/2002	161	53.20	169.00	0.92	168.58	0.92	0.00

Table 43. cont.

Date	$\Delta$ time days	Br <sup>-</sup> mg/L	Na <sup>+</sup>	Na <sup>+</sup>	Na <sup>+</sup>	Na <sup>+</sup>	$\Delta$ Rel Conc. Act - Dil
			Actual mg/L	Actual Rel Conc.	Dilution mg/L	Dilution Rel Conc.	
8/14/2002	306	49.60	141.00	0.77	157.80	0.86	-0.09
9/26/2002	348	47.10	130.00	0.71	150.32	0.82	-0.11
10/21/2002	373	43.70	131.00	0.71	140.14	0.76	-0.05

Table 44. Tracer Test 5 Cation Exchange Capacity.

Date	$\Delta$ time days	Br <sup>-</sup> mg/L	Na <sup>+</sup>	Na <sup>+</sup>	Na <sup>+</sup>	Na <sup>+</sup>	$\Delta$ Rel Conc. Act - Dil
			Actual mg/L	Actual Rel Conc.	Dilution mg/L	Dilution Rel Conc.	
11/13/2002	0	61.80	183.00	1.00	183.00	1.00	0.00
1/7/2003	54	63.60	191.00	1.04	188.06	1.03	0.02
3/12/2003	119	62.30	186.00	1.02	184.41	1.01	0.01
5/3/2003	170	62.90	186.00	1.02	186.09	1.02	0.00
7/15/2003	242	56.90	177.00	0.97	169.23	0.92	0.04
8/25/2003	282	60.80	175.00	0.96	180.19	0.98	-0.03
10/20/2003	337	53.50	163.00	0.89	159.67	0.87	0.02
12/22/2003	399	51.20	158.00	0.86	153.21	0.84	0.03
2/18/2004	455	40.00	144.00	0.79	121.73	0.67	0.12
3/23/2004	490	34.20	142.00	0.78	105.43	0.58	0.20

Table 45. Tracer Test 6 Cation Exchange Capacity.

Date	$\Delta$ time days	Br <sup>-</sup> mg/L	Na <sup>+</sup>	Na <sup>+</sup>	Na <sup>+</sup>	Na <sup>+</sup>	$\Delta$ Rel Conc. Act - Dil
			Actual mg/L	Actual Rel Conc.	Dilution mg/L	Dilution Rel Conc.	
6/14/2004	0	75.55	202.00	1.00	202.00	1.00	0.00
7/19/2004	35	71.60	182.00	0.90	191.93	0.95	-0.05
9/13/2004	91	72.65	174.00	0.86	194.60	0.96	-0.10
10/26/2004	134	77.70	182.00	0.90	207.48	1.03	-0.13
12/6/2004	175	69.08	171.00	0.85	185.48	0.92	-0.07
2/3/2005	234	72.81	171.00	0.85	195.01	0.97	-0.12
4/12/2005	302	62.75	165.00	0.82	169.35	0.84	-0.02
6/14/2005	365	62.51	163.00	0.81	168.74	0.84	-0.03
9/22/2005	465	49.83	142.00	0.70	136.40	0.68	0.03

The change in relative concentrations of Na<sup>+</sup> actual and Na<sup>+</sup> dilution were compiled and plotted on a graph against time, as shown in Figure 13. A strong deviation between relative concentrations would entail a linear relationship with an R<sup>2</sup> value close to 1.0. Figure 13 shows no such relationship. The relative concentrations of Na<sup>+</sup> dilution and Na<sup>+</sup> actual did not deviate from one another, therefore CEC is considered insignificant at this EVA ISM.

