Joint Technical Advisory Group Meeting
University of Miami and Florida Atlantic University

Funded by the Hinkley Center for Solid and Hazardous Waste Management (HCSHWM)
and the Solid Waste Authority of Palm Beach County

DATE: **Friday, October 19, 2018**
TIME: **10:00 am**
WHERE: **Solid Waste Authority of Palm Beach County**
Administration Building Auditorium
7501 N. Jog Road, West Palm Beach, FL 33412

Directions from I-95
- Take I-95 to 45th Street
- Turn West on 45th Street to the end
- Follow the curve over the bridge (N. Jog Road)
- Turn West at the green sign that says "Solid Waste Authority Administration"

Directions from Florida's Turnpike (SunPass Only)
- Take Florida's Turnpike to Exit 107 (SR 710 Beeline Hwy)
- At the traffic signal continue straight (N. Jog Road)
- Turn West at the green sign that says "Solid Waste Authority Administration"

MEETING AGENDA
Friday, October 19, 2018

10:00 – 10:15 am	Opening Address and Introduction of Participants	Helena Solo-Gabriele Daniel Meeroff
10:15 – 10:25 am	Overview of University of Miami Studies	Helena Solo-Gabriele
10:25 – 11:00 am	Characterization of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Leachate	A. Jones H. Zhang
11:00 – 11:15 am	Open Forum	Participants
11:15 – 11:25 am	Overview of Florida Atlantic University Studies	Daniel Meeroff
11:25 – 11:55 am	Electrochemical Oxidation Treatment of Leachate	Md. Fahim Salek
11:55 – 12:25 pm	Development of Biosensor for Odor Detection	Sharmily Rahman
12:25 – 12:55 pm	Examination of Leachate Collection System Clogging	Bishow Shaha
12:55 – 1:15 pm	Open Forum	Participants
1:15 pm	Adjourn, Thank You	Daniel Meeroff

Please RSVP (or suggest an alternate) to
dmeeroff@fau.edu and hmsolo@miami.edu

For more information:

Dr. Daniel E. Meeroff Tel.(561)297-2658 http://labees.civil.fau.edu
Or
Dr. H. Solo-Gabriele Tel.(305)284-3467, office (305)989-9103, cell http://www.coe.miami.edu/hmsolo/?page_id=769

To connect from your computer, register at **https://swa.adobeconnect.com/tag10-19-18/event/event_info.html**

Attendance: Dr. Meeroff, Dr. Solo-Gabriele, Wester Henderson, Amy Hightower, Bishow Shaha, Md Fahim Salek, Sharmily Rahman, Dan Schauer, Manuel Hernandez, James Telson, Mary Beth Morrison, Ramana Kari, Nicole Robey, Mark Eyeington, Amede Dimonnay, Nate Mayer, Athena Jones, Ashley Thomson, Dave Phillips, David Meyers, El Kromhout, Elisabeth Hawley, Hilary Thornton, John Merrill, Johnsie Lang, Kavitha Dasu, Mary Maurer, Morlon Barlaz, Neil Coffman, Ram Tewari, Robert Sterner, Rohan Sethi, Laura Barrett

Minutes:

1. Opening address by H. Solo-Gabriele and D. Meeroff was followed by introduction of the group members and attendees both in person and virtual (10:04 am) They both thanked the Solid Waste Authority of Palm Beach County for providing the meeting location and for the audiovisual support. Those connected via Adobe Connect could not introduce themselves. A list of names for individuals participating virtually was read during the meeting address. All participants, in person and virtual, were thanked.

2. H. Solo-Gabriele introduced PFAS in leachate research. Athena Jones joined the presentation over the teleconference line to discuss the rationale. H. Solo-Gabriele gave a primer on PFAS naming conventions and properties. Then addressed the sampling and analytical procedures conducted at the USEPA lab in Research Triangle Park. Next, H. Solo-Gabriele presented results from this study and compared to Lang et al. 2017, pointing out that 70 ng/L is the current drinking water standard for PFAS+PFOA, one order of magnitude (700 ng/L) higher was an expected outcome, and 1100 ng/L was the Lang et al. 2017 published national average. The Florida samples were higher than the national average. Audience questions were about:
   - Did the initial filtration step remove any PFAS-like compounds that were adsorbed to the solids?
   - What treatment was conducted? Were PFAS precursors not destroyed but converted to other PFAS-like products?
   - Age of landfill trends?
   - Were PFAS in biosolids a source at landfills? What about in recyclables?
   - Additional questions and answers from the audience are detailed in the following page.
3. D. Meeroff introduced the FAU research group and asked the TAG members to visit the research website to comment on previous research final reports that have just been released.
4. F. Salek introduced his electrochemical oxidation of leachate research. He presented results of pretreatment with Fenton followed by EOx. A question from the audience was related to how this process would deal with PFAS/PFOA. It was agreed to produce an influent/effluent series of samples for testing.
5. S. Rahman presented on her biosensor experimental plan. A question about other gasses than hydrogen sulfide, and S. Rahman will be testing ammonia, methane, carbon dioxide, and hydrogen sulfide mixtures in nitrogen. There was mention of a 500 ppbv methane sweeping regulation, which will be taken into account.
6. B. Shaha presented on his leachate clogging research. He presented alternative sources of dilution water, issues related to using NEFCO water for dilution (solids removal required), pH adjustment using carbon dioxide or LFG, his discovery of two types of solid clogs ("hard" and "loose"). He noted that pH increased, while alkalinity and calcium decreased during incubation. There were questions about the biological aspect of leachate clogging and what disinfection techniques might be effective in leachate, adding chemicals to inactivate pathogens is problematic in leachate and injection wells, but what about design guidance for reducing exposure to air or eliminating air in LCS, what about the 2 MG/month flow from Dyer Park would it be useful as a dilution water source, are VFAs involved, heat sterilization may inadvertently increase Ca precipitation, does LSI increase going down the well is there a temperature change, should the results be compared to another facility such as Miami-Dade Blackwater Plant.
7. Dr. Solo-Gabriele and Dr. Meeroff thanked the participants and the hosts at SWA and then adjourned for lunch (12:35 pm).

Questions and Answers (paraphrased):

Elisabeth Hawley: Have you included total oxidizable precursor (TOPs) analysis for your samples?

Response: Not in this set of analyses. TOPs analyses would be an excellent set of analyses to include. TOPs would include all of the PFAS precursors in bulk. It would be helpful in analyzing before and after treatment to get a bulk reading of all fluorinated species. The current method of targeted analyses could miss the PFAS precursors that would convert to the targeted species that are measured.

Elizabeth Hawley: The City of New York has analyzed over 200 landfills for PFAS. The lead is Martin Brand at NYSDEC Office of Remediation and Materials Management.

Response: We will work towards tracking down that study.

Ram Tewari: Though focus of the study is landfill leachate, does recyclability of the products with PFAS is a concern. Other concern is regarding beneficial utilization of biosolids.

Response: In terms of biosolids, studies have shown that PFAS through the wastewater treatment process tend to accumulate in biosolids. The biosolids are typically land applied and thereby potentially serving as a means to redistribute PFAS into the environment. It would be of interest to trace PFAS through the recycling process.

Ram Tewari: How does deep well injection of landfill leachate impact

Response: There are landfills that dispose leachate through deep well injection. The impacts are not known however.

El Kromhout: Other concern is regarding beneficial utilization of biosolids?

Response: The samples came from landfills in Florida. The names of the landfills are kept anonymous.

