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**MANAGEMENT OF SUBSURFACE  
REDUCTIVE DISSOLUTION UNDERNEATH LANDFILLS**

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Report # ??  
FINAL REPORT

## **ACKNOWLEDGEMENTS**

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## **LIST OF ABBREVIATIONS, ACRONYMS & UNITS OF MEASUREMENT**

AOP: *Advanced Oxidation Process*  
APO: *Aerated Photochemical Oxidation*  
BDL: *Below Detection Limits*  
BMP: *Best Management Practice*  
BOD<sub>5</sub>: *Biological Oxygen Demand in mg/L*  
BTEX: *Benzene, Toluene, Ethylbenzene, and Total Xylenes*  
C&D: *Construction and Demolition Waste*  
CB: *Conduction Band*  
CCA: *Copper, Chromium, and Arsenic*  
CFR: *Code of Federal Regulations*  
C<sub>0</sub>: *initial concentration in mg/L or M*  
COD: *Chemical Oxygen Demand in mg/L*  
DC: *Direct Current*  
DO: *Dissolved Oxygen in mg/L as O<sub>2</sub>*  
DSS: *Decision Support System*  
DST: *Decision Support Tool*  
ED: *Electrodialysis*  
EDCs: *Endocrine Disrupting Compounds*  
EDTA: *Ethylenediamine Tetraacetic Acid*  
EP: *Energized Process*  
FAC: *Florida Administrative Code*  
FDEP: *Florida Department of Environmental Protection*  
FGDL: *Florida Geographical Data Library*  
Flux: *in units of gpd/ft<sup>2</sup>*  
FTIR: *Fourier Transform Infrared Spectroscopy*  
GAC: *Granular Activated Carbon*  
GUI: *Graphical User Interface*  
HCSHWM: *Hinkley Center for Solid and Hazardous Waste Management*  
HRT: *Hydraulic Retention Time*  
IACUC: *Institutional Animal Care and Use Committee*  
IMA: *Iron Mediated Aeration*  
KHP: *Potassium Hydrogen Phthalate or Potassium Acid Phthalate*  
Leachate Production: *in units of gallons per day per acre*  
MAP: *Magnesium Ammonium Phosphate*  
MBR: *Membrane Bio-Reactor*  
MF: *Microfiltration*  
MGD: *Million Gallons per Day*  
MIEX: *Magnetic Ion Exchange*  
MINCF: *Minimum Confidence Factor*  
MSW: *Municipal Solid Waste*  
MWCO: *Molecular Weight Cut-Off*  
n/a: *not available*  
NF: *Nanofiltration*

nm: *wavelength in nanometers*  
nr: *not recorded*  
OCUCLUS: *FDEP Division of Waste Management Document Management System*  
PAC: *Powdered Activated Carbon*  
pBOD<sub>5</sub>: *Particulate Biological Oxygen Demand in mg/L*  
pCOD: *Particulate Chemical Oxygen Demand in mg/L*  
pH: *-log[H<sup>+</sup>] in standard units*  
PIMA: *Photochemical Iron-Mediated Aeration*  
POTWs: *Publicly Owned Treatment Works*  
Q: *flowrate in m<sup>3</sup>/s*  
RCRA: *Resource Conservation and Recovery Act*  
Redox: *Oxidation-reduction reaction*  
RO: *Reverse Osmosis*  
SBR: *Sequencing Batch Reactor*  
SC: *Specific Conductivity in S/m*  
SWANA: *Solid Waste Association of North America*  
t<sub>1/2</sub>: *Half life in minutes*  
TAG: *Technical Advisory Group*  
TCLP: *Toxicity Characteristic Leaching Procedure Test*  
TDS: *Total Dissolved Solids in mg/L*  
TKN: *Total Kjeldahl Nitrogen in mg/L as N*  
TN: *Total Nitrogen in mg/L as N*  
TSS: *Total Suspended Solids in mg/L*  
UF: *Ultrafiltration*  
UIC: *Underground Injection Control*  
US: *Ultrasound*  
USEPA: *United State Environmental Protection Agency*  
UV: *Ultraviolet*  
VB: *Valence Band*  
VOCs: *Volatile Organic Compounds*  
W: *Watts*  
ZVI: *Zero-Valent Iron*  
λ: *Wavelength*

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FINAL REPORT  
09/01/2010 – 02/29/2012

# **ANNUAL REPORT**

September 1, 2010 – February 29, 2012

PROJECT TITLE:       MANAGEMENT OF SUBSURFACE REDUCTIVE  
DISSOLUTION UNDERNEATH LANDFILLS

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KEY WORDS:       Landfills, iron, oxidation, solid waste management, dissolution, ferrous, ferric, groundwater

## **ABSTRACT**

High concentrations of iron have recently been observed in groundwater and soils around municipal solid waste landfills in Florida. The levels have been attributed to reductive dissolution from native iron in the soil perhaps caused by a shadowing effect of the landfill liner, which inhibits the reaeration of the shallow aquifer beneath the landfill. The goal of this research was: 1) to investigate the key parameters governing reductive dissolution of iron; 2) to develop a list of engineering management alternatives for controlling the release of iron in-situ; and 3) to conduct laboratory experiments on methods for iron and co-contaminant removal from groundwater at landfill impacted sites. A priori, the groundwater circulation well technology shows promise as a relatively low cost and potentially effective management technology for elevated levels of iron in the subsurface. The technology introduces air into the zone of influence to stimulate microbially mediated processes to biogeochemically convert dissolved iron to relatively immobile Fe(III) species. In the first year of the research, a bench scale model was developed to test multiple parameters such as aeration rate, soil type, removal efficiency, zone of influence, etc. The models were tested using soil from Boca Raton and from Polk County.

## **EXECUTIVE SUMMARY**

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COMPLETION DATE:       02/29/2012

### **OBJECTIVES**

Elevated concentrations of iron have been observed in groundwater monitoring wells down gradient of lined landfills in different regions of Florida and elsewhere (Jones Edmunds and Associates, Inc. 2008; Peebles and Tumlin 2008; Wang and Stone 2008). The source of the iron contamination is either: 1) directly released via leachate, or 2) naturally-occurring mobilized from soil due to changes in soil chemistry caused by the presence of the landfill. The goal of this research is: 1) to investigate the key parameters governing reductive dissolution of iron; 2) to develop a list of engineering management alternatives for controlling the release of iron in-situ focused on minimizing the potential disturbance to the system, limiting treatment costs, and producing the most effective results; and 3) to conduct laboratory experiments on methods for iron and co-contaminant removal from groundwater at landfill impacted sites.

### **RATIONALE**

Many landfill sites across Florida are detecting elevated levels of iron in the subsurface. These are found to be above the State Groundwater Cleanup Target Level of 3.0 mg/L. This iron is attributable to either leaking landfill leachate or some natural source related to the presence of the landfill itself. Wang and Stone (2008) analyzed groundwater and leachate samples for iron and several geochemical parameters including: pH, oxidation reduction potential (ORP), dissolved oxygen, turbidity, ammonia, nitrate, chloride, sulfate, sulfide, carbonate, and metals, from four landfills located in central and north Florida. The major solute compositions for groundwater were compared to those in the

leachate using Stiff Pattern plots. They found that groundwater iron positively correlates with reduction indicators (such as the detection of ammonia, lower ORP, and neutral pH) or turbidity. However, when the maximum iron levels from the leachate are calculated, the values do not account for the observed concentrations of iron in the groundwater. Thus, indicating that the source of the dissolved iron may be the result of natural mobilization from the soil due to reducing conditions induced by the presence of the landfill liner. It is hypothesized that for lined landfills, the reductive dissolution of iron may be attributed to man-made changes in the natural hydrology resulting from the use of impermeable liners and the installation of storm water management infrastructure, which impede the natural progress of recharge water to the shallow portions of the aquifer. It is speculated that reductive dissolution mobilizes the naturally-occurring iron due to changing redox conditions in the groundwater underneath the landfill or due to changes in soil pH. Iron can exist in the environment in different forms, most commonly as either the oxidized form ( $\text{Fe}^{3+}$ ) or the reduced form ( $\text{Fe}^{2+}$ ). Iron (III) is relatively insoluble becoming part of the soil matrix. In the presence of reducing conditions, some of the immobile  $\text{Fe}^{3+}$  can be converted to readily soluble  $\text{Fe}^{2+}$  (Pedersen et al. 2005; Benner et al. 2002). When the groundwater is exposed to reducing conditions with low concentrations of dissolved oxygen and nitrate, bound  $\text{Fe}^{3+}$  is slowly released into groundwater, resulting in increases in soluble  $\text{Fe}^{2+}$  levels by Le Châtelier's principle (which will tend to favor the production of more ferrous iron at steady state reducing conditions). Also, in the subsurface, a number of biological reactions occur which are stimulated by the presence of iron as a micro-nutrient, allowing iron-reducing bacteria, for example, to dominate the native microflora and release even more naturally-occurring iron. Water temperature may be a critical factor affecting the metabolic activity of the iron bacteria, which are facultative psychrophiles with growth initiation between 5-9°C and inhibition of growth at 34°C (Cullimore and McCann 1978).

The release of bound iron has been quantified under similar reducing conditions to those described here but at smaller scale (Al-Hobaib et al. 2006), and a one dimensional reactive transport model has been developed to predict the biogeochemical behavior of iron reduction and release to groundwater in reducing environments (Razzak et al. 2009). Furthermore, a packed column, sedimentation, membrane filtration method has been proposed for removal of this elevated iron in the subsurface (Sim et al. 2001), but our research team is confident that there are more practical and cost-effective approaches that exist but have not been applied to this problem.

Depending on the source of the iron, other engineering alternatives may also be applicable. Since no evidence has been found to link this observation to leachate contamination (Townsend 2008), it is therefore plausible that iron is being liberated from the soil due to reductive dissolution. If the main cause is iron bacteria, this can be controlled by dosing periodically with disinfectants like chlorine. If the release of soluble iron is related to a general lack of iron bacteria, which is limiting in-situ microbially-mediated bioprecipitation, then options such as micro-aeration, chelation with organic acids, or pH control may be effective, in theory. Some iron may be present in colloidal form. Unlike ferric iron, which will generally agglomerate, tiny particles of colloidal iron will resist coagulation and aggregation. Their large surface area and charge relative to

their small mass causes individual iron colloids to actually repel each other. Their small size, then, makes them difficult to filter, and a coagulating agent may be required to adequately remove or trap these particles. If the major culprit is soluble ferrous iron, ion exchange and oxidation followed by filtration should be effective. The latter approach may be achievable by simple aeration, the addition of an oxidizing agent, or any number of advanced oxidation methods as is being currently tested in the Laboratories for Engineered Environmental Solutions (Lab.EES) at FAU.

In the previous project, "*Management of subsurface reductive dissolution underneath landfills*," we partnered with Polk County to investigate the incidence of elevated levels of iron detected in monitoring wells located in the vicinity of the phase III landfill. It was postulated by Jones Edmunds & Associates, Inc. (2008) that the source of the iron was related to iron-rich soils used to bring the site to grade ("clean fill"). They based this hypothesis on the fact that the volatile organic compounds, semi-volatiles, and pesticides that would not be expected to be associated with the clean fill, were not detected in the groundwater sampling, but the metals that would be associated with soil material were detected. Iron and arsenic were detected at similarly high levels around Phase III before waste was even placed in the landfill, providing further evidence that these constituents are not derived from waste or leachate.

So when iron dissolution is detected, and leachate leaking from the liner can be eliminated as a source, we need to establish that reducing conditions are in fact occurring in the subsurface. Looking at the water quality samples, it was clear that oxidation reduction potential (ORP) and dissolved oxygen (DO) were lower in impacted wells (Townsend 2008), pH and manganese levels were higher, and elevated iron concentrations correlated with ammonia, lower ORP, and pH (Wang and Stone 2008). The conclusion is that reducing conditions are observed. Therefore, the iron which is either local or imported from fill is mobilizing from the iron-rich soils and ending up in the monitoring wells in very high levels.

It is clear that if the fate of released iron depends on the biogeochemistry, then we would see a strong influence of pH, redox, and microbial conditions on iron speciation. If the main cause of iron mobilization is microbiological in nature, then the natural organic material in the soils will be the primary food source that is consumed by microorganisms that will utilize all of the available oxygen in the subsurface leading to reducing conditions that foster iron mobilization. If the landfill gas (mainly methane) is entering the system and somehow displaces the oxygen and adds organic matter to the soil, then this could stimulate the microbially mediated reductive dissolution of iron. Finally, if the presence of the landfill cuts off recharge of oxygen to the subsurface, this would have the effect of artificially boosting the mobilization of iron in the subsurface. Natural aquatic systems can vary greatly in pH, redox conditions, microbiological communities, and organic content. Chemical equilibrium modeling software provides a more robust assessment and can predict equilibrium concentrations of the iron species, but chemical equilibrium is unlikely in these types of natural systems, and furthermore the influence of microbiology is difficult to model in dynamic systems.

## METHODOLOGY

A preliminary set of engineering alternatives was developed to evaluate feasibility as an effective management option for landfills. Depending on the source of the iron, many engineering alternatives may be applicable. If the iron mobilization is caused by iron bacteria for example, this can be controlled by dosing periodically with disinfectants like chlorine. If the release of soluble iron is related to a general lack of iron bacteria, which is limiting in-situ microbially-mediated bioprecipitation, then options such as micro-aeration, chelation with organic acids, nutrient addition, or pH control may be effective, in theory.

Our laboratory also conducted bench scale experiments using the groundwater circulation well technology to obtain preliminary data using Boca Raton and Polk County soils. The units were tested in an attempt to develop design considerations such as air flow rate, zone of influence, treatment times, and process removal efficiency. Groundwater samples were spiked with 100 mg/L iron, and subsamples were collected periodically and analyzed for dissolved iron to quantify process removal efficiency.

## RESULTS

Initial testing of soil samples revealed that Boca Raton were representative compared to historical data. The Polk County soil samples were also confirmed to have elevated levels of iron according to geotechnical surveys that were conducted of the entire landfill site by a private engineering firm. The results for preliminary bench scale testing were inconclusive due a catastrophic failure of the dissolved iron analytical method. Numerous attempts were made to obtain usable data from the month-long tests including sending out the samples to a certified third party laboratory and collaborating with the University of Florida and Hach Chemical Company.

## CONCLUSIONS

Soil and groundwater sample analyses were obtained from existing landfill locations in Florida experiencing elevated levels of subsurface contamination, including Polk County and Broward/Palm Beach Counties. A set of laboratory scale experiments were developed to evaluate the process efficiency of groundwater circulation well technology. Testing for several weeks of treatment was conducted. Using a control soil collected in Boca Raton, FL, the groundwater circulation well was able to demonstrate an extremely rapid conversion of iron resulting in a 1.0-log removal occurring between 2 – 24 hours. The experiment was continued beyond 72 hours, but iron removal from 72 - 264 hours of running time showed arbitrary results because of a difficulty encountered with the iron speciation. After consulting with colleagues from the University of Florida, it was determined that the ferrous iron test needs to be modified and a total iron test using ICP-MS should be run for iron speciation in our samples. So we plan to develop and implement this protocol in year two. First, we will conduct method development tests to confirm results using spiked iron samples and Boca Raton soils. Then we will run the

feasibility tests using the contaminated soils and groundwater samples to develop the appropriate treatment conditions for scale-up, including parameters such as air flow rate, radius of influence, treatment time, and process removal efficiency. The effects of soil variations will be investigated by comparison with Boca Raton soils and by collecting samples from various locations and times of the year.

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# 1. INTRODUCTION

Recently elevated concentrations of iron have been observed in groundwater monitoring wells down gradient of lined landfills in Florida (Timmons et al. 2008; Wang and Stone 2008; Townsend 2008). The source of this iron contamination has not been verified yet, but is potentially associated with the presence of the landfill by either one or both of the following mechanisms: 1) the source of the iron is direct release of iron from the municipal solid waste leachate, or 2) the source is from naturally-occurring iron mobilized from the soil due to changes in soil chemistry or local hydrology. After the source is determined, the immediate question is if iron is being mobilized, is this a sign that other, potentially more toxic metals, like arsenic, are also being transported downstream too? If this is the case, then how do we control these releases?

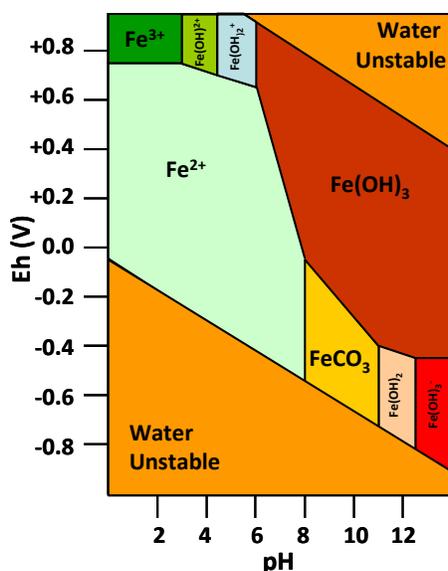


Figure 1. Eh-pH diagram showing Fe stability fields at 25°C. Modified from Upchurch et al. (1991).

In order to better understand this phenomenon, we must investigate the biogeochemistry of iron in the subsurface. Iron can exist in the environment in different forms, most commonly as either the oxidized form (Fe<sup>3+</sup>) or the reduced form (Fe<sup>2+</sup>). Ferric iron (Fe<sup>3+</sup>) is relatively insoluble and is typically bound as part of the soil matrix. In the presence of reducing conditions, some of this immobile Fe<sup>3+</sup> can be converted to readily soluble Fe<sup>2+</sup> (Pedersen et al. 2005; Benner et al. 2002). The iron content of soils is typically in the range of 0.5% to 5%, dependent upon the local geology, transport mechanisms, and overall geochemical history (Vance 1994). It is well known that iron in its various forms (Figure 1) is ubiquitous in Florida soils and is a micronutrient. Nevertheless, a groundwater cleanup target level and secondary maximum contaminant level (non health-based) has been established at 0.3 mg/L (62-777 FAC). For aquifers that are not used to supply drinking water but contain elevated levels of naturally occurring contaminants such as iron, the State of Florida has “groundwater of low yield/poor quality” criteria. In this case, the adjusted target level is 3.0 mg/L (62-777 FAC). Because iron is not considered a major health risk, the bigger concern from a public health perspective would be the co-liberation of iron-

associated arsenic or other metals (Delemos et al. 2006). The Florida Department of Environmental Protection (FDEP) sponsored a study by Gadagbui and Roberts (2002) to develop human health-based standard for iron in groundwater. An approach similar to that used for other non-carcinogens in the development of groundwater cleanup target levels (GWCTL) was used by the authors to recommend a GWCTL for iron of 4.2mg/L. According to FAC 62-701.530 semi-annual groundwater monitoring (for iron) is required at Class I landfill monitoring wells in Florida. In addition, surface water monitoring is also required as per FAC 62-701.510. According to data reported by Rhue et al. (2008), groundwater iron levels in Florida have been routinely measured in the range of 10 – 100 mg/L.

Chen and co-workers reported total iron concentrations in Florida soils (1999). The data are summarized in Table 1.

Table 1. Summary of total iron sampling in selected Florida soils (Chen et al. 1999).

County	Horizon	Order	Soil Series	Date Sampled	Total Fe (mg/kg)
Broward	Oa1	Histosols	Lauderhill	11/18/1971	14,226
Broward	Oa1	Histosols	Lauderhill	08/01/1972	4453
Broward	Ap	Entisols	Dade	05/05/1980	102
Palm Beach	Oap	Histosols	Okeelanta	01/28/1971	4452
Palm Beach	Oap	Histosols	Terra Ceia	01/28/1971	6306
Palm Beach	A	Entisols	Basiner	03/01/1973	218
Palm Beach	Ap	Alfisols	Boca	10/01/1973	450
Palm Beach	A	Alfisols	Holopaw	03/06/1974	279
Palm Beach	A	Spodosols	Oldsmar	03/06/1974	151
Polk	A1	Alfisols	Non-designated	10/20/1976	765
Polk	Ap	Spodosols	Zolfo	10/27/1977	243
Polk	Ap	Spodosols	Immokalee	12/14/1981	165
Polk	A1	Entisols	Astatula	12/06/1983	375
Polk	Ap	Entisols	Candler	12/07/1983	1647

Some samples were analyzed for iron concentrations in soils near landfills in Northwest Florida as reported by Subramaniam (2007). These data are summarized in Table 2.

