QUARTERLY PROGRESS REPORT

[March 01, 2019 – May 31, 2019]

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

PRINCIPAL INVESTIGATORS:

Youneng Tang, Ph.D., Assistant Professor
Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering
2525 Pottsdamer Street Suite A130, Tallahassee FL 32310; Tel: 850-4106119; Fax: 850-4106142; ytang@eng.famu.fsu.edu

Tarek Abichou, Ph.D., P.E., Professor
Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering
2525 Pottsdamer Street Suite B314, Tallahassee FL 32310; Tel: 850-4106661; Fax: 850-4106142; abichou@eng.famu.fsu.edu

PROJECT WEBSITE: https://www.eng.famu.fsu.edu/~ytang/project9.html

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 severe 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:

In the first two quarters, we designed and tested six lab-scale landfills. In this quarter (*i.e.*, the third quarter), we continued to test the six lab-scale landfills. We have completed most of Task 1 and some of Task 2. Based on the progress, we anticipate to complete all three tasks as scheduled by August 31, 2019.

Task 1: Test of six lab-scale landfills until H_2S is generated

Results overview: Figure 1 is photo of the six lab-scale landfills. Landfill L0 was the control (with no drywall in it). Landfills L1 to L5 were similar landfills with drywall in them. The week numbers in Task 1 refer to the number of weeks after adding seed leachate to landfills in December 2018. The solid waste decomposition started immediately after we added the seed leachate in the second quarter. Three processes in anaerobic digestion, including hydrolysis, acidogenesis and acetogenesis, dominated in the second quarter (from Week 1 to Week 10). Methanogenesis and sulfate reduction (*i.e.*, odor production) became significant in the third quarter (this quarter, from Week 11 to Week 22). The reaction rates were different in the six landfills. According to the sulfate reduction rates, the six landfills can be rearranged by the descending order of sulfate reaction rate: L5 > L1 > L3 > L2 > L4 > L0 (see Figure 2a), and the sulfate reaction rate represents the overall biological reactions rates, which is further discussed below.

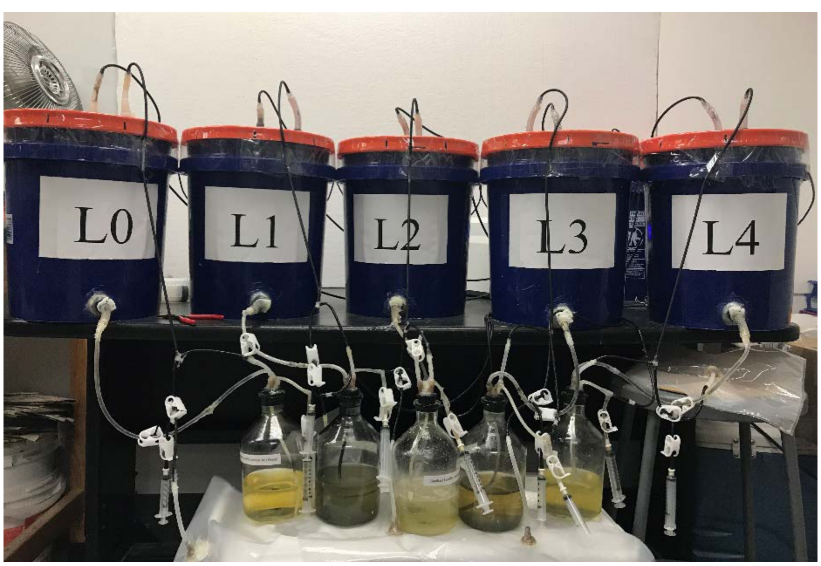


Figure 1. A photo of six landfills and leachate. Landfill L5 is behind Landfills L3 and L4.

1.1 Landfill odor generation (*i.e.*, sulfide production)

Sulfur species (sulfate, sulfite, and sulfide) in the leachate: As shown in Figure 2a, the six landfills can be rearranged by the descending order of sulfate reduction rate: L5 > L1 > L3 > L2 > L4 > L0 (see Figure 2a). The sulfate reduction was negligible in L0. Leachate from the three landfills having the highest sulfate reduction rates (*i.e.*, L1, L3, and L5) was black (Figure 1) due to the formation of metal sulfides (*e.g.*, iron sulfide), a sign of sulfate reduction to sulfide (Figure 2b). Sulfite was below the detection limit of 0.02 mg S/L.

