

Assessment of Groundwater Monitoring Data from the Aucilla Landfill and the Cause of the Elevated Iron Concentrations

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1.0 Introduction

A trend has been noted in several surficial groundwater monitoring wells at the Aucilla Area Solid Waste Facility in Madison County, Florida: iron concentrations have been increasing. Particularly, surficial wells 2S, 7S and 8S have concentrations of iron above the secondary drinking water limit of 0.3 mg/L (the historical data for iron concentrations in these three wells are presented in Appendix A). The iron concentrations in these wells also exceed the 4.2 mg/L health-based criterion for iron recently developed for FDEP. These wells are located adjacent to an operating Class I lined landfill unit.

The possible cause of the elevated iron concentrations was investigated. As part of routine groundwater monitoring at the site, additional sampling parameters were analyzed to help evaluate the possible cause (sampling date: August 24, 2005). These data, along with historical data from the site were evaluated.

2.0 Methods

The following parameters were examined for 9 different surficial monitoring wells adjacent to the Class I landfill cell:

- Oxidation reduction potential (mV)
- Total iron (mg/L)
- Ferrous iron (Fe^{+2} ; mg/L)
- Dissolved Oxygen (mg/L)
- pH (standard units)
- Total Organic Carbon (mg/L)
- Ammonia nitrogen (mg/L)
- Nitrate nitrogen (mg/L)
- Chloride (mg/L)
- Sodium (mg/L)
- Sulfate (mg/L)
- Sulfide (mg/L)
- Alkalinity (mg/L)
- TDS (mg/L)
- Conductivity (umhos/cm)
- Manganese ($\mu\text{g/L}$)

These parameters include some already required as part of routine monitoring at the site, as well as additional parameters to assist in the data evaluation. Based on the results, the monitoring wells were grouped in to two different groups. The first group included those wells which exceed the FDEP health-based standard of 4.2 mg/L for iron (2S, 7S, and 8S). The second group included those wells which were below the FDEP health-based standard (6S, 9S, 10S, 12S, 13S and 14S).

3.0 Results and Discussion

Appendix A presents the historical iron concentration data for the three impacted wells. Appendix B presents the table of raw data for the wells and parameters of interest for August 24, 2005 sampling event). Appendix B presents comparison bar charts for each of these monitoring parameters.

3.1 Iron Concentrations

Iron concentrations in monitoring wells 2S, 7S and 8S all have elevated iron concentrations. Figure A-1 shows the dramatic increase in recent years in iron concentrations in 2S. As shown in Figure A-2, iron concentrations in 7S have also steadily increased since the first sampling event. Iron concentrations in samples from monitoring well 8S were already somewhat elevated in the first sampling events. The concentrations of iron measured in the August '05 sampling event were similar to the historical data (see Figure C-1 in Appendix C). Concentrations in wells 2S, 7S and 8S were elevated (47, 27 and 20 mg/L respectively) with respect to wells 6S, 9S, 10S, 12S, 13S and 14S (all less than 0.03 mg/L with the exception of 13S at 0.5 mg/L).

Iron exists in a variety of different forms in the environment. The concentrations described above represent the total concentration of iron in the samples collected, regardless of species (oxidized Fe^{+3} or reduced Fe^{+2}) and regardless of whether the iron is dissolved or suspended. In previous efforts to determine whether the suspended particles (e.g., fine soil particles) were the source of the iron, both filtered and unfiltered samples were analyzed for iron in the elevated wells (April 2005). No difference was observed in the filtered and unfiltered samples; the nature of the elevated iron was thus determined to be dissolved (see the figure in Appendix D). Unless otherwise stated, the groundwater analysis results described in this document represent unfiltered measurements.

As will be described in greater detail in subsequent sections, iron in native soils will typically be present in the +3 valence state. Under reducing conditions, insoluble Fe^{+3} can be released as soluble Fe^{+2} . In an attempt to shed light on the observations, dissolved iron with a valence state of +2 was measured (Fe^{+2}) using a colorimetric technique. The results are similar to the total iron concentration results, with Fe^{+2} being elevated in those samples where total iron was elevated (see Figure C-2). In one of the three elevated wells (7S), the results suggest that nearly all of the iron was present as Fe^{+2} . In the other two elevated wells, the measured Fe^{+2} represented a smaller fraction of the total iron; this is believed to be in part a result of oxidation of the Fe^{+2} to Fe^{+3} during the process of sampling and during the time between sampling and analysis (24 hours or less).

Several different hypotheses might explain the cause of the elevated iron concentrations. These are outlined as follows:

Hypothesis A. The elevated concentrations of iron are a result of leachate contamination, with leachate representing the source of the iron. Given that the landfill is a double-lined facility, this would mean that the landfill cell is leaking or that leachate was in some other fashion discharged outside the boundary of the cell.

Hypothesis B. The elevated concentrations of iron are a result of leachate contamination, with leachate causing the formation of reducing conditions that thus liberates Fe^{+2} from the soil. This phenomenon has been proposed as the source of elevated iron at some unlined construction and demolition debris facilities in Florida. In the same manner as hypothesis A, this would mean that leachate was released from the lined landfill cell in some fashion.

Hypothesis C. The elevated concentrations of iron are a result of reducing conditions that developed in the groundwater because of changes in site hydrology and/or hydrogeology brought on by the presence of the lined landfill cell and supporting structures. In this hypothesis, iron is liberated from native soil into groundwater because reducing conditions develop ($\text{Fe}^{+3} \rightarrow \text{Fe}^{+2}$), but the development of these reducing conditions does not take place because of a release of leachate to the environment.

These hypotheses are explored in the following sections.

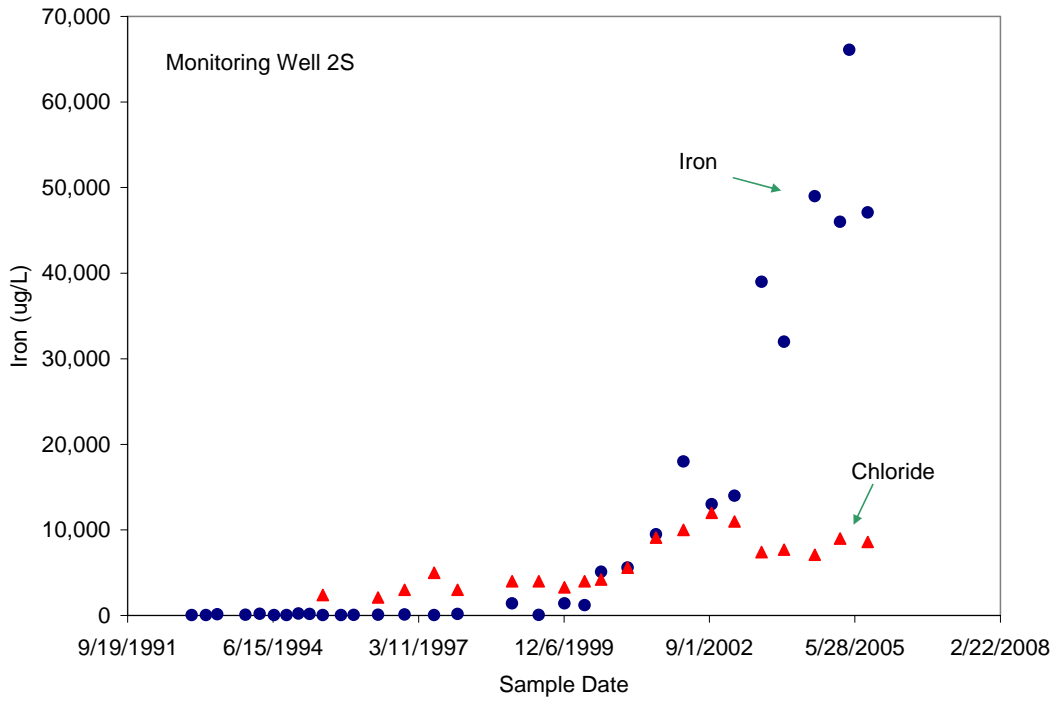
3.2 Indication of Leachate Contamination

The iron concentration in the leachate sample collected from the main leachate sump was 38 mg/L. Historically, leachate samples collected from the Class I sumps at the landfill have ranged from 1.4 to 90 mg/L (1,400 to 90,000 ug/L) with an arithmetic average of 35 mg/L. This concentration is on the same magnitude as the impacted groundwater wells. If the source of the elevated iron in the groundwater was leachate from the landfill, the iron concentrations would be expected to be much lower as a result of simple dilution (based on TDS and electrical conductance measurements, dilution would be at least an order magnitude). Thus from a very simple analysis of the data, the elevated iron concentrations do not appear to be the result of iron in the leachate (hypothesis A is not supported). However, given that leachate could also impact the oxidation/reduction chemistry, a more thorough examination is required.