Table 2. Summary of Iron Concentration in Soils Near Landfills in Northwest Florida (Subramaniam 2007)

County	Landfill	Status	Total Fe (mg/kg)
Bay	Steelfield	Active	49.6
Calhoun	Calhoun County	Closed	84.1
Escambia	Perdido	Active	39.4
Franklin	Franklin County Central	Active	65.8
Gadsden	Quincy-Byrd	Active -Class I closed	46.4
Gulf	Five Points	Active – NL	91.2
Holmes	Holmes County	Closed	34.0
Jackson	Springhill	Active	43.8

Leon	US 27 South	Active	68.8
Liberty	Liberty County	Active -Class II closed	119.9
Okaloosa	Baker	Closed	83.2
Santa Rosa	Santa Rosa Central	Active	94.0
Santa Rosa	Santa Rosa Holley	Closed	67.3
Wakulla	Lower Bridge	Active -Class I closed	90.0
Walton	Walton County Central	Active	84.3

In Florida, soils form primarily in sandy and loamy marine sediments (Myers and Ewel 1990). These types of soils are characterized by high hydraulic conductivity and low reactivity. Soil elemental compositions vary widely, reflecting differences in local, site-specific formation processes (Thornton 1982). Iron is a major constituent of the earth's crust, varying between 500 – 5000 mg/kg and averaging 3800 mg/kg in soils worldwide (Vance 1994). Iron occurs largely as ferromagnesium minerals that tend to dissolve readily and release iron, which can form precipitates such as ferric oxides and hydroxides, which are commonly found in soils near the surface. Ma, Tan, and Harris (1997) reported iron concentrations in the range of 60 to 4000 mg/kg in typical Florida soils.

## 1.1 PREVIOUS STUDIES OF IRON DISSOLUTION IN FLORIDA

In Florida, elevated iron has been found in groundwater monitoring wells at the several landfill sites in the northwest region of the state, including the Aucilla landfill (Madison County, Florida), the Klondike landfill (Escambia county, Florida), and the Baker landfill (Okaloosa County, Florida). Furthermore, some surficial wells around these landfill units have measured concentrations of iron above the secondary drinking water standard of 0.3 mg/L. The iron concentrations in these wells also exceed the 4.2 mg/L health-based criterion for iron recently developed for FDEP. These wells are located adjacent to either operating lined landfill units or discontinued unlined landfill units.

Townsend (2008) analyzed data from the Aucilla Area Solid Waste Facility in Madison County, FL and found iron levels measured from impacted groundwater monitoring wells varied from 0.03 – 47 mg/L. These values were then compared to conservative tracers (chloride, sodium, conductivity, total dissolved solids) and also volatile organic compounds such as benzene. Figure 2 shows a plot of chloride tracer versus iron levels. Although the iron levels are creeping up over time, the chloride concentrations remain relatively constant. If the source of the iron was a release of leachate, then the chloride signal would have followed the same trend, but it did not. Townsend (2008) also measured the iron concentrations in the leachate and found them to be on the order of 35 mg/L (range = 1.4 - 90 mg/L), which is much too low to account for the observed iron concentrations given the ambient dilution computed from conservative tracers. When the maximum iron levels from leachate samples taken from four other landfills in central and north Florida were calculated, the values did not account for the observed concentrations of iron in the groundwater either (Wang and Stone 2008), even when the variability caused by field sampling methods, redox-sensitive parameters, well construction materials (non-steel), and landfill construction methods were taken into consideration.

In some instances, other conservative indicators of leachate contamination, such as chloride, sulfate, ammonia, and sodium did not correlate with the elevated levels of iron. Thus the enhanced iron levels have not been causally linked to leachate contamination. Therefore, requiring facilities to conduct liner repairs or mandating advanced treatment of leachate will have no effect.

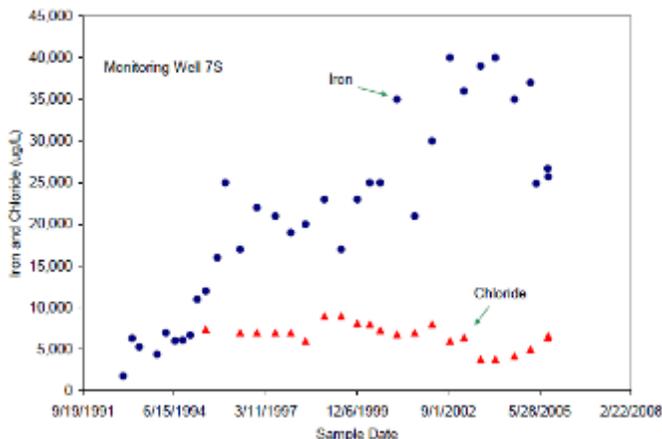


Figure 2. Relationship between historical iron levels and chloride levels in monitoring well 7S at the Aucilla Area Solid Waste Facility in Madison County, FL (Townsend 2008).

Given that no evidence has been found to correlate the observed elevated iron levels with leachate, it is plausible that iron is being liberated from the soil due to reductive dissolution. Townsend (2008) found that oxidation reduction potential (ORP), dissolved oxygen (DO), and ammonia were lower in impacted wells at the Aucilla Area Solid Waste Facility, while nitrate, pH, and manganese were higher. These observations indicate reducing conditions favorable to the growth of iron-reducing bacteria in the subsurface. Wang and Stone (2008) analyzed groundwater and leachate samples for iron and several geochemical parameters including: pH, ORP, DO, turbidity, ammonia, nitrate, chloride, sulfate, sulfide, carbonate, and metals, from four landfills located in central and north Florida. The major solute compositions for groundwater were compared to those in the leachate using Stiff Pattern plots. They found that groundwater iron showed positive correlations with reduction indicators (such as the detection of ammonia, lower ORP, and neutral pH) or turbidity (Wang and Stone 2008). Thus, indicating that the source of the dissolved iron may be the result of natural mobilization from the soil due to reducing conditions induced by the presence of the landfill liner.

Another incidence of iron dissolution occurred in Polk County at the North Central Landfill Class I Phase III, which is an approximately 2,000-acre site located approximately midway between Lakeland and Winter Haven. The facility, which began operation in 1976, includes active and closed Class I and Class III disposal facilities and a materials recovery facility for processing recyclables. Starting in 2008, soil and groundwater samples were collected and laboratory analyses confirmed the presence of elevated levels of iron (Jones Edmunds & Associates, Inc. 2008). The monitoring well readings for groundwater iron taken from the site for the period from March 2003 through August 2008 exceed the Cleanup Target Level (CTL) which is 3000 µg/L as shown in Table 3.

Table 3. Groundwater monitoring well iron levels collected from the site for the period from the North Central Landfill in Polk County, FL during the period of March 2003 through August 2008.

<b>Well No.</b>	<b>Iron levels (µg/L)</b>
CW-15	3390
CW-16	23,500
CW-17	53,800
CW-18	40,200
CW-20	85,100
SW-12A	7180
SW-101	4160
SW-102	38,400
SW-103	5860
SW-104	59,400
SW-105	21,800
SW-106	68,700
SW-107	41,000
SW-108	26,000
SW-109	7860

These monitoring wells were designed for surficial aquifer monitoring, made of 2-inch diameter PVC varying in depth from 17-39 ft. The average iron concentrations were found to be 32,400 µg/L ± 25,700 µg/L. The well locations listed in the table are shown spatially in Figure 3, Figure 4, and Figure 5. For comparison purposes, we obtained water quality data reported from the shallow aquifer in Palm Beach County in a USGS report (WRI 76-119 by Scott 1977) from 18 raw water wells for the coastal ridge and eastern sandy flatlands and found a historical average concentration of 1230 µg/L ± 1470 µg/L. Taking historical data from Monarch Hill Landfill in Pompano Beach, FL provided by Sermin Unsal (Environmental Licensing Manager from Broward County Department of Planning and Environmental Protection) from sampling conducted in 2001 to 2011, we find an average of 2540 µg/L ± 4580 µg/L.

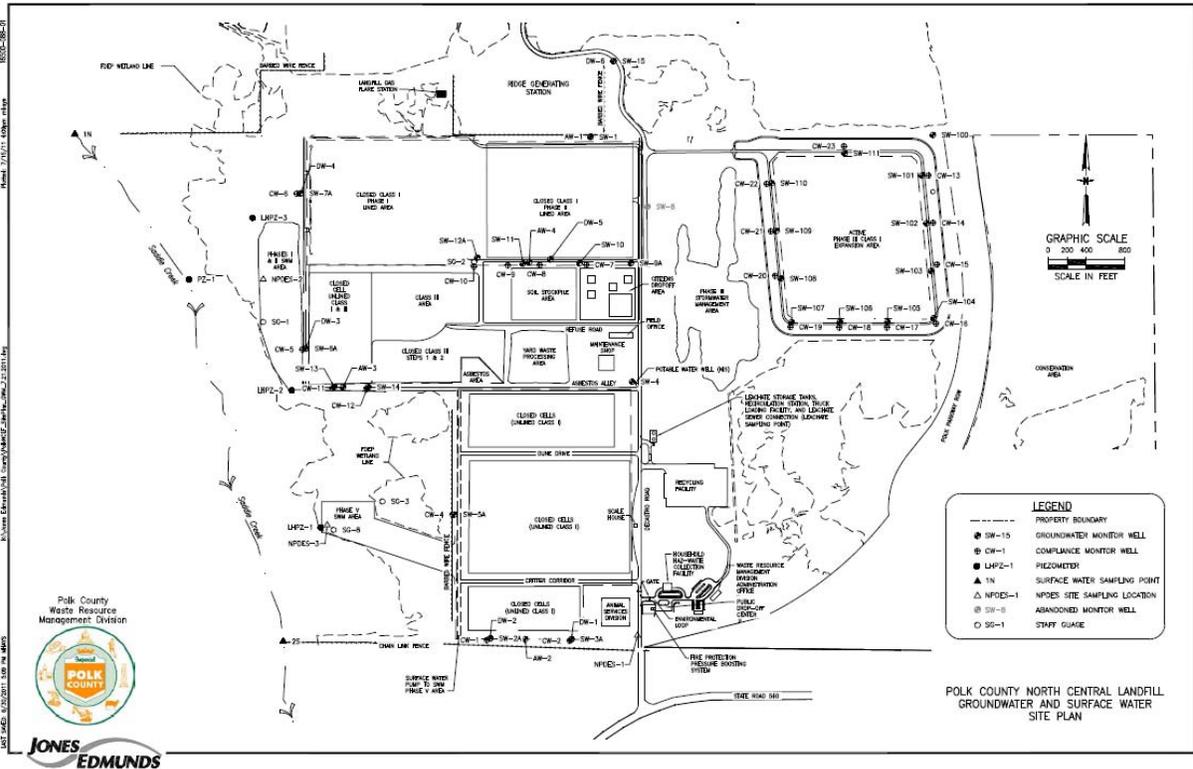


Figure 3. Polk County North Central Landfill groundwater and surface water site plan map (Jones Edmunds & Associates, Inc. 2008).

In Polk County there is an intermediate aquifer system in which there is an occurrence of carbonate beds more than 5 feet thick that are confined above and below by clays. The intermediate confining unit is 100 ft thick and the upper confining unit is about 50 ft thick in the area of the landfill site (Barr 19932). The first 30 feet below grade tends to be Plio-Pleistocene undifferentiated sediments (sandy clay and clayey sand).

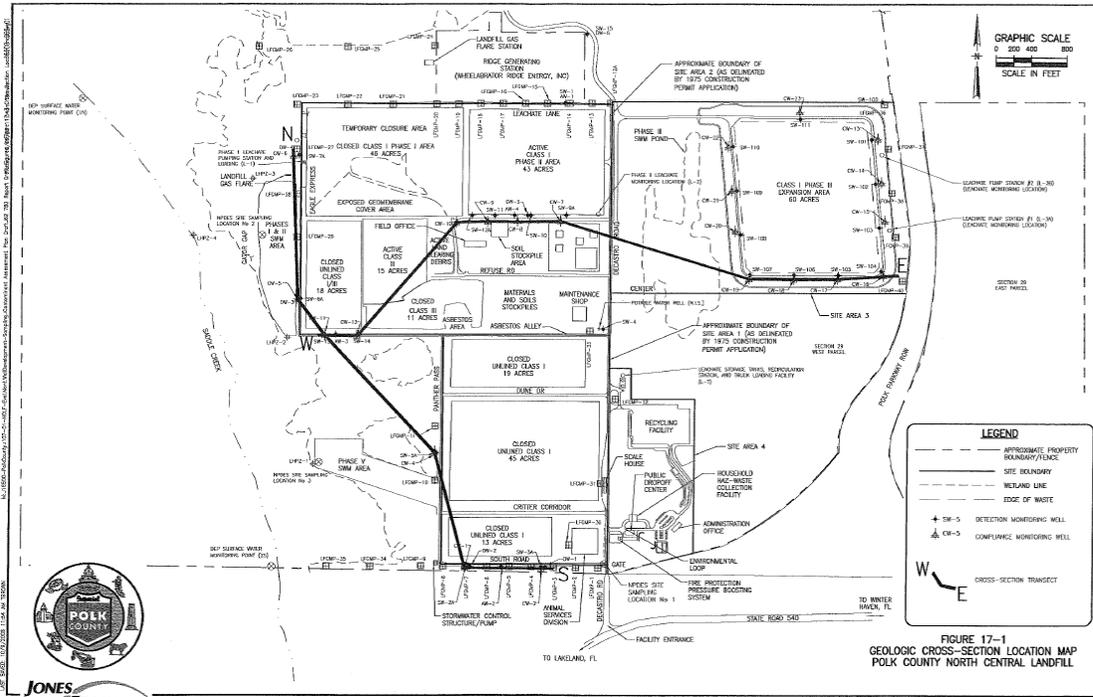


Figure 4. Polk County North Central Landfill geologic cross-section and location of detection monitoring wells and compliance monitoring wells (Jones Edmunds & Associates, Inc. 2008).

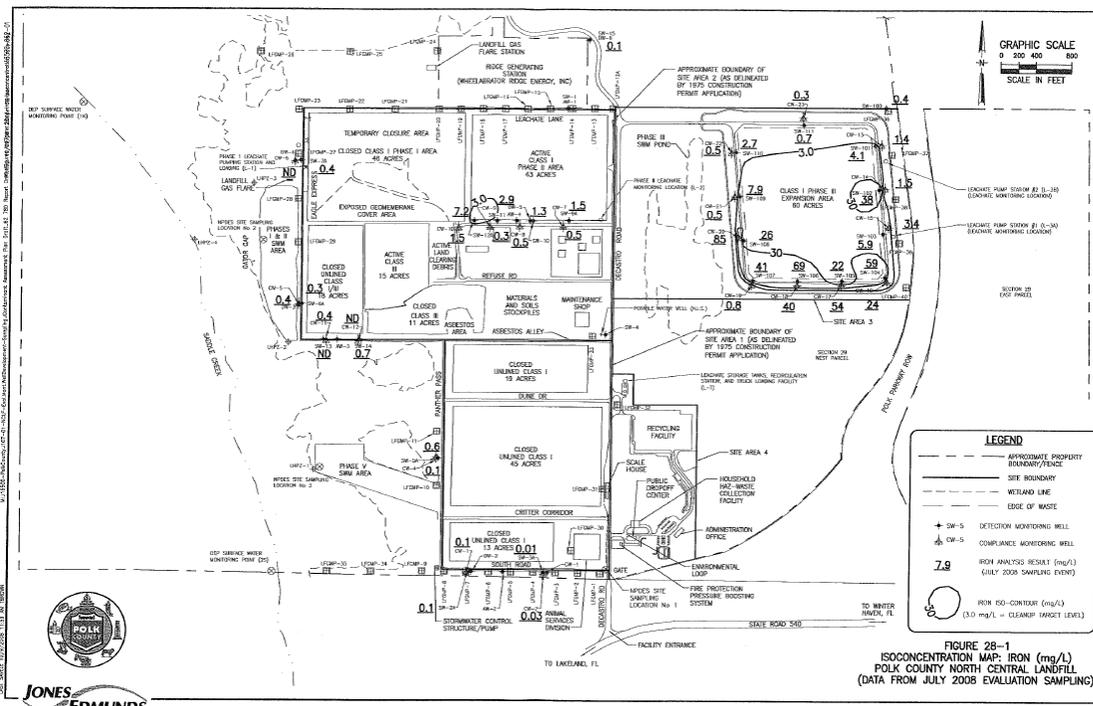


Figure 5. Polk County North Central Landfill iron concentration iso-contours from July 2008 sampling events (Jones Edmunds & Associates, Inc. 2008).

In this case, there were 22 wells which showed detections for iron, and also there were detections of ammonia, arsenic, antimony, and TDS above the groundwater cleanup target levels. For ammonia the groundwater cleanup target level of 2.8 mg/L was exceeded in SW-106 and SW-108. Compliance wells were installed downgradient and of those, CW-8 and CW-20 detected ammonia above 2.8 mg/L. Arsenic was detected at concentrations above drinking water standard of 10 µg/L in five wells and subsequently in 2 of the compliance wells installed downstream of the detections, but no levels above the groundwater cleanup target of 100 µg/L. TDS was detected above the drinking water standard of 500 mg/L in 17 wells and 16 compliance wells. Of these, only iron seemed to require a remedial strategy according to Florida State Statutes.

It was postulated by Jones Edmunds & Associates, Inc. (2008) that the source of the iron was related to iron-rich soils used to bring the site to grade (“clean fill”). They based this hypothesis on the fact that the volatile organic compounds, semi-volatiles, and pesticides that would not be expected to be associated with the clean fill, were not detected in the groundwater sampling, but the metals that would be associated with soil material were detected. Iron and Arsenic were detected at similarly high levels around Phase III before waste was even placed in the landfill, providing further evidence that these constituents are not derived from waste or leachate.

The practice of mud waving, which involves compacting the soil into the local organic mud to provide a more stable foundation by displacing the mud and water, also tends to provide an ample source of available carbon under saturated anaerobic conditions. These conditions promote the microbially-mediated reduction of iron(III) to iron(II) and the reduction of the associated arsenic(V) to arsenic(III) and the production of ammonia. Thus the iron and associated redox-sensitive or adsorbed metals (like arsenic) will mobilize in the subsurface. The compliance wells that were installed here after the iron detects seemed to show that the recharge rate inside the new wells was very poor. They attributed this to deliberate lowering of the groundwater table by a nearby control structure, but this phenomenon could also be related to plugging of the aquifer caused by biological growth stimulated by the iron rich environment as well as the presence of sparingly soluble ferric oxyhydroxides near the well. The plan of action is to modify the zone of discharge and continue with a modified monitoring plan with input from FDEP.

So when iron dissolution is detected in the subsurface, and no there is no evidence that the source is directly from leachate, the source may be natural. Therefore, we need to establish that reducing conditions are in fact occurring. The telltale signs of reducing conditions are: oxidation reduction potential (ORP) and dissolved oxygen (DO) are lower in impacted wells (Townsend 2008) and pH, ammonia, and manganese levels are higher in impacted wells (Wang and Stone 2008).

## **1.2 MECHANISMS FOR REDUCING CONDITIONS**

To understand if this is possible, we investigated mechanisms that are known to create reducing conditions in the subsurface. These mechanisms include: 1) changes in redox conditions in the groundwater or changes in soil pH caused by biogeochemical processes, or 2) changes in local hydrology.

### 1.2.1 Redox Conditions

When the groundwater is exposed to reducing conditions with low concentrations of dissolved oxygen and nitrate, bound  $\text{Fe}^{3+}$  is slowly released into groundwater, resulting in increases in soluble  $\text{Fe}^{2+}$  levels by Le Châtelier's principle (which will tend to favor the production of more mobile ferrous iron at steady state reducing conditions). Upstream of the landfill, during periods of rainfall, stormwater will percolate through the soil and displace any available air within the pore spaces of the vadose zone. This will have the effect of reducing the native iron species to the more soluble ferrous form, which will tend to mobilize downstream. Rising groundwater elevations can have a similar effect, even though the tiny amounts of dissolved oxygen in stormwater will tend to minimize the magnitude of the reducing effect (Peebles and Tumlin 2008). Conversely, the iron may then readily convert to the insoluble ferric form when more air is introduced into the pores during: 1) extended periods of drought, 2) lower groundwater elevations, or 3) areas where the groundwater table has been dropped intentionally. This would have the effect of trapping the mobilized iron in the oxidized form at concentrations that are enhanced with respect to the upstream background. When the groundwater levels rise again, this ferric iron becomes mobile again and can be liberated downstream. If this is the case, then a seasonal periodicity in groundwater concentrations would be expected.

Hydric soils are defined as soils that formed under conditions of saturation, flooding, or ponding long enough during the growing season to develop anaerobic conditions in the upper zone (USDA Soil Conservation Service 1987). The redox potential (Eh) of the soil can be monitored to determine if anaerobic conditions occur (Ponnamperuma 1972). Because soils and other biological systems are rarely at redox equilibrium, redox potential measurements cannot be used to accurately predict the activity of specific oxidized and reduced components of the system (Patrick et al. 1996). According to McBride (1994), platinum Eh electrodes respond quickly to some redox couples such as  $\text{Fe(III)} - \text{Fe(II)}$ . Although redox potential cannot be relied on to reflect the thermodynamic reaction potentials, it can be used as a general guide to redox reactions taking place in the soil. The National Technical Committee for Hydric Soils (NTCHS) developed the technical standard for identifying hydric soils. Smith (2004) used a mathematical relationship to determine the Eh required for anaerobic conditions based on the slope of the thermodynamically predicted oxygen line lowered to extend through the  $\text{Fe(OH)}_3 : \text{Fe}^{2+}$  line at pH 7 to ensure the equation represented anaerobic conditions for most soils. Many factors can affect the rate of reduction in soils, including the amount and forms of organic matter, amount and forms of iron species, microbial activity, and concentrations of manganese and nitrate present (Ponnamperuma 1972). For the most part, typical Florida soils are characterized by relatively high levels of subsurface iron oxides with low dissolved oxygen and basically strongly reducing conditions (Chen 1999) as shown in Figure 6.

