STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

SRS *In Situ* Bioremediation Techniques and F-area Post Molasses Injection Analysis

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

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FLORIDA INTERNATIONAL UNIVERSITY

ABSTRACT

There are many contaminants present in the surface and subsurface of sites that were involved with weapons manufacturing and atomic energy related activities, such as the Savannah River Site. Therefore, developing a cost effective bioremediation technique for such sites is of vital importance for the well-being of the natural systems and human communities around it. This report will explore some of the techniques that are in the process of being tested and implemented at the Savannah River Site. These include humate addition to a copper contaminated creek to restore the natural system of the creek, humate addition to the underground water system to change the mineralogy of the subsurface and achieve the attenuation of radionuclides in the groundwater, and lastly, molasses addition to create a reduced zone that would induce the immobilization of uranium present in the groundwater. Furthermore, it will explore the importance of long term effectiveness and how monitoring is an important part of developing these technologies because it demonstrates the viability of the technology as a long term solution for *in situ* remediation of the site.

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1. INTRODUCTION

Groundwater contamination at the Savannah River Site is a cause of major concern. Especially considering the proximity of the site to the Savannah River, the main water source for many people in South Carolina, it is not surprising that it is the target of major remediation efforts. *In situ* bioremediation technologies are being researched, developed and implemented in several groundwater plumes in hopes of achieving a cost effective way of dealing with the underground contamination. The main goal is to accomplish long term remediation without degrading the overall water quality or drastically changing the ecosystem of the region. *In situ* remediation involves treating the contaminants in place at the site, meaning without transporting it out of the ground. The main factors that influence *in situ* remediation, and therefore are important while considering the development of a new technology or the implementation of an existing one, are the equilibrium relationships between contaminant phases, factors controlling biological and geochemical processes, contaminant characteristics affecting reductive and oxidative conversion parameters and chemical and biological availability. The technologies can be implemented either at the source, along the pathway or at the receptor of the contamination. Sometimes, as it is with some of the technologies discussed in this report, bioremediation and physical technologies are combined. For example, pump and treat technologies are used to introduce nutrients or so-substrates to stimulate bioremediation. In this report, several *in situ* remediation techniques are discussed, such as the addition of humate sources to a contaminated creek and to a contaminated groundwater plume, and the addition of molasses to a contaminated groundwater plume. The injections of a foreign substance to any ecosystem will cause changes in the mineralogy and water chemistry of said ecosystem. Some of these changes are desired, such as the reduction of uranium from aqueous U(VI) to insoluble U(IV). In this case, the uranium is sequestered in mineral form underground which prevents it from being transported with the groundwater flow, stopping any further spread of the contamination. Other changes, however, might have negative impacts and careful monitoring should be made in order to ensure that the positive benefits outweigh the negatives.

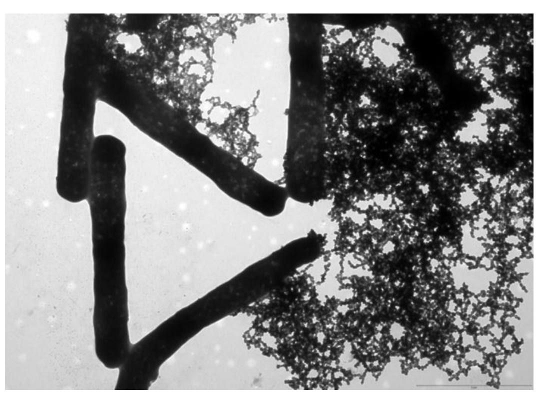

Figure 1. Uranium reduction (image from ARCADIS presentation).

$$UO_2^{2+}{}_{(aq)} + 2e^- = UO_{2(c)}$$

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2013, a DOE Fellow intern, Valentina Padilla, spent 10 weeks doing a summer internship at Savannah River National Laboratory located in Aiken, South Carolina, under the supervision and guidance of Dr. Miles Denham. The intern was given the opportunity to collaborate in several sampling events where she learned different sampling methods and techniques. These sampling events are a vital part of ongoing research on different *in situ* remediation techniques currently being implemented at the site. She concentrated her research on the F-area of the site, where molasses injections were made by ARCADIS in previous years with the purpose of creating a reduced zone that would facilitate the bioremediation of U(VI) and other contaminants. She analyzed the wells and developed a depth profile of the area that gives valuable information on the current conditions and what changes have occurred in the soil and groundwater since the original molasses injections occurred. To further contribute to the research, Valentina also performed a microcosm study using core samples from the F-area that is intended to provide useful information about the mineralogical changes caused by molasses addition to the subsoil.

3. SITE HISTORY

Site Overview

The Savannah River Site (SRS) is located in South Carolina adjacent to the Savannah River. The site was built during the 1950s to refine nuclear materials, mainly tritium and plutonium-239, for the nation's defense during the cold war period. It covers an extensive area of 310 square miles (800 km^2) and is one of the main employers for the area, employing over 10,000 people. Five reactors were built on the site; the reactors produced the nuclear materials by irradiating target materials with neutrons. Other facilities on the site included two chemical separation plants, a heavy water extraction plant, a nuclear fuel and target fabrication facility and waste management facilities. The production of nuclear material was discontinued in 1988. However, the site has remained operational ever since with non-defense related activities such as providing nuclear material for the space program, and contributed to medical, industrial and research efforts.

Figure 2. Savannah River Site.

Present Condition

The Savannah River Site is currently owned by the U.S Department of Energy (DOE) and was placed on EPA's National Priority List (NPL) of contaminated sites in 1989. At this time, its major focus is the cleanup activities related to work done in the past for the nation's nuclear buildup. The Savannah River National Laboratory was created in 1951 to provide research and development support for the startup operation of the Savannah River Site. It was certified as a national laboratory on May 7, 2004, and it currently plays a vital role in the country's environmental management, specifically in the areas of cleanup technologies and hazardous materials disposition, and dealing with the cold war legacy. There has been a great deal of progress in the cleanup efforts since the 1980s;

however, there is a lot more work left to be done. The main concern at the site are the high-level-waste tanks, which store highly radioactive liquid waste and are considered by the DOE and the South Carolina Health and Environmental Control (SCDHEC) as “the greatest human health risk in South Carolina.” The underground contamination, however, is related to the large volume of radiological waste created by previous operations of the nuclear reactors and their support facilities. Although most of the plumes are currently being addressed with different remediation technologies, more research is needed to achieve a cost effective way of dealing with the contamination. It is predicted that the cleanup process will take several more decades to be completed.

4. SAMPLING EVENT I
H12 Outfall Study: Monitoring the Effectiveness of Humate for Copper Detoxification

This project is the implementation of using humate as a remedial method for mitigating copper toxicity in surface water. The goal is that the humate addition will reestablish the natural food chain of the creek. Surface water samples were collected in the H-area of the Savannah River Site from the H-12 Outfall for customized chronic toxicity tests and analysis of the biotic ligand model (BLM) parameters. A YSI probe model 6820 was used to collect basic parameters from the creek such as pH, dissolved oxygen (DO), temperature, specific conductivity and oxidation-reduction potential (ORP). Samples were collected from the middle of the creek using a pump system powered by a generator. These results will provide technical information that will validate the efficiency of the humate detoxification technology.

