# Letter of Transmittal



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To: Susan Pelz, PE	From: Jon Powell
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Date: 8/31/2010			
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From:	***************************************	***************************************		
Jon Powell, PE				

#### Dear Susan:

I am pleased to provide you with two (2) copies of the Natural Attenuation with Monitoring Plan for the Central County Solid Waste Disposal Complex on behalf of Sarasota County Environmental Services, Solid Waste Operations. I can be reached at the telephone number above or at <a href="mailto:jpowell@iwcs.biz">jpowell@iwcs.biz</a> if you have questions. I anticipate that Sarasota County will be in touch with you soon to develop a schedule to discuss the contents of the report.

Best Regards,

Jon Powell

Dept. Of Environmental Protection

SEP 0 1 2010

Southwest District

# NATURAL ATTENUATION WITH MONITORING PLAN FOR THE CENTRAL COUNTY SOLID WASTE DISPOSAL COMPLEX

Prepared for:



# FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION SOUTHWEST DISTRICT

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4030 West Boy Scout Boulevard, Suite 700 Tampa, Florida 33607

On behalf of:

# SARASOTA COUNTY ENVIRONMENTAL SERVICES SOLID WASTE OPERATIONS

4000 Knights Trail Road Nokomis, Florida 34275

DRAFT - August 2010

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#### 1. Introduction

#### 1.1 Purpose

Sarasota County (the County) owns and operates the Central County Solid Waste Disposal Complex (the site), located in Nokomis, Florida. Elevated concentrations of iron, arsenic and total ammonia (collectively referred to herein as *constituents of concern (COCs)*) have been measured in groundwater in the vicinity of the site's lined Class I landfill area. A site assessment report (SAR) describing exceedances of groundwater regulatory thresholds at the site was prepared and submitted to the Florida Department of Environmental Protection (FDEP) under the provisions of Rule 62-780.600, Florida Administrative Code (FAC) in July 2009 (PBS&J 2009). The SAR proposed natural attenuation with monitoring (NAM) as the remediation strategy to address the groundwater standard exceedances.

The County contracted with Post, Buckley, Schuh, and Jernigan, Inc. (PBS&J) and its subcontractor Innovative Waste Consulting Services, LLC (IWCS) to develop a NAM plan for the County to submit to the FDEP. This report presents a detailed justification of NAM as an appropriate site rehabilitation strategy under the provisions of Rule 62-780 as well as the NAM plan.

#### 1.2 Site Description

The site opened in 1998 with a 55-acre lined cell (Phase I) on an approximately 6,000-acre complex located in Sections 1 through 4 and 9 through 16 of Township 38 South, Range 19 East (Figure A-1 in Appendix A). Waste disposal has occurred in this cell since 1998. The construction of second lined cell (Phase II) was recently completed and waste placement began on 16 August 2010. Phase II is located west of Phase I and is approximately 58 acres. The site's related facilities include a construction and demolition debris recycling facility, a yard waste composting area, and a waste tire processing facility. A layout showing the locations of different site features is presented in Appendix A.

#### 1.3 Summary of Previous Groundwater Assessments

The groundwater monitoring program at the site began in 1998; historical groundwater monitoring parameter trend charts are presented in Appendix B. Because of elevated levels of arsenic, total ammonia and iron in certain monitoring wells, the County initiated groundwater monitoring on a quarterly basis beginning in 2008, and conducted a contamination evaluation in 2008 per the requirements of Rule 62-701, FAC. The contamination evaluation report, submitted to the FDEP in October 2008, indicated that the FDEP's water quality standards were violated beyond the facility's permitted zone of discharge (PBS&J 2008). The County entered into a consent order with the FDEP in October 2008 to resolve the groundwater contamination issue. The consent order required the County to conduct a site assessment and submit a SAR to the FDEP. The SAR was submitted to the FDEP in July 2009. An addendum to the SAR is currently being prepared and will be submitted to the FDEP under separate cover.

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# 1.4 Report Organization

This report is organized into seven (7) sections as summarized in Table 1-1.

**Table 1-1. Report Organization** 

Section Content Description					
Section	•				
Section 1.0	<ul> <li>A description of the purpose of this report</li> </ul>				
	A brief description of the site				
	A summary of the relevant previous groundwater assessments				
Section 2.0	<ul> <li>A list of the regulatory criteria that must be met to propose NAM as a appropriate site rehabilitation strategy</li> </ul>				
	<ul> <li>An evaluation of the regulatory criteria along with justifications of the appropriateness of NAM as a site rehabilitation strategy</li> </ul>				
	A life-cycle cost estimate of a remedial alternative				
Section 3.0	<ul> <li>A description of the site hydrogeological data relevant to this report</li> </ul>				
	<ul> <li>A description of groundwater monitoring activities and regulatory actions</li> </ul>				
	<ul> <li>An assessment of the historical groundwater and leachate quality data to identify parameters that have exceeded the regulatory groundwater quality thresholds</li> </ul>				
	<ul> <li>A quantitative assessment to evaluate whether leachate release from the lined cells is the cause of the groundwater contamination</li> </ul>				
	An assessment of the site soil data				
Section 4.0	<ul> <li>Introduction of reductive dissolution of iron from site soils as a plausible cause for the groundwater standard exceedances of COCs</li> </ul>				
	<ul> <li>A review of the literature documenting cases in Florida and elsewhere where elevated levels of COCs have been measured in the groundwater from reductive dissolution of naturally-occurring iron minerals</li> </ul>				
	<ul> <li>An analysis of the historical groundwater and soil data from the site to evaluate the correlation between the arsenic and iron concentrations and total ammonia and iron concentration to evaluate whether elevated levels of arsenic and total ammonia in groundwater are related to the corresponding iron levels</li> </ul>				
·	<ul> <li>A summary of the findings of the laboratory studies conducted by University of Florida researchers to evaluate the role of reductive dissolution of iron in elevated levels of COCs in the groundwater</li> </ul>				
- Winness	<ul> <li>Contaminant fate and transport modeling to assess whether reductively-dissolved iron would be amenable to natural</li> </ul>				

Section	Content Description
	<ul> <li>attenuation as it percolates through the oxygenated surficial aquifer zone surrounding the impacted area</li> <li>Results of the sorption tests conducted on soil samples collected from the site and fate and transport modeling to assess whether the naturally-occurring soil surrounding the impacted area has the ability to sorb COCs from the impacted groundwater</li> </ul>
Section 5.0	<ul> <li>Approach for the selection of temporary point of compliance well locations</li> </ul>
	<ul> <li>Fate and transport modeling to assess the plume migration of COCs in relation to the proposed temporary point of compliance wells</li> </ul>
Section 6.0	Proposed NAM plan
Section 7.0	A list of the references cited in the report

Additional information and data relevant to the assessment are presented in appendices included at the end of the report. Appendix A presents site layouts. Appendix B presents historical groundwater monitoring parameter trend charts. Appendix C presents a life-cycle cost analysis of a remedial alternative.

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# 2. Justification of Natural Attenuation with Monitoring

#### 2.1 Review of NAM Requirements

Rule 62-701, FAC requires routine monitoring of groundwater at landfill sites for several water quality parameters and outlines corrective action provisions in the event any of the monitored parameters exceeds the background levels or the water quality standards established by the FDEP. If the water quality standards are exceeded at the groundwater monitoring detection wells, the rule requires the initiation of contamination evaluation and water quality monitoring at the permitted zone of discharge. If water quality standards are exceeded at the permitted zone of discharge, the Rule requires corrective actions to comply with Rule 62-780, which mandates the initiation of a site assessment within 60 days of the discovery of the water quality violation. The water quality standard for iron, arsenic and total ammonia was exceeded outside the permitted zone of discharge of the site. The County contracted with PBS&J to conduct a site assessment in 2009 to evaluate the exceedances. A SAR was prepared by PBS&J and submitted to the FDEP in July 2009.

Rule 62-780 requires the identification and proposal of a risk-based corrective action (RBCA) as a part of the site assessment – RBCAs listed in Rule 62-780 are as follows:

- No Further Action (NFA) (with or without engineering and/or institutional controls),
- NAM, and
- Active Remediation.

Rule 62-780 also outlines criteria that should be evaluated when selecting and proposing a rehabilitation strategy. The rule allows for NAM as a site rehabilitation strategy, subject to the following individual site characteristics:

- The current and projected use of the affected groundwater and surface water in the vicinity of the site and the current and projected land use of the area affected by the contamination,
- The exposed population,
- The location of the plume,
- The degree and extent of contamination,
- The rate of migration of the plume,
- The apparent or potential rate of degradation of contaminants through natural attenuation, and
- The potential for further migration in relation to the site's property boundary.

Table 2-1 lists the regulatory criteria that must be met to propose NAM as a remedial strategy.

#### Table 2-1. NAM Applicability Criteria from Rule 62-780.690(1), FAC

- # Criteria Description
- (a) Free product is not present or free product removal is not technologically feasible and no fire or explosive hazard exists as a result of a release of non-aqueous phase liquids;
- (b) Contaminated soil is not present in the unsaturated zone, except that applicable leachability-based soil CTLs may be exceeded if it is demonstrated to the Department that the soil does not constitute a continuing source of contamination to the groundwater at concentrations that pose a threat to human health, public safety, and the environment, and it is demonstrated that the rate of natural attenuation of contaminants in the groundwater exceeds the rate at which contaminants are leaching from the soil. The determination shall be based upon individual site characteristics and demonstrated by USEPA Test Method 1312 (SPLP), or USEPA Test Method 1311 (TCLP) if the contamination is derived from used oil or similar petroleum products, followed by the appropriate analyses of the leachate, and based upon groundwater modeling, site stratigraphy, or site assessment results;
- (c) Contaminants present in the groundwater above background concentrations or applicable CTLs are not migrating beyond the temporary point of compliance or migrating vertically, which may contaminate other aquifers or surface water resources or result in increased site rehabilitation time;
- (d) The physical, chemical, and biological characteristics of each contaminant and its transformation product(s) are conducive to natural attenuation;
- (e) The available data show an overall decrease in the contamination; and
- (f) One of the following is met:
  - 1. The site is anticipated to achieve the applicable No Further Action criteria of Rule 62-780.680, F.A.C., as a result of natural attenuation in five years or less, the background concentrations or the applicable CTLs are not exceeded at the temporary point of compliance as established pursuant to subsection 62-780.690(2) or 62-780.690(3), F.A.C., and contaminant concentrations do not exceed the criteria specified in Chapter 62-777, F.A.C., Table V; or
  - 2. If the criteria of subparagraph 62-780.690(1)(f)1., F.A.C., are not met, the appropriateness of natural attenuation with monitoring may be demonstrated by the following:
    - a. A technical evaluation of groundwater and soil characteristics, chemistry, and biological activity that verifies that the contaminants have the capacity to degrade under the site-specific conditions. A listing of the site-specific conditions and geochemical parameters, as applicable, is provided in Chapter 62-777, F.A.C., Table IV;
    - b. A scientific evaluation (historical data or modeling results, as appropriate; the model used shall be demonstrated to be appropriate for the site conditions) of the plume migration in relation to the temporary point of compliance as established pursuant to subsection 62-780.690(2) or 62-780.690(3), F.A.C., an estimation of expected annual reductions in contaminant concentrations in monitoring wells, and an estimation of the time required to meet the applicable No Further Action criteria of Rule 62-780.680, F.A.C. Available technical information (including historical water quality data) shall be used for model calibration; and
    - c. A life-cycle cost analysis of remedial alternatives.

#### 2.2 Justification of NAM

This section presents an assessment of the applicability of NAM as a site rehabilitation approach based on:

- an evaluation of groundwater and soil analytical data for the site (presented in detail in Section 3.0),
- a review of the pertinent technical literature (Section 4.0),
- the results of the University of Florida's research on reductive dissolution (Section 4.0),
- fate and transport modeling conducted to evaluate aquifer reaeration and sorption as natural attenuation mechanisms for the COCs (presented in Section 4.0), and
- fate and transport modeling conducted to assess plume migration of COCs with respect to the proposed temporary point of compliance (presented in Section 5.0).

Rule 62-780 allows fate and transport models to be used to support the appropriateness of NAM as a remedial strategy. The criteria listed in Table 2-1 are presented below along with a discussion of each criterion with respect to its impact on NAM applicability.

#### 2.2.1 Free Product Presence and Removal

The first criterion that must be met for NAM to be an allowable site rehabilitation strategy is that "free product is not present or free product removal is not technologically feasible and no fire or explosive hazard exists as a result of a release of non-aqueous phase liquids." Free product is defined in Rule 62-780.200(21) as "the presence of a non-aqueous phase liquid in the environment in excess of 0.01 foot in thickness, measured at its thickest point." Non-aqueous phase liquids (NAPLs) are organic compounds (or a mixture of compounds) that are immiscible (resistant to mixing) in water (US EPA 1991) and that are sometimes present at contaminated sites where large amounts of organic liquids have been disposed (e.g., leaking petroleum tanks, dry cleaner sites). Since the presence of these highly concentrated organics would serve as a source for ongoing environmental contamination, they should be removed if appropriate. The COCs at the site (iron, arsenic and total ammonia) are inorganic and as described later in the report appear to originate from the existing site soils. The investigations conducted previously at the site show that free product is not present at the site and thus this criterion is met (PBS&J 2009).

#### 2.2.2 Soil Assessment

The second criterion that must be met for NAM to be an appropriate remedial strategy is that "Contaminated soil is not present in the unsaturated zone". Similar to the free product criterion, the purpose of this criterion is to ensure that contaminated soils (e.g., contaminated soil placed on site, or soil contaminated as a result of a discharge to on-site soils) do not remain on site and thus serve as an ongoing source of contamination. For the most part, the soil at the site is the natural site soil and is not hauled from outside sources for the site's development. The site was a Greenfield site before landfill development and there is no evidence of any previously-existing contamination. This criterion is met because the source of the groundwater exceedances at the site is the

natural site soils. As additional justification, soil analytical data were analyzed with the results summarized as follows.

Per 62-780.200(11), FAC "contaminated" or "contamination" means the presence of free product or any contaminant in surface water, groundwater, soil, sediment, or upon the land, in concentrations that exceed the applicable cleanup target levels (CTLs) specified in Rule 62-777, FAC. Many soil samples were collected from the unsaturated zone and characterized for total iron, arsenic, copper, chromium, lead, and nitrogen contents as a part of the Contamination Evaluation and Site Assessment studies at the landfill in 2008 and 2009, respectively, to assess whether the contaminated soil was present at the site (PBS&J 2008, PBS&J 2009). When the 95% UCLs of the constituent concentrations were compared to the respective soil cleanup target level (SCTL) and the background concentrations of these constituents in Florida soils reported in the literature (Ma et al. 1999), none of the constituents exceeded the respective SCTL and all were well below the respective average background concentrations reported for Florida soils. The SPLP was performed on 16 of the soil samples collected in 2008 and 2009 and SPLP leachate samples were analyzed for arsenic, total ammonia, and nitrate. None of the samples exceeded the GWCTL for total ammonia and nitrate. Arsenic was not detected in 13 out of the total 16 samples. Only 1 out of the 16 samples exceeded the GWCTL for arsenic. The maximum arsenic concentration measured for any SPLP leachate was 0.011 mg/L, just above the GWCTL of 0.01 mg/L. Iron was not measured in SPLP leachate. These data are presented and discussed in Section 3.0.

The data demonstrate that the soil at the site does not contain the COCs at concentrations greater than the direct exposure and leachability CTLs specified in Rule 62-777, FAC and therefore by definition is not contaminated.

#### 2.2.3 Migration of Contaminants Outside of the Temporary Point of Compliance

The third criterion that a site must meet for NAM to be an allowable site rehabilitation strategy is as follows: "contaminants present in the groundwater above background concentrations or applicable CTLs are not migrating beyond the temporary point of compliance or migrating vertically, which may contaminate other aquifers or surface water resources or result in increased site rehabilitation time."

The potentiometric surface elevation of the upper Floridan aquifer is reportedly higher than the water table in the surficial aquifer system around the site. The contaminants from the surficial aquifer system, therefore, are not expected to migrate vertically downwards and contaminate other aquifer systems at the site; more details are presented in Section 3.0. Appendix A presents several figures depicting the location of the temporary point of compliance (TPOC) wells as well as the arsenic, ammonia, and iron plumes after 200 years based on fate and transport modeling. The approach taken in the TPOC well location selection (described in more detail in Section 5.0) was to place the wells such that the contamination plume will not migrate beyond the TPOC. As the figures in Appendix A show, the modeled plume of the COCs is contained within the TPOC even after a period of 200 years.

#### 2.2.4 Natural Attenuation of COCs

The fourth criterion that a site must meet for NAM to be an allowable site rehabilitation strategy is as follows: "the physical, chemical, and biological characteristics of each contaminant and its transformation product(s) are conducive to natural attenuation."

The two processes that will naturally attenuate COCs at the site are sorption to the soil and aquifer reaeration. The ability of these two processes to result in natural attenuation of the COCs is demonstrated through contaminant fate and transport modeling in Section 4.0. Modeling results using site-specific partitioning coefficient data support that sorption of the COCs to the naturally-occurring soil will be a dominant removal mechanism and that further removal occurs as the reductively-dissolved iron oxidizes and precipitates out as iron minerals when the soil aquifer returns to the natural oxygenated environment away from the landfill. Based on the review of the literature and correlation of arsenic and total ammonia concentration with iron concentration in groundwater, arsenic and total ammonia concentrations are expected to decrease with decreasing iron concentrations because of sorption on ferric oxides and hydroxides or co-precipitation with iron to revert back to previous forms in the natural soil. In addition, total ammonia not otherwise removed will undergo nitrification over time in a more oxidized environment, thereby undergoing nitrification and denitrification to ultimately transform to nitrogen. The COCs and their transformation products are expected to be conducive to natural attenuation.

#### 2.2.5 Contaminant Concentration Trend

The fifth criterion that a site must meet for NAM to be an allowable site rehabilitation strategy is as follows: "the available data show an overall decrease in the contamination."

The site's groundwater quality data collected to date do not currently show an overall decrease in the concentration of the COCs. The fate and transport modeling conducted as part of this report suggests that the concentration of COCs will decline as the plume moves away from the landfill and through the portion of the surficial aquifer undergoing active reaeration via sorption and oxidation and precipitation of the reduced iron. The iron release will decline once the majority of iron that has a propensity to reductively dissolve and become solubilized is released from the soil matrix.

#### 2.2.6 Natural Attenuation Rate Assessment

The last criterion that the site must meet for NAM to be an allowable site rehabilitation strategy is as follows:

One of the following is met:

1. The site is anticipated to achieve the applicable No Further Action criteria of Rule 62-780.680, F.A.C., as a result of natural attenuation in five years or less, the background concentrations or the applicable CTLs are not exceeded at the temporary point of compliance as established pursuant to subsection 62-780.690(2)

- or 62-780.690(3), F.A.C., and contaminant concentrations do not exceed the criteria specified in Chapter 62-777, F.A.C., Table V; or
- 2. If the criteria of subparagraph 62-780.690(1)(f)1., F.A.C., are not met, the appropriateness of natural attenuation with monitoring may be demonstrated by the following:
  - a. A technical evaluation of groundwater and soil characteristics, chemistry, and biological activity that verifies that the contaminants have the capacity to degrade under the site-specific conditions. A listing of the site-specific conditions and geochemical parameters, as applicable, is provided in Chapter 62-777, F.A.C., Table IV;
  - b. A scientific evaluation (historical data or modeling results, as appropriate; the model used shall be demonstrated to be appropriate for the site conditions) of the plume migration in relation to the temporary point of compliance as established pursuant to subsection 62-780.690(2) or 62-780.690(3), F.A.C., an estimation of expected annual reductions in contaminant concentrations in monitoring wells, and an estimation of the time required to meet the applicable No Further Action criteria of Rule 62-780.680, F.A.C. Available technical information (including historical water quality data) shall be used for model calibration; and
  - c. A life-cycle cost analysis of remedial alternatives.

Criterion 1 requires the site to achieve No Further Action (NFA) criteria in 5 years or fewer. One of the criteria of NFA is that the groundwater contaminants do not exceed the less stringent of (a) the CTLs specified in FAC 62-777 or (b) background levels. The Site will achieve NFA when the process of iron release (and related release of arsenic and ammonia) through reductive dissolution ceases or becomes minimal and when the released COCs are returned to the solid phase via precipitation or sorption. Based on the technical evaluation of the natural attenuation mechanisms and the modeling presented in subsequent sections, NFA is not anticipated to be reached within 5 years. Therefore, criterion 1 was not used for justification of NAM as an approach.

An assessment of criterion 2 is presented as follows:

a) Technical Evaluation of Contaminants' Capacity to Degrade. The term "degrade" normally applies to organic compounds that are biologically or chemically transformed to less harmful organic compounds or converted to carbon dioxide. Two of the COCs, iron and arsenic, would not "degrade" but would change form and revert back to their original condition in the environment and total ammonia would either revert back to its original mineral or bound form, or would be "degraded" by transformation to another nitrogen compounds such as N<sub>2</sub> gas. These COCs are not organic and thus would not fit the classic definition of "degrade." The COCs are released from naturally-occurring minerals at the site because of the hydrogeochemical change — specifically decrease in the atmospheric oxygen transfer to the aquifer system — induced by site development activities. The modeling conducted as a part of this report evaluated the impact

of sorption and aquifer reaeration on fate and transport of COCs. The lab tests and modeling results suggest that the COCs will be sorbed to the naturally-occurring soil in the undisturbed areas surrounding the developed area. In addition, the modeling results suggest that iron will oxidize and precipitate out and its concentration would decrease with distance from the landfill. The COCs are expected to be removed from the groundwater and return to their stable state in the environment, which has the same ultimate impact as degradation. The COCs that are being released from the part of the site that has been developed would be transported and deposited in the undisturbed natural area of the site.

- b) Scientific Evaluation of Plume Migration with Respect to the Temporary Point of Compliance. Fate and transport modeling was conducted to evaluate plume migration with respect to the TPOC. Plumes of the COCs were contained within the TPOC after a 200-year modeling period. More details on the TPOC well location selection approach and justification, as well as modeling inputs and results are presented in Section 5.0. The site is expected to achieve NFA criteria and reduction in the concentration of COCs in monitoring wells only after the iron mass that has propensity to undergo reductive dissolution is released. The data and tools to make an accurate estimation of the time that the naturally-present iron minerals will continue to reductively dissolve, however, are not available. The exact time period that the site will reach the concentrations needed to achieve NFA or annual reduction in COCs concentration, therefore, can not be estimated at this point. However, substantial evidence is available (presented in Sections 4.0 and 5.0) to conclude that the COCs would be naturally attenuated via sorption and aquifer reaeration as the impacted groundwater percolates through the surficial aquifer soil in the undisturbed areas surrounding the developed areas of the site.
- c) Life-cycle cost analysis of the remedial alternatives. A life-cycle cost analysis of a pump-and-treat system as a remedial alternative was conducted based on site-specific groundwater flow rate, an assumed iron release rate, and assumed operational lifetime of 30 years. The system would consist of groundwater extraction wellpoints, a lined aeration pond and a settling pond impacted groundwater would be pumped out, aerated, and the precipitated iron would be removed and disposed while the treated water would percolate back into the surficial aquifer. The capital cost for system construction was approximately \$1.8 million and the annual operation and maintenance cost was estimated to be \$57,700. Appendix C provides further details of the cost estimate.

#### 2.3 Summary

Several criteria must be met for NAM to be considered an allowable strategy to address groundwater contamination per Rule 62-780. Existing monitoring data show that free product and contaminated soil are not present at the site. The nature of the contamination that exists at the site (inorganic compounds) and the technical assessment

of the biogeochemistry associated with each of the COCs suggests that these chemicals will ultimately be transformed, reverting back to a chemical form that will result in a reduction of their respective concentrations in groundwater at the site within the proposed TPOC. The technical discussion and modeling show that sorption to the naturally-occurring soil and natural reaeration of the surficial aquifer will lead to a reduction in the concentration of the COCs. Based on the discussion above, NAM is concluded to be an appropriate rehabilitation strategy for the site.

## 3. Review of Site Hydrogeology and Monitoring Data

#### 3.1 Site Hydrogeology

The hydrogeologic units at the site consist of the surficial aquifer system, the intermediate aquifer system, and the Floridan aquifer system. Ardaman & Associates (2008), based on site-specific borings, reported that the surficial aquifer system thickness ranges from approximately 14 to 16.5 ft and mostly consists of fine sand, fine sand with silt, and silty fine sand. The potentiometric surface elevation in the Upper Floridan aquifer is reported to be always higher than the water table, suggesting that the groundwater does not flow from the surficial aquifer system to the Floridan aquifer system.

The groundwater flow direction varies somewhat and ranges from west to south-southwest. The average hydraulic gradient in the surficial aquifer system in the site's Phase II area is reported to range from 0.0005 to 0.0011; the steepest gradients have been reported to range from 0.003 to 0.006. Site-specific hydraulic conductivity of the surficial aquifer system is reported to range from 0.25 ft per day to 4.1 ft per day. The effective porosity of the surficial aquifer has been reported to be 0.25. Based on the steepest gradient range, hydraulic conductivity range and the effective porosity, the maximum groundwater velocity in the surficial aquifer is expected to range from 1.1 ft to 36 feet per year. The storage coefficient has been reported to range from 0.15 to 0.19.

### 3.2 Timeline of Site Activities, Monitoring Activities, and Regulatory Actions

The groundwater monitoring system for the period of 1998 to 2007 consisted of one background well (MW-1), seven detection wells (MW-2, MW-4, MW-8, MW-9, MW-10, MW-11, MW-12), and two piezometers (MW-3 and MW-5); MW-1, MW-4, MW-8, MW-10, MW-11, and MW-12 were replaced with MW-1R, MW-4R, MW-8A, MW-10R, MW-11R, and MW-12R, respectively, at various points during this period. For simplification the replacement wells are identified by the original well IDs in this report. Monitoring of MW-2 and MW-4 was discontinued in 2001 and 2007, respectively. The groundwater monitoring during this period was conducted semi-annually per the site's permit requirements. The monitoring wells listed above were sampled on a quarterly basis in 2008 and part of 2009. Since August 2009, wells have been sampled semi-annually.

Twenty additional wells (GW-1 through GW-16 and DGW-1 through DGW-4), referred to herein as *CE wells*, were installed in 2008 outside of the facility's zone of discharge as part of contamination evaluation. Fifteen additional wells (GW-17 through GW-31) were installed and sampled in 2009 as a part of the site assessment; CE wells that were not abandoned for the site's Phase II construction were also sampled as a part of the site assessment. Six detection wells (MW-15 through MW-20) were installed in 2009 for monitoring groundwater quality for Phase II. Eight additional wells (PW-1 through PW-

8) were installed in June 2010 as part of the SAR addendum that is being prepared in parallel with this report.

Table 3-1 identifies the installation date, the abandonment date (if applicable), and the well type of all the groundwater monitoring wells at the site. The site layout presented in Appendix A shows locations the groundwater monitoring wells described above and listed in Table 3-1.

Table 3-1. Groundwater Monitoring Wells at the Site

Well ID	Installation Date	Abandonment Date	Well Type
MW-1/MW-1R	1998		Background well
MW-3			Piezometer
MW-2	1998	2001	Detection well
MW-4	1998	2007	Detection well
MW-5			Piezometer
MW-8/MW-8A	1998		Detection well
MW-9	1998		Detection well
MW-10/MW-10R	1998		Detection well
MW-11/MW-11R	1998	2009	Detection well
MW-12/MW-12R	1998	2009	Detection well
CW-8A, CW-9, CW-10R	2008		Compliance wells
CW-11R	2008	2009	Compliance well
GW-1 through GW-8	2008	2009	Temporary wells
GW-9 through GW-16	2008		Temporary wells
DGW-1 and DGW-2	2008		Deep temporary wells
DGW-3 and DGW-4	2008	2009	Deep temporary wells
GW-17 through GW-31	2009		Temporary wells
MW-15 through MW-20	2009		Phase II detection well
PW-1 through PW-8	2010		Permanent wells

#### 3.3 Evaluation of Groundwater Monitoring Data

The groundwater monitoring data for the background well, detection wells and the CE wells collected from 1998 through 2010 were compiled to assess data distributions and the frequency of GWCTL exceedances for different parameters. Table 3-2 lists monitoring parameters that were measured above the GWCTL at least once for a given monitoring well. It also lists the GWCTLs and the number of measurements that exceeded the GWCTL. A table summarizing these exceedances for individual wells is presented in Appendix B. Trend charts for each of the parameters are also presented in Appendix B.

Table 3-2 shows that arsenic, iron, total ammonia, and total dissolved solids (TDS) frequently exceeded the respective GWCTL in multiple wells. GWCTL exceedances for

iron, arsenic, and total ammonia have been recorded at the site dating as far back as 1998 when many of the wells were first installed (refer to the trend charts presented in Appendix B for more details). Sodium, chloride, sulfate, zinc, aluminum, manganese, vanadium, and lead have recorded exceedances, as well. However, these exceedances have been far less frequent comparatively. The water quality data for wells PW-1 through PW-8 were obtained from Dunkelberger (2010), details of which will be provided to the FDEP under separate cover as part of an addendum to the SAR.

Table 3-2. Summary of GWCTL Exceedances by Constituent Between 1998 and 2010

Constituent	# of Detections	GWCTL (mg/L)	# of GWCTL Exceedances	Well(s) where GWCTL Exceedance Occurred
Arsenic	184	0.05 up to	82	MW-1, 8, 9, 10, 11, 12, 13,
		12/31/2004		15, 16, 17, 19, 20, CW-8,
		and 0.01		9, 10, 11, PW-7 and 8
		thereafter		
Iron	215	0.3	214	MW-1, 2, 4, 8, 9, 10, 11,
				12, 13, 15, 16, 17, 18, 19,
				20, CW-8, 9, 10, 11, PW 1
				through 8
Total	215	2.8	109	MW-8, 9 , 10, 11, 12, 15,
ammonia				16, 17, 19, 20, CW-8, 9,
				10, 11, PW-7
TDS	216	500	156	MW-1, 2, 8, 9, 10, 11, 12,
				13, 15, 16, 17, 18, 19, 20,
				CW-8, 9, 10, 11, PW-1, 2,
		· · · · · · · · · · · · · · · · · · ·		4, 5, 7, 8
Sodium	204	160	22	MW-1, 12, 16, PW-1, 5, 7
Chloride	201	250	23	MW-1, 12, 16, PW-5, 7
Manganese	29	0.05	3	MW-15, PW-4, 8
Sulfate	49	250	6	MW-12, 15, CW-10
Zinc	59	5	8	MW-1, 2, 4, 8, 9, 10, 11,
				12
Lead	16	0.015	4	MW-8, 9, 20
Aluminum	2	0.2	2	MW-17, 18
Vanadium	1	0.049	11	MW-20

A box-and-whisker plot was constructed for various parameters to compare concentrations among the background, detection, and compliance wells. These plots provide a visual portrayal of the statistical distribution of the data. Figure 3-1 presents a definition sketch of the box-and-whisker plot. The line inside the box represents the median. The top of the box represents the 75<sup>th</sup> percentile and the bottom of the box represents the 25<sup>th</sup> percentile. The lines that extend upward and downward (whiskers) from the box represent the 90<sup>th</sup> and 10<sup>th</sup> percentiles, respectively. The outliers are presented individually outside the whiskers.

Figures 3-2, 3-3, and 3-4 show box-and-whisker plots of arsenic, iron, total ammonia, TDS, sodium, and chloride data collected from 1998 through 2010. These plots also show concentration distributions of these parameters in leachate samples collected from the site from 1998 through 2009 as part of routine monitoring.

As shown in Figures 3-2, 3-3 and 3-4, the background well (MW-1) exhibited exceedances of iron, TDS, sodium, and chloride, indicating that the groundwater naturally contains elevated concentrations of these parameters.

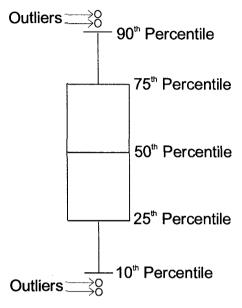


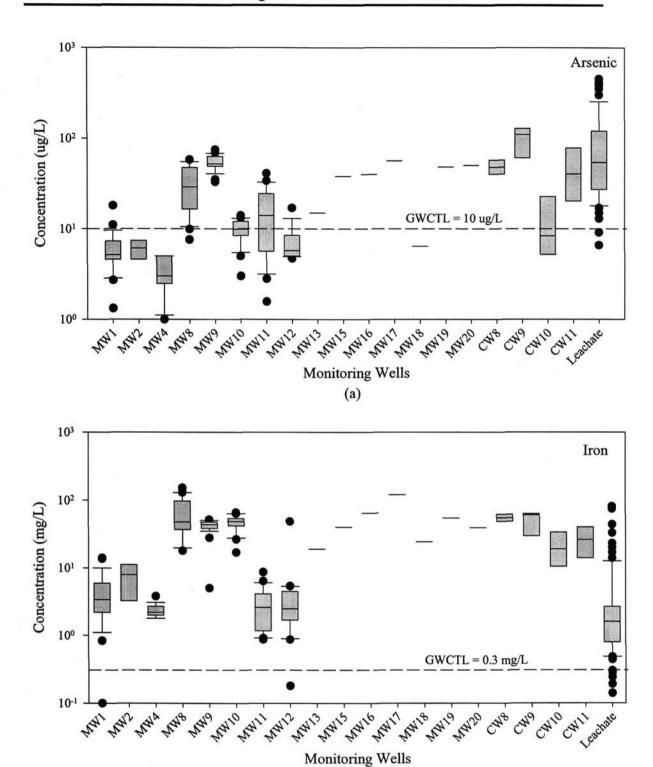
Figure 3-1. Box-and-Whisker Plot Definition Sketch

Figures 3-2 and 3-3 show the iron, arsenic, and total ammonia concentrations measured in the detection wells located south of Phase I were higher than those recorded at the wells located on the other three sides of Phase I. As the groundwater at the site is reported to flow generally in the west to south-southwest direction, the presence of the lined cell appears to impact iron, arsenic, and total ammonia concentrations in groundwater as groundwater flows beneath the lined cell.

The site layout and the reported groundwater flow direction shows that the compliance wells are located down gradient of the respective detection wells, i.e. compliance wells are located farther from the landfill than the detection wells. As demonstrated with the modeling results presented in Section 4.8, the contaminant concentration in the well located farther would always be less than or equal to those measured at the well located closer to the source. As can be seen from Figures 3-2 and 3-3, the median iron, arsenic and total ammonia concentrations in the compliance wells were, for the most part, greater than the median concentrations in the respective detection wells suggesting that landfill is not the sole cause of elevated levels of these parameters in groundwater. The median concentration of arsenic in CW-9 was significantly greater than that in leachate suggesting leachate release from the landfill is not a significant cause of arsenic exceedances at the site. As the nitrate and nitrite concentrations measured in groundwater were much lower than those of total ammonia, the reduction

of naturally-occurring nitrate and nitrite in groundwater does not seem to be a major cause of the elevated concentrations of total ammonia measured in groundwater; refer to Figure B-1 in Appendix B for nitrate and nitrite concentrations measured at the site.

Figure 3-4 shows that all but three exceedances for sodium and chloride were in the background well MW-1. As shown in Appendix B, the sodium, chloride and TDS concentrations in MW-1 decreased by more than an order of magnitude in 2007. The concentrations of these constituents since 2008 have been less than the respective GWCTLs. Similar to iron, arsenic and total ammonia, another interesting observation worth noting is that for the most part the median concentration of sodium and chloride in the compliance wells were greater than that of the respective detection wells (e.g., median chloride concentration in MW-8 was lower than the median chloride concentration in CW-8).



(b)

Figure 3-2. Box-and-Whisker Plot of (a) Arsenic, and (b) Iron

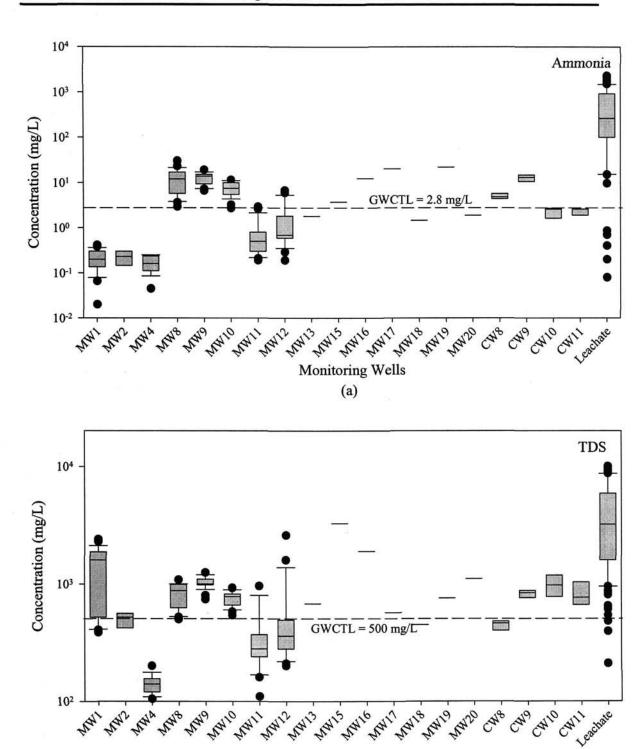
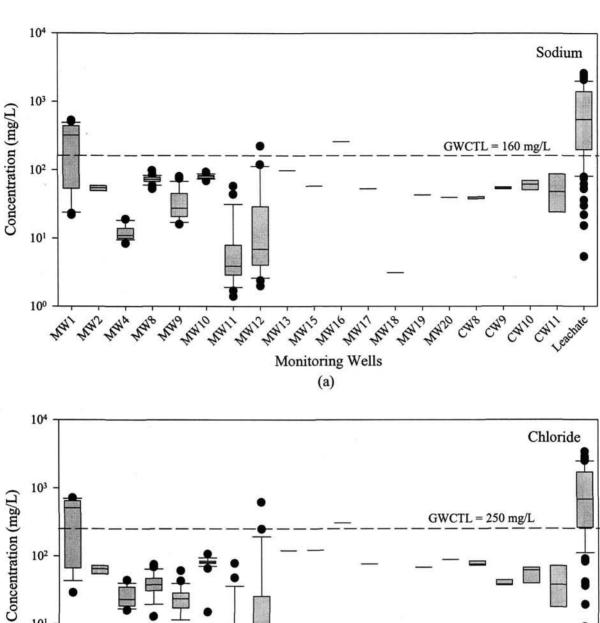


Figure 3-3. Box-and-Whisker Plot of (a) Total Ammonia, and (b) Total Dissolved Solids (TDS)

Monitoring Wells (b)



Nonitoring Wells

(b)

Figure 3-4. Box-and-Whisker Plot of (a) Sodium, and (b) Chloride

#### 3.4 Assessment of Leachate Release as a Cause of Groundwater Contamination

This section presents an assessment of whether a leachate release from the landfill could be a cause of groundwater contamination at the site. In this contamination pathway the leachate would leak from the liner system and mix with the groundwater, thus impacting groundwater quality. The concentration of constituents in the mixture is expected to be less than the concentration in the leachate because of dilution.

There are several indicator parameters commonly used to assess whether leachate migration is the cause of groundwater contamination at municipal solid waste (MSW) landfills. Strong indicators of leachate contamination include soluble salts (such as chloride), total ammonia, and organic chemicals (e.g., volatile organic compounds (VOCs)). In this evaluation, it was assumed that the chemical constituents measured in the leachate samples were representative of the leachate in the landfill.

The ratio of iron and arsenic concentrations to chloride concentrations were calculated for groundwater and leachate samples. In the event that leachate release is the major contributor to groundwater contamination, the chemical concentration ratio for groundwater should be similar to the ratio for leachate. Figure 3-5 presents box-and-whisker plots of arsenic-to-chloride and iron-to-chloride ratios for leachate and groundwater well MW-8, which is one of the detection wells that has shown substantial increases in arsenic and total ammonia concentrations over time. The concentration ratio of both the contaminants in leachate was significantly different than the concentration ratio in groundwater suggesting that the leachate is not a major factor in groundwater contamination at the site.

Organic compound (e.g., VOCs, Semi-VOCs) analytical data for leachate and groundwater were compiled and analyzed to identify correlations between their concentrations in leachate and groundwater. A wider range of organic compounds were detected in leachate samples — more than 75 organic compounds were detected individually or in combination in at least one sample. A list of the compounds detected and the detection frequency is presented in Appendix B. Toluene, total xylene, naphthalene, ethylbenzene, benzene, acetone, and 1, 4-dichlorobenzene were detected in more than 30 leachate samples collected from 1998 through 2009; approximately 70 leachate samples collected since 1998 were analyzed for organic compounds. Box-and-whisker plots of these compounds are presented in Figure 3-6. It should be noted that acetone is used as a laboratory solvent for analysis of organic compounds and its detection may be a result of laboratory contamination or interference.

These compounds were for the most part not detected or detected infrequently since 1998. The six organic compounds that were occasionally detected in groundwater were: acetone, dichloromethane, xylene, toluene, carbon disulfide, and bis (2-ethylhexyl) phthalate. Acetone and bis (2-ethylhexyl) phthalate was detected in ten and five samples, respectively, collected from 1998 through 2009. All five detections for bis (2-ethylhexyl) phthalate occurred in the July 2009 sampling event at Phase II detection wells. Dichloromethane, xylene, toluene, and carbon disulfide were detected in two, two, one, and one sample(s), respectively, collected from 1998 through 2009; the

maximum xylene and toluene concentrations reported (for the samples that had detectable concentrations) were 0.32 and 0.2  $\mu g/L$ , respectively. The toluene concentration in leachate at the site reportedly ranged from 0.1 to 300  $\mu g/L$  and the total xylene concentration ranged from 0.29 to 210  $\mu g/L$ . Frequent detection of these compounds in leachate and the near absence of these compounds in groundwater indicates that leachate release is not a major contributor to the groundwater impacts measured at the site.

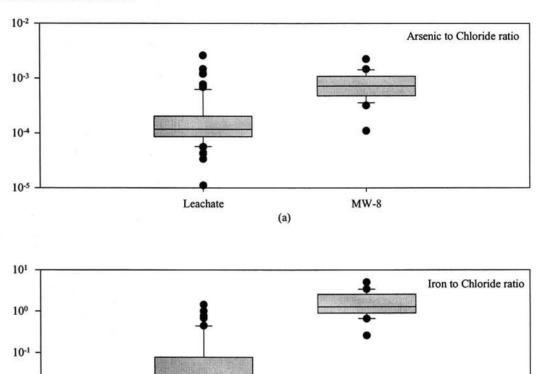


Figure 3-5. Box-and-Whisker Plot of (a) Arsenic-to-Chloride Ratio, and (b) Iron-to-Chloride Ratio

(b)

Leachate

MW-8

Iron, arsenic and total ammonia concentrations in many of the CE wells were greater than the respective detection well – this observation does not support the hypothesis that landfill leachate is a major contributor to groundwater impacts at the site. The maximum groundwater velocity was estimated to range from 1.1 to 36 ft per year. Neglecting diffusion, the maximum distance that the contaminants introduced into groundwater with a hypothetical leachate release could migrate in 12 years (1998 through 2009) is approximately 435 ft from the landfill. However, GW-15 and GW-16 (which had their highest recorded arsenic concentrations in 2009) are located approximately 500 ft and 1100 ft, respectively, from the edge of Phase I. Also, the Phase II detection wells exhibited exceedances even before waste place began in Phase

10-2 -

10-3

II. Based on the groundwater velocities estimated for the site, leachate release, if any, from either Phase I is not expected to migrate to these wells within the time frames exceedances have been recorded at these wells. These measurements further substantiate the observation that a leachate release is not a major contributor to groundwater contamination at the site.

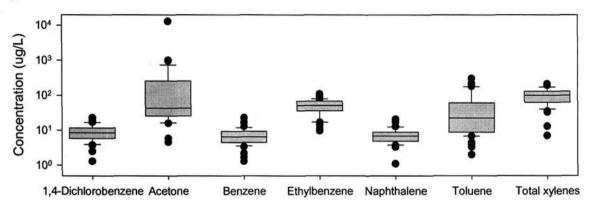


Figure 3-6. Box-and-Whisker Plot of Selected Organic Compounds in Leachate

#### 3.5 Evaluation of Soil Data

Many soil samples were collected from the unsaturated zone and characterized for total iron, arsenic, copper, chromium, lead, and nitrogen as a part of the Contamination Evaluation and Site Assessment studies at the landfill in 2008 and 2009, respectively, to assess whether the contaminated soil was present at the site.

The 95% UCL of the constituent concentrations were calculated and compared to the respective SCTLs and the background concentrations of these constituents in Florida soils as reported in the technical literature (Ma et al. 1999). Table 3-3 presents the number of samples, concentration range, 95% UCL of the measurements, SCTLs and Florida background concentrations. Figure 3-7 presents the box-and-whisker plot of the concentration distribution of arsenic, iron, chromium, copper, lead and nitrogen along with the SCTLs.

None of the constituents listed above exceeded the commercial/industrial SCTL. The 95% UCL of these constituents was well below the respective SCTL (residential and commercial/industrial), suggesting that the soil did not pose a human health risk via the direct exposure pathway. The 95% UCL of the constituent concentrations was well below the respective average background concentration reported for Florida soils suggesting that these constituents are present in site soils at background levels for Florida and not caused by an anthropogenic release.