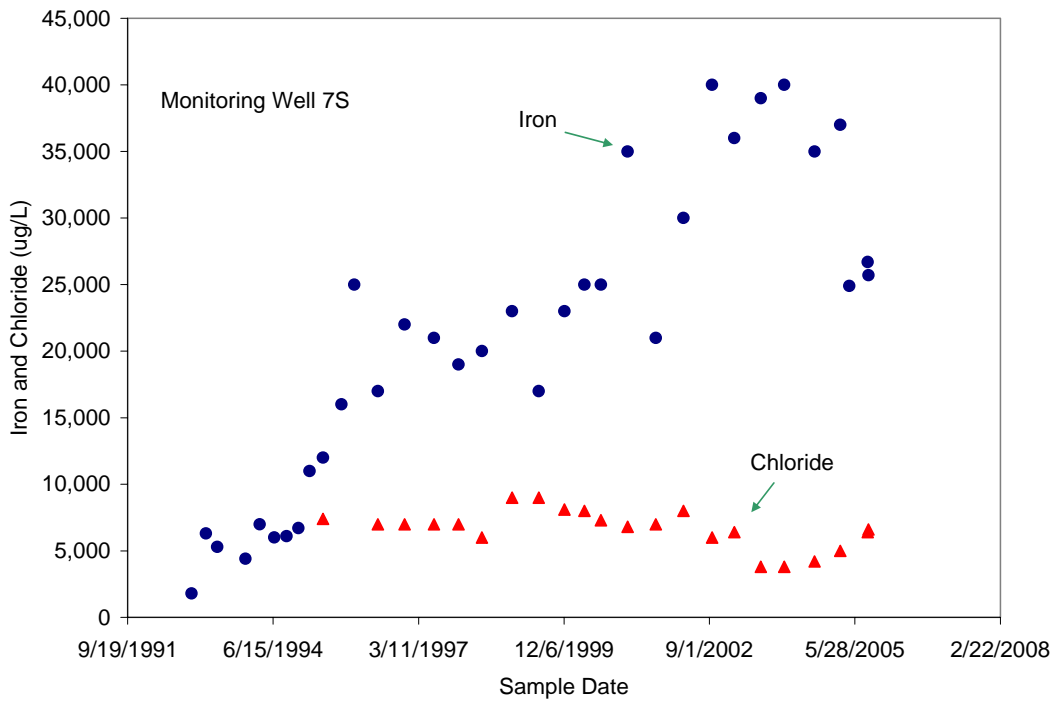
Many of the water quality parameters analyzed in groundwater monitoring wells are naturally occurring elements, and elevations in concentrations of these elements may in some cases simply be a result of the native soils. When assessing whether the source of groundwater contamination is a discharge from a landfill, it is helpful to look at concentrations of chemicals that are strong indicators of leachate. Two groups of indicator parameters were evaluated as part of this assessment: organic pollutants and soluble salts.

Anthropogenic chemicals such as organic pollutants are one group of indicator chemicals. Volatile organic compound (VOC) concentrations in all of the groundwater monitoring wells, including the iron-impacted wells, were for the most part all below detection limit. VOCs were routinely encountered at low concentrations in the samples collected from the Class I leachate sumps. For example, 18 of 32 leachate samples in the historical data set were found to have benzene at concentrations greater than the detection limit. In 32 samples of groundwater from each well, benzene was detected 0 times for monitoring wells 2S, 7S, and 8S. The VOC results do not support the hypothesis that leachate has been discharged to the groundwater.

Soluble salts, specifically chloride and sodium, were also evaluated. Chloride and sodium are good indicator parameters for leachate because, unlike VOCs, they are normally very high in concentration in landfill leachate (in the August 2005 leachate, chloride = 1370 mg/L and sodium = 790 mg/L). Although chloride and sodium are naturally occurring elements, because of their solubility they are normally low in concentration in groundwater and they are less likely to be impacted by changes in geochemical conditions (oxidizing or reducing conditions or pH). In the following figure, iron and chloride concentrations are plotted on the same graph for monitoring well 2S.



Iron and Chloride Changes in 2S



Iron and Chloride Changes in 7S

Both of the above figures show that the dramatic increase in iron concentrations over time do not correlate with a dramatic increase in chloride concentrations.

Figures C-9 and C-10 show the August 2005 concentrations of chloride and sodium for the monitoring wells. The concentrations were very low compared to the leachate concentrations and there was no calculated statistical difference (using the student t test) between the iron-impacted wells and those not impacted by iron. The chloride and sodium data do not support the hypothesis that leachate has been discharged to the groundwater.

In summary, the available data regarding VOC concentrations and the soluble salts do not support the hypothesis that leachate has entered the groundwater (hypotheses A and B). It is true, however, that the concentrations of several different water quality parameters are different between the iron-impacted wells and those wells not impacted. In the next section, explanations for these changes are provided based on changes in oxidation and reduction chemistry.

3.3 Changes in Groundwater Quality as a Result of Oxidation and Reduction Chemistry

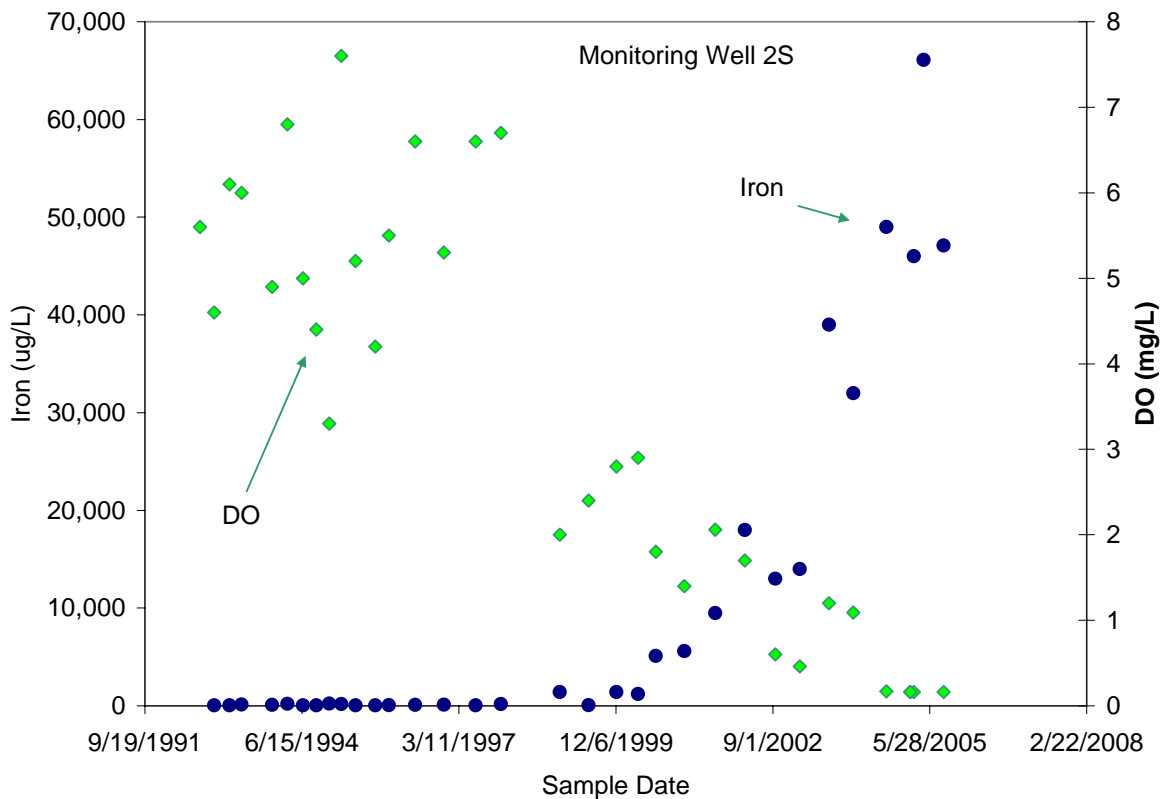
In the environment (including the groundwater environment), a number of biological reactions occur in which organic matter is consumed as part of the life cycle of different bacteria. These bacteria use utilize a variety of different compounds as electron acceptors. Since some electron acceptors are energetically more favorable than others, some bacteria out compete other bacteria depending on which electron acceptors they use. This concept is a basic component of most water chemistry texts, and has been used to describe different zones that occur in groundwater underneath landfills that have been contaminated leachate. In appendix E, these reactions are presented (from Stumm and Morgan).