Figure 3. YSI Model 6820.

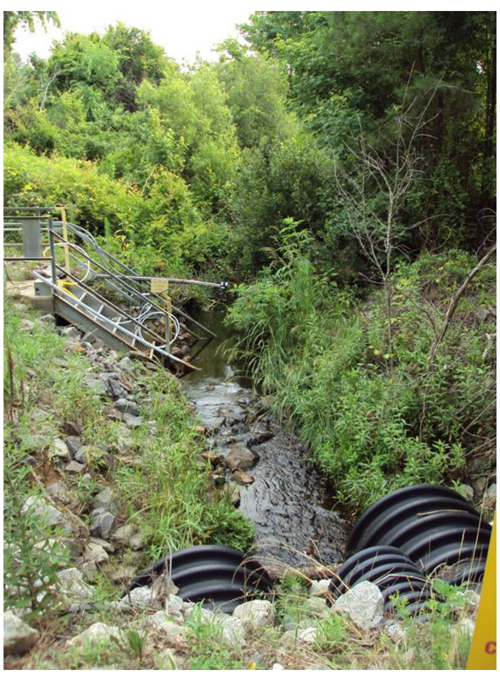

Figure 4. H12 copper contaminated creek.

Figure 5. H12 sampling.

5. SAMPLING EVENT II
Post Injection Monitoring: Field Test of Humate as an Enhanced Attenuation Amendment for Radionuclides in Groundwater

Humate injections, consisting of approximately 2000 liters of a humate solution, were made earlier this year into a well downgradient of the F-area seepage basins. The goal of the technology is for the humate addition to enhance sorption of the existing uranium and other radionuclides. The main contaminant targets are uranium, strontium and iodine. Three wells were sampled during this sampling event, the ninth sampling event after the original humate injections two months ago. The depth to water and other water parameters were measured and recorded using a YSI probe. The water was then purged, to avoid the collection of any stagnant water, and samples were taken.

From the monitoring of the water color and pH, there is indication that most of the humate has been flushed out of the subsurface system, but some still remains. More monitoring is still necessary to corroborate the hypothesis that the remaining humate will absorb into aquifer minerals and will enhance sorption of the contaminants of interest.

Figure 6. Humate injection site.

6. F-AREA DEPTH PROFILE ANALYSIS

The ARCADIS demonstration at the F-area is an implementation of enhanced anaerobic reductive precipitation (EARP) that targets metals and radionuclide contaminants. It is also known as *in situ* reactive zones (IRZs), and they work by introducing an innocuous food-grade carbon substrate, in this case molasses, to the groundwater advective flow distribution. This addition of molasses produces anaerobic conditions through microbial action. Because uranium is a redox-sensitive radionuclide, its mobility is dramatically affected by the redox status of the subsoil. The treatment then works by establishing a pH gradient that minimizes the mobility of uranium by reducing the aqueous U(IV) present in the groundwater into the insoluble U(IV) form. Although this report focuses on uranium, other key contaminants are technetium and nitrate, which are also targeted by this technology. Below is a diagram of the conceptual implementation of the ARCADIS technology at a site with an existing uranium pump and treat system. The injections of molasses were performed monthly from April 2010 through January 2011, and the groundwater chemistry and contaminant concentrations were monitored afterwards for several months.

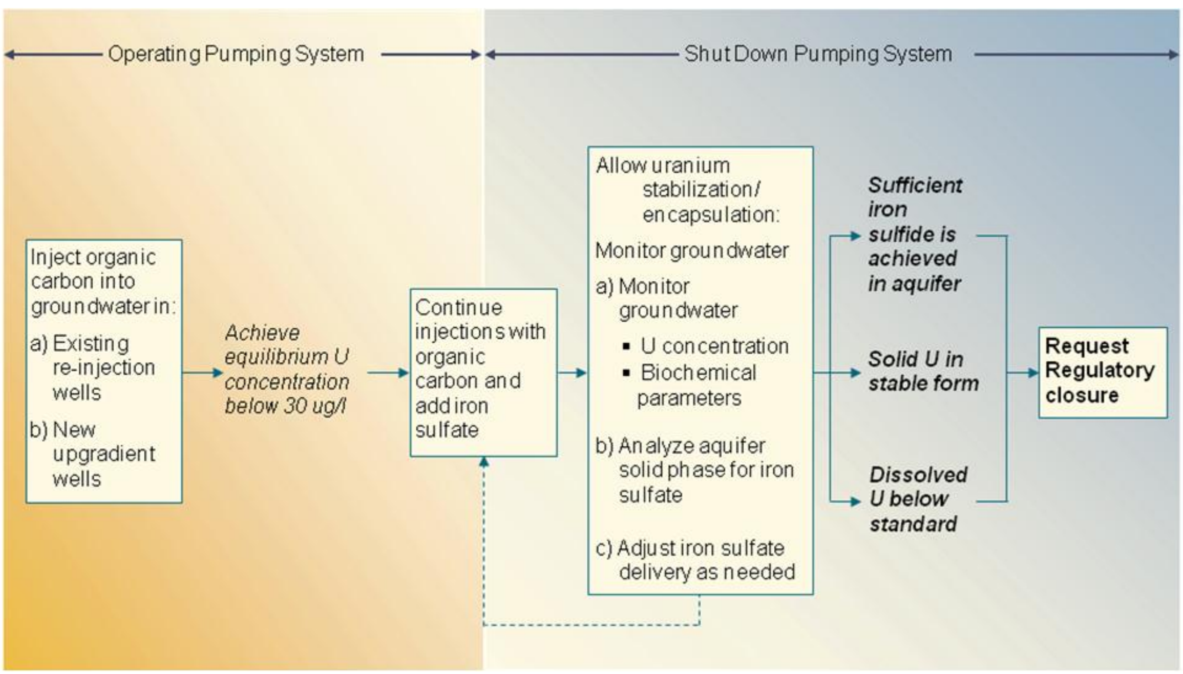

Figure 7. Implementation of ARCADIS technology at site with uranium pump and treat system.

One of the main challenges with the technology, however, is that it is difficult to demonstrate the long term effectiveness of the technology after the molasses of injections have stopped and the uranium levels in the water have been lowered to standards (15 pCi/L or 30 ug/L). In other words, since the natural tendency of uranium is to be in the aqueous form, it is unknown if it will stay in the insoluble form long enough for the technology to be considered successful and for it to be a cost effective way of dealing with the uranium contamination.

Since the project was left unfunded after several months following the molasses injections, the period where re-oxidation occurred and what effect this had on reduced uranium was left unmonitored. Without monitoring data during this critical period, the longevity of the project could not be proven.

Figure 9. F Area at SRS.

