

State University System of Florida
Florida Center for Solid and Hazardous Waste Management
PROJECT SUMMARY

TITLE: Soils underneath Florida Landfills and their Role in the Occurrence and Fate of Iron and Arsenic in Groundwater

COMPLETION DATE: July 31, 2007

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CONSULTANT: Helena Solo-Gabriele

AFFILIATION: University of Miami, Department of Civil, Environmental and Architectural Engineering

OBJECTIVES: The primary objectives of this project are to quantify the contribution that soils beneath landfills can make to iron in groundwater and to evaluate the ability of soils beneath C&D debris landfills to retain and hold arsenic against leaching. Elevated iron concentrations have been noted at a growing number of facilities in the state, both lined and unlined, but the source of the iron is unknown. This study will attempt to relate the chemical, physical, and hydrologic properties of these soils to their iron releasing potential. The second issue is the fate of As from CCA-treated wood at C&D debris landfills. The ability of soils to retain arsenic depends on the chemical and physical properties of the soil as well as the chemical properties of the surrounding solution, such as redox potential and presence of organic and inorganic ligands. These factors will be quantified to the extent possible and utilized in an existing transport model to evaluate the leaching potential of arsenic beneath C&D Landfills.

METHODOLOGY: An extensive literature survey will be conducted on this topic. The fundamental concepts of oxidation and reduction chemistry will be presented in a document that is aimed at audiences with little chemistry background. Laboratory experiments on various Florida soils will be conducted in the lab and the data generated will be used in a solute transport model to evaluate this issue. All of the information will be compiled into a comprehensive report.

RATIONALE: Several landfill sites in Florida are experiencing elevated iron concentrations in the groundwater wells. The iron rich soil is being hypothesized as source of iron. Similarly the disposal of arsenic treated wood in unlined C&D landfills is a concern for potential groundwater contamination due to arsenic (As) leaching from the wood. The two issues are interrelated since changes to the redox conditions can have a strong impact on the fate of both As and Fe. The fate of As is very much tied to chemistry of iron; iron soils have a strong ability to adsorb arsenic from water. The fact that reducing condition under landfills may cause iron to be released suggests that As will also be released and might be more mobile than expected based on soil properties alone.

ACCOMPLISHMENTS: The principal investigator's research area is the remediation of contaminated soils, waters, and aquifers. He is specialized in the colloidal and physical chemistry of soils, and the interaction of various soil pollutants with clays and clay minerals. Drs. Townsend and Solo-Gabriele's have conducted previous research for the Center on topics related to landfills, arsenic and the environment.

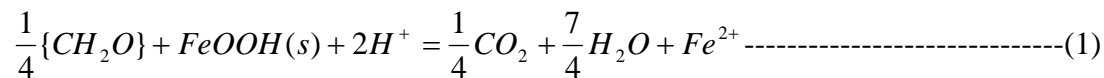
SOILS UNDERNEATH FLORIDA LANDFILLS AND THEIR ROLE IN THE OCCURRENCE AND FATE OF IRON AND ARSENIC IN GROUNDWATER

Introduction and Background

Two topics of current interest in Florida pertain to the role of soils underneath Florida landfills and their impact on groundwater quality: (1) the mobilization of naturally-occurring iron from soils under and around landfills and (2) the fate of arsenic from unlined C&D debris landfills.

Mobilization of naturally-occurring iron. The elevation of iron concentrations in groundwater monitoring wells at landfill sites have been noted at a growing number of facilities in the state, both lined and unlined. The hypothesis that has been proposed by many is that the source of this iron is not the landfill leachate, but the native soils beneath the landfill. It is speculated that the iron becomes mobilized as a result of changing pH and/or redox conditions in the groundwater underneath the landfill. In the case of unlined (C&D debris) disposal facilities, reducing conditions can develop as a result of leachate migration into the groundwater. In the case of lined landfills, the reducing conditions are thought to develop as a result of changes to the natural hydrology that result from the use of a liner and possibly from other site changes such as the installation of storm water control ponds.