In summary, the data collected for the groundwater wells at Aucilla support the hypothesis that reducing conditions are developing underneath the lined landfill cell and resulting in the liberation of iron.

The most energetically favorable reaction will be aerobic respiration where oxygen is used as an electron acceptor.

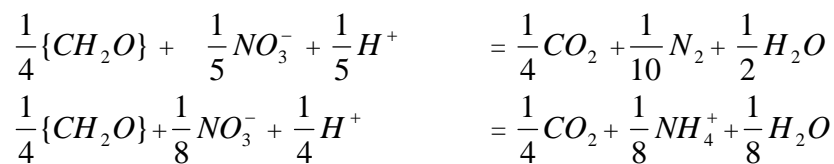


As show in Figure C-4, the dissolved oxygen is lower in the iron impacted wells in comparison to the unimpacted wells (August 2005 sampling date). The following figure plots the concentration of iron and the concentration of dissolved oxygen for monitoring well 2S. There is a clear correlation between decreasing DO concentrations and increasing iron concentrations.



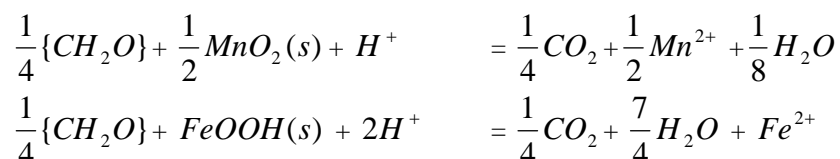
Iron and DO Changes in 2S

The next most energetically favorable reactions are nitrate reduction and denitrification.



Dissolved N_2 was not measured, but nitrate and ammonia concentrations were (see Figures C-7 and C-8). The results are exactly as one would suspect based on the formation of reducing conditions: nitrate is higher in the unimpacted wells compared to the iron-impacted wells, while the opposite is true for ammonia.

The reduction of oxidized manganese and iron from the solid phase to the dissolve phase would be expected as the next most favorable reactions and this is what occurs.



The elevation of iron has already been described, and this exact phenomenon is also observed for manganese (see Figure C-16).

The next most energetically favorable reaction is sulfate reduction. Sulfate concentrations are not lower in the iron-impacted wells (see Figure C-11 for sulfate and C-12 for sulfide), which indicated that the dominant bacterial species were the iron reducing bacteria. Sulfate concentrations, in fact, appeared to be somewhat greater in the iron-impacted wells, suggesting that perhaps the sulfate was being liberated from the mineral matrix as a result of the other biogeochemical reactions. Sulfate concentrations were not above the groundwater cleanup target level.

The changes in the other water quality parameters are also consistent with the reactions described above. The probe-measured oxidation reduction potential (ORP) is lower in the iron impacted wells as would be expected (Figure C-3). Note that in the above reactions, protons (H^+) are consumed, and the pH of the iron-impacted wells is increased (again as would be expected; Figure C-5). Alkalinity is greater in the iron-impacted wells (Figure C-13), a result of the CO_2 produced during the biological reactions described above. The specific conductance and TDS are also somewhat higher in the iron-impacted wells, which is very likely the result of the iron, manganese and carbonates that have increased as a result of the reactions described above. As described previously, chloride and sodium concentrations, major contributors to TDS and conductance in leachate, are not elevated in the iron-impacted wells. The increase in total organic carbon (TOC; Figure C-6) in the iron-impacted wells is hypothesized to be a result of the fermentation reactions that occurs just prior to the iron reduction reaction (see Appendix E).

4.0 Summary and Conclusion

Iron concentrations have been documented to be increasing in several groundwater monitoring wells down-gradient of a lined Class I landfill unit at the Aucilla Area Solid Waste Facility in Madison County. Several hypotheses were explored to assess the cause of the increased iron concentrations. There is no evidence that leachate has impacted groundwater (based on VOCs and soluble salts). The quality of the groundwater has changed, and these changes are consistent with the formation of chemically reducing conditions between points up-gradient and down-gradient of the lined landfill unit. Given the absence of any evidence that leachate is the cause of these reducing conditions, the most plausible cause is the presence of lined landfill unit itself. The liner will act to cut off the normal cycle of water infiltration into the surficial aquifer. Existing dissolved oxygen will be consumed through naturally occurring biological reactions, resulting the predominance of other bacterial species that use electron acceptors other than oxygen. The data suggest that iron reducing bacteria are active and are liberating dissolved iron from the soil to the groundwater.