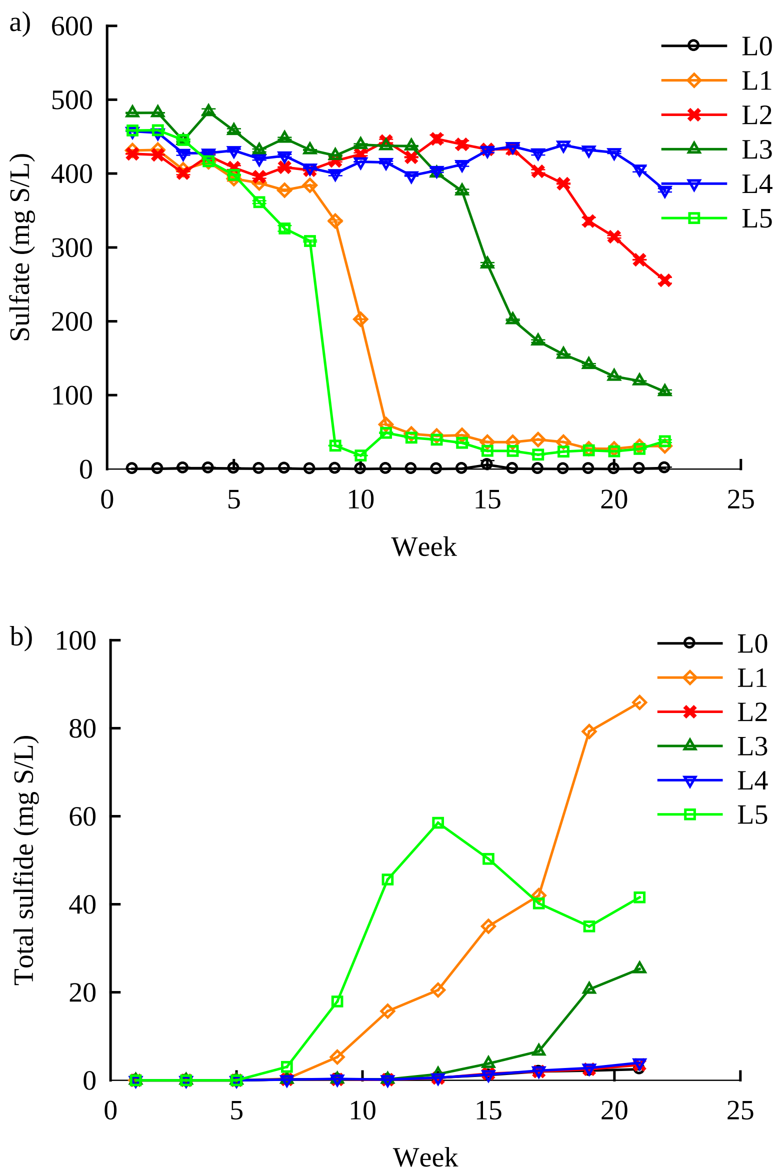


Figure 2. Concentrations of sulfur species in the leachate.

Hydrogen sulfide in the headspace: The H_2S concentration in the headspace is shown in Figure 3 with ppmv (*i.e.*, parts per million by volume) as unit, which is consistent with the odor threshold unit (Ko et al., 2015). The odor threshold for H_2S ranges from 0.0005 to 0.3 ppmv (Ko et al., 2015; Agency for Toxic Substances and Disease Registry, 2008). L1, L3 and L5 had higher H_2S concentrations than the other landfills, which corresponded well with the sulfate reduction trend (Figure 2a). The H_2S concentrations in L2 and L4 started to increase since Week 19, reaching 30 ppmv and 330 ppmv, respectively, in week 22. The H_2S in those two landfills are expected to increase in the near future. Task 1 would be completed once all landfills except for the control landfill L0 have significant sulfide production.

