SUMMARY: SUSTAINABLE MANAGEMENT OF POLLUTANTS UNDERNEATH LANDFILLS

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Elevated levels of iron have been observed in groundwater and soils around municipal solid waste landfills in Florida. The levels have been attributed to reductive dissolution of the native chemistry in the soil perhaps caused by a shadowing effect of the landfill liner, which inhibits the reaeration of the shallow aquifer beneath a properly lined landfill. In this study, the research team will refine a preliminary list of potential engineering management alternatives for controlling the release of contaminants in-situ and conduct laboratory experiments on management methods for dealing with this issue. In a previous research grant, "*Management of subsurface reductive dissolution underneath landfills*," funded by the Hinkley Center, an innovative groundwater circulation well technology was investigated for control of iron releases in-situ.

The source of the elevated iron contaminations has not been verified yet, but is potentially caused by either one or both of the following mechanisms: 1) direct release of iron from the municipal solid waste leachate, or 2) naturally-occurring iron mobilized from the soil due to changes in soil chemistry or local hydrology. It is clear from our previous literature review as part of the previous project, "*Management of subsurface reductive dissolution underneath landfills*," 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 microbially-mediated, 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 (CO_2 + CH_4) 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.

Regardless of the source of the elevated iron, the next step is to develop an effective strategy for remediation. The research team will focus on identifying viable engineering alternatives that will minimize the potential disturbance to the system, limit treatment costs, and produce the most effective results. 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; and 3) to conduct laboratory experiments on methods for iron and co-contaminant removal from groundwater at landfill impacted sites.

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PROGRESS REPORT
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Project Title: Sustainable Management of Pollutants Underneath Landfills
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Progress to Date:

- **Task 1**. **Conduct a literature search of key parameters governing reductive dissolution**. Ahmed Al Basri is conducting a review of the historical data from landfills experiencing iron dissolution problems as well as the known causes of reductive dissolution such as: biogeochemical, microbial, hydrologic, soil chemistry (pH, Eh, iron sequestration, iron mobility), and leachate pollution. In addition, the literature review covers temperature effects, changes in local hydrologic conditions, landfill gas effects. Al Basri is also investigating literature on the co-liberation of toxic metals with iron to evaluate the potential problem of arsenic levels. From the literature review, it was determined that many landfills can create an effect that increases iron mobility by blocking the oxygen from percolating into the soil or by releasing high levels of organic seepage and iron from leaks in the liner. These releases can motivate the local microbial fauna to increase their consumption of the existing oxygen and increase the redox potential. This would have the effect of mobilizing the iron downstream some short distance. However, there are still unpredictable factors that play a vital role in increasing the redox potential and the lack of knowledge of the specific microbiological profile of the soil underneath the landfill make it very difficult to attribute the reductive dissolution to a specific cause.

  Task 2. Refine a list of engineering alternatives for managing elevated iron levels. Ahmed Al Basri is continuing his literature review based on the previous work done by former graduate students Richard Reichenbach and André McBarnette. Mr. Al Basri has focused his search on the literature review of in-situ management methods for iron mitigation that are currently available. These include but are not limited to: aeration, oxidation agents, chelation/iron sequestration, pH control, bioprecipitation/bioremediation, zero valent iron, trench fill, ion exchange, advanced oxidation, recirculating well technology, and others like adsorptive filtration. These alternatives will be evaluated for process efficiency, ease of operation, minimal site disturbance, and environmental considerations. Iron can be treated in soil by different methods depending on the form of the iron in addition to the cause of the elevated iron. For example, if the main reason for the elevated iron levels is determined to be microbial in nature, then disinfection can be a suitable treatment process. Other techniques include but are not limited to: chelation, pH control, permeable reactive barriers, advanced oxidation, and aeration. Of those, in-situ aeration via a groundwater circulation well seems to be the most promising technique as the iron contamination is generally found to occur in a limited shallow area with the groundwater less than 13 meter deep in most cases.