Iron is a naturally-occurring element in many Florida soils. As a chemical species, iron can exist in the environment in many different forms. Iron in soils typically occurs in the more oxidized Fe^{+3} form as opposed to the Fe^{+2} form. In the oxidized form, the iron is relatively immobile and stays as part of the soil matrix. When reducing condition convert some of the oxidized iron to a more reduced form ($Fe^{+3} \rightarrow Fe^{+2}$), the iron may become liberated from the native soil matrix into groundwater (Pedersen et al. 2005; Benner et al. 2002; Zachara et al. 2001).



In the environment (including the groundwater environment), a number of biological reactions occur in which organic matter is consumed as part of the life cycle of different bacteria. These bacteria utilize a variety of different compounds as electron acceptors. Since some electron acceptors are energetically more favorable than others, some bacteria out compete other bacteria depending on which electron acceptors they use. For example, iron reducing bacteria (IRB) are known to out-compete sulfate reducing bacteria (SRB) (Lovley, 1991). This concept is a basic component of most water chemistry texts, and has been used to describe different zones that occur in groundwater underneath landfills that have been contaminated with leachate.

When the groundwater gets into reducing conditions with low concentration of oxygen and nitrate, Fe(III) is slowly released from soil and rocks to groundwater, resulting in increases in dissolved Fe(II) concentrations. Increasing Fe(II) concentrations in groundwater has also been reported by the Minnesota Pollution Control Agency (1999).

The fate of arsenic discharged from unlined C&D debris landfills. Current research in Florida suggests (Solo-Gabriele et al., 2003; Townsend et al., 2004; Townsend et al., 2005; Khan et al., 2006) that As will leach from CCA-treated wood and will be mobile in environments such as those found beneath C&D debris landfills. This has been demonstrated in landfill simulations,

indicating that As contamination in the groundwater at these sites will be a concern. Current groundwater monitoring data do not indicate any widespread problem, however. Preliminary groundwater pollutant transport modeling demonstrates that As may reach concentrations above the current groundwater cleanup target level in years to come, but that the results are highly dependent on the ability of the underlying soil to retard the As. The ability of the soil to retain As was cited by the Wood Science Council as the primary reason why CCA-treated wood disposal in unlined landfills is not a concern. However, soils in Florida vary widely in their ability to retain As, which depends heavily on their clay and metal oxide contents. Florida is dominated by soils with sandy textured surface horizons, which can at some sites; extend vertically downward to considerable depths. If a landfill happens to be situated over this type of material, the potential for As contamination of groundwater may be quite high. Recent studies of phosphate retention in Florida soils is of considerable importance in this regard since the chemistry of arsenate and phosphate are so similar. Leaching of phosphate in soil columns has documented the magnitude of the problem (Rhue et al., 2006) and a similar approach should prove useful for predicting leaching and groundwater contamination potential for As beneath landfills.

A second issue of considerable importance, especially with respect to As, is the effect of redox conditions that result from the presence of a landfill and the impact that these changes can have on the fate of As and Fe in groundwater. In well aerated systems, the thermodynamically stable form of As is As(V), arsenate. In this form it is chemically very similar to phosphate and adsorbs strongly to oxides of Fe and Al commonly found in soil and aquifer systems. In this form, it exhibits very little tendency to leach. However, unlike phosphate, arsenate readily undergoes reduction in anaerobic environments to the As(III) state, arsenite. Whereas As(V) is an anion in typical groundwater systems, As(III) is molecular at $\text{pH} < 9$. Because of its weak acid character, As(III) is weakly retained in soils and is, therefore, quite mobile in the environment. Thus the potential for groundwater contamination from As under reducing conditions is quite high. Studies of As movement in soils adjacent to old cattle dip vats have been observed As plumes well over 100 m from the vat in cases where a seasonally high water table created reducing conditions for several months out of the year. In drier sites or sites with more clay and metal oxides, movement was severely curtailed (Thomas, 1998). Arsenic dips have not been used in Florida since the 1940s so the extent of the plumes down gradient from these vats gives some indication of the rate at which arsenic is expected to move through our sandy soils.

