QUARTERLY PROGRESS REPORT

[September 01 2018 - November 30 2018]

PROJECT TITLE: Using Nitrate Produced from Leachate to Control Landfill Odors

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Project summary: One common and persisting problem with landfilling is odors. Hydrogen sulfide gas (H_2S) is usually the major cause of the odors. A significant amount of H_2S is generated when municipal solid waste (MSW, rich in organic matters) is co-disposed of with sulfate (SO_4^{2-})-laden wastes such as construction & demolition (C&D) waste, fines from materials recovery facilities, and ashes from coal combustion and MSW incineration. The odor problem is even worse in Florida because of frequent hurricanes and tropical storms, which usually leave millions of cubic yards of storm debris that contain a lot of organic matters and drywall (rich in gypsum, $CaSO_4$) as people are usually not interested in separating garbage after a hurricane. Conventional odor-control products are designed to react, absorb, or mask odors; they deal with odors after generation. The PIs propose to use nitrate (NO_3^-) to inhibit H_2S generation before odors become an operational issue, which is a novel and environmentally friendly approach. To make this approach more sustainable and economically feasible, the PIs further propose to convert ammonium (NH_4^+) in the leachate to nitrate and then apply the nitrate-containing leachate to the landfill to suppress H_2S generation at the source.

Work Accomplished during this Reporting Period:

During this period, we completed part of Task 1 by 1) designing five lab-scale landfills, 2) preliminarily testing one of the five landfills to make sure that the design was reasonable and 3) setting up all the five landfills.

1) <u>Designing five lab-scale landfills</u>

We designed five lab-scale landfills, including four identical landfills containing simulated storm debris (*i.e.*, the mixture of municipal solid waste and drywall, Figure 1) and one control landfill, which included the same municipal solid waste, but not drywall. Each landfill (35 cm in height and 29 cm in diameter) contained the following layers: (from bottom to top) gravel, geotextile, waste, geotextile, and gravel. All landfills were capped to maintain anaerobic condition.