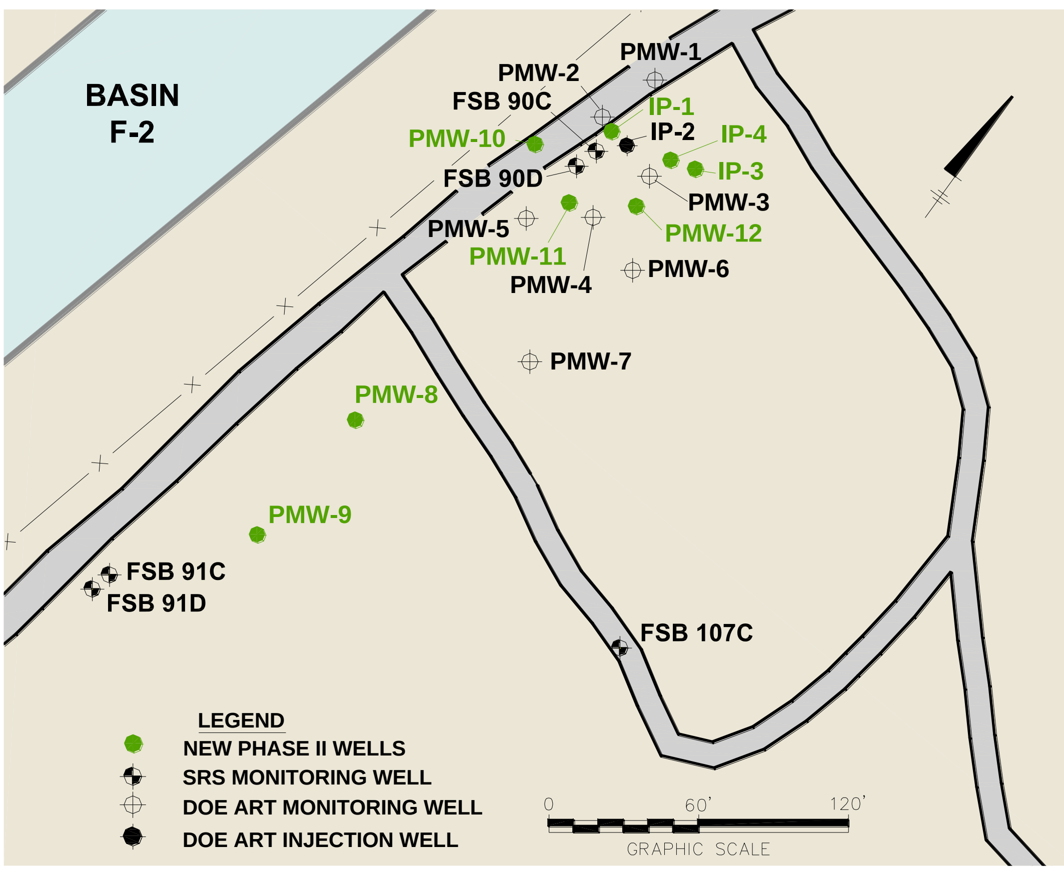

Figure 8. Well layout for molasses injections.

The results from the monitoring made by ARCADIS for several months after the initial injections showed that reducing conditions were developed in the treatment zones as desired and the key contaminant (uranium, technetium, and nitrate) had decreased dramatically in the reactive zones. Evidence of methanoginesis was seen throughout most of the reactive zone. A substantial reducing zone had persisted for at least four months after the last injection; however, a change to less-reducing conditions was beginning to occur at the up gradient edge of the zone.

In an effort to resume monitoring of the area, and gain understanding of what changes have occurred to the mineralogy and water chemistry, a depth profile of several wells was made during this internship. The wells profiled were PMW-9, PMW-11 and PMW-12. The following information was collected on the wells at 1-foot intervals inside the screen: depth to water, specific conductivity, pH, DO (%), DO (mg/L), ORP and temperature. The results are shown in the following tables. Graphs were constructed for each parameter to represent the changes in respect to the depth of the well.

Figure 10. YSI probe used for F area well profiling.

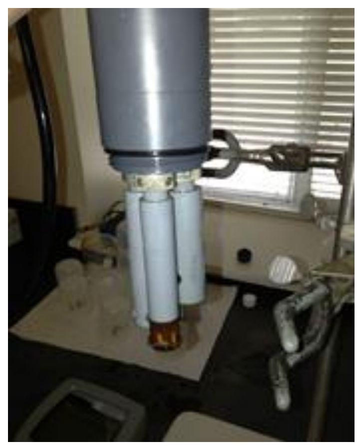

Figure 11. YSI probe Internal membranes.

Figure 12. YSI probe output monitor.

Well PMW-9

WELL ID:	PMW-9
Date:	7/1/2013
YSI Model:	600XL-B-O
SN:	03J0434
Screen (ft):	66'-86'
Stick Up (in):	30.5625
Stick Up (ft):	2.546874
Depth to water (ft):	69.87
Depth to water from ground (ft):	67.32313

Table 1. PMW-9 Depth Profile

Depth (ft)	Depth from Ground (ft)	Sp. Cond. (µS/cm)	pH	DO (%)	DO (mg/L)	ORP (mV)	Temp (˚C)
71	68.45313	115	4.83	80.7	7.35	192.1	19.9
72	69.45313	111	4.68	77.4	7.09	203.2	19.36
73	70.45313	109	4.61	75.1	6.94	204.9	19.14
74	71.45313	107	4.6	73	6.75	203.9	19.05
75	72.45313	106	4.6	70.4	6.52	200.5	19.03
76	73.45313	107	4.7	68	6.3	192.5	19.02
77	74.45313	108	4.81	65.8	6.1	161.8	19.02
78	75.45313	108	4.9	64.8	6.01	147	19.02
79	76.45313	109	4.92	63.7	5.9	147.8	19.02
80	77.45313	109	4.97	62.1	5.75	145.6	19.02
81	78.45313	109	4.97	61.5	5.69	148	19.02
82	79.45313	164	5.93	48.8	4.52	-37.8	19.03
83	80.45313	197	6.25	41.6	3.85	-113.6	19.03
84	81.45313	203	6.32	39.6	3.66	-116.3	19.03
85	82.45313	205	6.36	38.4	3.56	-121	19.03
86	83.45313	205	6.38	37.5	3.47	-124.2	19.03
87	84.45313	205	6.41	36.6	3.38	-126.2	19.03
88	85.45313	205	6.42	35.7	3.31	-128.2	19.03
89	86.45313	228	6.45	34.9	3.24	-141.8	19.04