Thomas (1998) placed As-contaminated soil in columns under reducing conditions and showed that both Fe and As leached from the columns. Little or no detectable Fe or As was leached from aerobic columns. There appeared to be no lag between the appearance of the Fe and that of the As. There was little or no detectable Al leaching from the columns, suggesting that most of the As that was mobilized from the soil was associated with Fe. The Fe was undoubtedly in the Fe(II) state, but the valence state of the As was not measured. However, it is believed that the As is initially released from the oxides as As(V) and is subsequently reduced to As(III) microbially.

As stated in previous paragraphs, Fe present in the system affects the dissolved As concentrations. Presence of sulfides in anaerobic conditions has also been shown to influence the Fe and As chemistry. O'Day et al. (2004) has shown that the ratio of reactive iron to sulfur in the systems controls the distribution of solid phases capable of removing arsenic from

solutions when conditions change from oxidized to reduced, the rate of which is influenced by microbial processes. Because of the difference in solubility of iron versus arsenic sulfides, precipitation of iron sulfide may remove sulfide from solution but not arsenic if precipitation rates are fast. Field et al. (2004) has also shown that the extent of As mobility will depend on concentration of sulfides generated from sulfate reduction. A few recent laboratory and field studies (Delemos et al., 2006; Keimowitz et al., 2005) have also shown a correlation between dissolved iron and arsenic concentrations under reducing conditions.

Objectives

The following specific project objectives are proposed.

1. Conduct a thorough literature search on issues pertaining to the role of naturally occurring soils under landfills in attenuating or immobilizing pollutants.
2. Conduct experimental research to test the hypothesis that iron in soils underneath landfills can be liberated by changes in oxidation reduction potential (ORP) and to relate the amount of iron released to chemical and physical properties of the soil.
3. Conduct experimental research to assess the potential for Florida soils to adsorb arsenic under both oxidizing and reducing conditions. Arsenic sorption coefficients will be measured for a range of Florida soils typical of those found at landfill sites in Florida.
4. Conduct more extensive modeling to assess the potential impact of As leaching from C&D debris disposal facilities on groundwater quality.

Research Team

Dr. R. Dean Rhue will serve as the principal investigator for the proposed research. Dr. Rhue's research area is the remediation of contaminated soils, waters, and aquifers; he is specialized in the colloidal and physical chemistry of soils, and the interaction of various soil pollutants with clays and clay minerals. A major research area for Dr. Rhue has been the fate and transport of arsenic from old cattle-dipping vats in Florida. Dr. Timothy Townsend will serve as a co-principal investigator and Dr. Helena Solo-Gabriele will serve as a project advisor. Drs. Townsend and Solo-Gabriele have been investigating the impact of arsenic in CCA-treated wood on the Florida environment for 10 years. Dr. Townsend has also been involved in several projects related to iron mobilization at Florida landfills.

Methods

The methodology is broken down into tasks to meet the objectives described above.

Task 1.

A review of existing literature on the issues pertaining to the role of naturally occurring soil underneath landfills will be conducted. Target literature will include peer reviewed journals, solid waste industry publications, government reports, and consultant engineering reports. The University of Florida and the University of Miami library systems will be utilized for this search, as will the World Wide Web. The literature search will focus on the role of naturally occurring soils to both attenuate and mobilize pollutants.

Task 2.

Samples of representative Florida soils will be collected, including samples from existing landfill locations in the state where the problem of high iron concentrations in groundwater is occurring. A set of laboratory experiments will be designed to measure the amount of iron that these soils can liberate under reducing conditions similar to that would take place under a landfill. The soils will be leached in batch leaching settings under controlled reducing conditions. Zero head space, airtight conditions will be created for biological reduction of iron, small amount of cellulose will be added to the soil sample to provide ample electron donor for the microbial reactions. Few samples will also be leached with reducing conditions controlled using reducing agents (e.g., sodium thiosulfate). The amount of iron released over time will be measured. Chemical parameters to be measured will include total Fe, Fe^{+2} , total Mn, pH, and ORP in the leachate. Exchangeable fraction of iron in the soil sample (after leaching tests) will be measured using the 0.5N HCl as the extraction fluid. Measures of extractable soil iron will be made using extractants such as ammonium oxalate (pH 3) and citrate-dithionate to determine if the amount of iron released can be predicted from measures of extractable iron as has been shown by van Bodegom et al. (2003). Dissolved iron concentrations in these experiments will be compared with actual groundwater iron concentrations for similar soils at landfill to determine if iron concentrations in the groundwater are likely to be coming from the soil or if other sources are likely. Samples and data from landfill sites will be gathered with assistance from FDEP, the landfill operators, and the consulting engineers involved at these sites.