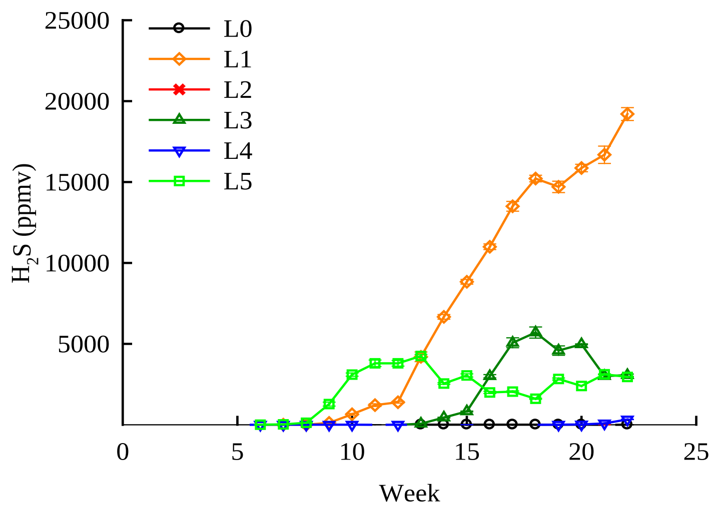


Figure 3. Concentration of hydrogen sulfide in the headspace.

1.2 Landfill solid waste decomposition (*i.e.*, carbon conversion)

Carbon species (acetate, chemical oxygen demand (COD), and dissolved organic carbon (DOC)) in the leachate: Figure 4 shows the concentrations of carbon species, including acetate, COD and DOC. The three parameters were decreasing due to organic decomposition and dilution by simulated rainwater. The trend of the three species was similar to the trend of sulfate: the highest reaction rate (*i.e.*, decreasing rate) in Landfill L5, followed by Landfill L1 and the others.

Carbon species (CH_4 and CO_2) in the headspace: Rapid increase in CH_4 started from Week 8 (Figure 4d), particularly for L1 and L5. The trend was similar to the trend of acetate consumption, suggesting CH_4 production by Equation 1 (Mora-Naranjo et al., 2004). The percentage of CO_2 was increasing in the first eight weeks due to hydrolysis, which released CO_2 (Figure 4e).