Mary Beth Morrison: What was the type of treatment of the landfill treatment?

Response: The landfill leachates were treated using an aeration process. One was a batch treatment process the other was a continuous flow process. Both used aeration with sedimentation for the purpose of removing ammonia from the leachate. Both leachates are sent to wastewater treatment plants after treatment.

Amede Dimonnay: Did results how a relationship with the age of landfill?

Response: In this study the levels of PFAS were dominated by landfill type with ash leachates characterized by lower levels of PFAS relative to other landfills. Given the small number of samples within a landfill type, we were unable to see effects of age. A study conducted in Austria indicated that there were differences between PFAS leachates levels for open landfills versus closed landfills. We would expect differences in terms of the changes in the PFAS industry over time. For very old landfills, before 1940s, levels should be non-existent because PFAS had not yet been produced. After this time, landfills that were opened would have received primarily PFOA and PFOS. With the conversion to alternatives, new landfills would contain the alternatives to PFOA and PFOS.

Response from Johnsie Lang (via chat): In my national survey we found six PFASs tested that demonstrated significantly higher concentrations in leachate from younger waste compared to older waste. All other PFASs did not differ with waste age.

Manny Hernandez: Is it right to say that C&D and Class III landfills have higher PFAS levels relative to MSW? C&D and Class III landfills are not as highly regulated in terms of bottom liners relative to MSW landfills.

Response: We do not have enough data to show that there is a significant difference in PFAS between the different landfill types. However, given the types of waste found in C&D and Class III (e.g., carpet, wood with sealants, etc.) it would make sense that these type of landfills would have more PFAS. In order to show this, we will need to sample more landfill leachates.

Hilary Thorton: The Dalton Landfill in Georgia has conducted a study to evaluate PFAS in biosolids. This area is impacted by carpet manufacture.

Response: We will work towards getting a copy of the study. Thanks.

We Welcome You
to the October 19, 2018

Joint UM and FAU
Hinkley Center TAG Meetings

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COLLEGE OF ENGINEERING & COMPUTER SCIENCE
Florida Atlantic University

AGENDA
FRIDAY, OCTOBER 19, 2018

- 10:00 am Introductions
- 10:15 am PFAS in Landfill Leachate
- 11:00 am Questions/Answers
- 11:15 am Introduction of FAU Studies
  - Electrochemical Oxidation Treatment of Leachate
  - Biosensor for Odor Detection
  - Leachate Collection System Clogging
- 12:55 pm Questions/Answers

PFAS PRESENTATION

MIAMI

RESEARCH TEAM AND HINKLEY CENTER

RESEARCH TEAM MEMBERS

Name	Affiliation and Address	Phone Number	Email
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Athena Jones	Graduate Student University of Miami		a.jones18@umiami.edu
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HINKLEY CENTER

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TAG COMMITTEE

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Characterization of *Per- and Poly-fluoroalkyl Substances* (PFAS) in Landfill Leachate and Preliminary Evaluation of Leachate Treatment Processes

Dr. Helena Solo-Gabriele
Professor

Athena Jones
Ph.D. Student

Hekai Zhang
M.S. Student

University of Miami
College of Engineering
Dept. of Civil, Architectural & Environmental Engineering

Project funded by: Hinkley Center for Solid and Hazardous Waste Management

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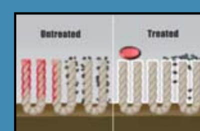
OUTLINE OF DISCUSSION

I. Research motivation
II. Background of PFAS
III. Research Objectives
IV. Results to Date

PFAS USES

- **PFOA** or **C8**
  - Used in Teflon-making process
- **PFOS**
  - Used in Scotchguard
  - Hydrophobic and lipophobic



ALTERNATIVES TO PFOA AND PFOS (FTOH)

- FTOH is used in wrappers for fast food, pizza box liners, and microwave popcorn bags

SOURCES OF PFAS CONTAMINATION

- Waterproof coatings and sealants
- Non-stick surfaces, cookware
- Food packaging, esp. fast food
- Teflon: floss, non-stick bandages, plumbers tape,

RESEARCH MOTIVATION

- PFAS can be inhaled, ingested, or absorbed via skin
- PFAS are found virtually everywhere in the world and in the blood serum of >99% of Americans
- Toxicological studies have linked PFAS in serum to adverse health effects

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HEALTH IMPACTS
MEDICAL CONDITIONS LINKED TO PFAS

Health Outcomes
- Kidney & bladder cancer
- Liver tumors and cancer
- Thyroid diseases
- Hormonal changes
- Increased cholesterol

- Different impacts by gender
- Children may be at greater risk
- Developmental impacts largely unknown

Units: ng/L

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HEALTH IMPACTS
RECOMMENDED EXPOSURE LIMIT

EPA issued (MAY 2016) a non-enforceable health advisory of 70 ppt (ng/L) PFOA+PFOS concentration in drinking water

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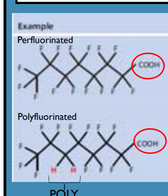
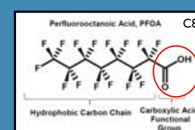
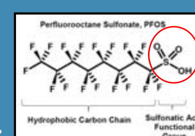
PFAS CHEMISTRY
STRUCTURE



- **Poly- or Per-fluorinated alkyl substances (PFAS)**
  (Depending on partial or full fluorination)
- **Acid functional group + alkyl group**
  (Fluorinated carbon chain or alkyl group)
- **C-F bounds make compounds extremely persistent**
  (Resistant to hydrolysis, photolysis, and biodegradation)





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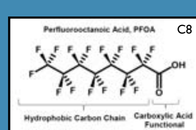
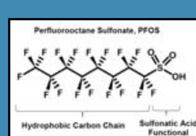
PFAS PERSISTENCE

- Persistent due to C-F bonds
- The half-life of
  - PFOA in water is 92 years
  - PFOS in water is 41 years
- First manufactured in 1940s.
- Phase out:
  - PFOA (2015) from 8 manufacturers
  - PFOS (2002) from its only manufacturer





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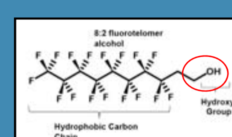
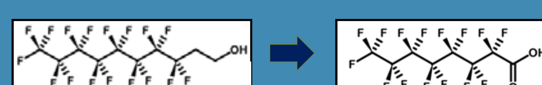
PFOA, PFOS ALTERNATIVES (FTOH)

- PFOA can also be formed from degradation of fluorotelomers (FTOH)





FTOH

PFOA

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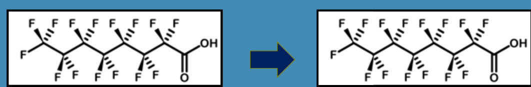
PFOA, PFOS ALTERNATIVES (PFHXA)

- PFHxA Perfluorohexaonic acid (C6)
- More mobile
- Shorter half-life but more may be needed to achieve same benefit



PFOA PFHxA

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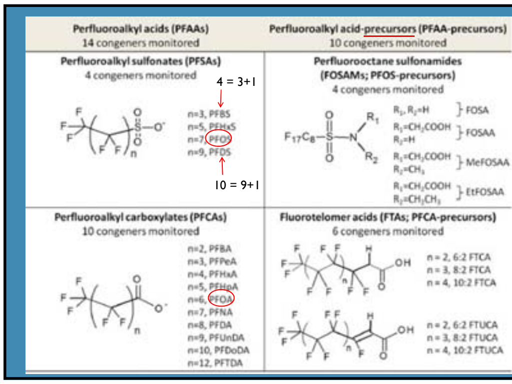
PFAS



