STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

An Assessment of Long-Term Monitoring Strategies and Developing Technologies

DOE-FIU SCIENCE & TECHNOLOGY
WORKFORCE DEVELOPMENT PROGRAM

Date submitted:

December 20, 2019

Principal Investigators:

Anilegna Nunez Abreu (DOE Fellow Student)
Florida International University

Grover Chamberlain, Mentor
Department of Energy Headquarters

Florida International University:

Ravi Gudavalli Ph.D. Program Manager
Leonel Lagos Ph.D., PMP® Program Director

Submitted to:

U.S. Department of Energy
Office of Environmental Management
Under Cooperative Agreement # DE-EM0000598

FIU | Applied Research Center
FLORIDA INTERNATIONAL UNIVERSITY

ABSTRACT

This technical report consists of a description of two projects developed at the United States Department of Energy's Office of Environmental Management (DOE-EM) in the summer of 2019, as well as the practical application of each and further work that needs to be done. Both projects were done under the mentorship of employees from both DOE-EM Office of Subsurface Closure based in Germantown, Maryland and from the Savannah River National Laboratory.

The first project aims to provide both a qualitative and quantitative assessment of the Direct Mercury Analyzer (DMA-80) in comparison to Cold Vapor Atomic Absorption Spectroscopy (CVAAS) and off-site sampling in order to effectively assess the instrument and aid in future method selection for the determination of total mercury. The quantitative assessment was done by using a simple cost analysis comparison through the form of a return on investment index. On the other hand, the qualitative assessment was done by examining the instrument's overall productivity, sensitivity, reliability, efficiency, and waste production. Ultimately, the assessment deemed the DMA to be a more effective instrument in comparison to its adversaries.

The second project, a work in progress, assesses a new long-term monitoring approach being developed by a team in the Savannah River Site. The approach is meant to create more proactive ways of monitoring contaminant remobilization. In this report, an attempt is made to create the foundations of a return on investment index that assesses the approaches' practicality without diminishing the assessment of the effectiveness of the approach itself. As this is a work in progress, future efforts must be made to complete the quantitative assessment.

The final project was a trip to Savannah River National Laboratory to get a firsthand tour of the site as well as learn about the variety of projects being carried out throughout the site. Tour consisted of three days in which multiple presentations were given discussing the site's role within the environmental remediation efforts for the United States.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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 2019, a DOE Fellow intern Anilegna Nunez Abreu spent 10 weeks doing a summer internship at DOE-EM under the supervision and guidance of Senior Program Manager, Grover Chamberlain and Director of Technological Development, Kurt Gerdes. The intern's project was initiated on June 1, 2019, and continued through August 10, 2019 with the following interdisciplinary objectives: (1) developing a quantitative and qualitative assessment of proposed integrated systems-based approaches to long-term monitoring, (2) creating a benefit analysis of the use of the Direct Mercury Analyzer instrument for total mercury analysis, and (3) gaining first-hand oversight of current site development through a guided tour of the Savannah River Site.

3. RESEARCH DESCRIPTION

2.1. Direct Mercury Analyzer (DMA-80) Instrument Assessment

Introduction

Mercury contamination has become a priority challenge for the US Department of Energy's Office of Environmental Management (EM). In sites like the Oak Ridge Reservation (ORR) and Savannah River Site (SRS) mercury contamination has posed two distinct yet prevalent issues, summarized below in a general manner.

In ORR large amounts of mercury where used in the 1950s throughout the 1970s resulting in release into the surrounding environment. Though remediation efforts have been in place since the 1980's elevated concentrations of mercury remain in facilities, nearby soil and groundwater, and in surface water (streams, banks, and sediments). Presently, concentrations in certain areas exceed the states' regulatory limits and guidelines, including toxic and bioaccumulate methylmercury, thus posing a potential threat to the biota and people in the surrounding area.

Meanwhile, in SRS the use of mercury as a catalyst and as a precipitating agent for nuclear separations processing have been ongoing for years. Waste solutions, containing high levels of mercury, are discharged into High-Level Waste Tanks (HLW) for storage and disposal. Recently, analytical data found there to be significantly higher levels of mercury concentrations especially organomercury such as methylmercury. The predominance of organomercury reduces the effectiveness of the current mercury removal operations and mercury immobilization operation being performed in SRS. More generally, complex mercury speciation and transformations in the Liquid Waste System coupled with limited information on such processes, and strict regulatory requirements pose long-term challenges for SRS and DOE-EM.