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \text{Equation 1}$$

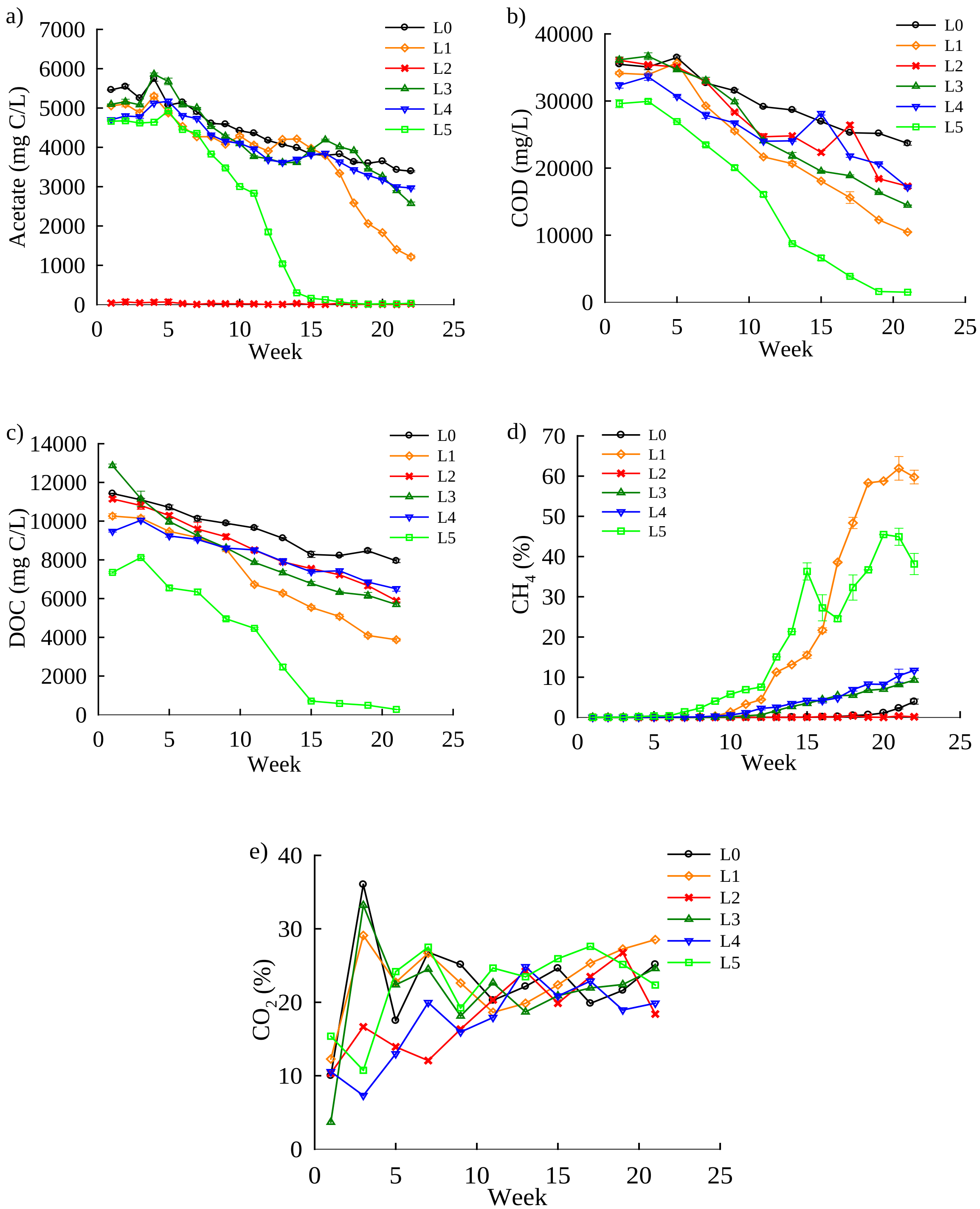


Figure 4. Concentrations of carbon species in the leachate (a, b, c) and headspace (d, e).

1.3 Nitrogen conversion in the leachate

Nitrogen species (ammonium and dissolved organic nitrogen (DON))**:** In the first eight weeks, the concentration of ammonium was increasing due to hydrolysis and acidogenesis (Figure 5a) (Price et al., 2003). Similarly, the concentration of DON, released during the decomposition of organic matters, increased simultaneously (Figure 5b). After Week 8, the ammonium and DON concentrations were decreasing due to the depletion of organic matters and dilution by the simulated rainwater. The other two nitrogen species, including nitrate (<1.5 mg N/L) and nitrite (< the detection limit of 0.01 mg N/L), were negligible since the reactors were anaerobic (dissolved oxygen < the detection limit of 0.1 mg/L): Any nitrate or nitrite, if produced from the solid waste decomposition, would have been reduced to nitrogen gas.