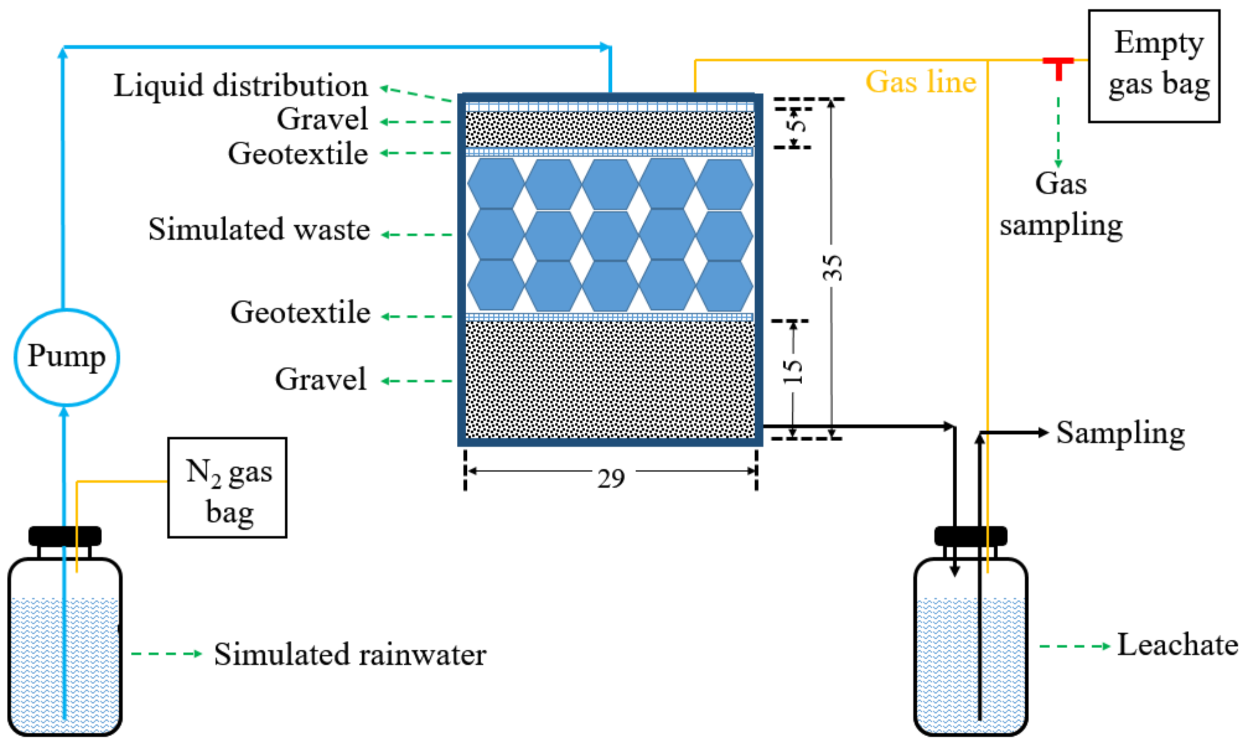

Figure 1. Schematic diagram of the lab-scale landfills. Note: the unit of the dimension is cm.

The total weight of simulated storm debris in each landfill was 2 kg, corresponding to a thickness of ~15 cm. The composition of the storm debris is shown in Table 1, and adapted from Barlaz (1998) and Lee et al. (2006). Food waste consisted of bread (35%), boiled rice (25%), cabbage

(25%) and boiled pork (15%) (Xu et al., 2011). Glass was obtained from the clean broken glassware in the laboratory. Old newsprint was collected from the Florida State University Library. Grass, leaves, and branches were collected from a local household. All other materials were obtained from a local material recovery facility (the Marpan Recycling Center in Tallahassee, FL). Those materials were broken or shredded into small pieces and the size was on the order of 2 cm wide by 3 to 7 cm long, allowing the material to be well mixed prior to reactor loading.

Table 1. Composition of solid waste mixture in the lab-scale landfills

Categories	**Component**	**Composition (wet weigh)**	**H_2O content**
Drywall, major source of sulfate (10%)	Drywall	10%	1%
Municipal solid waste, MSW (90%)	Grass	7%	70%
	Leaves	3%	30%
	Branches	3%	10%
	Wood	6%	20%
	Food	18%	70%
	Plastic	8%	2%
	Metal	7%	3%
	Glass	5%	2%
	Coated paper	1%	5%
	Old newsprint	9%	5%
	Corrugated containers	19%	5%
	Office paper	4%	5%

Gravel (0.5 – 1.5 cm in diameter) was placed at the bottom (15 cm in thickness) for leachate collection, and on the top (5 cm in thickness) for even liquid distribution. Geotextiles (Mirafi 140N, TenCate Geosynthetics, USA) were placed between gravel and simulated storm debris to prevent clogging and assist even liquid distribution. Perforated tubing was place on top of the gravel to distribute simulated rainwater.

To accelerate solid decomposition in landfills, we added leachate (3.1 L and 3.2 L for the control and other landfills, respectively) to increase the moisture content and provide seed at the beginning of the experiments. The leachate was from a local landfill containing both MSW and C&D debris (Apalachee Solid Waste Management Facility, Tallahassee, FL). The volume of leachate we added to the landfills was calculated following Equation 1, which was based on the need for increasing the moisture to 70% for suitable waste decomposition (Hernández-Berriel et al., 2010).

$$(W_S + W_L) \times 70\% = W_S \times P_W \times P_{H_2 0} + W_L \quad \text{Equation 1}$$

where W_L was the total weight of leachate to add, W_S was the total weight of solid components, P_W was the wet weight percentage of each solid component, and P_{H2O} was the H_2O content of each solid component (Table 1).