In summary, both ORR and SRS have very unique challenges concerning mercury contamination. However, the initial step within resolving these challenges deals with the characterization and monitoring of mercury in both environments. Performing mercury analysis and speciation can be a costly and laborious process, nevertheless, essential to effectively manage mercury challenges. Being able to quantify the amounts of total mercury present in the area of interest is an essential portion of the complex development of an effective mercury speciation approach. Hence, the purpose of this investigation is to present and assess the efficiency of a potential instrument that can aid in identifying total mercury and thus, in part, supporting the development of an effective procedure for mercury analysis.

DMA-80

The Direct Mercury Analyzer (DMA-80) is an instrument that determines the amount of total mercury in a given sample. It can analyze up to 40 samples at a time with an average of a 7-minute analysis period per sample. The system requires little to no sample preparation thus decreasing the possibility for error during analysis and produced minimal waste.

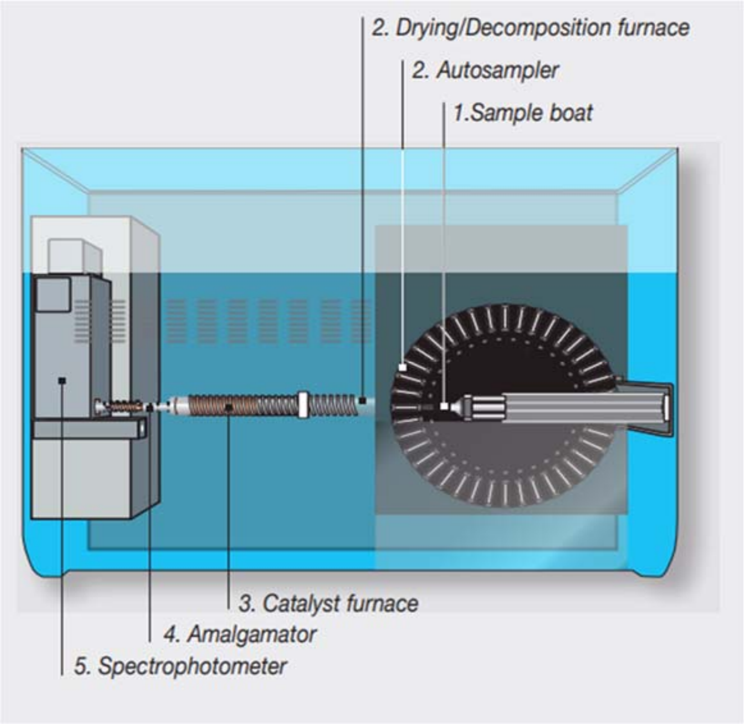


Figure 1 Milestone DMA-80 "How It Works" diagram

Infographic

In order to holistically assess the effectiveness of the DMA-80, an infographic was created that compares the instrument to its predecessor, the CVAAS, initially used in the Savannah River National Laboratory (SRNL), and off-site sampling, a current method being used in SRNL for Low Level Waste Systems (LWS).

The infographic (APPENDIX A.) presents a qualitative and quantitative evaluation of the benefits of using the DMA-80 in comparison to its competitors. To provide a compelling and effective evaluation the procedures necessary to use each instrument being compared where listed, as well as the advantages or disadvantages that each method had over the DMA-80. For the quantitative analysis two simple return on investment index where created that assess the monetary advantages of using the DMA-80 for both mercury challenges posing DOE. Ultimately it was determined that by using the DMA-80 for measuring total mercury for tank waste samples, as opposed to the current off-site analysis being used, the return on investment (not taking into account the time value of money) would be 1,575%. On a similar note, using the DMA-80 for environmental samples would give a 54% return on investment, thus reducing costs by 30%. All calculations where performed based on 700 sample estimates due to the fact that there is a minimum number of samples that should be sent off for off-site analysis for tank Waste Mercury. In terms of environmental mercury, calculations where based off of 200 total mercury samples and 100 methylmercury samples respectively. ORNL already has a DMA-80 on site thus the cost for onsite assessment of total mercury is very low and could not be specifically determined. However, the amount saved on labor and offsite analysis sendoff was determined to amount to an estimated $9,000 savings amount. The return on investment indexes and a summary of estimated costs for analysis are presented below.