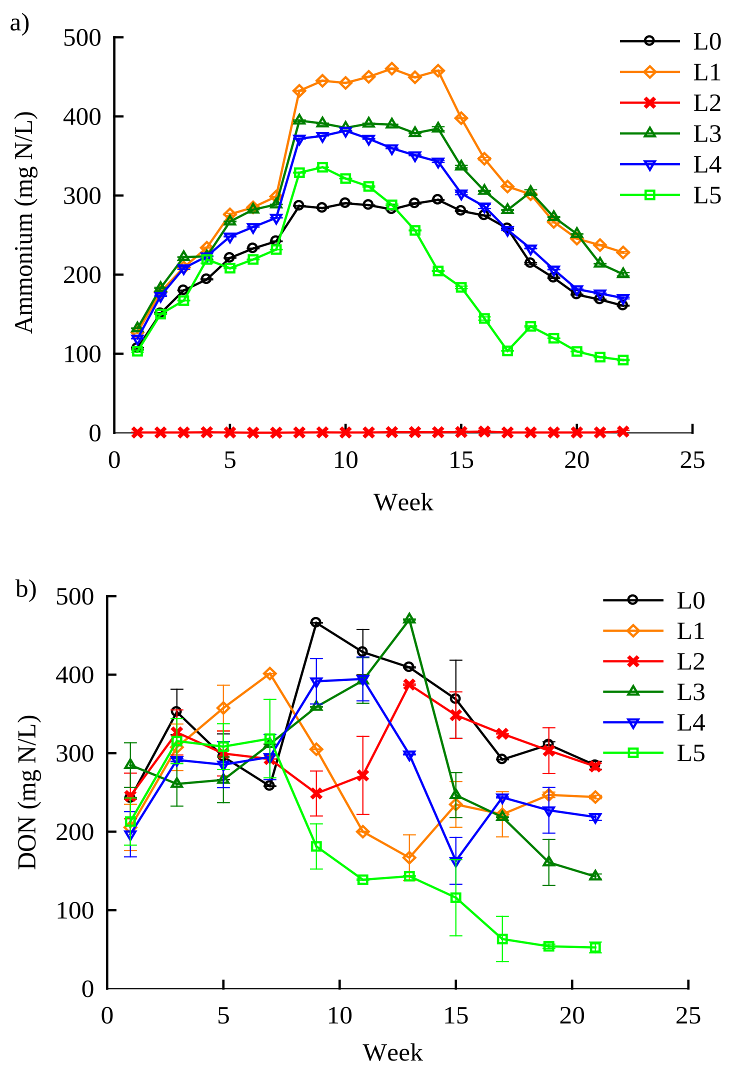


Figure 5. Concentrations of nitrogen species in the leachate.

1.4 Other parameters

pH: The low pH values (*i.e.*, around 5.4) of leachate in all six landfills during the first eight weeks (Figure 6), compared to 7.8 in the seed leachate, was caused by the generation of acetate, CO_2, and release of proton in the solid decomposition processes (Staszewska and Pawłowska, 2010). After the eighth week, the pH increased due to the consumption of acetate and proton for methanogenesis, and the reduction of sulfate.

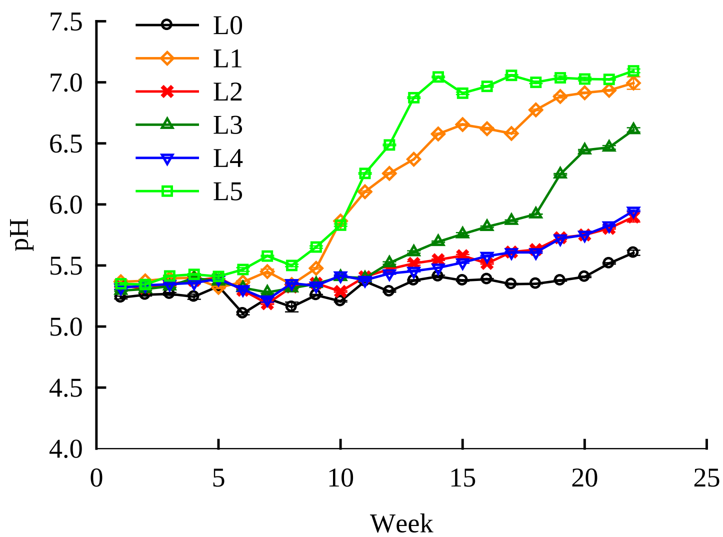
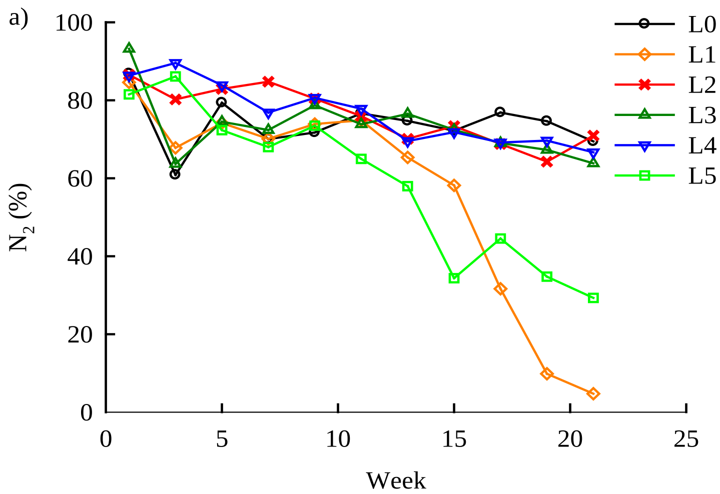