Task 3. Conduct laboratory experiments on selected treatment technologies for managing iron dissolution. The Laboratories for Engineered Environmental Solutions (Lab.EES) is equipped with the capability to conduct laboratory-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 (see **Error! Reference source not found.**). In the previous project, "*Management of subsurface reductive dissolution underneath landfills,*" the groundwater circulation well technology was the focus of preliminary investigations. The conditions for the testing were refined, and testing for several weeks of treatment was conducted. However, a major problem arose with the protocol for quantifying the concentration of iron in the well. 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 use this protocol in task 3. Currently, feasibility tests are being conducted using the contaminated soils and groundwater samples collected in year one to develop the appropriate treatment conditions for scale-up, including parameters such as: aeration conditions, mixing, radius of influence, depth, drawdown, hydraulic grade line, hydraulic conductivity, porosity, and process removal efficiency at the end of the treatment time of several weeks. The effects of soil variations will be investigated by comparison with Boca Raton soils and by collecting samples from various locations at the Polk County landfill at different times of the year. Initial tests have been conducted to determine the process removal using soil samples from Boca Raton and Polk County. It was found that both of the soil types have an aggressive capacity to absorb the spiked iron which was prepared using an iron reference material (1000 mg/L $FeCl_3$ dissolved in HCl). So it was decided that each of the soil aquaria should be spiked continuously with iron solution until equilibrium is reached in each tank with a stable aqueous concentration. For two of the four aquaria, the aqueous iron levels reached a satisfactory level of stability to allow initiation of testing. The other two are still being monitored. The first 2 aquaria contain soils collected on 11/09/2011 from the southeast (aquarium 1) and southwest (aquarium 2) corner of the Polk County landfill site, while the other two under observation were both collected in 05/11/2011 from the southeast (aquarium 3) and northeast (aquarium 4) corner of the Polk County landfill.

The aquaria were initially filled with soil that had been sundried for one week and then spiked with surface water containing 100 mg/L of total iron. The soil and water samples were left to equilibrate to a constant soil moisture content and aqueous iron level. This process took nearly 4 weeks. Then the samples were re-spiked with aqueous iron until the iron levels reached steady state. The results of iron saturation testing are found in Figures 1-4. In each aquarium, the ratio of the measured aqueous iron concentration versus the cumulative mass of iron added is plotted. When the ratio levels off or when the slope of the line is near to zero, it is determined that saturation has been reached.

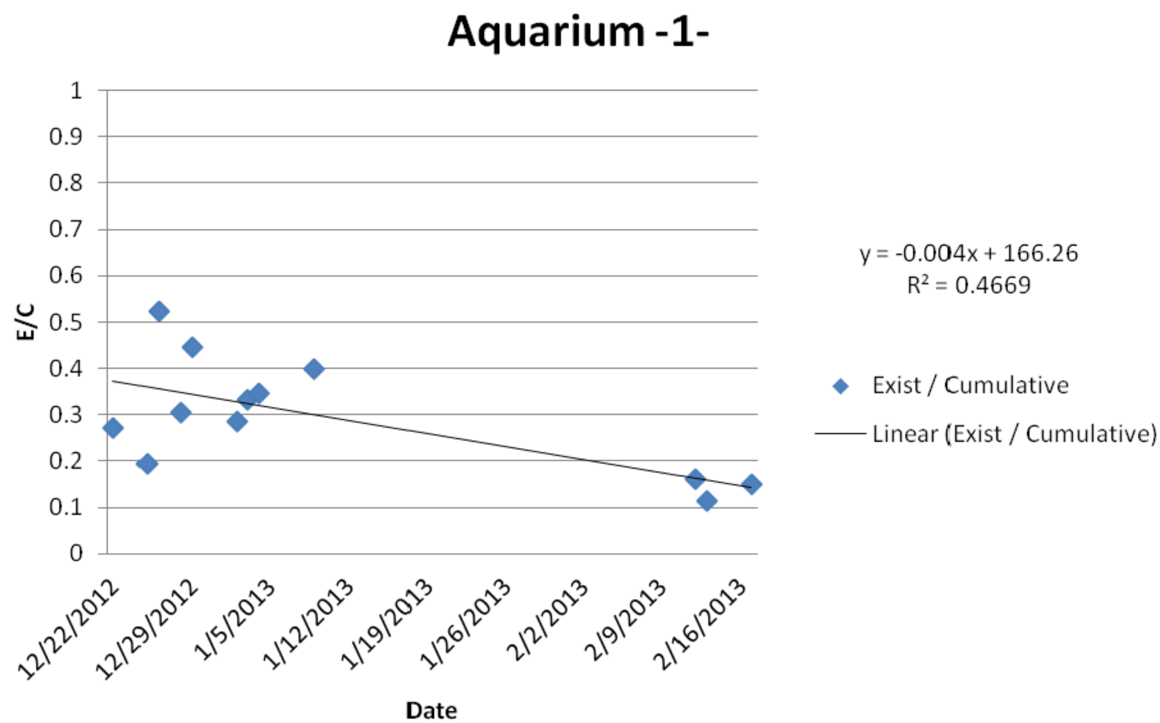

Figure 1. Results of saturation testing in aquarium 1 (Soil Sample: SE 11/09/2011).