Table 1 Tank Waste Mercury Analysis

	Estimated Cost Per Sample	Estimated Annual Costs
Off-site Analysis	$1,400	$420,000
On-site Analysis	$700	$210,000

Return on Investment DMA for Tank		
Investment ($)	Savings ($)	Category
$300,000		Instrument Purchase and Deployment
$100,000		Associated Investment
	6,300,000	Inhouse Strategy using DMA
1575%		Return On Investment

Table 2 Environmental Mercury Analysis

	Estimated Cost Per Sample Total Mercury	Estimated Cost Per Sample Methylmercury	Estimated Annual Costs
Off-site Analysis	$100	$200	$30,000
On-site Analysis	$	$	$21,000

Return on Investment DMA for Environmental		
Investment ($)	Savings ($)	Category
$50,000		Instrument Purchase and Deployment
		Associated Investment
	270,000	Inhouse Strategy using DMA
54%		Return On Investment

2.2. Return on Investment for Integrated Systems-Based Approaches to Long-Term Monitoring

Introduction

After World War II the United States was left with the monumental challenge of trying to remediate soil and groundwater that was contaminated as a result of a variety of activities associated with nuclear weapons production. Today, still one of the greatest challenges for DOE-EM, the remediation of large complex groundwater plumes of metals and long-lived radionuclides is estimated to have a projected lifecycle cost of $22 billion. One of the greatest contributors to these costs, and what this project focuses on, is coming from monitoring these contaminants after they've been attenuated.

To better understand what long-term monitoring (LTM) is, Figure 2 below is a simplified overview of the decision-making process that occurs before deciding whether to implement long-term monitoring strategies. Essentially, after pump and treat, a remediation technique used to treat contaminated groundwater, remedial action objectives (RAO's) are assessed. If the RAO's have not been met but if the plume has declined during treatment, monitored natural attenuation (MNA), a strategy that relies on natural process to attenuate contaminant migration, is considered. If it is determined that MNA will meet RAO's then the strategy is implemented and alongside it, long-term monitoring, the collection of data over a period of time, is introduced usually through the use of wells and water stations to monitor changes in contaminants.

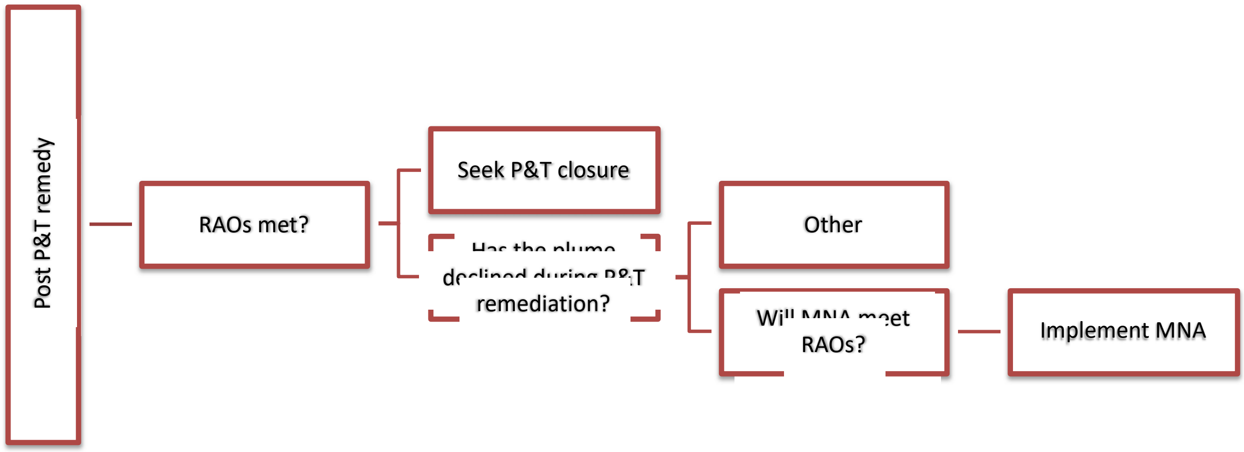


Figure 2 Simplified Decision-Making Process for Implementing MNA

LTM for even one plume, however, can last up to decades until contaminants are effectively attenuated. Current monitoring approaches, which consist of collecting data from wells to determine whether there have been changes in contaminant concentration or location, have proven to be costly and insufficient. This is mostly because the data collected can only inform scientists of when the contaminant conditions have changed, thus leading to "reactive" decisions once a problem becomes prevalent rather than "proactive" decisions used to prevent a problem from occurring in the first place. In addition to the data being insufficient to make proactive decisions, sample collections are costly and labor some.