Figure 6. pH of leachate from all six lab-scale landfills

Other gases and gas production rate. The O_2 concentration in all landfills was below the detection limit of 0.1 mg/L, indicating an anaerobic condition in the landfills. N_2 was the major gas before methanogenesis dominated, because the system was flushed with N_2 at the beginning of experiment to eliminate O_2. The percentage of N_2 decreased, particularly in L1 and L5 (Figure 7a), due to the generation of CH_4 and CO_2. H_2 generation is usually negligible (Toerien and Hattingh, 1969), since the consumption rate of H_2 is much more rapid than the generation rate. The gas production rate was large at the beginning because of the gas generation from the seed leachate. It quickly dropped until Week 8 and then increased due to methanogenesis (Figure 7b).



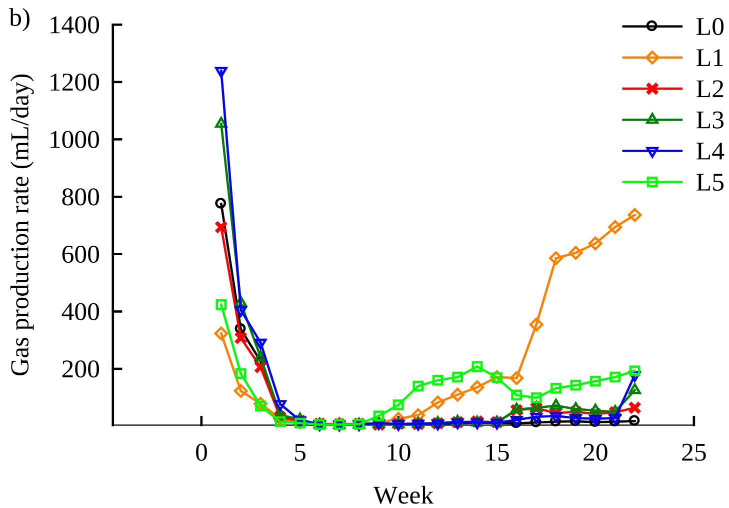


Figure 7. N_2 percentage (a) and gas production rate (b) in the headspace of the landfills.

Task 2: Test of one lab-scale leachate treatment biological reactor until ammonium is converted to nitrate

Results overview: One lab-scale leachate treatment biological reactor was set up to treat the leachate collected from a local landfill. The week numbers in Task 2 refer to the number of weeks after the beginning of reactor operation in April 2019. The conversion of ammonium to nitrate in the leachate started in Week 2 and has been increasing since then. We expect that all the ammonium in the leachate will be converted to nitrate, which will be used in Task 3.

2.1 Design and operation of the lab-scale leachate treatment biological reactor

The lab-scale leachate treatment biological reactor was a 3.5-gallon (*i.e.*, 13.2 L) bucket containing 8 L leachate collected from the local landfill. The reactor was operated in a batch mode as shown in Figure 8. Activated sludge from a local wastewater treatment facility was added to the biological reactor to reach an initial concentration of 4,000 mg MLSS/L (mg mixed liquor suspended solids/liter) in the reactor, which is a typical biomass concentration in the aeration tank in a municipal wastewater treatment plant (Reynolds and Richargds, 1996). A magnetic stirring bar was placed at the bottom of the reactor to accelerate aeration and mixing. A lid was used to cover the reactor to minimize vaporization. Air was continuously pumped into the leachate to enhance aeration.