Appendix A
Historic Iron Data for
Monitoring Wells 2S, 7S and 8S

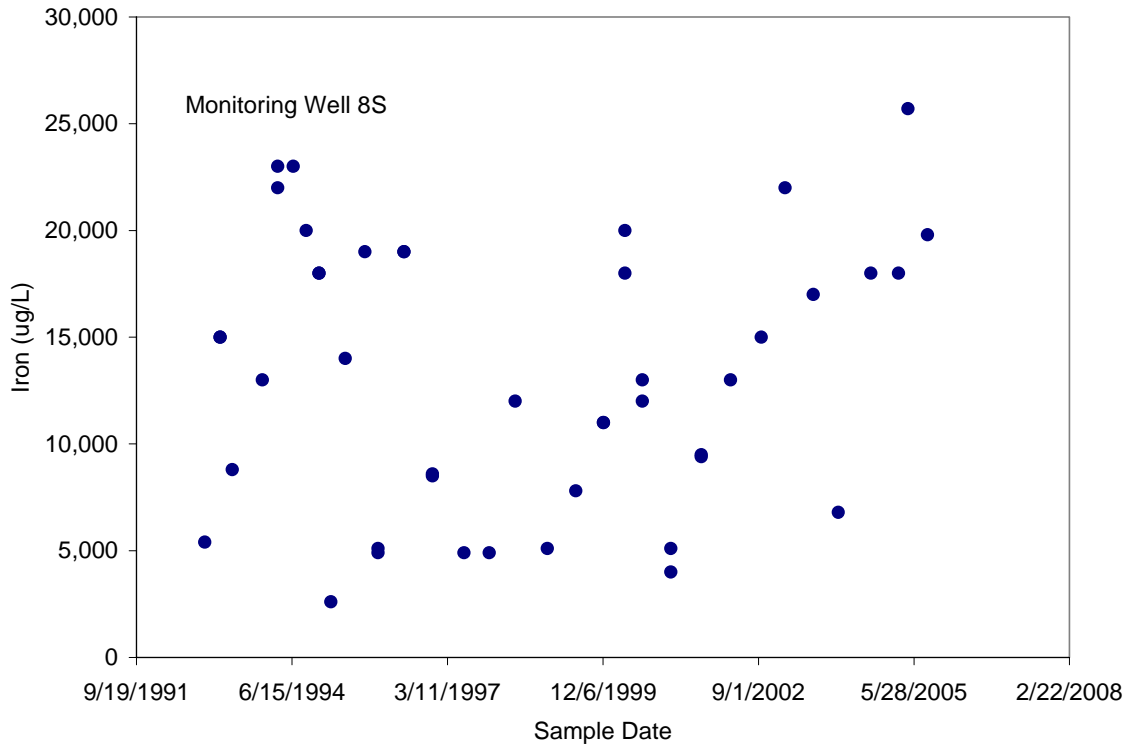


Figure A-3. Historical Iron Concentrations in Monitoring Well 8S

Appendix B.
Summary Data Table

Parameter	ORP	Total Fe	Fe +2	DO	pH	TOC	Ammonia	Nitrate	
Standard	(1)	0.3 mg/L**	(1)	(1)	6.5-8.5**	(1)	2.8*** mg/L	10* mg/L	
Units	mV	mg/L	mg/L	ppm	S.U.	mg/L	mg/L	mg/L	
Monitoring Wells	2S	-85.5	47.1	2.864	0.16	5.51	4.8	0.74	0.17
	7S	9.3	26.7	24.0	0.10	5.46	5.0	1.2	<0.009
	8S	12.7	19.8	2.308	0.47	5.32	6.1	1.8	<0.009
	6S	219.9	<0.02	0.010	2.46	3.99	<1.0	<0.003	2.5
	9S	176.3	<0.02	0.016	0.13	3.77	<1.0	<0.003	1.5
	10S	133.6	<0.02	0.008	0.72	4.07	<1.0	<0.003	2.7
	12S	277.6	<0.02	0.019	1.79	4.03	<1.0	<0.003	5
	13S	23.9	0.63	0.487	0.48	4.72	1.3	<0.003	1
	14S	488.7	0.0241	0.028	0.20	4.38	<1.0	<0.003	0.74
Sump 1	-116.7	38.3	2.3	0.40	6.75	760	329	<0.045	
Sump 2	-180.2	4.0	2.0	0.47	6.69	150	480	<0.018	

Parameter	Chloride	Sodium	Sulfate	Sulfides	Alkalinity	TDS	Conductivity	Manganese	
Standard	250** mg/L	160* mg/L	250** mg/L	(1)	(1)	500** mg/L	(1)	50** µg/L	
Units	mg/L	mg/L	mg/L	ug/L	mg/L	mg/L	umhos/cm	µg/L	
Monitoring Wells	2S	8.6	2	47.4	4.0	73.9	180	336	1100
	7S	6.4	2.4	8.9	3.0	49.6	88	156	340
	8S	8.8	4.2	3.1	32.0	45.9	102	104	1100
	6S	7.9	3.2	1.3	<1	<4	70	75	8.1
	9S	11.3	1.8	1.4	1.0	<4	40	87	3.4
	10S	5.7	3.1	1.4	<1	<4	50	60	2.8
	12S	7	1.4	1.2	1.0	<4	60	97	8.9
	13S	5.9	1.5	2.4	5.0	<4	60	56	36
	14S	6	1.9	2.6	4.0	7.6	54	64	13
Sump 1	1370	790	7.3	25	2340	3480	8053	1400	
Sump 2	669	549	311	86	1780	2540	5247	1000	

- * Primary Drinking Water Standard
- ** Secondary Drinking Water Standard
- *** Groundwater Clean-up Target Level
- (1) No Standard

Appendix C
Summary Data Plots for
Recent Sampling Events

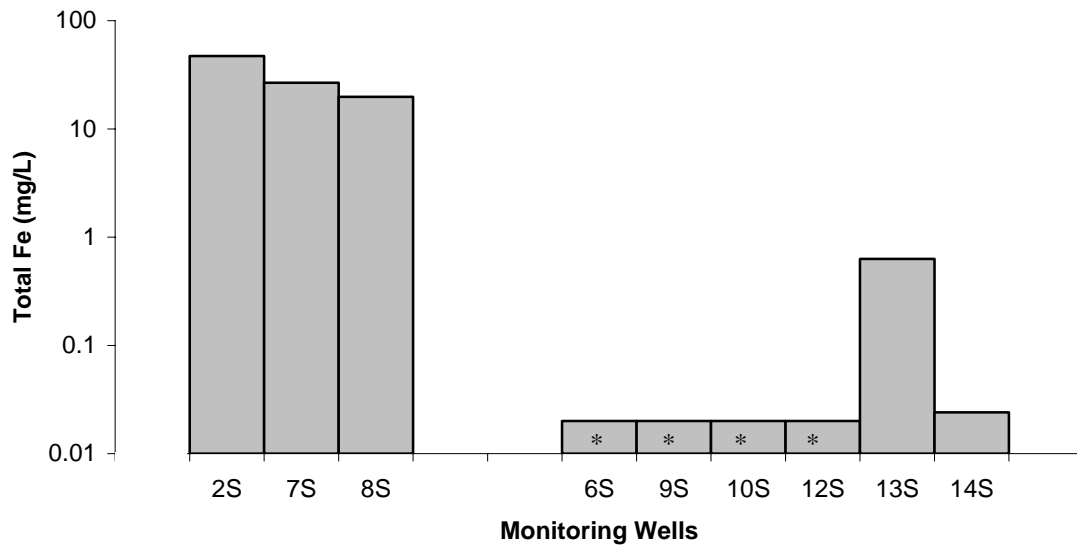


Figure C-1. Total Iron
 (* indicates samples that are below detection limit, 20 ug/L)

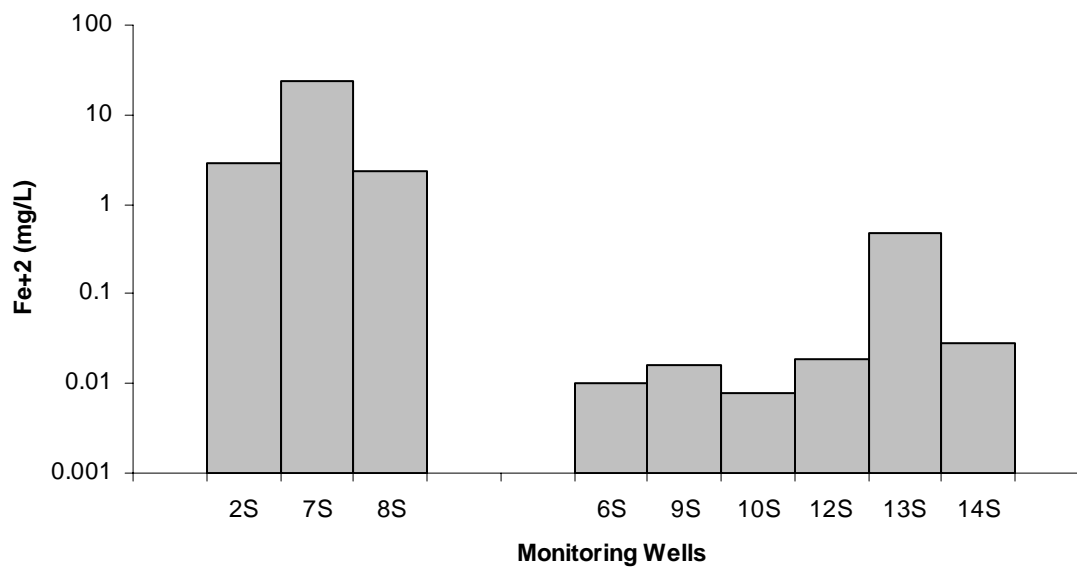


Figure C-2. Iron(II)