During the landfill operation, simulated rainwater was injected continuously into the landfills. The injection flow rate of 230 mL/week was calculated using Equation 2 (Liu and Sang, 2010), which corresponded to an annual precipitation of 75 cm/year with 24% infiltration (Holmes, 1984; Lang et al., 2017). The composition of the simulated rainwater was shown in Table 2, and adapted from Donn and Menzies (2005). The pH of simulated rainwater was 7.0±0.1.

$$Q = P \times \frac{\pi d^2}{4} \times 24\% \quad \text{Equation 2}$$

where, Q was the flow rate, P was the average annual precipitation, and d was the diameter of the lab-scale landfill.

Table 2. Composition (μmol/L) of the simulated rainwater

Species	$NaNO_3$	NaCl	Na_2SO_4	NH_4Cl	$CaCl_2$	$MgCl_2$	$KHCO_3$	HCl
Concentration	6	56	10	6	15	10	8	1

2) Preliminarily testing one of the five landfills to make sure that the design was reasonable

To test if our design was reasonable, we set up and tested one landfill containing simulated storm debris as shown in Figure 2.

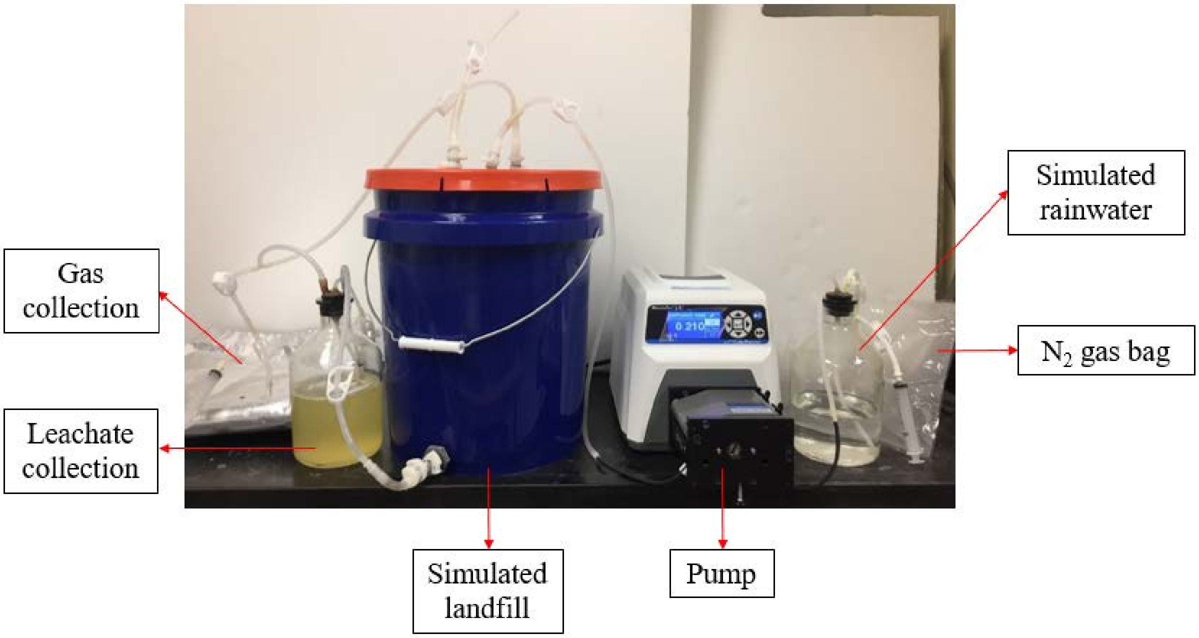

Figure 2. The landfill used in the preliminary test

Leachate and gas from the landfill were collected and characterized. The characterization focused on nitrogen, sulfur, and carbon species, but also included pH. The measurement methods are summarized in Table 3.