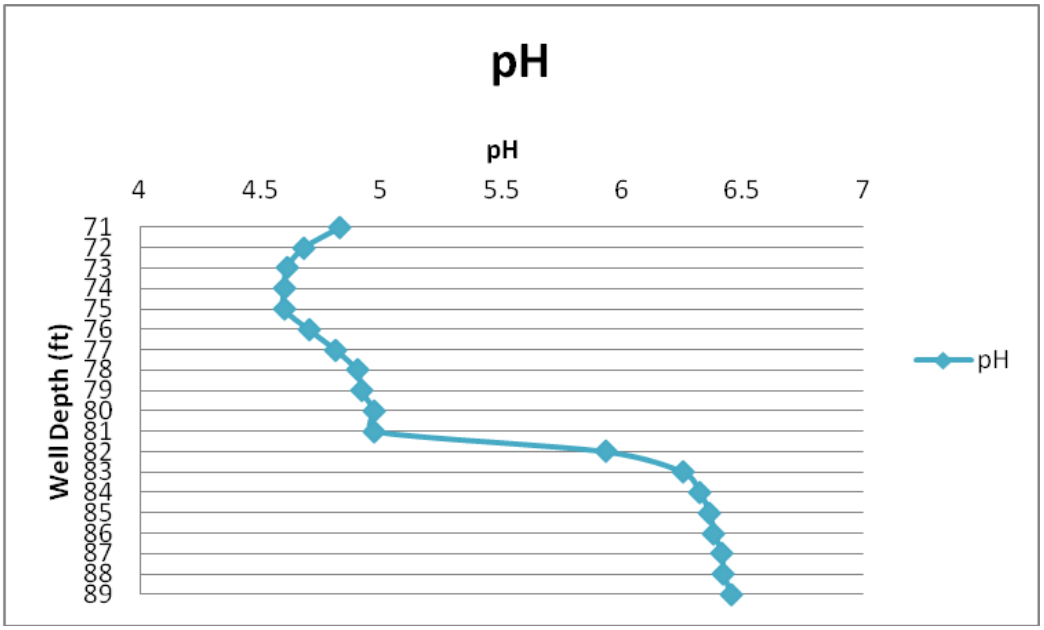

Figure 13. PMW-9 pH Vs. Depth.

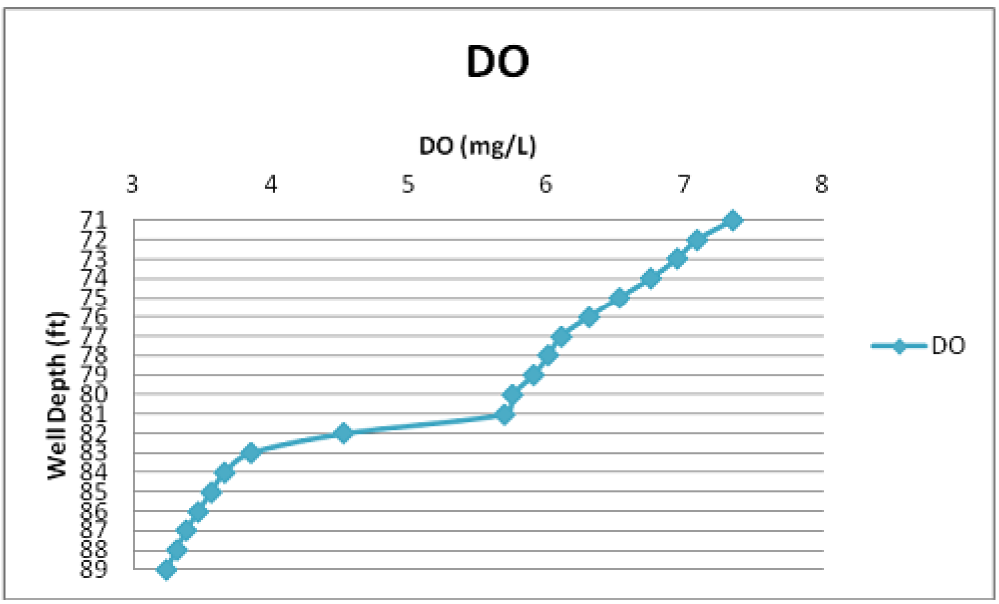

Figure 14. PMW-9 DO Vs. Depth.

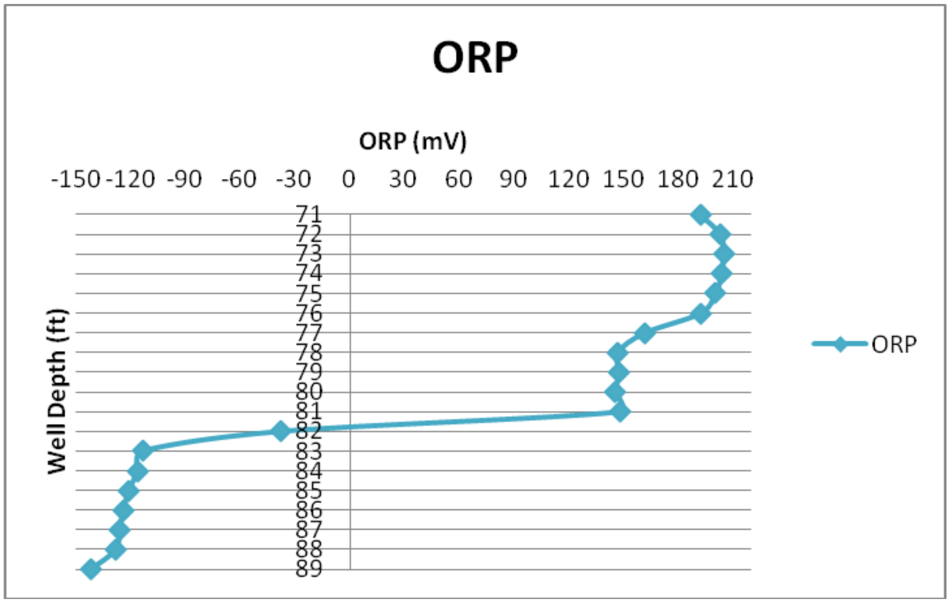

Figure 15. PMW-9 ORP Vs. Depth.

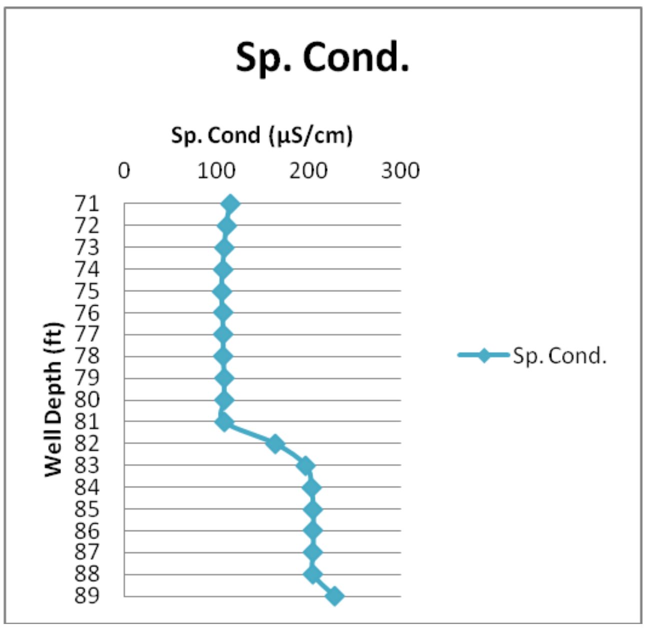

Figure 16. PMW-9 Sp. Conductivity Vs. Depth.