To address this challenge, and to foster more proactive solutions, a new Long-Term Monitoring Paradigm was developed by a team in SRNL to reduce the number of monitoring wells by 80% and replace these wells with a more efficient and cost-effective approach consisting of a site-specific monitoring network. This approach aims to enhance the effectiveness and serviceability of LTM all while being feasible. Figure 3 and Figure 4 describe the detriments of the traditional LTM paradigm as well as summarize the benefits of the new paradigm.

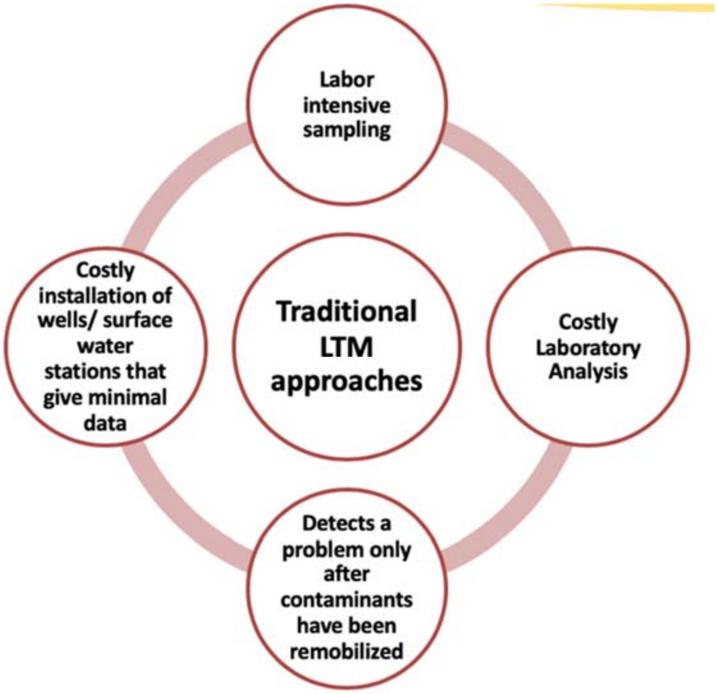


Figure 3 Traditional LTM Approach Detriments

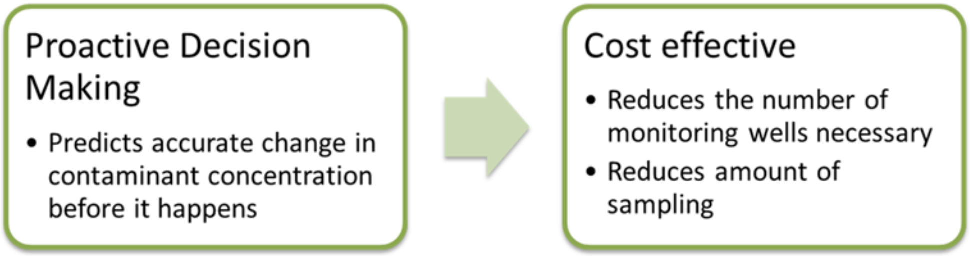


Figure 4 Advantage Overview of New Paradigm

This project focuses on developing the basis for a return on investment index that will aid sites in accounting for the best suited site-specific approaches and in return allow them to calculate a return on investment percentage of using said approaches.