Benskin et al. 2012

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DETECTION OF PFAS IN ENVIRONMENT

- PFAS have been detected in low quantities in the arctic ice cap
- In rivers not affected by production facilities: 2.2 – 46 ng/L
- In rivers downstream of chemical production facilities: 4,500 – 19,400 ng/L
- Leachate from landfill that receives PFAS wastes: 140,000 ng/L

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DETECTION OF PFAS IN LANDFILL LEACHATE

Table 1: Concentrations (ppt) of PFOA and PFOS in untreated landfill leachates

	U.S. (Huset et al. 2011)	Finland (Perkola and Sainio 2013)	Spain (Fuertes et al. 2017)	Germany (Busch et al. 2010)	China (Yan et al. 2015)
No. of Landfills	6	2	4	22	5
PFOA	660	170	600	150	280 to 214,000
PFOS	110	110	20	30	1100 to 6000

EPA Health Advisory Level = 70 ng/L (PFOA+PFOS)

U.S. National Study of 70 PFAS' in 95 Landfill Leachate Samples, Lang et al. 2017

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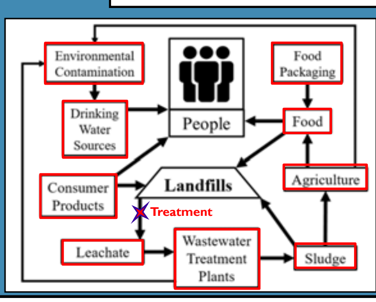
CYCLE OF PFAS CONTAMINATION



- **Landfills** are a central component of the exposure cycle
  - accumulation of PFAS
- **Leachate** treated in **WWTP**
- **Sludge** from **WWTP** applied in **agriculture**

(inspired by Oliaei et al. 2013)

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RESEARCH OBJECTIVES

1. Sample and analyze leachate samples for PFAS from
   - Landfills
   - Leachate treatment systems
2. Unique features
   - Measured leachates from Class III, C&D, WTE ash landfills.
   - Measured gas condensates.
   - Measured full-scale landfill leachate treatment systems

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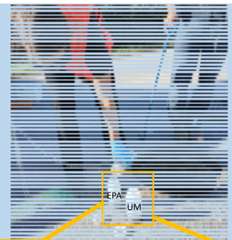
Leachate Sampling

Sample Collection

- Collect two, 0.5 liter samples of leachate from landfills throughout State of Florida. Age of landfill, composition of fill, and climate to be considered
- UM sample: basic physical-chemical parameters (pH, COD)
- EPA sample: First batch, freeze and ship. Second batch, filter, freeze and ship.



EPA for PFAS Analysis

UM for characterization

Sampling at Landfills

Sampling Apparatus:

- 30 ft. of zinc coated chain
- Detachable chain, clasps, + hose clamp to hold bottles
- Soiled portions can be easily replaced
- Sampled from manholes up to 30 feet deep with only 1 to 2 inches of leachate

Contamination Avoidance

- PFAS are found in many scientific products
- Products specifically avoided include:
  - Blue ice packs, solvent gloves, hand lotions (on day of sampling), certain labels, all Teflon items
  - Everything used was questioned prior for possible PFAS contamination

Contamination Avoidance

- Bottles capped and stored in Ziploc bags prior to entering field
- Blanks prepared using DI water from machine with no Teflon parts
- Separate sample taken for leachate characterization

Contamination Avoidance

- One trip blank (closed throughout sampling)
- One sample blank per sample (left open near each site during sampling)
- One lab blank (created at EPA lab and processed as all other blanks)

Sampling at Landfills

First Set		Second Set	Group
MSW + Gas Condensate	→	MSW Gas Cond (not reanalyzed)	I
Class III	→	Class III (reanalyzed)	I
C&D	→	C&D (reanalyzed)	I
MSW	→	MSW (reanalyzed)	I
		MSW (new and old)	II
		MSW (old)	II
		MSW Influent	III
		MSW Effluent	III
		MSW+C&D Influent	V
		MSW+C&D Effluent	V
		Ash	IV
		Ash	IV

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Leachate Characterization

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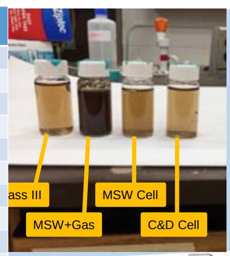
Leachate Characterization

Leachate Type	Facility ID	Age	pH	COD
MSW Gas Cond	I	21	7.3	14,000
Class III	I	26	7.6	2,700
C&D	I	25	7.6	2,000
C&D Influent	V		8.1	4,600
C&D Effluent	V		8.0	4,100
MSW	I	12	6.9	8,800
MSW (new and old)	II	17	7.7	3,800
MSW (old)	II	27	7.7	3,800
MSW Influent	III	34	7.5	1,800
MSW Effluent	III	34	8.1	700
Ash	IV	18	6.2	4,200
Ash	IV	18	6.4	4,300



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Process of PFAS Analysis

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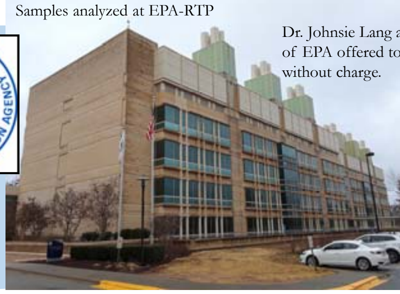
Samples analyzed at EPA-RTP



Dr. Johnsie Lang and Dr. Mark Strynar of EPA offered to analyze 20 samples without charge.

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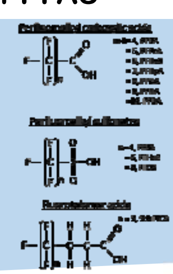
Targeted Analysis for 11 PFAS

- Carboxylic acid PFAS (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA)
- Sulfonated PFAS (PFBS, PFHxS, PFOS)
- 5:3 fluorotelomer carboxylic acid (5:3 FTCA)



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Calibration Curve

- Standards received from Wellington Labs were used to prepare …
  - Calibration curve
  - Internal standard
- Standards contained various classes of PFAS of varying carbon chain lengths

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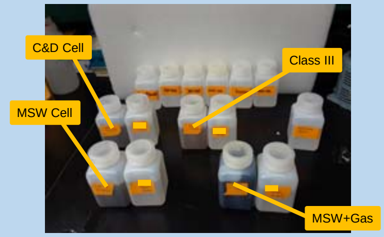
Filtration

- Internal standard was added to all samples, blanks, and calibration curve samples before filtration



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Filtration

- All samples, blanks, and calibration solutions were filtered using glass fiber filters.
- The MSW pump station + gas condensate presented a challenge & had to be double filtered

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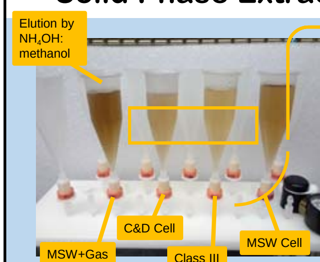
Solid Phase Extraction (SPE)



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LC/MS/TOF

- Liquid chromatography, mass spectrometry, time of flight
- Targeted analyses
  - Carboxylic acid PFAS (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA)
  - Sulfonated PFAS (PFBS, PFHxS, PFOS)
  - 5:3 fluorotelomer carboxylic acid (5:3 FTCA)