Well PMW-11

WELL ID:	PMW-11
Date:	7/1/2013
YSI Model:	600XL-B-O
SN:	03J0434
Screen (ft):	68'-78'
Stick Up (in):	29
Stick Up (ft):	2.4166657
Depth to water (ft):	69.87
Depth to water from ground (ft):	67.4533343

Table 2. PMW-11 Depth Profile

Depth (ft)	Depth from Ground (ft)	Sp. Cond. (µS/cm)	pH	DO (%)	DO (mg/L)	ORP (mV)	Temp (˚C)
71	68.58	143	4.31	71.9	6.47	292.9	20.5
72	69.58	141	4.19	70.8	6.48	304.9	19.61
73	70.58	140	4.14	67.1	6.17	300.8	19.4
74	71.58	140	4.14	65.5	6.03	299	19.36
75	72.58	140	4.13	64.4	5.93	300.1	19.35
76	73.58	140	4.13	63.8	5.87	300	19.34
77	74.58	140	4.14	63	5.79	296.2	19.34
78	75.58	140	4.15	62.4	5.74	295.6	19.34
79	76.58	140	4.16	61.7	5.68	289.6	19.34
80	77.58	140	4.16	62.3	5.72	282.2	19.34
80.3	77.88	140	4.5	58.4	5.37	204.9	19.34

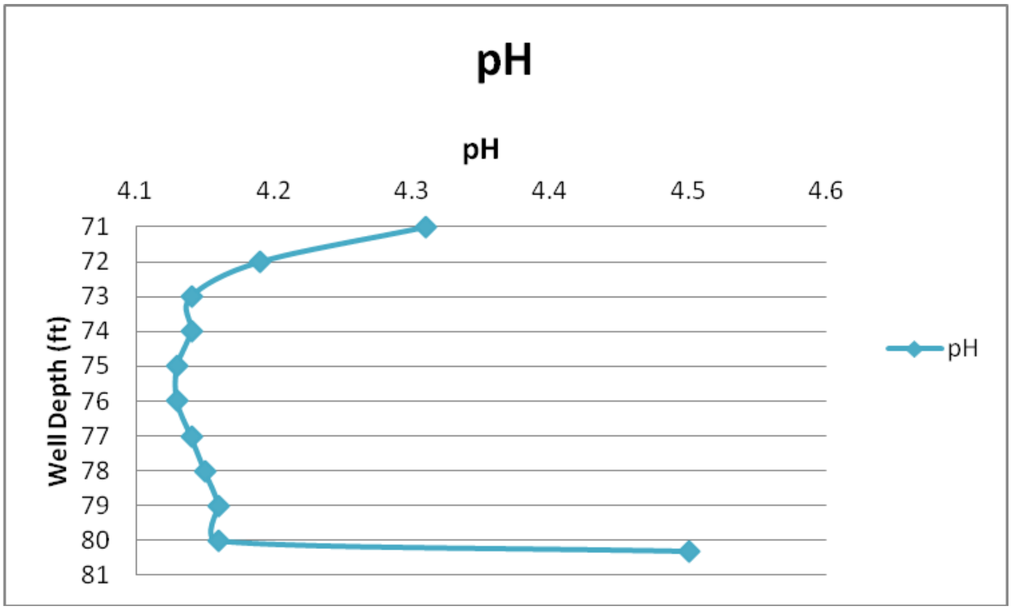

Figure 17. PMW-11 pH Vs. Depth.

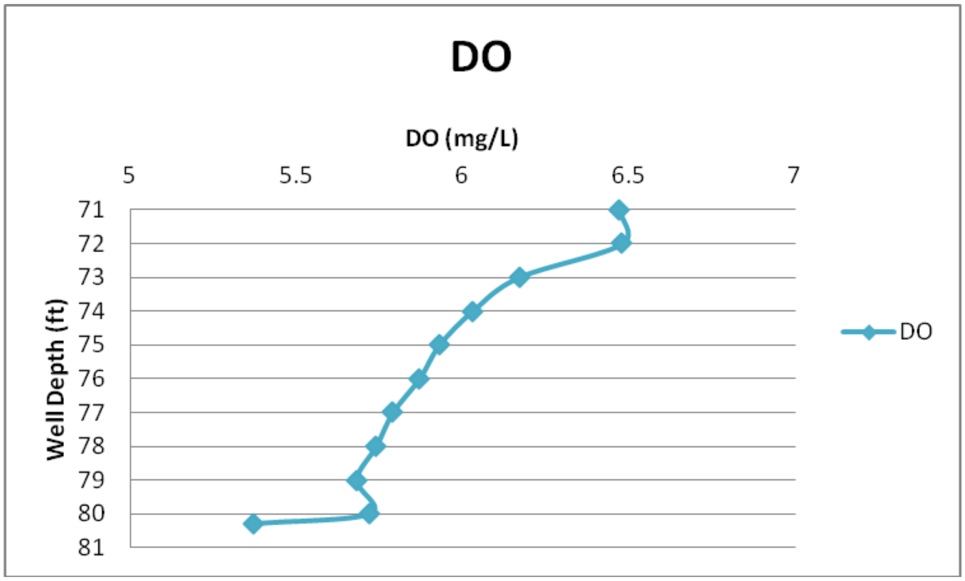

Figure 18. PMW-11 DO Vs. Depth.

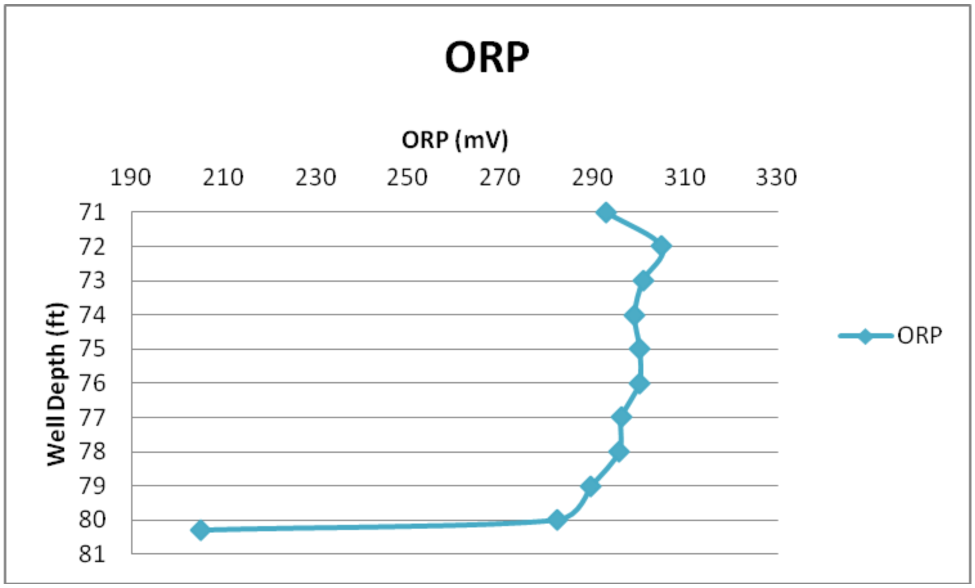

Figure 19. PMW-11 ORP Vs. Depth.