Survey

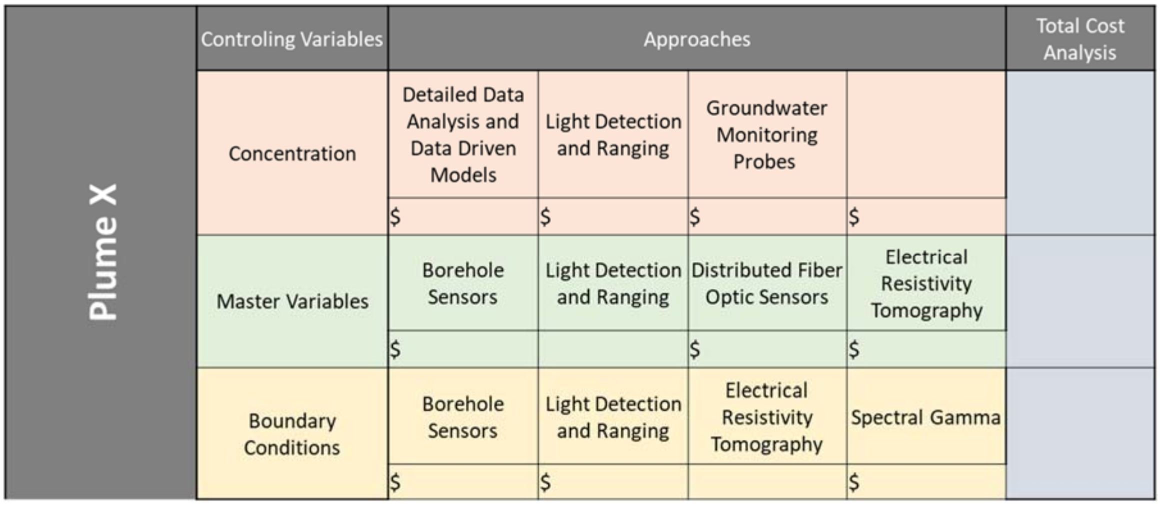
One of the key obstacles that the implementation of the new paradigm faces is stakeholder approval. Since the traditional long-term monitoring approach is well known, and because monitoring contaminants is crucial to the success of remediation, it is important to address stakeholder's concerns regarding the solidity of the proposed paradigm. To better understand stakeholder concerns and expectations, a survey was created to distribute to various Legacy Management Project Managers, gathering at an SRS meeting, asking them a variety of questions regarding the unique characteristics at their sites. Future work must be done to assess the responses of the survey, which can be found in APPENDIX B.

Return on Investment Index

The return on investment index was created on the basis that "Plume X" can be any plume in question. The first contributing factor to determining which approach is best suited for Plume X is assessing the “controlling variables” which are: concentration, master variables, and boundary conditions. These variables are the conditions that need to be monitored to determine whether contaminant conditions have changed. To explore this concept thoroughly refer to *Shifting the Paradigm for Long Term Monitoring at Legacy Sites to Improve Performance while Reducing Cost* which can be found in references. After determining the controlling variables, approaches to monitoring such variables can be determined from a list of possible approaches.

The future recommendations for this project include creating a shortlist of possible approaches based on controlling variables. Additionally, determining estimated costs for each approach in a manner that can be replicated based on individual monitoring life expectancy. If these tasks are completed the ROI coupled with the measured cost of current (traditional) monitoring strategies put in place at the site in question can provide a significant comparison between the feasibility of using the new paradigm in comparison to traditional approaches. Figure 5 below is a demonstration of the ROI in progress.

Table 3 LTM ROI Index



	Controling Variables	Approaches				Total Cost Analysis
Plume X	Concentration	Detailed Data Analysis and Data Driven Models	Light Detection and Ranging	Groundwater Monitoring Probes		
		$	$	$	$	
	Master Variables	Borehole Sensors	Light Detection and Ranging	Distributed Fiber Optic Sensors	Electrical Resistivity Tomography	
		$		$	$	
	Boundary Conditions	Borehole Sensors	Light Detection and Ranging	Electrical Resistivity Tomography	Spectral Gamma	
		$	$		$	

2.3 Savannah River Site Tour

The final project discussed in this report is the site tour of the Savannah River National Laboratory (SRNL) in South Carolina. The tour was an excellent opportunity to gain first-hand insight on how DOE site functions. The tour was very holistic, many locations such as the H-Area, F-Area, and individual labs were shown. Additionally, the visit also consisted of various presentations that described the range of projects being carried out within different sectors of SRNL. Within the visit, interns got the opportunity to get guidance from two of the researchers, who the projects discussed above, were based on. A DOE Fellow alumnus was also present during the visit, thus allowing for insight on career development post-graduation and fellowship.

Pictures of the site tour can be seen below (12) and visit agenda can be seen in Appendix C below:

Figure 5 F-Area Basin 1 and 2

Figure 6 DOE EM-HQ Intern Group Photo

Figure 7 Interns at SRNL

Figure 8 Dr. Brian B. Looney conducting site tour

Figure 9 M-Area

Figure 10 H-Area

4. CONCLUSION

This internship provided an excellent opportunity for professional development as well as gave interns an effective insight into how a cabinet-level department of the US functions. The projects carried out allowed for a concrete understanding of the various roles within the Department of Energy's Environmental Management office as well as gave insight to the roles that each individual site plays within DOE. Each project has room for future work to be done by future interns. Throughout both projects there where a variety of other remarkable opportunities that could not be addressed in detail in this report such as seeing first-hand development of new technologies that are the future of environmental remediation efforts, meeting inspiring professionals and gaining the advice of how to do well in the workforce, and many others. The internship also provided various professional development opportunities throughout the summer such as Resume Workshops, and Financial Literacy Workshops. Ultimately, the DOE-HQ Internship created a supportive environment for both personal and professional growth.