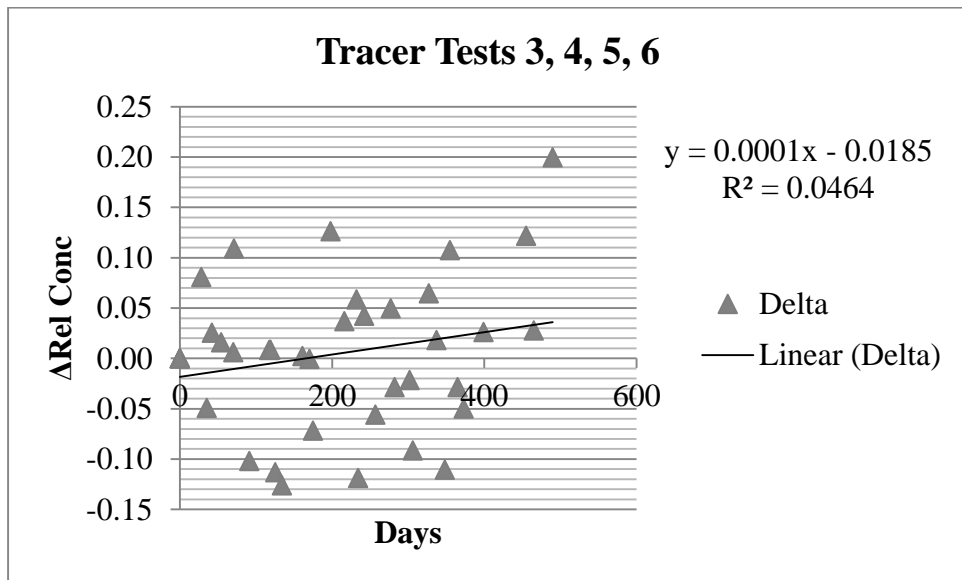


Figure 13. Cation Exchange Capacity Consideration.



# Appendix E

## Final Dataset

The following tables present the data chosen as the final dataset.

Table 46. Tracer Test 1 Final Data.

Date	Δtime days	Na <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	K <sup>+</sup> mg/L	Ca <sup>2+</sup> mg/L	Mn <sup>2+</sup> mg/L	Fe <sup>2+</sup> mg/L	NH <sub>4</sub> -N mg/L	pH	F <sup>-</sup> mg/L	Cl <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	CO <sub>3</sub> <sup>2-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	NO <sub>3</sub> -N mg/L	Br <sup>-</sup> mg/L	SiO <sub>2</sub> mg/L	IC mg/L	OC mg/L	TC mg/L
12/1/1997	0	12.7	41.0	349	119	0.678	0.112	0.012	7.40	0.670	9.80	321.8	1.11	64.6	135.2	76.4	25.6	69.7	7.29	77.0
12/27/1997	26	8.1	32.9	279	97.6	0.546	0.047	0.067	7.42	0.670	9.17	329.2	1.06	66.7	116.7	68.0	23.5	71.1	2.78	73.9
1/30/1998	59	13.2	31.7	289	93.7	0.561	<0.007	not done	7.30	0.640	9.63	312.4	0.75	70.0	106.6	62.1	23.8	69.3	2.91	72.2
2/27/1998	86	13.2	29.1	237	84.4	0.547	<0.007	<0.010	7.29	0.690	9.10	329.2	1.32	83.2	103.7	65.8	18.8	65.9	8.08	74.0
3/27/1998	116	11.4	24.0	189	73.6	0.464	<0.007	0.060	7.48	0.690	9.46	282.8	0.90	99.5	69.4	44.5	21.6	60.5	2.90	63.4
4/30/1998	149	13.4	24.3	179	73.1	0.487	0.035	0.024	7.58	0.726	8.65	262.9	1.05	124.9	53.5	44.6	23.7	55.4	3.55	59.0
5/26/1998	175	11.1	22.7	155	65.7	0.462	<0.007	0.754	7.54	0.690	7.65	243.0	0.84	154.0	36.3	40.0	23.3	51.5	3.23	54.8
6/23/1998	202	12.0	23.9	155	71.8	0.453	<0.007	<0.010	7.66	0.860	8.36	231.0	1.08	190.5	19.4	37.3	24.9	48.2	17.3	65.5
8/4/1998	243	6.4	19.1	129	58.7	0.359	<0.007	<0.010	7.64	0.990	8.19	224.3	0.89	202.6	6.4	32.1	22.3	46.9	27.1	74.0
8/30/1998	269	10.4	20.8	130	62.8	0.384	<0.007	<0.010	7.71	1.01	8.17	227.9	1.09	227.7	0.81	33.1	24.5	47.3	23.3	70.6

Table 47. Tracer Test 2 Final Data.