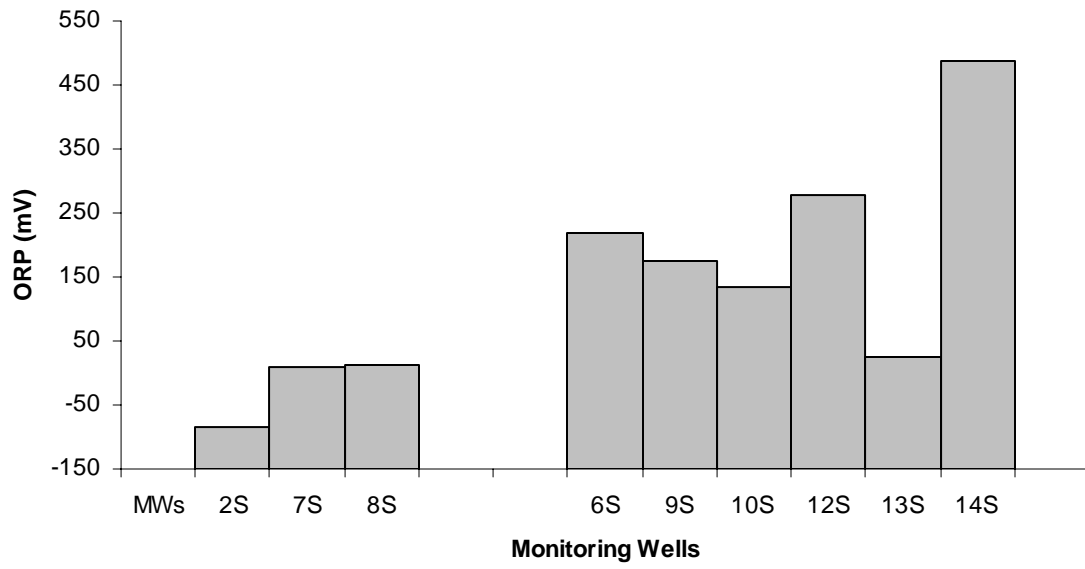


Figure C-3. Oxidation Reduction Potential

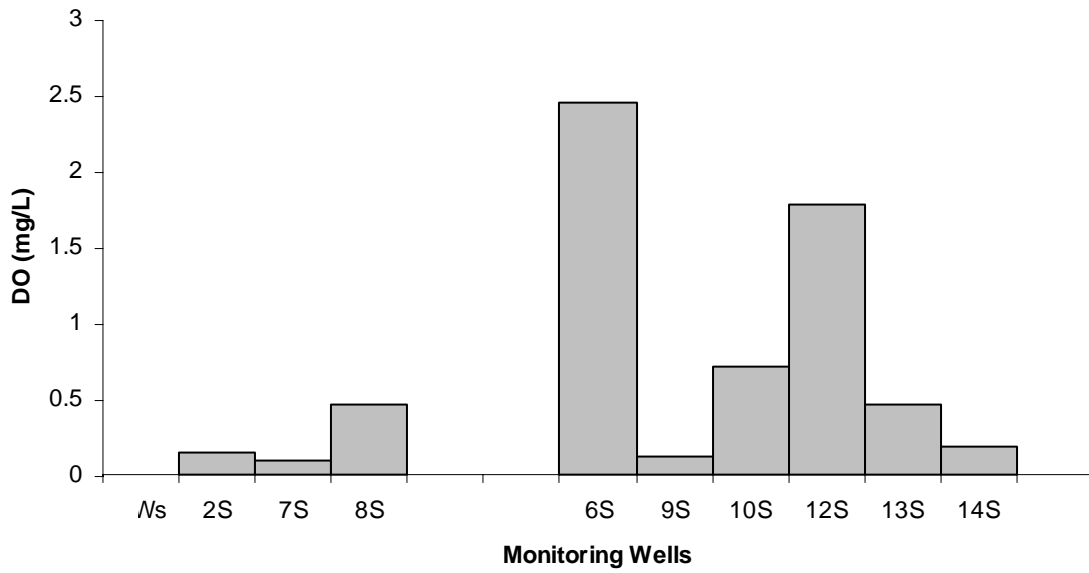


Figure C-4. Dissolved Oxygen

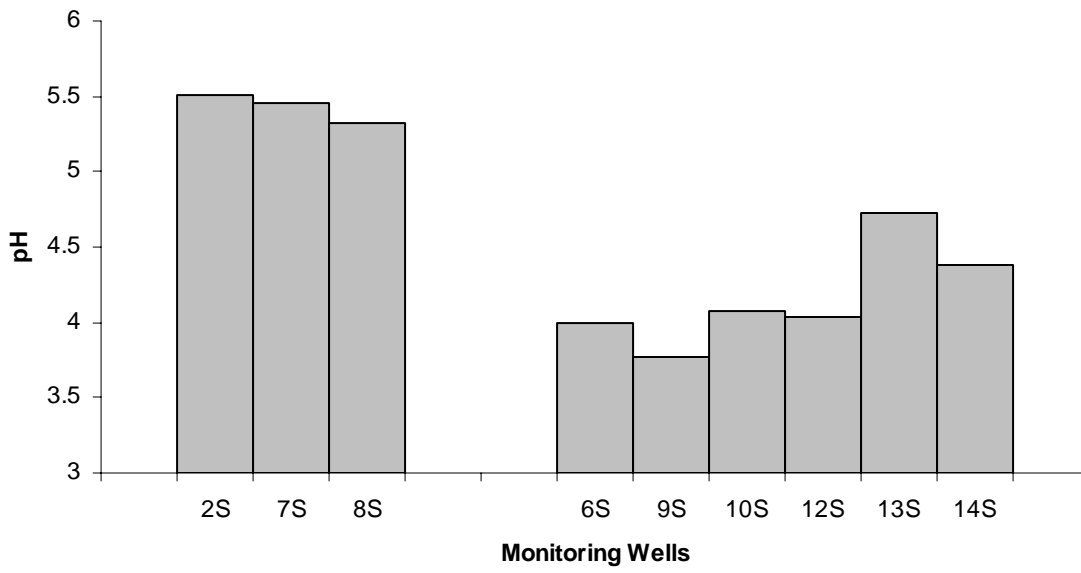


Figure C-5. pH

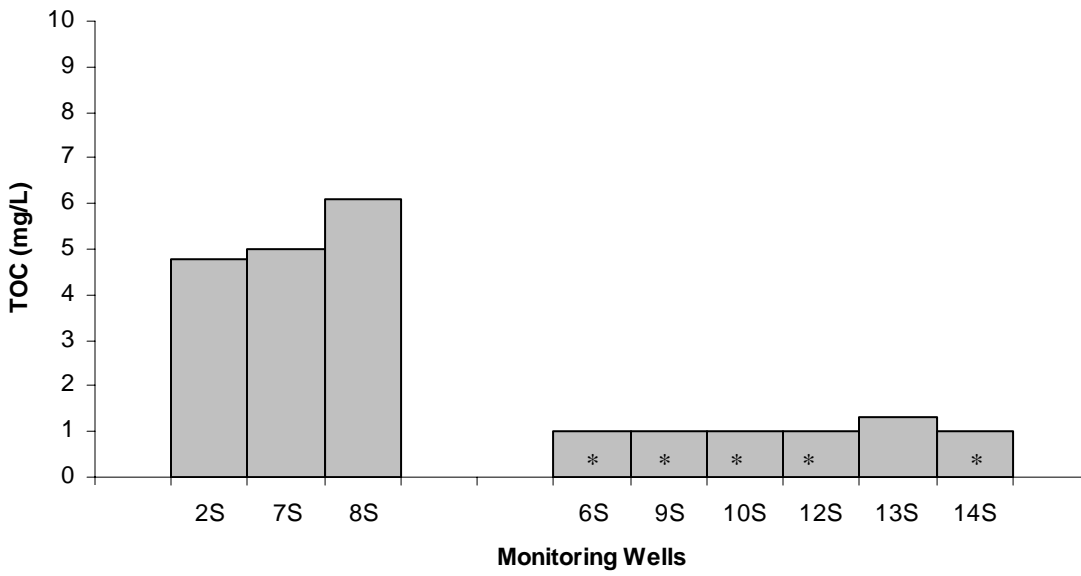


Figure C-6. Total Organic Carbon (TOC)
 (* indicates samples that are below detection limit, 1 mg/L)