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Visits to EPA-RTP

- First Visit – January 2018, Athena Jones was mentored
- Second Visit – July 2018, Helena Solo-Gabriele was mentored

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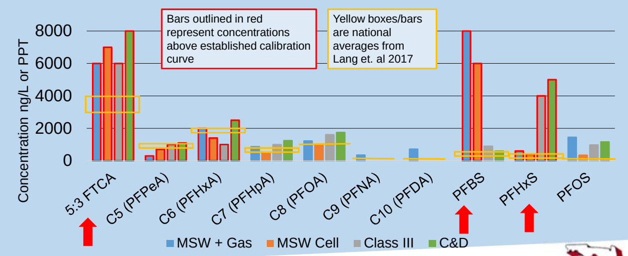
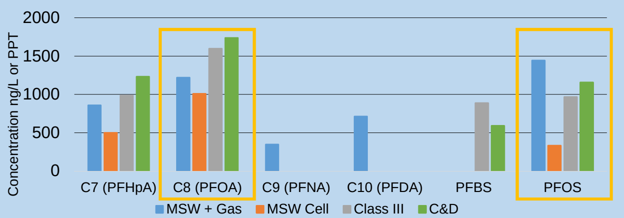
Results

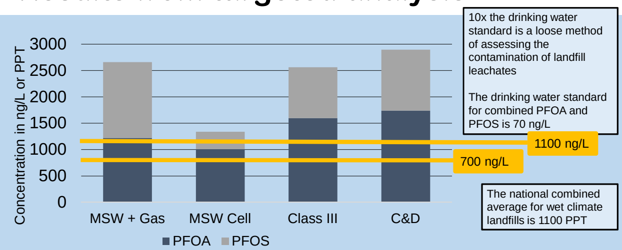
Results from targeted analysis (1st trip)



Results from targeted analysis (1st trip)

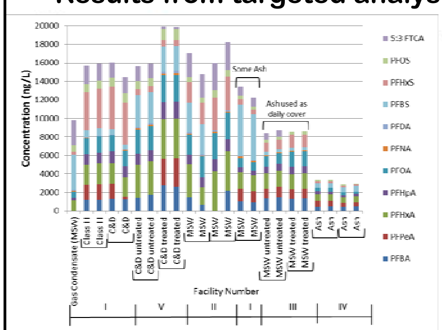


Results from targeted analysis



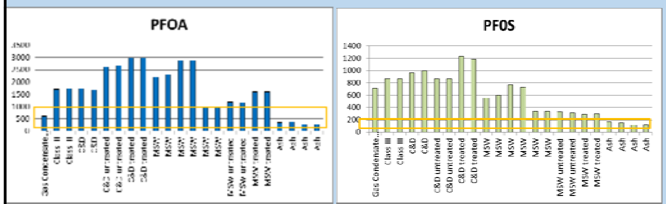
Results (2nd EPA visit)

Results from targeted analysis (2nd trip)



- Ash has lowest levels of PFAS
- MSW mixed with ash has lower PFAS in comparison to MSW only
- C&D/Class III leachate similar to MSW leachate
- Treatment of C&D leachate increases PFAS

Individual PFAS Species



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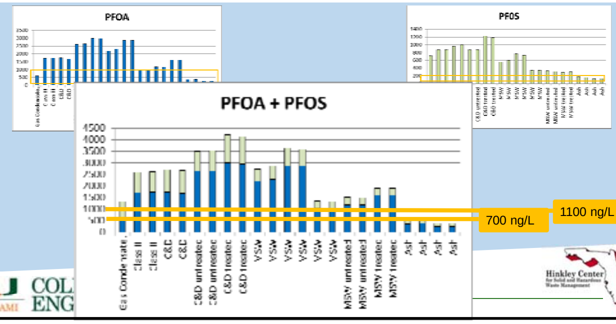
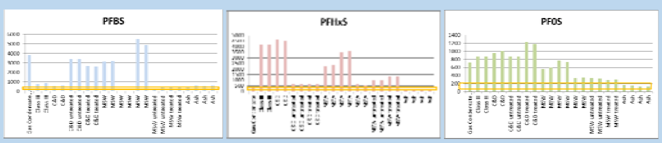
Individual PFAS Species



Hinkley Center

Individual PFAS Species



Levels of PFAS with sulfonatic acid groups tend to be high

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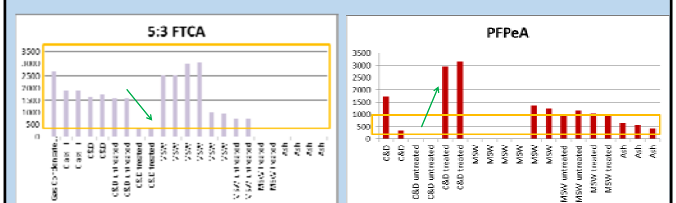
Individual PFAS Species



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Next Steps

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Next Steps

- Submitted proposal to EPA Star Grant Competition (w/T. Townsend)
- Write and submit manuscript from first phase with EPA-RTP
- Second study set with EPA-ORD (scheduled for Oct. 18 start)
  Samples to be analyzed for 26 PFAS plus BOD, COD/Ammonia, Conductivity, pH, Temperature, Metals, TOC, TDS, TS.
- Host third TAG meeting during summer of 2019

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Acknowledgements

- Hinkley Center for funding this research opportunity
- Johnsie Lang & Mark Stryner of ORISE/EPA for critical help in sample analysis
  - (Oak Ridge Institute for Science and Education)
- Landfill staff who helped with sample collection
- TAG members for giving their time and expertise to make this project a success
- University of Miami office staff who aided in shipping samples and acquiring materials

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Thank you, questions?

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Technical Advisory Group Meeting

1. "Electrochemical Oxidation of Leachate"
2. "Odor Biosensor"
3. "Leachate Collection System Clogging"

Daniel E. Meeroff, Ph.D.
Department of Civil, Environmental & Geomatics Engineering

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Daniel Meeroff, Ph.D.

- **Professor & Associate Chair, Department of Civil, Environmental & Geomatics Engineering, FAU**
  - **Director of the Laboratories for Engineered Environmental Solutions (Lab.EES)** http://labees.civil.fau.edu
  - **College Liaison, Undergraduate Research & Community Engagement**
- **Research Interests**
  - Environmental Engineering
  - Water/Wastewater Treatment Technologies
  - Utilities Resiliency
  - Water Quality & Aquatic Toxicity
  - Solid/Hazardous Waste Management
  - Water Use Efficiency and Pollution Prevention Strategies
  - Industrial Wastewater & Leachate Management
  - Air Quality Management
  - STEM Education Research

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Recent Funded Research

- **Hinkley Center funding for leachate clogging, food waste diversion, industrial waste treatment, air quality monitoring**
- **Environmental Research and Education Foundation funding for biosensor development**
- **NSF Electron Beam Processing research**
- **City of Wellington phosphorus loading from on site treatment and disposal systems**
- **AECOM/URS disposal well resiliency project**
- **Industry funded algae control demonstration projects**
- **NSF STEM Education Grant (LEARN Program)**

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Agenda

1. Introductions/Opening Remarks	*Dr. Meeroff*
2. Electrochemical Oxidation of Leachate	*Salek*
3. Odor Biosensor	*Rahman*
4. Leachate Clogging	*Shaha*
5. User Input/Open Forum	*Everyone*