The trend line shows that the gradient is less than 0.5% (slope = 0.4%) for the tested sample (Aquarium 1), so this sample was selected for initiation of groundwater circulation well feasibility testing.

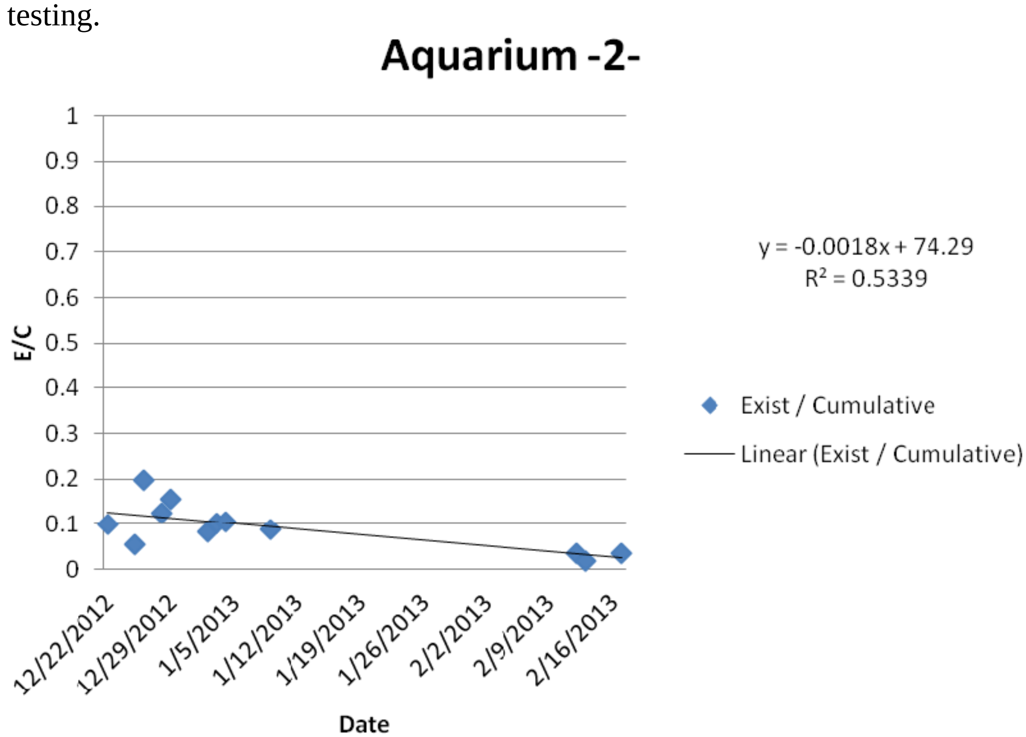

Figure 2. Results of saturation testing in aquarium 2 (Soil Sample: SW 11/09/2011).

The second aquarium set of data shows a trend line with a gradient is less than 0.5% (slope = 0.18%), so this sample was also selected for initiation of groundwater circulation well feasibility testing.