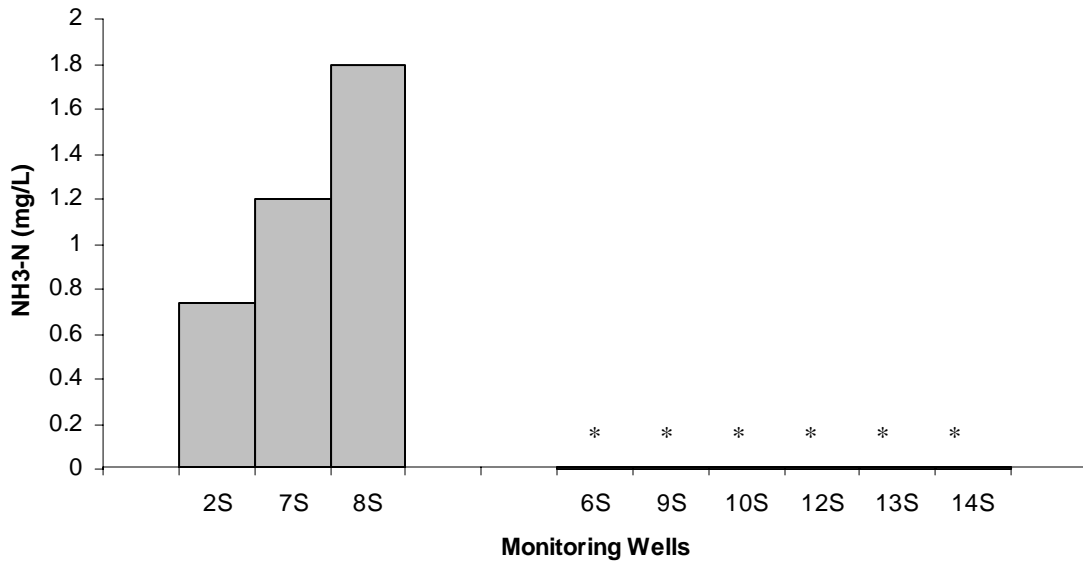


Figure C-7. Ammonia Nitrogen
 (* indicates samples that are below detection limit, 0.003 mg/L)

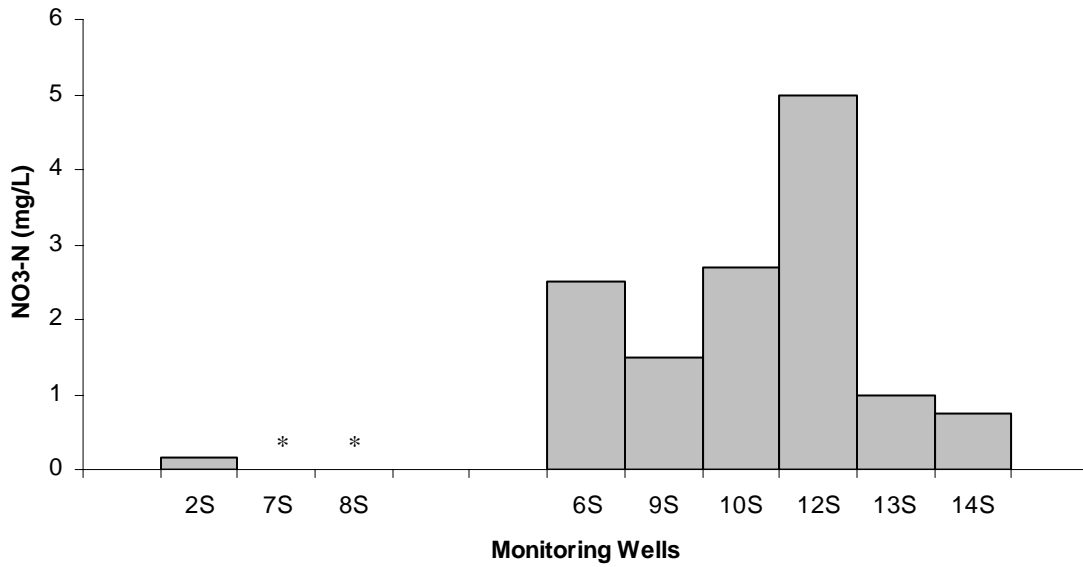


Figure C-8. Nitrate Nitrogen
 (* indicates samples that are below detection limit, 0.009 mg/L)