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Current Projects

1. **"Investigation of Electrochemical Oxidation for Treatment of Landfill Leachate"**
2. **"Development of a biosensor for measuring odorants in the ambient air near solid waste management facilities"**
3. **"Leachate Collection System Clogging"**
4. **"Investigation of Effective Odor Control Strategies"**
5. **"Beneficial Reuse Solutions for Landfill Operations and Management"**

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"Landfill Leachate Treatment by Advanced Electrochemical Oxidation"

Daniel E. Meeroff, Ph.D.
Md Fahim Salek
Department of Civil, Environmental & Geomatics Engineering

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Introduction

- Leachate is a liquid that passes through a landfill and extracts constitutes from it
- Potential threat to soil, surface water and groundwater
- Current disposal practices are deep-well injection, on-site treatment or mixing with municipal wastewater
- Leachate volume totaled 2.2 billion gallons in 2013 and 2.1 billion gallons in 2014 in Florida
- Approximately 92% of Florida active landfills discharge leachate to wastewater treatment plant and 3% discharge directly to water body after onsite treatment

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Electrochemical Oxidation

- Electrochemical oxidation (EOx) is an oxidation process that occurs through the application of external voltage
- Recently, EOx has been successfully used for treating wastewater from tanneries, power plants, municipal areas, and landfills
- This process involves direct oxidation of pollutants at the anode as well as indirect oxidation by hydroxyl radicals, chlorine, hypochlorite ion, and other oxidants generated in the matrix

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Objectives

1) Conduct testing to determine the efficiency of EOx coupled with other pre-treatment process to remove selected parameters of interest (such as COD/BOD, ammonia, turbidity) for safe discharge or reuse of the treated leachate

2) Assess and monitor any halogenated byproducts generated during the treatment process

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Tasks

1. Collect data on electrochemical oxidation
2. Perform laboratory scale experiments
3. Assess treatment performance
4. Assess byproduct generation
5. Develop final recommendations and preliminary cost analysis

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Task 1. Collect Data on Electrochemical Oxidation

Anode Material	Current Density (Am^{-2})	Volume of Sample (L)	Time (h)	COD Removal %	Ammonia Removal %	Cl^- mg/l	Authors
Ti/RuO2-IrO2	260 A m-2	0.2	1.5	44	50	831	H. Zhang et. Al (2011)
Ti/IrO2-RuO2	80 A m-2	0.12	4	20	N/A	6150	E. Turro et. Al (2011)
	160 A m-2			40			
	320 A m-2			35			
Ti/RuO2-IrO2	300 A m-2	0.8	N/A	20	35	3702	H. Zhang et. Al (2011)
	900 A m-2			10	85		
Graphite carbon	800 A m-2	0.5	4	65	N/A	N/A	M. Bashir et. Al (2009)
BDD	2571 A m-2	10	8	50	30	2574	A. Anglada et. Al (2011)
Ti/Pt	400 A m-2	0.25	1	63	80	5500	F. Feki et. Al

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Task 2. Perform Laboratory Scale Experiments

Treatment Process Flow Diagram

Origin Clear AOx → Magneli EOx

Ozone Oxidation → Magneli EOx

Fenton Coagulation → Origin Clear AOx

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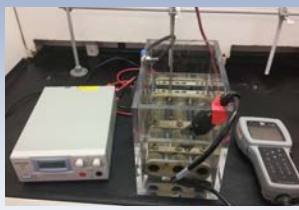
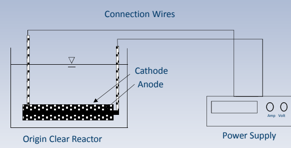
Experimental Set-up of Origin Clear Reactor





Schematic Diagram of Origin Clear Reactor

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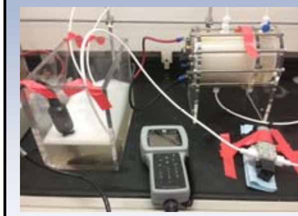
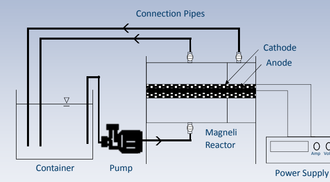
Experimental Set-up of Magneli Reactor





Schematic Diagram of Magneli Reactor

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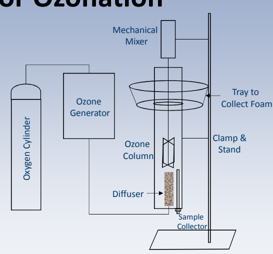
Experimental Set-up for Ozonation



Schematic Diagram of Ozone Unit

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Test Details

Origin Clear Reactor	
Ampere Range	25-29 Amps
Voltage Range	5 Volts
Electrooxidation Time	60 mins
Anode Material	Titanium coated with IrOx and RuOx
Sample Volume	4 liters

Magneli Reactor	
Ampere Range	30 Amps
Voltage Range	5-6 Volts
Electrooxidation Time	30-45 mins
Anode Material	Titanium coated with IrOx and RuOx
Flow	4 liters/min
Sample Volume	4 liters
Current Density	75 mA/cm^2

Ozone Reactor	
Dose	20 g/h
Feed	Oxygen
Pressure	5 psi
Column height	2 feet
Sample Volume	4 liters

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Sample Details

Sample Details	
pH	7-7.5
COD	6000-9500 mg/l O_2
BOD_5	500-600 mg/l O_2
BOD_5/COD	0.05-0.70
NH_4	2500-3200 mg/l
Chloride	12.5-13.8 g/l
Turbidity	1000+
Conductivity	29-57 mS/cm

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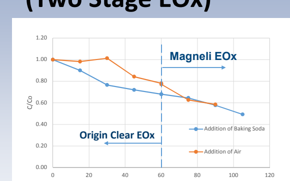
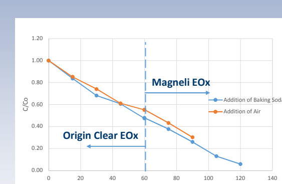
Assess Treatment Performance (Two Stage EOx)



COD Removal



Ammonia Removal

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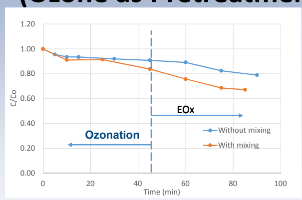
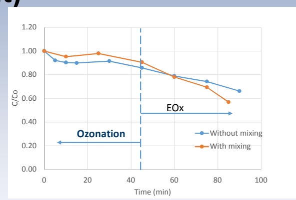
Assess Treatment Performance (Ozone as Pretreatment)



COD Removal



Ammonia Removal

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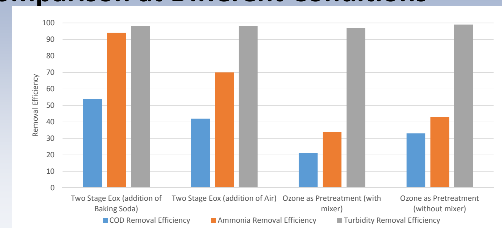
Assess Treatment Performance Comparison at Different Conditions



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Current Work

1) Fenton Coagulation

2) After Settlement

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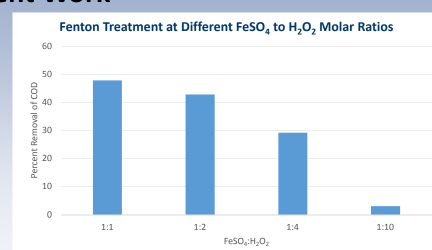
Current Work