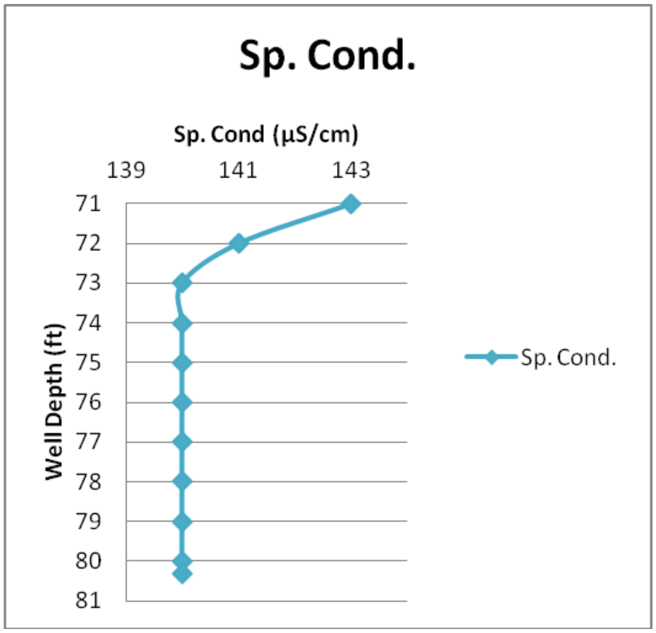

Figure 20. PMW-11 Sp. Conductivity Vs. Depth.

Well PMW-12

WELL ID:	*PMW-12*
Date:	7/1/2013
YSI Model:	600XL-B-O
SN:	03J0434
Screen (ft):	68'-78'
Stick Up (in):	27.5
Stick Up (ft):	2.291666
Depth to water (ft):	69.11
Depth to water from ground (ft):	66.81833

Table 3. PMW-12 Depth Profile

Depth (ft)	Depth from Ground (ft)	Sp. Cond. (µS/cm)	pH	DO (%)	DO (mg/L)	ORP (mV)	Temp (˚C)
70	67.71	139	4.12	74.4	6.72	309	20.33
71	68.71	139	4.02	70.7	6.47	322	19.63
72	69.71	137	3.99	68	6.25	331.6	19.45
73	70.71	138	3.99	66.1	6.08	321.8	19.4
74	71.71	137	4.1	63.4	5.83	171.3	19.37
75	72.71	134	4.2	61.3	5.66	141.3	19.35
76	73.71	134	4.21	60.8	5.6	133.2	19.35
77	74.71	134	4.23	60.1	5.53	128.3	19.35
78	75.71	134	4.23	59.5	5.47	125.3	19.35
79	76.71	134	4.24	59.3	5.46	123.1	19.35
80	77.71	135	4.35	58.9	5.42	109.6	19.35
80.3	78.01	172	5.35	52.1	4.79	-43.6	19.36

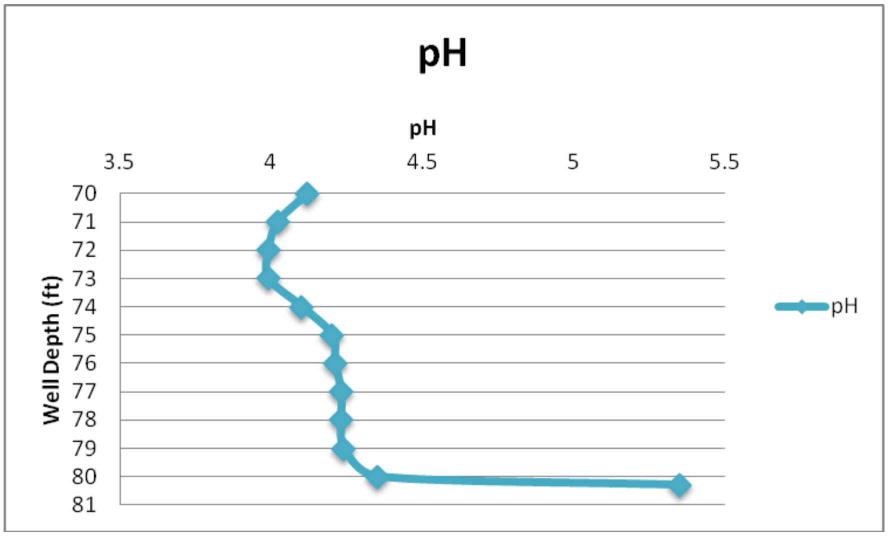

Figure 21. PMW-12 pH Vs. Depth.

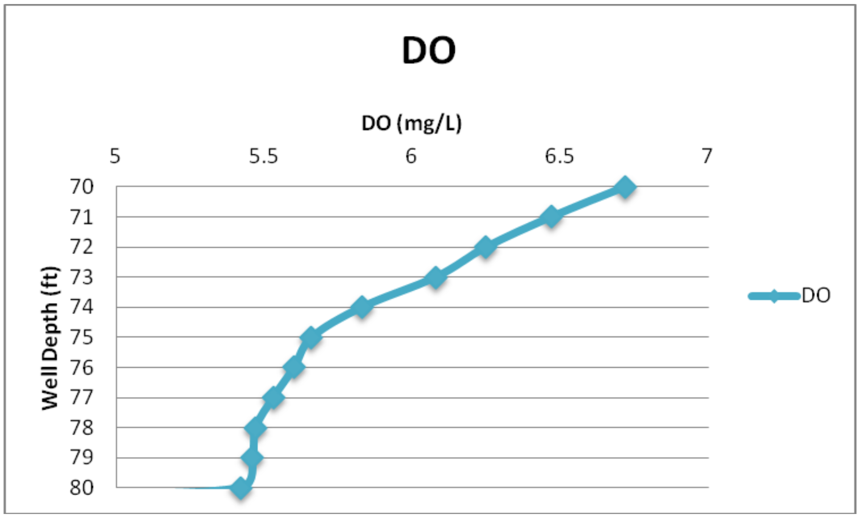

Figure 22. PMW-12 DO Vs. Depth.