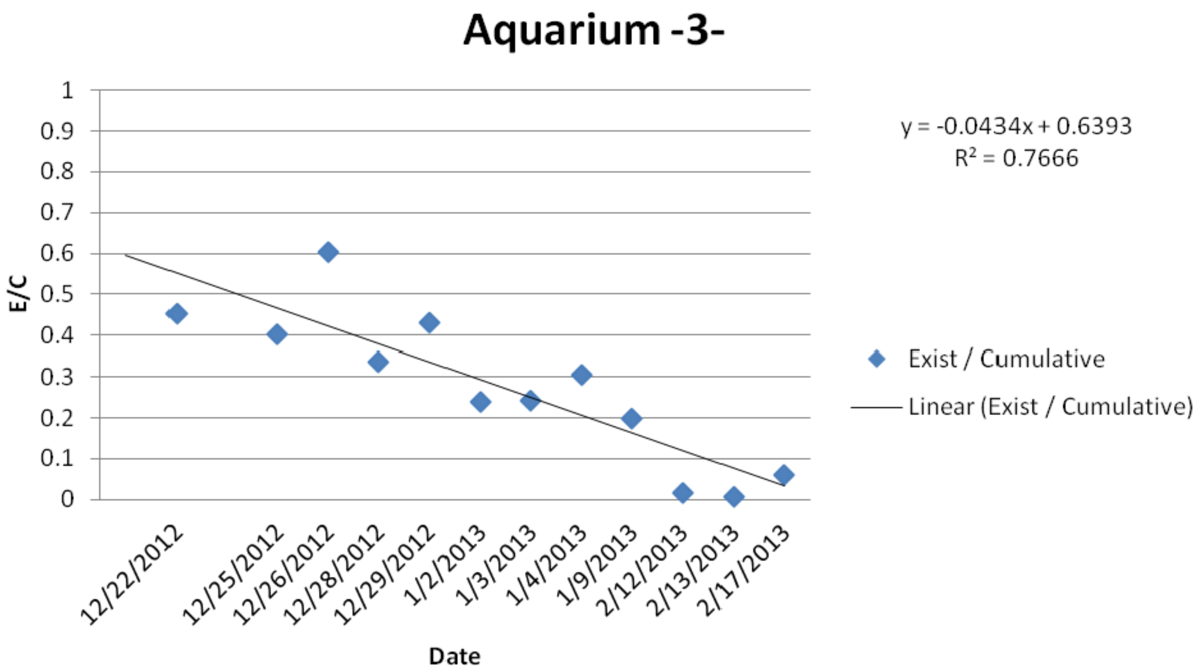

Figure 3. Results of saturation testing in aquarium 3 (Soil Sample: SE 05/11/2011).

The third Sample (Aquarium 3) shows a 4.3% gradient, which exceeds our 0.5% criterion, so it is still being spiked and monitored.

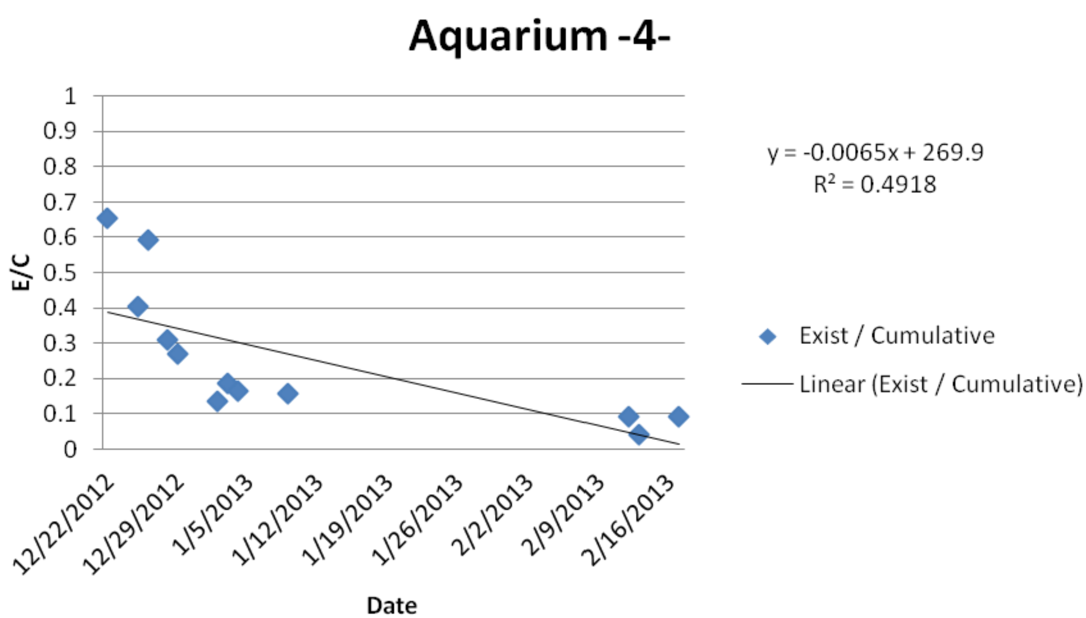

Figure 4. Results of saturation testing in aquarium 4 (Soil Sample: NE 05/11/2011).

Aquaruim 4 has a gradient of 0.65%, which exceeds our criterion, so it is also continuing to be spiked and monitored.

Aquarium 1 and Aquarium 2 were started at the same time. Water samples were collected from the groundwater circulation well and tested for total iron at periodic time intervals to determine the degredation kinetics of the aeration process. Aquarium 1 showed rapid iron removal (Figure 5).