Date	Δtime days	Na <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	K <sup>+</sup> mg/L	Ca <sup>2+</sup> mg/L	Mn <sup>2+</sup> mg/L	Fe <sup>2+</sup> mg/L	NH <sub>4</sub> -N mg/L	pH	F <sup>-</sup> mg/L	Cl <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	CO <sub>3</sub> <sup>2-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	NO <sub>3</sub> -N mg/L	Br <sup>-</sup> mg/L	SiO <sub>2</sub> mg/L	IC mg/L	OC mg/L	TC mg/L
10/27/1998	0	6.6	32.4	328	91.3	0.622	<0.007	<0.010	7.6	0.460	6.00	343.4	1.62	59.30	105.5	110.9	25.8	72.1	0.6	72.7
12/1/1998	34	9.0	31.4	290	88.6	0.603	<0.007	<0.010	7.07	0.460	6.03	291.8	0.41	65.30	100.6	111.0	25.5	69.7	0	69.5
1/16/1999	79	8.5	32.0	356	90.6	0.590	<0.007	0.051	7.04	0.490	5.78	305.7	0.40	81.60	95.3	110.9	26.3	73.9	8.2	82.1
2/15/1999	108	9.0	29.5	302	84.5	0.535	<0.007	0.030	7.44	0.530	5.96	316.9	0.99	79.10	89.3	110.3	23.8	68.2	4.2	72.3
3/12/1999	135	7.6	29.0	264	83.1	0.535	<0.007	<0.010	7.78	0.550	6.10	348.1	2.33	88.80	78.3	108.9	21.6	71.8	6.2	78.0
4/17/1999	170	9.1	28.1	268	80.4	0.508	<0.007	0.646	7.47	0.580	6.48	306.4	1.00	91.30	70.6	95.7	23.7	65.6	9.1	74.7
5/25/1999	208	9.2	27.0	231	78.0	0.486	<0.007	1.40	7.66	0.580	6.05	312.6	1.55	89.60	62.3	94.6	21.7	65.2	0.6	65.8
6/23/1999	236	9.5	27.1	226	78.3	0.494	<0.007	0.121	7.56	0.560	5.61	296.8	1.17	107.50	50.0	83.5	24.4	62.7	1.9	64.6
7/20/1999	263	9.2	23.7	196	67.5	0.432	<0.007	<0.010	7.72	0.580	5.57	307.2	1.61	127.80	33.8	73.4	19.4	63.7	1.8	65.5
8/17/1999	290	9.7	23.0	191	65.3	0.414	<0.007	0.027	7.56	0.650	5.93	302.5	1.08	134.50	23.2	63.5	22.9	63.9	1.8	65.7
10/26/1999	359	9.9	20.3	177	57.2	0.291	<0.010	<0.010	7.62	0.790	5.87	292.9	1.11	146.00	7.77	50.3	21.4	61.4	7.2	68.6
11/30/1999	393	9.7	19.6	178	55.8	0.297	<0.010	0.016	7.39	0.770	5.91	284.6	0.63	156.40	1.86	47.9	20.5	62.0	8.5	70.5
2/19/2000	472	9.4	20.8	154	59.7	0.378	<0.010	<0.010	7.53	0.710	6.00	291.1	0.92	158.20	0.02	39.0	25.9	61.8	0.5	62.3
6/7/2000	580	8.0	20.0	131	57.4	0.402	<0.010	<0.010	7.60	0.560	7.77	297.7	1.10	133.10	0.02	33.1	23.7	62.6	2.2	64.8

Table 48. Tracer Test 3 Final Data.

Date	Δtime days	Na <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	K <sup>+</sup> mg/L	Ca <sup>2+</sup> mg/L	Mn <sup>2+</sup> mg/L	Fe <sup>2+</sup> mg/L	NH <sub>3</sub> -N mg/L	pH	F <sup>-</sup> mg/L	Cl <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	CO <sub>3</sub> <sup>2-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	NO <sub>3</sub> -N mg/L	Br <sup>-</sup> mg/L	SiO <sub>2</sub> mg/L	IC mg/L	OC mg/l	TC mg/L
9/4/2000	0	177	33.8	11.5	88.8	0.550	<0.010	<0.010	7.34	0.500	5.20	363.80	0.96	40.2	109.0	66.8	27.4	79.9	4.8	84.7
10/2/2000	28	172	32.9	12.0	86.9	0.558	<0.010	<0.010	7.54	0.510	5.08	385.01	1.57	49.0	86.5	59.1	25.5	81.5	1.0	82.5
11/15/2000	71	179	33.4	13.4	91.6	0.572	<0.010	<0.010	7.95	0.560	5.54	391.09	4.08	80.1	81.0	59.9	28.6	79.9	1.6	81.5
1/9/2001	125	155.5	30.5	14.5	81.35	0.5325	<0.010	<0.010	7.68	0.520	4.84	377.26	2.00	130	69.5	66.2	24.85	78.5	0.7	79.2
3/22/2001	198	174	33.7	15.6	92.4	0.604	<0.010	<0.010	7.71	0.620	4.55	369.18	2.21	186	47.8	56.7	27.4	76.6	6.3	82.9
4/26/2001	232	160	32.4	14.9	89.7	0.588	<0.010	<0.010	7.71	0.650	5.40	306.52	1.81	212	37.0	55.9	26.3	63.6	4.0	67.6
6/11/2001	277	150	31.5	15.0	87.0	0.578	<0.010	<0.010	7.63	0.660	5.22	342.67	1.64	240	25.0	52.6	25.6	71.7	1.7	73.4
7/31/2001	327	141	30.5	14.9	83.5	0.564	0.029	<0.010	7.68	0.560	4.61	352.75	1.84	256	10.2	47.9	25.8	73.4	2.8	76.2
8/29/2001	355	131	28.5	14.7	77.1	0.523	<0.010	<0.010	7.81	0.660	5.30	300.82	2.02	259	2.83	40.9	24.9	61.9	20.9	82.8