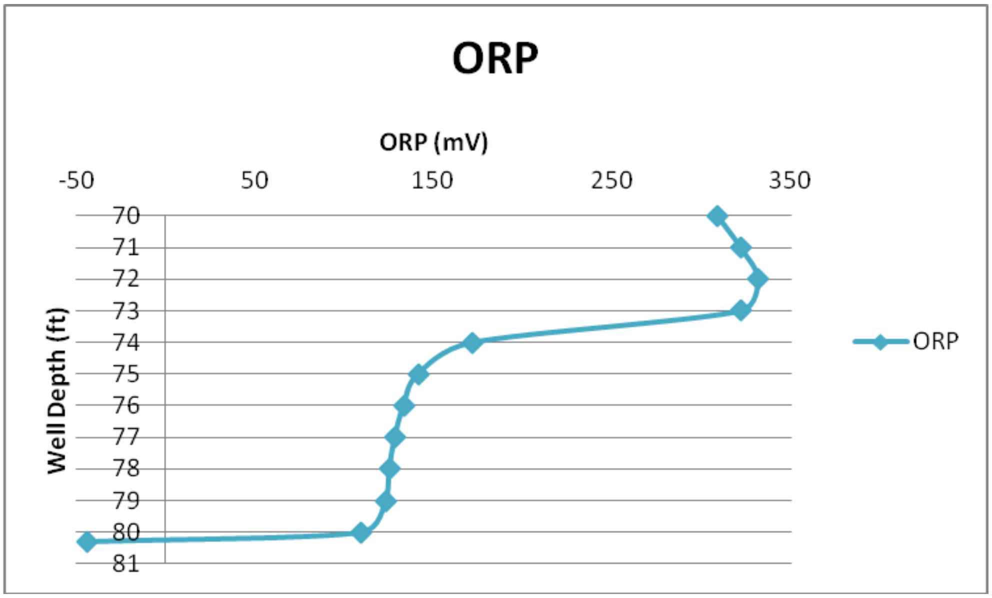

Figure 23. PMW-12 ORP Vs. Depth.

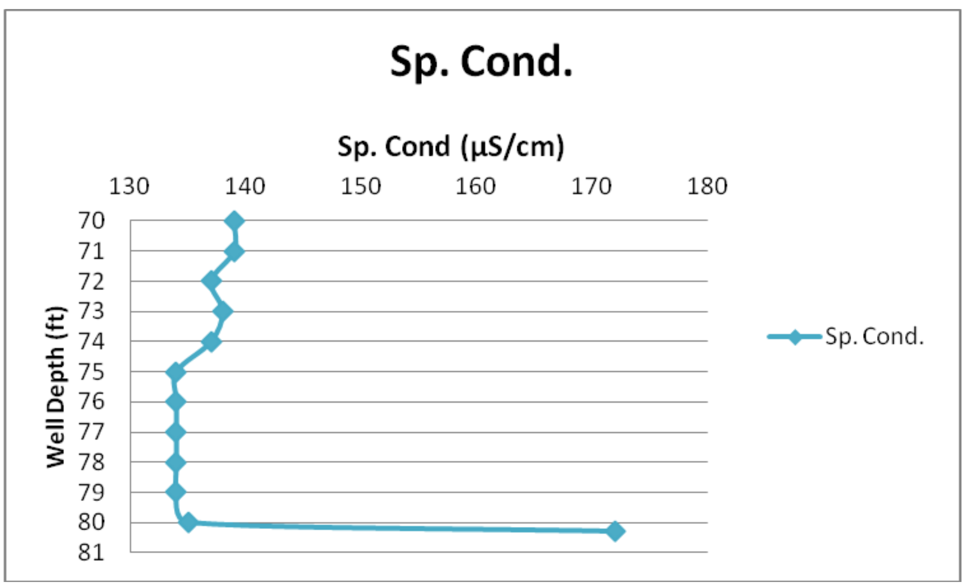

Figure 24. PMW-12 Sp. Conductivity Vs. Depth.

From these results, it can be concluded that there is a redox gradient depicted by the graphs. The results are somewhat unexpected, especially the comparison of well PMW-9 to the other two wells. The bottom part of the PMW-9 well exhibits a marked increase in conductivity and pH while also showing a marked decrease in DO and ORP, more so than the other two wells. This is interesting because this behavior was expected on the other two wells (PMW-11 and PMW-12), which are located at the injection site, not at PMW-9 which is located more at a a side gradient to the injection site. It can be hypothesized that the trailing edge of the reduced zone would probably be somewhere between PMW-11 and PWM-12. Additional sampling of these wells is needed for further understanding of the changes that have happened since the last molasses injection.

7. MICROCOSM STUDY

Microcosm Theory

A microcosm study was designed and performed to support the research on the ARCADIS work, the molasses injections to the F-area wells. The schematic design of the microcosmic experiment is shown below. Two centrifuge tubes were used, and holes were perforated on the caps. A small tube was used to connect both centrifuge tubes and was inserted tightly through the holes on the caps; tape was placed around it to prevent any gas exchange. One of the centrifuge tubes contained the sediment and the solution addition while the other contained only DI water. The purpose of the second centrifuge tube containing only DI water was for the small connecting tube to be inserted below the water level, allowing any gases to escape from the sediment sample in the first centrifuge tube while preventing any air from entering. This was done as a cost effective way to make the system anaerobic.

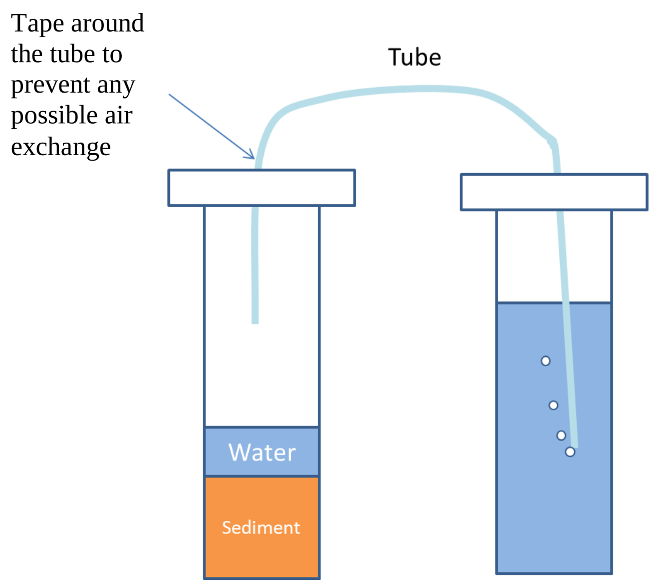

Figure 25. Microcosm set up.

Microcosm Study Set Up

To test if the set up was working properly, a preliminary test microcosm study with two different soil samples from the F-area was done. The composition of the set up is as follows: 20 mL of sediment of each of the sediments were added to separate centrifuge tubes, plus a 10 mL solution mixture containing DI water, 0.014 g of $NaNO_3$ (equivalent to 200 mg/L), and 7 g of molasses (equivalent to 20% by weight of the solution).

Figure 26. Sediment samples.

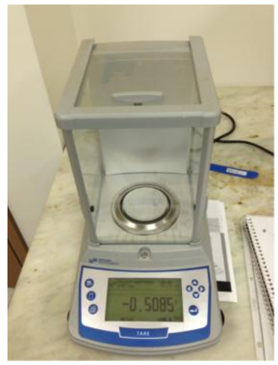

Figure 27. Weighing balance.

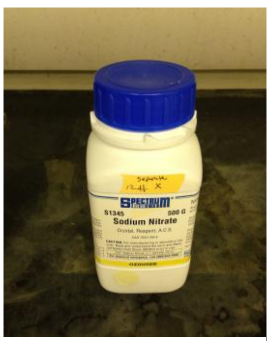

Figure 28. Sodium nitrate.

Figure 29. Molasses.