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Task 4: Assess Byproduct Generation

1. **Treating leachate can produce halogenated byproducts like THMs as high as 20,000 ppb, extremely higher than the USEPA's MCL [1]**
2. **Depending on pH and anode material, the oxidation mechanism follows two routes: Electrochemical conversion or electrochemical combustion. By maintaining pH >7 combustion can be favored, which will generate less halogenated byproducts [2]**
3. **Generated gas can be trapped and analyzed using gas chromatography-mass spectroscopy to study further treatment requirements to eliminate byproducts**

[1] Li, Nanzhu & Deng, Yang. (2012). Formation of Trihalomethanes (THMs) during Chlorination of Landfill Leachate. International Journal of Environmental Pollution and Remediation. . 10.11159/ijepr.2012.002.
[2] A. Anglada, A. Urtiaga, I. Ortiz, Contributions of electrochemical oxidation to wastewater treatment: fundamentals and review of applications, Journal of Chemical Technology and Biotechnology 84 (2009) 1747-1755

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Next Steps

1) **To study the detection using LC-MS or GC-MS and treatment of halogenated byproducts**
2) **Cost analysis and comparison with other existing methods**

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Discussion Question

- Challenges:
  - Controlling the foam produced during the process
  - Managing the sludge produced during Fenton coagulation/oxidation
  - Managing the potential byproducts

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Thank You

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"Development of a Biosensor for Measuring Odorants in the Ambient Air Near Solid Waste Management Facilities"

Daniel E. Meeroff, Ph.D.
David M. Binninger, Ph.D.
Sharmily Rahman

Department of Civil, Environmental & Geomatics Engineering

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INTRODUCTION

- Detecting and quantifying odor at landfills and industrial facilities is difficult because of subjectivity in the analytical method
- As of now, no truly objective method of monitoring nuisance odors is readily available at low cost
- Human odorant binding proteins are used to carry odorants in the human olfactory network, so they could be used as biosensors to objectively measure odorants
- Project has the potential to make odor investigations more manageable for landfill operators

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OBJECTIVES

- Develop a novel technology that uses human odor binding protein (hOBP2A) biosensor to objectively quantify odors
  - This could standardize odor identification and establish reasonable, objective standards for odor severity
- Expose biosensor to selected model odorants
  - Both single and mixtures of odorants
- Determine positive/negative spectrophotometric response and concentration dependence/Beer's Law quantitation

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Proposed Approach

- hOBP2A can bind with odorants in the µM-range
- The protein can be marked with a fluorescent tag (1-AMA)
- Odor intensity measurement is based on the inverse relationship between bound odorants and unbound proteins (non-specific)
- The fluorescent tag response is expected to follow an inverse concentration-dependence and follow Beer's Law (quantitative)
- Potentially reversible with a slight change in pH

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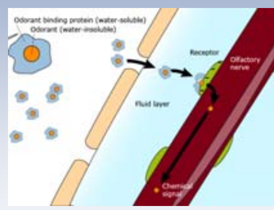
hOBP2A

- Binds to odorants to deliver them to the olfactory receptors
- Stable to temperature, organic solvents, and proteolytic digestion
- Broad binding affinity
- Can be expressed in bacterial systems at low cost & easily purified



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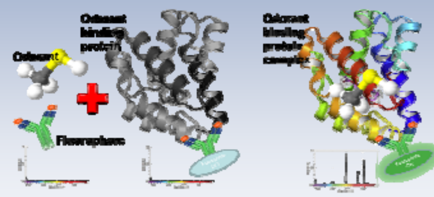
MECHANISM



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TASK 1: DEVELOP BIOSENSOR COMPLEX

I. 
- Obtain purified hOBP2A from Dr. Binninger and his team

II. 
- Apply fluorescent tag (1-AMA) to the protein

III. 
- Dilute biosensor in buffer solution

hOBP2A + 1-AMA + Buffer solution → Biosensor complex

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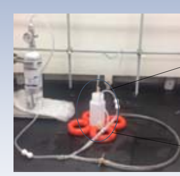
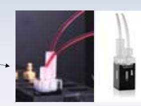
TASK 2: DEVELOP EXPOSURE CHAMBER



Prototype of exposure chamber (version 1)

No need for pipette if spigot available



Flow-through cuvette

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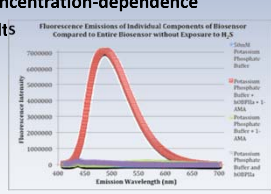
TASK 3: PROTEIN SENSITIVITY EXPERIMENTS

- Begin with H_2S to replicate previous experiments
- Determine spectroflurometry-based concentration-dependence
- Verify with previous experimental results



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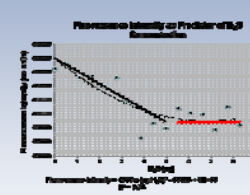
Previous Work Showed a Saturation Limit

- Signal seems saturated from 5 – 10 µg H_2S
- Under these conditions, the maximum quantitation limit appears to be ~4-5 µg H_2S
- Possible reasons
  - Reaching equilibrium, the reaction reverses and causes the fluorophore to release the protein
  - Relative binding affinity of competing gasses
  - Sampling error



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TASK 3: PROTEIN SENSITIVITY EXPERIMENTS

- Verify previous findings
  - Determine if the calibration and quantitation range are accurate and reproducible
  - Determine the optimal ratio of hOBP2A:fluorophore (currently 1:1)
    - Test with different mixtures (concentration) of protein and fluorophore
    - Exposing the system to higher concentrations of odorants
    - Conduct more trials

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TASK 4: PROTEIN SENSITIVITY ON MIXTURES

- How do other odorants bind with the biosensor complex?
  - Check with pure compounds (e.g. NH_3) and mixture of "standard" landfill gas containing H_2S, CO_2, NH_3 and N_2
  - Check the binding capacity of the biosensor complex being exposed to acidic and basic odorants (pH change)

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EXPECTED RESULTS

- To determine the concentration of unknown odorants from landfills using hOBP2A protein biosensor with fluorometry
- Verify how the process works with H_2S
- Demonstrate that the method works with other model odorants and mixtures
- Bring about improvements to conventional odor investigation methods

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"Investigation of Leachate Management Solutions at the Solid Waste Authority of Palm Beach County"

Daniel E. Meeroff, Ph.D.
Bishow Shaha, MSCV

Department of Civil, Environmental & Geomatics Engineering

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Agenda

- Current work
- Results
- Future work

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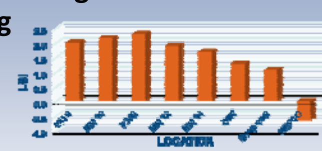
Task 1. Impacts of Flow Regime on Geochemical Rocking



- Water quality did not change from 2013-2016 study
- NEFCO wastewater appears to be reducing scaling in the injection well due to its low pH
- It appears likely that groundwater dilution reduces precipitation potential from flushing effect

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Mass Balance Calculations

- Leachate volumes vary between 20-90 gpm
- NEFCO volumes vary between 50-125 gpm
- Mass balance calculations were performed to calculate LSI and RI
  - Leachate in 10 gpm increments
  - NEFCO in 25 gpm increments at pH 4.5, 5.0, and 5.5

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Mass Balance Calculations Results

Flow, gpm		LSI based on NEFCO pH		
Leachate	NEFCO	pH = 4.5	pH = 5.0	pH = 5.5
70	50	0.6	0.8	1.0
70	75	0.2	0.5	0.7
70	100	-0.1	0.2	0.5
70	125	-0.3	0.1	0.4