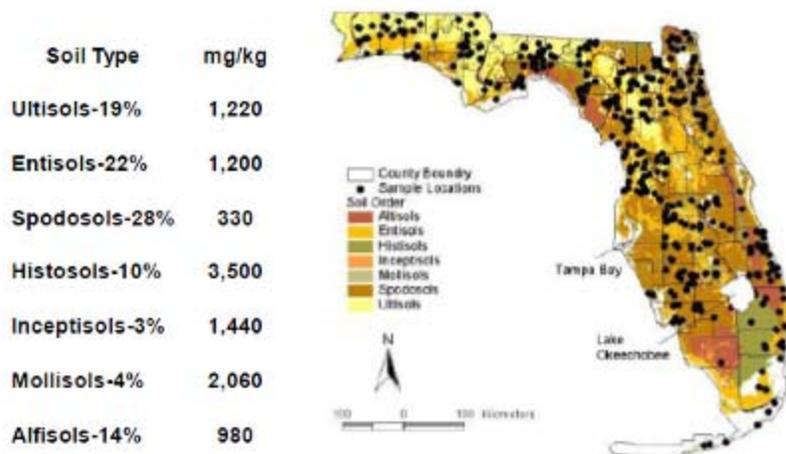


Figure 6. Spatial distribution of total iron concentrations in typical Florida soils (Chen 1999).

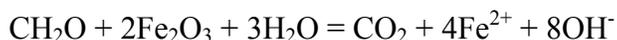
### 1.2.2 Soil pH

Changes in soil pH to acidic conditions can also liberate bound iron by helping to dissolve iron precipitates. Iron in its various forms is reactive and readily reflects changes in surrounding Eh/pH conditions. This is particularly true in soil and groundwater systems that have been environmentally impacted with hydrocarbons (Vance 1994). Ferric hydroxide, or  $\text{Fe}(\text{OH})_3$ , which is the direct result of ferrous iron oxidation and precipitation, is relatively immobile in the subsurface. With time, this ferric hydroxide becomes mineralized to: a) amorphous hydrous ferric oxide ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ), b) maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), c) lepidocrocite ( $\gamma\text{-FeOOH}$ ), d) hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), and e) goethite ( $\alpha\text{-FeOOH}$ ), in order of decreasing solubility. Amorphous hydrous ferric oxide at neutral pH and oxidizing Eh conditions has a solubility of  $0.6 \mu\text{g/L}$ , which is three orders of magnitude greater than that of goethite. Thus, mineralized forms of ferric iron can also contribute to the liberated dissolved iron under these conditions. However, these theoretical concentrations are much lower than those observed in monitoring wells, and would only account for an insignificant fraction of the mobilized iron.

Soil pH directly affects soil redox potential (Eh). The pH affects the Eh differently in soils than in solutions because the pH can be buffered by silicates, carbonates, and insoluble oxyhydroxides that are not involved in redox reactions (Bohn 1969). During reduction, a general increase in pH occurs. Because most soils contain more Fe(III)-oxides than any other oxidant under oxygen limited or oxygen-free (anaerobic) conditions, reduction of Fe(III) is mainly responsible for the increase in soil pH upon reduction (Ponnampertuma 1972).

The soil pH is important because it affects the availability of nutrients, the growth of microorganisms responsible for breaking down organic matter, and many chemical transformations in the soil. Soil pH thus affects the availability of chemicals and nutrients. Soils that have a pH below 5.5 generally have a low availability of calcium, magnesium, and phosphorus; however, the solubility of iron and boron would be high at that pH range (Argo 2003). Soil pH also affects the diversity and density of microorganisms. A pH of 6.6 to 7.3 is favorable for microbial activities that contribute to the availability of nitrogen, sulfur, and phosphorus in soils. Iron bacteria, except *T. ferrooxidans*, generally grow well over the pH range

of 5.4 to 7.2 (Hasselbarth and Ludemann 1972). If soils have a pH outside the appropriate range, certain chemical pesticides may become ineffective, changed to an undesirable form, or may not degrade as expected, which may result in toxicity or mobility of the material. Many heavy metals can also become more water soluble under acidic conditions and will tend to move downstream, and in some cases move into aquifers (underground sources of drinking water) or nearby surface water. Soil pH is one of several properties used as a general indicator of soil corrosivity. Management of soils often alters the natural pH because of acid-forming nitrogen fertilizers, or removal of bases (potassium, calcium, and magnesium). Soils that have sulfur-forming minerals can produce very acidic soil conditions when they are exposed to air. These conditions often occur near recent activity where the soil has been drained. So, when Eh/pH changes cause reducing conditions, this favors the formation of more soluble Fe(II), which becomes mobile. Furthermore, sorbed trace metals typically associated with iron oxides like arsenic will tend to be released. With respect to microbially-mediated iron reduction which follows the following reaction (Chen et al. 2007) with the molecule CH<sub>2</sub>O representing a generic organic chemical:



Consequently, the pH of the systems should tend to increase by production of hydroxide as the reaction proceeds.

### 1.2.3 Biogeochemical Processes of Iron

Amorphous hydrous ferric oxide can be described as an amphoteric ion exchange medium, meaning that when pH conditions change, it has the capability to offer hydrogen ions (H<sup>+</sup>) or hydroxyl ions (OH<sup>-</sup>) for cation or anion exchange, respectively. Sorption behavior is primarily related to pH within the typical range of 5.0 to 8.0. Given the typical soil concentrations, the iron in one cubic yard of soil is capable of adsorbing from 0.5 to 5 pounds of soluble metals as cations, which can later be released due to changes in pH. Ferric iron can also form soluble complexes with many inorganic and organic ligands, including humic acids, fulvic acids, tannic acids, phosphates, and even catechols, which are byproducts of the biodegradation of aromatic petroleum hydrocarbons. The yellow/orange coloration of groundwater at some sites contaminated with petroleum hydrocarbons is due to the release of ferric-catechol complexes (Vance 1994). Because complexed ions typically react more slowly than uncomplexed forms, the complexed iron may take months to complete the same reaction. In other words, the iron is released more slowly and can tend to build up during certain conditions depending upon the pH, temperature, dissolved oxygen, and the presence of other soluble ions. The lower the pH and temperature, the longer the time required for completion of the oxidation reaction. Increasing dissolved oxygen, decreases the time required for oxidation. As with redox conditions, if this phenomenon is pH-driven, then a seasonal periodicity in groundwater concentrations would be expected.

In the subsurface, a number of biogeochemical reactions utilize redox couples between ferrous and ferric iron. Organic material can be biodegraded with ferric iron as the terminal electron acceptor, resulting in the production of reduced soluble ferrous iron. Anaerobic conditions are required as is the presence of ferric iron in a suitable form. Under these conditions, iron-reducing

bacteria can dominate the native microflora and release even more naturally-occurring iron. Water temperature may be a critical factor affecting the metabolic activity of these microorganisms, which are facultative psychrophiles with growth initiation between 5-9°C and inhibition of growth at 34°C (Cullimore and McCann 1978). Under oxygen poor conditions, iron-fixing bacteria can still oxidize ferrous iron to ferric iron via either the extraction of carbon dioxide from ferrous bicarbonate leaving insoluble ferric hydroxide, or the utilization of organically-bound iron complexes as a carbon source, leaving precipitated ferric hydroxide. This could be confirmed using upstream and downstream groundwater temperatures and microbiological sampling.

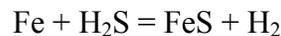
It is known that in the subsurface anaerobic zone, the dominant species are sulfate and iron reducing bacteria (Chen et al. 2007), but the composition of the microbial flora beneath landfills has not been fully explored. However, investigations involving the characterization of bacterial communities found within contaminant plumes of landfills have been conducted (Albrechtsen, Heron, and Christensen 1995; Röling et al. 2001; van Breukelen and Griffioen 2004; Lin et al. 2007). In the Netherlands, a high diversity of iron-reducing bacteria *Geobacteraceae* (Lin et al. 2005) was found in the contaminant plume, while *Protobacteria* were dominant upstream. Gram-positive bacteria made up the majority of the species beneath the landfill, and downstream the *Protobacteria* reappeared, however they were different species compared to upstream (Röling et al. 2001). In a Danish landfill, researchers noted an increase of iron and sulfate reducing bacteria closer to the landfill (Albrechtsen, Heron, and Christensen 1995; van Breukelen and Griffioen 2004), and contamination by anoxic landfill leachate tends to show distinct zones of sulfate reducing and iron reducing bacterial prevalence (Cozzarelli et al. 2000).

Biochemical iron processes compete with geochemical processes in the subsurface, potentially governing the iron release near landfills where landfill leachate interacts with the soil. This is because the additional organic material presumably from the leachate can serve as an energy source as well as a carbon source for adapted microorganisms. Iron-reducing bacteria and sulfate reducing bacteria coexist in the subsurface and compete for the same resources, so we can find separate zones of dominance rather than mixed matrices. Some of the most common species include: *Desulfovibrio*, *Thiobacillus*, *Crenothrix*, *Leptothrix*, *Gallionella*, *Shewanella*, and *Hydrogenomas* (Chen et al. 2007). A recent study of landfill soils in northwest Florida found that the bacterial populations averaged  $5.0 \times 10^5$  CFU per gram of dry soil, It was found that ferrous iron was released when landfill leachate contacted with iron rich soils in the presence of cultured iron-reducing bacteria, and minimal ferrous iron release was observed in the absence of the bacteria, which indicates that iron release is a microbially-mediated process (Chen et al. 2007).

In Florida, soils are mainly characterized as poorly drained Myakka sandy soils (USDA NRCS 2003). Myakka soils are spodospl, acid soils characterized by a subsurface accumulation of humic material and aluminum and iron oxides. Although Myakka soils are widely extensive in Florida, they are rarely found in other states (USDA NRCS 2003). Researchers from Florida State University have demonstrated that a pure culture of *Shewanella oneidensis* strain as well as enrichment cultures of iron-reducing bacteria are capable of conserving energy for growth with the structure Fe(III) bound in smectite clay as the sole electron acceptor (Kostka et al. 2002).

When conditions permit, microbially-mediated iron reduction and release may be the mechanism for elevated iron observations in groundwater. Near landfills, there is also a possibility of iron release due to the oxidation of metallic iron (Sridharan 1988; Reardon 1995), which can occur under both aerobic and anaerobic conditions. Usually, iron oxidation is a chemical oxidation process, which can be accelerated by anions found in leachate such as chloride, carbonate, and sulfate, for example. However, since leachate can cause depletion of dissolved oxygen of the contaminated groundwater owing to the high oxygen demand, chemical oxidation of metallic iron is most likely to occur under anaerobic conditions (Powell et al. 1995; Phillips et al. 2000).

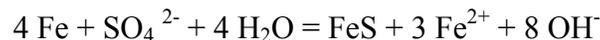
Many studies have also investigated the interactions of microorganisms with metallic iron under both aerobic and anaerobic conditions. The oxidation/corrosion process is more associated with zero-valent iron to ferric iron, which is stimulated by microorganisms (Morales et al. 1993; Hernandez et al. 1994). Due to the limited solubility of oxygen in groundwater, particularly near landfills where high concentrations of BOD and COD deplete dissolved oxygen, and the rapid reduction of molecular oxygen by Fe(0) and Fe(II), the oxidation usually occurs under anaerobic environments. Although under anaerobic conditions, iron corrosion rates driven by electrochemical reactions may be reduced, microbially-mediated anaerobic corrosion of iron may occur at rates exceeding those seen under oxygenated conditions (Lee et al. 1995). Anaerobic iron oxidation is frequently linked to the activity of sulfate-reducing bacteria (Dinh et al. 2004). Two iron oxidation mechanisms may occur simultaneously to different extents. An indirect mechanism can occur in which oxidation of iron is governed by hydrogen sulfide found in high concentrations in subsurface reducing conditions in the presence of sulfate-reducing bacteria. The reaction is as follows:



Because sulfate-reducers use organic compounds (shown here as CH<sub>2</sub>O) and H<sub>2</sub> for sulfate reduction, the net reaction is:



The direct mechanism is commonly attributed to sulfate-reducing bacteria such as *Desulfovibrio* species or other *Methanobacterium*-like microorganism, which can grow with organic substrate or H<sub>2</sub>. These microbes can obtain electrons from metallic iron in a more direct manner than via free hydrogen:



For iron oxidation by both mechanisms, Fe(OH)<sub>2</sub> or FeCO<sub>3</sub> may precipitate in addition to FeS. For the microbially mediated liberation of ferrous iron in the subsurface several things need to happen. First, an appropriate microbial consortia must exist with iron-reducing and sulfate-reducing bacteria like *Shewanella* sp. and *Desulfovibrio* sp. present. Next the appropriate food source must be available, which could be provided by leachate, and finally, the appropriate environmental conditions must exist, such as reducing conditions, pH, etc. D'Angelo and Reddy (1999) found that microbial biomass carbon was also correlated with reduction rates in saturated soils.

It turns out that microbial incubations and geochemical analyses can be used to map redox zones of elevated iron (USGS 2000), and a study conducted by the USGS (Christenson and Cozzarelli 2003) mapped redox zones with respect to iron levels at the Norman Landfill Research Site in Oklahoma. They found that when they inhibited the growth of bacteria in the samples, no release of iron occurred.

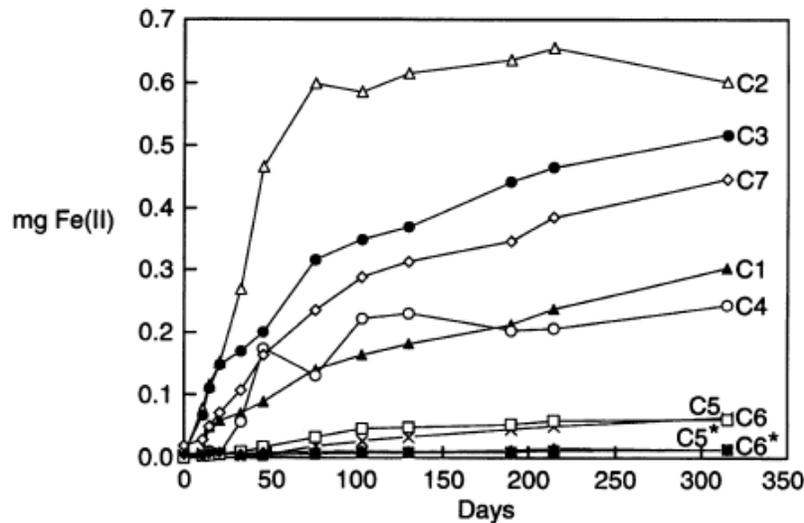


Figure 7. Dissolution of iron from samples taken from the Norman Landfill Research Site in Oklahoma. Samples C5\* and C6\* were bacteria inhibited controls (Christenson and Cozzarelli 2003).

Although one of the earliest studies on microbial Fe(III) reduction, by Starkey and Halvorson (1927) concluded that Fe(III) reduction was abiotic, no subsequent studies have demonstrated that Fe(III) can be abiotically reduced by changes in dissolved oxygen or pH (Lovley 1991). Recent studies have shown that in anaerobic, nonsulfidogenic environments in which Fe(III) reduction is occurring, Fe(III) reducers enzymatically catalyze nearly all of the Fe(III) reduction (Lovley 1993). The mechanisms by which electrons are transported from microorganisms to Fe(III) were studied by Nevin and Lovley (2002). Previously it was thought that Fe(III)-reducing microorganisms must come into direct contact with Fe(III) oxides in order to reduce them. However, research now suggests that electron-shuttling compounds and/or Fe(III) chelators may alleviate the need for direct contact between Fe(III)-reducing microorganisms and Fe(III) oxides (Nevin et al. 2002). It is believed that many different Fe(III)-reducing microorganisms participate in this process. Nevin and Lovley (2002) demonstrated that *Shewanella* may release a compound that permits electron transport to Fe(III) oxides that are not in direct contact with those microorganisms.

In soil and groundwater, a number of biological reactions occur in which organic matter is consumed as part of the life cycle of different microorganisms. These microorganisms utilize a variety of different compounds as electron acceptors. Because some electron acceptors are energetically more favorable than others, some microorganisms out compete other

microorganisms depending on which electron acceptors they use. In many respects, microbially mediated redox reactions that occur in groundwater environments are similar to those that occur beneath landfills (Christensen 2000). It is also known that iron-reducing bacteria are capable of mediating the release of other contaminants that may be adsorbed to ferric oxides (Senior 1995).

#### 1.2.4 Soil Composition

According to Lovley (1993), Fe(III) is one of the most abundant potential electron acceptors for organic matter decomposition in many aquatic sediments and subsurface environments. It has been found that the redox potential in wetland soils low in organic matter content may take longer to reach a level that is characteristic of reduced conditions (Smith 2004; Scott et al. 1998; Ponnampertuma 1972; Ugwuegbu et al. 2001). In submerged soils the decomposition of organic matter is almost entirely the work of facultative and obligate anaerobes. Since anaerobic bacteria operate at a much lower energy level than aerobic organisms, both organic matter decomposition and assimilation are slower in submerged soils than in aerobic soils (Ponnampertuma 1972). Smith (2004) found using hydric soils from North Carolina that soils with >30 g/kg of total organic carbon (TOC) took less time to develop anaerobic conditions than soils having < 30 g/kg TOC.

Other studies have also shown that the time to reduction in wetland soils is correlated to the amount and composition of organic matter that is present in the soil (Nevin and Lovley 2002; Smith 2004; Lovley and Phillips 1998; Pracht et al. 2001). It is possible that the chemical composition of organic matter in the soil could be an important factor regarding the rate of reduction in soils. One theory indicates that rates of organic matter oxidation and Fe(III) reduction are faster in the presence of organic matter than in their absence because of electron shuttling by humic substances, alleviating the need for Fe(III) reducing microorganisms to contact insoluble Fe(III) oxides (Nevin and Lovley 2002). According to Brady and Weil (2002), fulvic acid is the humic substance most susceptible to microbial attack followed by humic acid and then humin. Humic substances may further aid Fe(III) reduction by augmenting the reduction of forms of Fe(III) otherwise inaccessible to Fe(II)-reducing microorganisms. For example, reduction of the crystalline Fe(III) oxides goethite and hematite has been shown by Lovley and Phillips (1998) to be accelerated in the presence of humic substances.

Thermodynamics predicts that more soluble iron oxides such as ferrihydrite provide more energy upon reduction than crystalline iron oxides (Lindsay, 1979). Lowe et al. (2000) suggested that in a salt marsh, poorly crystalline Fe(III) oxyhydroxides are the main terminal electron acceptors for microbial Fe(III) reduction. Lovley (1991) found that hydroxylamine-extractable Fe(III) oxides were strongly correlated to microbial Fe(III) reduction in soils. The hydroxylamine-extractable Fe(III) contains organically bound Fe and some poorly crystalline Fe, indicating that these forms are the primary source of reducible Fe(III). Roden (2003) found that the surface area of Fe(III) oxides determined which forms of iron were more reducible in soils. His research showed that rates of reduction were higher on synthetic ferrihydrite than on synthetic goethite.

The carbon to nitrogen ratio (C/N) could also affect the rate of reduction in wetland soils. Microbial reduction was shown to increase with decreasing C/N ratios (Gaunt et al. 1997). Generally stabilized organic matter has a greater C/N ratio than fresh organic matter. Wetland

plants typically have a C/N ratio > 50, and as plant matter decays in the soil, carbon dioxide is evolved, which lowers the soil pH, while nitrogen is retained causing the C/N ratio to decrease (stabilizing at 15-25) (Nair et al. 2001).

Soils high in nitrate (> 275 mg/L) have positive redox potentials for several weeks after submergence, and soils low in organic matter (< 1.5%) or high in Mn (> 0.2%) maintain positive redox potentials even 6 months after submergence. Soils low in active Mn, Fe, and with > 3% TOC attained Eh values of -200 mV to -300 mV within 2 weeks of submergence (Ponnamperuma 1972).

The amount of manganese and nitrate in the soil may have a significant effect on the time it takes for Fe(III) to be reduced under anaerobic conditions. The reduction of elements in submerged soils proceeds in a sequence predicted by thermodynamics. Oxygen is the first component to be reduced, followed by nitrate, then Mn(IV)-oxide minerals, then Fe(III)-oxides, then sulfate, and finally carbon dioxide (Ponnamperuma, 1972). According to Lovley (1991), net Fe(III) reduction does not occur in the presence of Mn(IV) and nitrate. The suppression of net Fe(III) reduction in the presence of Mn(IV) has been attributed to the rapid Mn(IV) oxidation of Fe(II) and a lower concentration of electron donors, such as organic matter, in the presence of Mn(IV) (Lovley and Phillips, 1998). Native or added Mn(IV) retards the decrease in Eh of flooded soils and prevents the buildup of high concentrations of Fe(II) and other reduction products (Ponnamperuma, 1972). Furthermore, Zaharieve et al. (1988) suggest that manganese decreases soluble ferrous iron.