The SPLP was performed on 16 of the soil samples collected in 2008 and 2009 and the SPLP extract was analyzed for arsenic, total ammonia, and nitrate. Figure 3-8 presents the box-and-whisker plot of the SPLP concentration distribution of arsenic, total ammonia and nitrate along with the GWCTLs. None of the samples exceeded the GWCTL for total ammonia and nitrate. Arsenic was not detected in 13 of the total 16 samples. Only one out of the 16 samples exceeded the GWCTL for arsenic. The

maximum arsenic concentration measured for any SPLP leachate was 0.011 mg/L, just above the GWCTL of 0.01 mg/L. Iron was not measured in the SPLP leachate.

Table 3-3. Comparison of Measured Soil Concentrations to SCTL and Florida Background Concentrations

Constituent	Number of Samples	Detection Limit (mg/kg) <sup>1</sup>	Concentration Range (mg/kg)	95% UCL (mg/kg)	Residential SCTL (mg/kg) <sup>2</sup>	Florida Background Concentration (mg/kg)
Arsenic	77	0.22 – 0.27 (28)	0.22 - 8.9	1.14	2.1 (7)	1.34±3.77
Chromium	51	0.22 – 0.26 (4)	0.22 – 25	8.84	210	15.9±30.6
Copper	51	0.065 – 0.082 (46)	0.065 - 1.3	0.24	150	6.10±22.1
Iron	27	0.12 (0)	16 – 6,800	2,161	53,000	49 – 39,600 (range)
Lead	51	0.22 – 0.26 (16)	0.22 - 3.8	1.45	400	11.2±26.3
Nitrogen	51	4-100(1)	32.9 – 3,700	637	N/A	N/A

<sup>&</sup>lt;sup>1</sup> Number in the parenthesis is the number of samples that were below the detection limit.

<sup>&</sup>lt;sup>2</sup> Number in the parenthesis is the number of samples that exceeded the respective residential SCTL.

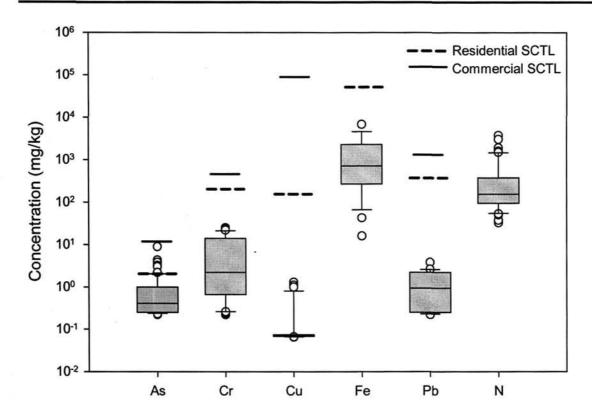


Figure 3-7. Box-and-Whisker Plot of Total Concentrations in Soil for Various Parameters

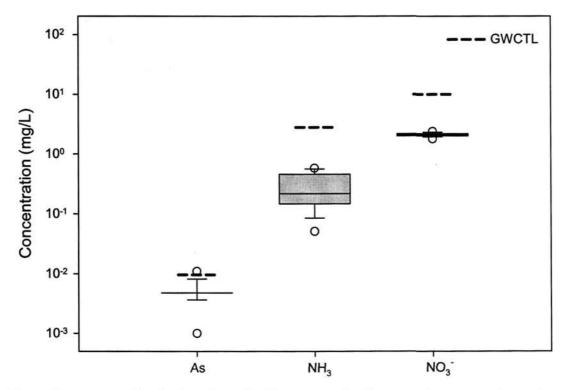


Figure 3-8. Box-and-Whisker Plot of Soil SPLP Results for Arsenic, Ammonia, and Nitrate

## 4. Processes Controlling Natural Attenuation

#### 4.1 Groundwater Impacts from On-Site Soils

The data presented in the previous chapter, along with the information provided in previous reports on the site, show that some groundwater wells at the site routinely exceeded the FDEP GWCTLs for iron, arsenic and total ammonia. Given that all solid waste disposal areas are lined per Florida's solid waste rules and are thus designed to prevent leachate migration into the environment, and given that the evaluation presented in the previous sections concludes that leachate does not appear to be the cause of groundwater exceedances at the site, this leads to the speculation that these groundwater exceedances are the result of the release of naturally-occurring elements from site soil. In this section, the mechanisms that could result in the release of iron, arsenic and total ammonia from soil into the groundwater at the site are explored.

Several landfills throughout Florida are currently observing GWCTL exceedances in groundwater monitoring wells for iron. Given iron's relatively low GWCTL (0.3 mg/L), the relatively abundant nature of iron in Florida's environment, and the fact that the GWCTL was based on a secondary drinking water standard, historically such exceedances were not a major priority of environmental enforcement. However, the tie to surface water deterioration issues in the Florida Panhandle and the development of a risk-based water quality threshold for iron by the FDEP-contracted toxicologists (4.2 mg/L) raised the issue of iron contamination to a new level of awareness. This has spurred research into the phenomena related to the release of iron from soils as a result of landfill construction and operation.

The process that has been largely attributed to being responsible for iron release at landfill sites is known as "reductive dissolution." In this process, reducing conditions develop in the surficial aquifer at a landfill site and transform the oxidized solid-phase iron to reduced dissolved-phase iron. The reactions associated with reductive dissolution and how landfill construction and operation might promote such reactions are discussed in more detail below, but this phenomenon has been observed and described at other landfill sites around the country. In most cases, the focus of these other sites is the release of arsenic: as iron is released into solution, any arsenic sorbed to the iron is also released. The fundamental underlying reaction, however, is reductive dissolution of iron minerals.

Many of the sites where iron dissolution has occurred (in Florida and reported in the technical literature) are old, unlined landfills. But growing evidence shows that similar problems can occur at lined landfill sites as well. University of Florida researchers have worked on a landfill site in north Florida where the groundwater data clearly show the release of iron after the placement of a lined landfill unit, with no evidence of leachate contamination from the landfill. Similar evidence has been reported for other lined landfills in the Florida Panhandle, as well as sites in the FDEP's Southwest District (e.g., Polk County's North Central Landfill). In the remainder of this section, a more detailed explanation of the scientific mechanism of reductive dissolution is presented, along with

other evidence collected from the site in previous studies. This section also presents iron fate and transport modeling that was conducted to evaluate whether iron will precipitate out of the groundwater when migrating through the oxygenated aquifer. Fate and transport modeling was also conducted to assess to whether the natural site soils would sorb the COCs and naturally attenuate the contamination. This section ends with a description of how NAM can represent an appropriate RBCA for sites with iron exceedances (along with arsenic and total ammonia exceedances resulting from iron reductive dissolution).

### 4.2 Development of Reducing Conditions Underneath a Landfill

#### 4.2.1 Fundamentals of Redox Biology and Chemistry

In the environment (including the groundwater environment), several biological reactions occur in which organic matter is consumed as part of the life cycle of different bacteria. These bacteria utilize a variety of compounds as electron acceptors. Under natural conditions, aerobic organisms (those using oxygen) are predominant. But when the oxygen is removed from the system, organisms that use other electron acceptors can begin to thrive. The following list presents electron acceptors used by different organisms, in order of most favorable to least (i.e., organisms that use electron acceptors higher on the list can outcompete organisms that use electron acceptors lower on the list).

• Oxygen 
$$\frac{1}{4}\{CH_2O\} + \frac{1}{4}O_2 = \frac{1}{4}CO_2 + \frac{1}{4}H_2O$$

• Nitrate 
$$\frac{1}{4}\{CH_2O\} + \frac{1}{8}NO_3^- + \frac{1}{4}H^+ = \frac{1}{4}CO_2 + \frac{1}{8}NH_4^+ + \frac{1}{8}H_2O$$

• Manganese 
$$\frac{1}{4}\{CH_2O\} + \frac{1}{2}MnO_2(s) + H^+ = \frac{1}{4}CO_2 + \frac{1}{2}Mn^{2+} + \frac{1}{8}H_2O$$

• Iron 
$$\frac{1}{4}\{CH_2O\} + FeOOH(s) + 2H^+ = \frac{1}{4}CO_2 + \frac{7}{4}H_2O + Fe^{2+}$$

• Sulfate 
$$\frac{1}{4}\{CH_2O\} + \frac{1}{8}SO_4^{2-} + \frac{1}{8}H^+ = \frac{1}{4}CO_2 + \frac{1}{8}HS^- + \frac{1}{4}H_2O$$

• Carbon dioxide 
$$\frac{1}{4}\{CH_2O\} = \frac{1}{8}CH_4 + \frac{1}{8}CO_2$$

As implied above, the chemicals used as electron acceptors are reduced in the process. Oxygen is reduced to carbon dioxide. Nitrate is reduced to ammonium. Oxidized manganese (Mn<sup>+4</sup>) is transformed to reduced manganese (Mn<sup>+2</sup>). Oxidized iron (Fe<sup>+3</sup>) is converted to reduced iron (Fe<sup>+2</sup>). The changes to the chemical conditions underneath a landfill can result in the disruption of the equilibrium developed in the soil-groundwater system, and thus a release of soil-bound elements to the water can occur.

#### 4.2.2 Development of Reducing Conditions as a Result of Landfill Construction

The soils underneath a landfill naturally contain a variety of inorganic chemicals. Prior to the construction of a landfill, the concentrations of these chemicals in the groundwater in contact with these soils tend to be low because a state of chemical equilibrium has been reached over the many years during which water has been flowing. However, the geochemical conditions may change with the construction of a landfill. One chemical change that has been noted in groundwater at landfills is the development of reducing conditions, when oxygen is no longer available for microbial decomposition of naturally-occurring organic matter.

In general, there are several factors that can lead to the development of reducing conditions at a landfill. First, leachate may be migrating and the organic matter in leachate can consume the dissolved oxygen in groundwater. Second, landfill gas can both contribute organic matter to the groundwater and act to force air from underneath the landfill, further limiting oxygen recharge. Finally, the presence of the landfill (lined and unlined areas) may be contributing to reducing conditions by limiting oxygen transport from the atmosphere to the groundwater.

#### 4.3 Reductive Dissolution of Iron

Iron is the second most abundant metal in the lithosphere and is a biogeochemically active element. Despite the fact that it usually represents less than 5% of the soil, its high surface area and small size make it highly reactive in soil-water systems. Florida soils are known to naturally contain iron minerals such as hematite and goethite. In these minerals, the iron is the oxidized form, referred to as the Fe<sup>3+</sup> form or the ferric form; these minerals are in the solid phase.

Iron in soils typically occurs in the more oxidized  $Fe^{3+}$  form as opposed to the  $Fe^{2+}$  form. When reducing conditions convert some of the oxidized iron to a more reduced form  $(Fe^{3+} \rightarrow Fe^{2+})$ , the iron may become liberated from the native soil matrix into groundwater by a biological reaction as follows (Pedersen et al. 2006; Benner et al. 2002; Zachara et al. 2001; Lovley 1991):

$$\frac{1}{4}\{CH_2O\} + FeOOH(s) + 2H^+ = \frac{1}{4}CO_2 + \frac{7}{4}H_2O + Fe^{2+}$$

In this reaction, solid-phase ferric iron (Fe<sup>3+</sup>) is transformed to dissolved ferrous iron (Fe<sup>2+</sup>). Much research has been conducted to investigate Fe<sup>3+</sup> reduction under anaerobic conditions. Albrechtsen and Christensen (1994) studied the reduction of Fe<sup>3+</sup> in groundwater samples taken at a landfill in Denmark. Suspended anaerobic aquifer sediments were tested for iron reduction by measuring the concentration of dissolved Fe<sup>2+</sup>. Fe<sup>3+</sup> did not reduce in samples inoculated with inactive sediment or when bacteria were killed by formaldehyde or by chloroform. The level of Fe<sup>2+</sup> was significant in samples where live bacteria were present. Bonneville et al. (2004) investigated the relationship between the microbial reduction kinetics and solubility of Fe<sup>3+</sup> oxyhydroxides and found that solubility is the rate-controlling parameter with regard to reductive dissolution of Fe<sup>3+</sup> oxyhydroxides. Fredrickson et al. (1998) studied the

reduction of hydrous ferric oxide and the formation of biogenic Fe<sup>2+</sup> minerals using a batch experiment with well-defined aqueous solutions. The reduction of iron was measured against time. The results indicated that the composition of aqueous media in which microbial iron reduction occurred had a significant impact on the rate and extent of iron reduction.

Although less investigated, a number of non-biologic iron reductive dissolution mechanisms have been reported in the literature (e.g. Suter et al. 1991; Poulton et al. 2004; Peiffer and Gade 2007) based primarily on laboratory studies.

### 4.4 Relationship with Arsenic

The release of iron into groundwater may not by itself be a problem, but in some cases, other chemicals that are bound to the iron mineral matrix may be released as well, such as arsenic. Arsenic is potentially a larger regulatory concern because unlike iron, it is a carcinogen and has a primary drinking water standard.

Arsenic, along with iron and manganese, is an inorganic element that potentially exists naturally in the aquifer matrix in different forms. The forms of arsenic present in soil depend on the type and content of minerals present, the pH, and the redox potential. In general, under oxidizing conditions, arsenic occurs primarily in the +5 valence state in soil and is strongly adsorbed by clays and iron oxides in soil. Under reducing conditions, arsenic is primarily in the +3 valence state and is more mobile. Arsenic is sensitive to reducing conditions and some organisms can use As<sup>5+</sup> as an electron acceptor which results in the transformation to As<sup>+3</sup>. The redox equation of As<sup>3+</sup>/As<sup>5+</sup> is:

$$H_3 AsO_4 + 2H^+ + 2e^- \rightarrow H_3 AsO_3 + H_2 O$$

However, the more likely cause for naturally-occurring arsenic to increase in concentration in the groundwater stems from the propensity for arsenic to bind with iron compounds in soil (DeLemos et al. 2006). Previous research has found that arsenic adsorbs readily in oxygenated environments to several iron minerals, namely iron oxides and iron oxyhydroxides. When reducing conditions develop in the groundwater, the Fe<sup>3+</sup> present in the iron oxides and oxyhydroxides can be reduced to the more soluble ferrous iron (Fe<sup>2+</sup>), thus releasing the sorbed arsenic into the groundwater (USGS 2004; Parisio et al. 2006). Deuel and Swoboda (1972) found that reducing an untreated black clay soil led to the release of arsenic and that the arsenic release was associated with iron oxide dissolution. De Vitre et al. (1991) found a rapid increase in pore-water arsenic concentrations with depth in lake sediment and a concurrent increase in dissolved iron.

Reductive dissolution of iron has been reported to be a major cause of groundwater contamination with arsenic in the Ganges Plain of north India and Bangladesh (McArthur et al. 2001, Horneman et al. 2004, Acharyya et al. 1999, Anawar et al. 2002, Bose and Sharma 2002). The mobilization of arsenic as a result of changes to geochemical conditions was investigated at MSW landfill sites in the United States (USGS 2004). One way arsenic mobilizes is through reductive release (which is typically coupled with the

dissolution of iron oxides in soil). In other words, it has been shown that reducing conditions can cause iron hydroxides to be released, and as a result, arsenic also becomes mobilized.

To evaluate the correlation between iron and arsenic present in the soil at the site, the measured arsenic concentration was plotted as a function of iron concentration in the soil. Figure 4-1 presents the relationship between iron and arsenic concentrations in the soil samples collected at the site (refer to Section 3.5 for more details). The plot shows that the arsenic concentration in soil is strongly related ( $r^2 = 0.95$ , excluding two outliers) to the soil iron content potentially because of arsenic sorption on the solid-phase iron mineral as described above; the soil samples with greater iron concentration would tend to bind more arsenic.

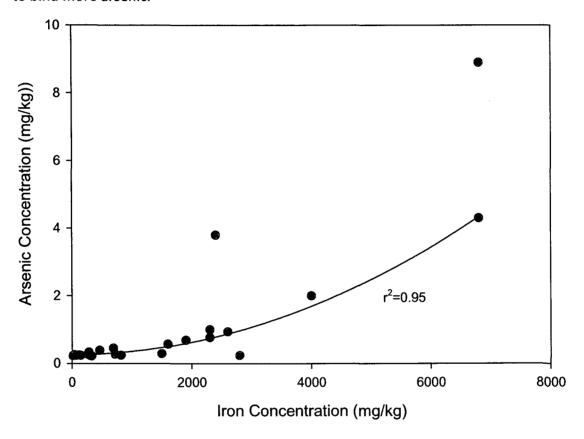


Figure 4-1. Soil Arsenic Concentration as a Function of Soil Iron Concentration

The arsenic concentrations in groundwater — historically measured at the site as part of the routine groundwater monitoring, compliance evaluation, and site assessment — were plotted as a function of the measured iron concentrations (Figure 4-2). Figure 4-2 suggests that, in general, the greater arsenic concentration was associated with a greater iron concentration potentially because of dissolution of arsenic with dissolution of the solid-phase iron via reductive dissolution. The presence of elevated arsenic levels with elevated iron concentrations indicates that the two are interrelated.

Another worthwhile observation is that arsenic concentrations were significantly lower in samples with an iron concentration less than the 35 mg/L than those in samples with an iron concentration greater than the 35 mg/L range. Figure 4-3 shows box-and-whisker plots of arsenic concentrations for iron >35 mg/L and <35 mg/L. It can be seen that arsenic concentrations for samples with iron concentration <35 mg/L are significantly lower than the arsenic concentration with iron concentration >35 mg/L, which once again indicates a relationship between the concentrations of iron and arsenic in groundwater at the site.

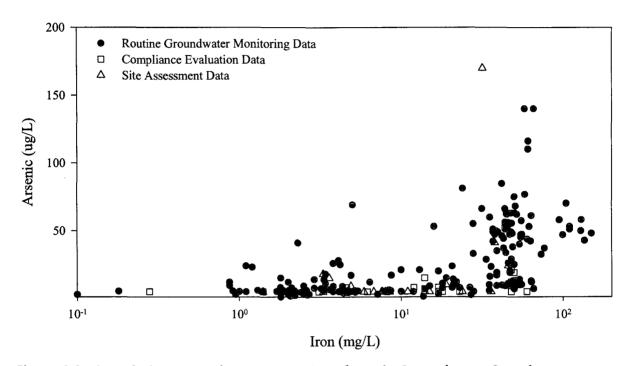


Figure 4-2. Arsenic Concentration as a Function of Iron in Groundwater Samples

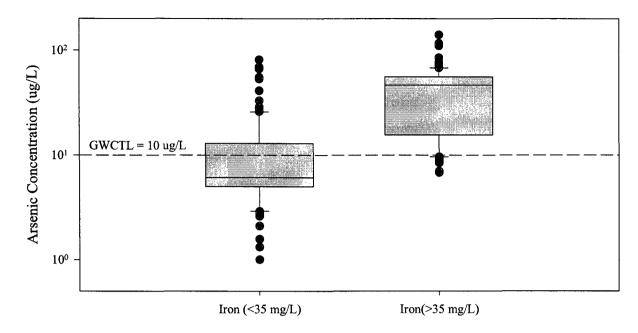


Figure 4-3. Box-and-Whisker Plot of Arsenic Concentration for Iron < 35mg/L and Iron > 35 mg/L

# 4.5 Relationship with Ammonia

The reductive dissolution of iron and the associated release of arsenic are mechanisms that have been described previously in the literature, most particularly to explain the release of arsenic at old landfill sites. While the concept of reductive dissolution as being caused simply by the presence of landfill construction (without a leachate discharge) is relatively unique to Florida, the basic science of the iron and arsenic chemistry is well established.

Based on a review of the literature, the release of ammonia under similar conditions has not been explored in the same manner. The presence of ammonia complicates the issue since ammonia is typically thought of as an indicator parameter in MSW landfill leachate. During MSW landfill decomposition, nitrogen-rich proteins in food waste are converted in the anaerobic environment to ammonia where it tends to increase in concentration with time (it is conserved in the anaerobic landfill environment). The analysis in Section 3 does not indicate that a leachate discharge is the cause of groundwater exceedances at the site.

Ammonia will exist in a different form depending on the pH, either as a cation  $NH_4^+$  (ammonium) or as a dissolved gas,  $NH_3$ . At the pH typically measured in the groundwater at the site, nearly all ammonia will occur as ammonium. Several mechanisms can account for the association of iron with ammonium. First, some literature suggests that ammonium can co-precipitate with iron as part of an iron mineral precipitate (Sahrawat 2004; Ivanov et al. 1997). Through this mechanism, if iron minerals containing ammonium are reductively dissolved, ammonium would be released into solution as well if other adsorption sites are not available. Second, since

ammonium is a cation, it may naturally be bound to soil particles through ion exchange.  $NH_4^+$  could be exchanged with  $Fe^{+2}$  if large concentrations of the  $Fe^{+2}$  ion were released into solution (as would occur when reductive dissolution occurs), thus increasing the ammonium ion concentration in solution.

The total ammonia concentrations in groundwater — also historically measured at the site as part of the routine groundwater monitoring, compliance evaluation, and site assessment — were plotted as a function of the measured iron concentrations (Figure 4-4). Figure 4-4 suggests that, in general, the greater total ammonia concentration was associated with greater iron concentration potentially because of dissolution of ammonium with the solid-phase iron dissolution via reductive dissolution. Similar to the arsenic-iron relationship, the presence of elevated total ammonia levels with elevated iron concentrations indicates that the two are interrelated.

Furthermore, total ammonia concentrations are significantly lower in samples with iron concentration less than 35 mg/L than those of samples with iron concentration greater than 35 mg/L. Figure 4-5 shows box-and-whisker plots of total ammonia concentrations for iron >35 mg/L and <35 mg/L. It can be seen that total ammonia concentrations for samples with an iron concentration <35 mg/L are significantly lower than the total ammonia concentration with an iron concentration >35 mg/L, which indicates a relationship between the concentrations of iron and total ammonia in groundwater.

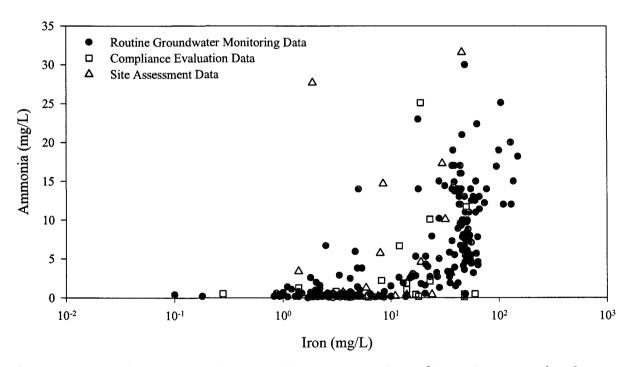


Figure 4-4. Total Ammonia Concentration as a Function of Iron Concentration in Groundwater

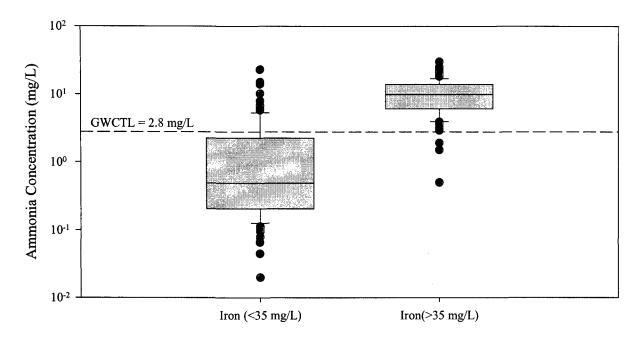


Figure 4-5. Box-and-Whisker Plot of Total Ammonia Concentration for Iron <35 mg/L and Iron >35 mg/L

# 4.6 2008 University of Florida Study

In 2008, the University of Florida conducted research to assess whether the natural soil could serve as a source of the elevated iron, arsenic and total ammonia concentrations in groundwater at the site (Townsend et al. 2008); a copy of the report describing the research findings was submitted to the FDEP as an attachment of the Contamination Evaluation Report (PBS&J 2008). Townsend et al. (2008) collected soil samples (soil borings and bulk samples) - from both the vadose and saturated zones - from different areas of the site for laboratory testing. Soil boring samples (SPT 1 through SPT 6) were analyzed for the following parameters: total organic matter; total and extractable iron, arsenic, and nitrogen; 30-day biological reductive dissolution for iron, arsenic and total ammonia; 1-day chemical reductive dissolution for iron, arsenic, and total ammonia; soil mineralogy; and iron reducing bacteria. The bulk soil samples were used to conduct batch tests to evaluate iron release in presence and absence of dissolved oxygen and without an external microbial seed and organic source over time, and column tests to assess the release of iron, arsenic and total ammonia under groundwater flow conditions and in the presence and absence of dissolved oxygen. The outcomes of the study were as follows:

- Total iron and arsenic contents of the soil samples from the site were within the typical range of most Florida soils.
- As shown in Figure 4-6, ferrous iron release under reducing conditions was substantially greater than release with de-ionized water and the SPLP extraction solution; iron release was evaluated with SPLP extraction, deionized water extraction, biological reductive dissolution, and chemical

reductive dissolution. The reductive reagent ( $Na_2S_2O_4$ ) was used to create abiotically-reducing conditions whereas an anaerobically digested seed and 5 g of additional cellulose were used to create biological reducing conditions. The results suggest that iron in the soil at the site can be released under reducing conditions.

- The results of the iron-reducing bacteria assay indicated a greater iron-reducing bacteria count in samples from and near the areas where the highest iron concentration in groundwater was recorded. The finding suggests that reductive dissolution of iron likely has a significant impact on iron release into groundwater at the site.
- The dissolved iron concentration increased with time in the absence of dissolved oxygen in both column and batch tests, again suggesting the iron would release under reducing conditions. These tests also suggest that the organic matter naturally present in soil was enough to create reducing conditions in the absence of an oxygen supply.
- As shown in Figure 4-7, the dissolved arsenic concentration increased with time in the biological reductive dissolution test suggesting that arsenic releases with iron under reducing conditions.

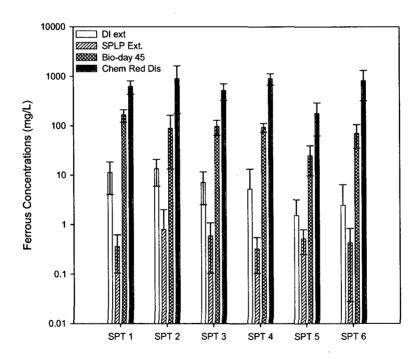


Figure 4-6. Comparison of Iron Release with Different Extraction Methods (Townsend et al 2008)

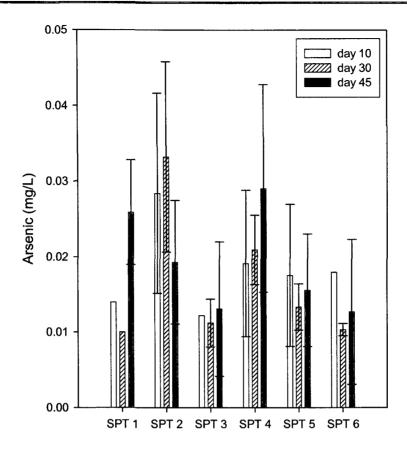


Figure 4-7. Arsenic Concentrations during a Biological Reducing Test (Townsend et al 2008)

• The study reported that ammonia (more specifically ammonium ions) was naturally present in the soil. Figure 4-8 shows the relationship between total ammonia and ferrous ion; higher concentrations of total ammonia were found in solution with higher ferrous iron concentrations. The results suggest that total ammonia is also bound to the iron oxide minerals to an extent and is released into solution when these minerals dissolve through reductive dissolution.

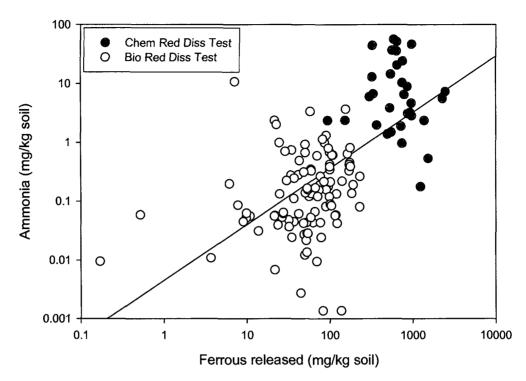


Figure 4-8. Relationship between Total Ammonia and Ferrous Released during Chemical and Biological Reductive Dissolution Testing

In summary, the results suggest that reductive dissolution of iron minerals in the site soils, which resulted in the release of iron, arsenic and total ammonia into groundwater, is a plausible explanation for the groundwater exceedances of these chemicals at the site. The fact that organic matter is associated with the iron minerals as well suggests that an external source of organic matter, such as leachate, is not required for the reaction to occur. The decrease in the amount of oxygen present triggers this reaction. The researchers hypothesized that the construction of the lined landfill cell, along with associated site development and other site activities (e.g., storage piles of cover soil), have sufficiently decreased the vadose zone oxygen content in some areas of the site that conditions suitable for accelerated iron-reducing bacteria have developed, which has in turn resulted in the release of iron, arsenic and total ammonia into the groundwater.

## 4.7 2009 University of Florida Follow-up Report

A follow-up study was conducted by Townsend et al. (2009) to further examine the hypothesis that iron reductive dissolution from on-site soils could occur simply through a decline in dissolved oxygen content even in the absence of an external input of organic matter and to examine the long-term effects of the decreased dissolved oxygen conditions on the release of iron (and other related constituents); a copy of the report is presented in Appendix D. The impact of external sources of organic matter, specifically yard trash, on reductive dissolution was also explored via batch tests and column tests.

The result of column tests on site soils confirmed that reductive dissolution of iron can occur with a decrease in dissolved oxygen influx even without any external input of organic matter. The column tests showed a temporary increase in iron concentration which was accompanied by an increase in total ammonia concentration. The fraction of iron reductively dissolved was found to be smaller than that observed in previous tests where an external source of organic matter was present. The amount of iron released was not sufficient to produce a measurable increase in arsenic concentration. Mass balance calculations as part of the study suggested that reductive dissolution, even at the lower release rates observed in the absence of external organic matter, could result in groundwater iron concentrations similar to those observed at the site. Measurements from the columns over time found iron release to spike and then decrease, which supported the hypothesis that given time, groundwater concentrations of iron should return to previously-existing levels.

The results of batch tests where yard trash extract (created using yard trash collected from Sarasota County) was used as a source of organic matter found an enhancement in reductive dissolution. These results suggest that external inputs of organic matter, such as those that might occur from stockpiled yard trash or as a result of site development activities, could influence the rate and extent of reductive dissolution.

Overall, the follow-up study supported the hypothesis that reductive dissolution is a plausible mechanism for the release of iron, arsenic, and total ammonia in the absence of any landfill discharge or external organic matter. Reductive dissolution can occur with a decrease in dissolved oxygen, and while the degree of reductive dissolution is limited, these levels can still result in groundwater exceedances. External sources of organic matter that might naturally enter the groundwater at a site (e.g., from yard trash operations, stockpiled organic soils, vegetation and muck from site development) may also play a role in the degree to which reductive dissolution occurs.

# 4.8 Fate and Transport Modeling of Reaeration as a Iron Natural Attenuation Process

#### 4.8.1 Overview

In the previous section, reductive dissolution was introduced as a plausible mechanism that could cause mobilization of the COCs (iron, arsenic and total ammonia) at the site. The decline in the oxygen recharge (herein referred to as *reaeration*) of the surficial aquifer system resulting from the liner system construction and operations such as earthwork (e.g., soil stockpiling, compaction) was identified as the potential cause of the reductive dissolution of iron at the site.

It is further anticipated that as the impacted groundwater migrates through the oxygenated aquifer, the reduced iron would oxidize and precipitate out of the groundwater. As discussed in the previous section, arsenic has a strong tendency to sorb on ferric oxides and hydroxides that are present in the native soil and would also form with the oxidation of the reduced iron. Similarly, total ammonia is reported to coprecipitate with iron. Arsenic and total ammonia concentration in the soil as well as

groundwater at the site were found to be strongly related to iron concentration. Reduction in dissolved arsenic and total ammonia concentration is, therefore, expected with dissolved iron oxidation and precipitation. The impact of sorption on the fate and transport of COCs is evaluated in the next section.

Modeling was conducted to evaluate the fate and transport of iron with aquifer reaeration as its concentration and speciation is expected to have an influence on the fate and transport of arsenic and total ammonia. The specific objectives of the modeling described in this section was to assess whether iron concentrations would decline over time and distance with reaeration of the surficial aquifer system. Simplified two-dimensional iron fate and transport modeling was conducted.

#### 4.8.2 System Description

A simplified two-dimensional system was modeled to meet the modeling objectives. Figure 4-9 presents a schematic of the system modeled.

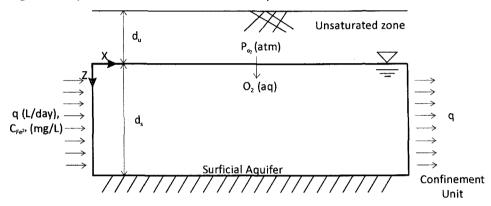


Figure 4-9. Schematic of the Modeled System

Groundwater with a reduced iron (i.e., ferrous ion or  $Fe^{2+}$ ) concentration of  $C_{Fe}^{2+}$  (mg/L) enters the saturated aquifer at a constant flux of q (L per day per m²) at x=0. Reduced iron is transported laterally due to advection (transport due to the bulk motion of water) and diffusion (movement of a chemical from an area of high concentration to an area of lower concentration). Oxygen with a partial pressure of  $P_{O2}$  (atm) above the water table enters the saturated aquifer at z=0 and diffuses across the depth of the aquifer because of the concentration gradient. The reduced iron is expected to oxidize in the presence of dissolved oxygen and precipitate out as either hematite ( $Fe_2O_3$ ), goethite (FeOOH), or amorphous  $Fe(OH)_3$  because of the low solubility of these compounds in water. The simulation of the reduced iron oxidation and subsequent precipitation requires modeling of the following phenomena:

- Groundwater flow,
- Transport of Fe<sup>2+</sup> and dissolved oxygen, and
- Reaction of Fe<sup>2+</sup> and dissolved oxygen.

Note that groundwater recharge and sorption of reduced iron in native soils would decrease reduced-iron concentrations in the impacted groundwater as it moves away

from the landfill; however, these phenomena were not modeled in order to assess the impact of aguifer reaeration on the natural attenuation of iron.

#### 4.8.3 Model Description

Rule 62-780 allows the use of fate and transport models listed either in an ASTM guidance document (ASTM 1999) or in a list of models maintained by the FDEP to support the appropriateness of NAM. IWCS used MODFLOW (Version 2005) and PHT3D (Version 2.0) models for assessing the fate and transport of reductively dissolved iron; these models are listed directly or as components of other models in the ASTM document. MODFLOW is a three-dimensional finite-difference model that simulates steady and unsteady groundwater flow in aquifer systems (unconfined or confined or a combination of these).

PHT3D is a three-dimensional, reactive multicomponent transport model which couples the solute transport model MT3DMS (Version 5.2) (Zheng and Wang, 1999) and the USGS geochemical code PHREEQC-2 (Version 2.14) (Parkhurst and Appelo, 1999). PHT3D can simulate a broad range of equilibrium and kinetically-controlled biogeochemical processes, including aqueous complexation, redox reactions, mineral precipitation/dissolution, and ion exchange reactions.

Visual MODFLOW 2009.1 Pro (developed by Schlumberger Water Services (Waterloo, Ontario, Canada)), was used as the graphical user interface to input the modeling data, run the models, and analyze the modeling results. The program first simulates groundwater flow using MODFLOW to calculate flow velocity at various spatial coordinates and the user-specified time steps. The velocity values are used by the contaminant transport model (PHT3D) to simulate the spatial distribution of contaminants (species) transport and reactions at various time steps determined by the model; PHT3D uses MT3DMS to simulate the transport and distribution of various species at the model-determined time steps and calls PHREEQC-2 to simulate the reactions among various species present in the system at the time steps specified by the user for MODFLOW simulations.

#### 4.8.4 Model Input Parameters

The models require specification of the system dimensions, head and species concentration within the system at time, t = 0 (referred to herein as the *initial condition*) and head and species concentration at the system boundaries (referred to herein as boundary conditions), and several other inputs to simulate fate and transport of various species (e.g.,  $Fe^{2+}$ , dissolved oxygen, etc.) as a function of time.

The surficial aquifer thickness at the site has been reported to range from 14 ft to 16.5 ft (Ardaman & Associates 2008). A depth of 16 ft was selected for modeling. As the diffusion coefficient of oxygen in air is almost 10,000 more than that in water, the unsaturated zone is expected to have an insignificant impact on the transport of oxygen for reduced iron oxidation in the saturated zone as long as it is exposed to the atmosphere. Therefore, the unsaturated zone depth was assumed to be zero. In other

words, the water table was assumed to be at the existing grades. The lateral extent of the aquifer modeled was 500 ft.

Table 4-1 presents the values of various aquifer properties and flow parameters used for modeling along with the range reported for the site by Ardaman & Associates, Inc. (2008). A constant head of 16.55 ft and 16 ft was specified at x=0 and 500 ft, respectively. These heads were specified to create a hydraulic gradient of 0.0011 ft/ft. A recharge (1 mm per year) was specified at the water table (z=0) to facilitate oxygen influx. A no-flow boundary condition was specified at the aquifer bottom (z=16 ft). A head of 16.3 ft was assigned everywhere in the domain as the initial head (at t=0).

Table 4-1. Groundwater Flow Parameters Used in Modeling

Symbo I	Parameters	Value Used for Modeling	Range Reported for the Site
Ks	Hydraulic conductivity in the saturated zone	2 ft/day	0.25 - 4.1 ft/day
N	Aquifer porosity	0.25 (v/v)	0.25 (v/v)
I	Aquifer hydraulic gradient	0.0011 ft/ft	Average 0.0005 – 0.0011 ft/ft Maximum 0.003-0.006 ft/ft
S <sub>s</sub>	Storage coefficient	0.15	0.10-0.19

#### 4.8.5 Fate and Transport Simulation Inputs

As a first step for the model setup, the chemical species whose fate and transport was to be simulated were selected from the PHREEQC-2 database. The following species were selected for the modeling:

- Dissolved oxygen (O(O))
- Gas-phase oxygen (O<sub>2</sub>(g))
- Ferrous ion (Fe<sup>2+</sup>) (reduced iron)
- Ferric ion (Fe<sup>3+</sup>) (oxidized iron)
- Hematite (Fe<sub>2</sub>O<sub>3</sub>)
- Goethite (FeOOH)
- Fe(OH)<sub>3</sub>
- Chloride (Cl<sup>-</sup>)

Apart from the concentrations of the user-specified species, the model also calculates pH and pe (electron activity). The model runs were conducted for a temperature of 25 °C, consistent with the average temperature of the groundwater monitoring samples collected (detection and compliance wells) historically at the site.

The model accepts concentration values only in moles per liter (mol/L). The initial concentrations of all the species except O(O), hematite, pH, and pe in the system were

assumed to be zero. Historical groundwater monitoring data suggests that pH and dissolved oxygen have ranged from 4.61 to 7.77 and 0.07 mg/L to 9.3 mg/L, respectively (refer to Appendix B for historical groundwater monitoring data summary and plots). The initial dissolved oxygen content was assumed to be 4 mg/L (0.00025 mol/L). The initial pH of the system was assumed to be 6. For a system at 25 °C, the pe is related to oxidation reduction potential (ORP) as follows:

ORP, 
$$E_h$$
 (in millivolts (mV)) = 59 x pe (eqn 4-1)

Based on the measurements taken at the site during the Contamination Evaluation and Site Assessment conducted in 2008 and 2009, respectively, the ORP has been reported to range from -196 mV to 125 mV. The lower ORP (i.e., more negative) values are indicative of reducing conditions, and higher ORP values are indicative of oxidizing conditions. An initial pe of 2 (ORP = 118 mV) was specified to represent the oxidizing condition of the aquifer before it is influenced by the influx of reduced-iron-laden groundwater from the up-gradient aquifer zone where reductive dissolution of iron is occurring.

As discussed earlier in the report, the 95% UCL of the mean iron concentration in the soil samples collected from the site as part of the Contamination Evaluation conducted in 2008 was calculated to be approximately 2,200 mg/kg. Assuming a soil bulk density of 1,700 kg/m³ and that 100% of iron in the soil is present as hematite, the hematite content of the soil was calculated to be 5.4 g/L of bulk soil (approximately 0.035 mol/L of bulk soil). The initial hematite content of the surficial aquifer was specified to be 0.035 mol/L of bulk soil. It should be noted that specification of an initial hematite concentration is not expected to impact the fate and transport of the incoming reduced iron. The intent of specifying the initial hematite content in soil was to demonstrate that this iron will not dissolve in an oxygenated environment.

A concentration or flux (concentration gradient) of each species needs to be specified at each of the system boundaries. At the x=0 boundary, a constant reduced-iron concentration of 150 mg/L (0.002686 mol/L), pH of 6 and pe of -4 (ORP = -236 mV) were specified. It should be noted that 150 mg/L represents the highest iron concentration measured to date for the site. It should be further noted that the 150 mg/L may not represent the maximum concentration that would occur at the site. Not enough data and tools are available in the existing literature to predict the maximum concentration of iron that would occur at the site under the reductively dissolving environment. The model requires the water composition at the boundary to be charge-balanced. A chloride concentration of 190.5 mg/L (0.005372 mol/L) was specified at this boundary to make the composition of incoming groundwater charge-neutral. The concentration of all the other species, including dissolved oxygen, was assumed to be zero at this boundary.

The groundwater and dissolved contaminants exited the system at x=500 ft at a rate such that the head at this boundary was always equal to the specified head at this boundary. At the bottom of the surficial aquifer system (z=16 ft boundary), the flux (concentration gradient) of all the species across this boundary was specified to be zero.

At the water table (z=0 boundary), a constant dissolved oxygen concentration was specified by setting a groundwater recharge rate of 0.039 inches (1 mm) per year with a dissolved oxygen content of 16,000 mg/L (1 mol/L), pH of 6, and pe of 2. The partial pressure of oxygen was specified at 0.20 atm assuming the oxygen content of air above the water table is 20% (by volume) which is slightly lower than the oxygen content of atmospheric air. The model uses Henry's law to relate the partial pressure of oxygen in air to the dissolved oxygen content in water. If the dissolved oxygen content is greater than the equilibrium dissolved oxygen content at the specified partial pressure, the model transfers the dissolved oxygen to the air phase and stores it at the transfer location. The air-phase oxygen is not transported with water and is transferred back to the water if the dissolved oxygen content falls below its equilibrium concentration at the location the air-phase oxygen is stored.

Dispersion is the phenomenon of the spreading of a contaminant beyond the region it would migrate due to advective flow alone. Dispersion depends on the coefficient of hydrodynamic dispersion, which is the sum of the coefficient of mechanical dispersion and the coefficient of molecular diffusion. The coefficient of mechanical dispersion is the product of the groundwater velocity and media dispersivity. The dispersivity is a characteristic property of the media only and is not dependent on fluid properties. The Peclet number ( $P_e$ ) (eqn 4-2) is an indicator of the relative contribution of mechanical dispersion and diffusion in overall dispersion of contaminant. For  $P_e$ <1, mechanical dispersion can be neglected and diffusion is the dominant dispersion mechanism.

$$P_e = \frac{Vd}{D_d}$$
 (eqn 4-2)

Where,  $P_e$  = Peclet number, V = Linear groundwater velocity (ft/day), d= mean grain size (ft), and  $D_d$  = Diffusion coefficient of species in water (ft²/day). The maximum groundwater velocity for the site was reportedly 36 ft/yr (Ardaman & Associates 2008). Soil classification reported in soil boring logs presented in Ardaman & Associates (2008) suggests that more than 50% of the soil by mass has a particle size less than 0.0156 ft (4.75 mm). Akgerman and Gainer (1972) summarized the published values of diffusion coefficients of air in water at 25 °C and reported a range of 2.07 x  $10^{-5}$  cm²/s to 2.60 x  $10^{-5}$  cm²/s (1.93 x  $10^{-3}$  to 2.41 x  $10^{-3}$  ft²/day). Based on these inputs,  $P_e$  for the site was estimated to be less than 0.75. For these conditions, the mechanical dispersion is insignificant in comparison to diffusion. The coefficient of hydrodynamic dispersion can be approximated as  $0.67D_d$  for these flow conditions (Domenico and Schwartz 1990). Thus, the hydrodynamic dispersion for the site is expected to range from 0.0013 to 0.0016 ft²/day. The models were run using a diffusion coefficient of 0.0014 ft² per day and a dispersivity value (i.e., mechanical dispersion) of 0.

Table 4-2 lists all the inputs described above.

Table 4-2. Input Parameters Used in Aquifer Reaeration Modeling

Symbol	Parameter	Value Used for Modeling
System [	Dimensions	
ds	Saturated surficial aquifer depth	16 ft
du	Unsaturated surficial aquifer depth	0 ft
Χ	Horizontal extent of surficial aquifer	500 ft
<u>Aquifer I</u>	Properties	
Ks	Hydraulic conductivity in the saturated zone	2 ft/day
η	Porosity	0.25 (v/v)
Ss	Storage coefficient	0.15
D	Bulk diffusion coefficient	0.0014 ft²/day
Boundar	y Condition at x=0	
	Reduced iron concentration	150 mg/L (0.002686 mol/L)
	рН	6
	pe (ORP)	-4 (-236 mV)
	Chloride	190.5 mg/L (0.005372 mol/L)
	Dissolved oxygen	0 mg/L
	Head	16.55 ft
<u>Boundar</u>	y Condition at z=0	
	Reduced iron concentration	0
	рН	6
	pe (ORP)	2 (118 mV)
	Chloride	0
	Dissolved oxygen	16,000 mg/L (1 mol/L)
	Recharge	1 mm/year
Initial Co	endition (t=0)	
	Reduced iron concentration	0
	pH	6
	pe (ORP)	2 (118 mV)
	Chloride	0
	Dissolved oxygen	4 mg/L (0.00025 mol/L)
·····	Hematite	5.4 g/L of bulk soil (0.035 mol/L bulk soil)

#### 4.8.6 Results

To assess the magnitude of the impact of aquifer reaeration on iron fate and transport, the model was run to simulate reduced-iron fate and transport without reaeration. This was accomplished by specifying the top of the water table as a zero-flux boundary condition rather than a recharge boundary condition. All the other boundary conditions were the same as described earlier in this section. Figure 4-10 presents the distribution of reduced iron at the end of the 5<sup>th</sup>, 10<sup>th</sup>, 20<sup>th</sup>, and 40<sup>th</sup> year. As expected, reduced iron moved as a vertical front with time.