- If the role of NEFCO as dilution water has a beneficial influence, then we need to determine the effect of solids and where best to connect it to the LCS

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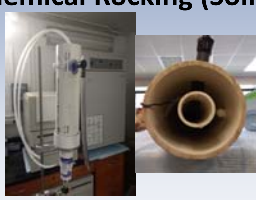
Task 1. Impacts of Flow Regime on Geochemical Rocking (Solids Handling)



NEFCO water volume = 4 L
Flow rate = 1.75 gpm
Measured capacity = 2.8 L
Input dia = ¾ inch
Discharge pipe dia = ½ inch

Lab scale model

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Task 1. Impacts of Flow Regime on Geochemical Rocking (Solid Handling)

Time (Min)	Turbidity		TSS	
	Single pass	Batch	Single pass	Batch
0	18.1	18.1	80	80
5	13.9	-	80	80
10	12.1	12.3	20	25
15	12.2	16.2	40	75

- Turbidity reduction ≈ 30%
- TSS reduction ≈ 70%
- The solids that accumulated looked like biological sludge and were highly adhesive to surfaces

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Task 1. Impacts of Flow Regime on Geochemical Rocking (Solids Handling)

- Findings:
  - Based on 6MG/month NEFCO flow
    - Initial TSS = 80 mg/L
    - TSS after solid separation = 20 mg/L
  - Solid before separation ≈ 130 lb/day
  - Solid after separation ≈ 30 lb/day
  - Estimated solids to be handled = 100 lb/day
  - We plan to conduct more cyclone separator tests to refine these values and further analyze the solids collected to determine their properties

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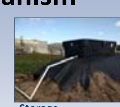
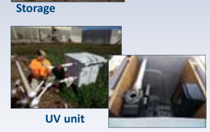
Task 2. Impacts of Biological Activity as a Clogging Trigger Mechanism

Field Setup



Storage



UV unit

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Task 2. Impacts of Biological Activity as a Clogging Trigger Mechanism

- **Experimental Methodology:**
- **Onsite leachate reservoir ≈ 900 gallons**
- **Measure weight of 1" dia pipe sections**
- **Flow in each side = 26-28 lpm**
- **Flow through 1" bypass ≈ 6 Lpm (max possible = 12-15 Lpm)**
- **UV fluence = 40 mJ/cm^2·s**
- **Sample collection at 0, 15, 30, 60, 90, and 120 minutes**
- **HPC count in the laboratory**

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Task 2. Impacts of Biological Activity as a Clogging Trigger Mechanism

UV Experiment_DAY 1_04/30/2018

Sample ID	Time, min	pH	Cond.	Sp. Cond.	TDS, g/L	Temp. C
0	0	7.18	41.99	39.61	25.75	28.13
15,C	15	7.06	43.69	39.75	25.88	30.27
30,C	30	7.1	44.43	40.17	26.11	30.54
60,C	60	7.07	44.97	40.22	26.16	31.16
90,C	90	7.08	44.20	40.39	26.25	29.98
120,C	120	7.03	44.76	40.24	26.17	30.91
Average		**7.09**	**44.01**	**40.06**	**26.05**	**30.17**
St. Dev		0.05	0.99	0.28	0.18	0.99
15,U	15	7.08	43.67	40.01	26.02	29.85
30,U	30	7.11	43.69	40.02	26.01	29.88
60,U	60	7.09	44.61	40.27	26.18	30.70
90,U	90	7.04	44.50	40.12	26.09	30.73
120,U	120	7.02	44.60	40.26	26.16	30.70
Average		**7.07**	**44.21**	**40.14**	**26.09**	**30.37**
St. Dev		0.03	0.44	0.11	0.07	0.41

*C-control side, U- UV side (treated)

ID	HPC/mL
Control	24,000
UV_30	20,000
UV_60	22,000
UV_90	<20,000

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Task 2. Impacts of Biological Activity as a Clogging Trigger Mechanism

Removable pipe section (1") 1 ft long

Orange/reddish jelly-like substance

ID	W_1,g	W_2,g	ΔW, g
Control side	215	218.1	3.1
UV side	245	249.3	4.3

- **UV side had a dry thin layer of scale**
  - **Likely related to locally elevated temperature from UV lamp**
- **Formation of calcium carbonate scale seems to be enhanced by alternate submerged and dry conditions**

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Task 2. Impacts of Biological Activity as a Clogging Trigger Mechanism

- **Findings:**
  - **Although disinfection was observed in the lab, no disinfection was observed using the field UV unit**
    - **Possibly low transmittance due to high TSS, color, turbidity, and humic/fulvic acid (NOM) content**
- **To further investigate the biological trigger, FAU will conduct heat sterilization trials in the lab**

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Task 3. Impacts of pH Adjustment for Enhanced Precipitate Control

- pH changes:

Factors	Change in pH
Addition of CO_2	-
Addition of acid (HCl)	-
Sitting in open air	+
Turbulence (500 rpm)	+
Aeration	+
Addition of base (NaOH)	+

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Task 3. Lab Experiments with Carbon Dioxide

Laboratory setup

Experimental setup:

- **Gas cylinders (103 L, 600 L)**
  - **0-49.99% CO_2**
  - **15% CO_2, 15% CH_4, balance N_2**
  - **Adjustable flow valve (0.1-7.0 Lpm)**

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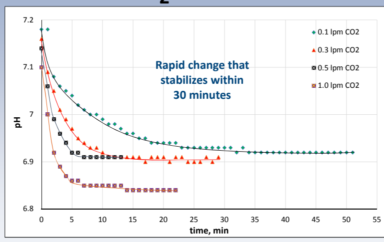
Task 3. Effect of CO_2 Gas Addition on pH



pH changes over time

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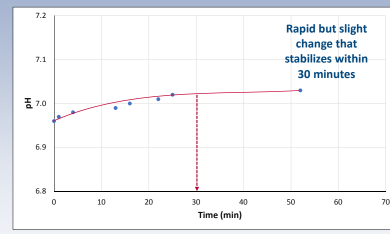
Task 3. Leachate Exposed to Open Air



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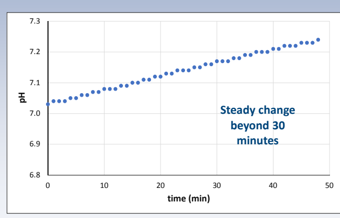
Task 3. Leachate Exposed to Mechanical Turbulence (500 rpm)



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Visual Inspection (Day 7)

Experimental setup:

- CO_2 addition at different rates
- 200 mL sample
- Incubated at 35°C, 7 days
- Volume of leachate, scale, weight, water quality data collected at day 0 and day 7

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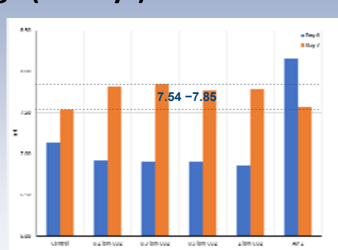
pH change (Δ7 days)



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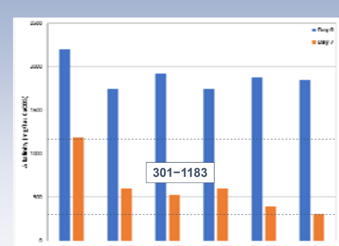
Alkalinity (Δ7 days)



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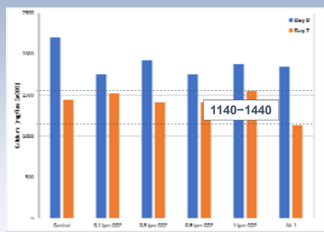
Calcium (Δ7 days)



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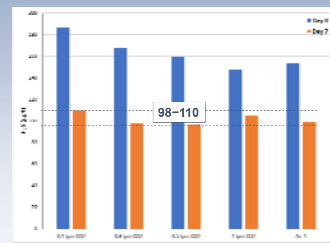
H_2S (Δ7 days)



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Scale Rate Calculation (Δ7 days)

- Two types of scale formed
  - “Loose” floating thin layers
  - “Hard” scale attached to the beaker surface
- Expressed in grams of scale formed per liter of leachate sample (g/L)
  - To calculate this scale rate, only “hard” attached scale was included
  - Future work will attempt to quantify the “loose” material contribution
- Questions:
  - How does the “loose” scale form?
  - What is its composition and how does it float?
  - How is it different than the “hard” scale that attaches to the surface?