Interactions with phosphorus also commonly occur in soil media. The affinity between iron(III) and  $\text{H}_2\text{PO}_4^-$  ions is known to be strong, and therefore the precipitation of  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  can easily occur under favorable conditions. Furthermore, phosphate anions compete with microorganisms for iron, and thus phosphate interferes with iron uptake and transport. Other interactions between iron and micronutrients are not well understood. A high sulfur content may result in low iron availability, depending on the soil environment (Kabata-Pendias and Pendias, 1992).

Given the complex biogeochemistry of subsurface iron, it may be difficult to predict the mechanisms at work, but the release of bound iron has been quantified under similar reducing conditions to those described here albeit at smaller scale (Al-Hobaib et al. 2006), and a one dimensional reactive transport model has been developed to predict the biogeochemical behavior of iron reduction and release to groundwater in reducing environments (Razzak et al. 2009).

### **1.2.5 Temperature Effects**

Low temperatures slow down SRB activity and thus reaction rates of reduction. In column experiments, SRB functioned effectively at 6°C, the lowest temperature tested (Tsukamoto et al. 2004). Cold-adapted species are able to function at temperatures as low as 4° C, and increased populations may offset lower activity (Higgins et al. 2003). According to Yao and Conrad (2000), the optimum temperature for Fe(III) reduction is between 32 and 41°C. At temperatures above and below this range, time to achieve reduction of iron is between 15 – 50 times slower. This effect was more noticeable in soils that had low organic content (less than 15 mg/g organic

carbon), indicating a relationship between the two parameters, likely caused by biogeochemical processes.

Low temperatures generally reduce sulfate-reducing biological activity. Bacterially-mediated reaction rates generally double with each 10° C increase, and this was confirmed in a permeable reactive barrier study (Doshi 2006). Installing biological components below grade, covering reactors with insulating material, or controlling cold winter inflows can minimize temperature effects. Sub-freezing ambient temperatures will not preclude effective treatment in most applicable bioremediation systems (Doshi 2006).

### **1.2.6 Co-liberation of Metals with Iron**

Although iron itself is not considered toxic, it is environmentally significant because of its interaction with other toxic metals. Iron oxides adsorb and form co-precipitates with many elements (i.e. zinc, lead, manganese, nickel, copper, cobalt, vanadium, molybdenum, chromium, and arsenic), and in fact is a major controlling factor in the distribution of metals under non-reducing conditions (Bodek et al. 1988). In soils and sediments where conditions are not strongly reducing, adsorption by solid iron oxides is one of the most important controls on the distribution of trace elements. In an aerobic sediment or water system, the metal bonding may be almost irreversible. If the oxides are dissolved by reduction, the adsorbed metals may be released and appear in solution, or they may be precipitated as some other phase, such as a sulfide (Bodek et al. 1988). However, if ferrous iron is present in large quantities, it can bind the sulfide to the extent that insufficient amounts are available to precipitate other heavy metals (Bodek et al. 1988). This would have the effect of releasing potentially toxic metals downstream. The forms of nitrogen present may also affect the availability of soil iron.

Francis and Dodge (1990) showed that five heavy metals (cadmium, chromium, nickel, lead and zinc) were solubilized from the iron (III) oxide-hydroxide, goethite ( $\alpha$ -FeOOH), by anaerobic nitrogen-fixing bacteria. The authors were able to show that the dissolution of the metals due to microbial reduction varied with the type of metal, with the cadmium and zinc being the most labile when co-precipitated with the iron oxide tested. The mechanisms of this action by the bacteria appear to be a biochemical reduction of the iron, resulting in a release of the metals.

Both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  readily form complexes with cyanide (i.e., ferrocyanide and ferricyanide), which can decompose in the presence of light to yield free cyanide (Broderius and Smith Jr. 1980). The decomposition of ferrocyanide also results in the elevation of the pH (Bodek et al. 1988). The iron cyanide complexes are of special concern at industrial sites (Theis et al. 1994). However, due to light attenuation processes in soils, it is not likely that this would be significant for soils contaminated with these complexes unless the contamination is very near the surface.

In soils, various trace elements are concentrated by iron oxides, including zinc, lead, manganese, nickel, copper, cobalt, vanadium, molybdenum, chromium, and arsenic. The adsorption is dependent on pH and is greatest at pH 4-5. Iron oxides also react with carbonates in soil systems (Kabata-Pendias and Pendias, 1984).

By far, the most troublesome of the trace metals associated with iron is arsenic. Arsenic in soil and groundwater is usually either in the form of the oxyanions: 1) arsenite with +3 charge or 2) arsenate with a +5 charge. Arsenate readily sorbs to soil minerals, particularly iron oxides and hydroxides. Arsenate sorption to iron oxides peaks around pH 5 - 7. Arsenite tends to sorb less strongly than arsenate. Arsenic can also form insoluble sulfide minerals. In most oxidizing or mildly reducing soils, arsenate is bound to ferric oxide-hydroxide minerals such as goethite, ferrihydrite, and hematite. A shift to strongly reducing conditions converts ferric iron to soluble ferrous iron, in effect releasing the arsenic and causing dissolved levels to increase. The same mobilization sequence is increasingly seen down-gradient of landfills in the US where reducing landfill leachate prompts the release of naturally occurring arsenic from soils. Petroleum spills in soils might have the same effect (Khandaker et al. 2009). Originally arsenic contamination was thought to come primarily from dissolution of arsenic-bearing sulfide minerals, but more recent work emphasizes the importance of reductive dissolution of the arsenic-containing Fe(III) hydroxide coatings. Degradation of aquifer organic material leads to strongly reducing conditions in the aquifer, which exacerbates the release of arsenic because of the breakdown of ferrihydrite and release of trace amounts of arsenic that are bound by the ferrihydrite (Khandaker et al. 2009). Arsenite typically forms aqueous  $\text{As}(\text{OH})_3$ ,  $\text{As}(\text{OH})_4^-$ , or  $\text{AsO}_2\text{OH}^{2-}$  depending on pH (Figure 8). Arsenite exists under anaerobic conditions, for example in water-logged soils. Under more oxidizing conditions arsenic converts to arsenate. Dissolved arsenate forms  $\text{AsO}_4^{3-}$ ,  $\text{HAsO}_4^{2-}$ , or  $\text{H}_2\text{AsO}_4^-$ . At  $6.9 < \text{pH} < 11.5$ ,  $\text{HAsO}_4^{2-}$  is the primary arsenate species. At  $2.2 < \text{pH} < 6.9$ ,  $\text{H}_2\text{AsO}_4^-$  is the primary arsenate species.

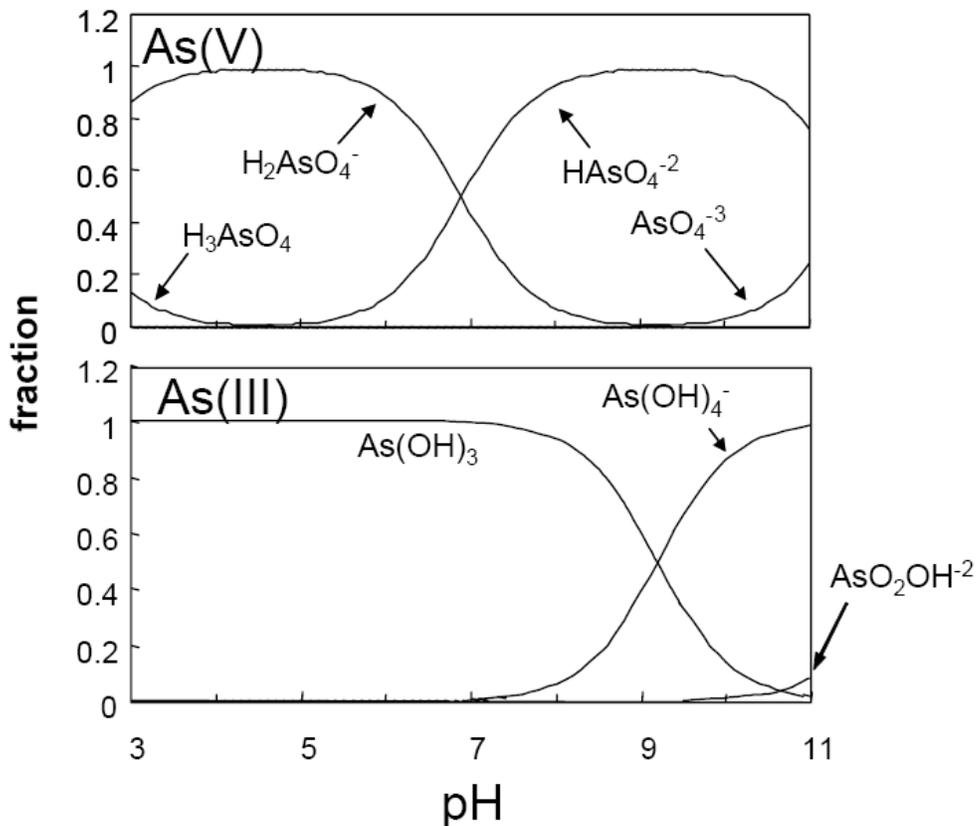


Figure 8. pH-dependent speciation of As(V) and As(III) at 25°C (Khandaker et al. 2009).

Figure 9 compares arsenate and arsenite speciation against redox and pH-dependent soil iron mineralogy. The stability of iron minerals is particularly important because of their tendency to sorb arsenic. At pH 7 surface waters and near-surface waters range from 0.7 down to 0.3 V. Bogs, organic rich waters, water-logged soils and deep groundwaters range from 0.3 down to -0.2 V.

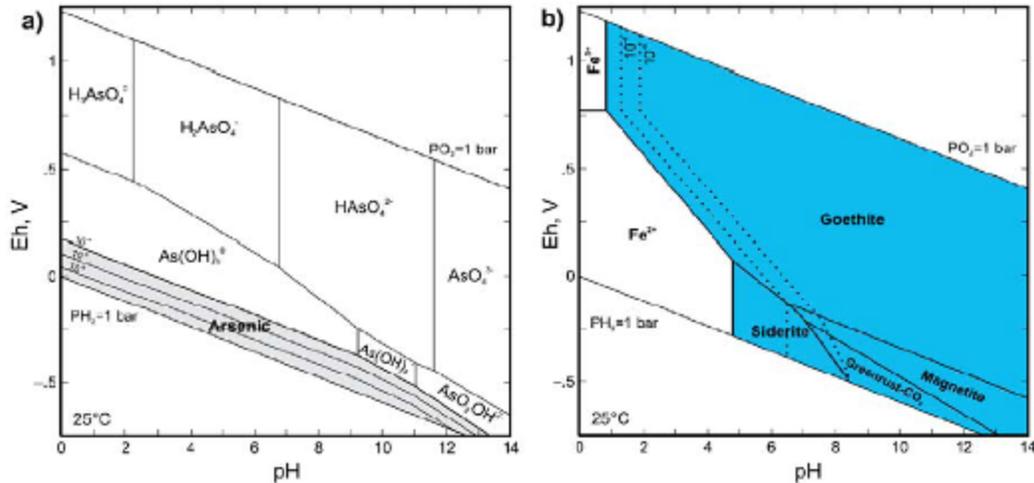


Figure 9. Eh-pH diagrams for arsenic and iron at 25°C for iron-reducing systems (from U.S. Environmental Protection Agency 2007). These paired diagrams show the relative distribution of potentially adsorbing arsenic species (left) relative to representative types of Fe-bearing sorbents (right) that are predicted to occur as a function of Eh and pH. (a) System As-H<sub>2</sub>O, with  $\Sigma As$  contoured from  $10^{-8}$  to  $10^{-4}$ ; region for elemental arsenic is shaded gray. (b) System Fe-C-H<sub>2</sub>O (no sulfur) with  $\Sigma Fe$  contoured from  $10^{-2}$  to  $10^{-6}$  and  $\Sigma C=10^{-3}$ ; Hematite and Wüstite are suppressed.

Dissolution of otherwise immobile sorbed arsenic can result from: 1) a rise in pH in high iron soil, 2) a drop in pH in alkaline soil, or 3) a change in redox potential. Arsenate, initially sorbed to iron (hydr)oxides under aerobic conditions, might be released and transported in groundwater if a shift to anaerobic conditions were to cause the dissolution of the host iron oxide. However, over time and under anaerobic conditions, the arsenate might convert to less soluble arsenite. Under strongly reducing conditions, microorganisms may tend to methylate arsenic to a mobile form. Arsenic in water and soil may be reduced and methylated by fungi, yeasts, algae, and bacteria (Craig 1989; Aposhian 1997). Arsenic is a known carcinogen and mutagen and is known to cause fatigue and loss of energy as well as dermatitis (Metcalf and Eddy 2003). Inorganic arsenic is a recognized human poison, and large oral doses (above 60,000 ppb in water which is 10,000 times higher than 80% of U.S. drinking water arsenic levels) can result in death. Lower levels of inorganic arsenic (ranging from about 300 to 30,000 ppb in water; 100–10,000 times higher than most U.S. drinking water levels), cause irritation and discomfort (ATSDR 2007)

Iron oxides are known to adsorb heavy metals like arsenic and mercury. Amorphous hydrous ferric oxides can release iron but have a maximum solubility of 6  $\mu g/L$ , which is much too low to have any effect that could be measured at a monitoring well. But these oxides can act as an ion exchange medium and sorb up to 5 lb of metal cations per  $yd^3$  (Rhue 2008), and they can form soluble complexes with organic ligands naturally present like humics, fulvics, tannic acids, organophosphates, etc. These would slowly release iron over time, depending on seasonal

temperatures, pH, and dissolved oxygen levels. Delemos et al. (2006) noted a correlation between elevated arsenic levels and organic contamination in groundwater systems. This suggests that arsenic release from bound iron oxides caused by natural degradation of organic contaminants may be a widespread phenomenon.

### 1.2.7 Changes in Local Hydrologic Conditions

The final possibility is that for lined landfills, the reductive dissolution of iron may be attributed to man-made changes in the natural hydrology resulting from the use of impermeable liners and the installation of stormwater management infrastructure, both of which impede the natural progress of recharge water to the shallow portions of the aquifer, thus inhibiting the natural equilibrium in pH, temperature, DO, and other soil redox conditions.

Changes in local hydrology can be brought about by extended periods of drought, lower than normal groundwater elevations, areas where groundwater has been deliberately lowered, and changes to the geotechnical characteristics from imported fill. Any of these changes could bring about the localized redox conditions necessary to trap mobilized iron with respect to upstream subsurface conditions, and then release it when conditions change again. An example of natural iron dissolution can be seen in Figure 10 from the Yin-Yang Sea in Taiwan.



Figure 10. Photograph of natural iron dissolution from the nearby iron-rich uplands into the Yin-Yang Sea, Taiwan. (Photo by Min-Ming Chen)  
([http://culture.teldap.tw/culture/index.php?option=com\\_content&view=article&id=184](http://culture.teldap.tw/culture/index.php?option=com_content&view=article&id=184))

Iron is a naturally occurring metal in the surface soils of Florida. In some areas of Florida, it is readily obvious that the soil contains important concentrations of iron because of the noticeable orange-red color. But color alone is not the only factor. Once the soils or groundwater are exposed to air, reduced iron in the form of Fe(II) may oxidize and convert to Fe(III) and precipitate. Expanding on this concept, factors such as rainfall and groundwater elevation can also have a profound effect on the fate of iron in the subsurface. During periods of rainfall, stormwater will percolate through the soils at varying degrees and displace the available air in

the pore space of the soils, which will have an electrochemically reducing effect, despite the dissolved oxygen in the rain water that minimizes the reducing effect. Conversely, during extended periods of drought and low groundwater elevation, the soils may convert to Fe(III) when air is reintroduced into the soil-pore space.

There is an anthropogenic condition that appears to mimic drought. The condition may be created by a relatively large cap on the surface from the construction of lined landfill, parking lot, building, airport, etc. Assuming there is no significant reduction in groundwater levels, the groundwater flowing beneath the structure no longer has the opportunity for unrestricted air and stormwater exchange. This has the effect of creating an artificial localized reducing environment in the saturated zone where iron converts into the more soluble Fe(II) and mobilizes out of the formation, liberating naturally-occurring iron from the soil into the groundwater. This soluble form of iron would be expected to remain mobile until the groundwater receives an oxygen infusion via infiltrating precipitation, or when the groundwater discharges into open surface water body. The oxygen infusion causes the ferrous iron to precipitate or convert electrochemically to ferric iron. If the groundwater table near the landfill rises and falls naturally. Then the local iron in the subsurface would follow a periodic trend in which during the seasonal high water table, the conditions would favor reduction and mobilization of iron, and during the seasonal low water table, the conditions would tend to trap the iron locally in the ferric form.

### **1.2.8 Summary of Reducing Condition Effects**

It is clear from our literature review that if the fate of released iron depends on the biogeochemistry, then we would see a strong influence of pH, redox, and microbial conditions on iron speciation. If the main cause of iron mobilization is microbiological in nature, then the release of organic matter in leachate or natural organic material in the soils could be a food source that is consumed by microorganisms to utilize all of the available dissolved oxygen in the subsurface, leading to reducing conditions that accelerate iron mobilization. If landfill gases like methane enter the system and somehow displace the oxygen and add to the organic matter in the soil, then this could also stimulate the microbially-mediated reductive dissolution of iron. Finally, if the presence of the landfill cuts off recharge of oxygen to the subsurface, this would have the effect of artificially boosting the mobilization of iron in the subsurface. Natural aquatic systems can vary greatly in pH, redox conditions, microbiological communities, and organic content, so chemical equilibrium modeling software provides a more robust assessment and can predict equilibrium concentrations of the iron species. However, chemical equilibrium is unlikely in these types of natural systems, and furthermore the influence of microbiology is difficult to model in dynamic systems.

## **1.3 IRON IN LEACHATE**

Landfill leachate is defined as any liquid that has passed through or emerged from solid waste and contains soluble, suspended or miscible materials removed from such wastes (40 CFR Part 257). Leachate is the liquid that percolates through the landfill and is captured by the leachate collection system in the case of modern sanitary landfills or directly transmitted to the ground beneath the bottom of a landfill in the case of older landfills and dumps. This material consists of: 1) primary leachate, which is the liquid content of the waste placed in the landfill that

percolates through the waste by the force of gravity, 2) secondary leachate, which is formed when water entering the landfill (principally from precipitation) percolates through the portions of the landfill that are not capped and becomes contaminated via contact with the contents of the landfill, and 3) metabolic water, which is created by the microbial degradation of waste materials over the active life of the landfill. Basically landfill leachate is a high strength wastewater characterized by elevated levels of dissolved and suspended materials (organic or inorganic compounds, such as heavy metals, ammonia, dissolved and suspended solids, COD and BOD, etc.). The composition of municipal landfill leachate exhibits noticeable temporal and site-specific variation in chemical and microbiological characteristics, attributable to a combination of factors including landfill age, type of waste, rainfall, temperature, pH, depth of fill, and compaction (USEPA 1995; Viraraghavan and Singh 1997).

Several reviews have been conducted with the goal of collecting information regarding leachate composition according to the location (i.e. the climate and especially the precipitation rate), the age of the landfill, or the type of wastes. Different data sets are available from different parts of the world (Akesson and Nilsson 1997, Al-Yaqout et al. 2005, Amokrane et al. 1997, Bekbölet et al. 1996, Bernard et al. 1997, Bila et al. 2005, Calli et al. 2005, Geenens et al. 2000, Gonze et al. 2003, Hickman 2003, Imai et al. 1998, Ince 1998, Kim et al. 1997, Kjeldsen et al. 2002, Lin et al. 2000, Mohammad et al. 2004, Moraes and Bertazzoli 2005, de Morais and Zamora 2005, O’Leary and Walsh 1995, Oweis and Kehra 1998, Tammemagi 1999, Tatsi et al. 2003, Tchobanoglous and Kreith 2002, Reinhart and Grosh 1998, Reinhart and Townsend 1998, Silva et al. 2003, Silva et al. 2004, Statom et al. 2004, Steensen 1997, Ward et al. 2002, Westlake and Phil 1995, Wichitsathian et al. 2004, Wu et al. 2004, Youcai et al. 2002) and are summarized in Table 4.