Figure 4-11 presents the 5 mg/L-concentration contour after 5<sup>th</sup>, 10<sup>th</sup>, 20<sup>th</sup>, and 40<sup>th</sup> year of the simulation. The rationale for selection of the 5 mg/L concentration for defining the iron plume is presented later in this section. As can be seen from Figures 4-11 and 4-12, the concentration varied as a function of the x-coordinate and was constant across

the depth (z-coordinate). Therefore, the iron transport in this case can be considered as one dimensional transport.

As a quick check, the reduced iron plume migration rate was estimated by neglecting diffusive flow. The plume under this assumption will migrate at the groundwater flow velocity. The groundwater flow velocity for the modeled scenario was estimated using the following equation:

$$v = \frac{Ki}{\eta}$$
 (eqn 4-3)

Where,

v = groundwater velocity (ft/day),
 K = Hydraulic conductivity (ft/day),
 i = hydraulic gradient (ft/ft), and
 η = porosity (v/v)

Based on hydraulic conductivity (2 ft per day) and porosity (0.25) values used for the modeling and the simulated hydraulic gradient of 0.0011 ft/ft, the groundwater velocity would be approximately 3.2 ft per year. In the absence of diffusive flow (i.e., the advective flow only condition), the iron plume would migrate 16 ft, 32 ft, 64 ft, and 128 ft in 5, 10, 20, and 40 years, respectively. As can be seen from contour plots presented in Figure 4-10 the contours associated with iron concentrations ranging from 90 to 105 mg/L migrated at the rate estimated above. Contours with iron concentration less than 90 mg/L migrated at a rate greater than that predicted based on groundwater velocity (advective flow) because of diffusion.

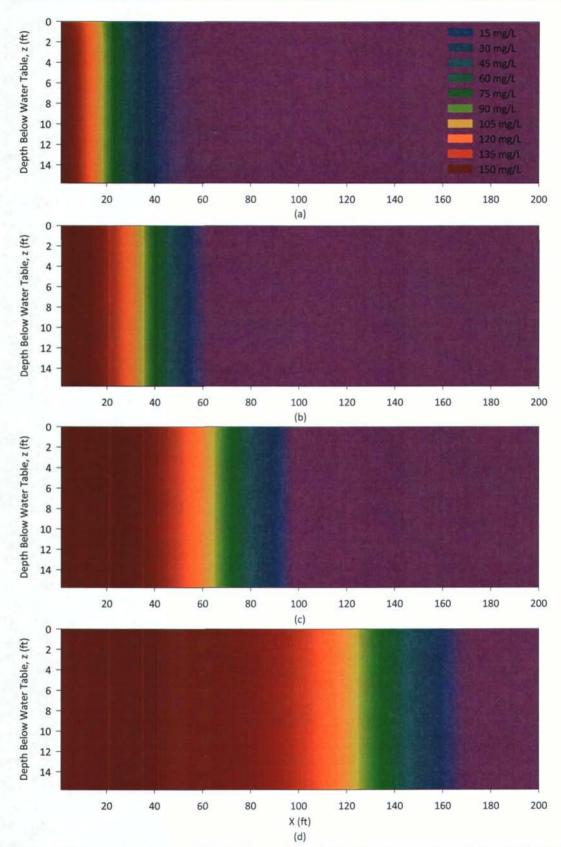


Figure 4-10. Reduced Iron Distribution without Aquifer Reaeration at the End of (a) 5 years, (b) 10 years, (c) 20 years, and (d) 40 years

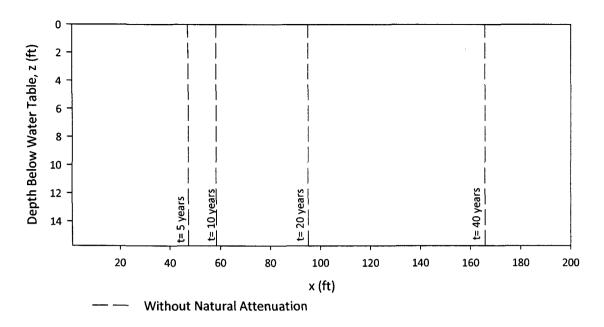


Figure 4-11. Location of 5 mg/L Concentration Contour at the End of 5<sup>th</sup>, 10<sup>th</sup>, 20<sup>th</sup> and 40<sup>th</sup> Year

Figure 4-12 presents the temporal variation of iron concentrations at 50 ft, 100 ft and 200 ft from the source (x=0). It can be seen that the concentration at 50 ft reached a maximum value of 150 mg/L (source concentration at x=0) in approximately 25 years. The iron plume reached 100 ft around the 20<sup>th</sup> year. The iron concentration, however, did not increase to its maximum concentration within the simulation duration of 40 years at this location. The 200-ft location was not impacted within the simulation duration of 40 years. The concentrations at a given x were the same across the aquifer depth as described above. It is shown that the concentration of iron at a well located farther from the source is always less than or equal to the concentration observed in a well located closer to the source.

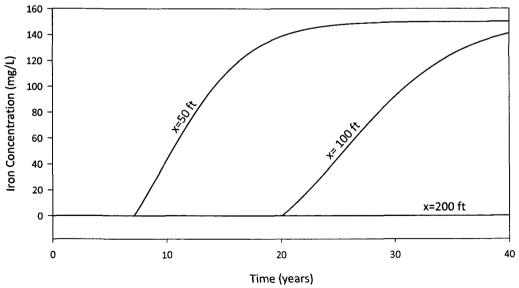


Figure 4-12. Temporal Variation of Iron Concentration at x=50, 100, and 200 ft

To assess natural attenuation of iron through reaeration, a model run was conducted by specifying the top of the water table as a constant oxygen concentration boundary condition. Figure 4-13 presents the distribution of reduced iron at the end of the 5<sup>th</sup>, 10<sup>th</sup>, 20<sup>th</sup>, and 40<sup>th</sup> year; these timeframes were picked to illustrate the temporal migration of the iron plume when subjected to natural attenuation through aquifer reaeration. As Figure 4-13 shows, the iron concentration at any given x increased with depth as expected.

Figure 4-14 presents the distribution of oxygen at the end of the 5<sup>th</sup>, 10<sup>th</sup>, 20<sup>th</sup>, and 40<sup>th</sup> year. By comparing iron and dissolved oxygen distributions in Figure 4-13 and 4-14, respectively, it can be seen that the iron concentration was negligible in the oxygenated aquifer and vice versa. These results suggest that the reduced iron is likely oxidized in the presence of dissolved oxygen and thus precipitates out. The distribution of hematite, goethite, and amorphous Fe(OH)<sub>3</sub> was analyzed to identify the form of iron precipitate resulting from oxidation. Both goethite and amorphous Fe(OH)<sub>3</sub> were found to be zero throughout the simulation's duration. The hematite concentration was found to increase from its initial value of 0.035 mol/L at the iron-oxygen interface suggesting that the reduced iron was oxidizing and precipitating out as hematite in the presence of oxygen. The hematite concentration at 200 ft did not change from its initial value (0.035 mol/L) suggesting that the iron mineral did not dissolve; this location was not impacted by the iron plume.

Figure 4-15 presents a comparison of the iron plume (defined as the 5 mg/L contour line) extents at the end of 5<sup>th</sup>, 10<sup>th</sup>, 20<sup>th</sup>, and 40<sup>th</sup> years with and without aquifer reaeration. The 5 mg/L contour was selected for this comparison as the contours associated with lower iron concentrations output by the model were not smooth. As expected, a portion of the reduced iron was oxidized and precipitated out of the solution with aquifer reaeration. It should be noted that the iron plume did not reach steady state at the end of 40 years and is expected to continue moving laterally with time until steady state is attained. The plume depth will shrink with lateral distance and will ultimately approach zero.

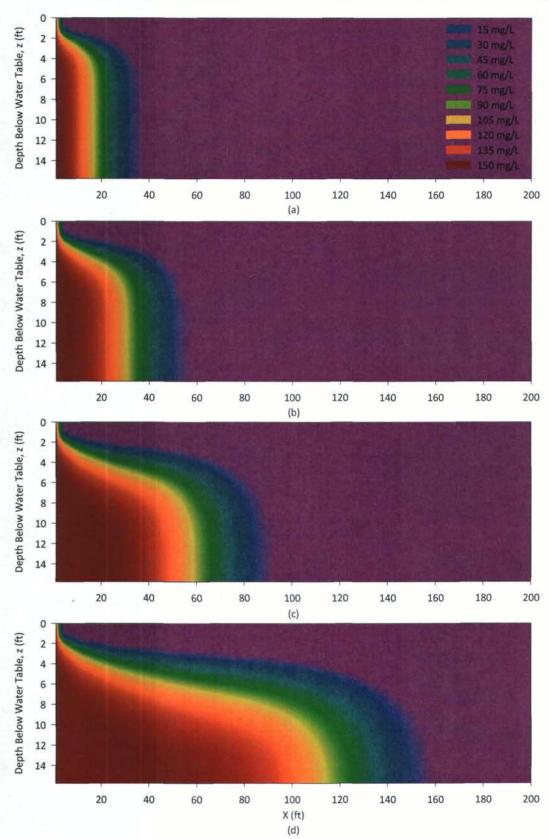


Figure 4-13. Reduced Iron Distribution with Aquifer Reaeration at the End of (a) 5 years, (b) 10 years, (c) 20 years, and (d) 40 years

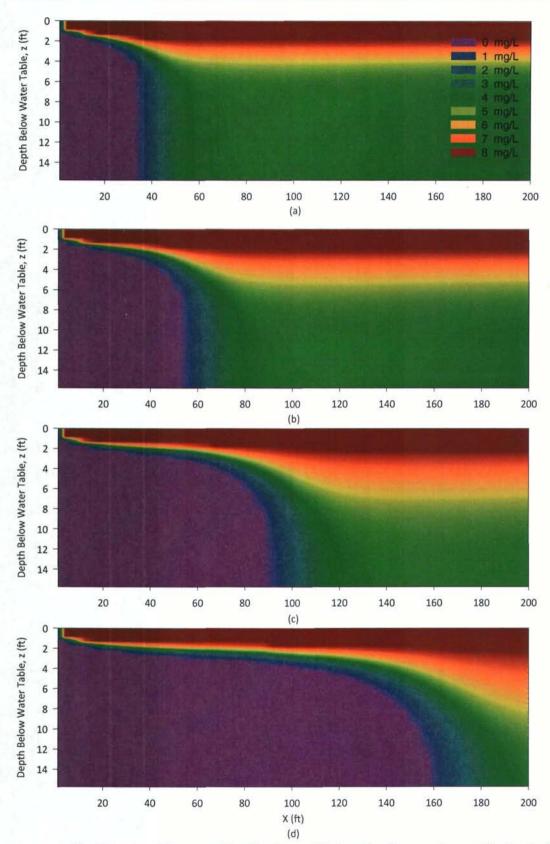


Figure 4-14. Dissolved Oxygen Distribution with Aquifer Reaeration at the End of (a) 5 years, (b) 10 years, (c) 20 years, and (d) 30 years

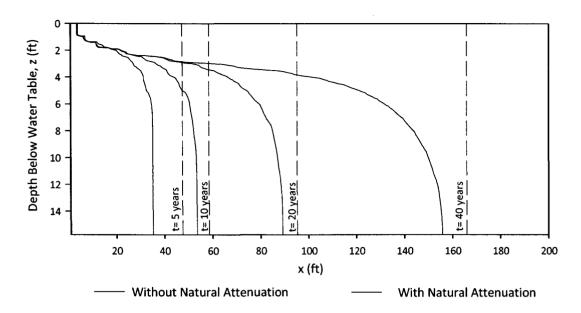


Figure 4-15. Progression of Reduced Iron Plume with and without Aquifer Reaeation

Figure 4-16 shows the iron concentration at 50 ft from the source (x=0); concentrations at depths of 0, 2, 4, 6, 8, 10, and 12 ft below the water table are shown. It can be seen that the iron concentration increased and reached steady-state values approximately at the same time at all depths. The steady-state concentration varied with depth unlike the simulation without aquifer reaeration. It can be seen that the steady-state concentration increased from 0 mg/L at 2 ft below the water table to 150 mg/L (source concentration) at approximately 10 ft below the water table.

Figure 4-17 presents the depth-weighted-average iron concentration at the end of the 40<sup>th</sup> year. The depth-weighted-average iron concentration (calculated at the end of the 40<sup>th</sup> vear) at a given x represents the iron concentration of a sample collected at the end of 40<sup>th</sup> year from a fully-screened well located at that x. For both the cases, the concentration at a point located farther from the source was always less than or equal to the concentration at a point closer to the source. It can be seen that the concentration for the case without reaeration reached the maximum concentration of 150 mg/L up to x=75 ft; 150 mg/L represents the steady-state concentration for this case. The depth-weighted-average concentration for the case with aquifer reaeration was significantly lower than the case without aquifer reaeration. As expected, the difference between the iron concentration with and without reaeration increased with the lateral distance from the source. The percent difference between the iron concentrations with and without reaeration was calculated at various lateral distances from the source at the end of 40<sup>th</sup> year. The percent difference between the iron concentration with and without reaeration ranged from less than 1% at x=1 ft to more than 60% at x=120 ft. The concentration data presented in Figure 4-17 suggests that aquifer reaeration has a significant impact of on the fate of the reduced iron.

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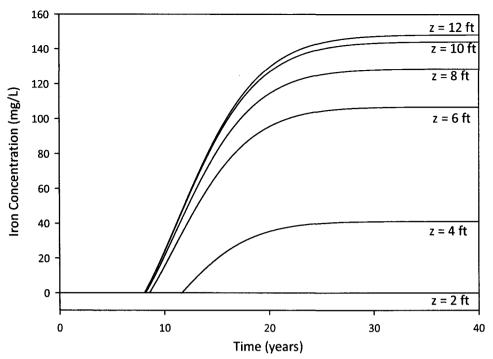


Figure 4-16. Temporal Variation in Reduced Iron at Different Depths at x= 50 ft

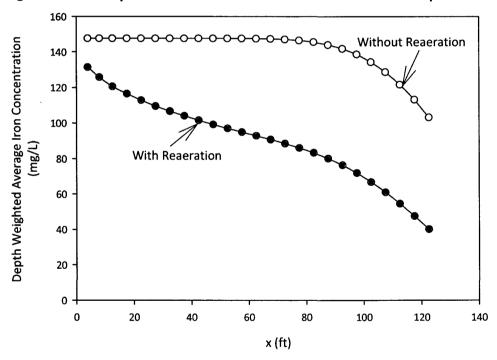


Figure 4-17. Comparison of Depth Weighted Average Iron Concentration with and without Aquifer Reaeration

### 4.8.7 *Summary*

The fate and transport of dissolved iron was modeled with and without aquifer reaeration. The simulations were conducted using MODFLOW and PHT3D models. The modeling results are summarized as follows:

- The dissolved iron migrated away from the source with time and without a decrease in concentration with distance in the absence of aquifer reaeration. The iron concentration did not vary across the depth of the aquifer in this case.
- The dissolved iron concentration decreased with increasing distance from the source and with aquifer reaeration. The iron concentration increased with depth. The plume was observed to reduce in thickness with distance from the source and was located near the lower section of the aquifer. The modeling results suggest that aquifer reaeration has a significant impact on dissolved iron fate and transport.
- The iron concentration at a point located farther from the source was always less than or equal to that at a point located closer to the source.

# 4.9 Fate and Transport Modeling of Sorption as a Natural Attenuation Process for the COCs

#### 4.9.1 Overview

The sorption of the iron, arsenic and ammonium by the naturally-occurring soil is another likely mechanism of natural attenuation of the COCs at the site. As discussed earlier in this section, arsenic has a strong tendency to sorb on ferric oxides and hydroxides that are present in the native soil and would also form with the oxidation of the reduced iron. Similarly, ammonium is reported to co-precipitate with iron. Soil samples were collected from the site to measure the partitioning coefficient ( $k_d$ ) of iron, arsenic, and ammonium; the partitioning coefficient or distribution coefficient is the measure of sorption affinity of a contaminant to soil. Modeling was conducted to evaluate the fate and transport of the COCs based on the lab-measured  $k_d$  values. The specific objective of the modeling conducted in this section was to assess the magnitude of the impact of sorption of COCs by surficial aquifer soils on the plume migration — modeling was conducted using a simplified two-dimensional scenario.

Although the available site data such as hydraulic conductivity, porosity, velocity, COC concentrations, and surficial aquifer depth were used as modeling inputs, the model runs did not account for site features such as cell dimensions and did not simulate the location of the contaminant plume with respect to these site features. The fate and transport modeling accounting for these site features is presented in Section 5.0. Additionally, since the objective of the modeling presented in this section was to assess the impact of sorption, other processes that may impact the fate and transport of the COCs such as aquifer reaeration, and dilution were not simulated. The model results, therefore, should not be interpreted as a comprehensive fate and transport simulation of the site.

#### 4.9.2 Partitioning Coefficient Measurement

IWCS collected soil samples from nine locations at the site in June 2010 to measure the site-specific partitioning coefficients for iron, arsenic, and ammonium; a map showing the sampling locations are presented in Appendix A. Four of the sampling locations (S-1, S-5, S-8, and S-9) were close to four of the additional wells (PW-1, PW-2, PW-3, and PW-

6) drilled to delineate the plume of the COCs and the other five were located between these wells. At each of the sampling locations a borehole was hand-augered until a standing water-column was encountered in the borehole and a sample of the soil below the water table was collected in a 2-L Nalgene polyethylene bottle. The hand auger bucket was thoroughly cleaned and rinsed with distilled water after each sample was collected.

The samples were labeled, stored in an ice-filled cooler, and transported to the University of Florida Solid and Hazardous Waste laboratory. The analysis was performed in accordance with ASTM D 4646-03. A sub-sample of each sample was air-dried for 7 days and the rest were stored in a cooler at 4 °C. Air-dried samples were sieved through a 2-mm screen. A sub-sample of the sieved (<2 mm) air-dried samples was oven-dried to determine the moisture content of the air-dried samples.

For ammonium's k<sub>d</sub> measurement, a known mass of ammonium chloride was dissolved in a known volume of deionized water to prepare an ammonium solution (referred to herein as *solute solution*). A 12.5-gram (oven-dried basis) sub-sample of the sieved (<2 mm) air-dried samples was added in a 500-mL container and 250 mL of the ammonium solution was added to the container to achieve a 1:20 soil-to-solution ratio and the solution pH was measured (referred to herein as *initial pH*). The containers were capped and agitated continuously for 24±0.5 hours on a rotary extractor rotating at 29±2 rounds per minute. The solution pH was measured and then filtered using a 0.45-µm membrane filter. The filtrates and the solute solution were preserved, stored, and analyzed for total ammonia. All the nine samples and a laboratory blank (ammonium solution without soil) were analyzed in triplicate.

The procedure described for ammonium  $k_d$  was repeated for arsenic and reduced iron  $k_d$  measurements. Table 4-3 presents the compound used for the solute solution preparation, initial solute concentration, and the analysis method for ammonium, arsenic, and iron tests.

**Table 4-3. Sorption Tests Parameters** 

Solute	Compound Used	Initial Solute Solution Concentration (mg/L)	Analysis Method
Ammonium	NH <sub>4</sub> Cl	28.7 mg/L NH <sub>4</sub> +	HACH Method 10031
Arsenic	Na <sub>2</sub> HAsO <sub>4</sub> .7H <sub>2</sub> O	0.285 mg/L As <sup>5+</sup>	EPA Method 3010a EPA Method 6010c
Reduced Iron	FeCl <sub>2</sub> .4H <sub>2</sub> O	128.857 mg/L Fe <sup>2+</sup>	HACH Method 8146

The k<sub>d</sub> value was calculated using the following equation:

$$k_d = \frac{(A-B)V}{M_s B}$$
 (eqn 4-4)

where, A = initial concentration of the solute defined as mean concentration of the blanks (mg/L), B = final concentration of the solute after 24 hours in contact with the soil (mg/L), V = volume of solution (mL),  $M_s$  = mass of air-dried soil on an oven-dried basis (g), and  $k_d$  = distribution coefficient (mL/g)

For reduced iron and ammonium  $k_d$  tests, the final solute concentration in the blanks was within 10% of the initial concentration. The average final arsenic concentration in the blanks (0.239 mg/L), however, was approximately 16% less than the initial blank arsenic concentration (0.285 mg/L). An aliquot of the filtrates was acid-digested prior to arsenic analysis using inductively-coupled plasma atomic emission spectroscopy. The analysis of the blank filtrates before and after acid digestion suggested that the average arsenic concentration in the blank filtrates before digestion (0.276 mg/L) was within 4% of the initial arsenic concentration in the blank (0.285 mg/L) and the loss in arsenic concentration was associated with the acid-digestion process. For a lower  $k_d$  estimate, the final blank concentration (0.239 mg/L) was used in place of the initial concentration for the arsenic  $k_d$  value calculation. Figure 4-18 presents the box-and-whisker plot of the measured  $k_d$  values. The figure shows that the  $k_d$  value is constituent-dependent and ranges over orders of magnitude even for a single constituent.

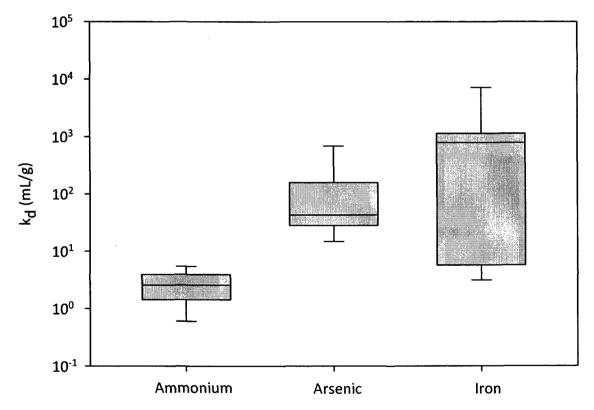


Figure 4-18. Distributions of the Measured k<sub>d</sub> Values

#### 4.9.3 In-Situ Density Measurement

The site-specific sorption modeling required specification of the in-situ density of the soil. The site-specific in-situ soil density was measured using the rubber balloon method (ASTM D 2167-08). The method entailed taking a background reading on the apparatus

base plate placed at the measurement location. Figures 4-19 (a) and (b) below show the base plate and placement of the rubber balloon apparatus over the base plate for taking volume readings, respectively. A 1-ft deep borehole was hand-augered through the annulus of the base plate and the soil withdrawn from the borehole was weighed. The rubber balloon apparatus was placed over the base plate to take the final reading. The borehole volume (V) was estimated by subtracting the initial reading from the final reading. A sample of the soil withdrawn was collected in an air-tight glass jar for moisture content measurement. The in-situ dry density of the soil was calculated using the following equation:

$$\rho = \frac{M(100 - MC)}{100 \ V}$$
 (eqn 4-5)

where, M= mass of the soil withdrawn from the borehole (kg), V= borehole volume (L), and MC= percent moisture content (wet weight basis).

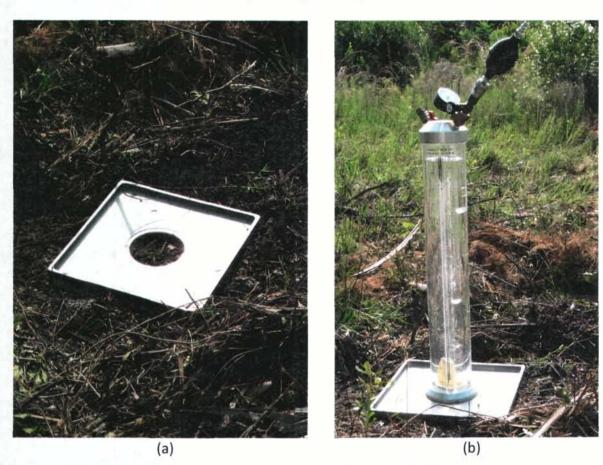


Figure 4-19. Rubber Balloon Apparatus (a) Base Plate, and (b) Placement over the Based Plate for Volume Measurement

The estimated in-situ dry density ranged from approximately 840 to 1,700 kg/m $^3$  (52 to 105 lb/ft $^3$ ). The average in-situ dry density was estimated to be approximately 1,200 kg/m $^3$  (75 lb/ft $^3$ ).

### 4.9.4 Modeling System Description

Figure 4-21 presents a schematic of the system modeled.

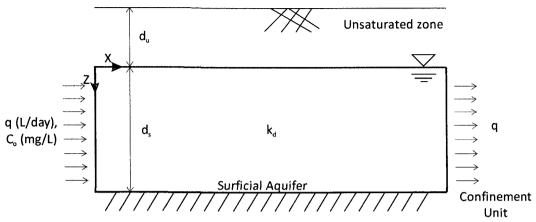


Figure 4-20. Schematic of the Modeled System

Groundwater with a concentration of COCs of  $C_o$  (mg/L) enters the saturated aquifer at a constant flux of q (L per day per  $m^2$ ) at x=0 and are transported laterally due to advection and diffusion. The COCs are sorbed by the soil as these migrate through the surficial aquifer. As noted in Section 4.8, aquifer reaeration and groundwater recharge would potentially decrease the concentration of iron in the impacted groundwater as the distance from the landfill area increases – these effects were not impacted as part of this modeling run since the objective was to isolate the effect of sorption on natural attenuation.

#### 4.9.5 Model Description

Identical versions of MODFLOW and Visual MODFLOW were used in the sorption investigation as described earlier in Section 4.8 – MT3DMS (Version 5.2) was used for contaminant transport modeling. Similar to the aquifer reaeration modeling, the system dimensions, initial conditions, boundary conditions, and other inputs were needed to evaluate the impact of sorption on natural attenuation.

The system dimensions and the groundwater flow simulation inputs used were the same as for the aquifer reaeration modeling presented in the previous section. A  $k_d$  value of  $10^{-6}$  L/mg was used to model sorption. As presented earlier, this value represented the lower end of the  $k_d$  values measured for soil samples collected from the site. The sorption was modeled as an equilibrium-controlled linear isotherm reaction. A constant head of 16.55 ft and 16 ft was specified at x= 0 and 500 ft, respectively. These heads were specified to create a hydraulic gradient of 0.0011 ft/ft. The surficial aquifer top and bottom boundaries (z= 0 and z=16 ft) were treated as zero-flux boundaries.

A concentration or flux (concentration gradient) of each species was specified at each of the system boundaries. The modeled scenario is a two-dimensional fate and transport case; therefore, four boundary conditions were specified. At the x=0 boundary, a constant iron, arsenic, and total ammonia concentration of 150 mg/L, 0.3 mg/L, and 30 mg/L, respectively, was specified. It should be noted that these concentration values

represent the higher end of the concentrations of these COCs measured to date for the site. The groundwater and dissolved contaminant exited the system at x=500 ft at a rate such that the head at this boundary was always equal the specified head at this boundary. The flux of all the three species across the top and the bottom of the surficial aquifer was specified to be zero. A head of 16.3 ft was assigned everywhere in the domain as the initial head (at t=0). The initial concentrations of all the species were assumed to be zero. Table 4-4 lists all the inputs described above.

**Table 4-4. Input Parameters Used in Sorption Modeling** 

Symbol	Parameter	Value Used for Modeling
System D	Dimensions	
d <sub>s</sub>	Saturated surficial aquifer depth	16 ft
$d_u$	Unsaturated surficial aquifer depth	0 ft
X	Horizontal extent of surficial aquifer	500 ft
<u>Aquifer F</u>	Properties	
Ks	Hydraulic conductivity in the saturated zone	2 ft/day
η	Porosity	0.25 (v/v)
S <sub>s</sub>	Storage coefficient	0.15
D	Bulk diffusion coefficient	0.0014 ft²/day
k <sub>d</sub>	Partitioning coefficient	10 <sup>-6</sup> L/mg
ρ	Dry soil density	1,200 kg/m³
Boundar	y Condition at x=0	
	Iron concentration	150 mg/L
	Arsenic concentration	0.250 mg/L
	Total ammonia concentration	30 mg/L
	Head	16.55 ft
Boundar	y Condition at z=500	
	Head	16.00 ft
Initial Co	ndition (t=0)	
	Iron, Arsenic, Total ammonia concentration	0

#### 4.9.6 Results

To assess the magnitude of the impact of sorption on the fate and transport of COCs, the two simulations—one with sorption and the other without sorption—were conducted. For model runs simulating the fate and transport without sorption, a  $k_d$  =0 was specified. All the other inputs were the same as described earlier in this section. Figure 4-21 presents the distribution of reduced iron at the end of the  $5^{th}$  and  $40^{th}$  year with and without sorption. As expected, reduced iron moved as a vertical front with time for both simulations (with and without sorption). The iron front without sorption moved as far as 140 ft from the source in 40 years. However, it moved less than 30 ft from the source in 40 years with sorption. As shown in Figures 4-22 and 4-23, a similar difference in the arsenic and total ammonia front migration was observed. The model suggests that sorption corresponding to even a low value of the site-specific  $k_d$  measurements had a dramatic impact on the fate and transport of the COCs.

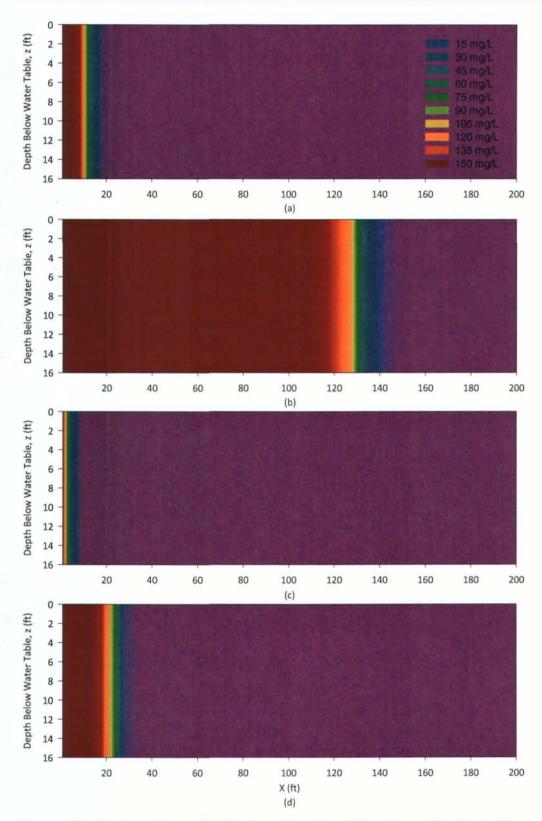


Figure 4-21. Reduced Iron Distribution (a) without Sorption at the End of 5 years (b) without Sorption at the End of 40 years, (c) with Sorption at the End of 5 years (d) with Sorption at the End of 40 years

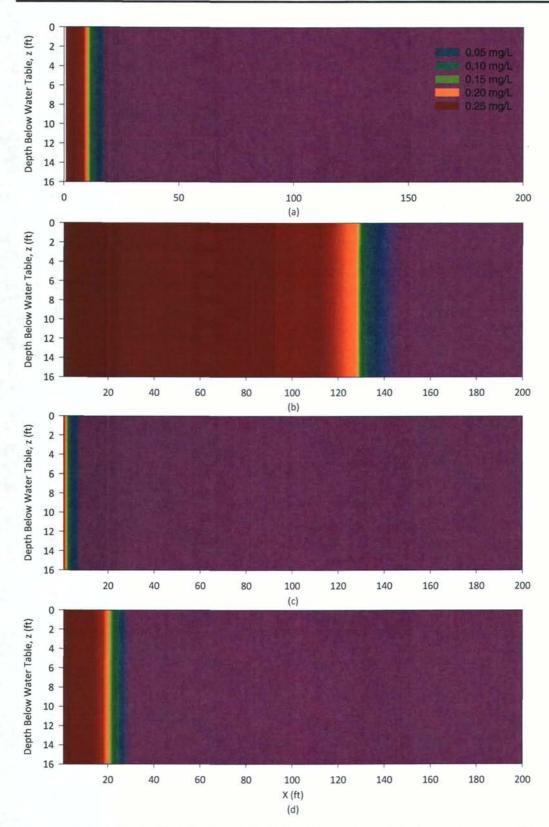


Figure 4-22. Arsenic Distribution (a) without Sorption at the End of 5 years (b) without Sorption at the End of 40 years, (c) with Sorption at the End of 5 years (d) with Sorption at the End of 40 years

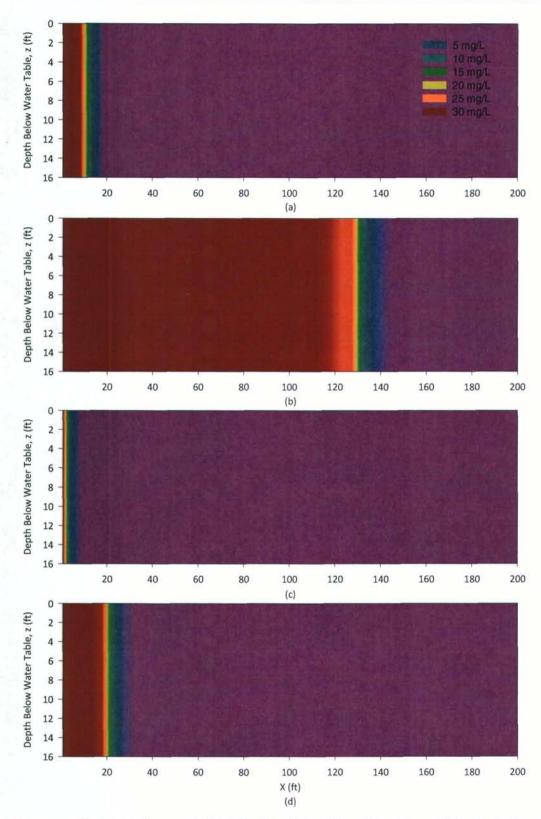


Figure 4-23. Total Ammonia Distribution (a) without Sorption at the End of 5 years (b) without Sorption at the End of 40 years, (c) with Sorption at the End of 5 years (d) with Sorption at the End of 40 years

# 4.10 Comparison of Relative Impact of Reaeration and Sorption as Natural Attenuation Processes

By comparing Figures 4-10(d) and 4-21(d), which present iron distribution at the end of 40<sup>th</sup> year for attenuation with aquifer reaeration and with sorption, respectively, it can be seen that for the same groundwater flow and contamination source conditions sorption results in a greater degree of attenuation than aquifer reaeration at the site.

# 4.11 Potential for NAM as an Effective Remedial Strategy

Ideal sites for employing NAM to manage risk are those with COCs that are amenable to concentration reduction with time and distance through a combination of natural physical, chemical, and biological processes and those located a sufficient distance away from a receptor of concern. Several mechanisms can result in natural attenuation, including sorption to the soil, chemical transformation and biological decomposition. A classic example of natural attenuation is the case of an old landfill that has low concentrations of VOCs that are expected to degrade with time and distance away from the landfill.

Reductive dissolution, which has been demonstrated to be the cause of the groundwater exceedances, will be amenable to natural attenuation as follows:

- The cause of iron reductive dissolution is a reduction in oxygen concentrations because of landfill construction and related Site activities, as the impacted groundwater travels into non-impacted areas, oxygen concentrations should increase over time and distance to natural levels. This will in turn result in the eventual transformation of the dissolved-phase iron (Fe<sup>2+</sup>) to a solid-phase iron mineral (Fe<sup>3+</sup>). Thus iron concentrations in the groundwater will decrease as distance from landfilling activities increases.
- The amount of iron in the soil under the landfill that can be released through reductive dissolution is finite, so at some point the source will decrease, and thus the concentration of iron in the surrounding groundwater will decrease with time.
- Iron that enters the groundwater will exist as Fe<sup>2+</sup>, an ion which will react with other minerals in the soil, and thus be subject to natural attenuation as any metal ion would.
- Some of the arsenic released during the dissolution of iron minerals will reprecipitate with iron minerals (existing or newly precipitated) that are transformed back to the solid phase; arsenic will thus naturally attenuate through sorption and precipitation.
- Some of the ammonium released during the dissolution of iron minerals will reprecipitate with iron minerals that are transformed back to the solid phase –
  ultimately, ammonium would naturally attenuate via sorption and precipitation.
  Furthermore, ammonium will be subject to biological redox reactions when the
  groundwater becomes oxygenated, with an ultimate conversion to nitrogen gas

# 5. Temporary Point of Compliance Selection

#### 5.1 Overview

Based on the evidence presented in the previous sections of this report, NAM appears to be a feasible remedial approach to address the groundwater impacts at the site. However, as discussed in Section 2.0, Rule 62-780 allows NAM only if all of the specific criteria listed Rule 62-780.690 (1) are met. The assessment of a few of the criteria listed in Rule 62-780.690 (1) require an assessment of the migration of COCs with respect to the TPOC. This section presents the approach used to establish the TPOC, the proposed TPOC well locations and the fate and transport modeling used to assess the migration of COCs with respect to the selected TPOC wells.

#### 5.2 TPOC Establishment

The decline in the oxygen recharge of the surficial aquifer system resulting from the liner system construction and operations such as earthwork (e.g., soil stockpiling, compaction, stormwater pond) was identified as the cause of the reductive dissolution of iron at the site. The fact that most of the monitoring wells located within the areas that have been developed as a part of the site construction operation have recorded concentration of COCs greater than the background well (MW-1) suggest that the naturally-occurring soil at the site is susceptible to reductive dissolution when subjected to alterations which can decrease oxygen transfer between the aquifer and the atmosphere. Figure 5-1 presents the area that has been developed from its natural state as part of the site's construction and operation.

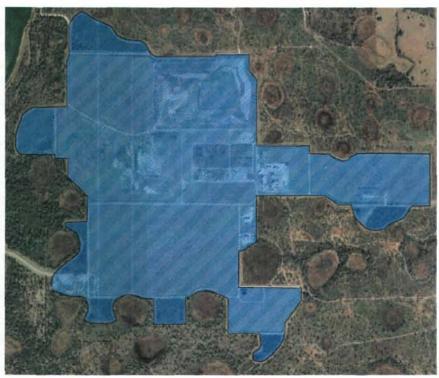


Figure 5-1. Area Developed at the Site for Operations

The attenuation of the COCs is expected to occur as these constituents travel through the soil in undisturbed areas. Some attenuation would be expected to occur beneath the developed areas. However, the degree of natural attenuation expected beneath the developed areas is anticipated to be less than the attenuation the COCs in the soil below the undisturbed natural areas surrounding the developed area. To assess whether natural attenuation of COCs occurs through the undisturbed areas, the installation of four groundwater monitoring wells in the undisturbed area is proposed. These wells will be located about 500 to 1,000 ft downgradient of the edge of the disturbed area as shown in Figure 5-2. These wells are proposed as the TPOC until the site achieves the No Further Action criteria of Rule 62-780.680(1), 62-780.680(2), or 62-780.680 (3), FAC or until NAM is determined to not be an effective rehabilitation strategy for the site, whichever occurs first.

Rule 62-780.690(2) allows temporary relocation of the point of compliance to the property boundary, or to the plume edge when the plume is within the property boundary while NAM is proceeding provided human health, public safety, and the environment are protected. The proposed TPOCs are located within the property boundary. As no public or private well located within the area bounded by the TPOC (please see the SAR for more details) draws water from the surficial aquifer, the proposed TPOC, therefore, is anticipated to be protective of human health, public safety, and the environment.

Seven stormwater management ponds are located within the zone bounded by the TPOC wells - these ponds store the stormwater runoff up to a control elevation which is above the water table elevation and ultimately the stored water percolates and mixes with the groundwater. The COCs that may be present in stormwater pond-groundwater mix would attenuate as they seep through the undisturbed zone soil before migrating outside the TPOC. The ponds would discharge the stormwater-groundwater mix to surface waters when the water elevation is above the control elevation, which can be expected to occur after a large storm event. Because of the low groundwater velocity, the groundwater would be significantly diluted with the stormwater runoff before discharging to surface waters. Because of the anticipated low impact of stormwater pond on surface water quality, no well is proposed to monitor compliance with surface water standards.

# 5.3 Assessment of COCs Migration Relative to TPOC

## 5.3.1 Overview

Per Rule 62-780.690, FAC the following assessments must be made (pertaining to TPOC) for NAM to be allowable site rehabilitation strategy:

 Contaminants present in the groundwater above background concentrations or applicable CTLs are not migrating beyond the TPOC or migrating vertically, which may contaminate other aquifers or surface water resources or result in increased site rehabilitation time.



Figure 5-2. Proposed TPOC Wells

 A scientific evaluation (historical data or modeling results, as appropriate; the model used shall be demonstrated to be appropriate for the site conditions) of the plume migration in relation to the temporary point of compliance.

This section presents the fate and transport modeling conducted related to these assessments. As discussed in the previous section, the sorption process at the site is expected to dominate the natural attenuation of COCs. Therefore, only sorption was modeled for a more conservative assessment. Other process such as aquifer reaeration and dilution associated with groundwater recharge were not modeled.

#### 5.3.2 Model Description

MODFLOW (Version 2005) and MT3DMS (Version 5.2) were used for assessing the fate and transport of the COCs. Visual MODFLOW 2009.1 Pro was used as the graphical user interface to input the modeling data, run the models, and analyze the modeling results.

# 5.3.3 Model Input Parameters

The fate and transport of all the three COCs (iron, arsenic and total ammonia) was modeled. The models require specification of the system dimensions, initial condition,

the boundary conditions, and several other inputs to simulate fate and transport of iron, arsenic, and total ammonia as functions of time. This section describes the values of the input parameters used for the modeling effort.

The site layout and the associated coordinates were imported into the model as a shape file to define the model domain(s). The groundwater flow direction was assumed to be in the southwest direction and invariable for the model duration. The shape files were rotated by  $45^{\circ}$  to align the site so that the groundwater flow is in the southwest direction (from the top of the domain to the bottom of the domain). The site extents used for modeling are shown in Figure 5-3. An approximately 9,200 ft  $\times$  9,400 ft area was modeled. The figure also shows the grid size used for the modeling. On average a 50 ft  $\times$  50 ft spatial discretization was used for modeling.

A surficial aquifer thickness of 16 ft and a hydraulic gradient of approximately 0.0011 ft/ft were used for model run. The hydraulic gradient was created by specifying a constant head of 16 ft at the bottom-most row and a constant head of 26.2674 ft at the top-most row. The side boundaries were specified to be zero flux. Similarly, the top and bottom elevation of the aquifer were modeled as a zero-flux boundary condition.

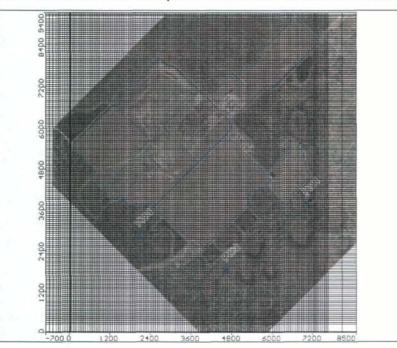


Figure 5-3. Site Area Used for Modeling

The nodes within the boundary of the developed area of the landfill were specified as the iron, arsenic, and total ammonia source with a constant concentration of 150 mg/L, 0.25 mg/L, and 30 mg/L, respectively, which are all at the higher end of the historically-measured concentrations of these constituents. Figure 5-4 shows that area that was modeled as a source of the COCs. All the nodes below this area were specified as constant concentration sources of the COCs to model soil beneath the developed area as the contamination source.

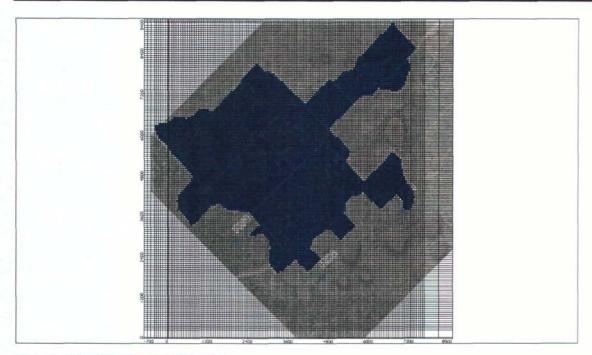


Figure 5-4. COC Source Extents

A  $k_d$  value of 0 was specified for nodes modeled as sources of COCs to model the case that soil under reductive dissolution would not sorb COCs, which is a conservative assumption as soil beneath the developed area would also be expected to sorb the COCs to some degree. A  $k_d$  value of  $10^{-6}$  L/mg (the lower end of that measured from site-collected soil samples) was used to model sorption of COCs in the undisturbed area (outside the extents of the disturbed area, the green area shown in Figure 5-5). The sorption was modeled as an equilibrium-controlled linear isotherm reaction.