5. ACKNOWLEDGMENTS

This internship was supported by the a variety of dedicated employees from the Department of Energy Headquarters Facility and Savannah River National Laboratory. A special thank you to Skip Chamberlain, Kurt Gerdes, Carol Eddy-Dilek and Brian B. Looney for mentoring the projects discussed in this report. Additionally, acknowledgments go to all EM-HQ interns who supported this project and made it come to life.

6. REFERENCES

Department of Energy. (n.d.). Retrieved September 26, 2019, from https://www.energy.gov/

Eddy-Dilek, C. (n.d.). *Innovative Strategy for Long Term Monitoring of Metal and Radionuclide Plumes-14380*.

Eddy-Dilek, Looney, C. A. *, Brian B, Kmetz, T., & John. (n.d.). *Shifting the Paradigm for Long Term Monitoring at Legacy Sites to Improve Performance while Reducing Costs*.

Edwards, R. (2018). *Evaluation and Impacts of Mercury in the SRS Liquid Waste System-Update*.

Ferrigno, D., Co, E.-T., Brown, K., Member, E.-T., Hanfling, R., Lahoda, E., … Leviton, A. (n.d.). *EM Tank Waste Subcommittee Report for SRS / Hanford Tank Report Number TWS #003 EMAB EM Subcommittee Report for SRS / Hanford Tank Waste Review Report Number TWS #003 EMAB EM-TWS SRS / Hanford Tank Waste*.

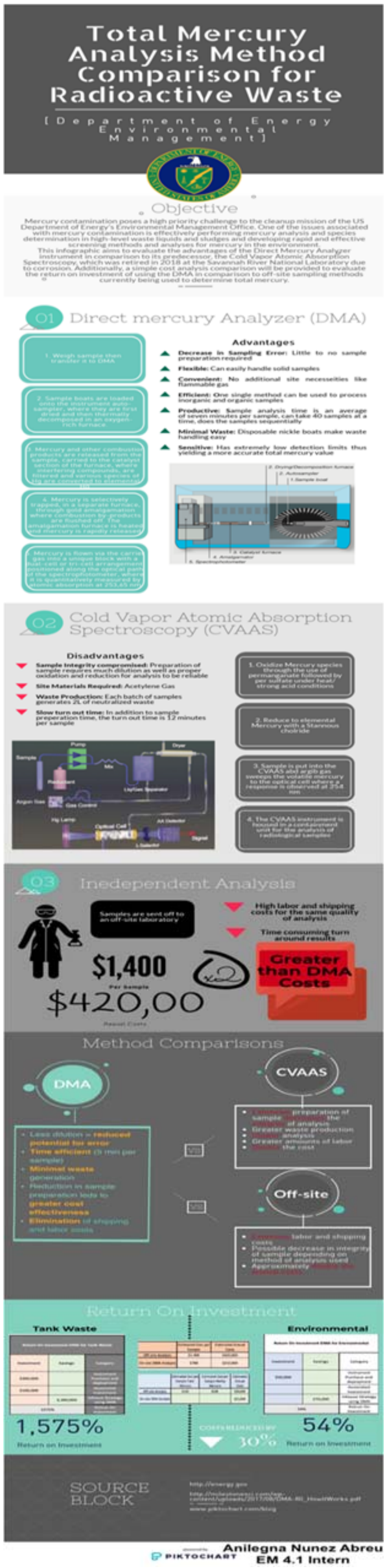
Gerdes, K. (n.d.). *Draft EM Tech Assistance Test Bed Slides*.

LabNote. (n.d.). The Milestone DMA-80: Innovation Delivered. Retrieved September 26, 2019, from https://milestonesci.com/direct-mercury-analyzer/

Oak Ridge National Lab. (n.d.). *Technology Plan to Address the EM Mercury Challenge*.