Table 4. Typical leachate water quality data from young and mature landfills (Tchobanoglous, Theisen, and Vigil 1993)

Constituent	Units	Young	Mature
Iron (Fe)	mg/L	50 – 1200	20 – 200
Ammonia-nitrogen	mg/L as NH <sub>3</sub> -N	10 – 800	20 – 40
BOD <sub>5</sub>	mg/L as O <sub>2</sub>	2000 – 30,000	100 – 200
COD	mg/L as O <sub>2</sub>	3000 – 60,000	100 – 500
pH	pH units	4.5 – 7.5	6.6 – 7.5
Alkalinity	mg/L as CaCO <sub>3</sub>	1000 – 10,000	200 – 1000
TSS	mg/L	200 – 2000	100 – 400

Other important constituents include: i) dissolved organic matter from methane (CH<sub>4</sub>) to volatile fatty acids (VFA) to more refractory humics and fulvics; ii) inorganic constituents, such as calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), iron (Fe<sup>2+</sup>), manganese (Mn<sup>2+</sup>), chloride (Cl<sup>-</sup>), sulfates (SO<sub>4</sub><sup>2-</sup>) and bicarbonates (HCO<sub>3</sub><sup>-</sup>) with heavy metals (arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel and zinc), in the microgram per liter range; iii) xenobiotic organic compounds from domestic and industrial sources, comprised of a broad variety of aromatic hydrocarbons, phenols, endocrine disrupting compounds (EDCs), pharmaceuticals, personal care products, pesticides, and chlorinated

aliphatics among others.

### 1.3.1 Constituents of concern, health risks, and environmental impacts

The available leachate quality data sets all lead to the same conclusion: the composition of leachate is highly variable and site specific. Differences can be as high as several orders of magnitude. According to 40CFR Part 258 – Criteria for Municipal Solid Waste Landfills, typical constituents of concern for monitoring programs include: pH, conductivity, dissolved oxygen, dissolved solids, biochemical oxygen demand, chemical oxygen demand, organic carbon, nutrients (ammonia, total kjeldahl nitrogen, total phosphorus), common ions, heavy metals, and organic priority pollutants. In this study, emphasis is placed on the following environmentally significant parameters of leachate quality: ammonia, BOD<sub>5</sub>, COD, TDS, and heavy metals concentration, as described in more detail below:

1. Ammonia (NH<sub>3</sub>) is a gas at standard temperature and pressure. It is mainly used to produce fertilizer and is generated during the anaerobic digestion of organic material. As it has a high solubility in water, ammonia gas readily transfers to leachate and forms soluble ionized ammonium (NH<sub>4</sub><sup>+</sup>). According to the USEPA (1986), levels of ammonia in the environment as low as 0.0017 mg/L are acutely toxic to freshwater fish. In leachate, it is thought that high levels of ammonia can originate from nitrogen-containing wastes mainly via the decomposition of protein. The majority of the total Kjeldahl nitrogen (TKN) found in leachate is typically in the form of ammonia, which can range from 0.2 to 13,000 mg N/L (Renou et al. 2008). Average ammonia-nitrogen in leachate may be present in concentrations on the order of 2000 mg/L (Englehardt et al. 2006). Levels this high are lethal to certain organisms. Furthermore, ammonia concentrations may persist in the leachate with time. This is why ammonia has been regarded as one of the most problematic constituents in leachate (Kjeldsen et al. 2002).
2. Biochemical Oxygen Demand (BOD<sub>5</sub>) is a test used to measure the concentration of biodegradable organic matter present in a sample of water. It is the amount of oxygen that would be consumed if all the biodegradable organics were oxidized by microorganisms.
3. Chemical Oxygen Demand (COD) is a test used to indirectly measure the amount of organic compounds (both recalcitrant and biodegradable). It is the amount of oxygen that would be consumed if all the organics were oxidized by a strong chemical oxidant such as dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>). Specific organics such as phthalate esters, volatile aromatics, aromatic sulphonates, chlorinated volatile hydrocarbons, phenols, cresols, and numerous other organic pollutants have been identified in various concentrations in landfill leachate (Jimenez et al. 2002).
4. Total Dissolved Solids (TDS) are the total amount of charged ions, including minerals, salts, or metals dissolved in water. TDS is directly related to the purity of water and its electrical conductivity. Excess dissolved solids are objectionable in drinking water because of possible physiological effects, unpalatable mineral tastes, and higher costs because of corrosion or the necessity for additional treatment.

5. Heavy metals include some of the trace metals such as cobalt, copper, manganese, vanadium, or zinc, which are required as micronutrients to sustain microbial populations, but excessive levels can be detrimental. Other heavy metals such as mercury, lead, or cadmium have no known vital or beneficial effect on microorganisms, and their accumulation over time are biotoxic and can cause serious illness in human populations. Heavy metals can be a significant concern in leachate, although Kjeldsen et al. (2002) reported that metals in leachate were found at concentrations at or below drinking water standards due to adsorption, precipitation and complexation processes occurring in the landfill. For example, chemically treated wood makes up about 6% of the wood waste stream in Florida, and this fraction is projected to increase to 25-30% by 2020 due to disposal of aging structures (Englehardt et al. 2006). Ash from the combustion of a wood solid waste containing as little as 6% CCA treated wood will fail the toxicity characteristic leaching procedure test (TCLP) according to Hinkley (2003), indicating that ash monofill leachate contains copper, chromium, and arsenic (CCA), and this material will also generate arsenic-contaminated leachate. Another source of toxic metals is electronic waste, potentially contributing lead, nickel, cadmium, and others to the leachate.

Taken together, these key constituents represent the potential for multiple chemical toxicity with synergistic, carcinogenic, and acutely toxic and genotoxic consequences (Park and Batchelor 2002). More than 100 hazardous chemicals have been isolated and identified in landfill leachate including aromatics, halogenated organics, phenols, pesticides, heavy metals, endocrine-disrupting compounds, pharmaceuticals, personal care products, and ammonium (Foo and Hameed 2009). Many of those on the list are capable of bioaccumulation, persistence, and reactivity in the environment. Toxicity studies confirmed the presence of 133 different chemicals, of which 24% were carcinogenic, 16% were mutagenic, and 8% were teratogenic (cited in Foo and Hameed 2009). However, toxicity tests conducted with *Daphnia* (Atwater 1983), freshwater fish (Wong 1989), luminescent bacteria (Devare and Bahadir 1994) and other organisms found that ammonia-nitrogen is the dominant constituent with regards to toxicity.

Table 5 summarizes the variability of constituents found in leachate. Specific conditions are not indicated in the table, as the summary serves point out the wide variety of leachate water quality that can be found.

Table 5. Extreme values for the composition of leachate developed through review of technical literature

Parameters	Units	Concentration		
		Range	Average	Median
Iron	mg/L as Fe	20-2100	700	40
Ammonia	mg/L as NH <sub>3</sub> -N	BDL* - 8750	830	750
BOD <sub>5</sub>	mg/L as O <sub>2</sub>	BDL* - 80,800	4000	190
COD	mg/L as O <sub>2</sub>	0.4 – 152,000	10,300	4200
Conductivity	µS/cm	5.2 – 95,000	13,100	8,600
Lead (Pb)	mg/L	BDL* - 5.0	0.1	0.1
pH	pH units	2.0 – 11.3	7.5	7.5
TDS	mg/L	0.1 – 88,000	11,000	7600
TSS	mg/L	10 – 45,000	840	950

BDL\* = below detection limit.

Source: Adapted from Akesson and Nilsson (1997), Al-Yaqout et al. (2005), Amokrane et al. (1997), Bekbölet et al. (1996), Bernard et al. (1997), Bila et al. (2005), Calli et al. (2005), Geenens et al. (2000), Gonze et al. (2003), Hickman (2003), Imai et al. (1998), Ince (1998), Kim et al. (1997), Kjeldsen et al. (2002), Lin et al. (2000), Mohammad et al. (2004), Moraes et Bertazzoli (2005), Morais and Zamora (2005), O’Leary and Walsh (1995), Oweis and Kehra (1998), Tammemagi (1999), Tatsi et al. (2003), Tchobanoglous and Kreith (2002), Reinhart and Grosh (1998), Reinhart and Townsend (1998), Silva et al. (2003), Silva et al. (2004), Solid Waste Authority of Palm Beach County (2006), Statom et al. (2004), Steensen (1997), Ward et al. (2002), Westlake and Phil (1995), Wichitsathian et al. (2004), Wu et al. (2004), Youcai et al. (2002).

For comparison purposes, Table 6 shows the concentrations of the same constituents in a typical medium-strength untreated domestic wastewater and average concentrations of leachate.

Table 6. Comparison of the composition of untreated domestic wastewater and leachate

Parameters	Units	Medium Strength Wastewater**	Typical Leachate (from Table 5)	Florida Leachate	
				Average	Range
Iron	mg/L as Fe	4-20***	700	1770	0.3 - 9720
Ammonia	mg/L as NH <sub>3</sub> -N	25	830	500	BDL* – 1350
BOD <sub>5</sub>	mg/L as O <sub>2</sub>	190	4000	150	BDL* – 445
COD	mg/L as O <sub>2</sub>	430	10,300	3000	55 – 14,000
Conductivity	µS/cm	Not reported	13,100	11,600	1000 – 95,000
Lead (Pb)	mg/L	<0.0056	0.1	0.03	BDL* – 0.1
pH	pH units	7.0	7.5	7.5	2.0 – 11.3
TDS	mg/L	500	11,000	9300	900 – 88,000
TSS	mg/L	210	840	--	--

BDL\* = below detection limit.

\*\* Adapted from Metcalf and Eddy 2003

\*\*\*Adapted from Nielsen et al. 2007

It is clear that leachate is a highly concentrated waste stream. Compared to typical medium strength domestic wastewater, leachates contain similar constituents but at 1-2 orders of magnitude higher. The average TDS and TSS concentrations in leachate are respectively 22 and 4 times larger than medium strength wastewater, ammonia is 33 times more concentrated in leachate, and BOD<sub>5</sub> and COD are about 24 and 21 times larger in leachate than in the medium strength wastewater. The data collected emphasize the site specificity and the wide variability of leachate composition already outlined. This simple comparison demonstrates the obvious necessity of leachate treatment, when compared to raw sewage. It is suggested that that management of leachate will require treatment prior to safe discharge to the environment. However due to the elevated concentrations of certain constituents, the efficiency of the currently available treatment processes may not be sufficient to achieve the regulated (or target) effluent quality.

As this research addresses leachate specifically from Florida, the literature review was particularly focused on collecting data from Florida landfills. Previous research conducted by Ward et al. (2002) and Statom et al. (2004) among others were considered. In addition, data was collected from the Solid Waste Authority of Palm Beach County (leachate samples from 2004 to 2005). Several record reviews were conducted with Andrell Maxie at the FDEP Regional Office in West Palm Beach, FL, in addition to online searches using the OCULUS system. Furthermore, several reports were made available to FAU to extract laboratory results of leachate composition from landfills in St. Lucie, Okeechobee, Broward, and Miami-Dade counties, for instance. The results of this literature review are summarized in the Florida averages and ranges for leachate quality in Table 6.

The variability in both quality and quantity and the continual generation of leachate over a long period of time are the main issues in determining an effective management approach that includes adequate treatment. The composition of landfill leachate at a particular point in time depends heavily upon the nature of the waste characteristics, including (Kjeldsen et al. 2002; Foo and Hameed 2009):

- Degree of contouring and compacting of solid wastes
- Landfill operation and management (presorting, co-disposal with sludge or ash, ash monofill, type of daily cover material)
- Moisture content, temperature, pH, and oxygen level
- Microbial activity
- Flowrate of groundwater influx, surface water runoff, leachate recirculation, washdown water, and landfill irrigation
- Local precipitation patterns
- Chemical equilibrium and solubility of key constituents
- Internal processes such as hydrolysis, adsorption, biodegradation, dissolution, redox, gas generation, and fate and transport mechanisms
- Hydro-geological variations
- Age, maturity, design (size, depth and lining system), and operation of landfill
- Topography, vegetation, and spatial distribution of sampling points

### 1.3.2 Landfill Gas Effects

Winters and Paulsen (2009) found that construction of composite cells over clay-lined cells contributed to the escape of trapped landfill gas from older cells moving into the subsurface. This mechanism can likely mobilize iron simultaneously. In their experiments, they found that when the gas was removed by installing additional wells, the methane levels decreased (Figure 11) and the iron levels started to stabilize (Figure 12).

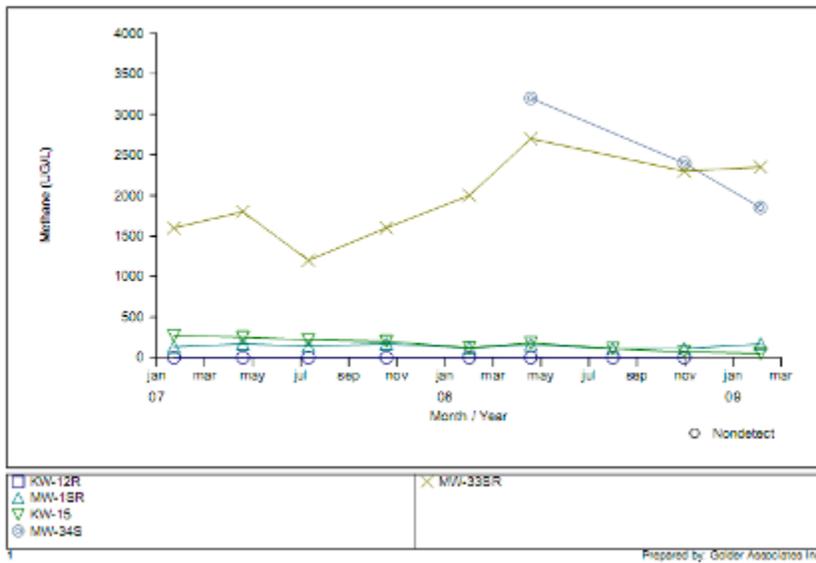


Figure 11. Measurements of methane gas levels detected in the subsurface after installation of additional landfill gas capture wells from 2002-2009 made by Golder and Associates.

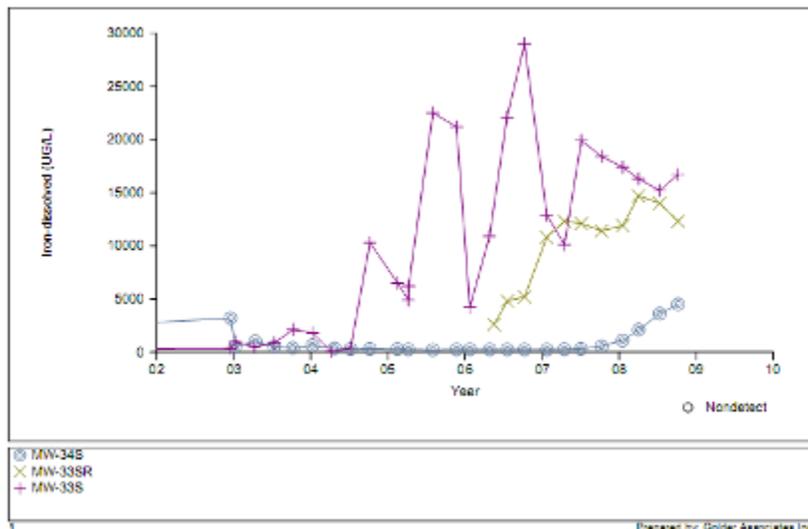


Figure 12. Measurements of dissolved iron levels from 2002-2009 made by Golder and Associates.

### **1.3.3 Landfill Leachate as a Source of Iron**

In terms of iron mobilization in leachate plumes from leaking landfill liners, we would expect to see high oxygen demand with subsequently low dissolved oxygen conditions and high levels of strongly reduced organic material. This large amount of organic material expected to be present in a typical leachate plume is an excellent energy source for local bacteria consortia. Iron is readily available to the bacteria for use as a terminal electron acceptor in the oxidation of this organic nutrient source. This microbially mediated redox, reduces the groundwater iron from ferric to ferrous, which has the effect of releasing the mobile ferrous iron into solution as well as any sequestered trace metals that were organically complexed.

A study of Florida landfills clearly showed that contact between landfill leachate and iron-rich soil does not cause a significant release of ferrous iron into solution in the absence of an appropriate microbiological community to mediate this process (Williams 2007).

If the source of elevated iron is associated with landfill leachate, then we would expect to see either elevated levels of other conservative tracers such as TDS, chlorides, etc.; elevated levels of other known leachate contaminants such as benzenes, ammonia, arsenic, etc.; or dilution effects compared to the measured leachate water quality, caused by the cleaner native groundwater that is receiving the discharge. That being said, there are also caveats to this assertion, which include the fact that there is uncontrollable variability caused by field sampling methods; a known lack of reliability of redox-sensitive parameters; variability in well construction materials statewide (steel materials would cause a confounding signal); and variations in landfill construction methods and operation.

So if there is no documented evidence that the source of the iron is landfill leachate, either directly as a result of leaking landfill liners or indirectly due to the presence of the landfill disrupting the natural hydrology of the subsurface, then repairing the liner system would have no effect, but large scale cost. So we must explore options for managing the iron levels that would have an effect.

## **1.4 ENGINEERING ALTERNATIVES FOR MANAGING IRON IN-SITU**

Once the iron dissolution is detected, it is usually necessary to determine the source and if co-liberation of toxic metals is also occurring before coming up with an effective management strategy to remediate the problem. According to Taiz and Zeiger (2002), plant roots have developed several mechanisms to naturally increase iron solubility, including soil acidification, reduction of ferric iron to ferrous iron, and the release of iron chelators. Following this example, we will investigate those options in more detail. Sim et al. (2001) found a packed column, sedimentation, membrane filtration system to be effective at removing iron from the subsurface, but our research team is confident that there are more practical and more cost-efficient approaches that exist but have not been applied to this scenario. The research team focused on identifying viable engineering alternatives with the potential to minimize disturbance, limit treatment costs, and produce the most effective results.

Conventional treatment for iron removal in soil and groundwater typically involves either pH adjustment or establishment of appropriate redox conditions to oxidize and precipitate iron in the groundwater. These processes fall under physical/chemical and biological treatment for the precipitation of iron. The most common treatment processes for iron removal focus on oxidation, dosing with alkali, and sedimentation. Another common treatment process for the passive treatment of groundwater with elevated levels of iron is dosing with lime (Lee et al. 2007; Danesh et al. 2008). Other methods in groundwater with high iron content include: bioprecipitation, sorption, ion exchange, and membrane processes (Gazea, Adam, and Kontopoulos 1996). Various in-situ and ex-situ remediation techniques have also been employed, e.g., solidification, stabilization, flotation, soil washing, electroremediation, bioleaching, and phytoremediation (Mulligan et al. 2001). Microbially-mediated treatment methods have also been applied to iron removal (Bernoth et al. 2000). Bio-reactors and permeable reactive barriers are also commonly employed. Constructed wetlands can also treat groundwater with high iron content, depending on the oxidation conditions (Doshi 2006). In the following sections, we will explore these engineering alternatives and evaluate them for process efficiency, ease of operation, minimal site disturbance, and environmental considerations.

### **1.4.1 Chemical Dosing**

The goal of chemical precipitation is to convert the soluble iron to insoluble precipitated forms like ferric hydroxides, oxides and oxyhydroxides. Dosing with alkaline agents can be used to artificially raise the pH in situ, to assist the precipitation process by increasing the amount of hydroxide available and neutralizing the effects of alkalinity loss during biodegradation, metal oxidation, and precipitation (Bertills and Sundlof 1995; Mercer and Tobiason 2008).

By far the most commonly used alkaline agent for reducing acidity and precipitating heavy metals in the groundwater is lime or limestone (calcium carbonate) (Cravotta and Trahan 1999). Limestone is selected due to its availability and relatively inexpensive cost. Other commonly used alkaline agents include hydrated lime (calcium hydroxide), soda ash (sodium carbonate), caustic soda (sodium hydroxide), and in some cases even ammonia gas (Bugajer and Danilas 1987).

Anoxic limestone drains treat groundwater using a subsurface zone packed with crushed limestone. Treated water from anoxic limestone drains typically is discharged into a settling pond or wetland to allow metals to precipitate and settle (Cravotta and Trahan 1999). However, anoxic limestone drains often experience armoring, i.e., strong adhesion and complete pacification by encrustation, causing the limestone to become inactivated and potentially clogging of the drain (Robbins et al. 1999). For effective operation, dissolved oxygen and Fe(III) concentrations are suggested to be less than 1.0 – 5.0 mg/L (Cravotta 2003). Limestone armoring can be substantially limited by adding sandstone into the drain (Sasowsky, Foos, and Miller 2000). An important percentage of the ferric oxides precipitated onto sandstone rocks when iron contaminated groundwater discharged onto both exposed limestone and sandstone (Sasowsky, Foos, and Miller 2000), such that iron preferentially adsorbs to sandstone at an order of magnitude higher compared to limestone (Sasowsky, Foos, and Miller 2000). However, it must be noted that these experiments were not conducted under low DO conditions.