Figure 5-5. Sorption Zone Used for Modeling

The initial concentrations of iron, arsenic, and total ammonia were assumed to be 5 mg/L, 0.005 mg/L, and 0.2 mg/L, respectively. The initial concentrations were selected based on the average concentration of these COCs in the background well (MW 1). Simulations were conducted at K=0.25 ft/day and K=4.1 ft/day, which is the lower and higher end of the hydraulic conductivity estimated at the site, respectively. The simulations were conducted for 200 years. Table 5-1 lists all the inputs described above.

Table 5-1. Input Parameters for Plume Migration Modeling

Symbol	Parameter	Value Used for Modeling						
System D	System Dimensions							
ds	Saturated surficial aquifer depth	16 ft						
du	Unsaturated surficial aquifer depth	0 ft						
<u>Aquifer P</u>	Properties Properties							
Ks	Hydraulic conductivity in the saturated zone	0.25 to 4.1 ft/day						
η	Porosity	0.25 (v/v)						
S <sub>s</sub>	Storage coefficient	0.15						
D	Bulk diffusion coefficient	0.0014 ft <sup>2</sup> /day						
k <sub>d</sub>	Partitioning coefficient	10 <sup>-6</sup> L/mg						
ρ	Dry soil density	1,200 kg/m³						
Source C	oncentration							
	Iron concentration	150 mg/L						
	Arsenic concentration	0.250 mg/L						
	Total ammonia concentration	30 mg/L						
Initial Co	ndition (t=0)							
	Iron concentration	5 mg/L						
	Arsenic concentration	0.005 mg/L						
	Total ammonia concentration	0.2 mg/L						

#### 5.3.4 Results

The plume extents of the COCs, defined by the respective initial concentration, are presented in Appendix A. The results show that the COCs are not expected to migrate outside the TPOC, even with a 200-year model simulation period. Therefore, the location of the four TPOC wells is appropriate and consistent with the requirements of Rule 62-780. As discussed earlier, the impacts of aquifer reaeration and dilution with recharge were not modeled. These factors will further slow the plume's migration. For the modeling results presented above, it was assumed that the undisturbed areas would not be developed over time. The TPOC selection was based on the assumption that the undisturbed areas of the Site would not be further developed. In the event that Site development occurs in currently undisturbed areas, new TPOC locations would be selected (on an as-needed basis) and submitted to the FDEP as part of a modified NAM Furthermore, the TPOC representing the area of the highest constituent concentrations (MW-8A) would likely have to be relocated as a development within the current disturbed area as more landfill cells are built - therefore, a new well would be selected (either an existing well or a new well) located in the area of highest concentration.

## 6. Proposed NAM Plan

The previous sections demonstrate that NAM is an appropriate remedial strategy for the site based on the requirements in Rule 62-780. The proposed NAM plan is as follows:

- Groundwater will be sampled from the four proposed TPOC wells (TPOC-1, TPOC-2, TPOC-3, TPOC-4), and MW-8A (these five wells are collectively referred to herein as NAM wells) on a semi-annual basis MW-8A was selected as a NAM well to satisfy the requirement of Rule 62-780.690(8)(a)(2) to include a well located in the area of highest concentration. The TPOC wells will be installed after the NAM plan is approved. Monitoring well MW-8A is located in the area of greatest contamination as can be seen from Figures 3-2 and 3-3. A map showing locations of the proposed TPOC wells is included in Appendix A. All samples will be collected in accordance with FDEP's most recent set of Standard Operating Procedures for Groundwater Sampling.
- One groundwater sample will be collected from each of the proposed NAM wells. Additionally, one blind duplicate sample will be collected from a random NAM well selected in the field on the day of the sampling event.
- Samples will be transported in an iced cooler under chain of custody protocol to a laboratory certified under the NELAC Institute.
- Water-level elevation readings will be measured at each of the five proposed NAM wells within 24 hours of initiating any groundwater sampling event. NAM sampling activities including water level measurements will be conducted with the routine groundwater sampling events.
- Analysis for a variety of field and laboratory parameters (shown in Table 6-1) will be conducted during each sampling event.

Table 6-1. Analytes and Corresponding Methodologies as Part of NAM

Field Parameter	Analytical Method		
рН	EPA 150.1		
Temperature	EPA 170.0		
ORP	ASTM D1498-00		
Specific Conductance	EPA 120.1		
Dissolved Oxygen	EPA 360.1		
Laboratory Parameter	Analytical Method		
Arsenic	EPA 6020B		
Iron	EPA 6020B		
Total Ammonia	EPA 350.1		
Total Dissolved Solids	SM 2540C		

- Within 60 days of sample collection, two copies of the quarterly NAM report will be signed, sealed, and submitted by a Professional Engineer or Professional Geologist registered in Florida to FDEP. The NAM report will include the following:
  - Brief background on the project and activities conducted
  - Laboratory analytical results and chain of custody documentation
  - Summary tables of all analytical results, corresponding CTLs, and detection limits
  - Site maps which illustrate the results
  - Water-level elevation information (summary table and flow map)
  - Conclusions and recommendations
- It is our understanding that the FDEP will establish action levels for COCs for the proposed NAM wells during the NAM plan approval process.

Table 6-2. Proposed Action Levels as Part of the NAM Plan

Well ID	Total Ammonia Action Level (mg/L)	Arsenic Action Level (μg/L)	Iron Action Level (mg/L)
TPOC-1, TPOC-2, TPOC- 3, TPOC-4	2.8	10	14
MW-8A	32	1,100	150

#### Notes:

- 1. MW-8A was selected as the well located in the area of the highest constituent concentration as required in Rule 62-780.690(8)(a)(2), as it was the location of the highest measured iron concentration.
- 2. Iron action level for the TPOC wells was based on the maximum measured concentration in background well MW-1.
- In the event of an exceedance of these action levels, confirmatory sampling will be conducted at applicable wells within 30 days of receiving the initial results. If the confirmatory sampling results show an exceedance(s) of the specified action level(s), the subsequent annual NAM report (described below) will include a proposal to perform a supplemental site assessment, continue the implementation of the NAM plan, or prepare and submit a Remedial Action Plan.
- On an annual basis, site analytical data will be evaluated to determine the
  concentration trend of COCs in the NAM wells. As described in Section 2.0, the
  site will achieve NFA criteria only after all the iron mass that has the propensity
  to reductively dissolve has been released. The data and tools are not available to
  assess the time frames the naturally-present soil will continue to release iron

- under reductive dissolution which is needed to assess annual reduction in COCs or time to achieve NFA criteria for the site.
- The proposed NAM plan implementation will continue until the site meets the NFA criteria 62-780.680(1), 62-780.680(2), or 62-780.680(3), F.A.C., for at least the last two consecutive sampling events.

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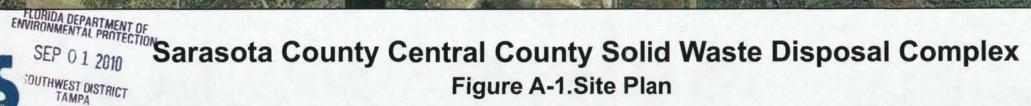
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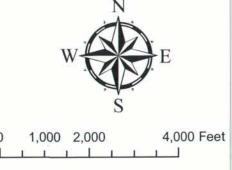
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Appendix A
Site Plans





OUTHWEST DISTRICT



Legend

Property Boundary

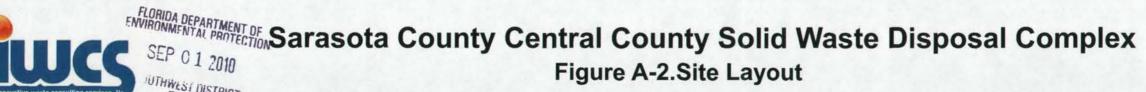
Developed Area







1,200 Feet







**Abandoned Wells** 

1,500 Feet

**Existing Wells** 

ENVIRONMENTAL PROTECTION Sarasota County Central County Solid Waste Disposal Complex **Figure A-3.Well Locations** 





SEP 0 1 2010 SOUTHWEST DISTRICT

ENVIRONMENTAL PROTECTION

SEP 0.1

Sep Figure A-4.Partitioning Coefficient Sampling Locations - June 2010





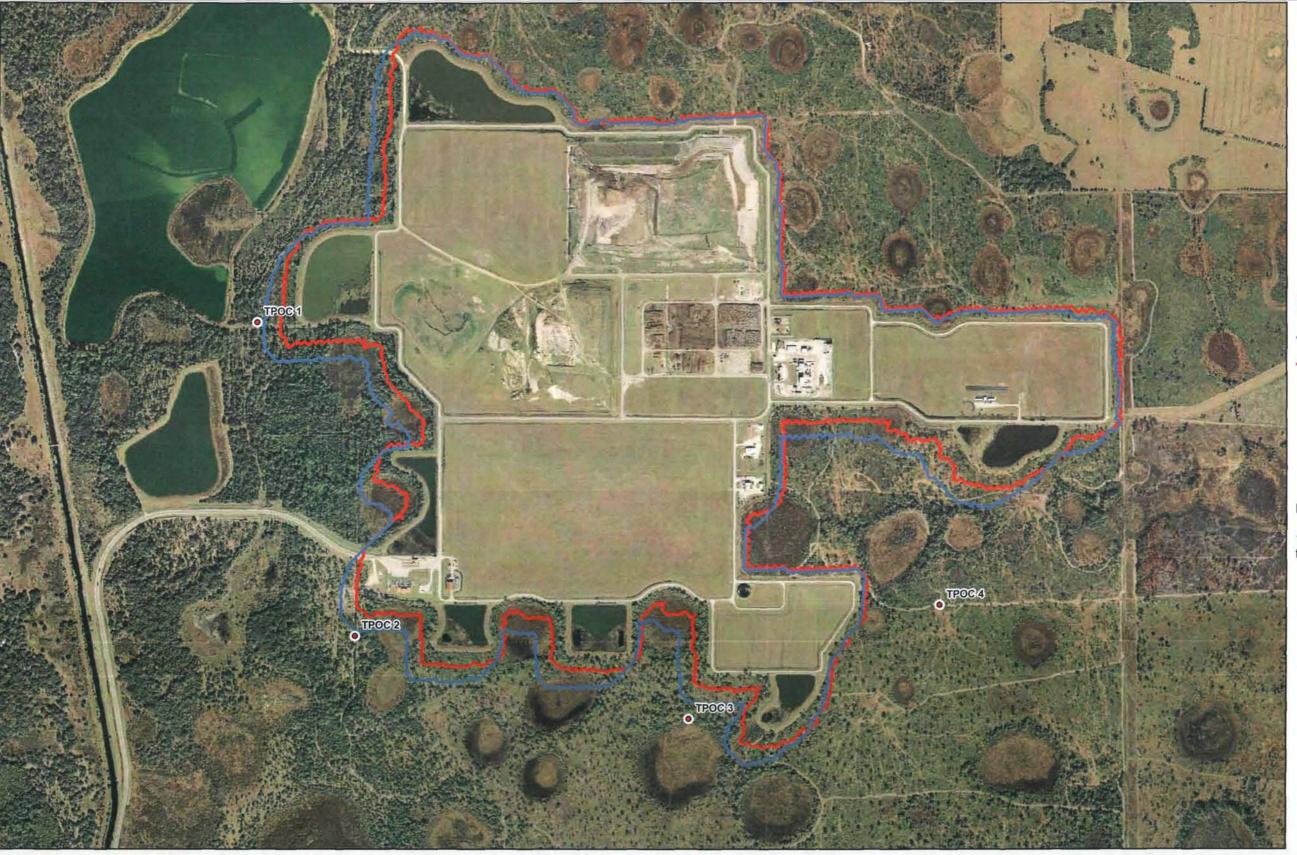
4,000 Feet

Property Boundary

Developed Area

SEP 01 2010 Sarasota County Central County Solid Waste Disposal Complex Figure A-5.Proposed TPOC Wells

SOUTHWEST DISTRICT





- K=4.1 ft/d,  $k_d = 10^{-6}$  L/mg - K=0.25 ft/d,  $k_d = 10^{-6}$  L/mg

### Notes:

 Groundwater flow was assumed to be towards the southwest.



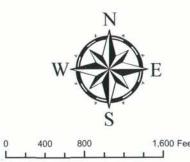
FLORIDA DEPARTMENT Sarasota County Central County Solid Waste Disposal Complex

SEP 0 1 2010

Figure A-6. Modeled Arsenic Plume Extent After 200 Years







 $K=4.1 \text{ ft/d}, k_d = 10^{-6} \text{ L/mg}$ 

K=0.25 ft/d, k<sub>d</sub> =10<sup>-6</sup> L/mg

### Notes:

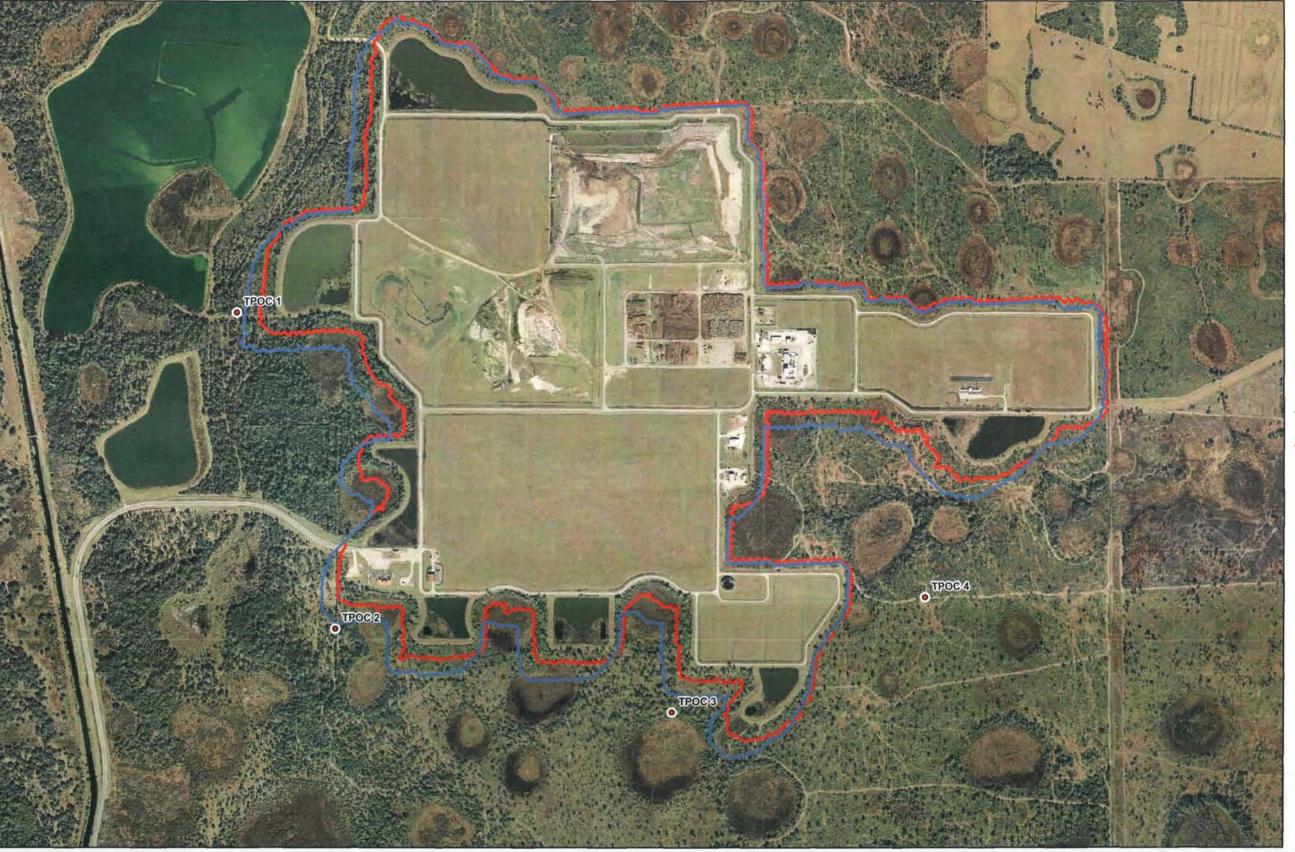
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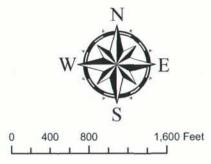


SOUTHWEST DISTRICT

SEP () 1 2010
Sarasota County Central County Solid Waste Disposal Complex Figure A-7. Modeled Ammonia Plume Extent After 200 Years







K=4.1 ft/d, k<sub>d</sub> =10<sup>-6</sup> L/mg

K=0.25 ft/d, k<sub>d</sub> =10<sup>-6</sup> L/mg

## Notes:

1. Groundwater flow was assumed to be towards the southwest.



ENVIRONMENTAL PROTECTION Sarasota County Central County Solid Waste Disposal Complex SEP 0 1 2010 Figure A-8.Modeled Iron Plume Extent After 200 Years MITHWEST DISTRICT

# Appendix B Groundwater and Leachate Quality Data Summary and Trend Charts

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Table B-1 Occurrence of GWCTL Exceedances by Well

Well ID	Constituent	# of Samples	# of Detections	Concentration Range (mg/L)		GCTL (mg/L)	# of GCTL Exceedances
				Minimum	Maximum		
MW - 1	Arsenic	24	16	0.00132	0.018	0.01	1
	Iron	24	23	0.1	13.7	0.3	23
	Ammonia (as N)	24	23	0.02	0.41	2.8	0
	TDS	23	23	386	2400	500	19
	Sodium	23	23	22	530	160	16
	Chloride	23	23	29	720	250	17
	Sulfate	4	4	4.7	15.7	250	0
	Zinc	16	12	0.0048	11.5	5	1
	Lead	11	0	0.0005	0.005	0.015	0
MW - 2	Arsenic	5	4	0.0042	0.00805	0.01	0
	Iron	5	5	1.79	14	0.3	5
	Ammonia (as N)	5	5	0.14	0.3	2.8	0
	TDS	5	5	410	570	500	3
	Sodium	5	5	46	59	160	0
	Chloride	5	5	51	74.3	250	0
	Sulfate	0	0	0	0	250	0
	Zinc	5	2	0.015	7	5	1
	Lead	5	2	0.0005	0.013	0.015	0
MW - 4	Arsenic	17	6	0.001	0.005	0.01	0
	Iron	17	17	1.8	3.8	0.3	17
	Ammonia (as N)	17	17	0.045	0.25	2.8	0
	TDS	17	17	105	200	500	0
	Sodium	17	17	8.4	19	160	0
	Chloride	17	17	16	44	250	0
	Sulfate	0	0	0	0	250	0
	Zinc	12	8	0.0035	11.4	5	1
	Lead	9	1	0.0005	0.005	0.015	0
MW - 8	Arsenic	25	25	0.0076	0.058	0.01	12
	Îron	25	25	18	150	0.3	25
	Ammonia (as N)	25	25	2.92	30	2.8	25
	TDS	25	25	500	1085	500	24
	Sodium	24	24	53	98	160	0
	Chloride	24	23	13	75	250	0

Well ID	Constituent	# of Samples	# of Detections		tion Range g/L)	GCTL (mg/L)	# of GCTL Exceedance
				Minimum	Maximum		
• •	Sulfate	6	3	0.036	50	250	0
	Zinc	19	11	0.0032	26.3	5	1
	Lead	14	6	0.0005	0.018	0.015	1
MW - 9	Arsenic	27	27	0.033	0.075	0.01	23
	Iron	27	27	5.02	52	0.3	27
	Ammonia (as N)	27	27	6.6	19	2.8	27
	TDS	27	27	740	1250	500	27
	Sodium	26	26	16	80	160	0
	Chloride	26	25	5	61	250	0
	Sulfate	6	5	0.036	25	250	0
	Zinc	14	5	0.0032	7.52	5	1
	Lead	13	1	0.0005	0.018	0.015	1
MW - 10	Arsenic	27	26	0.003	0.014	0.01	7
	Iron	27	27	17	66	0.3	27
	Ammonia (as N)	27	26	2.7	11.4	2.8	25
	TDS	27	27	540	928	500	27
	Sodium	26	26	69.2	93	160	0
	Chloride	26	26	15	107	250	0
	Sulfate	6	2	0.036	25	250	0
	Zinc	19	9	0.0032	7.17	5	1
	Lead	13	1	0.0005	0.0077	0.015	0
MW - 11	Arsenic	23	20	0.00157	0.041	0.01	3
	Iron	23	22	0.87	8.7	0.3	22
	Ammonia (as N)	23	23	0.19	2.91	2.8	1
	TDS	23	23	110	960	500	3
	Sodium	23	22	1.4	58	160	0
	Chloride	23	23	2.1	78	250	0
	Sulfate	3	3	110	170	250	0
	Zinc	13	6	0.0032	25.2	5	1
	Lead	9	1	0.0005	0.0056	0.015	0
MW - 12	Arsenic	22	13	0.0047	0.017	0.01	1
	Iron	22	21	0.18	49	0.3	20
	Ammonia (as N)	22	22	0.19	6.7	2.8	4
	TDS	22	22	200	2600	500	5

Well ID	Constituent	# of Samples	# of Detections		tion Range g/L)	GCTL (mg/L)	# of GCTL Exceedances
		·		Minimum	Maximum		
	Sodium	22	22	2	223	160	1
-	Chloride	22	22	2.1	620	250	1
	Sulfate	3	3	93	700	250	2
	Zinc	13	6	0.003	6.01	5	1
	Lead	9	1	0.0005	0.005	0.015	0
MW - 13	Arsenic	1	1	0.015	0.015	0.01	1
	Iron	1	1	19	19	0.3	1
	Ammonia (as N)	1	1	1.8	1.8	2.8	0
	TDS	1	1	680	680	500	1
	Sodium	1	1	98	98	160	0
	Chloride	1	1	120	120	250	0
	Sulfate	0	0	0	0	250	0
	Zinc	1	0	0.0232	0.0232	5	0
	Lead	2	1	0	0.0152	0.015	0
MW - 15	Arsenic	2	2	0.0287	0.0473	0.01	2
	Iron	2	2	33.6	46.9	0.3	2
	Ammonia (as N)	2	2	3.36	4.1	2.8	2
	TDS	2	2	3000	3540	500	2
	Sodium	1	1	58	58	160	0
	Chloride	1	1	122	122	250	0
	Sulfate	2	2	639	1010	250	2
	Zinc	0	0	0	0	5	0
	Lead	0	0	0	0	0.015	0
MW - 16	Arsenic	2	2	0.0324	0.0473	0.01	2
	Iron	2	2	55.9	73.6	0.3	2
	Ammonia (as N)	2	2	12.2	12.5	2.8	2
	TDS	2	2	1830	1970	500	2
•	Sodium	2	2	256	260	160	2
	Chloride	2	2	305	308	250	2
	Sulfate	1	1	9.2	9.2	250	0
	Zinc	0	0	0	0	5	0
····	Lead	0	0	0	0	0.015	0
MW - 17	Arsenic	2	2	0.0427	0.07	0.01	2
	lron	2	2	105	136	0.3	2
	Ammonia	2	2	15	25.1	2.8	2

Well ID	Constituent	# of Samples	# of Detections		ition Range g/L)	GCTL (mg/L)	# of GCTL Exceedances
				Minimum	Maximum		
	(as N)	··					<del></del>
	TDS	2	2	192	948	500	1
	Sodium	1	1 1	52.8	52.8	160	0
	Chloride Sulfate	1		75.7	75.7	250	0
		ılfate <u>1</u>	1	4.7	4.7	250	0
	Zinc	0	0	0	0	5	0
	Lead	0	0	0	0	0.015	0
MW - 18	Arsenic	2	1	0.005	0.00785	0.01	0
	Iron	2	2	20.7	28.1	0.3	2
	Ammonia (as N)	2	2	1.3	1.61	2.8	0
	TDS	2	2	292	605	500	1
	Sodium	1	1	3.12	3.12	160	0
	Chloride	1	_ 1	3.1	3.1	250	0
	Sulfate	1	1	1.3	1.3	250	0
	Zinc	0	_0	0	0	5	0
	Lead	0	0	0	0	0.015	0
MW - 19	Arsenic	2	2	0.0422	0.0541	0.01	2
	Iron	2	2	46.1	63.3	0.3	2
	Ammonia (as N)	2	2	21	22.4	2.8	2
	TDS	1	1	756	756	500	1
	Sodium	1	1	42.9	42.9	160	0
	Chloride	1	_1	67.8	67.8	250	0
	Sulfate	1	_1	10.11	10.11	250	0
	Zinc	0	_0	0	0	5	0
	Lead	0	0	0	0	0.015	0
MW - 20	Arsenic	2	2	0.0237	0.0767	0.01	2
	Iron	2	2	20.7	58.2	0.3	2
	Ammonia (as N)	2	2	0.56	3.2	2.8	1
•	TDS	2	2	1030	1180	500	2
	Sodium	1	1	39.5	39.5	160	0
	Chloride	1	1	87.9	87.9	250	0
	Sulfate	1	1	3.3	3.3	250	0
	Zinc	0	0	0	0	5	0
	Lead	1	1	0.0159	0.0159	0.015	1
CW - 8	Arsenic	7	7	0.0337	0.061	0.01	7

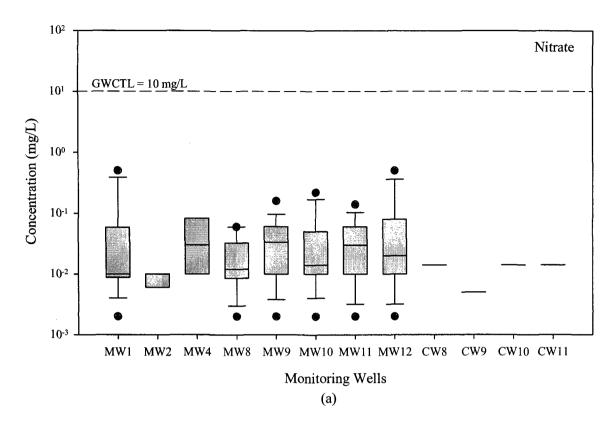
Well ID	Constituent	# of Samples	# of Detections		ition Range g/L)	GCTL (mg/L)	# of GCTL Exceedance
	Iron Ammonia (as N)			Minimum	Maximum		
		7	7	44.4	64		7
			7	4.2	6.7	2.8	7
	TDS		7	390	680	500	1
	Sodium	6	6	36	40.9	160	0
	Chloride	6	6	70	85	250	0
	Sulfate	4	4	0.75	28	250	0
	Zinc	0	0	0	0	5	0
	Lead	0	0	0	0	0.015	0
CW - 9	Arsenic	8	8	0.053	0.14	0.01	8
	Iron	8	8	16	65.9	0.3	8
	Ammonia (as N)	8	8	3.1	15	2.8	8
	TDS	8	8	720	976	500	8
	Sodium	6	6	46	56	160	0
	Chloride	6	6	30	44	250	0
	Sulfate	4	4	1.9	110	250	0
	Zinc	0	0	0	0	5	0
	Lead	0	0	0	0	0.015	0
CW - 10	Arsenic	8	8	0.0026	0.049	0.01	3
	Iron	8	8	2.03	39.7	0.3	8
	Ammonia (as N)	8	8	1.5	3.2	2.8	1
	TDS	8	8	670	2040	500	8
	Sodium	6	6	43	70	160	0
	Chloride	6	6	31	81	250	0
	Sulfate	4	4	28	260	250	1
	Zinc	0	0	0	0	5	0
	Lead	0	0	0	0	0.015	0
CW - 11	Arsenic	4	4	0.02	0.0846	0.01	4
	Iron	4	4	13	41.9	0.3	4
	Ammonia (as N)	4	4	1.9	2.82	2.8	1
	TDS	4	4	660	1100	500	4
	Sodium	4	4	24	91.8	160	0
	Chloride	4	4	15	78	250	_ 0
	Sulfate	2	2	17	23	250	0
	Zinc	0	0	0	0	5	0

Well ID	Constituent	# of Samples	# of Detections	Concentration Range (mg/L)		GCTL (mg/L)	# of GCTL Exceedances
		•		Minimum	Maximum		
	Lead	0	0	0	0	0.015	0

Table B-2 Summary of Organic Compounds Concentration Data in Leachate

Compound	No. of	Range		
·	Detects	Min (ug/L)	Max (ug/L)	
1,1,1-Trichloroethane	4	0.5	50	
1,1-Dichloroethane	25	0.26	27.2	
1, <u>2</u> -Dibromo-3-	2	0.005	0.023	
1,2-Dichlorobenzene	1	7	7	
1,2-Dichloroethane	14	0.1	5	
1,3-Dichloro propane	1	0.5	4.5	
1,4-Dichlorobenzene	41	0.19	23	
1-Methyl naphthalene	1	0.95	1.3	
2-Butanone	17	0.29	2400	
2-Chlorophenol	1	0.64	1.3	
2-Chloronaphthalene	1	0.88	8.9	
2-Hexanone	1	3	3	
2-Methyl naphthalene	4	0.94	1.5	
2-Methyl phenol	16	0.69	18.7	
2-Naphthylamine	7	0.9	10	
2,4-Dimethylphenol	2	1.5	4.5	
2,4-Dinitrotoluene	1	0.51	1	
2,4,5-T	1	0.097	0.24	
2,6-Dinitrotoulerne	1	1.2	8.1	
3&4-Methyl phenol	15	0.62	800	
3,3-Dichlorobenzidine	4	0.65	65.5	
4 Methyl-2-pentanone	18	0.21	74	
4,4-DDD	1	0.017	0.06	
4,4-DDE	1	0.01	0.03	
4,4-DDT	2	0.013	0.064	
4,5-TP(silvex)	1	0.09	0.09	
4-Chloroaniline	11	1.3	16.4	
4-Nitrophenol	1	20	20	
Acetone	34	0.91	13000	
Acetonitrile	7	6.7	240	
Acetophenone	9	1.4	5.4	
Acrolein	3	8.8	420	
Aldrin	1	0.01	0.06	
Anthracene	3	0.57	_ 1.6	
Benzene	45	0.23	23	
Benzo anthracene	1	0.014	0.086	
Benzylalcohol	4	0.96	11	
Bis(2-chloroethoxy)	2	0.78	20.9	
Bis(2-ethylhexyl)	26	0.76	36.7	
Butyl benzyl phthalate	1	5	<b>1</b> 5	

Compound	No. of	Range		
	Detects	Min (ug/L)	Max (ug/L)	
Carbon disulfide	17	0.25	16	
Chlorobenzene	11	0.15	1.3	
Chloroethane	5	0.5	26	
Chloromethane	2	3	6.3	
Chloroform	1	0.5	7.3	
Cis,1,2-Dichloroethene	26	0.15	46	
Cis,1,3-Dichloropropene	1	13	13	
Dibromochloropropane	1	0.03	0.03	
Dichloromethane	2	2.3	220	
Dichlorodiflouro methane	1	1.5	1.5	
Diethyl phthalate	14	0.48	4.2	
Dimethyl phthalate	1	1	1	
Di-n-butyl phthalate	4	0.39	8.1	
Ethylbenzene	60	0.12	110	
Ethylene dibromide	4	0.0052	67	
Methyl ethyl ketone	1	40	454	
Methyl butyl ketone	2	1600	11000	
Methyl Isobutyl ketone	2	50	170	
Methylene chloride	7	0.5	950	
Naphthalene	31	0.74	20.9	
Nitrobenzene	1	2	2	
N-Nitroso-di-n-	3	0.89	25.1	
O-Toluidine	7	1	26	
Parathion methyl	1	0.5	1.3	
Phenanthrene	2	0.49	73	
Pentachlorophenol	2	0.062	0.062	
Phenol	6	0.51	7.7	
Styrene	11	0.17	16	
Tetrachloroethene	3	0.5	5.4	
Tetrachloroethylene	1	2.5	7.9	
Toluene	62	0.1	300	
Total xylenes	49	0.29	210	
Trichloroethene	5	0.5	5.2	
Trichloroethylene	1	2.5	5.3	
Trichloroflouromethane	3	0.5	36	
Vinyl chloride	24	0.14	14	



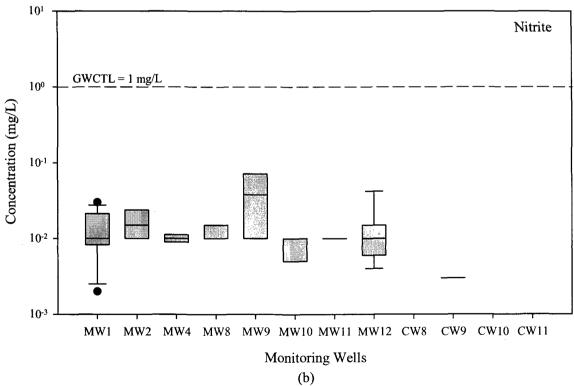
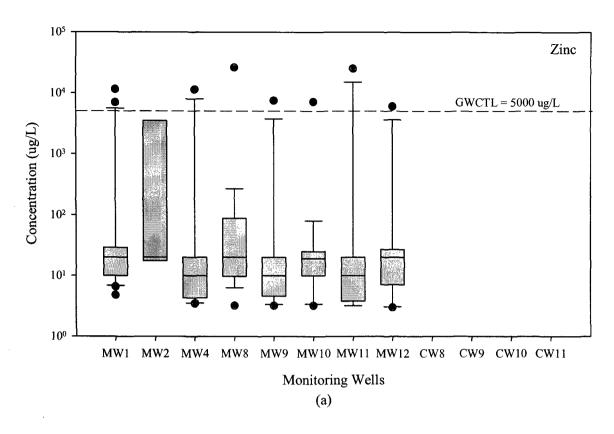


Figure B-1. Box and Whisker Plots (a) Nitrate and (b) Nitrite



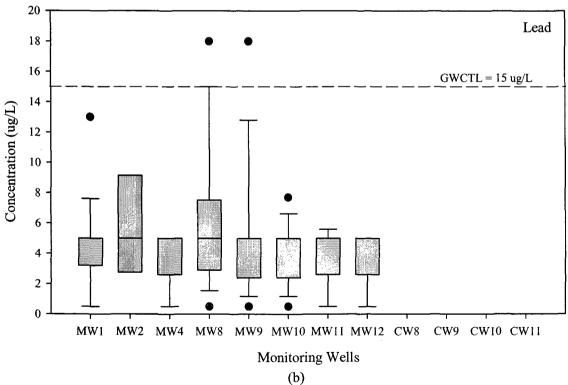


Figure B-2. Box and Whisker Plots (a) Zinc and (b) Lead

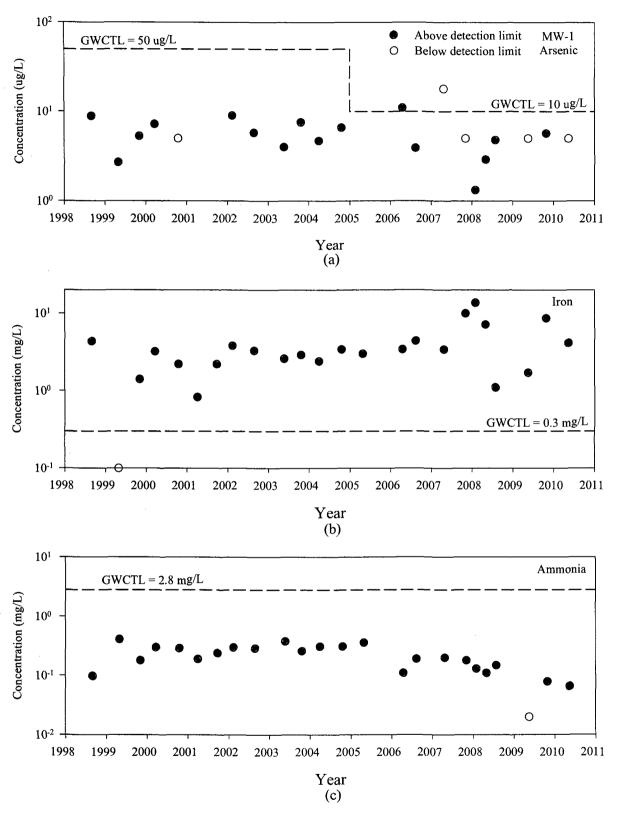


Figure B-3. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-1

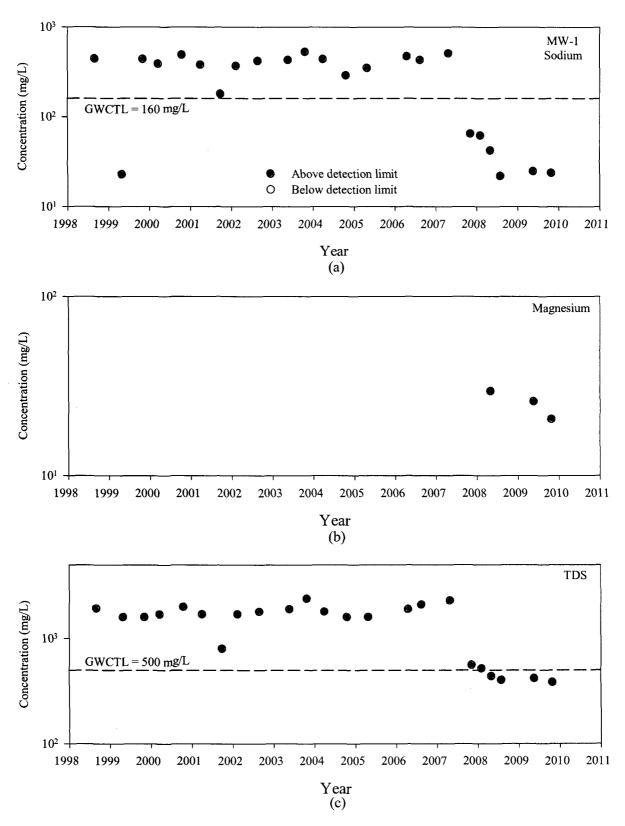


Figure B-4. Temporal Variation of (a) Sodium, (b) Magnesium, and (c) TDS for Monitoring Well MW-1

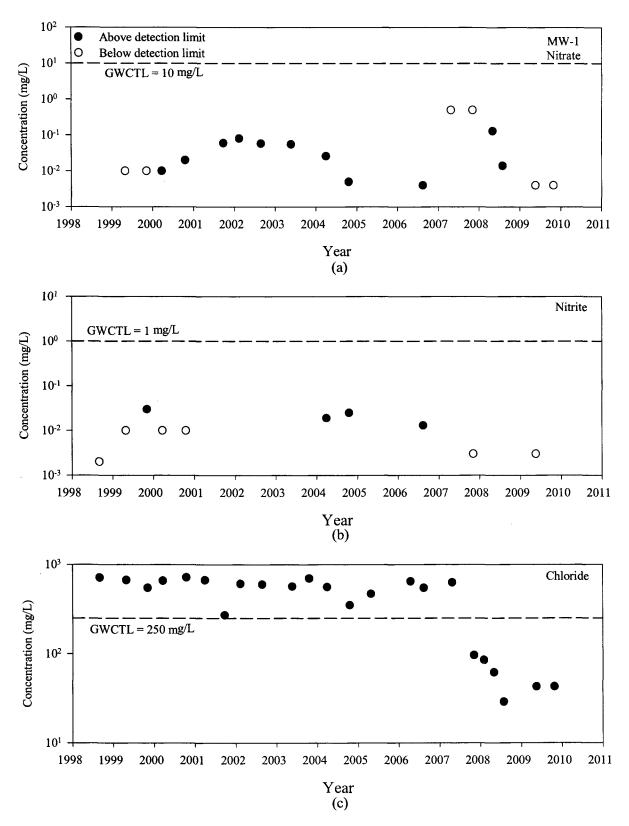


Figure B-5. Temporal Variation of (a) Nitrate, (b) Nitrite, and (c) Chloride for Monitoring Well MW-1

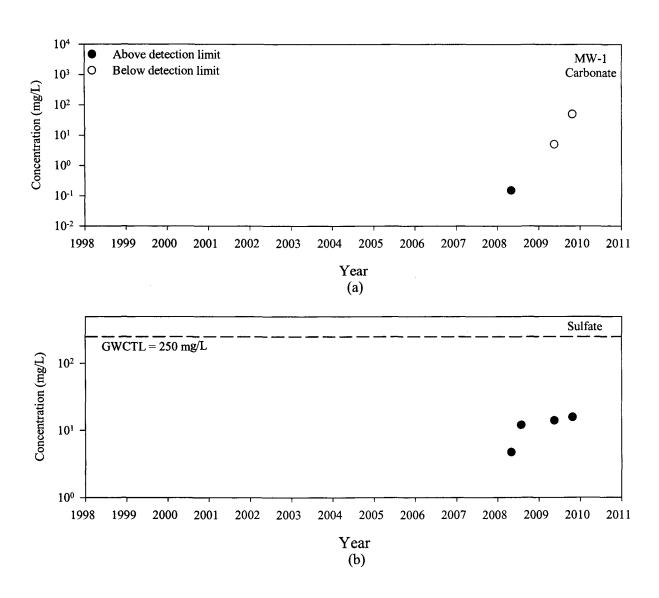


Figure B-6. Temporal Variation of (a) Carbonate, and (b) Sulfate for Monitoring Well MW-1

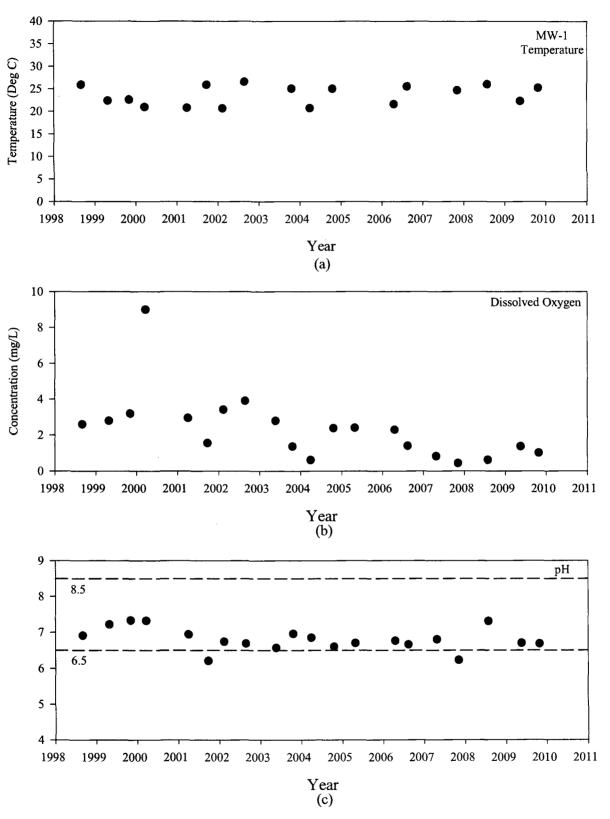


Figure B-7. Temporal Variation of (a) Temperature, (b) Dissolved Oxygen, and (c) pH for Monitoring Well MW-1

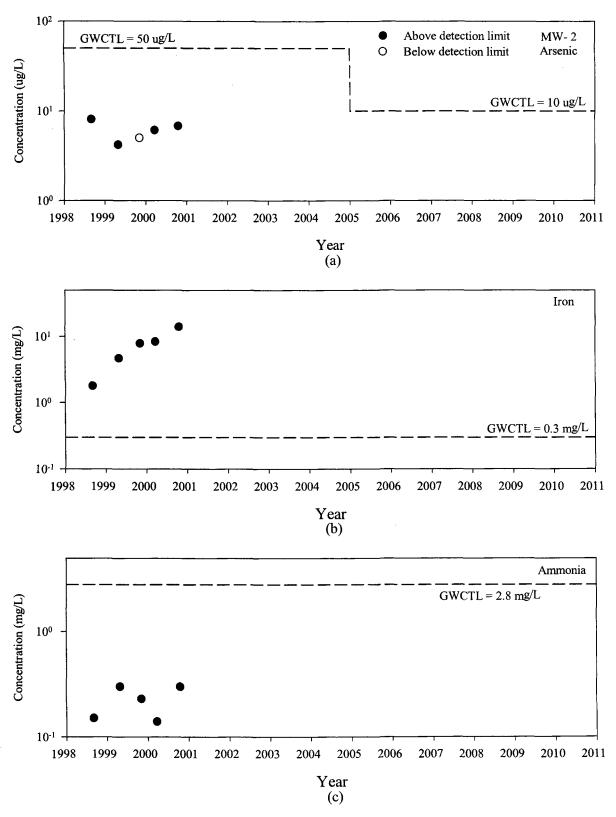


Figure B-8. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-2

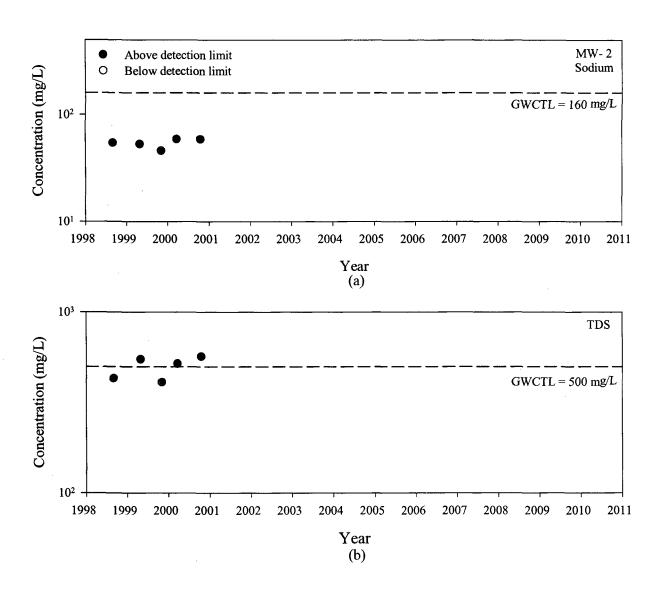


Figure B-9. Temporal Variation of (a) Sodium, and (b) TDS for Monitoring Well MW-2