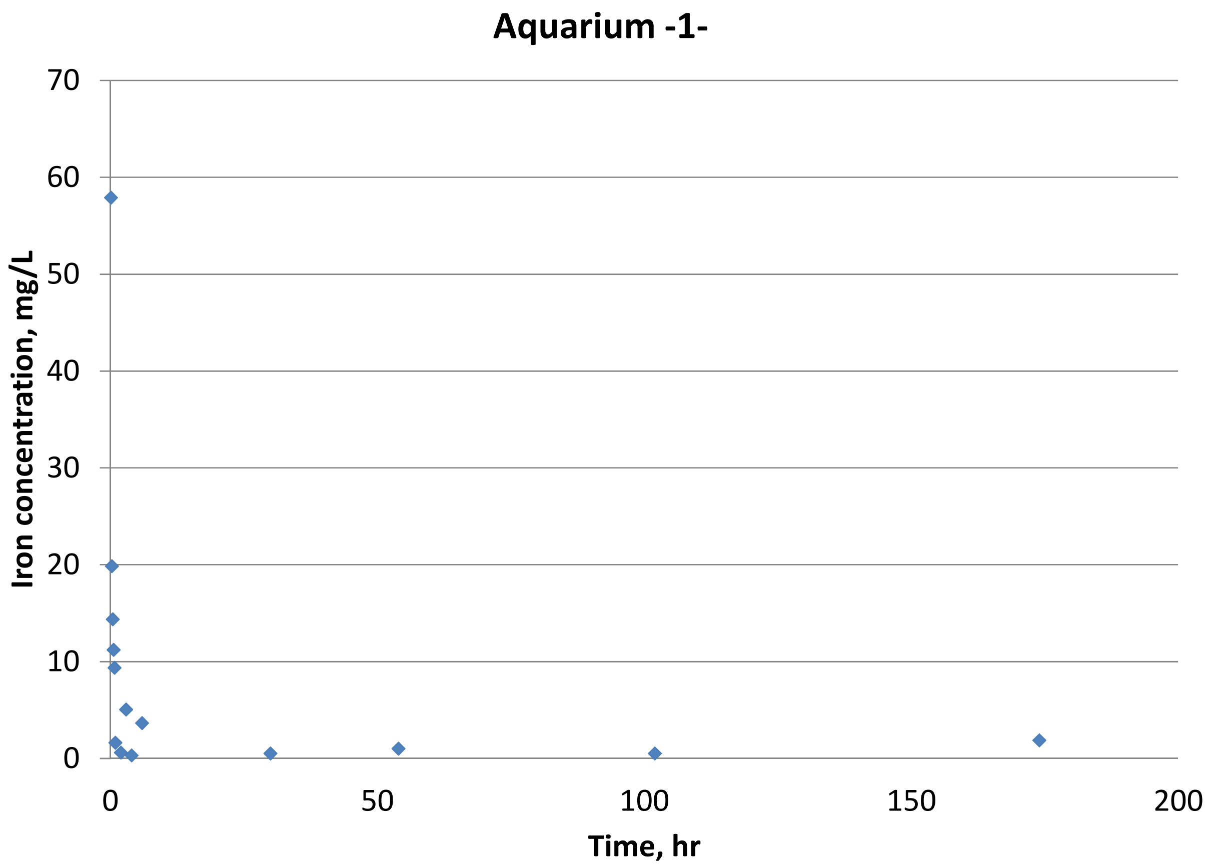

Figure 5. Results of iron removal testing using a groundwater circulation well in aquarium 1 (Soil Sample: SE 11/09/2011).

The removal of iron occurred rapidly in the first hour of operating the well, which is the same results obtained for the previous experment run in October 2012, but the effects of soil adsorption of iron made the reason for the observed removal unclear at that time. This experiment confirms the rapid removal of iron using this process. The initial first order iron decay rate constant is 2.4 hr^{-1} (r^2 = 0.89) for the first 2 hours of treatment.

The second sample showed similar results as the first aquarium but showed unstable iron readings from the beginning of running the experment because the initial iron concentrations in the aqueous phase were so low (17 mg/L compared to 55 mg/L for Aquarium 1). The initial first order iron decay rate constant is only 0.4 hr^{-1} for the first 2 hours of treatment, although the first order model does not show a good fit (r^2 = 0.06) because of the very low starting concentration.