Table 3. Summary of the sample measurement

Sample	Parameters	Methods	Reference
Leachate	NH_4^+	Ion chromatographic method	Rice et al., 2012
	NO_2^-	Ion chromatographic method	Rice et al., 2012
	NO_3^-	Ion chromatographic method	Rice et al., 2012
	Dissolved organic nitrogen (DON)	Equation 3[1]	
	SO_4^{2-}	Ion chromatographic method	Rice et al., 2012
	SO_3^{2-}	Ion chromatographic method	Rice et al., 2012
	$[S^{2-}]_{total}$[2]	Methylene blue method	Rice et al., 2012
	Chemical oxygen demand (COD)	Colorimetric method	Hach, 2014
	Dissolved organic carbon (DOC)	Wet oxidation method	Rice et al., 2012
	Acetate	Ion chromatographic method	Rice et al., 2012
	pH	Electrometric method	Rice et al., 2012
Gas	CO_2	Titration method[3]	Rice et al., 2012
	H_2S	Portable detector method[4]	
	CH_4	Gas chromatographic method	Rice et al., 2012
	N_2	Equation 4[5]	
	O_2	Electrometric method	Hach, 2015b
	volume	Syringe collection	Syringe

Notes:

1. Equation 3: DON = TDN – $[NH_4^+]$ – $[NO_2^-]$ – $[NO_3^-]$. The TDN was measured by the persulfate digestion method with Hach Total Nitrogen Reagent Set (Hach, 2015a).
2. $[S^{2-}]_{total}$ includes dissolved H_2S, HS^-, S^{2-} and acid-volatile metallic sulfides.
3. CO_2 was calculated from the concentration of carbonic acid based on Henry's Law, and the carbonic acid was derived from the measured alkalinity (Rice et al., 2012).
4. Using Jerome 631-X
5. Equation 4: $P_{N2} = 1 - P_{O2} - P_{CH4} - P_{H2S} - P_{CO2} - P_{H2O}$ (in which P_{H2O} = 3.13% at 25 ℃ (Wexler, 1976)).

The preliminary landfill worked well during the 60–day test. Leachate and gas were sampled and characterized on day 26. The results are summarized in Table 4. Sulfate reduction and solid decomposition were negligible at the time of sampling since $[S^{2-}]_{total}$ in the leachate and H_2S and CH_4 in the gas collection bag were negligible, suggesting that more time is needed to generate odors.

Table 4. Characterization of leachate and gas from the preliminary test

Sample	Parameters	Concentrations
Liquid	NH_4^+	180±1 mg N/L
	NO_2^-	BDL[1]
	NO_3^-	0.67±0.07 mg N/L
	DON	30.3±1.1 mg N/L
	SO_4^{2-}	212±1 mg S/L
	SO_3^{2-}	BDL
	$[S^{2-}]_{total}$	0.04±0 mg S/L
	COD	11,600±232 mg/L
	DOC	7,470±110 mg C/L
	Acetate	1,610±28 mg C/L
	pH	6.28±0.18
Gas	H_2S	BDL
	CH_4	0.04%
	CO_2	0%
	N_2	>96.59%
	O_2	<0.24%
	volume	<1 mL

Notes:

1. BDL: Below Detection Limit.
2. Detection limit of NO_2^- is 0.01 mg N/L. Detection limit of SO_3^{2-} is 0.02 mg S/L. Detection limit of H_2S is 0.003 ppm.

3) <u>Setting up all the five landfills</u>

After testing the preliminary landfill and knowing that the design was good and we were able to measure all parameters, we set up all five simulated landfills on November 24th, 2018 (Figure 4). Landfills 1 to 4 (L1 to L4) contained the simulated storm debris and landfill 0 (L0) was the control (without drywall). We anticipate to report the performance of the five landfills in the next quarterly report.