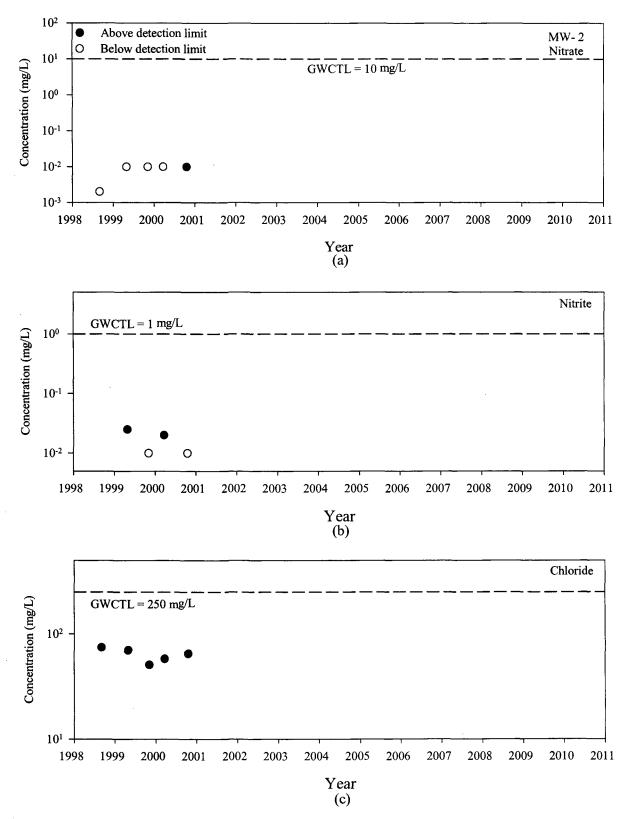
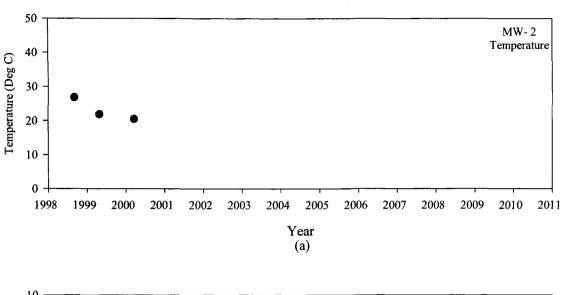
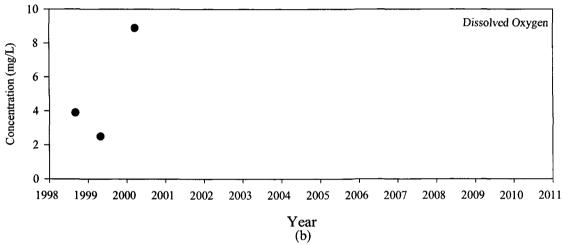


Figure B-10. Temporal Variation of (a) Nitrate, (b) Nitrite, and (c) Chloride for Monitoring Well MW-2





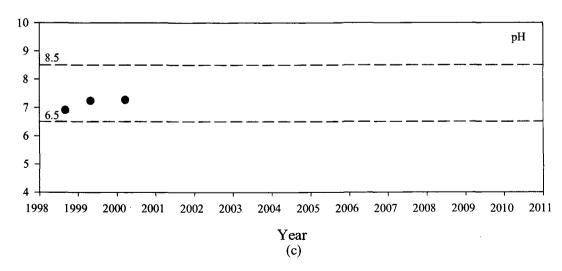


Figure B-11. Temporal Variation of (a) Temperature, (b) Dissolved Oxygen, and (c) pH for Monitoring Well MW-2

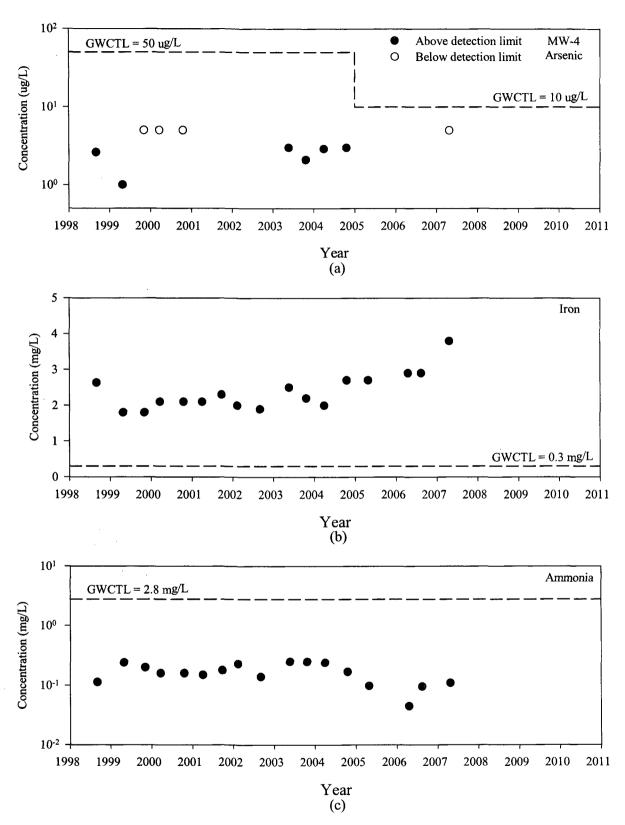


Figure B-12. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-4

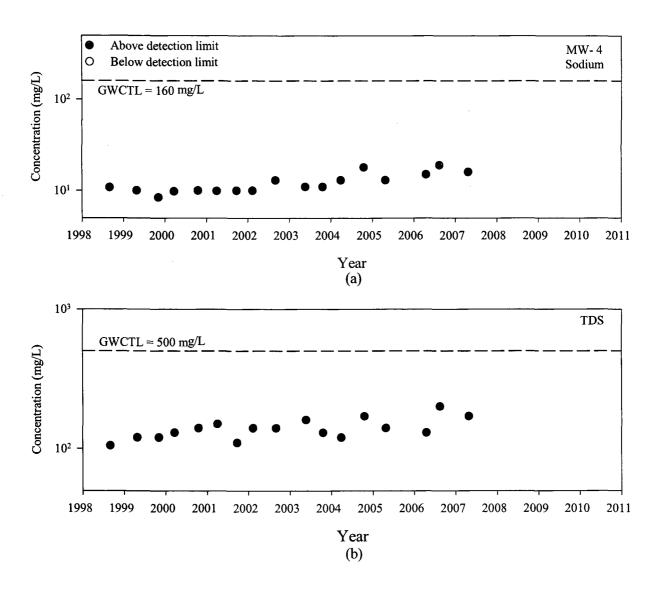


Figure B-13. Temporal Variation of (a) Sodium, and (b) TDS for Monitoring Well MW-4

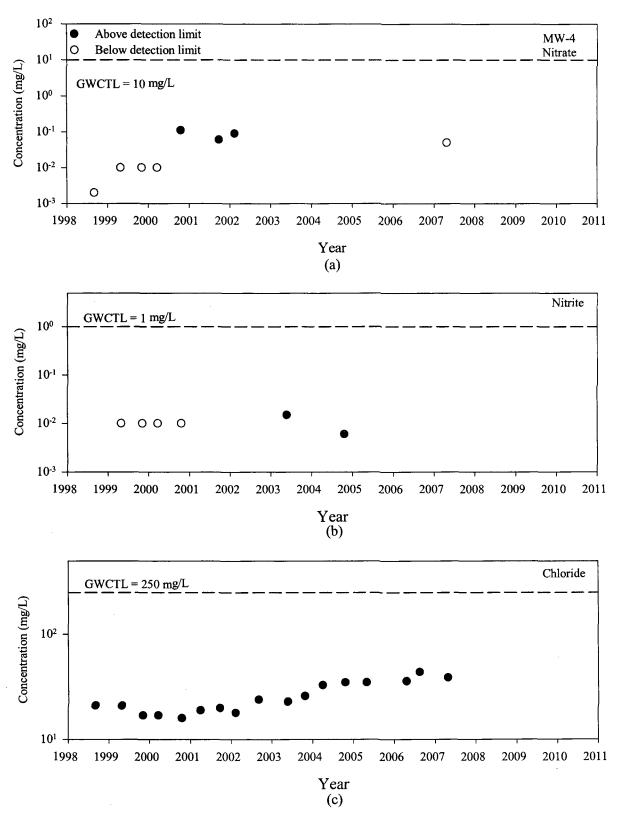


Figure B-14. Temporal Variation of (a) Nitrate, (b) Nitrite, and (c) Chloride for Monitoring Well MW-4

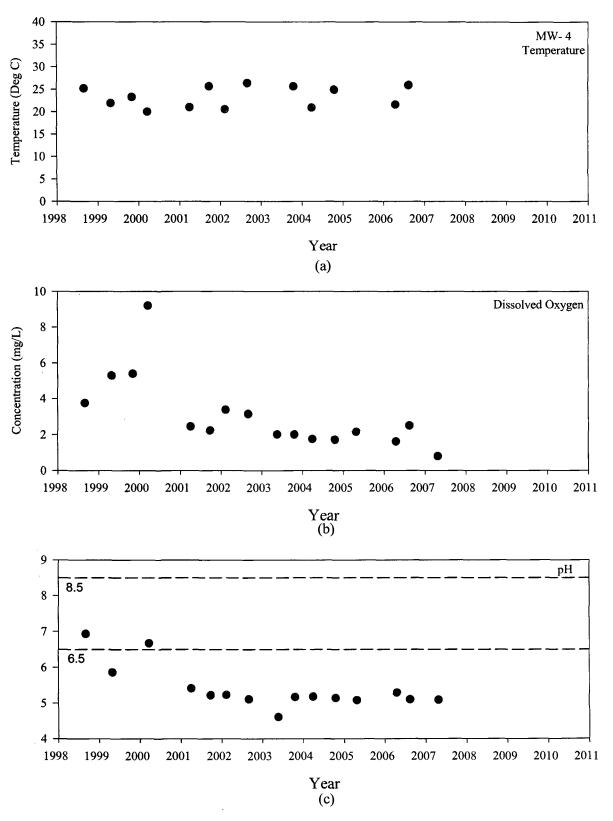


Figure B-15. Temporal Variation of (a) Temperature, (b) Dissolved Oxygen, and (c) pH for Monitoring Well MW-4

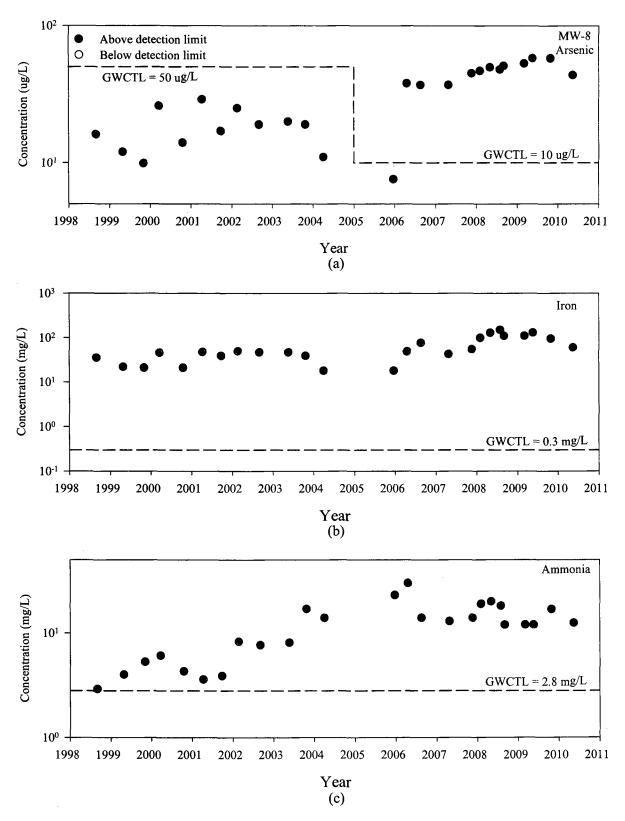


Figure B-16. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-8

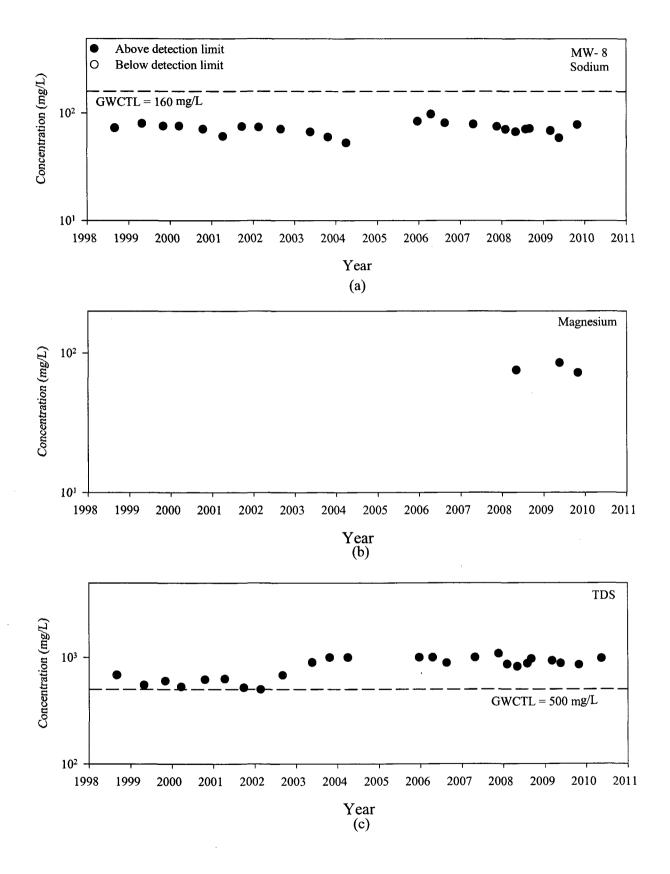


Figure B-17. Temporal Variation of (a) Sodium, (b) Magnesium, and (c) TDS for Monitoring Well MW-8

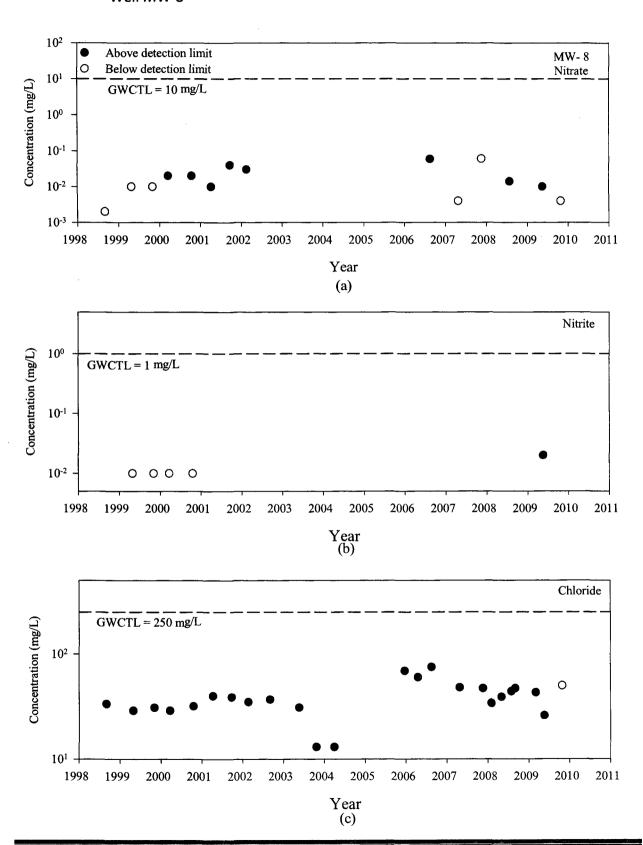


Figure B-18. Temporal Variation of (a) Nitrate, (b) Nitrite, and (c) Chloride for Monitoring Well MW-8

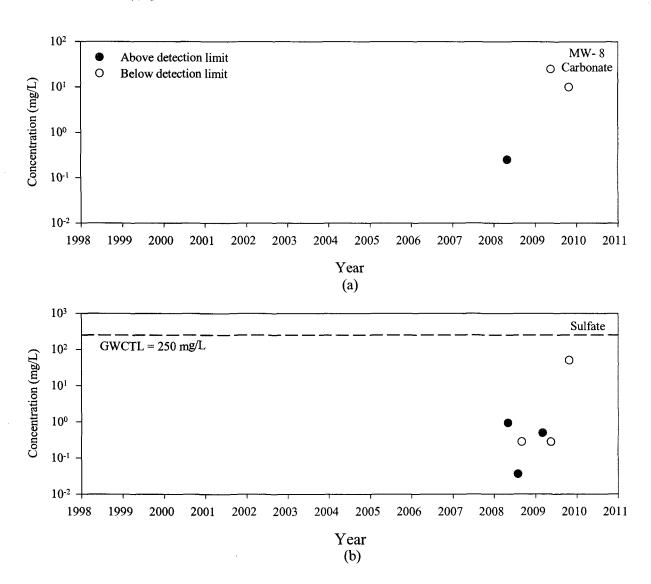


Figure B-19. Temporal Variation of (a) Carbonate, and (b) Sulfate for Monitoring Well MW-8

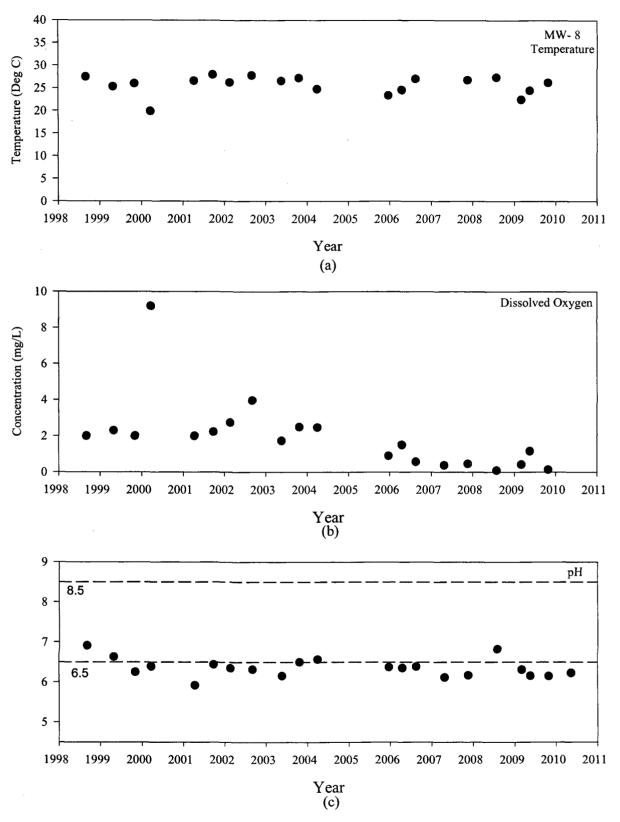


Figure B-20. Temporal Variation of (a) Temperature, (b) Dissolved Oxygen, and (c) pH for Monitoring Well MW-8

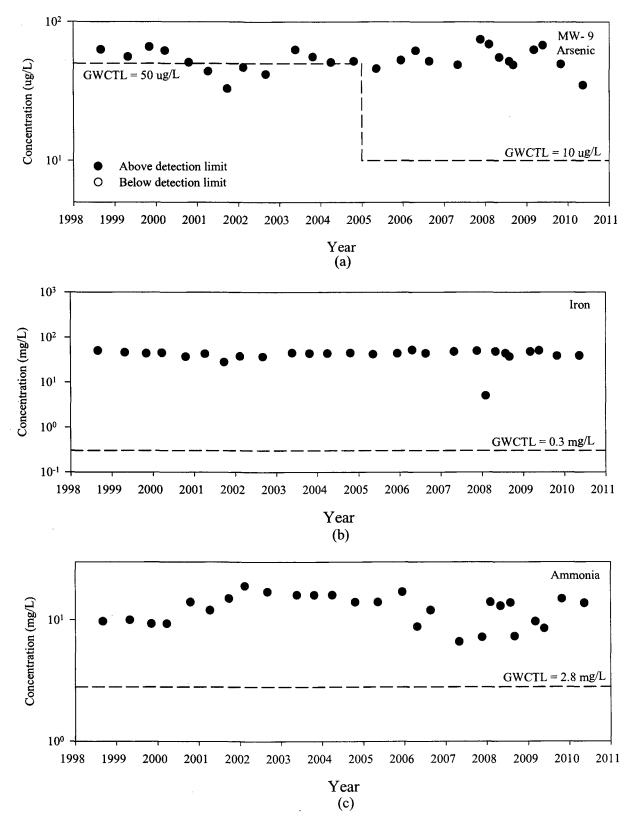


Figure B-21. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-9

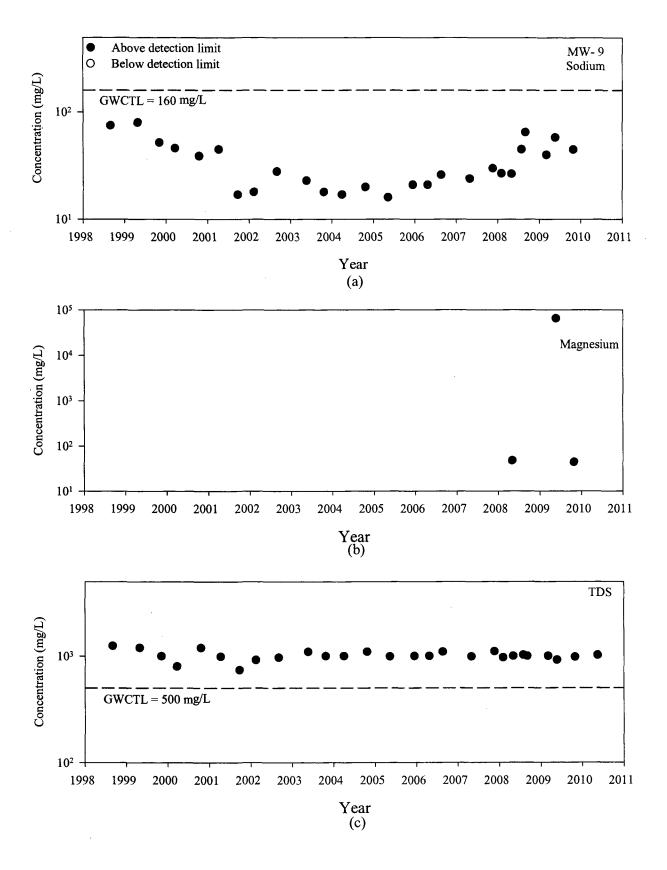


Figure B-22. Temporal Variation of (a) Sodium, (b) Magnesium, and (c) TDS for Monitoring Well MW-9

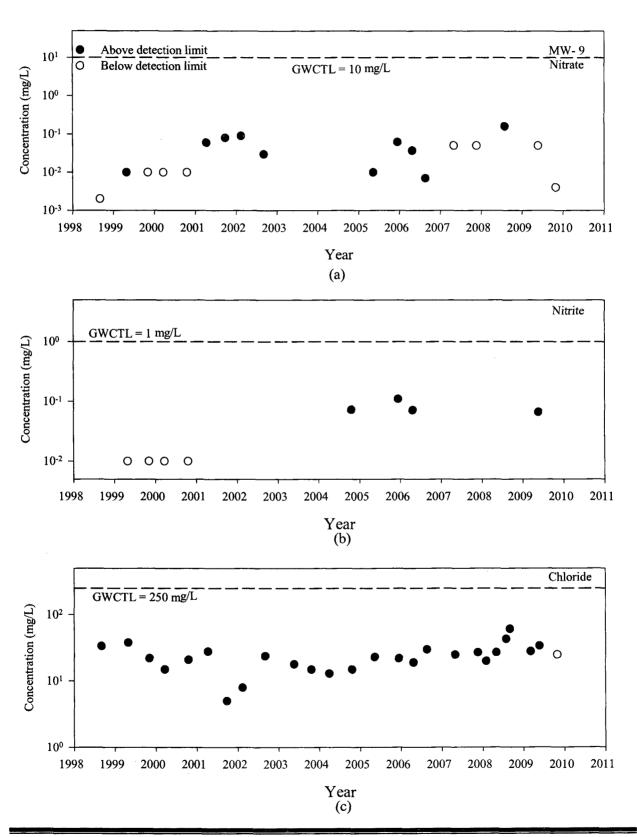


Figure B-23. Temporal Variation of (a) Nitrate, (b) Nitrite, and (c) Chloride for Monitoring Well MW-9

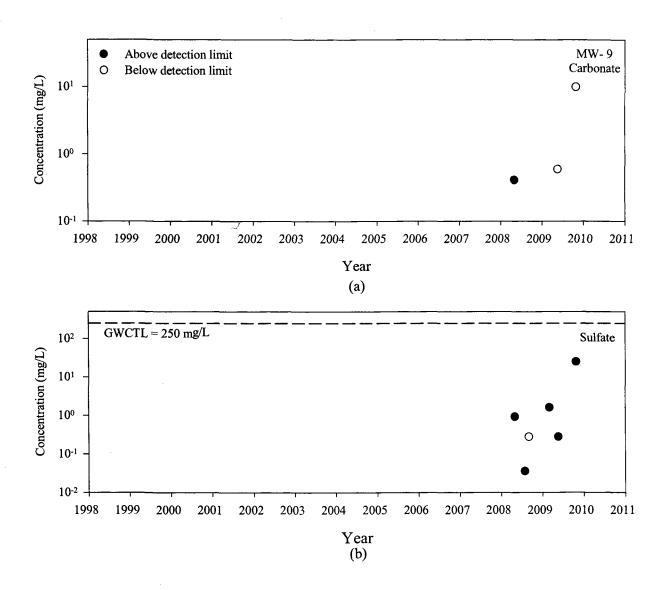


Figure B-24. Temporal Variation of (a) Carbonate, and (b) Sulfate for Monitoring Well MW-9

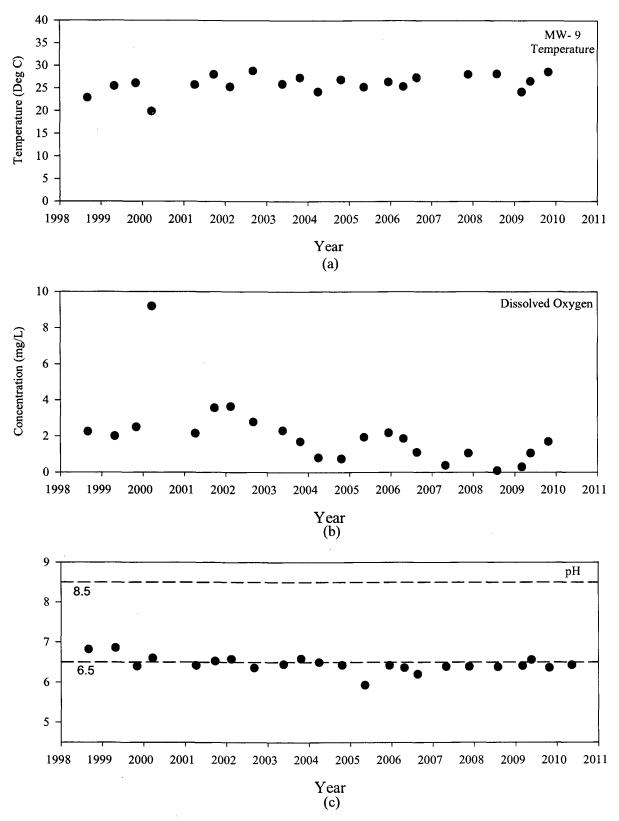


Figure B-25. Temporal Variation of (a) Temperature, (b) Dissolved Oxygen, and (c) pH for Monitoring Well MW-9

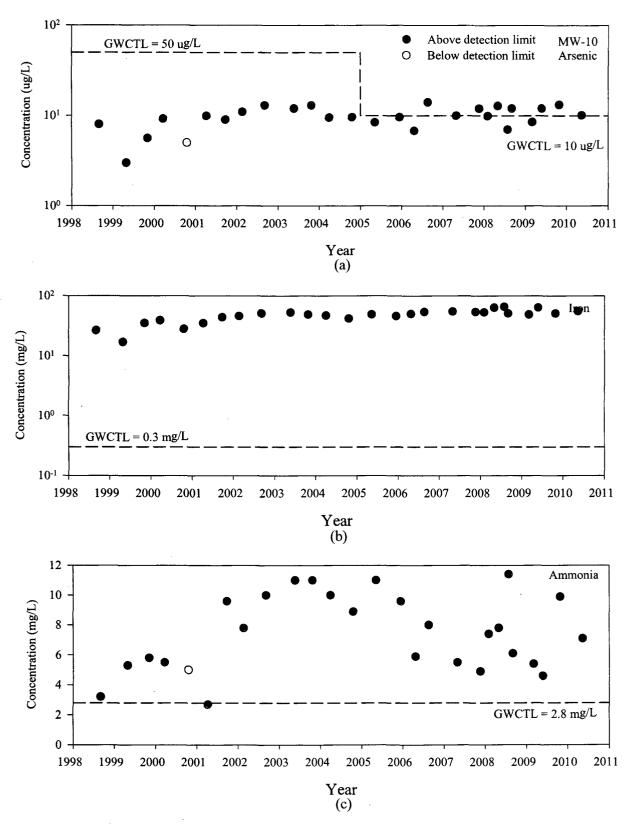


Figure B-26. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-10

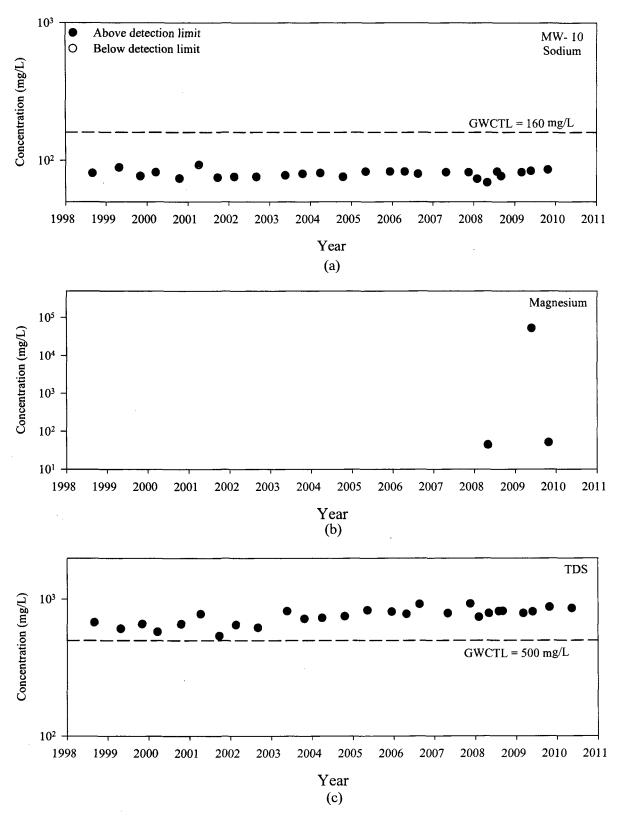


Figure B-27. Temporal Variation of (a) Sodium, (b) Magnesium, and (c) TDS for Monitoring Well MW-10

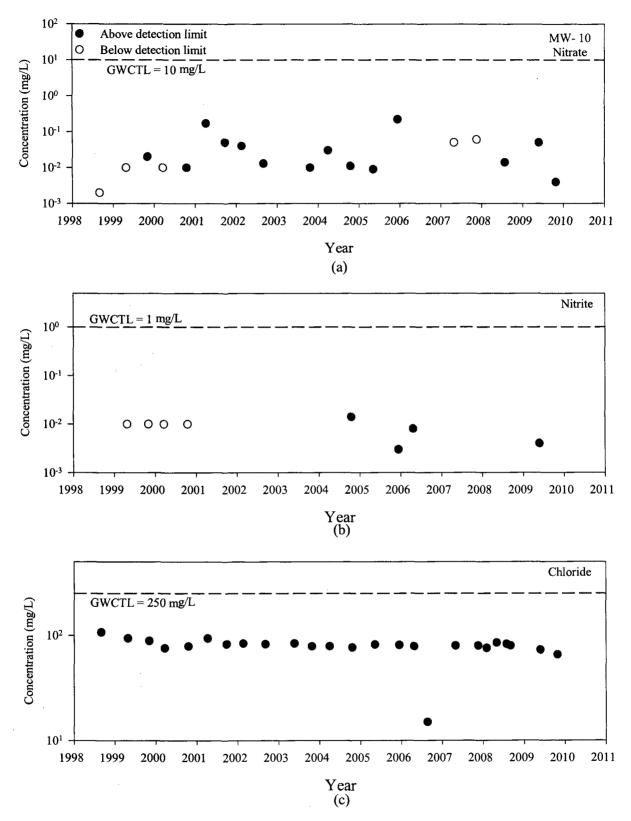


Figure B-28. Temporal Variation of (a) Nitrate, (b) Nitrite, and (c) Chloride for Monitoring MW-10

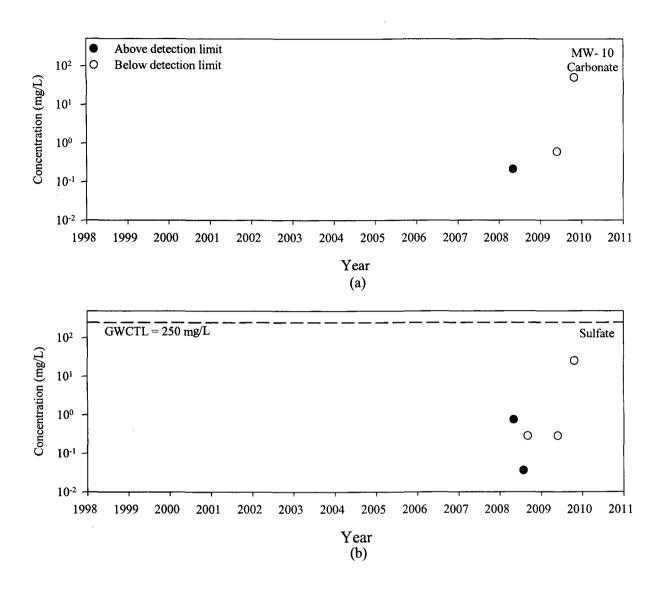
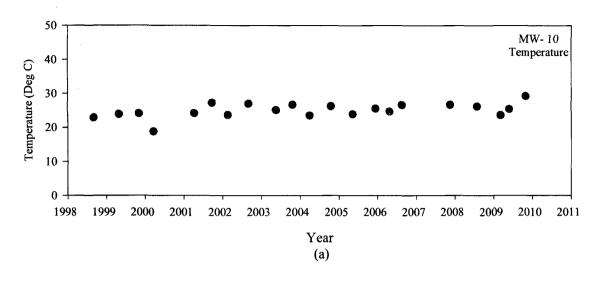
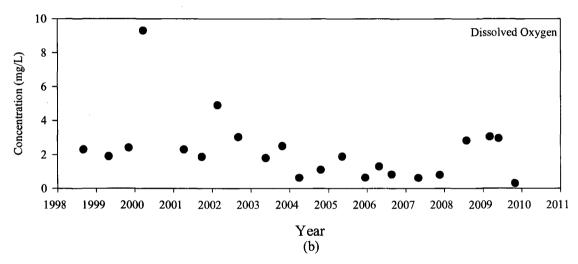


Figure B-29. Temporal Variation of (a) Carbonate, and (b) Sulfate for Monitoring Well MW-10





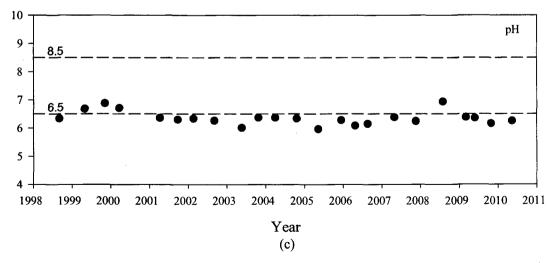


Figure B-30. Temporal Variation of (a) Temperature, (b) Dissolved Oxygen, and (c) pH for Monitoring Well MW-10

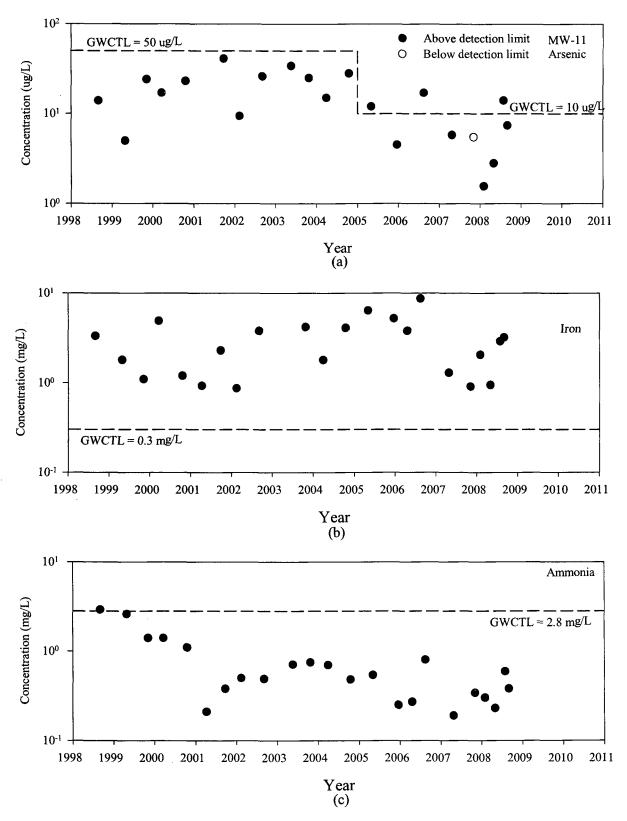


Figure B-31. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-11

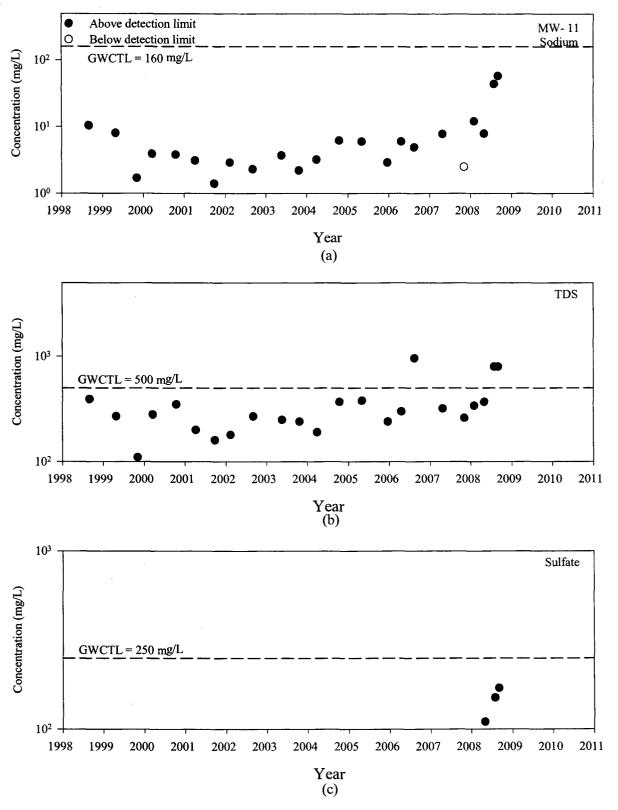


Figure B-32. Temporal Variation of (a) Sodium, (b) TDS, and (c) Sulfate for Monitoring Well MW-11

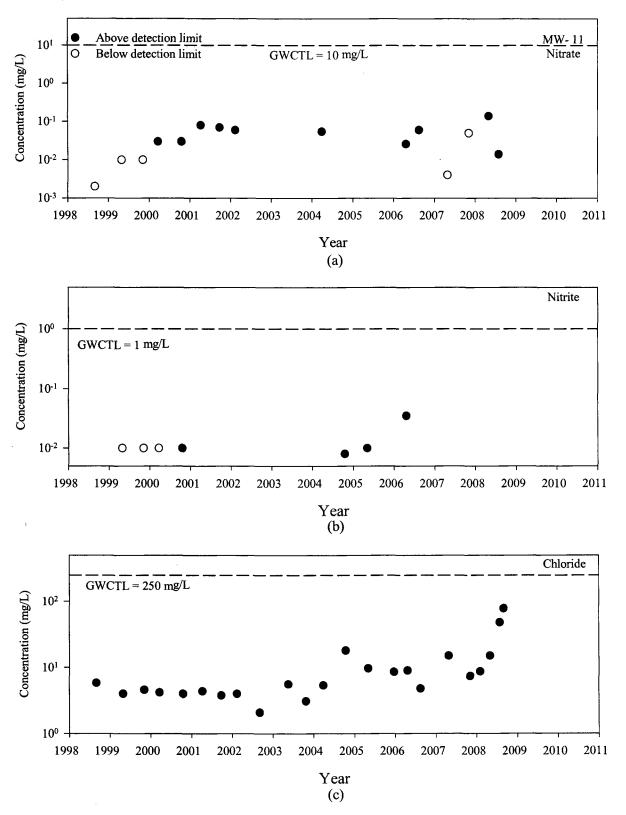


Figure B-33. Temporal Variation of (a) Nitrate, (b) Nitrite, and (c) Chloride for Monitoring Well MW-11

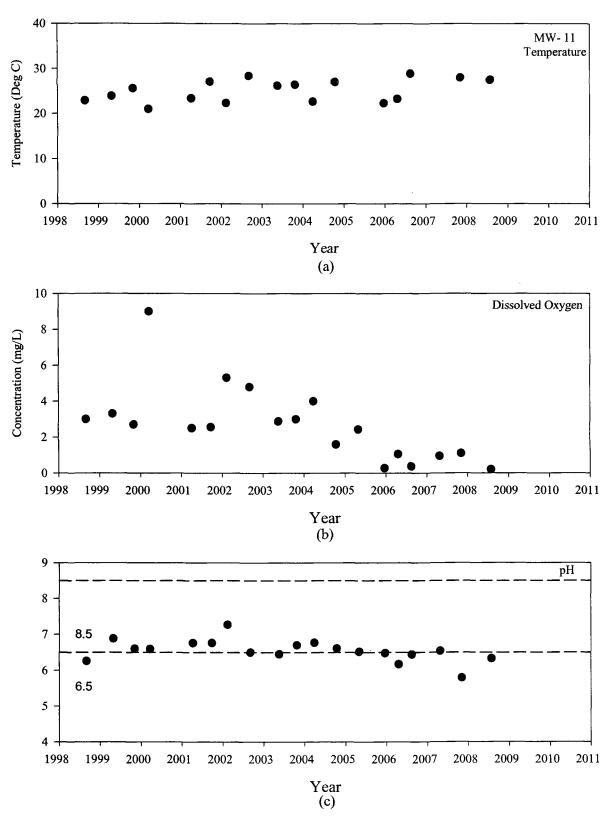


Figure B-34. Temporal Variation of (a) Temperature, (b) Dissolved Oxygen, and (c) pH for Monitoring Well MW-11

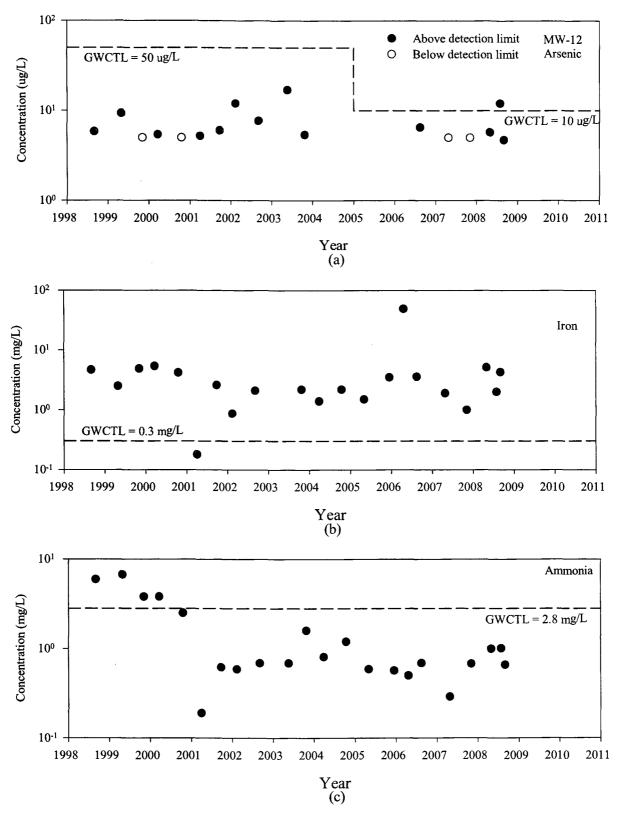


Figure B-35. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-12

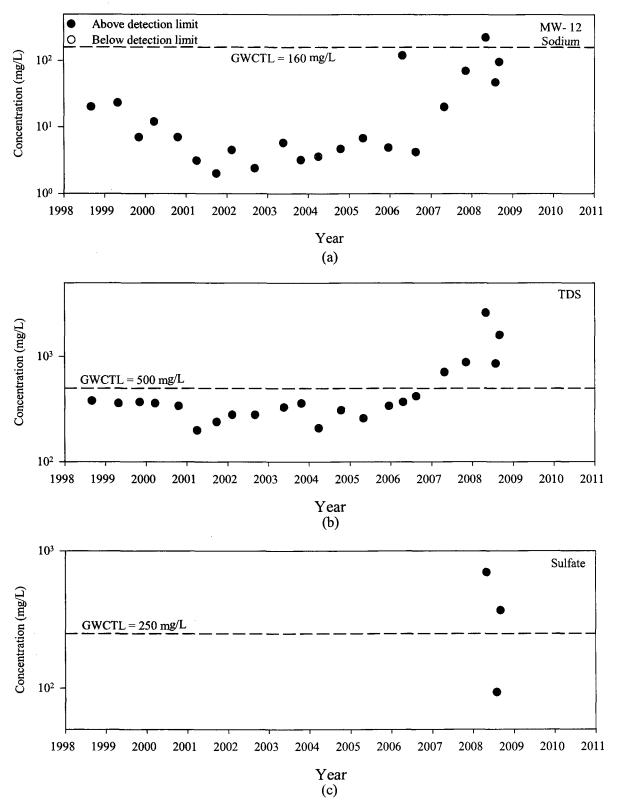


Figure B-36. Temporal Variation of (a) Sodium, (b) TDS, and (c) Sulfate for Monitoring Well MW-12