Table 49. Tracer Test 4 Final Data.

Date	Δtime days	Na <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	K <sup>+</sup> mg/L	Ca <sup>2+</sup> mg/L	Mn <sup>2+</sup> mg/L	Fe <sup>2+</sup> mg/L	NH <sub>3</sub> -N mg/L	pH	F <sup>-</sup> mg/L	Cl <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	CO <sub>3</sub> <sup>2-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	NO <sub>3</sub> -N mg/L	Br <sup>-</sup> mg/L	SiO <sub>2</sub> mg/L	IC mg/L	OC mg/l	TC mg/L
10/8/2001	0	184	33.0	4.7	88.2	0.547	<0.010	<0.010	7.23	0.520	5.41	343.31	0.70	42.05	95.6	58.4	27.3	77.6	2.3	79.9
11/20/2001	42	176	32.2	5.8	85.3	0.562	<0.010	6.84	7.38	0.500	5.18	342.09	0.96	71.3	87.2	54.1	26.6	74.5	2.6	77.1
12/18/2001	70	173	32.5	6.4	87.4	0.675	1.03	<0.010	7.26	0.490	2.60	332.82	0.76	99	81.8	54.3	27.9	74.6	3.8	78.4
2/5/2002	117	174	33.4	6.7	88.6	0.609	0.025	<0.010	7.48	0.500	5.22	348.60	1.24	136.5	66.0	54.5	26.1	74.5	3.1	77.6
3/19/2002	161	169	33.6	6.8	89.5	0.628	<0.010	<0.010	7.17	0.570	5.60	324.36	0.57	176	53.4	53.2	25.3	74.7	0.1	74.7
5/14/2002	216	176	34.7	7.4	91.5	0.651	<0.010	0.243	7.42	0.48	5.19	346.33	1.08	215	44.3	53.4	25.8	74.8	1.1	75.9
6/25/2002	257	155	32.6	6.7	86.2	0.632	<0.010	0.189	7.42	0.76	3.86	345.80	1.04	236.1	30.7	52.1	23.9	74.7	0.0	74.5
8/14/2002	306	141	30.5	6.7	80.0	0.584	<0.010	<0.010	7.59	0.520	5.34	350.04	1.47	260	20.3	49.6	22.5	73.6	1.1	74.7
9/26/2002	348	130	29.0	6.6	76.1	0.580	0.028	0.134	7.53	0.560	5.60	350.39	1.25	276	11.3	47.1	22.9	74.3	0.7	75.0
10/21/2002	373	131	29.9	6.9	80.3	0.607	0.040	<0.010	7.67	0.550	5.03	350.44	1.76	297	4.74	43.7	24.4	73.0	2.6	75.6

Table 50. Tracer Test 5 Final Data.