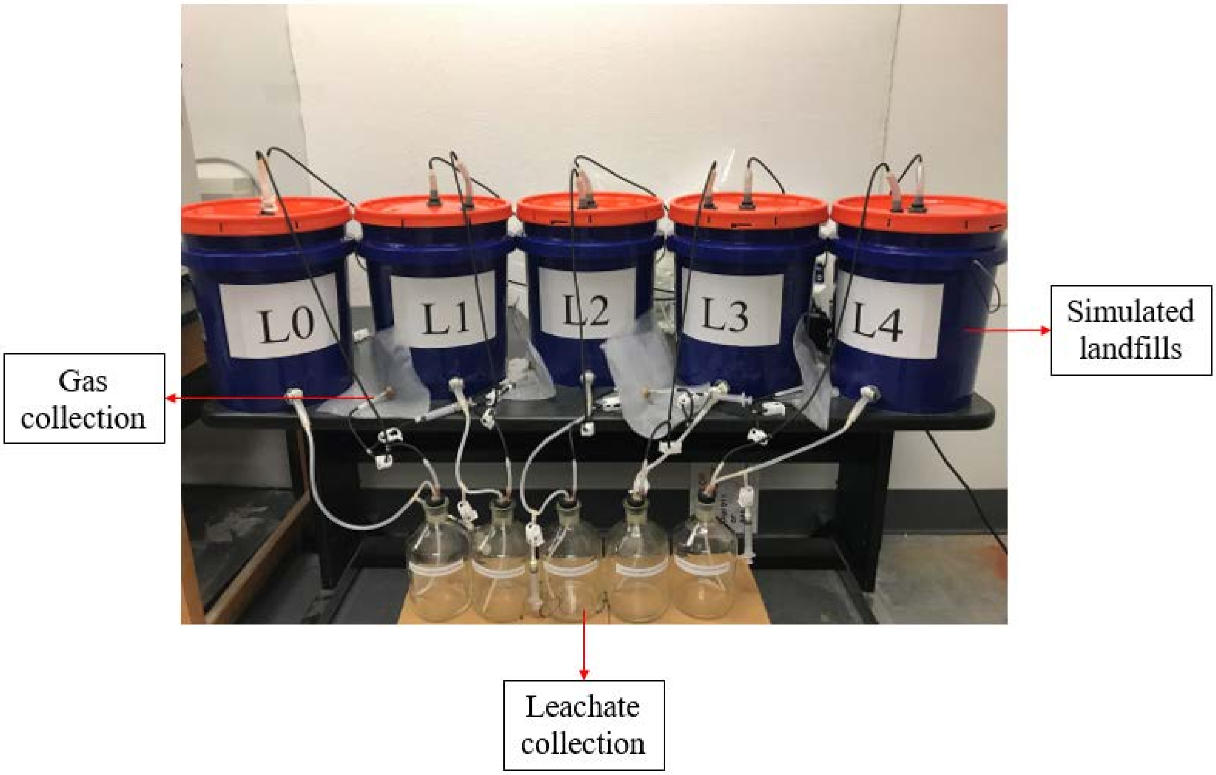

Figure 4. Five lab-scale landfills

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Xu, S.; Lam, H. P.; Karthikeyan, O. P.; Wong, J. W. C. Optimization of food waste hydrolysis in leach bed coupled with methanogenic reactor: Effect of pH and bulking agent. *Bioresource Technology*, 2011, 102, 3702-3708.

TAG Meetings (TAG-1):

- **Date of the meeting:** October 26, 2018.
- **Names/title/emails of participants:**

Name & Title	Affiliation	Contact Information
Owete S. Owete	FDEP	owete.owete@dep.state.fl.us
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Liang Li	FAMU-FSU COE	lli7@fsu.edu
Zhiming Zhang	FAMU-FSU COE	zz15@my.fsu.edu

- **List of TAG members who were unable to attend this meeting:** Ashvini Chauhan, Dean Chaaban, Joseph B. Cheatham, Joseph Dertien, Robert J. Wandell.
- **Link to the video recording/slides of the TAG meeting:** http://www.eng.fsu.edu/~ytang/project9.html

Metrics:

1. List research publications resulting from this Hinkley Center project.

   None.

2. List research presentations resulting from this Hinkley Center project.

   None.

3. List who has referenced or cited your publications from this project?

   None.