### 1.4.2 Biological Treatment

Biological processes like bio-filtration, bioprecipitation, and bioremediation allow a combination of aerobic biodegradation and physical retention of suspended particles by filtration (Štembal et al. 2005). This process is enabled by the activity of microorganisms, which are present in the groundwater microflora. Retention of biomass is achieved by water flow through a filter bed where the microorganisms create a biofilm, which acts like a biological reactor (Wang, Summers, and Miltner 1995; Gusek and Wildeman 2002). An advantage of natural immobilization of the microbes in a biofilm is the fact that cells are not permanently trapped within the filter, such that the dead microorganisms in the layer that sloughs off will eventually be washed out, maintaining the activity of the system at a high level, similar to a trickling filter. A well-established filter biomass requires an acclimation period of at least 3–4 weeks, and with filtration rates as high as 10–24 m/h, the removal of iron, manganese and ammonia from groundwater can be achieved in a single bio-filtration step (Štembal et al. 2005).

Doshi (2006) reviewed constructed wetlands as a viable method to remove iron using either 1) shallow surface flow systems with emergent vegetation to oxidize and precipitate iron or removal via sorption to biomass (USDA and EPA 2000; Eger and Wagner 2003), or 2) anaerobic wetlands systems using alkalinity addition to facilitate precipitation of metal sulfides (USDA and EPA 2000; Brenner 2001).

Sulfate-reducing passive bioreactors in Yellow Creek, Pennsylvania removed 98.9% of dissolved iron from 45 mg/L at pH 2.8 to 0.5 mg/L over a period of several years using a bioreactor pond with a 0.13 ha bottom area and 0.76 m deep. It is lined with one foot of compacted clay. The substrate is comprised of 50% wood chips, 30% limestone, 10% cow manure, and 10% hay. On exiting the bioreactor, the effluent eventually flows through a wetland settling system and rock filter before discharge. The bioreactor was designed for an average flow rate of 38 L/min (10 gpm), and the construction cost of the system was \$158,000 (Gusek 2005). Other bioreactor systems at Wheal Jane Tin Mine in Cornwall England, Surething Mine in Elliston, MT, Leviathan Mine in Markleeville, CA showed similar high removal of iron at 99% (Doshi 2006).

The major drawbacks to biological treatment include clogging with microbial biomass, temperature effects, space requirements, potential for odor problems ( $H_2S$  production), seasonal flow variability, and less control over reactor conditions

### 1.4.3 pH Control

For any treatment processes involving iron precipitation, it is very important to control the pH of the groundwater because pH impacts the solubility of iron and the kinetics of oxidation processes (Webster, Nordstrom, and Smith 1994). A soil pH below about 5.6 is considered low. Generally, the ideal pH range is between 6.0 and 7.0. Adding lime or finely ground limestone is a common method to increase the pH. The reaction rate increases when soil temperatures are warm and soil moisture is high. The amount of limestone to apply depends on the amount of organic matter and clay as well as the pH.

A soil pH that is more than about 8.0 is considered high. Soils that have a pH in this range are often also calcareous. The pH of these soils does not change until most of the calcium carbonate is removed. Acids that are added to the soil dissolve the carbonates and lower the soil pH. Treatments with acid generally are uneconomical for soils that have a content of calcium carbonate of more than about 5%. Phosphorus, iron, copper, and zinc become less bioavailable in calcareous soils.

Sulfate-reducing bacteria can survive in a wide range of pH conditions, but become less active below a certain pH (Doshi 2006). Jong and Parry (2006) found that SRB in laboratory scale bioreactors sustained sulfate reduction rates of 553-1052 mmol/m<sup>3</sup>/day when the pH was lowered from 6.0 to 4.0. However, when the pH was lowered to 3.5, this rate dropped to 3.35 mmol/m<sup>3</sup>/day. Tsukamoto et al. (2004) found similar results showing survival at pH 2.5 but severely limited growth rates at pH<3. More circumneutral pH, or at least pH>4, is generally required for effective microbially-mediated metal precipitation (Doshi 2006).

#### **1.4.4 Chelation/Iron Sequestration**

Chelating extraction of heavy metals from contaminated soils is another potentially viable treatment method. One effective way to use chelating agents is to excavate the soil and perform ex-situ soil washing, which is the physical separation of the clay and silt fraction containing the majority of the metals due to their high specific adsorption capacity as well as the extraction of metals by mineral acids or chelating agents (Peters 1999). In this process, the soil is removed from the site, treated in a closed reactor with the chelating agent, and after separation of the extraction solution that now contains the extracted heavy metals, the treated soil is returned to the site. The advantage of the method is the high potential extraction efficiency and the specificity for heavy metals. To keep treatment costs low, it is necessary to be able to recover and reuse the chelating agent for further extraction cycles. However, this process is clearly not in-situ and would not be suitable for the purposes described in this report.

Another potential application is to use chelating agents in conjunction with groundwater circulation wells or trench systems to help move the iron to the treatment location either in the well or the trench to possible pump and treat removal. Now, there are many factors to consider when comparing chelating agents for field-scale decontamination of polluted sites, these include: the ratio of chelating agent to toxic metals, pH, quantity of major cations extracted, specificity to the target contaminant, ecotoxicity, and cost. Most studies of chelation technologies have found that a ratio of greater than 1:1 to 5:1 between the chelant and the target metal is required to achieve adequate extraction (Norvell 1983; Elliot and Brown 1989; Steel and Pichtel 1998; Kim, Lee, and Ong 2003). Typically an excess of chelating agent is needed because of the presence of major cations in the soil matrix such as Mn, Mg, and Ca along with other toxic metals present in smaller amounts, all of which compete with the target metal and are extracted too (Papassiopi, Tambouris, and Kontopoulos 1999). Furthermore, some of the other constituents may have a stronger affinity for the chelating agent than the target metal, which will tend to complicate the process removal effectiveness. In some cases the ratio can be calculated from the concentration and volume of chelating agent and the mass of soil (Papassiopi, Tambouris, and Kontopoulos 1999). Some typical chelating agents that are used for this purpose include the persistent aminopolycarboxylic acids like EDTA, HEIDA, EGTA, DTPA, EDDHA, HEDTA, and CDTA

(Evangelou, Edel, and Schaeffer 2007). More recently, biodegradables such as EDDS and NTA have been proposed as an alternative, as well as naturally-occurring low molecular weight organic acids like citric acid, oxalic acid, malic acid, in addition to humic substances like humic acids, fulvic acids, and humins (Evangelou, Edel, and Schaeffer 2007).

By far, ethylene diamine tetraacetic acid (EDTA) has been the most widely used chelating agent due to its excellent extraction efficiency for mobilizing metals, but unfortunately, due to its low biodegradability (Bucheli-Witschel and Egli 2001), it is also very persistent in the environment. Nitrilotriacetic acid (NTA), the second most common chelating agent, is readily biodegradable, but is controversial due to possible adverse health effects (Ebina et al. 1986). So the trend is towards developing more easily biodegradable chelating agents like EDDS.

#### **1.4.5 Permeable Reactive Barriers**

A permeable reactive barrier is an application using reactive media (i.e. compost or filter media) that hosts metal oxidizing bacteria to remove specific contaminants of concern (Jambor and Raudsepp 2005; Ludwig et al. 2002). These barriers are placed in the path of groundwater flow to intercept the contaminated strata. Permeable reactive barriers have a subsurface reactive section for the groundwater to flow through and to be treated. In some cases, there are impermeable walls to direct the water flow to the reactive section. Permeable reactive barriers have been used to remove iron with possible permeable materials such as rocks in the form of amorphous ferric oxyhydroxide (Benner et al. 1997; US DOE 1998).

Permeable reactive barriers have been used to passively treat ground water containing organic and inorganic contaminants such as PCE, TCE, VOCs, radionuclides and metals (US DOE 2000). These barriers may use a variety of substrates to degrade, sorb, or precipitate contaminants directly or through microbial activity in the barrier. In a case study conducted at the Nickel Rim mine near Sudbury Canada, 68 – 94% removal of ferrous iron was recorded in mine tailings treated with this technology in the shallow aquifer system containing 200 – 2000 mg/L of ferrous iron. The reactive layer was 4 m thick, sandwiched between layers of sand approximately 1 m thick. The reactive layer contains 20% (by volume) municipal compost, 20% leaf mulch, 9% woodchips, 50% gravel, and 1% limestone. A clay cap 30 cm thick covered the top of the zone (Benner et al. 1999). The barrier measured a hydraulic gradient of 0.016, lower than the surrounding aquifer's hydraulic conductivity of 0.020, such that the ground water flows through the barrier at an average velocity of 16 meters per year. It was determined that iron was removed by sulfide formation and metal sulfide precipitation with a 90 day residence time.

The permeable reactive barrier also exhibited seasonal variation in performance. Sulfate and iron removal rates and alkalinity generation were higher in fall compared to the spring. This pattern was likely related to seasonal variation in temperature within the barrier, especially near the surface. Throughout a three-year study period, the temperature ranged from 2 to 29°C (at 1.0 m below the surface). Decreasing effectiveness over time was also noted. Sulfate reduction rates decreased 30% and iron removal rates decreased 50% in the first three years of operation. The slowing of sulfate reduction rates occurred most rapidly in the first three months of operation, and at a slower rate over the next 2 years. This pattern is typical of a model in which organic

matter of highest reactivity is preferentially consumed, lowering the overall reaction rate (Benner et al. 2002).

The case study performance data were used to produce a process-based reactive transport model. High correspondence between observed and simulated pore water and solid phase chemistry indicated that the conceptual model accounted for important processes. Seasonal and spatial temperature variation, low-flow zones, rapid depletion of labile organic carbon, mackinawite precipitation, and siderite formation were all modeled as important processes. Sulfide reactions with minerals down-gradient, gypsum formation, variation in organic carbon density, and specific mechanisms of organic carbon degradation were not modeled, and may further explain observed changes (Mayer et al. 2006).

#### 1.4.6 Aeration

In situ removal of iron can be accomplished effectively by aeration, which converts soluble ferrous iron to insoluble ferric species. One way to accomplish this is a process that involves the cyclical injection of volumes of oxygenated water into the aquifer. The injected water and some of the surrounding groundwater is then withdrawn leaving a lower concentration of iron in the subsurface. The mechanism of the reaction is still not well understood, but conversion to insoluble ferric species continues well after complete withdrawal of the oxygenated water (Appelo et al. 1999). For example, a case study performed in the Netherlands (van Beek 1980), cycled 1000 m<sup>3</sup> of oxygenated water with 7000 m<sup>3</sup> pumped out. A delayed rise in the iron concentration in the pumped groundwater indicated an increased efficiency with number of successive cycle runs. In theory, the ferrous iron sorbed onto iron oxyhydroxides gets oxidized by molecular oxygen and grows the sorption surface, which frees up more sorption sites to pick up ferrous iron from the groundwater upstream. Clogging is not generally observed with in situ iron removal, which is unexpected, but seems to be related to the self-regulating nature of the ferrous iron exchange and sorption mechanism (Appelo et al. 1999). So the design of the system is less related to the amount of oxidant in the injected water than it is to the amount of dissolved iron capable of consuming the oxidant.

Another conventional treatment for iron in groundwater consists of oxidation followed by filtration. Oxygen or stronger oxidants such as chlorine or permanganate. Table 7 summarizes the relative oxidation power of the species used in most conventional oxidation methods.

Table 7. Relative oxidation power of selected oxidizing species (Munter et al. 2001).

Oxidation Species		Relative Oxidation Power
Positively charged hole on titanium dioxide	( $h^+$ )	2.35
Hydroxyl radical	(OH·)	2.05
Ozone	(O <sub>3</sub> )	1.52
Hydrogen peroxide	(H <sub>2</sub> O <sub>2</sub> )	1.31
Permanganate	(MnO <sub>4</sub> <sup>-</sup> )	1.24
Hypochlorous acid	(HOCl)	1.10
Chlorine	(Cl <sub>2</sub> )	1.00

Oxidation tends to produce  $\text{FeOOH} \cdot \text{H}_2\text{O}$  precipitates, which can then be filtered using green sand (Lessard et al. 1999). However the process works effectively for total iron concentrations below 5 mg/L in the absence of dissolved organic material. At higher concentrations, the excessive amounts of precipitates tend to shorten filtration cycles and limit the effectiveness of the process (Ellis et al. 2000).

#### 1.4.7 Advanced Oxidation Processes

Advanced oxidation processes were defined by Glaze et al. (1987) as “near ambient temperature and pressure water treatment processes, which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification.” An AOP can utilize ozone ( $\text{O}_3$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), or other agents to oxidize the pollutants through the production of the hydroxyl radical ( $\text{OH}^\bullet$ ), which is a powerful and indiscriminate oxidant. The hydroxyl radical has a relative oxidation power of 2.05 compared to 1.00 for chlorine. Within milliseconds (Peyton and Glaze 1988, cited by Fang et al. 2005), hydroxyl radicals are capable of achieving complete mineralization (i.e. degradation of complex organics to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and mineral ions) of virtually all organic compounds (Feitz et al. 1998; Cho et al. 2002) rather than concentrate or transfer contaminants into a different phase. In this manner, pollutants that are only partially oxidized are decomposed into components that are more readily biodegradable and less toxic to common microorganisms found in a wastewater treatment plant for instance (Schulte et al. 1995; Morais and Zamora 2005).

An energized process is based on similar mechanisms as the AOPs but with the additional action of ultraviolet light, which may be either from a UV lamp or from natural sunlight. Addition of ultraviolet energy has been shown to enhance the production of the hydroxyl radical. Steensen (1997) explained that the use of iron (catalyst) or photo-energy (EP) improves oxidation power by accelerating the formation of hydroxyl radicals. Staehelin and Hoigné (1983) pointed out however, that “radical scavengers,” such as: carbonates species ( $\text{CO}_3^{2-} / \text{HCO}_3^-$ ) or alkyl compounds slow down the reaction rate because they interrupt the chain reaction. Maintaining a low pH to shift the carbonate equilibrium toward carbonic acid is important for these types of processes. Nevertheless, AOPs and EPs offer a robust and increasingly economically favorable alternative for treatment of wastewater contaminated with highly toxic organic constituents (Feitz et al. 1998). AOPs and EPs are known to handle many of the constituents typically found in leachate:

1. Elevated ammonia: EPs convert ammonia to nitrate through aeration or promote stripping of dissolved ammonia gases at suitably high pH (AWWA 1999).
2. High COD/BOD ratios: EPs convert refractory COD into readily biodegradable BOD (Suty et al. 2004), which is then mineralized by oxidation to simple products such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , etc. (Metcalf and Eddy 2003).
3. Heavy metals: EPs remove heavy metals such as: lead, arsenic, mercury, and cadmium through co-precipitation, adsorption, and redox mechanisms (Englehardt et al. 2002 and references therein).

4. pH toxicity: EPs limit pH impacts as a byproduct of aeration treatment via the natural buffering capacity of the carbonate system (AWWA 1999; Metcalf and Eddy 2003).
5. Volatile organic compounds: EPs can destroy recalcitrant organics and, because of their volatility or promote the stripping of VOCs during aeration, provided the appropriate conditions (AWWA 1999, Sutty et al. 2004).

Advanced oxidation processes can occur both with and without the addition of energy. If AOPs or EPs are used as a pre-treatment step before a biological treatment, it has been demonstrated that these types of oxidation processes can reduce the detention time required for subsequent biological treatment (Bila et al. 2005). Initial filtration or sedimentation is still often required as a pre-treatment step to remove solids that would interfere with the action of UV. One important drawback of AOPs is the high demand for electrical energy (e.g. ozonizers, UV lamps, ultrasound, etc.), which increases cost (Lopez et al. 2004). Also, for complete mineralization of pollutants to occur, high oxidant doses may be required. Silva et al. (2004) needed 3.0 g/L of ozone to attain significant toxicity decrease. Furthermore, some intermediate oxidation byproducts generated by incomplete mineralization can increase the toxicity of leachate.

The systems most commonly employed for advanced oxidation include: photo-Fenton (Kim et al. 1997; Lau et al. 2002; Morais and Zamora 2005; Dincer et al. 2008; Primo et al. 2008), UV/H<sub>2</sub>O<sub>2</sub> (Schulte et al. 1995; Steensen 1997; Shu et al. 2006), O<sub>3</sub>/UV (Bigot et al. 1994; Ince 1998; Qureshi et al. 2002), and photocatalytic oxidation (Konaka et al. 1999; Suri et al. 1999; Sturini et al. 2001; Munter et al. 2001; Pekakis et al. 2006; Sanchez et al. 2010). Advanced oxidation processes such as conventional Fenton, photo-Fenton and electro-Fenton are powerful advanced oxidation processes that effectively degrade refractory organics and persistent organic pollutants, which are difficult to decompose by processes other than biological systems. But alone, they appear to be limited and instead can really only be used as a pretreatment step to facilitate other downstream degradation processes. UV/H<sub>2</sub>O<sub>2</sub> is another powerful advanced oxidation processes that can effectively degrade refractory organics and persistent organic pollutants, but no ammonia, heavy metals, or suspended material are known to be removed with this technology. Ozone in concert with ultraviolet light radiation is another advanced oxidation technology, but has never been demonstrated to remove dissolved iron. Finally photocatalytic oxidation, to our knowledge, has not been demonstrated at field scale for treatment of highly variable, high strength contaminated waters. All of the advanced oxidation technologies are complicated to deploy in-situ due to the ultraviolet light radiation input, which must be provided using UV lamps, which increases the cost substantially.

#### **1.4.8 Groundwater Circulation Well Technologies**

If the iron is associated with co-liberated toxic metals like arsenic, then a process which induces circulation in the groundwater by means of either recirculation wells, or injection/extraction wells containing a reaction zone within the well itself could be an effective countermeasure against migration of the pollutants down gradient. Groundwater aeration, air sparging, or in-place air stripping are proven remedial technologies for removing volatile organic compounds from groundwater (Wyoming DEQ 1998). A similar process was proposed by Englehardt et al. (2002). During the extraction phase of the circulation, chelating agents are added to the water, if

needed, to assist in transporting contaminants more rapidly to the well for treatment. Anionic metal oxides, inorganic oxides such as nitrate, and radionuclides are generally soluble and mobile in the subsurface, and will also be transported to the well. Once in the reaction zone of the well, species that are present in zero-valent forms ( $Me^0$ ) will be oxidized over time by the continuous aeration provided, and removed by co-precipitation and adsorption processes. Volatile organic compounds (VOCs) would also be removed by either oxidation or phase transfer, and biological processes in the zone of influence will be accelerated by continuous aeration. This technology is an in situ remediation process that is successful in removing heavy metals, radionuclides, VOCs, and biodegradables. It is simple to operate, relatively rapid, and potentially inexpensive.

Also known as “in-well aeration,” this process involves injecting air into the bottom of a well or trench screened in the saturated zone. Conventional groundwater circulation wells work by forcing ambient air into the upper portion of a shallow groundwater aquifer through an injection well or sparger. A regenerative blower, positive displacement blower or oil-less compressor is usually used to overcome the hydraulic pressure and force the air into a saturated soil formation. Pilot testing is usually conducted to determine the optimum pressure and flow rate for these types of systems. As the injected air travels upward through the water column, bubbles form which remove volatile and semi-volatile organic compounds present. The upward movement of air also produces an airlift pump effect, as groundwater is pulled into the well from deeper screened portions and out of the well from shallower screened portions. Contaminant concentrations are reduced as groundwater circulates through the well, eliminating the need for pumping and treating the water at the surface. Just as with pump and treat systems, the low solubility of many contaminants and the inhibitory effect of slow mass transfer within heterogeneous geological conditions may retard the remediation process.

Groundwater circulation wells attempt to create a 3-dimensional circulation pattern in an aquifer by drawing ground water to the well, pumping the water through the well then reintroducing the water into the aquifer at a different elevation without pumping it above the ground. Distinct groundwater circulation patterns are established depending upon the operational geometry of the well and hydrologic conditions of the site. Figure 13 illustrates ideal circulation patterns that would be established with groundwater circulation wells as a function of horizontal groundwater flow velocities (Herrling et. al 1991a). The top illustration shows that under ideal conditions and in the absence of background flow, the circulation pattern forms symmetrical ellipsoids around the well. The middle and bottom diagrams show that as the horizontal component of the background flow velocity increases, the stream lines are skewed and the symmetry is lost, By comparison, it can be shown that increasing the background flow velocity will cause a decrease in the radius of the induced flow field. So the spacing of groundwater circulation wells is dictated by the horizontal groundwater velocity. Note that these diagrams illustrate the case of an idealized aquifer in which vertical flow is easily established. This may not be the case in many real-world situations.