Date	Δtime days	Na <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	K <sup>+</sup> mg/L	Ca <sup>2+</sup> mg/L	Mn <sup>2+</sup> mg/L	Fe <sup>2+</sup> mg/L	NH <sub>3</sub> -N mg/L	pH	F <sup>-</sup> mg/L	Cl <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	CO <sub>3</sub> <sup>2-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	NO <sub>3</sub> -N mg/L	Br <sup>-</sup> mg/L	SiO <sub>2</sub> mg/L	IC mg/L	OC mg/l	TC mg/L
11/13/2002	0	183	30.5	4.0	80.3	0.553	0.033	0.028	7.51	0.513	5.24	334.79	1.23	64.85	101	61.8	25.9	71.2	2.7	73.9
1/7/2003	54	191	33.2	5.2	85.4	0.637	0.028	<0.010	7.56	0.487	4.94	345.90	1.47	99.75	94.6	63.6	26.8	73.0	0.7	73.7
3/12/2003	119	186	33.1	5.5	87.2	0.656	0.023	<0.010	7.67	0.490	5.50	340.88	1.86	143.25	80.8	62.3	26.0	71.0	1.3	72.3
5/3/2003	170	186	34.0	5.9	89.4	0.697	0.029	<0.010	7.58	0.519	5.18	345.88	1.54	186	72.8	62.9	25.2	72.8	0.4	73.2
7/15/2003	242	177	33.9	5.5	89.5	0.710	<0.010	<0.010	7.42	0.474	4.89	329.22	1.03	203	54.6	56.9	25.0	71.1	1.5	72.6
8/25/2003	282	175	33.2	6.1	88.0	0.707	<0.010	<0.010	7.46	0.516	5.52	330.22	1.11	234.5	46.0	60.8	24.2	70.8	1.8	72.5
10/20/2003	337	163	31.9	6.2	84.5	0.685	0.049	<0.010	7.49	0.529	4.96	335.31	1.09	256	33.7	53.5	24.2	71.9	0.8	72.6
12/22/2003	399	158	31.8	6.5	85.2	0.769	0.570	<0.010	7.57	0.521	5.31	341.12	1.48	291	20.3	51.2	25.0	71.9	0.8	72.7
2/18/2004	455	144	29.0	6.2	76.7	0.651	0.019	<0.010	7.64	0.524	5.06	345.96	1.60	284.5	5.05	40.0	24.4	72.3	1.7	73.9
3/23/2004	490	142	27.6	6.1	72.8	0.620	0.019	<0.010	7.69	0.535	5.08	362.00	<1	266	0.58	34.2	23.9	not done	not done	not done

Table 51. Tracer Test 6 Final Data.

Date	Δtime days	Na <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	K <sup>+</sup> mg/L	Ca <sup>2+</sup> mg/L	Mn <sup>2+</sup> mg/L	Fe <sup>2+</sup> mg/L	NH <sub>3</sub> -N mg/L	pH	F <sup>-</sup> mg/L	Cl <sup>-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	CO <sub>3</sub> <sup>2-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	NO <sub>3</sub> -N mg/L	Br <sup>-</sup> mg/L	SiO <sub>2</sub> mg/L	IC mg/L	OC mg/l	TC mg/L
6/14/2004	0	202	32.0	2.4	83.3	0.666	<0.010	<0.010	7.52	0.464	3.61	325.46	1.27	62.7	107	75.55	23.1	69.1	3.5	72.6
7/19/2004	35	182	31.0	2.7	81.2	0.664	0.010	<0.010	7.53	0.472	3.61	318.34	1.25	69.6	99.9	71.6	22.0	67.5	7.5	75.0
9/13/2004	89	174	30.3	3.3	78.7	0.660	<0.010	<0.010	7.44	0.470	3.70	289.88	0.92	88.1	97.3	72.7	22.1	62.4	9.7	72.1
10/26/2004	132	182	31.8	4.1	82.9	0.700	<0.010	<0.010	7.31	0.461	3.66	316.85	0.76	112	94.7	77.7	22.7	70.1	5.2	75.3
12/6/2004	172	171	30.8	4.2	80.8	0.688	<0.010	<0.010	7.46	0.441	3.62	330.15	1.09	121	79.0	69.1	23.0	70.8	3.1	73.9
2/3/2005	229	171	30.5	4.6	81.6	0.700	0.010	<0.010	7.41	0.433	3.59	323.35	0.95	148	69.2	72.8	22.6	70.0	4.5	74.5
4/12/2005	298	165	30.9	4.6	83.9	0.733	<0.010	<0.010	7.46	0.451	3.60	324.96	1.09	164	54.5	62.8	22.4	69.7	6.4	76.1
6/14/2005	360	163	30.0	4.6	81.0	0.726	<0.010	<0.010	7.48	0.430	3.60	331.23	1.13	190	48.4	62.5	21.1	70.8	1.9	72.8
9/22/2005	458	142	28.9	4.6	77.6	0.704	<0.010	<0.010	7.50	0.452	3.66	331.27	1.15	187	27.7	49.8	22.2	70.6	4.4	75.0

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