After several weeks of the microcosm being monitored, it has been observed that even though there is some definite growth due to the molasses addition, it cannot be concluded that it is anaerobic bacteria because the bacterial growth in the microcosm is not showing signs of anaerobic bacterial growth, such as, sediment color change or foul smell. This can be due to several factors— the growth of the anaerobic bacteria might be really slow and perhaps the air that was inside the tubes is slowing the process significantly. Another possibility is that the system is not completely sealed off and oxygen is entering the system. Finally, it could be that the anaerobic bacteria were simply not present in any significant quantity on the sediment sample to begin with. The following pictures show the changes that occurred to the sediment and molasses within a four week spam.

Figure 30. Microcosm study week 1.

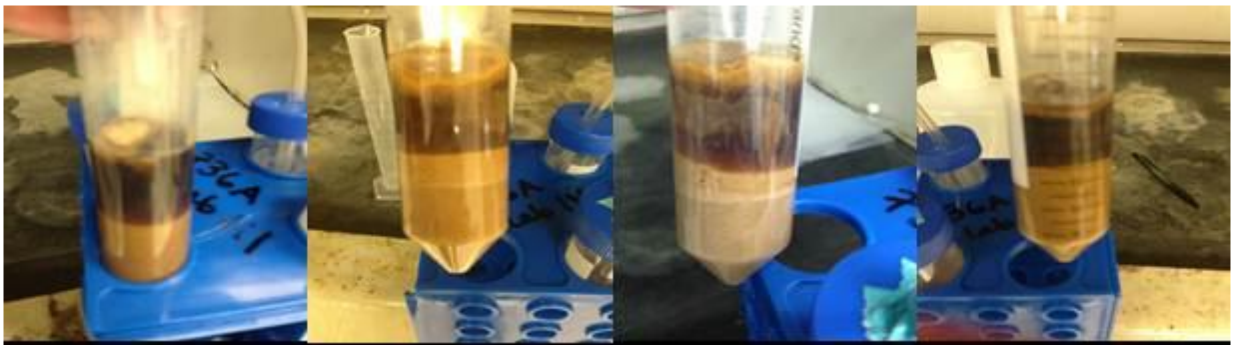

Figure 31. Microcosm study week 2.

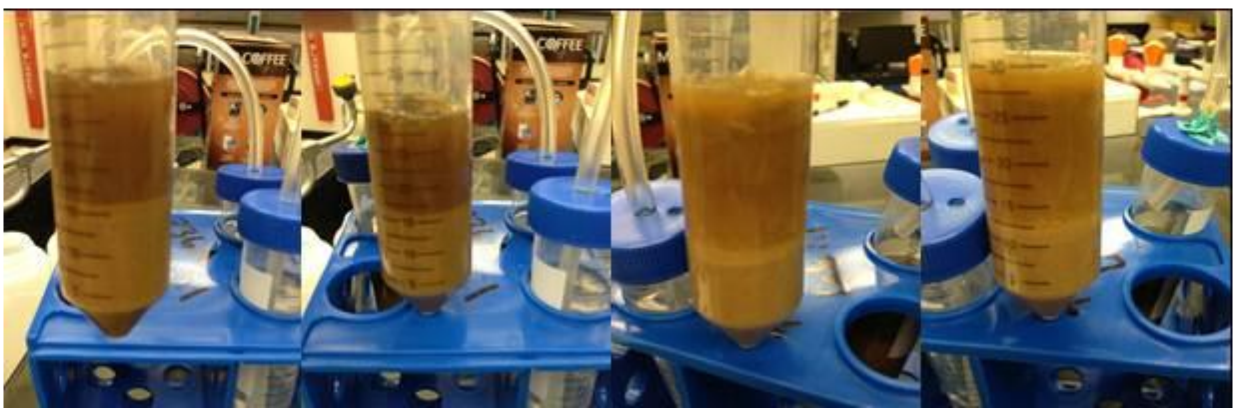

Figure 32. Microcosm study week 3.

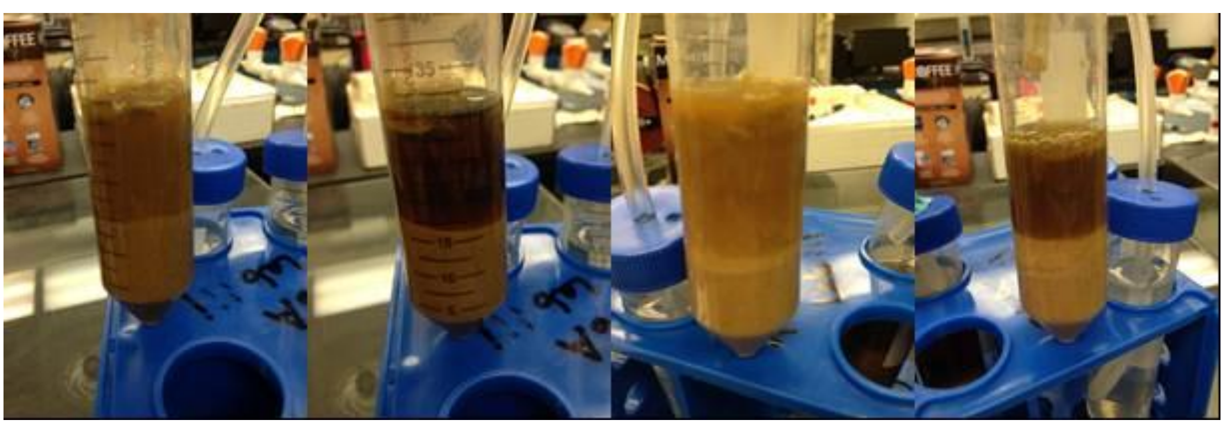

Figure 33. Microcosm study week 4.

As the microcosm study did not yield successful results, further changes to the set up have to be made to achieve anaerobic bacterial growth. The new set up will differ by placing the whole system inside a bag, which will be purged with nitrogen, along with the centrifuge tubes and connecting tubes, to guarantee an anaerobic environment.

Several core samples from a well closer to the molasses injection site were shipped back to the ARC facilities to continue the microcosm study. The core samples were obtained from the core facility from well FSB 91C—the closest well to the molasses injection site from where core samples were available. Six samples were retrieved at the following depths: 65, 80, 90, 95, 100 and 105 feet, respectively.

Figure 34. Core samples from FSB 91C.

Figure 35. Final Samples.

9. CONCLUSIONS

Metals and radionuclides, especially uranium, are a long term environmental problem that resulted from the legacy of uranium mining, weapons development, energy related activities and radioactive waste disposal. Even after extensive clean-up efforts, the concentration of these contaminates exceed the desired limits at some sites and might endanger biotic systems and human health. Although many studies have been made in the last twenty years regarding uranium bioremediation, and many advances in this area have been achieved, it is evident that there is still a need for additional remediation technologies that decrease dissolved contaminant concentrations within a reasonable timeframe and that serve as a long term remediation alternative. The research discussed in this report is a vital part of that process and seems promising for future developments. However, it is clear that more extensive research and monitoring are needed before these goals can be achieved.

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