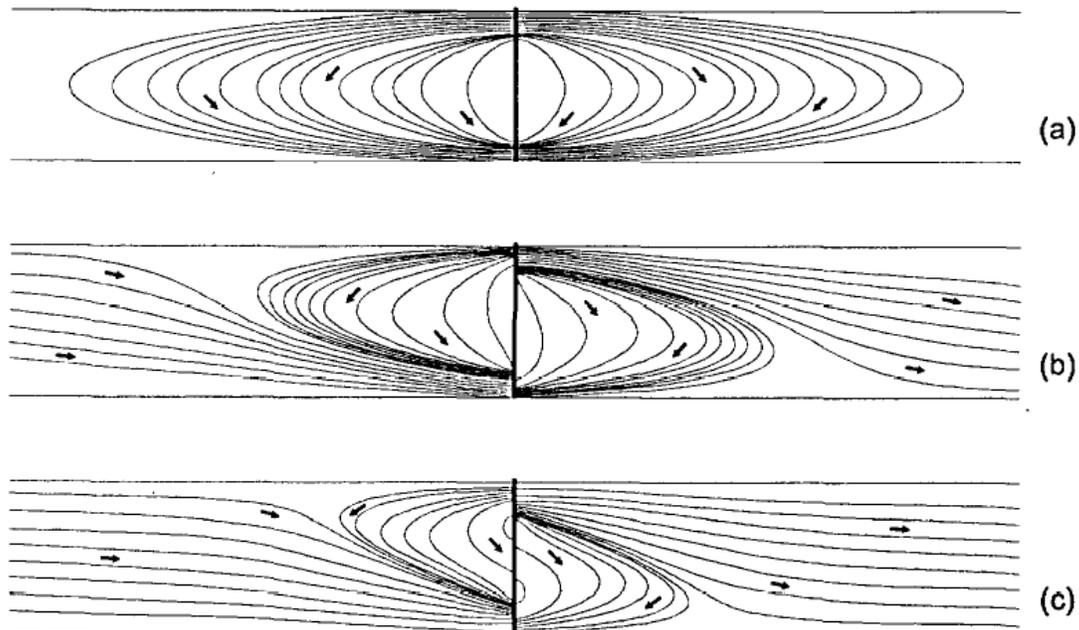


Figure 13. Idealized Circulation Pattern Around GCW system with Horizontal Groundwater Velocities of (a) 0.0 m/day, (b) 0.3 m/day and (c) 1.0 m/day (from Herrling et. al. 1991)

Groundwater circulation well systems are designed to provide treatment inside the well, in the aquifer, or a combination of both. For effective in-well treatment, the contaminants must be adequately soluble and mobile for transport by circulating groundwater. Current methods for in-well treatment include air stripping, activated carbon adsorption, and in-well bioreactors. Contaminants that cannot be mobilized effectively to the well can sometimes be treated in the aquifer. Most commonly, in situ treatment is achieved through biodegradation. Most often, as is the case with iron dissolution remediation, there is a combination of both in-well and in-aquifer treatment, with the relative percentages of removal by each mechanism being contaminant-, site-, and configuration-specific.

Most groundwater circulation well configurations incorporate air lift pumping to facilitate groundwater circulation, and air stripping to remove volatile contaminants from groundwater passing through the well. These systems will then transfer volatile contaminants from the aqueous phase to the vapor phase in the well. The off-gas often requires some level of treatment for contaminant vapor prior to discharge. Off-gas treatment can be achieved in situ by direct injection into the vadose zone. More often, the off-gas is treated above ground with any of a variety of processes. In the case of remediation of iron dissolution, the off-gas should not be a major issue unless contaminants such as hydrogen sulfide, ammonia, and other VOCs are also present in the aquifer, along with the iron.

Depending on the specific application, groundwater circulation systems may have several advantages such as the fact that treatment of the contaminated groundwater takes place below grade and does not require groundwater to be pumped out of the ground. Eliminating the need to pump groundwater to the surface is an attractive feature for two main reasons: 1) it may eliminate the need for a discharge permit, and 2) it will result in some energy cost savings from lifting water at sites with deep water tables.

Another advantage of groundwater circulation well systems over conventional pump-and-treat is that they induce a three-dimensional groundwater circulation zone that “sweeps” the aquifer. Pump-and-treat systems cause drawdown around the well, leaving contaminated zones that are not treated. In addition, pump-and-treat systems inherently draw water along preferential pathways in the subsurface, leaving contamination in lower permeability units. Because of this, pump-and-treat systems often become diffusion limited. Groundwater circulation well systems do not cause drawdown and they promote a circulation with both horizontal and vertical flow components that may cause more flux across lower permeable units. Another potential benefit is the simultaneous remediation of contamination above and below the water table. This is achieved by coupling the saturated zone treatment with soil vapor extraction (SVE) or bioventing.

The specifics of the well design, method of pumping, and method of treatment vary by configuration and are selected based upon site- and application-specific requirements. The most common method used to move groundwater in these kinds of systems is air lift pumping. Air lifts have an air line that extends to some depth below the water level in the well system. As air is injected, it mixes with the water and causes a decrease in the specific gravity of the fluid (Power 1992). The difference between the weight of the air-water fluid within the well and the water in the bottom of the well is replaced by water drawn in from the formation. Depending on the specific configuration, the pumped water is reintroduced into the aquifer either directly through the upper well screen or through a subsurface infiltration gallery. Since many of the driving mechanisms behind groundwater circulation wells are not fully understood, the subsurface investigation phase is critical. The specific data that should be collected and evaluated in order to assess feasibility include site specific criteria, contaminant characterization, soil related criteria, and groundwater related criteria (Wyoming DEQ 1998). In particular, the horizontal and vertical permeability of the saturated zone must be determined. Dissolved iron concentrations must also be measured because dissolved iron levels greater than 10 mg/L will tend to precipitate during the sparging operation and could in rare instances cause aquifer clogging, potentially reducing porosity and permeability in the surrounding aquifer (Wisconsin DNR 1993, Marley and Bruell 1995). Furthermore, well screens may become clogged by precipitated iron or by colonies of iron-reducing bacteria, gradually reducing the subsequent zone of influence of the system. It has been observed, however, that fouling of wells is rarely a problem, because they are essentially continuously being developed by the injected air. The types of systems have been conducted successfully at dozens of sites with high iron levels (Bass, Hastings, and Brown 2000).

It must be stated that this technology cannot be used to treat groundwater in a confined aquifer because the injected air would be trapped by the confining unit and would therefore not be able to escape to the unsaturated zone. The trapped air would then cause an increase in the downgradient movement of dissolved phase contamination. It is also important to note that the presence of fine grained materials or other geologic heterogeneities which may limit the migration of air to the water table surface, will adversely affect the efficiency of an air sparging system and may even promote dissolved and vapor phase contaminant migration.

After discussing construction and pilot testing recommendations with Jeff Ahrens of Geosyntec Consultants (personal communication 2011), we were able to narrow down the design parameters as follows:

- The air injection well(s) should generally be located in an area of significant groundwater contamination. Although, if the air injection wells are placed in a curtain to intercept a contaminant plume, the wells would be located on the downgradient end of the plume.
- The injection well(s) should not be placed in the vicinity of man-made air flow conduits, such as sewer or utility lines.
- The top of the screened interval must be placed significantly below the seasonally low water table to ensure that screen will not be exposed under any circumstance.
- Depth of the screened interval is also contingent on contamination depth. The top of the screened interval must be placed sufficiently below the contaminant plume or area to be targeted (generally from 5 to 15 feet below deepest contamination under low water table conditions). However, the depth should not be greater than 20 to 35 feet below the ground surface or greater than 10 feet below the water table.
- Screen length is typically 2 to 5 feet; increased screened intervals generally do not improve system efficiency since air tends to exit at the top of the screen.
- The filter pack should not extend more than 1 or 2 feet above the top of the screened interval. Filter pack material should be selected based on the average grain size of soils below the water table.
- Heat generated during air compression should be taken into account when selecting well and piping materials.
- The suggestion is to use galvanized pipe for the pressure side of the blower (typical pressures vary from 2 – 60 psig).
- A claw compressor type system is recommended for air delivery (typical air flow rates vary from 2 – 25 cfm).
- Well construction should ensure that short-circuiting of air is unlikely to occur across the bentonite seal and surface grout.
- The injection pressure should not exceed 3 times the static hydraulic pressure calculated at the top of the injection well screened interval. It is believed that turbulent flow occurs at higher pressures, potentially causing increased contaminant dissolution and plume migration downstream.
- The injection pressure should not exceed 80% of the total pressure exerted by the weight of the soil and water above the top of the screen. It is believed that higher pressures may produce fracturing in the sparging well annular seal or along weak joints in the soil, resulting in a loss of system efficiency.

#### **1.4.9 Summary of Technologies**

Depending on the source of the iron, other engineering alternatives may also be applicable. If the iron mobilization is caused by iron bacteria, this can be controlled by dosing periodically with disinfectants like chlorine. If the release of soluble iron is related to a general lack of iron bacteria, which is limiting in-situ microbially-mediated bioprecipitation, then options such as micro-aeration, chelation with organic acids, or pH control may be effective, in theory. Some iron may be present in colloidal form. Unlike ferric iron, which will generally agglomerate, tiny particles of colloidal iron will resist coagulation and aggregation. Their large surface area and charge relative to their small mass causes individual iron colloids to repel each other. Their small size, then, makes them difficult to filter, and coagulating agents may be required to adequately remove or trap these particles. If the major culprit is soluble ferrous iron, ion exchange or

oxidation followed by filtration should be effective. The latter approach can be achieved by aeration, the addition of an oxidizing agent, or any number of advanced oxidation methods. Also, adsorptive filtration methods can be employed under anoxic conditions to suppress the oxidation of ferrous iron and adsorb the ferric particles on anthracite media (Chaudhuri et al. 2008). The New River Solid Waste Association is in the process of testing waste materials available at landfill sites such as crumb rubber, lime rock, and recovered concrete aggregates as trench fill media for in-situ oxidative iron remediation. If the source of the iron is changes in local hydrology, then engineered systems can be employed to restore or mimic the effects of the previous hydrological conditions to counteract the effects of the landfill. Even pump and treat systems with packed columns, sedimentation tanks, and membrane filtration have been proposed (Sim et al. 2001), but the major drawbacks of each of these technologies provide strong limitations to adoption. The groundwater circulation well may be a viable option because it has potential to be able to create oxidation conditions in situ if the appropriate air flow and well spacing conditions can be worked out.

## **1.5 OBJECTIVES**

This research will focus on laboratory experiments to reduce iron pollution of the soils and groundwater under landfills by using recirculating aeration wells. This technology works by oxidizing the iron and converting it from the reduced iron(II) ferrous form, which is soluble in water to the insoluble iron(III) ferric form by pumping air into the soil. If the recirculating aeration wells are found to be successful in ameliorating the iron dissolution issue, a preliminary model for scale-up will be developed and the process will be evaluated for a preliminary cost analysis. The preliminary cost analysis will include the capital cost (recirculation well, aggregates, fittings, blowers, connection tubes, installation cost, etc.) and the operating cost (electricity, maintenance, operator fees, etc.).

## **2. METHODOLOGY**

### **2.1 INFORMATION COMPILATION**

Mr. Allan Choate provided a brief summary of the Polk County landfill facility. Phase 3 (60 acres) is currently active, receiving Class 1 waste since November 2006. The original facility was 100 acres of unlined landfill (pre-1985). Phase 1 is a single bottom liner (43 acres) and Phase 2 is double lined and consists of another 43 acres in final closure. Phase 3 has a 2 acre test liner with an array of 20 monitoring wells. This is where the iron/arsenic problem was first detected. The general direction of groundwater flow is from NE to SW. The facility is located in an area that was used for phosphate mines originally. The leachate is stored in an onsite storage tank and is pumped to the local POTW (Central Region WWTP) by gravity (5 miles). There are no pretreatment requirements according to a negotiated 5 year contract to dispose of the WWTP sludge residuals in exchange. This contract is renewable for up to 30 years. The amount of leachate generated is on the order of 20,000 gpd from the 150 lined acres on the site. This is down from 50,000 gpd after final closure of Phase 2. The Central Regional WWTP at the end of Eagle Lake Road in Winter Haven, FL. This facility is a 1.1 MGD permitted capacity contact stabilization system with rapid infiltration basins and irrigation disposal. Slug tests performed by Jones Edmonds in November 2004 revealed hydraulic conductivities on the order of 0.19 to 5.6 ft/day (average = 2.17 ft/day) (Jones Edmonds & Associates, Inc. 2005). The effective porosity is estimated at 0.2 and the gradient is southwesterly with an average of 0.0016. So the horizontal groundwater velocity =  $K_i/n = 0.017$  ft/day (6.3 ft/year), with a maximum of 13.6 ft/year. The vertical groundwater velocities were calculated using the HDR September 1998 biennial as a reference from well clusters SW-2, SW-3, SW-6, and SW-7 and assuming the variables from the vertical hydraulic conductivity tables in the 1995 Ardaman and Associates hydrogeology report. The range was +0.0367 ft/year downward to -0.1426 ft/year upward, with an average of -0.032 ft/year upward.

### **2.2 SOIL SAMPLING AND CHARACTERISTICS**

Soil samples were collected using a shovel after removing the top 15 cm since this zone is filled with plants, dirt, root residues, or other impurities. A conservative assumption that iron typically has a constant concentration for shallow depths near landfills was used in this case.

On February 25, 2011, Allan Choate (TAG Member) informed us that Polk County would like to participate in the study. On May 11, 2011, the principal investigator met with Polk County officials to obtain samples of leachate and soil for preliminary testing. Leachate samples were collected on May 11, 2011 from the combined leachate storage tank (south tank). Samples were collected in 2 liter plastic milk jugs that were rinsed three times with deionized water. Leachate was allowed to flow for approximately one minute before collecting the sample with zero head space and stored at 4°C until analyzed.



Figure 14. Leachate sample collection from Polk County facility on May 11, 2011.



Figure 15. Allan Choate assisting with the leachate sample collection on May 11, 2011.



Figure 16. Soil sampling from the downstream SE corner (left) and from the upstream NE corner (right) on May 11, 2011. The NE corner samples were taken just south of the monitoring wells that reported elevated iron readings.



Figure 17. Location of downstream SE corner Polk County landfill site on May 11, 2011.



Figure 18. Location of upstream NE corner Polk County landfill site on May 11, 2011.



Figure 19. Location of monitoring well for SE corner sampling location on May 11, 2011.

On November 9, 2011, Dr. Meeroff returned to the Polk County facility, and he and Mr. Choate collected additional soil samples from various locations at the site (Figure 8 and 9).



Figure 20. Southeast corner site at Polk County Landfill on November 9, 2011.



Figure 21. Southwest corner site at Polk County Landfill on November 9, 2011.

Samples were collected from the following locations:

- Polk County North Central Landfill
  - Northeast location (upstream): sampled collected on May 11, 2011
  - Southeast location (downstream due south): sample collected on May 11, 2011 and November 9, 2011
  - Southwest location (downstream in direction of groundwater flow): sample collected on November 9, 2011

Soil samples collected on May 11, 2011 have sandy consistency but they also have variations in color from dark black in the NE location to yellow in the SE location. Both NE and SE samples contain some impurities like small stones or some plant material. The soil collected on May 11, 2011 has a large component of sand. On November 9, 2011, the SE location showed a dark organic color. It had a clayey consistency with a dark yellow color that was almost gray when saturated with moisture. The SW location collected on November 9, 2011 had a clay-like consistency with a light yellow color.

For Boca Raton control soil and groundwater, samples were collected on the following dates as shown in Figure 22:

- Boca Raton FAU campus control site
  - Collected on June 6, 2011
- Boca Raton FAU campus canal water
  - Collected on December 10, 2011

Soil samples were collected in 5 gallon buckets, sealed, and stored at room temperature until analyzed.



Figure 22. (Left) Boca Raton surface water canal sample collected on December 10, 2011. (Right) Boca Raton soil sample collection on 06/10/2011.

### **2.3 BENCH SCALE EXPERIMENTS**

The FAU Laboratories for Engineered Environmental Solutions is equipped with an automated temperature controlled testing unit with the capacity of 3 sets of 8 aquaria (Figure 23). The aquarium model consists of a glass vessel with the following dimensions  $L = 11.5$  inches,  $W = 5.5$  inches, and  $D = 7.75$  inches, as shown in Figure 24.



Figure 23. Aquarium testing unit.



Figure 24. Close up of aquarium testing unit.

The soil was added to a depth of 5 inches, which makes it possible for water to be discharged from the discharge valve. In the center of this vessel, we set a one-inch diameter PVC pipe to create the annulus for the groundwater circulation well (Figure 25).



Figure 25. Construction of recirculating well installation.

Inside the annulus, a groundwater circulation well was placed, consisting of a clear vinyl tube with slits cut on both sides for aeration. The aeration well (outer tube) was 7-inches long, 0.5-inch inside diameter, 0.62-inch outside diameter. The well screen consisted of an upper and lower portion of a series of 10 slits 2.5 millimeters apart, cut using a razorblade. The well screen portions are 1-inch in height and separated by a 1-inch reaction zone from each other (Figure 26).

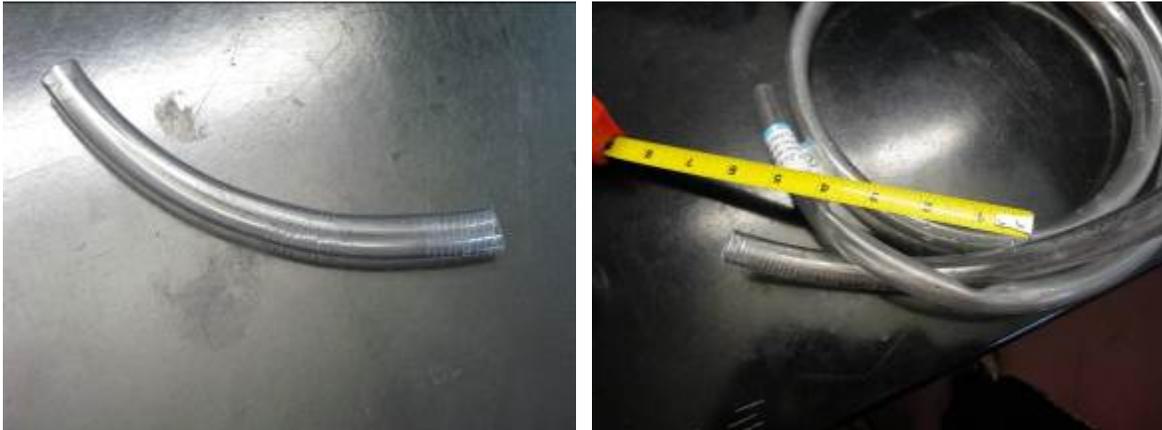


Figure 26. Construction of recirculation well slits for the recirculation zone.

The inner well for the tube-in-tube design was 9-inches long, and 0.25-inch outside diameter (0.170 inch inside diameter). Then a small opening (1/8") was made in the inner well to allow the lifted water and air bubble to escape and create the vertical circulation head. The air line is 72-inches in length with a 22-inch long 0.25-inch vinyl tubing connection to a standard bore three way stopcock with rotating male Luer lock (Figure 27) to control the air flow rate. From this valve, an anti-siphon anesthesia set tubing line with Luer lock adapters (Figure 28) was attached to deliver the aeration to the well using a 0.085-inch outside diameter vinyl tubing.

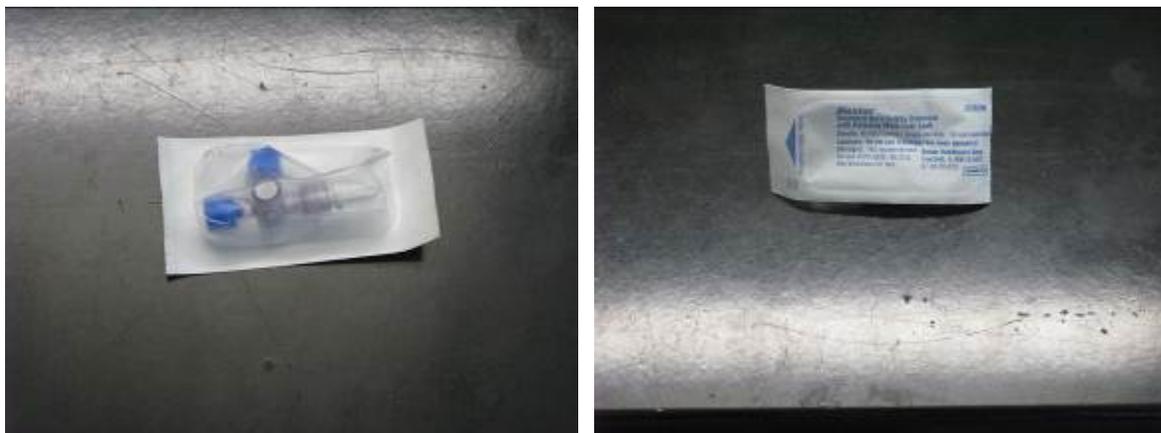


Figure 27. Closeup of standard bore three way stopcock with rotating male Luer lock.



Figure 28. Closeup of anti-siphon anesthesia set tubing line with Leur lock adapters used as the air delivery line.