Task 3.

Some of the soils used in this task may be the same as those in Task 2, but will be more representative of those found beneath Florida C&D debris landfills. A Phosphate model developed and used by the principal investigator in the past will be used for predicting As(V) mobility in different soil types. Adsorption coefficients for As (III) will be determined for these soils using accepted procedures from the literature. The retardation of arsenic movement will be measured using small columns using an anoxic, N_2 purged C&D debris leachate (and DI water) containing As (III). The PI's laboratory has designed and performed similar column experiments using soils from cattle dip vat sites; a strong correlation between the release of Fe and As were observed when a soil column was leached under reducing conditions (Thomas, 1998). Where possible, arsenic concentrations in the leachate will be speciated as As(V) and As(III) to determine is transformations are occurring in the column with respect to the form of arsenic.

Task 4.

A solute transport model, Migration of Organic/Inorganic Chemicals (MYGRT), will be used to assess the arsenic concentrations expected to occur down gradient of a hypothetical source (C&D landfill). MYGRT simulates a single contaminant, generated from a surface source and migrating downward through the unsaturated soil layer, mixing with the underlying groundwater, and then migrating horizontally down gradient through the aquifer. The software incorporates the processes of advection, dispersion, retardation, and decay. The source (in this case, leachate concentration) is defined as a function of time. After the soil and chemical parameters of the unsaturated/saturated layers are input, the model predicts the contaminant concentration as a function of time at any specified location along its path. The soil parameters used in the model runs will be those determined in Task 3 above. The input source leachate term will be based on

the work previously conducted by Drs. Solo-Gabriele and Townsend on As leaching from C&D debris landfills.

The MYGRT program is a collection of 22 analytical models. All of these models are based on analytical solutions to mass transport equations using the integral transform technique. The cases of spatial averaging (e.g., well screen averages) and zero dispersion is also solved. The integral transform method starts with the partial differential equation, boundary conditions, and initial conditions of a transport problem and proceeds to an exact solution of it. The aquifer can have a finite or semi-infinite thickness and one, two, or three dimensions can be simulated in the saturated zone. Model input information can be subdivided into four broad categories: source definition and description, unsaturated zone characteristics, saturated zone characteristics, and solute plume properties.

Timeline/Milestones

The project is proposed to begin on August 1, 2006 and to end on July 31, 2007, a total of 12 months. The following timeline is proposed.

The timeline for the project is broken down as follows:

	A	S	O	N	D	J	F	M	A	M	J	J
Project Planning and Kickoff	X											
Task 1. Literature Search	X	X	X									
Task 2. Iron experiments			X	X	X	X	X	X	X			
Task 3. Arsenic experiments			X	X	X	X	X	X	X			
Task 4. Modeling							X	X	X	X	X	
TAG Meeting			X							X		
Final Report											X	X

Benefits

The issues proposed for research are both of very current importance to landfill operators and the regulatory community in Florida. Both of these parties and the environmental community as a whole will benefit by better understanding the science behind the issues. The data derived will be valuable for future rulemaking activities and policy making.

Deliverables

The deliverables will include periodic progress reports, a final project report, and a project website. The investigators will also hold two technical advisory group meetings to present the plans and results for the research. The researchers will also make themselves available to present at FDEP workshops and meetings.

Possible Follow-up

Possible follow-up research to this project could include:

- Field experiment.
- Extensive Geochemical modeling.

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