Raubenolt, R., Fellow Student, D., Solomon, S., Paller, M., Looney, B., River, S., & Lagos, L. (n.d.). *Mercury Speciation via Diffusive Gradients in Thin-Films Technology DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM*.

APPENDIX A.



Total Mercury Analysis Method Comparison for Radioactive Waste

[Department of Energy Environmental Management]

Objective

Mercury contamination poses a high priority challenge to the cleanup mission of the US Department of Energy's Environmental Management Office. One of the issues associated with mercury contamination is effectively performing mercury analysis and species determination in high-level waste liquids and sludges and developing rapid and effective screening methods and analyses for mercury in the environment.

This infographic aims to evaluate the advantages of the Direct Mercury Analyzer instrument in comparison to its predecessor, the Cold Vapor Atomic Absorption Spectroscopy, which was retired in 2018 at the Savannah River National Laboratory due to corrosion. Additionally, a simple cost analysis comparison will be provided to evaluate the return on investment of using the DMA in comparison to off-site sampling methods currently being used to determine total mercury.

01 Direct mercury Analyzer (DMA)

1. Weigh sample then transfer it to DMA
2. Sample boats are loaded onto the instrument auto-sampler, where they are first dried and then thermally decomposed in an oxygen-rich furnace.
3. Mercury and other combustion products are released from the sample, carried to the catalyst section of the furnace, where interfering compounds, are filtered and various species of Hg are converted to elemental Hg.
4. Mercury is selectively trapped, in a separate furnace, through gold amalgamation where combustion by-products are flushed off. The amalgamation furnace is heated and mercury is rapidly released.
5. Mercury is flown via the carrier gas into a unique block with a dual-cell or tri-cell arrangement positioned along the optical path of the spectrophotometer, where it is quantitatively measured by atomic absorption at 253.65 nm

Advantages

- **Decrease in Sampling Error:** Little to no sample preparation required
- **Flexible:** Can easily handle solid samples
- **Convenient:** No additional site necesseities like flammable gas
- **Efficient:** One single method can be used to process inorganic and organic samples
- **Productive:** Sample analysis time is an average of seven minutes per sample, can take 40 samples at a time, does the samples sequentially
- **Minimal Waste:** Disposable nickle boats make waste handling easy
- **Sensitive:** Has extremely low detection limits thus yielding a more accurate total mercury value

02 Cold Vapor Atomic Absorption Spectroscopy (CVAAS)

Disadvantages

- **Sample Integrity compromised:** Preparation of sample requires much dilution as well as proper oxidation and reduction for analysis to be reliable
- **Site Materials Required:** Acetylene Gas
- **Waste Production:** Each batch of samples generates 2L of neutralized waste
- **Slow turn out time:** In addition to sample preperation time, the turn out time is 12 minutes per sample

1. Oxidize Mercury species through the use of permanganate followed by per sulfate under heat/ strong acid conditions
2. Reduce to elemental Mercury with a Stannous choiride
3. Sample is put into the CVAAS and argon gas sweeps the volatile mercury to the optical cell where a response is observed at 254 nm
4. The CVAAS instrument is housed in a containment unit for the analysis of radiological samples

03 Inedependent Analysis

Samples are sent off to an off-site laboratory

- High labor and shipping costs for the same quality of analysis
- Time consuming turn around results

$1,400

Per Sample

x2

$420,00

Annual Costs

Greater than DMA Costs

Method Comparisons

DMA

- Less dilution = reduced potential for error
- Time efficient (5 min per sample)
- Minimal waste generation
- Reduction in sample preparation leads to greater cost effectiveness
- Elimination of shipping and labor costs

VS

CVAAS

- [illegible] preparation of sample [illegible] the [illegible] of analysis
- Greater waste production
- [illegible] analysis
- Greater amounts of labor
- [illegible] the cost

VS

Off-site

- [illegible] labor and shipping costs
- Possible decrease in integrity of sample depending on method of analysis used
- Approximately [illegible]

Return On Investment

Tank Waste

1,575%

Return on Investment

COSTS REDUCED BY

30%

Environmental

54%

Return on Investment

SOURCE BLOCK

http://energy.gov

http://milestonesci.com/wp-content/uploads/2017/08/DMA-80_HowItWorks.pdf

www.piktochart.com/blog

powered by PIKTOCHART

Anilegna Nunez Abreu
EM 4.1 Intern

APPENDIX B.