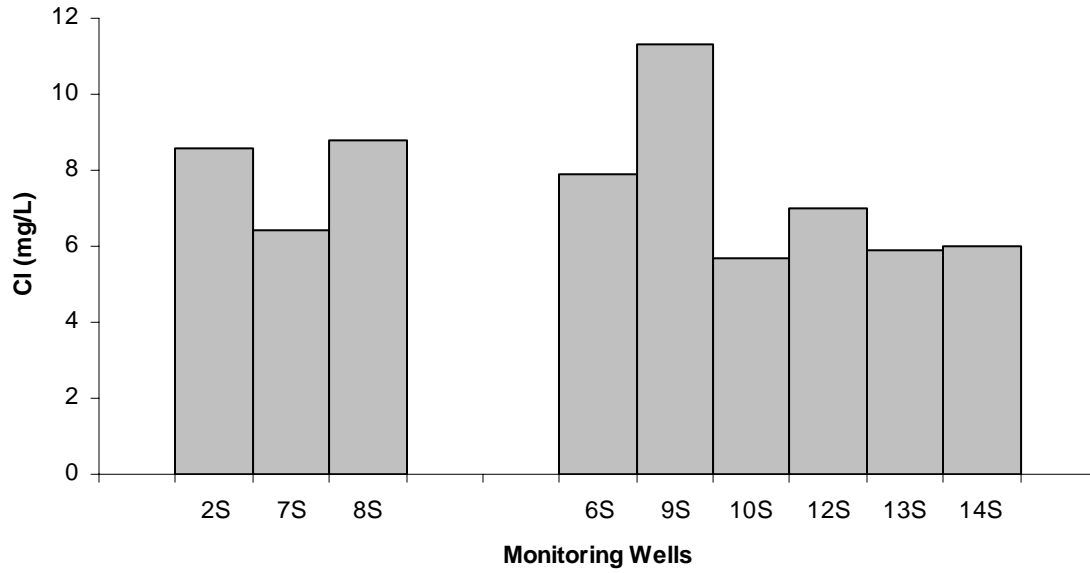


Figure C-9. Chloride

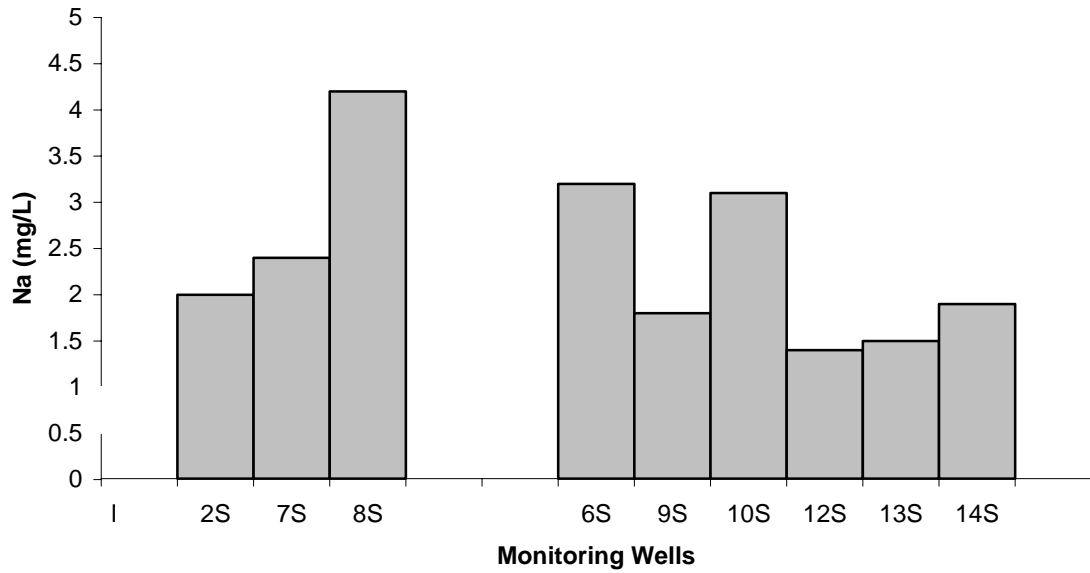


Figure C-10. Sodium

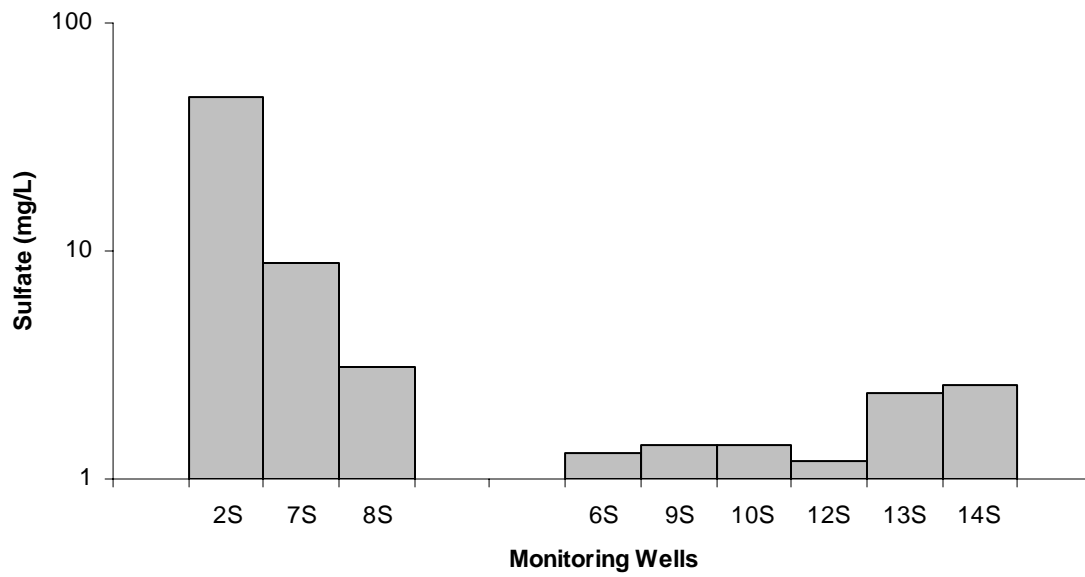


Figure C-11. Sulfate

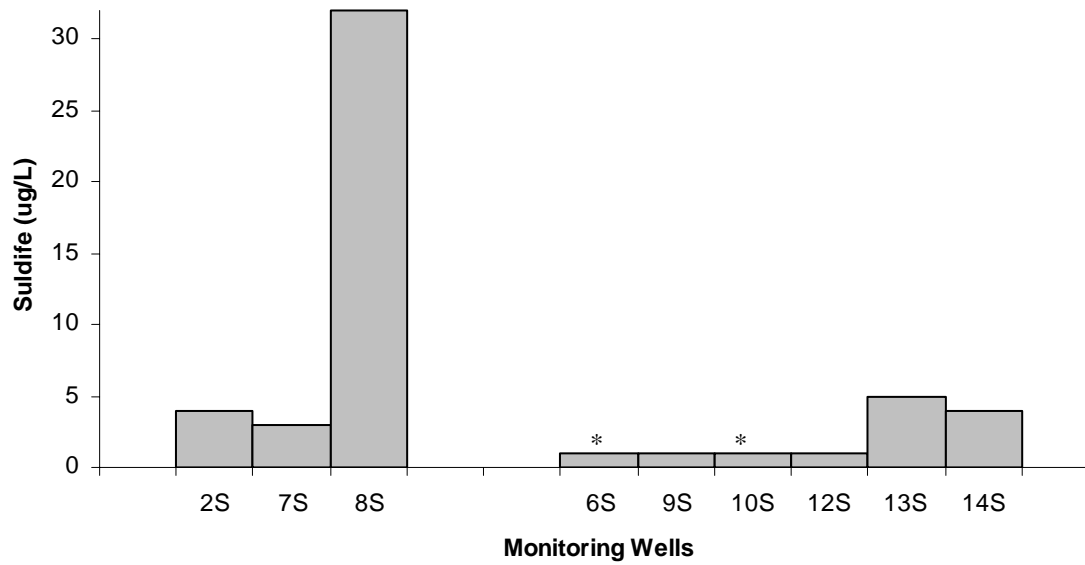


Figure C-12. Sulfide
 (* indicates samples that are below detection limit, 1 ug/L)

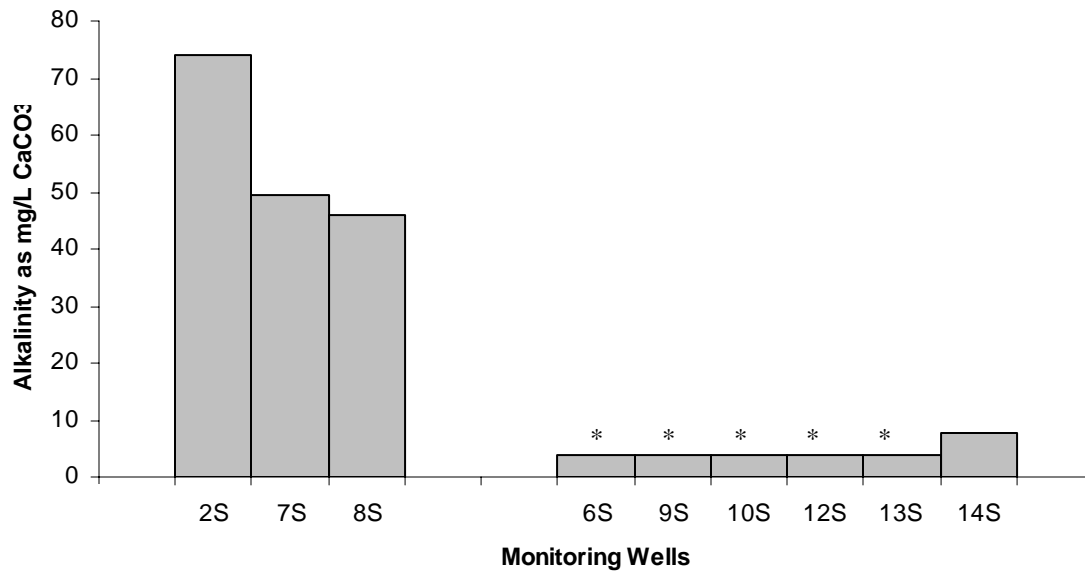


Figure C-13. Alkalinity
 (* indicates samples that are below detection limit, 1 mg/L)

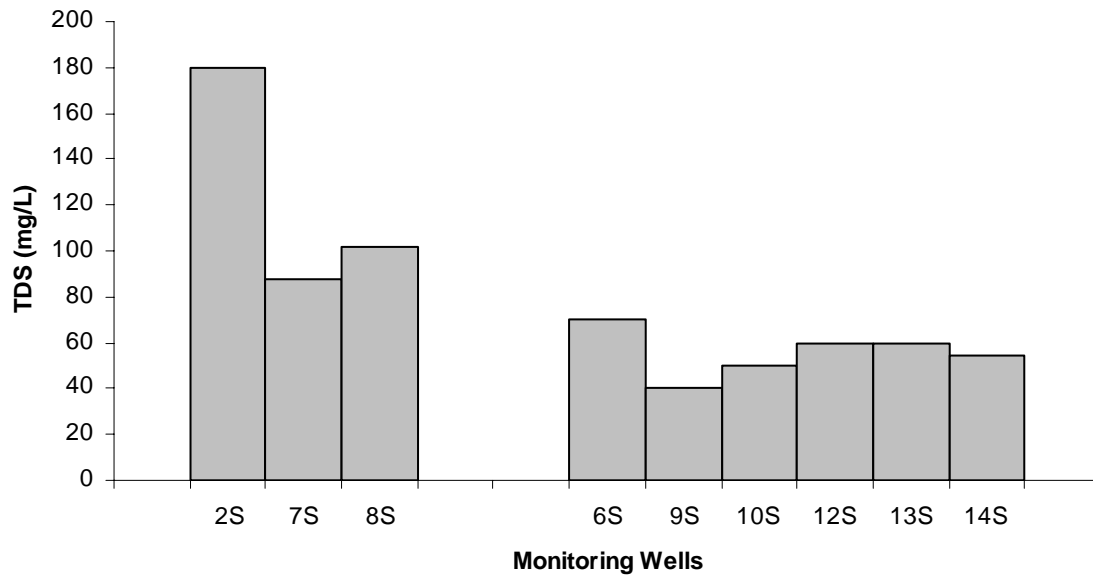


Figure C-14. Total Dissolved Solids (TDS)