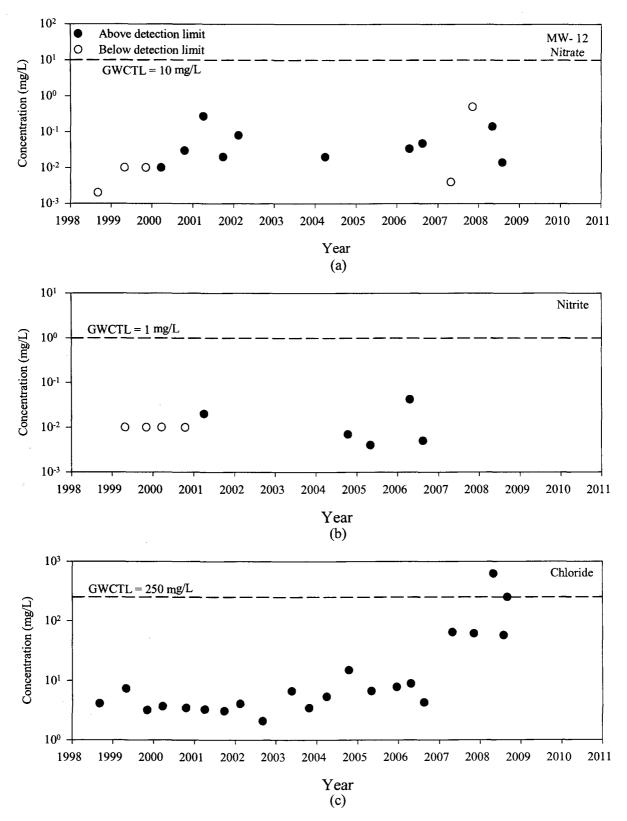


Figure B-37. Temporal Variation of (a) Nitrate, (b) Nitrite, and (c) Chloride for Monitoring Well MW-12

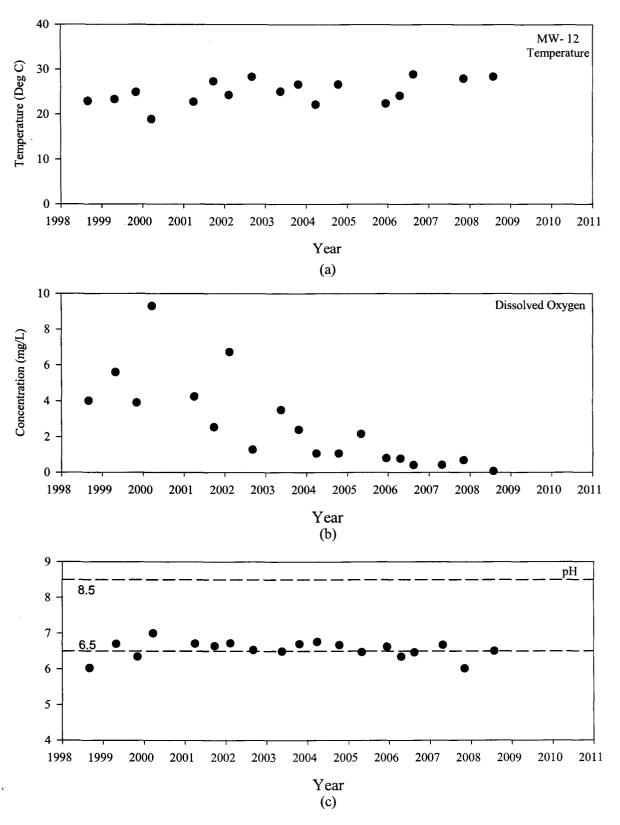


Figure B-38. Temporal Variation of (a) Temperature, (b) Dissolved Oxygen, and (c) pH for Monitoring Well MW-12

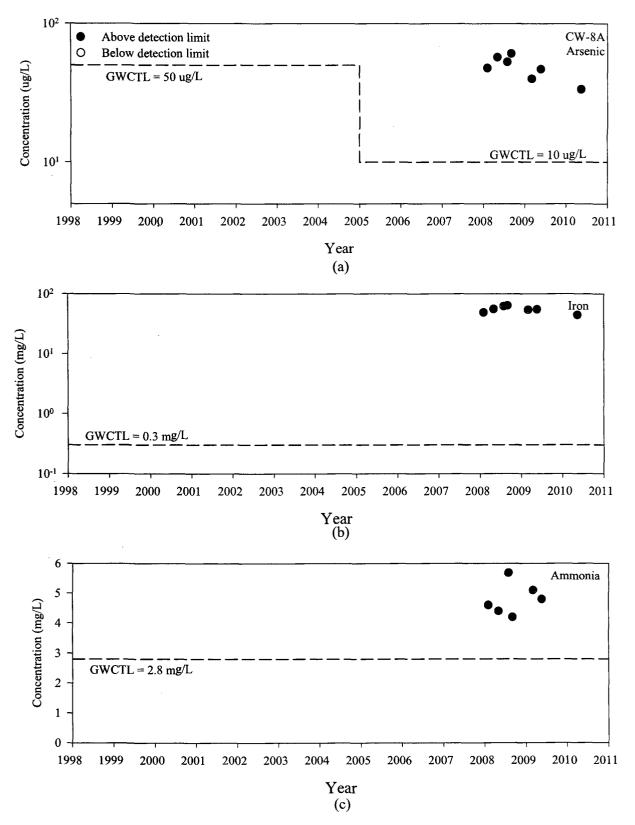


Figure B-39. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well CW-8

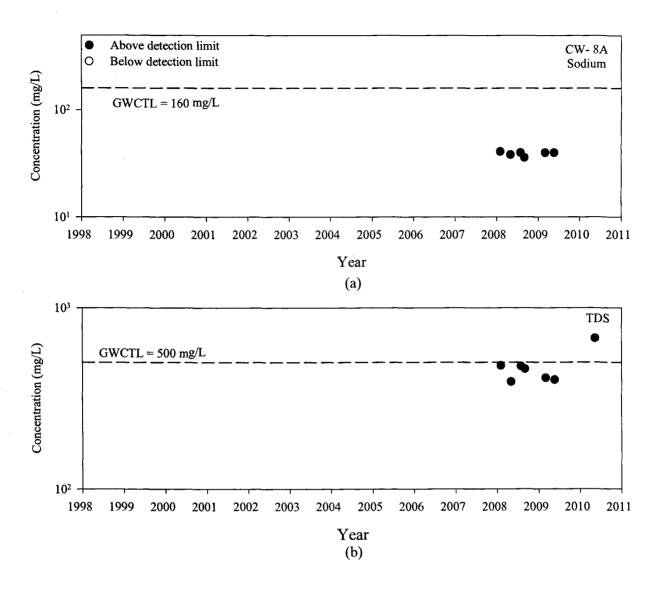


Figure B-40. Temporal Variation of (a) Sodium, and (b) TDS for Monitoring Well CW-8

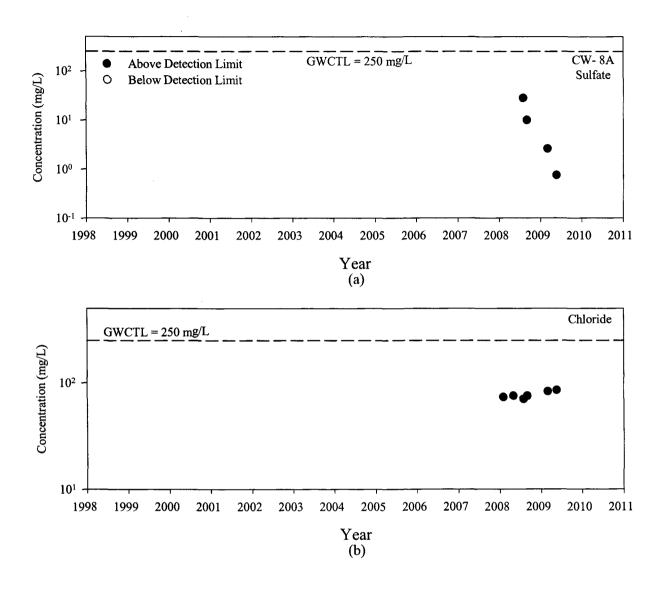


Figure B-41. Temporal Variation of (a) Sulfate, and (b) Chloride for Monitoring Well CW-8

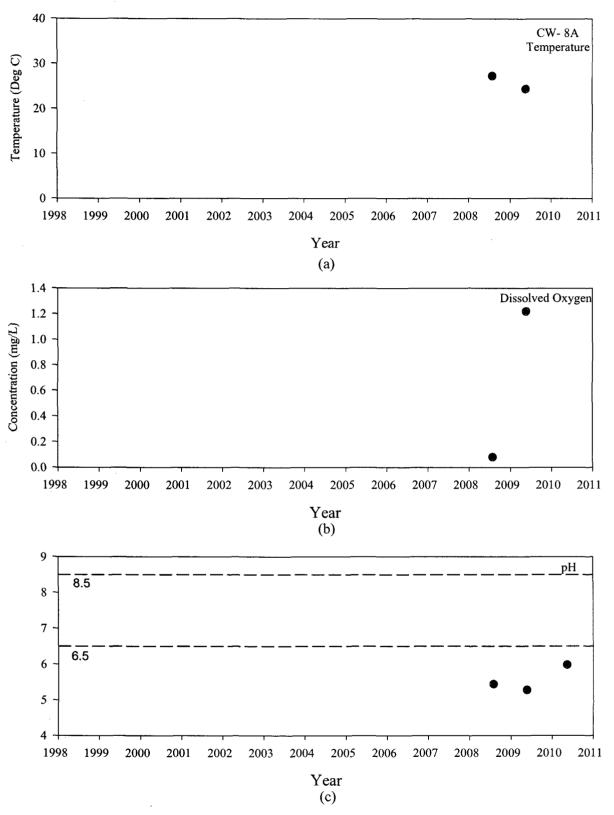


Figure B-42. Temporal Variation of (a) Temperature, (b) Dissolved Oxygen, and (c) pH for Monitoring Well CW-8

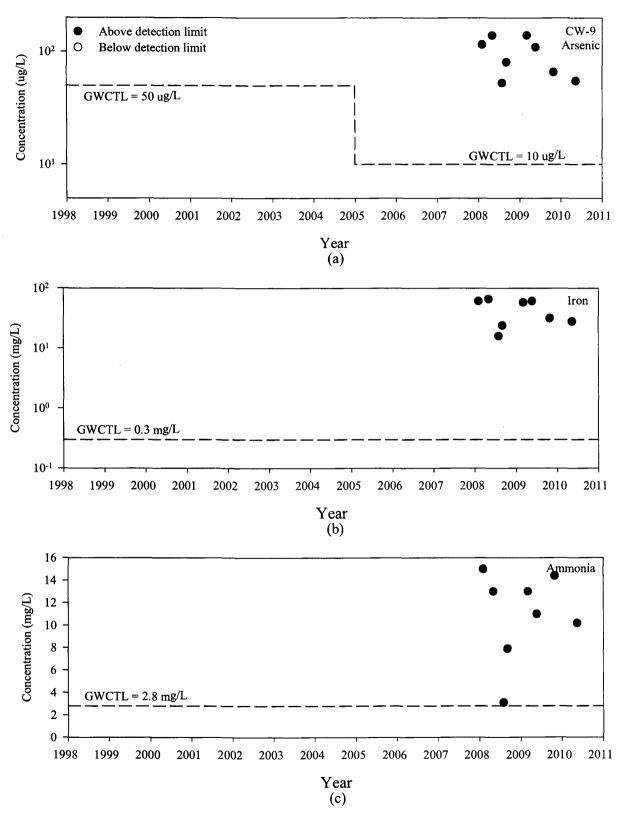


Figure B-43. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well CW-9

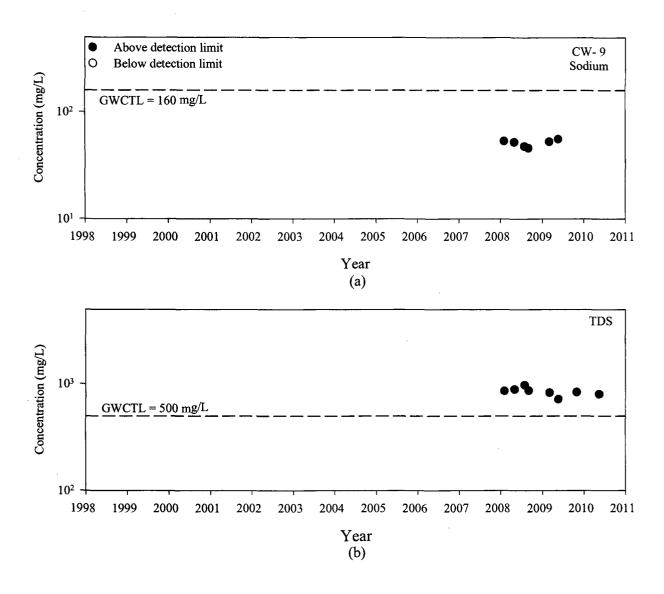


Figure B-44. Temporal Variation of (a) Sodium, and (b) TDS for Monitoring Well CW-9

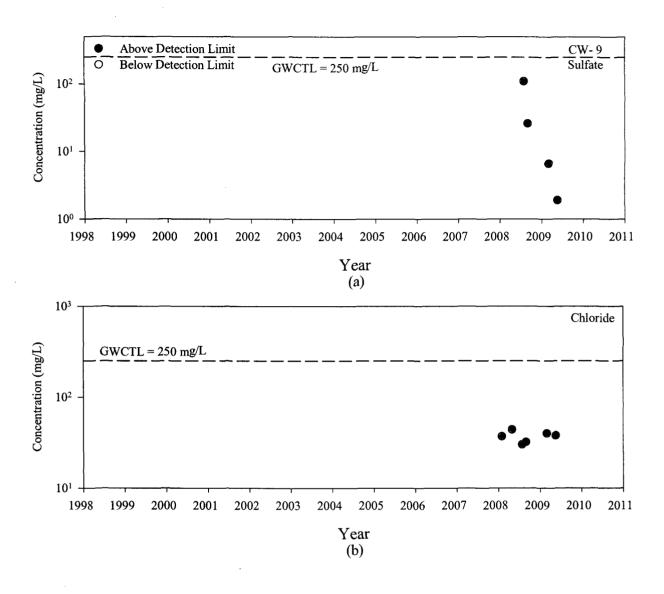


Figure B-45. Temporal Variation of (a) Sulfate, and (b) Chloride for Monitoring Well CW-9

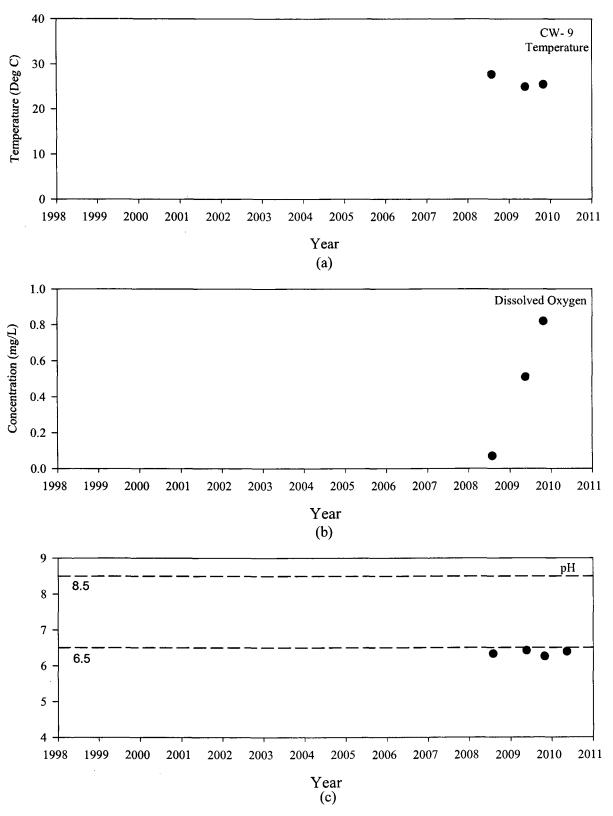


Figure B-46. Temporal Variation of (a) Temperature, (b) Dissolved Oxygen, and (c) pH for Monitoring Well CW-9

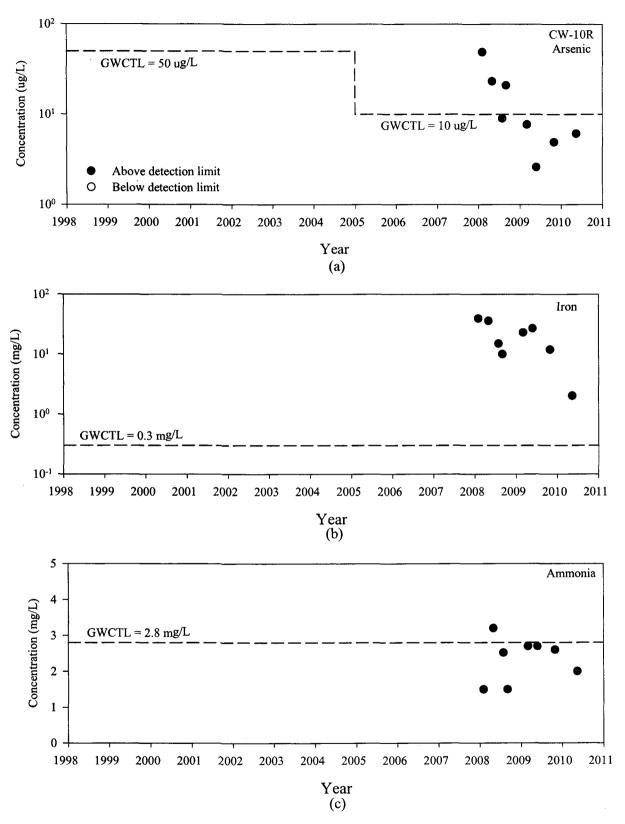


Figure B-47. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well CW-10

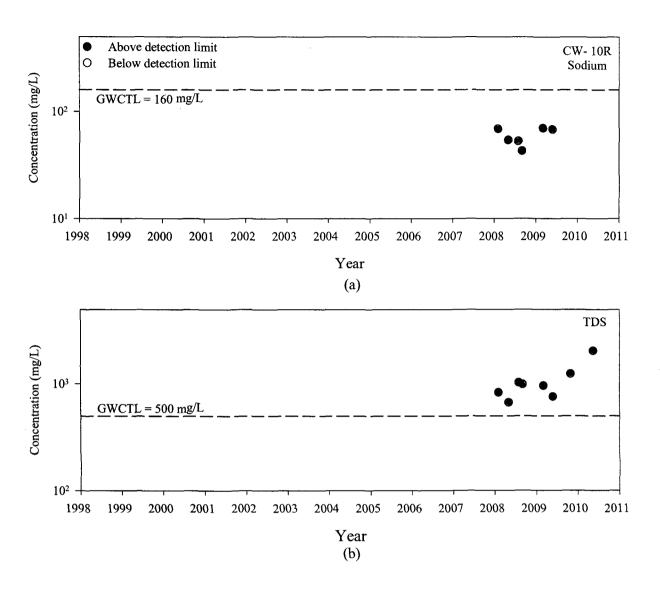


Figure B-48. Temporal Variation of (a) Sodium, and (b) TDS for Monitoring Well CW-10

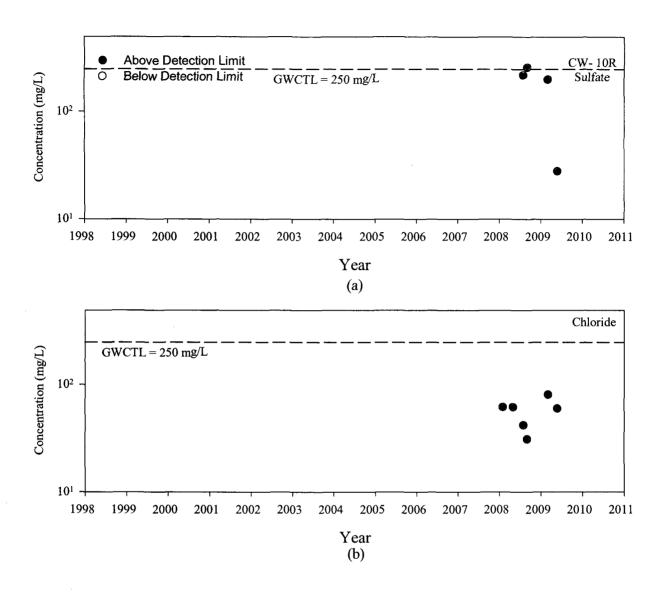


Figure B-49. Temporal Variation of (a) Sulfate and (b) Chloride for Monitoring Well CW-10

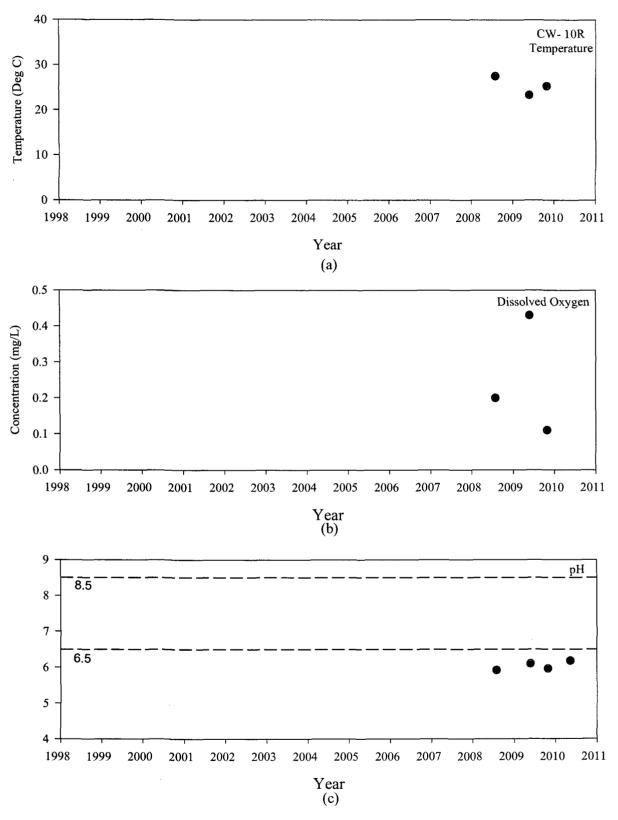


Figure B-50. Temporal Variation of (a) Temperature, (b) Dissolved Oxygen, and (c) pH for Monitoring Well CW-10

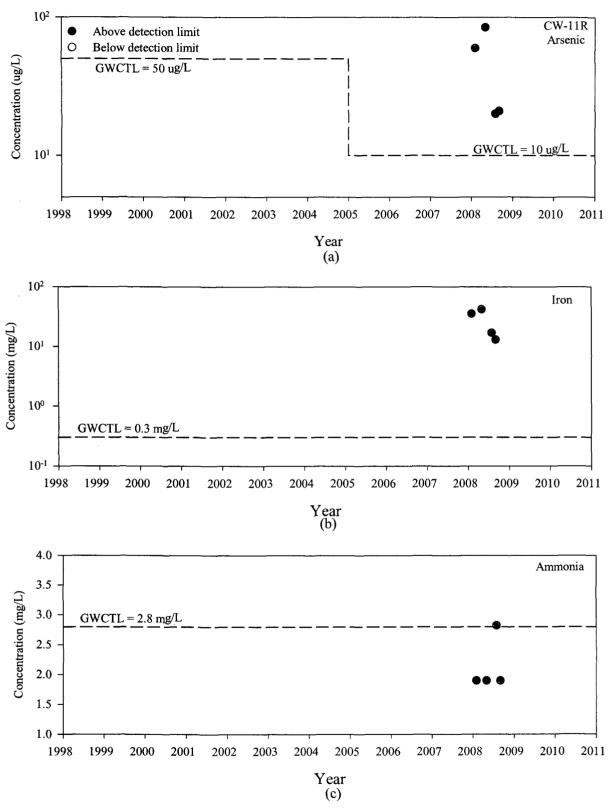


Figure B-51. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well CW-11

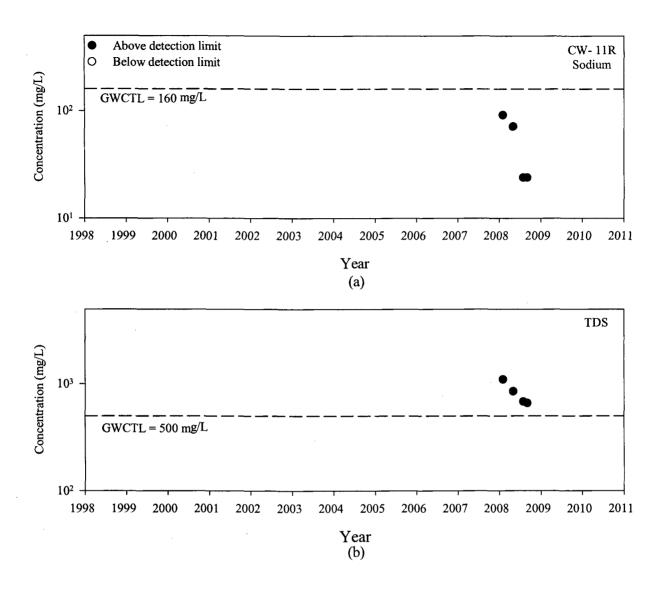


Figure B-52. Temporal Variation of (a) Sodium, and (b) TDS for Monitoring Well CW-11

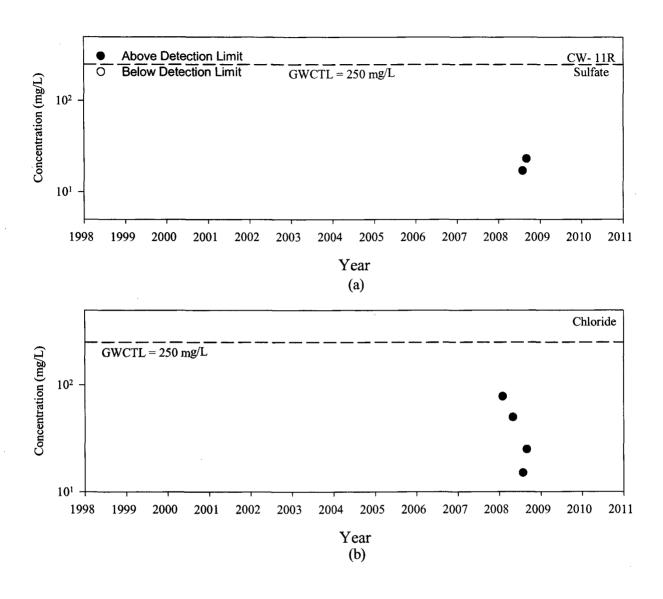
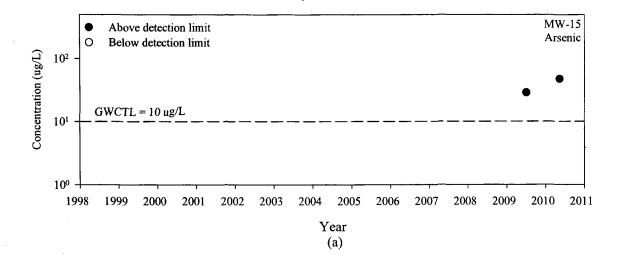
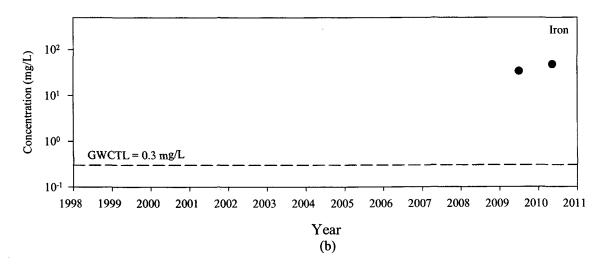


Figure B-53. Temporal Variation of (a) Sulfate and (b) Chloride for Monitoring Well CW-11





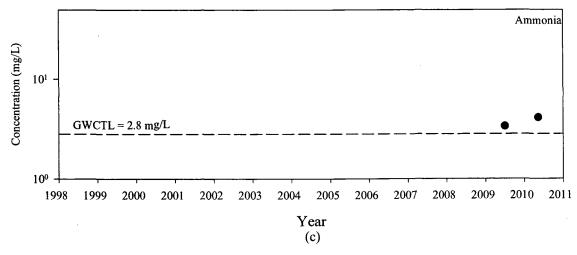


Figure B-54. Temporal Variation of (a) Arsenic, (b) Iron and (c) Ammonia (as N) for Monitoring Well MW-15

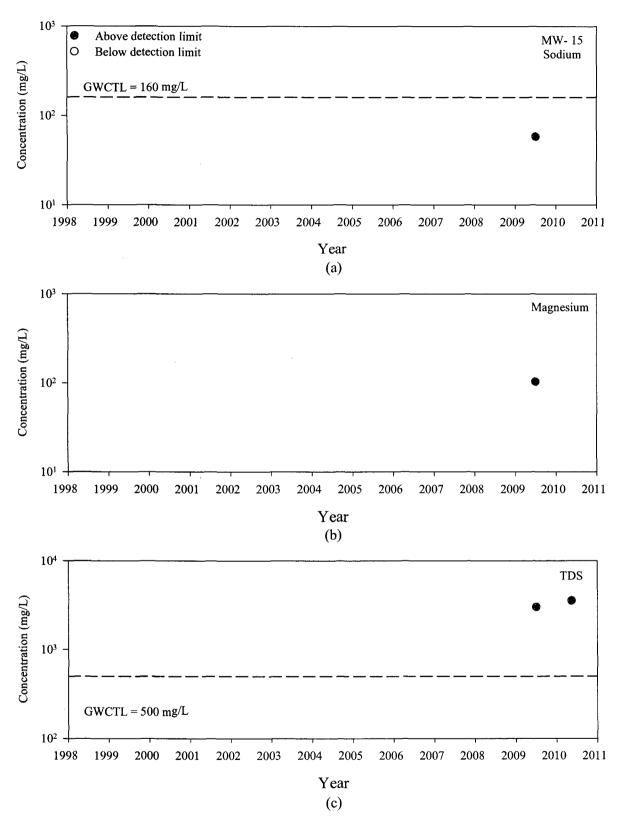


Figure B-55. Temporal Variation of (a) Sodium, (b) Magnesium, and (c) TDS for Monitoring Well MW-15

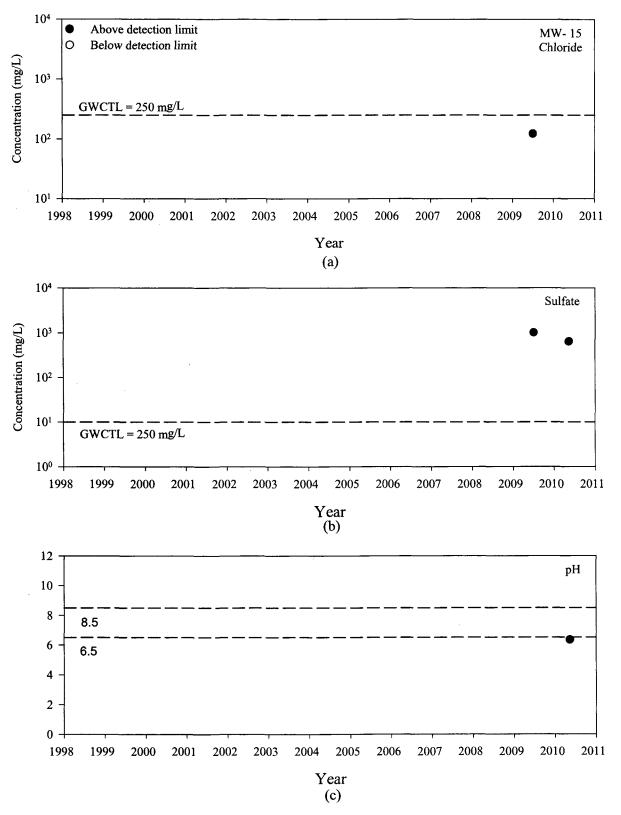


Figure B-56. Temporal Variation of (a) Chloride, and (b) Sulfate and (c) pH for Monitoring Well MW-15

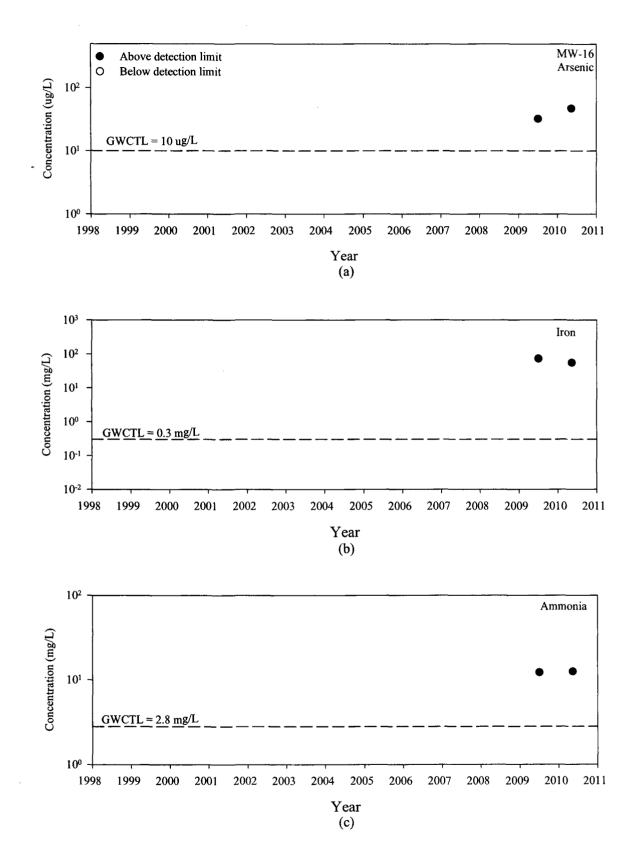


Figure B-57. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-16

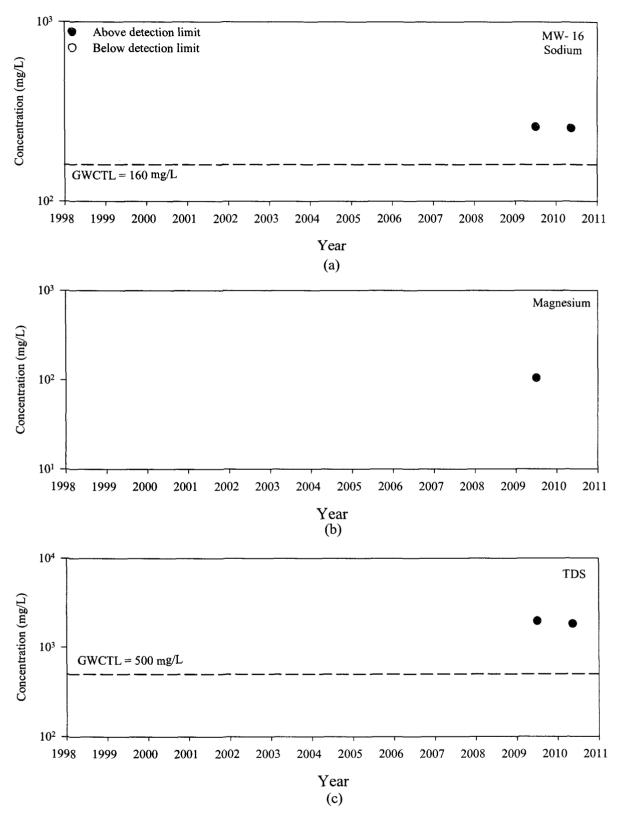


Figure B-58. Temporal Variation of (a) Sodium, (b) Magnesium, and (c) TDS for Monitoring Well MW-16

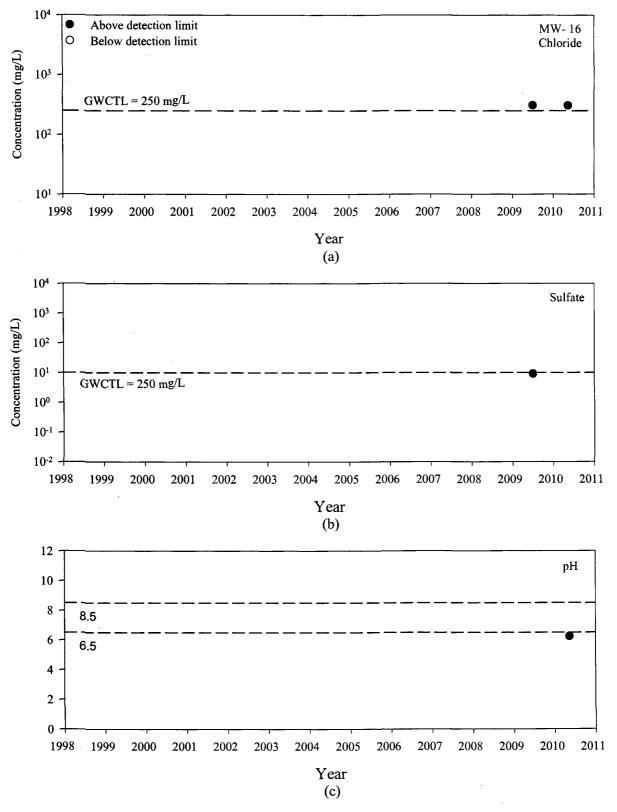


Figure B-59. Temporal Variation of (a) Chloride, and (b) Sulfate and (c) pH for Monitoring Well MW-16

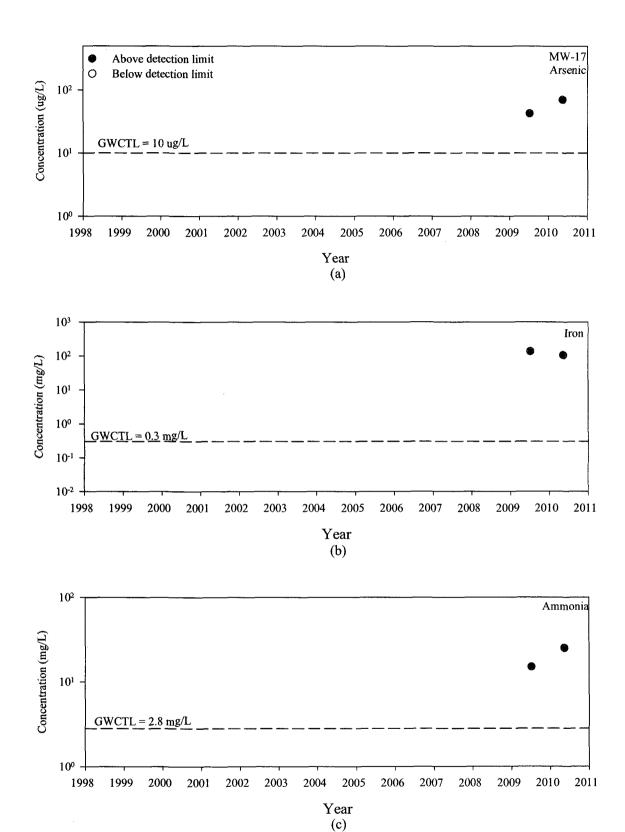


Figure B-60. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-17

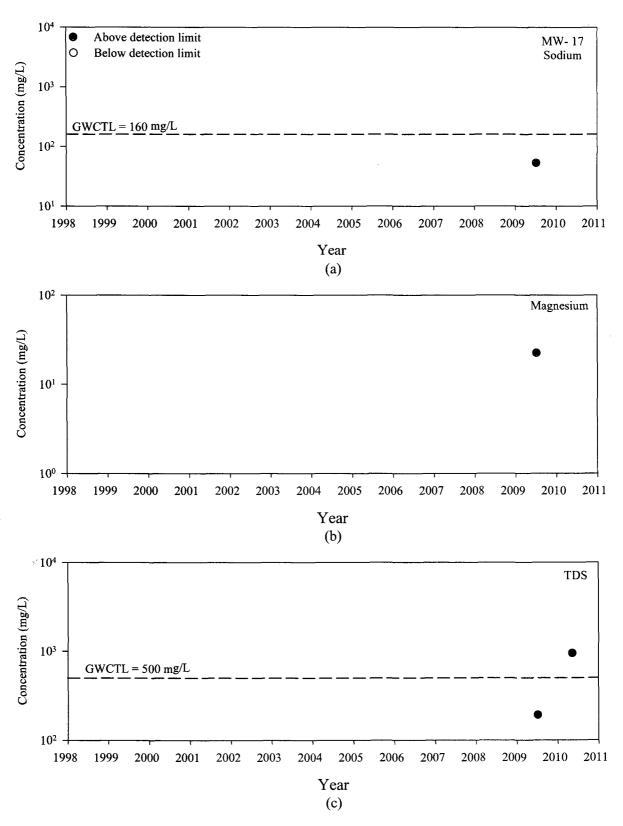


Figure B-61. Temporal Variation of (a) Sodium, (b) Magnesium, and (c) TDS for Monitoring Well MW-17

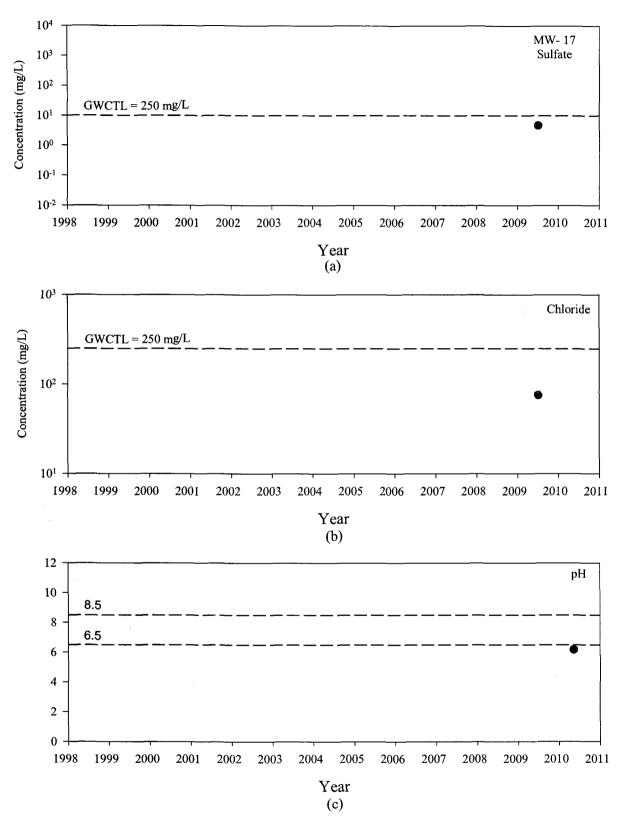
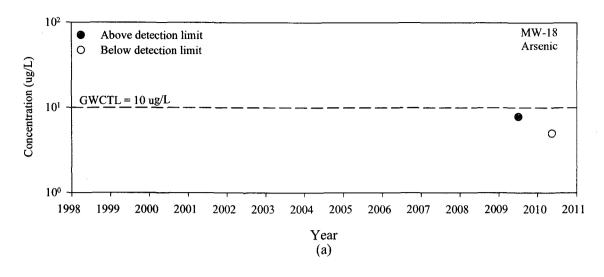
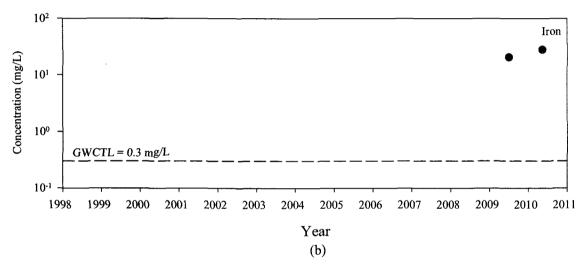


Figure B-62. Temporal Variation of (a) Sulfate, and (b) Chloride and (c) pH for Monitoring Well MW-17