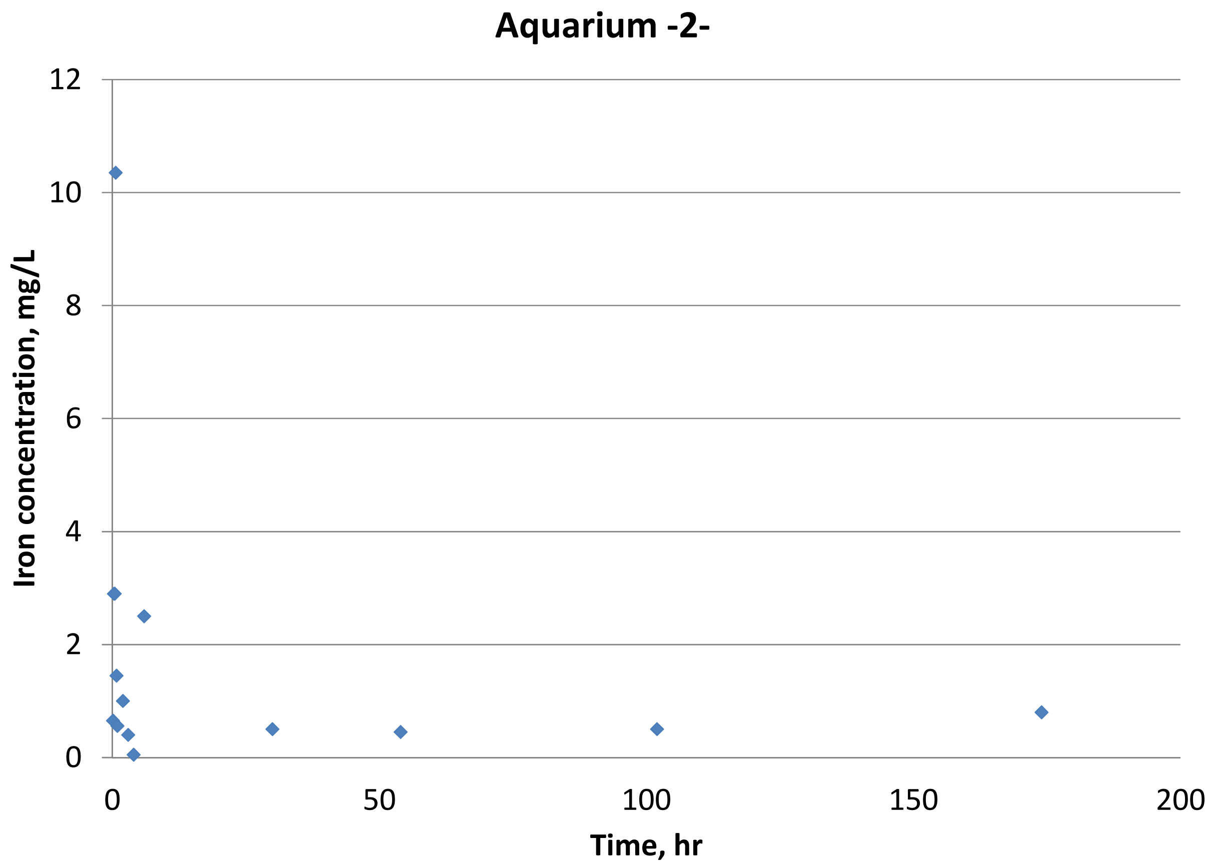

Figure 6. Results of iron removal testing using a groundwater circulation well in aquarium 1 (Soil Sample: SW 11/09/2011).

The other two aquaria have not been run to date and are continuing the spiking and monitoring process.

- **TASK 4. Develop final recommendations**. Using the data developed in Tasks 1-3, an assessment will be conducted to evaluate the recommended management approaches to deal with reductive dissolution issues underneath Florida landfills. If the recirculating aeration wells tested in task 3 are found to be successful in ameliorating the iron dissolution issue (with the goal of lowering the iron concentration to below 0.3 mg/L), the process will be evaluated for a preliminary cost analysis and a preliminary model for scale-up will be developed. 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.). No work has been initiated on this to date.

- **TASK 5. Prepare publication materials**. Interim and final reports will be developed and submitted. A plan will be developed for follow-up work based on comments from reviews of same. Furthermore, a scholarly publication will be developed, including but not limited to, a poster and a conference paper.

Research planned for the upcoming months:

- Complete the preliminary literature review.
- Complete aquarium-scale preliminary testing.
- Develop design model and cost estimates.