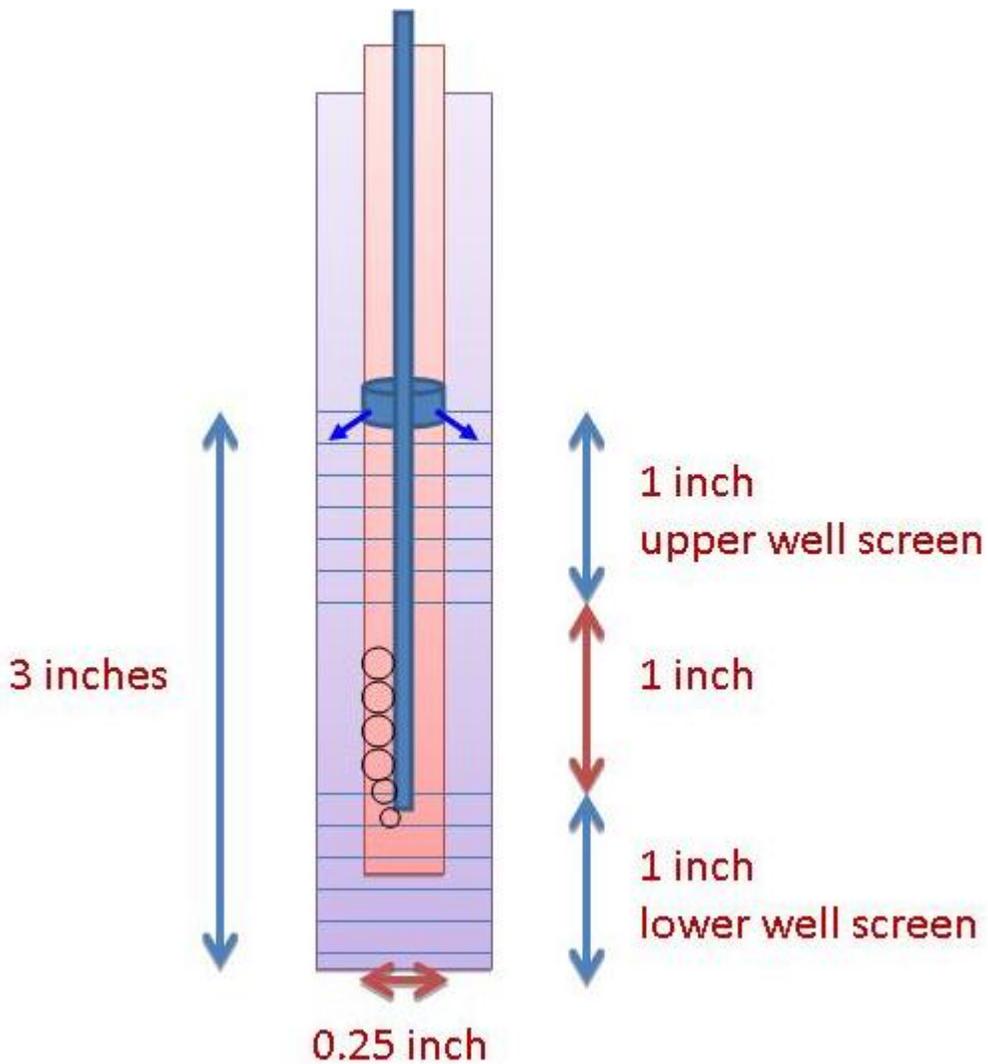


Figure 29. Cross sectional schematic showing dimensions of groundwater circulation well.

As you can see in Figure 30, an air pump (Elite 799, 1.0 cfm, 1 psi) was used to deliver the air. The pump was attached to an anti-siphon anesthesia set tubing line with Leur lock adapters by 0.25-inch outside diameter vinyl tubing. The smaller line 0.085-inch outside diameter vinyl tubing leaving from the connector was fitted into a shorter piece of 0.25-inch outside diameter vinyl tubing to act as the air lift zone. For tighter control of the air bubbles, a thin glass capillary tube of 0.037-inch outside diameter was attached to the end of the small line. A widow (1/8") was cut into the inner well to allow for air/water escape and to create the vertical circulation head.



Figure 30. (Left) Closeup of air pump used to deliver air to the groundwater circulation well (Elite 799, 1.0 cfm, 1 psi air pump). (Right) Closeup of the air delivery system for the well.

A hydraulic test was conducted to determine the aeration conditions, mixing, radius of influence, depth, drawdown, hydraulic grade line, hydraulic conductivity, porosity and other important parameters. This was conducted using a crystal violet dye test and by varying the air flow rate in a demonstration recirculation well (Figure 31). The most effective conditions were at full air flowrate of 1.0 cfm. At this flowrate, the dye was able to circulate approximately 19-20 mm from the edge of the beaker in the horizontal direction and about 20-30 mm in the vertical direction (Figure 32).

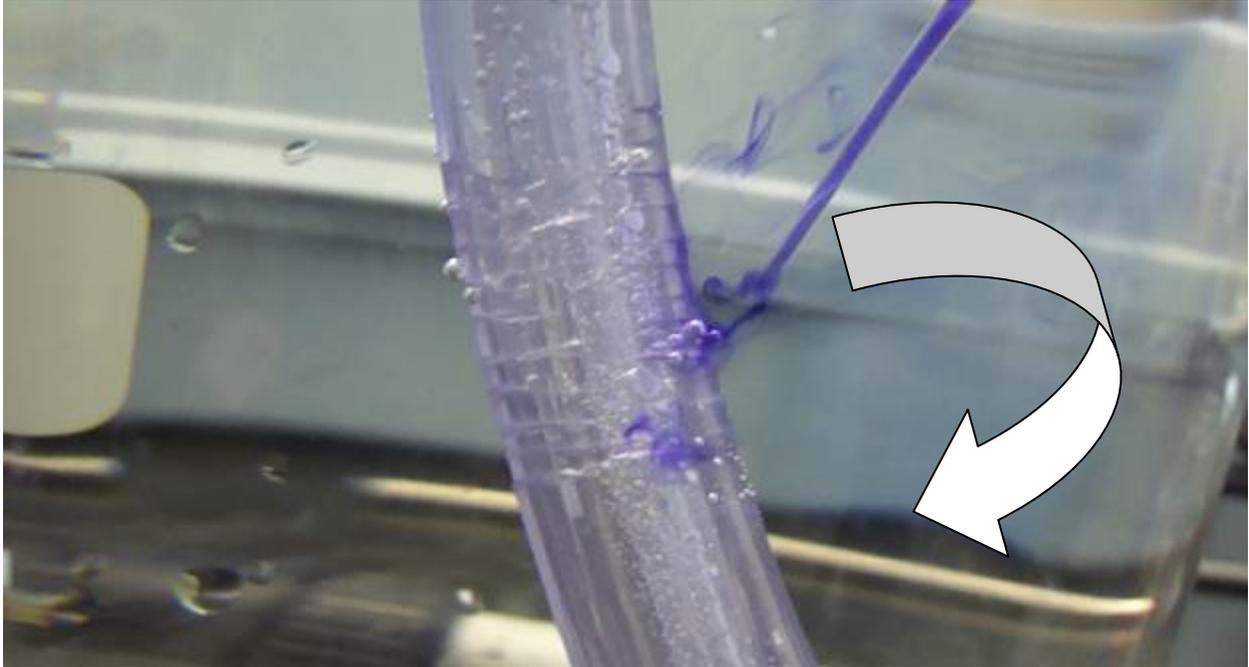


Figure 31. Close up of well screen testing using crystal violet dye.

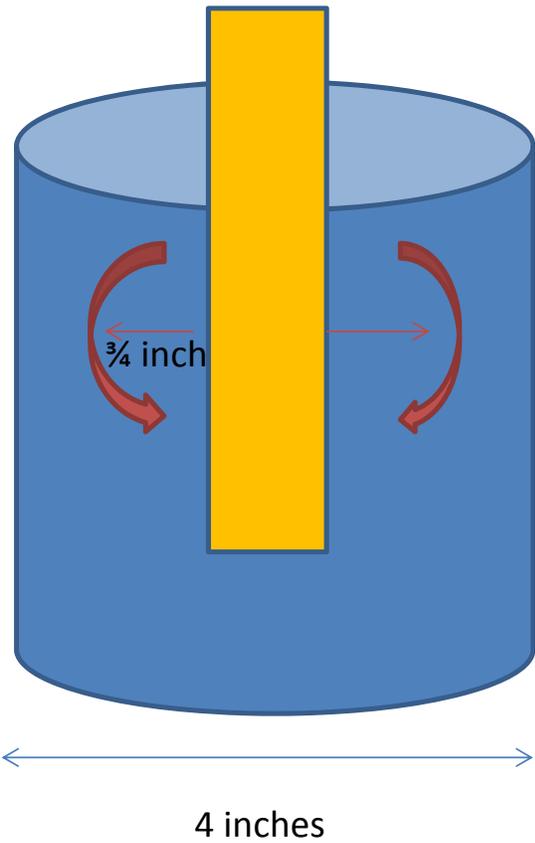


Figure 32. Schematic view of dye test circulation pattern.

The well was backfilled with a fine gravel aggregate medium to prevent the soil from plugging the well screen. The well tubing is attached to an air pump (Elite 799) to create the needed pressure of aeration. There is a three-way needle valve to control the air pressure delivered. This well is placed at 4 inches deep from the soil surface elevation. Once the well is installed, the aquarium is then saturated with water to permit air/water circulation in the soil.



Figure 33. Photograph of aquaria with groundwater circulation well.

The main target from this process is to convert the soluble iron (II) to insoluble iron(III) to reduce the dissolved iron levels in the well from the present value (0.03 – 47 mg/L) according to the monitoring well data from Townsend (2008) to the clean up target level, which is established as 0.3 mg/L (62-777FAC).

## 2.4 LABORATORY ANALYSES

In order to determine the iron levels in the soil samples and how much it may exceed the permissible limits, a spectrophotometric method was used after digestion following a modification of EPA Method 305B (APHA, AWWA, and WEF 2012), which is a hot block digestion of soil, sediment, tissue, or waste samples for total recoverable metals analysis.

First, the sample is homogenized by mixing with a small spade. Then a representative amount of sample is dried at 105°C in a drying oven. Sample weights for soil and sediment sample are reported on a dry weight basis. Therefore, the dry solids content was obtained in order to calculate the proper sample wet weight needed to obtain a final dry weight at least 0.5 g for digestion. First an appropriate amount (i.e. ~2 grams) of homogenized soil is placed on a pre-weighed aluminum dish. The weight is recorded to the nearest 0.001 g. Then the sample is heating in a drying oven at 105°C for at least 1 hour and then allowed to come to room temperature in a dessicator for at least one hour, before taking the final dry weight.

### 2.4.1 Digestion Procedure

After drying, a set of three subsamples (at least 0.5 g dry weight) is digested in 2.5 mL of 1:1 trace metal grade nitric acid ( $\text{HNO}_3$ ) added dropwise slowly to the soil samples in a test tube. All samples are refluxed in a heating block for 15 minutes at  $120^\circ\text{C}$ . Then they are allowed to return to room temperature for 30 minutes. At this point, another 2.5 mL of concentrated trace metal grade nitric acid ( $\text{HNO}_3$ ) is added and refluxed for 20 minutes at  $120^\circ\text{C}$  on the heating block with the caps on, and then for one additional hour at  $95^\circ\text{C}$  to concentrate the samples, making sure that the samples do not totally evaporate. Then the samples are allowed to come to room temperature with the addition of 1.0 mL of deionized water and 1.0 mL of 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). At this point the samples were returned to the hot plate for 90 minutes at  $95^\circ\text{C}$  or until effervesces subsides completely and then brought back to room temperature. After this acid digestion procedure, each subsample was reconstituted by rinsing with 10 mL of deionized water 3 times and inverting 8-10 times to mix the sample completely. Samples were filtered using Whatman  $0.45\ \mu\text{m}$  glass microfiber membranes with a vacuum filtration apparatus with plastic filter funnels. At this point, 1.0 M sodium hydroxide ( $\text{NaOH}$ ) was added dropwise (approximately 10-16 mL) to the samples to adjust the pH between 3-5 for the spectrophotometric method. Then the sample was diluted in the cuvette for spectroscopy.



Figure 34. Bench scale testing of soil and water iron levels.

### 2.4.2 Modified Phenanthroline Method for Determining Dissolved Ferrous Iron

Dissolved ferrous iron was analyzed using the Hach DR4000 UV/Vis spectrophotometer set to program 2165 Iron (FerroVer Method) at wavelength = 510 nm. Each aliquot was measured into a 10 mL cuvette. The contents of one FerroVer Iron Reagent Powder Pillow was added to the cuvette and swirled to mix. To each cuvette, 0.1 g of Iron RoVer reagent was added to counteract turbidity interference, as directed by the manufacturer for cases in which the turbidity of the sample created an interference. The samples turn orange-red in color when ferrous iron is present. All tests were zeroed using deionized water with an iron removal prefilter. After 3 minutes of reaction, the final reading of iron is read.

## 2.5 FEASIBILITY TESTING

For the first feasibility experiments, Boca Raton soil was used. Two aquaria were set up as described earlier. Then 3.56 grams of powdered iron (II) chloride tetrahydrate (FW=198.81212 g/mol) was first dissolved in 20 mL of concentrated HCl in 1.0 L of deionized water to make a 1000 mg/L stock solution. Then we added 400 mL of the stock solution to 3.6 L of canal water that was prefiltered using a 0.45-micron glass microfiber filter disk with plastic filter funnel. This was the spiked iron groundwater for the feasibility test, which was added to the aquaria containing the Boca Raton soil and groundwater circulation wells. The water was added using a perforated aluminum dish so as not to disturb the packed soil sample and the groundwater circulation well borehole during loading. Aquaria were loaded until saturation, and then the circulation air pump was started. After selected time intervals, groundwater samples were collected. Samples were collected using a 9 mm disposable borosilicate glass pipette with bulb and stored in a 40 mL IChem vial at pH <3 (using concentrated HCl). This same procedure was repeated using the Polk County soils as shown in Figure 35.



Figure 35. Aquarium testing setup with Polk County soil on the left and Boca Raton control soil on the right.

### 3. RESULTS AND DISCUSSION

This chapter explains in detail the results obtained from the experimental procedures that were described in the methodology section.

#### 3.1 RESULTS OF SOIL TESTING FOR IRON

Prior to experimentation, it was desired to determine the background iron concentrations in the Boca Raton soil control samples. The results of those experiments are summarized in Table 8. It is clear that the various samples collected are in the same order of magnitude as compared to historical samples in the area (Chen 1999). The measured concentration was generally low at between 180 - 300 mg/L

Table 8. Summary of soil iron concentrations in Boca Raton soils.

Sample Number	Fe(II) mg/kg
Sample #1	190
Sample #2	180
Sample #3	290
Sample #4	300
Average	239 ± 64
Chen 1999	330

The next set of measurements were made to determine the background iron concentrations in the soil samples collected from Polk County. The results of those experiments are summarized in Table 9. It is clear from the data that the soil collected from the southwest corner has the highest iron concentrations at around 2900 mg/kg, which is nearly 10 times the iron level detected in the Boca Raton soils. The next highest readings were from the northeast corner averaging 860 mg/kg, and the lowest readings came from the southeast corner (500 mg/kg for the May 11, 2011 sample and 660 mg/kg for the November 9, 2011 sample). For these tests, an iron reference calibration check sample was also analyzed. The value yielded 2.2% error, which is well within our expected tolerance for this method. The historical data for Polk County averaged 640 mg/kg (Chen et al. 1999) and nearly all of the samples measured were above this historical value.

Table 9. Summary of soil iron concentrations in Polk County soils.

Sample	Date	Fe(II) mg/L	Fe(II) mg/kg
SW.1	11/09/11	28	2640
SW.2	11/09/11	34	3160
SW.3	11/09/11	31	2900
NE.1	05/11/11	12	1120
NE.2	05/11/11	7.2	680
NE.3	05/11/11	8.4	790
SE.1	05/11/11	4.1	390
SE.2	05/11/11	5.8	550
SE.3	05/11/11	5.9	560
SEII.1	11/09/11	7.7	720
SEII.2	11/09/11	8.8	830
SEII.3	11/09/11	4.5	440

### 3.2 RESULTS OF GCW TESTING WITH BOCA RATON CONTROL SOILS

The first set of experiments used control soils collected in Boca Raton, FL. The initial concentration of iron in the soil was measured to be  $240 \pm 65$  mg/kg, which was similar to expected iron levels from historical records, which were found to average 300 mg/kg for this area. The results shown in Figure 36 demonstrate an extremely rapid conversion in the system resulting in a 1.0-log removal occurring between 2 – 24 hours. The experiment was continued beyond 72 hours, but iron removal from 72 - 264 hours of running time showed arbitrary results because of a difficulty with the iron speciation was found to occur at this stage. Independent certified lab results were also inconclusive. Due to the limitations of the phenanthroline colorimetric method and turbidity, pH, and stability issues in the matrix for analysis, the analytical results were brought into question.

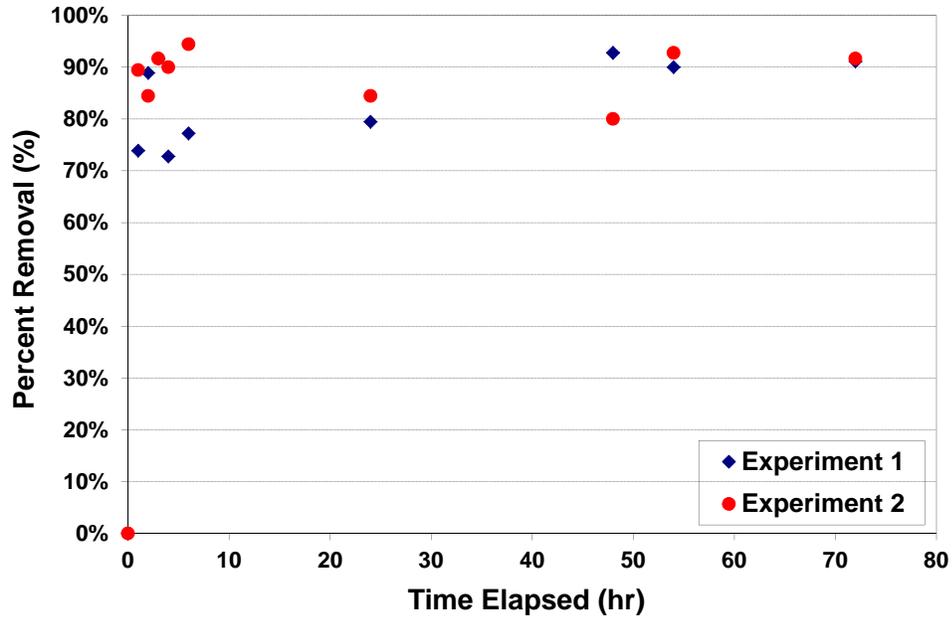


Figure 36. Results of GCW testing with Boca Raton control soil.

## **4. CONCLUSIONS AND RECOMMENDATIONS**

### **4.1 SUMMARY OF FINDINGS**

Soil and groundwater sample analyses have been obtained from existing landfill locations in Florida experiencing elevated levels of subsurface contamination, including Polk County and Broward County. A set of laboratory scale experiments have been developed to evaluate the potential process efficiency of selected engineering alternatives including the groundwater circulation well technology. The Laboratories for Engineered Environmental Solutions (Lab.EES) is equipped with the capability to conduct small scale subsurface testing using aquaria to simulate the reducing conditions underneath a landfill and evaluate in-situ management controls for attenuating the mobility of iron in the subsurface using groundwater circulation well technology. The conditions for the testing were refined, and testing for several weeks of treatment was conducted. Using a control soil collected in Boca Raton, FL, the groundwater circulation well was able to demonstrate an extremely rapid conversion of iron resulting in a 1.0-log removal occurring between 2 – 24 hours. The experiment was continued beyond 72 hours, but iron removal from 72 - 264 hours of running time showed arbitrary results because of a difficulty encountered with the iron speciation. After consulting with colleagues from the University of Florida, it was determined that the ferrous iron test needs to be modified and a total iron test using ICP-MS should be run for iron speciation in our samples. So we plan to develop and implement this protocol in year two. First, we will conduct method development tests to confirm results using spiked iron samples and Boca Raton soils. Then we will run the feasibility tests using the contaminated soils and groundwater samples to develop the appropriate treatment conditions for scale-up, including parameters such as air flow rate, radius of influence, treatment time, and process removal efficiency. The effects of soil variations will be investigated by comparison with Boca Raton soils and by collecting samples from various locations and times of the year.

### **4.2 RECOMMENDATIONS**

The following recommendations can be made from the completed study:

- Develop a workable testing protocol for iron speciation
- Determine the iron levels (total iron, ferrous and ferric) in the soil and groundwater for the sample sites already collected
- Run Polk County soils and Monarch Hill soils in the aquarium test for groundwater circulation well feasibility
- Develop design criteria for groundwater circulation wells for iron removal, specifically, determine the necessary reaction time, air flow rate, well design, soil conditions, etc.

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Ravi Kadambala  
Frederick Bloetscher  
Amede Dimonnay  
Allan Choate  
Juan Quiroz  
Dan Schauer  
Tom Peel  
Lee Martin  
Lee Casey  
Chad Fettrow  
James Leavor  
Marshall Seymore  
Charles Emery  
Dan Morrical  
John Booth  
Ray Schauer  
Richard Meyers  
Manuel Hernandez  
Marc Bruner  
Matt Zuccaro