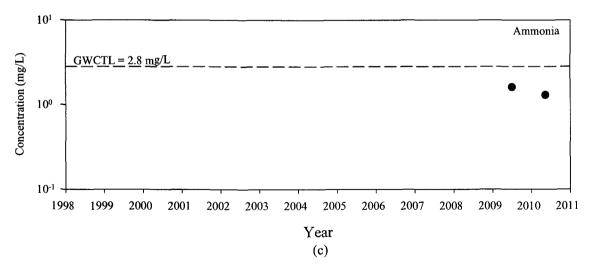


Figure B-63. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-18

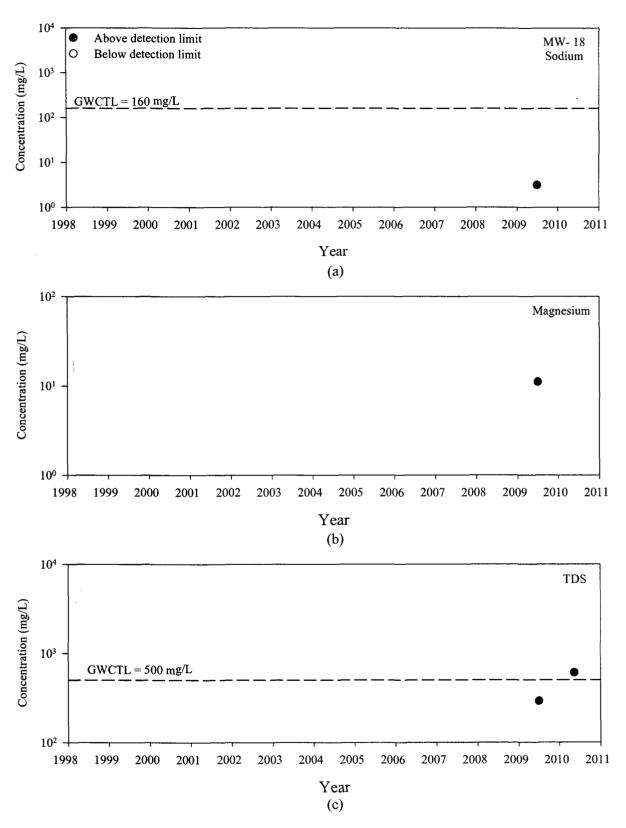


Figure B-64. Temporal Variation of (a) Sodium, (b) Magnesium, and (c) TDS for Monitoring Well MW-18

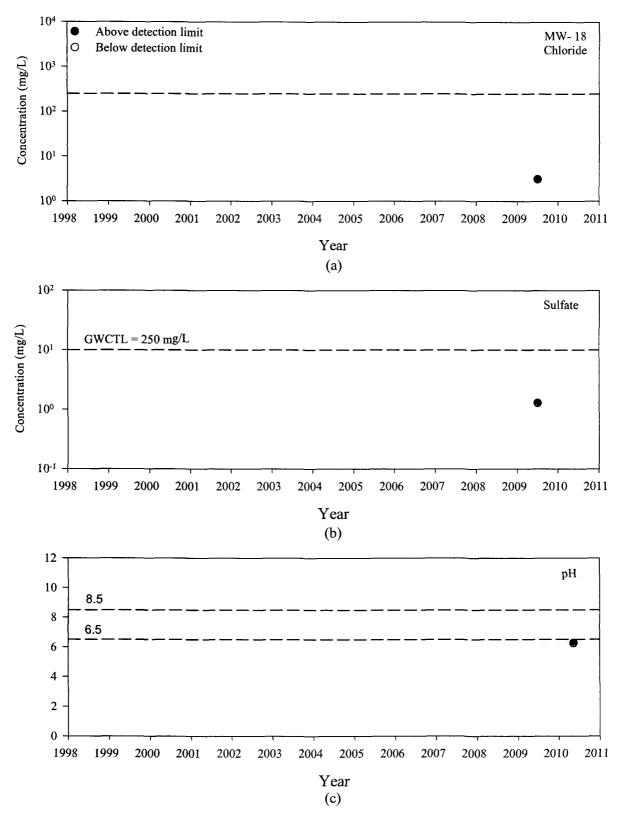


Figure B-65. Temporal Variation of (a) Chloride, and (b) Sulfate and (c) pH for Monitoring Well MW-18

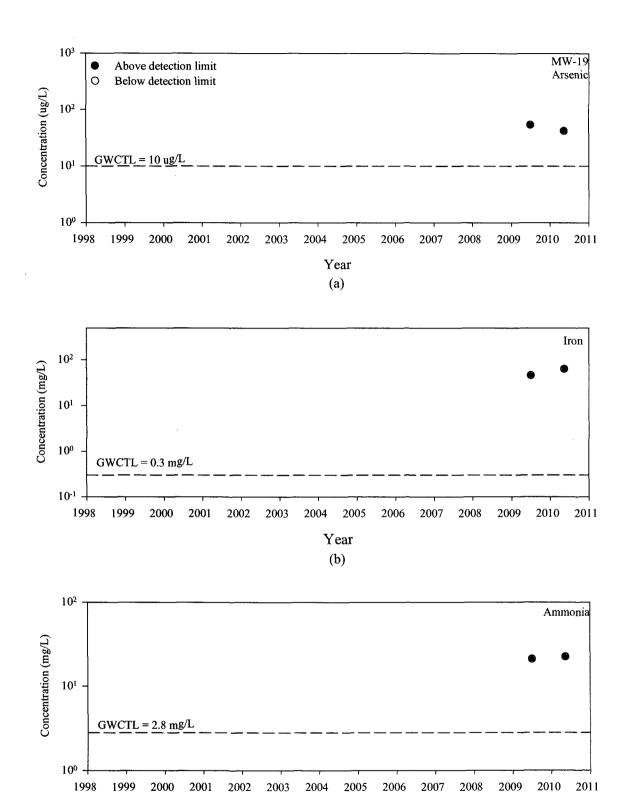


Figure B-66. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-19

Year (c)

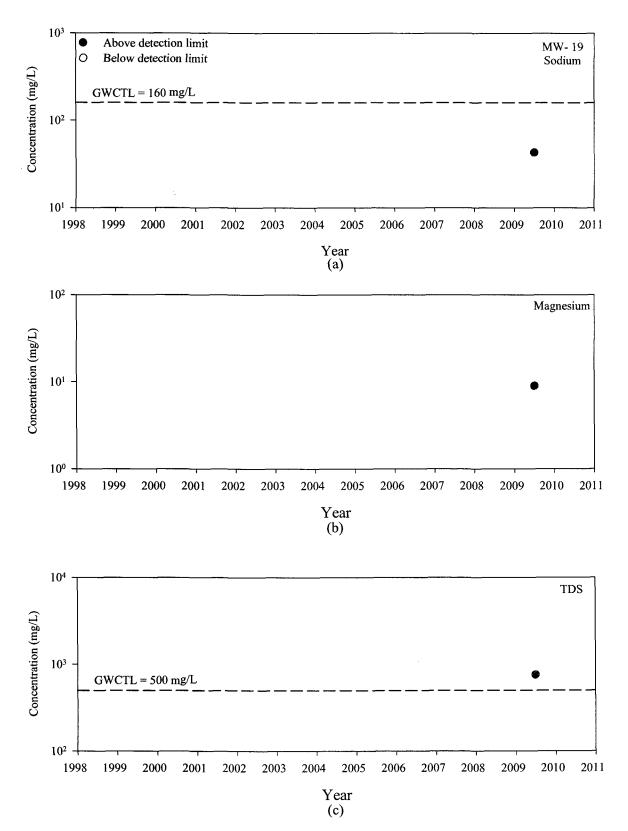


Figure B-67. Temporal Variation of (a) Sodium, (b) Magnesium, and (c) TDS for Monitoring Well MW-19

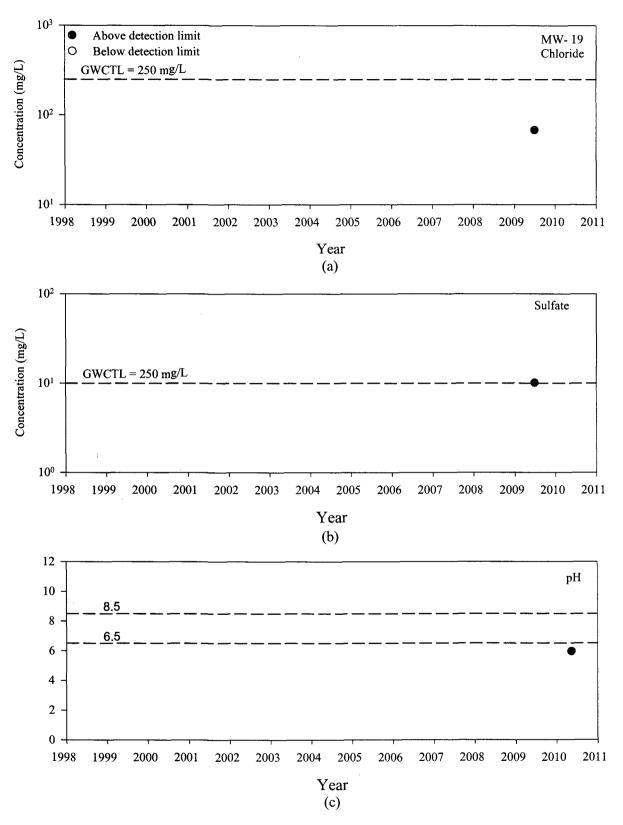
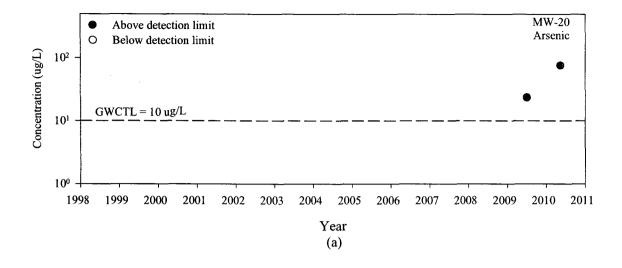
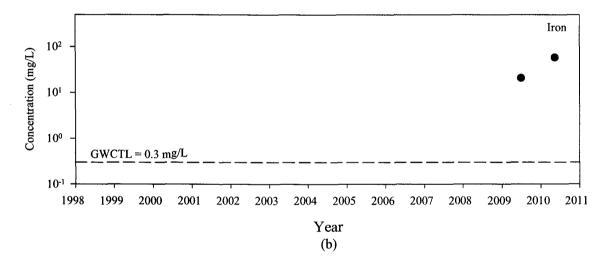


Figure B-68. Temporal Variation of (a) Chloride, and (b) Sulfate and (c) pH for Monitoring Well MW-19





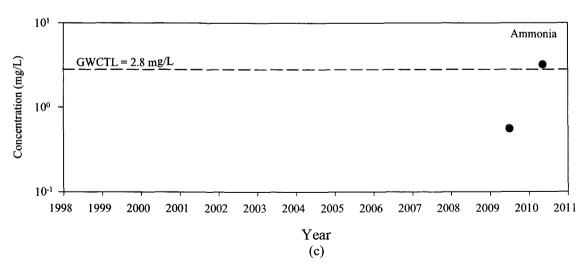


Figure B-69. Temporal Variation of (a) Arsenic, (b) Iron, and (c) Ammonia (as N) for Monitoring Well MW-20

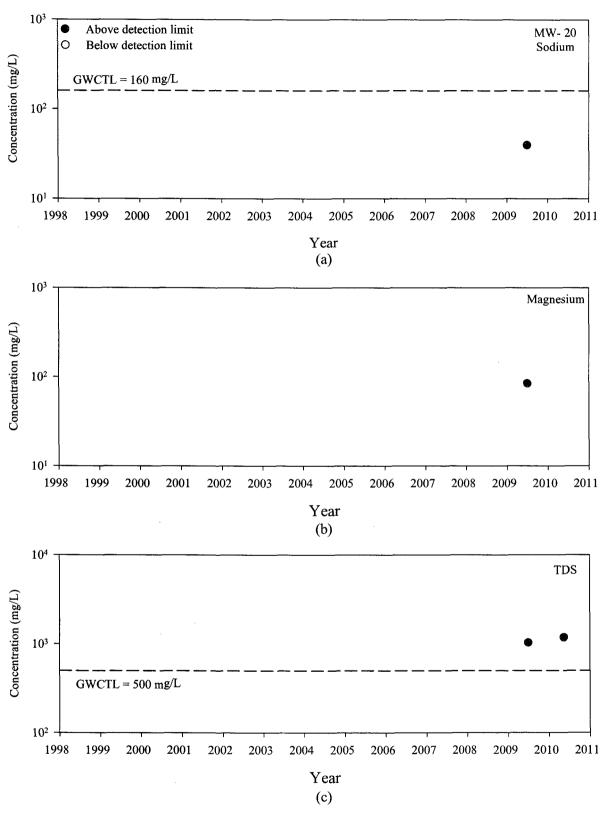


Figure B-70. Temporal Variation of (a) Sodium, (b) Magnesium, and (c) TDS for Monitoring Well MW-20

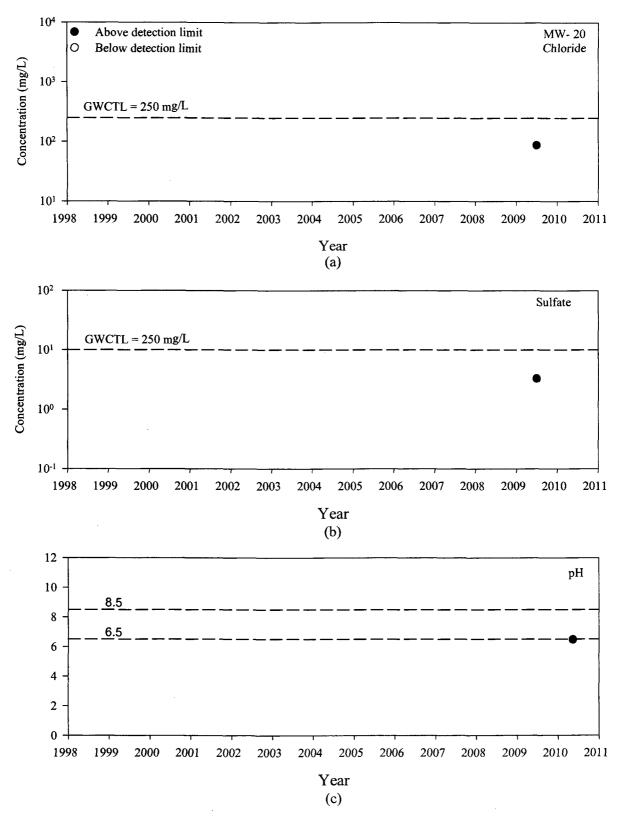


Figure B-71. Temporal Variation of (a) Chloride, and (b) Sulfate and (c) pH for Monitoring Well MW-20

# Appendix C Life-Cycle Cost Analysis of a Pump-andTreat System as a Remedial Alternative

INNOVATIVE WASTE CONSULTING SERVICES, LLC					
6628 NW 9th E	Blvd., Suite 3, Gain	esville, FL 32605,	USA		
Project Name: Sarasota County CCSWDC	Designed By:	вт	CHECKED BY: PJ/JP		
Appendix C – Pump and Treat Remedial Cost Estimation	Date:	08/13/2010	DATE: 08/26/2010		

# **Overview and Objectives**

As the Central County Solid Waste Disposal Complex (CCSWDC) is not expected to meet No Further Action criteria as described in 62-780.680(1), 62-780.680(2), or 62-780.680(3), FAC, within five (5) years, a life cycle remedial cost estimate was prepared to comport with Rule 62-780.690(1)(f)2, FAC.

This appendix describes the methodology used in preparing the cost estimate of a pump and treat system designed to extract groundwater across the down-gradient edge of the plume, convey extracted groundwater to aeration ponds and a subsequent sedimentation pond, and remove iron precipitate for disposal in a the CCSWDC's active lined cell.

## **Conceptual Design**

### **Groundwater Extraction Rate**

Groundwater will be extracted across the down gradient edge of the plume. The following equation was used to calculate the flow rate from the site:

$$Q = Aki$$

where,

 $Q = flow rate, ft^3/d$ 

A= cross-sectional area of the aquifer of interest, ft<sup>2</sup>

k= hydraulic conductivity, ft/d
i= hydraulic gradient, ft/ft

The cross-sectional area of the aquifer was calculated from the aquifer depth and the maximum source length perpendicular to the average groundwater flow direction – the surficial aquifer depth was assumed to be 16 ft based on information provided as part of the 2008 hydrogeological investigation of the site conducted by Ardaman and Associates. Furthermore, the maximum hydraulic conductivity (4.1 ft/s) and hydraulic gradient (0.0011 ft/ft) values reported in the Ardaman & Associates report were used. An approximate aquifer length perpendicular to the general groundwater flow direction (7,000 ft) was assumed based on the site dimensions. Based on these assumptions and the equation presented above, the groundwater extraction rate was calculated as follows:

$$Q = (7,000 \ ft \times 16 \ ft) \times 4.1 \frac{ft}{s} \times 0.0011 \frac{ft}{ft} = 505.12 \ \frac{ft^3}{d} = 3,778 \ gpd$$

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For the purpose of preparing this cost estimate, a daily flow rate of 4,000 gpd is required. Note that this is a figure that will be used as a part of this cost estimate only – in reality, aquifer pump tests would be initiated at the site as part of an initial remedial system design. Following the initial design, the pump-and-treat system's configuration and operations (such as number of extraction points, groundwater extraction rate, etc.) would be analyzed based on actual operational data and the system would be optimized in response to such results.

### **Sizing the Aerator**

To determine the required oxygen delivery rate for the treatment system, the stoichiometric mass of oxygen required to fully oxidize the aqueous Fe(II) in the extracted groundwater must first be calculated. Below are the half-cell reactions involved in this process. First, Fe(II) is oxidized to the non-aqueous Fe(III):

$$4Fe^{2+} \rightarrow 4Fe^{3+} + 4e^{-}$$

Delivery of O<sub>2</sub> to the aqueous phase results in the following reduction reaction:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

The two half-cell reactions can be combined and written as:

$$O_2 + 4H^+ + 4Fe^{2+} \rightarrow 2H_2O + 4Fe^{3+}$$

Therefore, one (1) mol of  $O_2$  is required to oxidize four (4) mol of Fe(II). Using this stoichiometric ratio, the assumed Fe(II) concentration of 150 mg/L (note that this concentration represents the upper end of the range of iron measurements conducted in groundwater at the site), and the groundwater extraction rate calculated earlier, the required oxygen delivery rate is calculated as follows:

$$\frac{0.150 \ g \ Fe(II)}{L} \times \frac{1 \ mol \ Fe(II)}{55.85 \ g \ Fe(II)} \times \frac{1 \ mol \ O_2}{4 \ mol \ Fe(II)} \times \frac{32 \ g \ O_2}{1 \ mol \ O_2} \times \frac{3.78 \ L}{gal} \times \frac{4,000 \ gal}{day} = \frac{325 \ g \ O_2}{day}$$

The stoichiometric oxygen delivery requirement is 325 g/day, or approximately 0.3 lb/hour. The aeration pond incorporates two (2) 3-hp self-aspirating floating aerators each capable of delivering 4.8 lb  $O_2$  per hour. Based on the stoichiometric oxygen demand and the expected oxygen delivery rate, approximately 32 times the required oxygen will be available to oxidize Fe(II).

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### Sizing the Aeration Pond and Sedimentation Pond

The aeration pond was sized based discussions with the aerator manufacturer Aeromix in August 2010, the design flow rate, and the desired hydraulic retention time. To accommodate two floating aerators, a 50 ft x 50 ft pond 7 ft deep with a 3:1 side slope configuration and a total volume of 256 ft<sup>3</sup>, or 51,700 gallons, was assumed. At 5 ft deep (2 ft of freeboard), the storage capacity is 112 ft<sup>3</sup>, or 22,600 gallons. The hydraulic retention time is then 5.7 days based on the calculated extraction rate.

A secondary (sedimendation) pond was also assumed which would allow for the settlement of the iron precipitate which would be periodically removed and taken to the active disposal cell at the CCSWDC. A 50 ft  $\times$  50 ft  $\times$  7 ft sedimentation pond with 3:1 side slopes was assumed. Assuming 2 ft of freeboard, the hydraulic retention time was calculated to be 5.7 days.

## **Life Cycle Cost Estimate**

A cost estimate for the pump and treat system described above is presented in Table 1. The total estimated capital cost of the pump and treat system is \$1.8 million.

**Table 1. Conceptual Pump and Treat Capital Cost Estimate** 

Item/Description	Unit	Unit Cost	Quantity	Totals
Excavate 50' x 50' x 7' aeration pond	CY	\$4.00	256	\$1,024
Excavate 50' x 50' x 7' sedimentation pond	СУ	\$4.00	256	\$1,024
Furnish and install 60 mil HDPE liner for two 50' x 50' x 7' ponds	SF	\$0.50	5,800	\$2,900
Floating Aerator	EA	\$8,000	2	\$16,000
Groundwater Extraction System Pump	EA	\$31,000	1	\$31,000
Groundwater Extraction Well Point Installation	LF	\$110.00	13,200	\$1,452,000
Surveying	LS	\$10,000	1	\$10,000

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Table 1 (Continued)

			Subtotal	\$1,513,948
Contingency (10%)	PCT	-	-	\$151,395
Engineering, Design,	1.6	6450.000	4	
Construction Assistance	LS	\$150,000	1	\$150,000
Total Capital Cost Estimate				1,815,343

The capital cost presented above is based on the best current available information. More rigorous design would need to be initiated to refine these costs, and the ultimate capital cost would be expected to increase or decrease following the results of start-up testing as part of overall system optimization.

Operations and maintenance (O&M) costs were estimated over a 30-year operational period that assumed a 3% annual increase in costs. It was assumed that the pump and treat system (pumps and aerators) will be operated continuously. Table 2 below shows the estimated annual O&M cost for the first year of operation. The total estimated lifetime (30 years) O&M cost was estimated to be approximately \$2.8 million. Note that the total lifetime O&M costs would be expected to vary based on the actual duration of system operation and other factors such as inflation. The estimate below did not account for other factors such as equipment replacement cost.

Table 2. Estimated Annual and 30-Year O&M Cost for Pump-and-Treat System

Annual Cost
\$5,000
\$7,700
\$20,000
\$25,000
\$57,700
\$2,746,854

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The mass of sediment generated annually in the sedimentation pond was calculated based on the design pumping rate and assumed iron concentration – it was estimated that approximately 2.2 kg/day or about 0.9 tons per year of iron precipitate would be generated and thus required to be removed and placed in the active Class I disposal cell at the CCSWDC.

Disposal costs were assumed to be negligible based on the anticipated 0.9 tons per year of precipitate generated. Furthermore, laboratory costs to test the sediment using the toxicity characteristic leaching procedure were not assumed but may be required to assess whether the material can be disposed of in the CCSWDC's active Class I cell.

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# **Appendix D**

University of Florida Follow-Up Evaluation of Groundwater Impacts at the Central County Solid Waste Disposal Complex (2009)

# Continued Work on the Sources and Causes of Groundwater Exceedances at the Sarasota County Central County Solid Waste Disposal Complex

Final Report

November 30, 2009

Timothy G. Townsend, PhD, PE (Principal Investigator)
Jae Hac Ko (Post Doctoral Associate)
Jianxia Hou (Graduate Research Assistant)

Department of Environmental Engineering Sciences University of Florida

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#### **EXECUTIVE SUMMARY**

Research was conducted to examine the potential for the release of naturally-occurring elements from soil at the Sarasota County Central County Landfill due to a process known as reductive dissolution. This work follows upon previous research demonstrating that soils at the site were susceptible to reductive dissolution, and that it was plausible that iron, arsenic, and ammonia exceedances could occur without a discharge from the landfill unit. The objectives of the current study were to further examine the hypothesis that iron reductive dissolution from onsite soils could occur simply through a reduction in dissolved oxygen content and to examine the long-term effects of the decreased dissolved oxygen conditions on the release of iron (and other related constituents). The impact of external sources of organic matter, specifically yard trash, on reductive dissolution was also explored.

The result of column tests on site soils confirmed that a reduction in dissolved oxygen, without any external input of organic matter, can result in reductive dissolution. The column tests resulted in a temporary increase in iron concentration which was accompanied by an increase in ammonia concentration. The fraction of iron reductively dissolved was found to be smaller than that observed in previous tests where an external source of organic matter was present, thus the amount released was not sufficient to produce a measurable increase in arsenic concentration (arsenic levels were relatively low in the soil). Mass balance calculations suggest that reductive dissolution, even at the lower release rates observed in the absence of external organic matter, could result in groundwater iron concentrations similar to those observed at the site currently. Measurements from the columns over time found iron release to spike and then decrease. This supports the hypothesis that given time, groundwater concentration should return to previously existing levels.

The results of batch tests where yard trash extract (created using yard trash collected from Sarasota County) was used as a source of organic matter found an enhancement in reductive dissolution. These results suggest that external inputs of organic matter, such as those that might occur from stockpiled yard trash or as a result of site development activities, could influence the rate and extent of reductive dissolution.

As a whole, the research supports the hypothesis that reductive dissolution is a plausible mechanism for the release of iron, arsenic, and ammonia in the absence of any landfill discharge

or external organic matter. Reductive dissolution can occur with a decrease in dissolved oxygen, and while the degree of reductive dissolution is limited, these levels can still result in groundwater exceedances. External sources of organic matter that might naturally enter the groundwater at a site (e.g., from yard trash operations, stockpiled organic soils, vegetation and muck form site development) may also play a role in the degree to which reductive dissolution occurs.

#### 1. Introduction

#### 1.1. Background

Measurements at the Sarasota County Central County Landfill indicate that the groundwater sampled from several wells contain concentrations of iron, arsenic and ammonianitrogen that exceed Florida's groundwater cleanup target levels (GWCTL). In the previous study "Assessment of the Source and Causes of Groundwater Exceedances at the Sarasota County Central County Solid Waste Disposal Complex," the Department of Environmental Engineering Sciences (EES) at the University of Florida (UF) investigated two potential sources for these chemicals: discharge from the landfill unit and leaching from the naturally occurring soils. Since the entire landfill area is lined, the potential for geochemical changes to the natural soil and aquifer environment were examined as a possible cause of the GWCTL exceedances. The report presented here provides the results of additional research on this subject.

# 1.2. Summary of Previous Results

In the previous study, a process known as reductive dissolution was examined as the potential cause of the release of dissolved iron into groundwater [1]. Reductive iron dissolution is a process where reducing conditions (these that typically occur in anaerobic or poorly aerated environments) cause the transformation of oxidized iron (Fe<sup>3+</sup>) to reduced iron (Fe<sup>2+</sup>). Since Fe<sup>3+</sup> is normally associated with a solid mineral and Fe<sup>2+</sup> is normally associated with dissolved iron, this process results in an increased iron concentration in the groundwater. The reductive dissolution process has been commonly observed at unlined landfill sites where leachate entering the groundwater promotes a reducing condition. More recent evidence also suggests that even lined landfills can cause this to occur by cutting off the natural flow of oxygen to the subsurface soils.

In the previous research, soil samples collected from the unsaturated and saturated zones at the landfill were found to contain iron minerals that were susceptible to reductive dissolution. Furthermore, the results suggested that arsenic and ammonia-nitrogen can also be released when iron is reductively dissolved. Preliminary data also supported the hypothesis that the reductive dissolution process could occur in the absence of external organic matter. The organic matter creates an oxygen demand as it is biologically decomposed, and as a result can create reducing conditions. The final conclusion of the report was that reductive dissolution, in the absence of any

landfill discharge, was a plausible mechanism for causing the elevated concentrations of iron, arsenic and ammonia at the site.

#### 1.3. Scope of Continued Investigation

The primary aims of the follow up investigation were two-fold. First, additional data were sought to confirm that reductive dissolution could occur in the aquifer at the site simply due to reduced dissolved oxygen levels, and to examine whether the conditions would return to previous conditions after a period of time. Second, the importance of external sources of organic matter (runoff from yard trash/mulch piles) was investigated. Since some of the highest arsenic concentrations were observed in areas where yard trash was stored, the impact of such organic matter on reductive dissolution was investigated.

#### 2. Materials and Methods

#### 2.1. Soil Preparation

The soil previously collected from Central County landfill in Sarasota County was used in this research. The sampling depth of the soil was approximately 36-43 inches, which is in the vicinity of the water table (37 inch below ground level). Prior to experimentation, the soil was airdried at room temperature for 4 days and manually mixed. Once the samples are well mixed, they were stored in sealed buckets.

#### 2.2. Experimental Methods

#### 2.2.1. Reductive dissolution test using sequential chemical reducing reagent

To test the fate of the naturally-occurring soil constituents under reducing conditions, sodium ascorbate (C<sub>6</sub>H<sub>7</sub>NaO<sub>6</sub>) or sodium borohydride (NaBH<sub>4</sub>) were used as chemical reducing reagents. Sodium ascorbate (0.05 M) or sodium borohydride (0.05 M) was used at a solid/water ratio of 1:20. When sodium borohydride was used, the pH of the solution was adjusted to 7. Soil (10 g) was measured and mixed with 200 milliliters (mL) of the abiotically reduced solution in a plastic bottle. The bottles were equilibrated on a rotating shaker for 24 hours at 30 rpm. All tests were carried out in triplicate. After equilibration, the supernatant was collected to measure ferrous iron, ammonia, total organic carbon (TOC), total iron and arsenic, pH and the oxidation reduction potential (ORP). The soil remaining in the bottle was mixed with the reducing solution and the testing process was repeated until the concentration of ferrous iron was under the method detection limit, this was done to determine the amount of total iron that could potentially be released.

#### 2.2.2. Reductive dissolution test under biologically reducing conditions

The fate of the naturally-occurring contaminants was measured under biologically reducing conditions over time. One hundred ten grams of soil were mixed with 140 mL of deionized water (DIW) in a glass serum bottle. One gram of cellulose and 10 mL of incubated seed solution were added immediately. The seed was obtained from an anaerobically operated soil column. The bottle was purged with nitrogen gas (N<sub>2</sub>) for approximately 3 minutes. The bottles were sealed and placed upside down to eliminate air intrusion. The bottles were shaken gently for one minute once each week. Samples were taken for analysis on days 10, 20, and 30. On the day

of sampling, the bottles were placed on a rotating shaker for two hours after which the mixture was filtered and analyzed. The pH, ORP, and Fe (II) were measured immediately after shaking. The remaining sample was preserved with HNO<sub>3</sub> acid and analyzed later using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) per US EPA SW 846 Method 6010B [2]. Data of these tests are presented in Appendix B – Biological Reducing Test.

#### 2.2.3. Soil column test

A soil column test was conducted to assess the release of iron, arsenic and ammonia from soils when exposed to O<sub>2</sub>-free water and evaluate the relationship between the two variables. The dimensions of the column and experimental setup are depicted in Figure 1. A total of five columns were packed with the soil described in Section 2.1 and a microbial seed was then added. The columns were fitted with a layer of geotextile and sand on the top and the bottom of the soil to prevent the sampling ports from clogging. The porosity and pore volume of soil packed in the columns are summarized in Table 1. De-aired water was added through the bottom port using a 140 mL syringe. Liquid samples were collected from the top of the columns using a 140 mL syringe with a check valve to minimize O<sub>2</sub> contact. Three columns (Column 1, 2, and 3) were packed with the Sarasota soil mixture and DI water (equivalent to nine pore volumes of the packed-soil) was used to remove suspended particles in water of the soil of the column before seeding. Flushing with DI water for Column 4 and 5 was not conducted before seeding for the purpose of checking if a measurable loss of iron mineral occurred from the flushing. Suspended solids in the effluent samples were separated using a centrifuge and filtration. The de-aired water addition and the sample collection were conducted every three or four days. The samples collected were immediately analyzed for DO, ferrous iron (Fe<sup>2+</sup>), and ammonia. Remaining samples were preserved with sulfuric acid or nitric acid for further analysis. The columns were stored in an anaerobic chamber which was purged with nitrogen gas  $(N_2)$ .

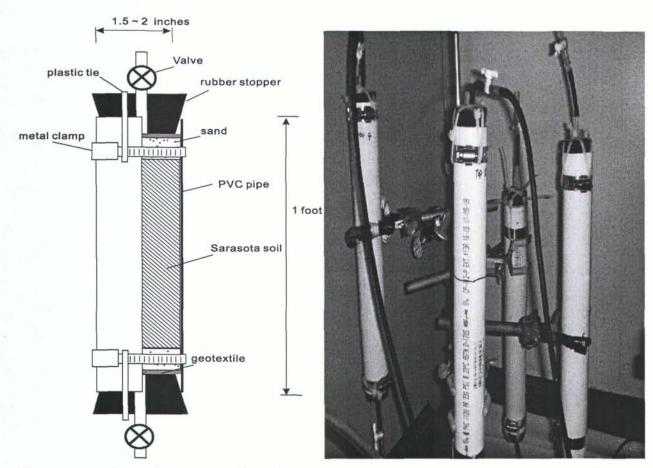


Figure 1. A schematic diagram of a soil column and a photograph of the experimental setup

Table 1. The porosity and pore volume of five columns

Parameters	Column 1	Colum 2	Column 3	Column 4	Colum 5
Added soil (g)	533	530	544	488	513
Filter sand (g)	55	53	49	123	106
Porosity of packed soil (%)	0.36	0.35	0.34	0.44	0.48
Pore Volume (mL)	110	107	104	120	135

## 2.2.4. Reductive dissolution test in the presence of external organic matter (yard trash extract)

#### 2.2.4.1. Preparation of yard trash extract

The County provided two 5-gallon buckets of size-reduced yard trash processed at the site. To generate yard trash extract, a yard trash sample (100g) was mixed with 2000 mL DIW in each glass bottle. The glass bottles with yard trash solution were rotated using a rotating shaker for 24 hours at 30 rpm. The supernatant (extract) was filtered to measure pH, TOC, and total metals.

#### 2.2.4.2. Reductive dissolution test under biologically reducing conditions using yard trash extract

A total of 110 grams of soil was placed in a glass serum bottle and 140 mL of yard trash extract was added with 10 mL of incubated seed solution. Solutions of 0%, 50%, and 100% yard trash extract were created by diluting yard trash extract with DIW. For example, a 50% yard trash extract solution contained 70 mL of yard trash extract and 70 mL of DIW before the addition of 10 mL of seed solution. A bottle with soil, yard trash extract solution, and seed was purged with N<sub>2</sub> and sealed. The bottles were kept in the incubator for 30 days, and were removed every 10 days for shaking. After 30 days, the supernatant was collected in each bottle and filtered to measure pH, ORP, Fe (II) and ammonia. The rest of the samples were preserved for further analysis in the same manner as described in section 2.2.3.

#### 2.2.4.3. Column tests using yard trash extract

Two out of the five columns described in section 2.2.3 were used for testing yard trash extract as a source of organic matter to enhance the microbial-mediated reducing conditions. Instead of adding de-aired DIW, yard trash extract was added into each column in a quantity equal to one pore volume of the column. Yard trash extract was added through the bottom port of the column using a 140 mL syringe. Liquid samples were collected from the top of the columns using a 140 mL syringe with a check valve to minimize O<sub>2</sub>-contact. Yard trash extract addition and sample collection were conducted periodically (weekly). Collected samples were immediately analyzed for DO, ferrous iron and ammonia. Remaining samples were preserved with sulfuric acid or nitric acid for further analysis. The columns were stored in an anaerobic chamber which was purged with nitrogen gas.

#### 2.3. Analytical Methods

#### 2.3.1. Soil quality analysis

#### 2.3.1.1. Soil pH

The pH of the soil sample was measured as per US EPA SW846 Method 9045D [2]. Twenty grams of soil were placed in a 50 mL beaker and 20 mL of DIW was added. The beaker was covered and the suspension was stirred continuously for 5 min using a magnetic stir rod on a stir plate. The soil suspension was then allowed to stand for about 1 hour to allow most of the suspended particles to settle out and pH of the supernatant was measured using an Accumet AP62 portable pH/mV/T meter equipped with a combination pH Electrode/ATC probe. The meter was calibrated using standard buffering solutions. Equilibrium between the electrode and sample was established by gently stirring the supernatant with the electrode until a steady reading was obtained.

### 2.3.1.2. Organic carbon

The measure of organic carbon in the soils was obtained following the Walkley-Black Method as described in the United States Department of Agriculture Soil Survey Methods Manual [3]. The soil sample (1g) was weighed in duplicate in a 250 mL Erlenmeyer flask. Ten mL of 1N potassium dichromate were then added to the sample, followed by thorough mixing. Twenty milliliters of the concentrated sulfuric acid were then added to this suspension and mixed. The sample was allowed to stand for one hour. Two-hundred milliliters of DIW and five drops of ferrous sulfate complex indicator were added to the soil suspension. When the indicator is added it gives the solution an orange color. Ferrous sulfate (0.5 N) was used for titration. Upon titration with 0.5N ferrous sulfate the orange color changes to green and finally to a reddish brown indicating the endpoint. Two blanks were included which served as standards. The percent of organic carbon was calculated as per the equation below:

$$OrganicCarbon(\%) = \frac{0.003g * N * 10mL * (1 - \frac{T}{S}) * 100}{ODW} = \frac{3(1 - \frac{T}{S})}{W}$$

Where:

N=Normality of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution T=Volume of FeSO<sub>4</sub> used in sample titration (mL) S=Volume of FeSO<sub>4</sub> used in blank titration (mL) ODW=Oven-dry sample weight (g)

#### 2.3.1.3. Total extractable ammonia

Five grams of soil were weighed and placed in 50 mL graduated centrifuge tubes containing 25 mL of 2 M KCl. The centrifuge tubes containing the soil and KCl mixture were shook for one hour and filtered through a Whatman #42 filter paper. The filtrates were analyzed for ammonium concentration C (mg/L) using the Hach Method 10023 [4]. The percentage of ammonium in soil was calculated as follows:

Ammonia in soil = 
$$\frac{cmg/L * 25mL * \frac{L}{1000mL}}{5g * 0.001 \frac{kg}{g}} = 5C$$

#### 2.3.1.4. Total iron

Total iron was determined using US EPA SW 846 Method 3050B: Two grams of soil with six replicates were placed in an Erlenmeyer flask. Ten milliliters of 1:1 nitric acid was added and the Erlenmeyer flask was covered with a watch glass. The flask was then heated on a hot plate without boiling. After 15 min, the Erlenmeyer flask was removed from the hot plate and an additional five mL of concentrated nitric acid was added. The flask was then placed back onto a hotplate for 30 minutes. If brown fumes were generated, five mL of concentrated nitric acid was added in a round robin format, until no more fumes were formed (generally four to five times). When brown fumes ceased, the Erlenmeyer flask was heated for an additional two hours or until the final volume of the mixture reached five mL. The Erlenmeyer flask was then removed from the hotplate, 3 mL of 30%  $H_2O_2$  was added (three times), and the solution was placed on the hotplate for two hours. Then 10 mL solution of concentrated HCl was added to the solution, after which the digestate was filtered through a Whatman #41 filter 21 into a 50 mL volumetric flask. After filtration the volumetric flask was then filled to 50 mL with additional deionized water. The samples were then analyzed using the Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES) as per US EPA SW846 method 6010B.

#### 2.3.1.5. Total nitrogen

The total nitrogen contained in the soil samples was analyzed using a Shimadzu Total Organic Analyzer equipped with Shimadzu Total Nitrogen Measuring Unit. The soils were first dried for 3 days in a 60°C oven. Pre-weighted soil samples were placed in the instrument and the temperature of the reaction chamber was increased to 900°C. The detection limit of nitrogen for

this method is  $60 \mu g/kg$  soil. The calibration curve was made using a series of standards and it was used to convert peak areas to actual concentrations of total nitrogen.

# 2.3.2. Water quality analysis

Liquid samples from the column test, biological reducing test, and sequential chemical reducing test were analyzed for pH, DO, ORP, ammonia-nitrogen, ferrous iron and total iron.

#### 3. Results and Discussion

# 3.1. Soil Quality of the Tested Soil

Bulk soil samples collected in the period of the previous research project for Sarasota County were well mixed and analyzed for soil quality prior to testing. The quality of the soil mixture was presented in Table 1. The soil pH was close to neutral. Moisture content of the soil was 2.1%. Total iron and arsenic of the soil was measured at 1,030 mg/kg and 0.44 mg/kg soil, respectively. Total nitrogen concentration was 17.4 mg/kg in the soil, but extractable ammonia measured to be 15.8 mg/kg. Total organic matter of mixed soil was 0.19%. The tested soil mixture had relatively low iron and arsenic concentrations when compared to those quality parameters (iron, 5,060 mg/kg; arsenic, 0.98 mg/kg) of the bulk soil reported in the previous project. This is because the soil sample containing the highest iron concentration among the bulk soil samples was used for tests in the previous study, but a mixture of the remaining bulk soil samples was used for this follow up study. More soil quality data are available in Appendix A-Soil Quality Data.

Table 2. The quality of the soil mixture used for this study

Parameters	Unit	Results
PH	-	7.8
Iron	mg/kg	1030
Arsenic	mg/kg	0.44
Organic content	%	0.29
Total extractable ammonia	mg/kg	15.8
Total nitrogen	mg/kg	17.4

#### 3.2. Iron Release During Sequential Chemical Reducing Test

This test was designed to measure the total amount of iron reductive dissolution under chemically reducing conditions. A sequential batch test with NaBH<sub>4</sub> or sodium ascorbate was used to measure the concentration of iron under chemically reducing conditions. The oxidation and reduction potential (ORP) of the solution was lowered below 0 mV after the reagent was added. Ferrous iron concentrations released from the soil samples are presented in Figure 2 (a) for sodium borohydride as a reducing agent and Figure 2 (b) sodium ascorbate as reducing agent. The left y-axis indicates the ferrous concentrations measured in the tested solutions (mg/L) and the right y-axis indicates the equivalent concentrations relative to the amount of iron released from the soil (mg/kg). A leachable amount of iron per chemical reducing test decreased with an

increasing number of chemical reducing tests using sequential chemical reagent. After the 4<sup>th</sup> test using each reducing agent, ferrous iron levels dropped below detection limit (0.01 mg/L). The total amount of ferrous iron released by the chemical reducing test with sodium borohydride was 14.9 mg/kg and was equal to 1.4% of total iron in the soil mixture. Total amount of ferrous iron released by the chemical reducing test with sodium ascorbate was 21.9 mg/kg and was equal to 2.1% of total iron in the soil mixture. Further detail of pH, ORP and TOC are presented in Appendix C - Chemical Reducing Test Data.

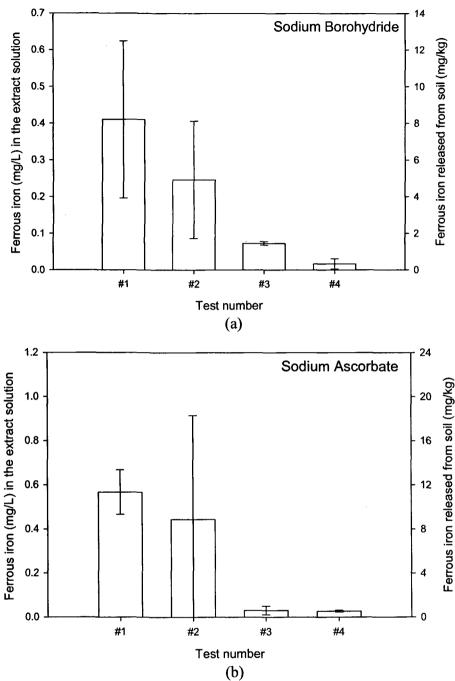


Figure 2. Ferrous iron release during sequential leaching test with chemical reducing reagent: (a) sodium borohydride and (b) sodium ascorbate.

# 3.3. Soil Column Test in the Absence of External Organic Matter

A total of five soil-packed columns were constructed and used to monitor iron release and iron-related parameters in the absence of external organic matter. Water quality parameters with cumulative pore volume for each column effluent are shown in Figures 3 through 7. Each column

shows an increase of ferrous iron, but the peak magnitude was temporary. In columns 1, 2, and 3, the iron increase was observed in the middle of the run. In columns 4 and 5, the increase is observed in the beginning. Overall ferrous iron levels in the effluents ranged from < 0.1 mg/L (below method detection limit) to 1.78 mg/L. As discussed in the previous report, ferrous iron increase is likely related to the increase of ammonia. The increase of ammonia in the effluent was coupled with the increase in ferrous iron. However, the magnitude of increase varied among the tested soil columns. Ferrous concentrations in the column effluents were not variable after passing several pore volumes of de-aired DIW through the column (5-6 pore volume for Column 4 and 5 and 9-10 pore volume for Column 1-3). DO of each column was maintained low by adding low-DO DIW (de-aired). In most of the experiments, DO in effluents were maintained lower than 4 mg/L, except in the beginning of the test. More water quality data are available in Appendix D- Soil Colum Experiments without an External Source of Organic Matter.

In Table 3, cumulative amounts of ferrous iron and ammonia-nitrogen in the effluent of each column for the test period was compared to total iron and total nitrogen of the soil packed in the column. The cumulative ferrous iron that leached from the soil in the columns ranged from 0.02% to 0.06% of total iron in the soil. The cumulative amount of ammonia-nitrogen released to the effluents ranged from 3.5% to 10.6% of total nitrogen in the soil.