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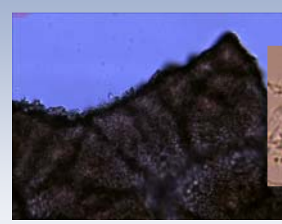
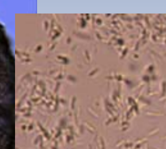
“Loose” Scale Under Microscope (400x)





Microbes

Floating precipitate layer, control

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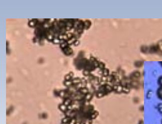
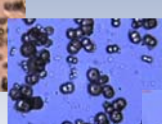
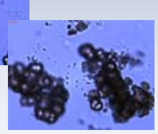
“Hard” Scale Attached to Beaker Surface (400x)



5 ml NaOH, PS/A



3 ml NaOH, MH8



5 ml NaOH, MH11

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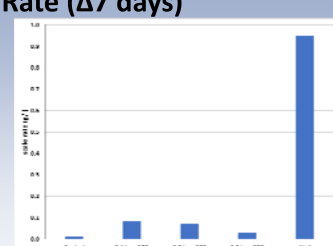
Scaling Rate (Δ7 days)



- Initial higher pH increases scale rate (Air 1)

Task 4. Impacts to the Deep Injection Well – Based on 2017-2018 Flows

Water Source	AVG Q 2017-2018	Min Q 2017-2018	MAX Q 2017-2018	pH	TDS	Alk	Ca	Cond	Temp	pHs	LSI	RI
P/S A	2,995,823	595,219	6,765,363	7.04	17,400	1,574	3,330	24.19	28.7	5.46	1.58	3.88
P/S B	3,522,549	1,274,142	7,276,223	6.85	6,670	3,058	630	12.04	34.2	5.76	0.70	5.50
P/S C	1,369,091	722,000	2,724,000	7.61	3,561	1,750	775	7.39	31.1	5.85	1.80	4.10
P/S D	1,257,000	579,000	2,167,000	7.03	3,608	2,100	600	8.52	30.0	5.9	1.10	4.80
DYER	1,741,582	617,000	3,769,000	7.11	2,303	1,618	565	3.55	28.4	5.99	1.10	4.80
CISW	780,696	137,408	1,405,417	6.95	1,015	371	404	1.29	29.0	6.65	0.30	6.35
ISW	1,771,997	168,897	3,369,288	6.95	1,015	371	404	1.29	29.0	6.65	0.30	6.35
Plant water	6,879,801	4,974,342	7,863,200	7.17	3,644	155	1,364	4.57	32.5	6.65	0.85	5.79
NEFCO	5,859,545	4,633,000	7,372,000	5.39	1,153	400	300	4.37	37.5	6.65	-1.26	7.91
AVG	26,178,084			7.22	4,176	1,010	972	6.82	32.3	6.13	0.85	5.15
MIN		13,701,008		7.10	3,769	733	984	6.34	33.6	6.15	0.98	5.28
MAX			42,711,491	7.35	4,721	1,341	986	7.50	31.1	6.05	0.88	4.91
DEEPWELL				7	6,200	1,190	1,110	11.70	33.7	5.9	1.1	4.80

Estimated LSI using mass balance

Actual LSI

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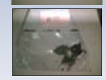
Task 4. Mineralogical and Biological Analysis of Deep Injection Well Biofilms

- Mineralogical analysis:
  - LSI increases with depth (0.81 to 1.42)
    - Higher precipitation potential the deeper we sampled
    - Composition of solids:
      - Quartz [SiO_2]
      - Calcite [$CaCO_3$]
      - Salts [NaCl, KCl]
      - Magnesioferrite [$Mg(Fe^{3+})_2O_4$]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Task 4. Mineralogical and Biological Analysis of Deep Injection Well Biofilms

- Biological analysis:
  - Anaerobic mesophilic methanogens were the most prevalent species
  - Sulfate-reducing bacteria was second most prevalent
  - A biofilm generating non-pathogenic amoebic protozoan was also found
  - Pseudomonas phage was the most prevalent virus found

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Future Work

- Task 1. Impacts of Flow Regime on Geochemical Rocking
  - NEFCO water is a promising alternative to ground water to supplement LCS dilution
  - Biological solids can be separated using cyclone separator (~100 lb/day)
  - Scope:
    - Experiments with varying Reynold's Number and flow depth in leachate bleed test using side by side pipe network
    - Solid analysis and cyclone tests to determine potential amount of solids deposition
      - Batch and single pass testing
      - Solid deposition rate

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Future Work

- Task 2. Impacts of Biological Activity as a Clogging Trigger Mechanism
  - UV unit did not achieve desired disinfection results
    - TSS, Turbidity, color, humic acids (low transmittance)
  - To determine the effect of microbial mediation, FAU will conduct laboratory experiments with heat sterilization
    - HPC plate count
    - Impacts on scale: laboratory tests
    - Field tests

Question: Does alternate dry and submerged condition enhance clogging/scaling issues?

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Future Work

- Task 3. Impacts of pH adjustment for Enhanced Precipitate Control
  - Slight increase in pH enhances scaling
  - Stagnation of leachate increases pH and subsequent scaling
  - Two different types of scale form: "Loose" floating and "Hard" attached to surfaces
  - Scope:
    - Quantify and determine mechanism of forming loose floating scale
      - How it forms?
      - How it floats?
      - Comparative compositional analysis of both types

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Future Work

- Task 4. Impacts to the Deep Injection Well
  - FAU conducted mineralogical and biological analysis of deep injection well samples
  - Scope:
    - FAU will continue monitoring the flows and loadings with current data
    - Conduct mass balance analysis to keep updated database
    - Conduct laboratory experiments to explore:
      - Pre treatment
      - Well rehabilitation

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Future Work

- Task 5. Perform other tasks for SWA as requested by SWA
  - FAU will continue monitoring leachate water quality
    - Periodic sample collection
    - Water quality analysis
    - Laboratory experiments
    - Update database
  - FAU will continue investigating leachate clogging issue
    - Explore the mechanism
    - Identify alternative management options

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Key Research

- How to best use NEFCO to supplement dilution with GW in the LCS?
- If rocking trigger is determined to be biologically mediated, how to exploit that to control clogging?
- Is “Loose” or “Hard” scale more problematic in terms of clogging?
- How to best protect the deep injection well?

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Thank you!

Questions??

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Funding Partners

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