4. How have the research results from this Hinkley Center project been leveraged to secure additional research funding?

   None.

5. What new collaborations were initiated based on this Hinkley Center project?

   After knowing the PI (Tang)'s ability to characterize materials used in civil engineering (i.e., drywall) and their degradation in the environment through this project, a colleague of the PI (i.e., Dr. Raphael Kampmann at the FAMU-FSU College of Engineering with expertise in materials) initiated collaboration with the PI and submitted a proposal to FDOT. The project is entitled 'Testing Protocol and Material Specifications for Basalt Fiber Reinforced Polymer Bars', and investigates the chemical degradation of Basalt Fiber Reinforced Polymer Bars subject to harsh environments.

6. How have the results from this Hinkley Center funded project been used (will be used) by the FDEP or other stakeholders? (1 paragraph maximum)

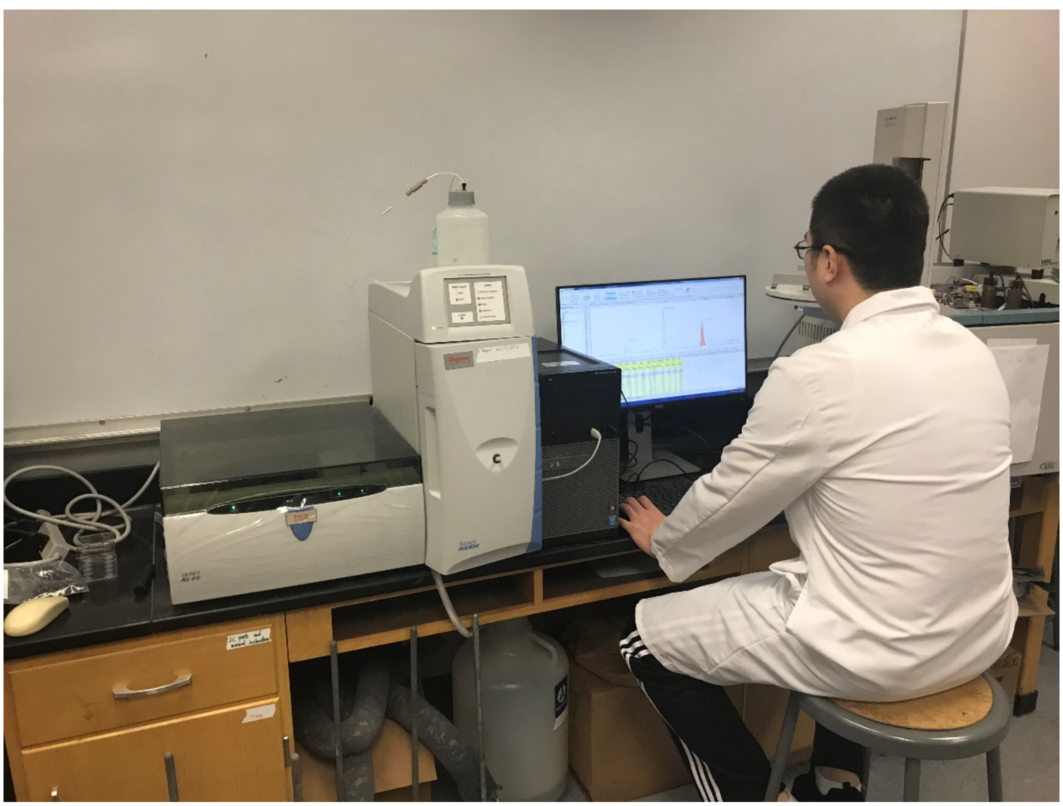
   None.

Pictures:

1) Research team for this project:

Professor Youneng Tang (PI) **Professor Tarek Abichou (co-PI)** **Zhiming Zhang (Graduate assistant)**

2) Lab work: anions measurement using Ion Chromatography by Zhiming Zhang



3) Lab work: lab-scale landfills setup by Zhiming Zhang