Long-Term Monitoring Survey 2019

Long Term monitoring is expected to be one of the largest costs for the Office of Environmental Management in the upcoming decade. Established approaches often use expensive monitoring wells whose samples are often redundant and encourage reactive decision making.

In order to foster more proactive solutions, a new Long-Term Monitoring Paradigm has been developed to reduce the number of monitoring wells by 80% and replace these wells with a more efficient and cost-effective approach consisting of the site-specific monitoring network.

The goal of this survey is to identify stakeholder's primary concerns when transitioning to a passive long-term monitoring approach as well as to inquire about current LTM practices in relation to metals and radionuclide contaminants in groundwater.

- Please tell us about your current long term monitoring approach: (such as frequency of sampling and/or O&M habits)
- How many wells do you sample?
- What is your monitoring/sample frequency?
    - Quarterly
    - semi-annual
    - annual
    - biannually
- Have you conducted a statistical well optimization study to optimize the location and frequency of well sampling? If yes, please explain.
- Are there any issues you have identified that need to be addressed with your current monitoring approach? If yes, please explain.
- What technical concerns do you have regarding metal and radionuclides contaminants in groundwater within your site? Do you believe that the current well network is effectively monitoring residual contaminant migration?
- Do you believe that the cost of your current approach will__________ over time?
    - increase
    - decrease
    - remain the same
- How open are you to a new approach for groundwater long term monitoring? (1 being not open, 5 being very open)

  1 2 3 4 5
- Have you considered the use of alternative measurements (such as Sensors, ERT, Spectral Geophysics, Remote Sensing, etc.)?
- What is your annual current cost for the following:
    - Capital cost:
    - O&M cost:
    - Labor cost:

        - Implementation cost:
- Which site do you work with?
- How long have you been working at that site?
- How satisfied are you with the current long term monitoring approach of that site? (1 being not good, 5 being very good)

  1 2 3 4 5
- What suggestions can you offer in regards to long term monitoring at the site you work for?
- If you feel comfortable with us contacting you to discuss your suggestions further, please provide name and email/phone number below.

APPENDIX C.

DOE-HQ Intern Site Visit
Savannah River National Lab Tour
Tuesday, July 23, 2019
FINAL Agenda

NOTE: Electronics, including cell phones, smartphones, two-way pagers, PDA's (Blackberry, Palm Pilot, iPads, etc.), laptop computers, thumb-drives, wireless/blue tooth devices, cameras (digital and film), voice recorders, fit bits anything with a USB port including some pedometers and data watches, etc. are NOT allowed inside the SRNL Limited Area security boundaries

Attire: Comfortable clothing and closed-toe shoes

Tour Participants: 14 - Skip Chamberlain, Latrincy Bates and Interns
SRNL Host(s): Brian Looney, Dennis Jackson, Hansell Gonzalez-Raymat

Time	Location	Escorts/Participants
8:00 am	**Arrive**	
	• Meet and Greet	All
	• 8:15 Presentation: Enhanced Attenuation of Uranium	Hansell Gonzalez-Raymat
	• 8:45 Presentation: M-Area VOC Treatment	Dennis Jackson
	• 9:15 Discussion	
	• 9:45 Government Van Arrives / Board Van	SRS Transportation
	• Enter SRS Using Normal Entry Procedures	Centerra-SRS PPD
10:00 am	Begin Driving Tour of SRS	Brian Looney
	• M Area	
	• F Area	
	• 11:30 Lunch: 766-H Cafeteria	
	• 12:30 G Area: Phytoremediation Site	
2:00 pm	**Arrive**	
	• Hg Laboratory Overview and Tour	Brian Looney
3:30 pm	**Visit: Day 1 Concludes**	

DOE-HQ Intern Site Visit
Savannah River National Lab Tour
Tuesday, July 23, 2019
FINAL Agenda

Tour Participants: 14 - Skip Chamberlain, Latrincy Bates, and Interns
SRNL Host(s): Bill Bates, Connor Nicholson, and Anna Knox

Time	Location	Escorts/Participants
8:45 am	**Arrive** • Meet and Greet	
9:00 am	**Presentations** • Bill Bates – Overview of Spent Fuel Activities at SRS • Connor Nicholson –Overview of D&D activities at SRS • Anna Knox – Overview of Reactive Barriers	
10:30 am	• Tour of Knox Lab	
12:00 pm	**Visit Concludes** • Depart SRS	