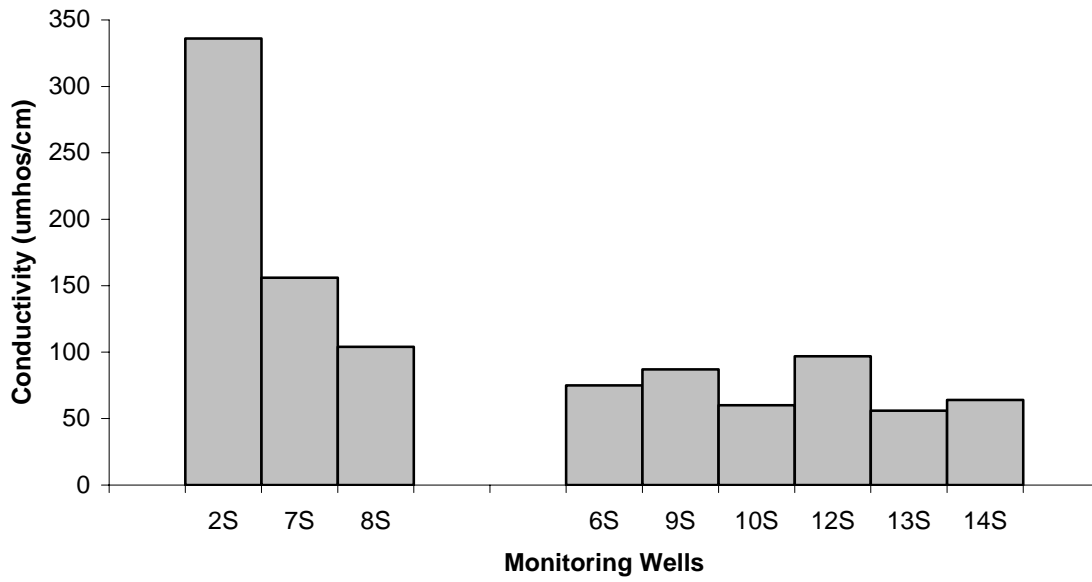


Figure C-15. Conductivity

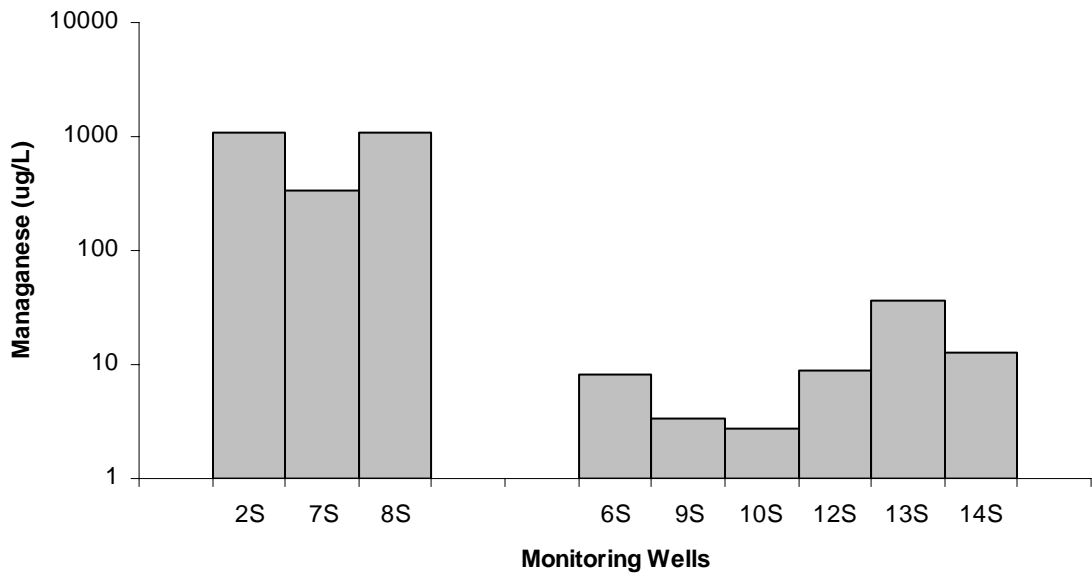


Figure C-16. Manganese

Appendix D
Comparison of Filtered and Unfiltered Iron Concentrations

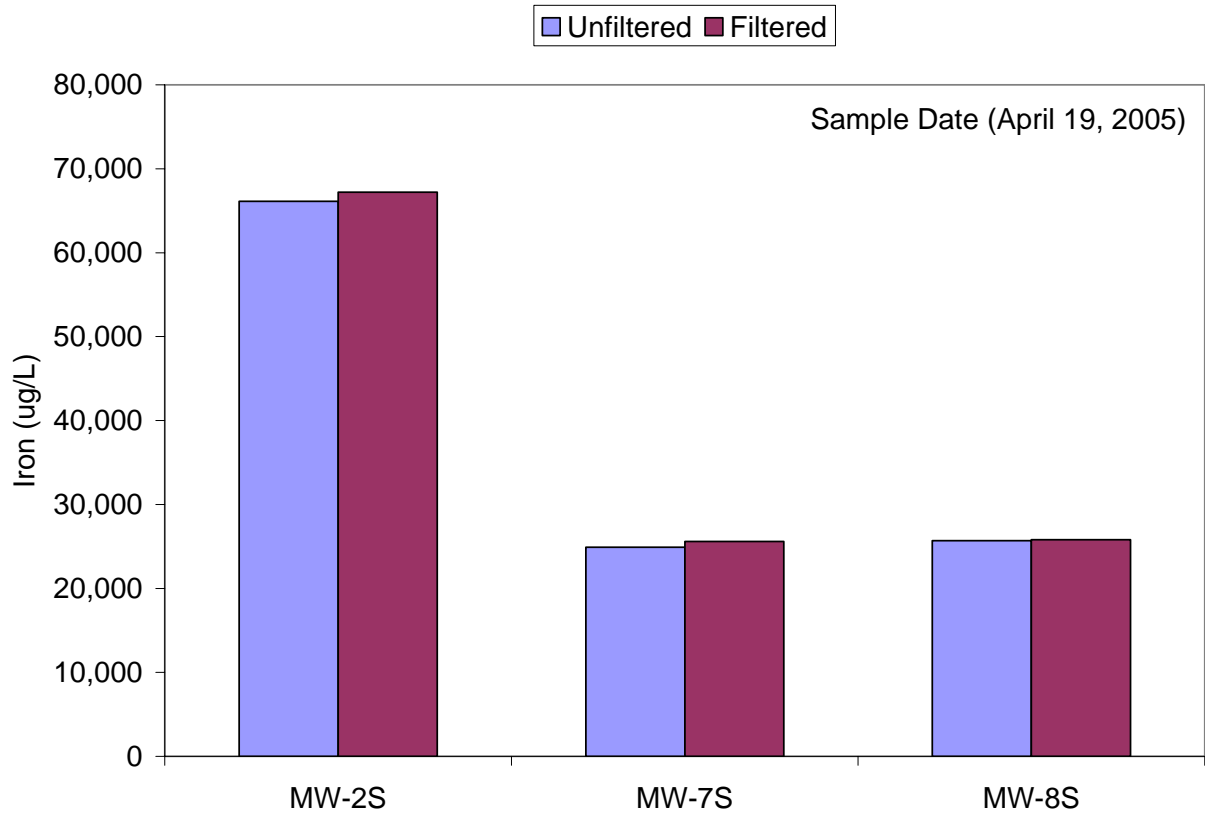


Figure D-1. Comparison of Iron Concentrations between Filtered and Unfiltered Groundwater Samples

Appendix E
Redox Reaction Chain

Sequence of Progressive Reduction of Redox Intensity by Organic Pollutants

O consumption (respiration)



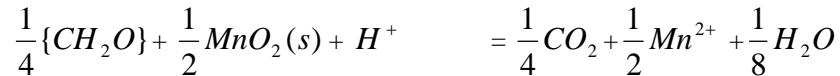
Denitrification



Nitrate Reduction



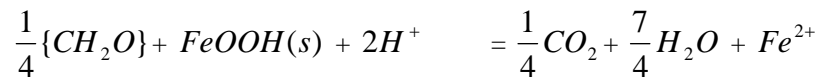
Production of Soluble Mn(II)



Fermentation



Production of Soluble Fe(II)



Sulfate reduction, production of HS



Methane Fermentation