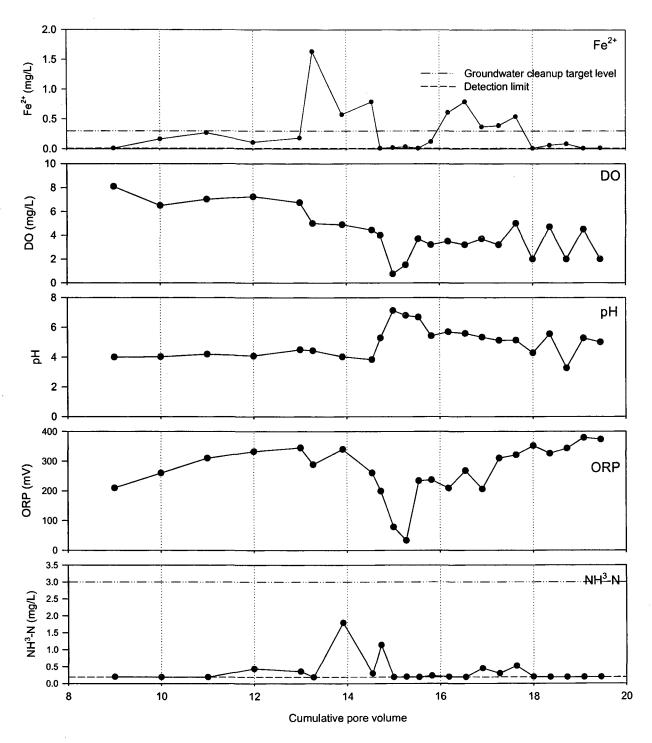


Figure 3. Selected water quality parameters measured from column 1.

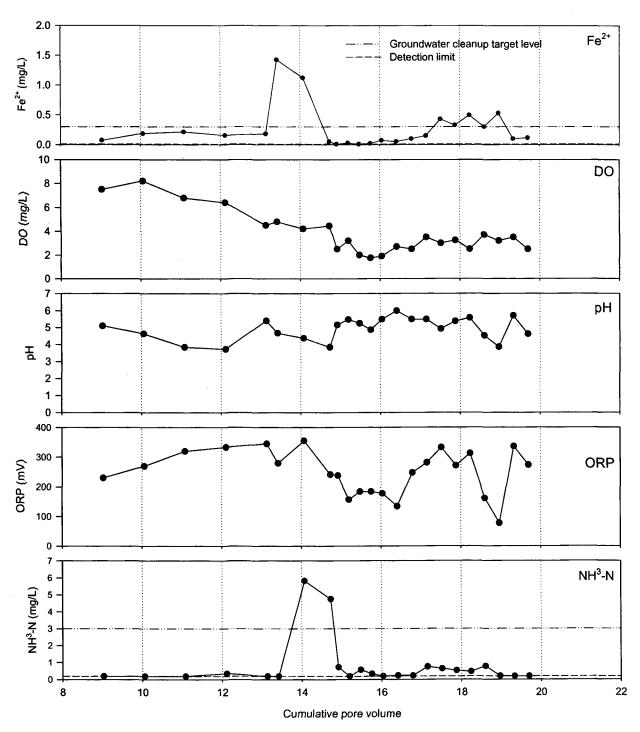


Figure 4. Selected water quality parameters measured from column 2.

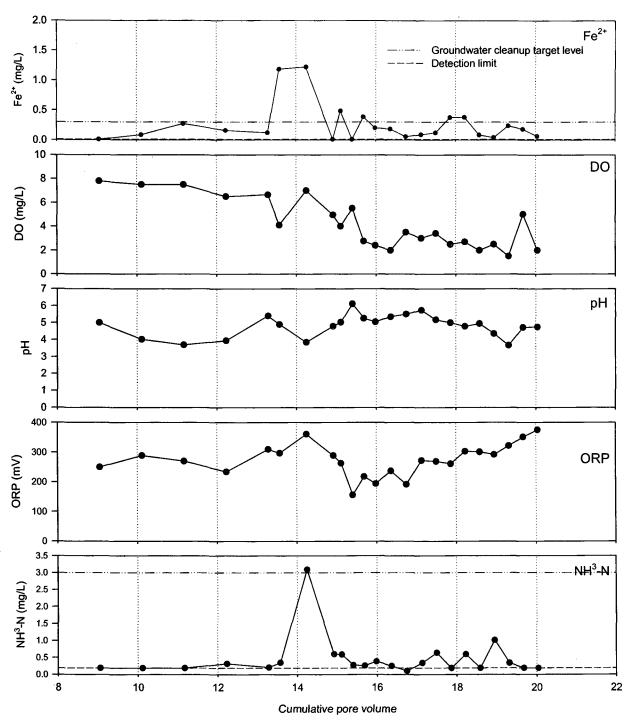


Figure 5. Selected water quality parameters measured from column 3.

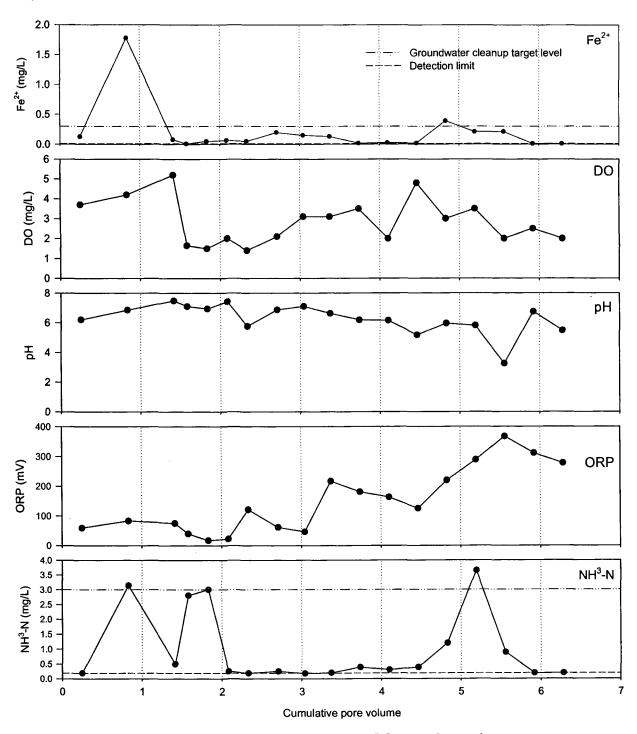


Figure 6. Selected water quality parameters measured from column 4.

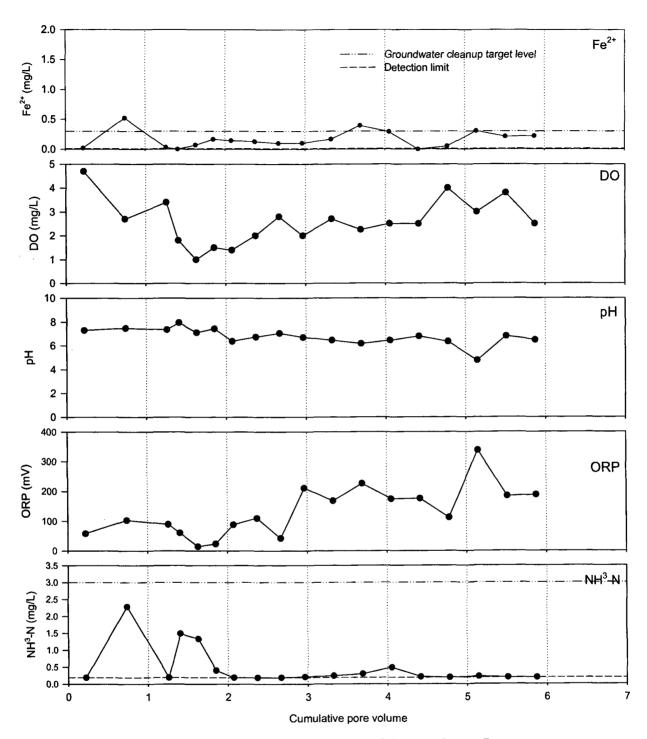


Figure 7. Selected water quality parameters measured from column 5.

Table 3. Cumulative amount of iron, ammonia-nitrogen, and TOC in effluent of each column

Column #	1	f selected parameters ent of each column	Soil packed in the column		
"	Fe <sup>2+</sup> (mg)	NH <sup>4+</sup> -N (mg)	Total iron (mg)	Total Nitrogen (mg)	
1	0.3	0.4	549	9.3	
2	0.3	1.0	547	9.2	
3	0.3	0.5	560	9.4	
4	0.2	0.7	502	8.5	
5	0.1	0.3	528	8.9	

## 3.4. Iron Release in Soil in the Presence of the External Organic Matter (Yard Trash Extract)

#### 3.4.1. Quality of yard trash extract

To generate yard trash extract, yard trash was mixed with DIW in a 2 L glass bottle. The bottle was rotated for 24 hours. The quality of yard trash extract is summarized in Table 4. The pH of the extract was 6.5. The extract contained negligible amounts of ferrous iron. Arsenic in the extract was around 0.01 mg/L. TOC of the extract averaged 650 mg/L. More water quality data are available in Appendix E - Yard Trash Extract (YTE) Experiments.

Table 4. Quality of tested yard trash extract

Parameters	Unit	Results
pH	-	6.5
Total iron	mg/L	0.6
Arsenic	mg/L	0.01
Ferrous iron	mg/L	< 0.01
Total organic carbon	mg/L	650

#### 3.4.2. Biological reducing test using yard trash extract

A biological reducing test for Sarasota soil mixture using yard trash extract was conducted to examine whether the yard trash extract impacted iron release from the soil. As presented in Figure 8, ferrous iron concentrations after the 30 day test increased. It was found that increasing the amount of yard trash extract added for the biological reducing test, increased the release of iron from the soil. An average of 5.17 mg/L ferrous iron was produced from the Sarasota mixture soil with a 100% yard trash extract solution (140 mL), but the concentration of ferrous iron decreased to 2.42 mg/L when the soil mixture was tested with a 50% yard trash extract solution. The presence of yard trash extract enhanced microbially-mediated reductive dissolution of iron.

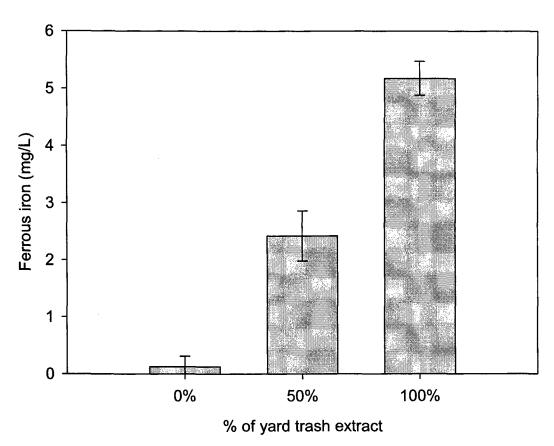


Figure 8. Ferrous iron concentration (mg/L) in biological reducing tests with different amount of yard trash extract.

Table 5. Selected parameters for biological reducing test using yard trash extract

Percent of yard trash extract in the solution	РН	ORP (mv)	DO (mg/L)	Fe <sup>2+</sup> (mg/L)
100 %	6.64 (± 0.12)	-74.33 (± 18.01)	0.65 (± 0.09)	5.17 (± 0.30)
50 %	6.77 (± 0.09)	-98.00 (± 31.43)	$0.70~(\pm~0.09)$	2.42 (± 0.44)
0 %	7.47 (± 0.49)	165.00 (± 16.37)	1.83 (± 0.38)	0.18 (± 0.22)

A figure in parenthesis indicates standard deviation

#### 3.4.3. Soil column test with the addition of yard trash extract

Two out of five soil columns used for soil column test (Section 3.3) were tested for the impact of yard trash extract on the effluent quality. Figure 9 and 10 show the effluent quality of column 3 and column 4 before and after adding yard trash extract, respectively. Ferrous iron concentration in the effluent of each column increased rapidly after the addition of yard trash extract. DO was stabilized in the range of 2-2.5 mg/L. The pH increased slightly in column 3, but was stable for column 4. A considerable decrease of ORP was observed in column 3 after the extract addition. The effluent quality results reveal that ammonia levels also increased with the addition of yard trash extract. More water quality data are available in Appendix E - Yard Trash Extract (YTE) Experiments.

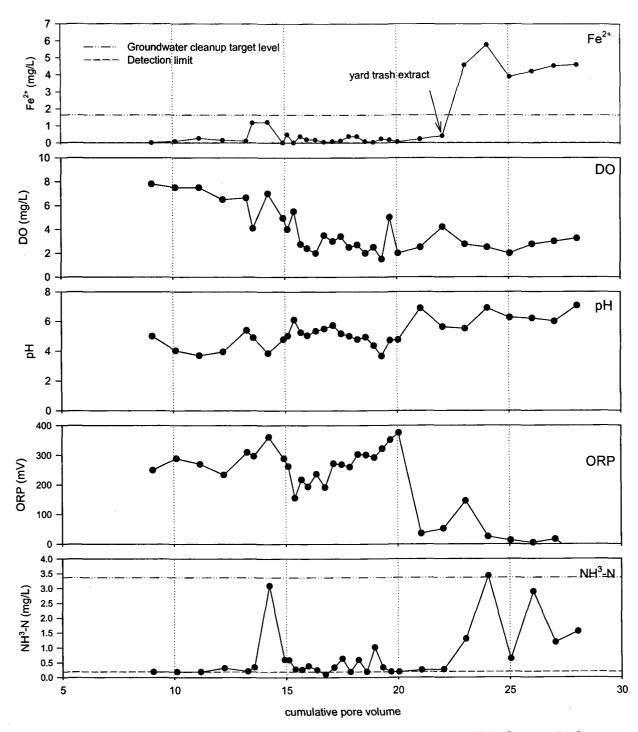


Figure 9. Selected water quality parameters measured from column 3 before and after adding yard trash extract.

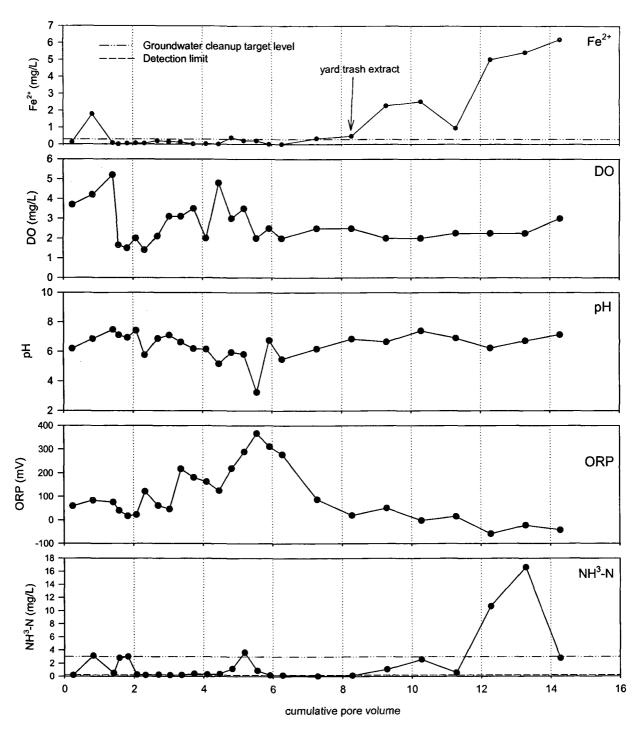


Figure 10. Selected water quality parameters measured from column 4 before and after adding yard trash extract.

## 4. Interpretation and Implications

In this project, the release of naturally occurring constituents in soil mixtures collected from Sarasota County was tested under various reducing conditions. Figures 11 and 12 show the summary of ferrous iron released (milligram of ferrous iron per kilogram of tested soil) and % of iron released in the different reducing conditions as compared to the total iron in the soil, respectively. The total amount of iron released under biologically reducing conditions (30 days) was much greater than those from column test without an external organic matter source (71 days). Compared to the total iron of 1,030 mg/kg in the soil samples, the amount of iron released from the biologically reducing conditions was 1.6% of the total iron in the tested soil, but those from the column tests ranged from only 0.01% to 0.03%.

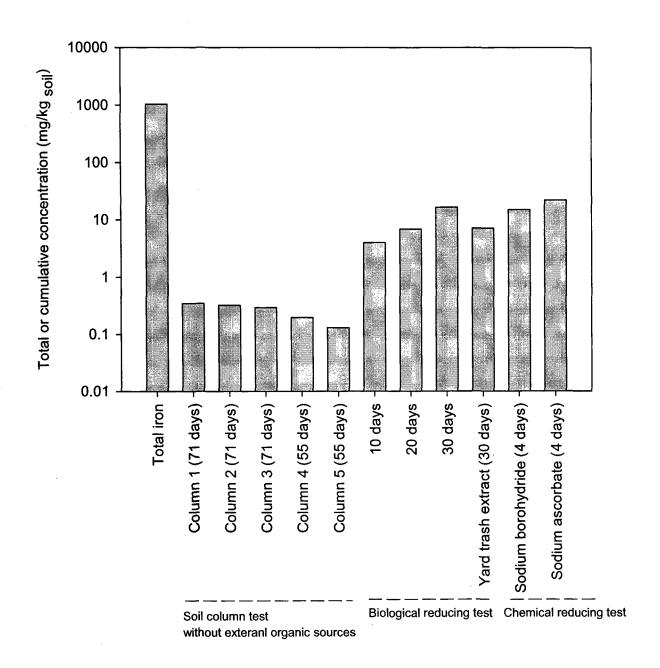


Figure 11. Summary of ferrous iron released (milligram of ferrous iron per kilogram of tested soil) in the different reducing conditions with total iron of the soil (the first bar in the chart).

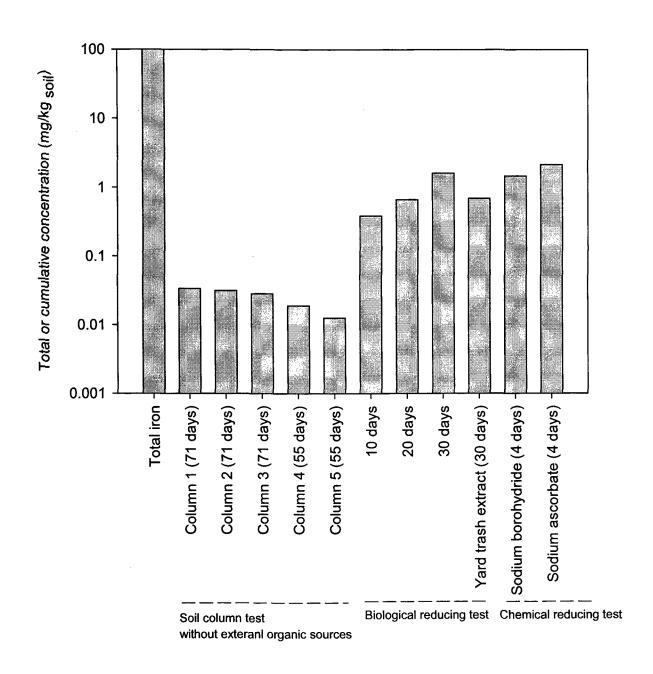


Figure 12. Summary of percent of ferrous iron released (% of total iron in the tested soil) in the different reducing conditions.

The following major observations are summarized based on the previous report and the new research:

- The soils at the site undergo reductive dissolution in the presence of external organic matter, including organic matter derived from yard trash.
- Arsenic and ammonia are observed to increase in concentration when iron reductive dissolution occurs. This was documented for arsenic in the first study. In the new study, the concentration of arsenic in the soil was too low for arsenic to be routinely detected. In the previous study, ammonia release was observed to be correlated with iron release in tests with external organic matter or chemical reducing tests. In the new study, ammonia release was examined without external organic matter and showed to be associated with iron release.
- The results of the column tests suggest that the increase in iron levels are temporary and will eventually return to previous conditions. This supports the theory stating natural attenuation may be an acceptable approach to controlling iron releases.
- The results of the column tests show that iron reductive dissolution does occur in the absence of external organic matter. However, the magnitude of this release is much less than conditions with external organic matter.

A question that comes about after examining the results is "can the amount of iron released in the absence of any external organic matter account reach the level of iron concentrations observed at the site?" Consider, for example, the results presented in Figure 4 where a spike of iron is observed up to 1.5 mg/L (a similar spike is observed for ammonia). Concentrations in the field are observed as high as 150 mg/L. A simple mass balance approach was used to examine whether the relatively small iron releases observed in the column studies could account for the concentration observed in the field. Consider a 1 m³ volume of soil, if the soil has a porosity of 0.4, dry bulk density of 1,800 kg/m³, and an iron content of 5,000 mg/kg, a release of 0.05% would result in a concentration of 11.3 mg/L. Figure 13 shows levels of iron in groundwater calculated using various iron release percentages with different amounts of total iron in soil.

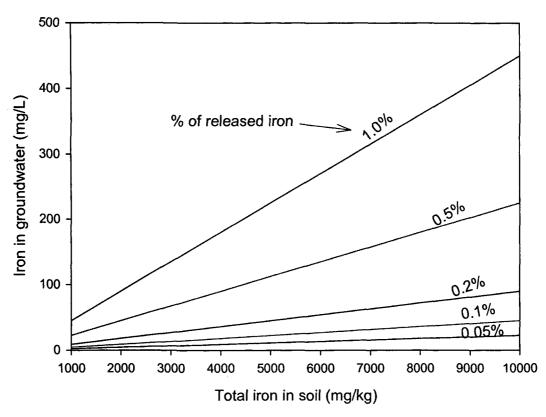


Figure 13. Computed levels of iron in groundwater with various iron release percentages and amounts of total iron in soil.

# 5. Summary and Conclusion

Research was conducted to examine the potential for the release of naturally occurring elements from soil at Sarasota County's Central County Landfill due to a process known as reductive dissolution. This work follows previous research which provided evidence that soils at the site were susceptible to reductive dissolution, and that it was plausible that iron, arsenic, and ammonia exceedances could occur without a leachate discharge from the landfill unit. The new work focused on further identifying the occurrence of reductive dissolution on-site soils subject only to a reduction in dissolved oxygen and examining the long-term consequences of such occurrences. The impact of extended sources of organic matter (specifically organic matter delivered from yard trash taken from the Sarasota county landfill) on reductive dissolution was also explored.

Bulk soil samples collected in the period of the previous research project for Sarasota County were well mixed and used for chemical reducing test with sequential reducing agent (sodium borohydride or sodium ascorbate), biological reducing tests (10 days, 20 days, and 30 days), soil column tests without an external source of organic matter, biological reducing tests with organic matter derived from yard trash, and soil column tests with an external source of organic matter. Total iron and arsenic of the soil was measured at 1,030 mg/kg and 0.44 mg/kg soil, respectively. Total nitrogen concentration was 17.4 mg/kg in the soil, but extractable ammonia measured 15.8 mg/kg. Total organic matter of mixed soil was 0.19%. The soil mixture released various amounts of naturally occurring constituents with different reducing conditions. The fraction of iron release from the soil ranged from 0.01 % to 0.21% of total iron in soil.

The results of soil column tests without an external source of organic matter showed temporal increases of ferrous iron from the effluents with relatively small peaks. The results suggest that the increase in iron levels were temporary and would return to previous conditions if there is no external source of organic matter. The results of the biological reducing test and soil column tests with organic matter derived from yard trash suggest that organic matter from sources such as yard trash or other vegetative material may also play a role in the extent and rate of reduction dissolution. Arsenic and ammonia are observed to increase in concentration when iron reductive dissolution occurs. In the new study, the concentration of arsenic in the soil was too low

for arsenic to be routinely detected. In the previous study, ammonia release was observed to be correlated with iron release in tests with external organic matter or chemical reducing tests.

The new research continues to support that reductive dissolution is a plausible mechanism for the release of iron, arsenic and ammonia even in the absence of both landfill discharge and external organic matter. Reductive dissolution can occur with a decrease in dissolved oxygen, and while the degree of reductive dissolution is limited, these levels can still result in groundwater exceedances at a magnitude similar to those observed at the county landfill site. External sources of organic matter that might commonly occur as part of the development and operation of a landfill site may also play a role in the occurrence and magnitude of these exceedances.

#### 6. References

- [1] Townsend, T.G., Kim H., Zhang, J., Yu, W., 2008. "Assessment of the Source and Causes of Groundwater Exceedances at the Sarasota County Central County Solid Waste Disposal Complex" Final report submitted to Sarasota County Environmental Services Solid Waste Operations.
- [2] U.S. Environmental Protection Agency, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW 846." Web source: <a href="http://www.epa.gov/waste/hazard/testmethods/sw846/online/index.htm">http://www.epa.gov/waste/hazard/testmethods/sw846/online/index.htm</a>.
- [3] U.S, Department of Agriculture. 1996. Chemical analyses, organic carbon (6A) Walkley-Black modified acid-dichromate organic carbon (6A1). p. 219–222. In Soil survey laboratory methods manual. Soil Survey Investigations Report no. 42, Version 3.0, January 1996. USDA. U.S. Gov. Print. Office, Washington, DC.
- [4] HACH, Ammonia- Nitrogen, Salicylate Method 1. Web. Source: <a href="http://www.hach.com/fmmimghach?/CODE%3ADOC316.53.0108015621%7C1">http://www.hach.com/fmmimghach?/CODE%3ADOC316.53.0108015621%7C1</a>

# **APPENDICES**

(Raw data)

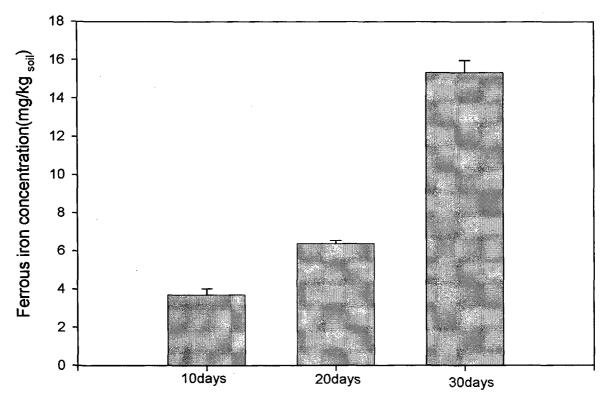
## Appendix A - Soil Analysis Data

#### A.1. Soil Quality Data (metal analysis)

Cations	Detection Limit	Soil 1	Soil 2	Soil 3	Mean	Standard deviation
Unit			mg			
Al	1.25	278.6	274.1	272.6	275.1	3.12
As	0.10	0.6	0.3	0.4	0.4	0.19
Ba	0.10	1.8	1.8	1.7	1.8	0.01
Ca	3.50	192.8	192.9	193.1	192.9	0.15
Cd	0.05	< 0.05	0.07	0.06	0.07	0.01
Cr	0.1	1.9	1.9	1.9	1.9	0.01
Cu	0.1	0.3	0.3	0.3	0.3	0.03
Fe	3.0	1032.5	1031.0	1027.0	1030.2	2.84
K	3.0	8.6	8.3	7.9	8.3	0.36
Mg	1.0	30.6	30.4	30.4	30.5	0.12
Mn	0.1	0.3	0.3	0.3	0.3	0.003
Ni	0.1	1.7	1.7	1.9	1.8	0.10
Pb	0.2	0.7	0.7	0.8	0.8	0.05

#### Appendix B - Biological Reducing Test

B.1 shows the amount of ferrous iron (mg/kg) released from soil samples under 10, 20 and 30 day biological reductive dissolution tests.



B.1. Amount of ferrous iron released during biological reducing test for 10, 20, and 30 days

B.2. Analytical results of biological reductive dissolution test for 10, 20, or 30 days.

Days	pН	ORP	DO	NH <sub>3</sub>	Fe <sup>2+</sup>	As
Days	p11	(mv)	(mg/L)	(mg/L-N)	(mg/L)	(mg/L)
Method Detection Limit	-	-	-	0.19	0.01	0.002
10	6	-26	1.5	10.08	3.1	0.03
10	6	-10	1	11.52	2.7	0.03
20	5.2	64	0.85	1.41	5.1	0:03
20	5.8	-8	0.75	0.86	4.9	0.04
20	4.9	63	1	0.12	11.7	0.04
30	4.9	93	0.8	0.25	12.4	0.04

## Appendix C - Chemical Reducing Test

C.1. Analytical results of chemical reductive dissolution test using sodium borohydride

Sample #	Test Number	pН	ORP	Fe <sup>2+</sup>	NH <sub>3</sub>	As	TOC
		P	(mv)	(mg/L)	(mg/L-N)	(mg/L)	(mg/L)
1	1	7.10	-89	0.17	0.52	0.007	19.4
2	1	6.98	-101	0.48	0.30	< 0.002	19.4
3	1	7.30	-96	0.58	<0.24	< 0.002	27.8
4	2	6.95	-188	0.17	<0.24	< 0.002	8.8
5	2	7.18	-54	0.14	<0.24	< 0.002	11.8
6	2	7.23	-90	0.43	<0.24	0.002	7.3
7	3	7.11	-123	0.08	< 0.24	< 0.002	7.8
8	3	7.36	-154	0.07	< 0.24	0.025	1.7
9	3	7.28	-80	0.07	<0.24	< 0.002	3.1
10	4	7.17	-139	< 0.01	<0.24	< 0.002	7.5
11	4	7.29	-147	0.03	<0.24	0.004	6.9
12	4	6.43	-10	< 0.01	<0.24	< 0.002	4.9

C.2. Analytical results of chemical reductive dissolution test using sodium ascorbate

Sample #	Test Number	PH	ORP	Fe <sup>2+</sup>	NH <sub>3</sub>	As
	1 000 1 (000 100 1		(mv)	(mg/L)	(mg/L-N)	(mg/L)
1	1	7.0	-65	0.45	<0.24	0.006
2	1	6.7	-76	0.63	< 0.24	0.006
3	1	6.7	-84	0.62	<0.24	0.007
4	2	6.3	-56	0.20	<0.24	0.001
5	2	6.3	-62	0.15	<0.24	0.004
6	2	6.5	-59	0.99	<0.24	0.003
7	3	6.8	-82	0.05	<0.24	0.002
8	3	6.8	-75	0.01	<0.24	0.002
9	3	6.8	-81	0.03	<0.24	0.003
10	4	7.0	-106	0.02	<0.24	0.004
11	4	7.0	-81	0.03	< 0.24	0.002
12	4	7.0	-83	0.03	< 0.24	0.006

## Appendix D - Soil Colum Experiments without an External Source of Organic Matter

#### D.1. Water quality data of Column 1

Date	Volume of sample (mL)	Pore volume	Cumulative Pore volume	pН	ORP (mv)	DO (mg/L)	TOC (mg/L)	NH <sub>3</sub> (mg/L-N)	Fe <sup>2+</sup> (mg/L)
5/19/2009	110	1.0	9.0	4.0	210	8.1	15.8	0.2	< 0.01
5/20/2009	110	1.0	10.0	4.0	260	6.5	17.4	<0.19	0.16
5/21/2009	110	1.0	11.0	4.2	310	7.0	14.5	< 0.19	0.27
5/22/2009	110	1.0	12.0	4.1	332	7.3	19.8	0.44	0.11
5/25/2009	110	1.0	13.0	4.5	345	6.8	20.2	0.36	0.18
6/4/2009	30	0.3	13.3	443	289	5.0	25.6	< 0.19	1.64
6/8/2009	70	0.6	13.9	4.0	340	4.9	40.7	1.79	0.58
6/10/2900	70	0.6	14.5	3.8	261	4.5	40.7	0.30	0.79
6/15/2009	20	0.2	14.7	5.3	199	4.0	10.2	1.14	< 0.01
6/19/2009	30	0.3	15.0	7.1	78	0.8	15.6	0.19	0.02
6/21/2009	30	0.3	15.3	6.8	33	1.5	21.6	0.20	0.04
6/23/2009	30	0.3	15.5	6.7	234	3.7	22.9	<0.19	< 0.01
6/26/2009	30	0.3	15.8	5.4	237	3.2	5.1	0.23	0.12
2/29/2009	40	0.4	16.2	5.7	209	3.5	12.2	0.20	0.61
6/30/2009	40	0.4	16.5	5.6	268	3.2	19.2	<0.19	0.79
7/6/2009	40	0.4	16.9	5.3	206	3.7	33.3	0.45	0.37
7/8/2009	40	0.4	17.3	5.1	310	3.2	9.6	0.30	0.39
7/11/2009	40	0.4	17.6	5.1	321	5.0	14.4	0.52	0.54
7/16/2009	40	0.4	18.0	4.3	352	2.0	10.2	0.20	< 0.01
7/21/2009	40	0.4	18.4	5.6	326	4.7	9.1	<0.19	0.06
7/25/2009	40	0.4	18.7	3.3	343	2.0	15.7	0.19	0.09
7/27/2009	40	0.4	19.1	5.3	379	4.5	24.5	< 0.19	0.01
7/29/2009	40	0.4	19.5	5.0	373	2.0	13.9	<0.19	0.02

### D.2. Water quality data of Column 2

Date	Volume of sample (mL)	Pore volume	Cumulative Pore volume	pН	ORP (mv)	DO (mg/L)	TOC (mg/L)	NH <sub>3</sub> (mg/L-N)	Fe <sup>2+</sup> (mg/L)
5/19/2009	110	1.0	9.0	5.1	230	7.5	11.0	<0.19	0.07
5/20/2009	110	1.0	10.1	4.6	269	8.2	13.2	<0.19	0.19
5/21/2009	110	1.0	11.1	3.8	320	6.8	25.6	<0.19	0.22
5/22/2009	110	1.0	12.1	3.7	333	6.4	13.5	0.35	0.16
5/25/2009	110	1.0	13.1	5.4	345	4.5	15.3	< 0.19	0.18
6/4/2009	30	0.3	13.4	4.7_	279	4.8	14.2	< 0.19	1.43
6/8/2009	70	0.7	14.1	4.4	355	4.2	25.5	5.82	1.12
6/11/2009	70	0.7	14.7	3.8	241	4.5	25.5	4.75	0.05
6/15/2009	20	0.2	14.9	5.2	238	2.5	11.7	0.72	< 0.01
6/19/2009	30	0.3	15.2	5.5	157	3.2	18.7	<0.19	0.03
6/21/2009	30	0.3	15.5	5.3	184	2.0	21.7	0.57	< 0.01
6/23/2009	30	0.3	15.8	4.9	184	1.8	18.1	0.33	0.02
6/26/2009	30	0.3	16.0	5.5	178	1.9	11.2	0.20	0.07
6/29/2009	40	0.4	16.4	6.0	134	2.7	16.2	0.23	0.05
6/30/2009	40	0.4	16.8	5.5	247	2.5	19.2	0.22	0.10
7/6/2009	40	0.4	17.1	5.5	281	3.5	16.4	0.74	0.15
7/8/2009	40	0.4	17.5	4.9	332	3.0	5.6	0.63	0.43
7/11/2009	40	0.4	17.9	5.4	271	3.3	10.9	0.52	0.33
7/16/2009	40	0.4	18.2	5.6	312	2.5	12.4	0.45	0.49
7/21/2009	40	0.4	18.6	4.5	161	3.7	20.5	0.77	0.30
7/25/2009	40	0.4	19.0	3.9	77	3.2	12.0	0.20	0.53
7/27/2009	40	0.4	19.3	5.7	336	3.5	13.4	<0.19	0.10
7/29/2009	40	0.4	19.7	4.6	273	2.5	9.8	<0.19	0.12

#### D.3. Water quality data of Column 3

Date	Volume of sample (mL)	Pore volume	Cumulative Pore volume	pН	ORP (mv)	DO (mg/L)	TOC (mg/L)	NH <sub>3</sub> (mg/L-N)	Fe <sup>2+</sup> (mg/L)
5/19/2009	110	1.1	9.1	5	250	7.8	10.90	<0.19	<0.01
5/20/2009	110	1.1	10.1	4.0	289	7.5	22.0	< 0.19	0.09
5/21/2009	110	1.1	11.2	3.7	270	7.5	13.1	<0.19	0.27
5/22/2009	110	1.1	12.2	4.0	234	6.5	19.4	0.32	0.16
5/25/2009	110	1.1	13.3	5.4	310	6.7	15.8	0.21	0.12
6/4/2009	30	0.3	13.6	4.9	297	4.1	20.1	0.35	1.19
6/8/2009	70	0.7	14.3	3.9	361	7.0	57.4	3.09	1.22
6/11/2009	70	0.7	14.9	4.8	289	5.0	22.2	0.60	< 0.01
6/15/2009	20	0.2	15.1	5.0	263	4.0	14.3	0.59	0.49
6/19/2009	30	0.3	15.4	6.1	156	5.5	13.5	0.28	0.01
6/21/2009	30	0.3	15.7	5.3	218	2.8	16.3	0.26	0.39
6/23/2009	30	0.3	16.0	5.0	194	2.4	12.5	0.38	0.20
6/26/2009	40	0.4	16.4	5.3	237	2.0	14.8	0.25	0.18
6/29/2009	40	0.4	16.8	5.5	192	3.5	20.1	0.10	0.06
6/30/2009	40	0.4	17.1	5.7	272	3.0	11.5	0.34	0.09
7/6/2009	40	0.4	17.5	5.2	269	3.4	15.6	0.64	0.12
7/8/2009	40	0.4	17.9	5.0	261	2.5	15.4	0.19	0.38
7/11/2009	40	0.4	18.2	4.8	303	2.7	23.7	0.60	0.38
7/16/2009	40	0.4	18.6	4.9	301	2.0	20.6	<0.19	0.08
7/21/2009	40	0.4	19.0	4.4	292	2.5	6.9	1.02	0.04
7/25/2009	40	0.4	19.3	3.7	322	1.5	26.6	0.34	0.24
7/27/2009	40	0.4	19.7	4.7	351	5.0	15.8	<0.19	0.18
7/29/2009	40	0.4	20.0	4.8	375	2.0	7.4	<0.19	0.06

D.4. Water quality data of Column 4.

Date	Volume of sample (mL)	Pore volume	Cumulative Pore volume	рН	ORP (mv)	DO (mg/L)	TOC (mg/L)	NH <sub>3</sub> (mg/L-N)	Fe <sup>2+</sup> (mg/L)
6/4/2009	30	0.3	0.3	6.2	59	3.7	20.4	<0.19	0.13
6/8/2009	70	0.6	0.8	6.9	83	4.2	59.9	3.15	1.78
6/11/2009	70	0.6	1.4	7.5	75	5.2	36.1	0.50	0.08
6/15/2009	20	0.2	1.6	7.1	40	1.7	7.9	2.81	< 0.01
6/19/2009	30	0.3	1.8	6.9	17	1.5	18.9	3.00	0.05
6/21/2009	30	0.3	2.1	7.4	22	2.0	37.1	0.25	0.06
6/23/2009	30	0.3	2.3	5.8	121	1.4	27.5	< 0.19	0.05
6/26/2009	45	0.4	2.7	6.9	61	2.1	25.0	0.25	0.20
6/29/2009	40	0.3	3.0	7.1	46	3.1	13.0	0.18	0.15
6/30/2009	40	0.3	3.4	6.6	217	3.1	16.9	0.20	0.13
7/6/2009	40	0.4	3.7	6.2	181	3.5	9.4	0.39	0.02
7/8/2009	40	0.4	4.1	6.2	163	2.0	47.5	0.30	0.03
7/11/2009	40	0.4	4.5	5.2	125	4.8	18.3	0.39	0.02
7/16/2009	40	0.4	4.8	6.0	220	3.0	13.7	1.20	0.39
7/21/2009	40	0.4	5.2	5.8	289	3.5	4.1	3.65	0.21
7/25/2009	40	0.4	5.6	3.3	367	2.0	10.8	0.89	0.21
7/27/2009	40	0.4	5.9	6.8	311	2.5	9.8	<0.19	0.01
7/29/2009	40	0.4	6.3	5.5	278	2.0	4.8	<0.19	< 0.01

### D.5. Water quality data of Column 5.

Date	Volume of sample (mL)	Pore volume	Cumulative Pore volume	рН	ORP (mv)	DO (mg/L)	TOC (mg/L)	NH <sub>3</sub> (mg/L-N)	Fe <sup>2+</sup> (mg/L)
6/4/2009	30	0.2	0.2	7.3	58	4.7	20.90	<0.19	0.02
6/8/2009	70	0.5	0.7	7.5	103	2.7	39.2	2.28	0.52
6/11/2009	70	0.5	1.3	7.3	89	3.4	31.5	<0.19	0.03
6/15/2009	20	0.1	1.4	7.9	60	1.8	32.6	1.49	< 0.01
6/19/2009	30	0.2	1.6	7.1	14	1.0	26.0	1.33	0.07
6/21/2009	30	0.2	1.9	7.4	23	1.5	21.8	0.40	0.17
6/23/2009	30	0.2	2.1	6.4	88	1.4	28.1	< 0.19	0.15
6/26/2009	40	0.3	2.4	6.7	110	2.0	39.4	< 0.19	0.13
6/29/2009	40	0.3	2.7	7.1	42	2.8	18.9	< 0.19	0.10
6/30/2009	40	0.3	3.0	6.7	211	2.0	13.7	0.21	0.10
7/6/2009	40	0.4	3.3	6.4	168	2.7	25.0	0.24	0.17
7/8/2009	40	0.4	3.7	6.2	226	2.3	18.5	0.30	0.39
7/11/2009	40	0.4	4.1	6.4	174	2.5	27.1	0.48	0.29
7/16/2009	40	0.4	4.4	6.8	176	2.5	17.3	0.21	< 0.01
7/21/2009	40	0.4	4.8	6.3	112	4.0	9.3	<0.19	0.05
7/25/2009	40	0.4	5.1	4.8	338	3.0	28.8	0.22	0.30
7/27/2009	40	0.4	5.5	6.8	184	3.8	19.8	< 0.19	0.21
7/29/2009	40	0.4	5.9	6.5	188	2.5	6.4	<0.19	0.22

## Appendix E - Yard Trash Extract (YTE) Experiments

#### E.1. Yard trash extract quality data (metal analysis)

Cations	Detection Limit	Sample 1	Sample 2	Mean	Relative percent difference
Unit		mg/l	L	%	
Al	0.025	0.97	1.17	1.07	18.7
As	0.002	0.009	0.012	0.010	24.6
Ca	0.07	35.62	72.71	54.17	68.5
Cd	0.001	0.003	0.004	0.004	16.4
Cr	0.002	0.01	0.01	0.01	66.5
Cu	0.002	0.03	0.07	0.05	84.4
Fe	0.06	0.60	0.61	0.60	1.0
K	0.06	107.17	190.93	149.05	56.2
Mg	0.02	10.35	24.48	17.41	81.1
Mn	0.002	0.12	0.25	0.18	71.0
Na	0.44	27.02	62.64	44.83	79.4
Ni	0.002	0.01	0.01	0.01	13.8
Pb	0.003	0.01	0.01	0.01	16.7

### E.2. Data of biological reducing test with yard trash extract (YTE)

Sample ID	Mixture	РН	ORP (mv)	DO (mg/L)	Fe <sup>2+</sup> (mg/L)
100% YTE 1	Soil (110g) + YTE (140 mL) + Seed (10mL)	6.7	-66	0.6	5.5
100% YTE 2	Soil (110g) + YTE (140 mL) + Seed (10mL)	6.5	-95	0.6	5.1
100% YTE 3	Soil (110g) + YTE (140 mL) + Seed (10mL)	6.8	-62	0.8	4.9
50% YTE 1	Soil (110g) + YTE (70 mL) + DIW (70 mL) + Seed (10mL)	6.8	-120	0.8	2.2
50% YTE 2	Soil (110g) + YTE (70 mL) + DIW (70 mL) + Seed (10mL)	6.7	-112	0.6	2.9
50% YTE 3	Soil (110g) + YTE (70 mL) + DIW (70 mL) + Seed (10mL)	6.9	-62	0.8	2.2
0% YTE 1	Soil (110g) + DIW (140 mL) + Seed (10mL)	7.1	169	1.5	< 0.01
0% YTE 2	Soil (110g) + DIW (140 mL) + Seed (10mL)	7.3	147	1.8	0.03
0% YTE 3	Soil (110g) + DIW (140 mL) + Seed (10mL)	8.0	179	2.3	0.34

### E.3. Water quality data of samples collected from Column 3 after adding yard trash extract (YTE)

Date	Addition	Volume of sample (mL)	Pore volume	Cumulative Pore volume	pН	ORP (mv)	DO (mg/L)	NH <sub>3</sub> (mg/L-N)	Fe <sup>2+</sup> (mg/L)
9/12/2009	DIW	104	1.0	21.0	6.9	35	2.5	0.25	0.22
9/17/2009	YTE	104	1.0	22.0	5.6	52	4.2	0.27	0.41
9/29/2009	YTE	104	1.0	23.0	5.5	146	2.8	1.30	4.58
10/5/2009	YTE	104	1.0	24.0	6.9	25	2.5	3.43	5.78
10/10/2009	YTE	104	1.0	25.0	6.3	12	2.0	0.63	3.90
10/20/2009	YTE	104	1.0	26.0	6.2	4	2.8	2.89	4.22
11/1/2009	YTE	104	1.0	27.0	6.0	16	3.0	1.19	4.54
11/13/2009	YTE	105	1.0	28.1	7.1	-38	3.3	1.55	4.6

#### E.4. Water quality data of samples collected from Column 4 after adding yard trash extract (YTE)

Date	Addition	Volume of sample (mL)	Pore volume	Cumulative Pore volume	рН	ORP (mv)	DO (mg/L)	NH <sub>3</sub> (mg/L-N)	Fe <sup>2+</sup> (mg/L)
9/12/2009	DIW	120	1.0	7.3	6.2	87.0	2.5	0.04	0.35
9/17/2009	YTE	120	1.0	8.3	6.9	20.0	2.5	0.14	0.49
9/29/2009	YTE	120	1.0	9.3	6.7	51.0	2.0	1.10	2.29
10/5/2009	YTE	120	1.0	10.3	7.4	-2.0	2.0	2.58	2.53
10/10/2009	YTE	120	1.0	11.3	6.9	15.0	2.3	0.57	0.95
10/20/2009	YTE	120	1.0	12.3	6.2	-59.0	2.3	10.69	5.02
11/1/2009	YTE	120	1.0	13.3	6.7	-23	2.3	16.63	5.44
11/13/2009	YTE	120	1.0	14.3	7.1	-43.0	3.0	2.77	6.2