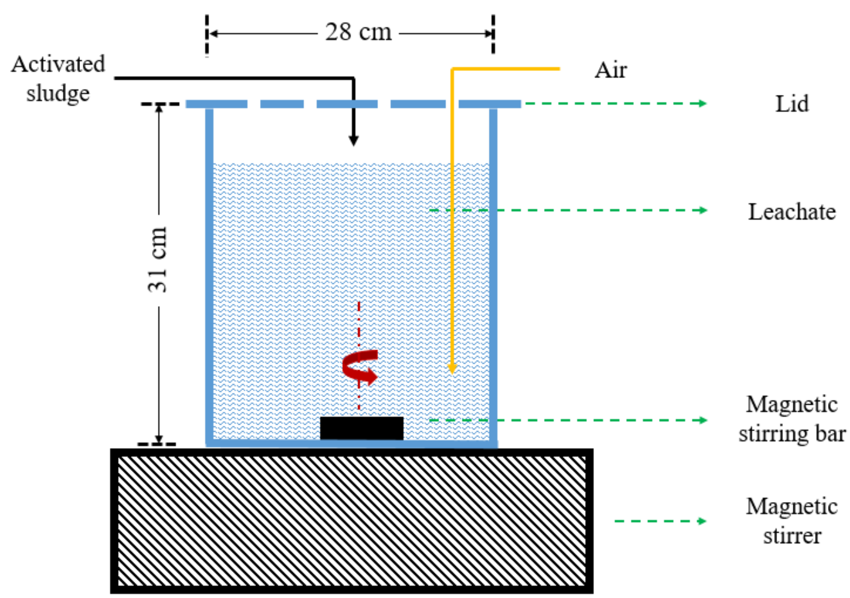


Figure 8. Schematic diagram of the lab-scale biological reactor

2.2 Leachate characterization at the beginning of the reactor operation

Leachate from the biological reactor was collected and characterized weekly. The characterization focused on nitrogen, sulfur, and carbon species, but also included pH. The measurement methods are summarized in Table 1. The leachate characteristics at the beginning of the reactor operation (right after sampling from the landfill) are summarized in Table 2.

Table 1. Summary of the measurement methods

Sample	Parameters	Methods	Reference
Leachate	NH_4^+	Direct ISE method	Hach, 2017
	NO_2^-	Ion chromatographic method	Rice et al., 2012
	NO_3^-	Ion chromatographic method	Rice et al., 2012
	DON	Equation 1[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
	COD	Colorimetric method	Hach, 2014
	DOC	Wet oxidation method	Rice et al., 2012
	Acetate	Ion chromatographic method	Rice et al., 2012
	pH	Electrometric method	Rice et al., 2012

Notes:

1. Equation 1: DON = TDN – $[NH_4^+]$ – $[NO_2^-]$ – $[NO_3^-]$. The TDN (total dissolved nitrogen) was measured by the persulfate digestion method with a Hach Total Nitrogen Reagent Set (Hach, 2015a).
2. $[S^{2-}]_{total}$ includes dissolved H_2S, HS^-, S^{2-} and acid-volatile metallic sulfides.

Table 2. Characterization of leachate at the beginning of reactor operation

Parameters	Concentrations
NH_4^+	111.0±0.5 mg N/L
NO_2^-	BDL
NO_3^-	226±2 mg N/L
DON	129±18 mg N/L
SO_4^{2-}	129±1 mg C/L
SO_3^{2-}	BDL
$[S^{2-}]_{total}$	BDL[1]
COD	1,033±29 mg/L
DOC	117±3 mg C/L
Acetate	107±3 mg C/L
pH	7.67±0.01

Note: 1. BDL = 0.1 mg S/L.

2.3 Leachate change during the reactor operation

***Carbon species (Acetate, COD, and DOC)*:** As expected, the acetate and COD were removed in the first five weeks due to aerobic degradation (Figures 9a and 9b) (Hershey et al., 2014). The slight increase of DOC was probably due to the conversion of particulate organic matter to dissolved organic matter (Figure 9c).

***Nitrogen species (ammonium, nitrite and nitrate)*:** The ammonium concentration in the leachate decreased (Figure 10a) and the trend corresponded well to the increase in nitrite and nitrate concentrations (Figures 10b and 10c), suggesting the biological conversion of ammonium to nitrite and nitrate. As an intermediate, the nitrite concentration was increasing rapidly during this stage. We expect the complete conversion from ammonium to nitrate within a short period based on the typical nitrification rate (Reynolds and Richargds, 1996).

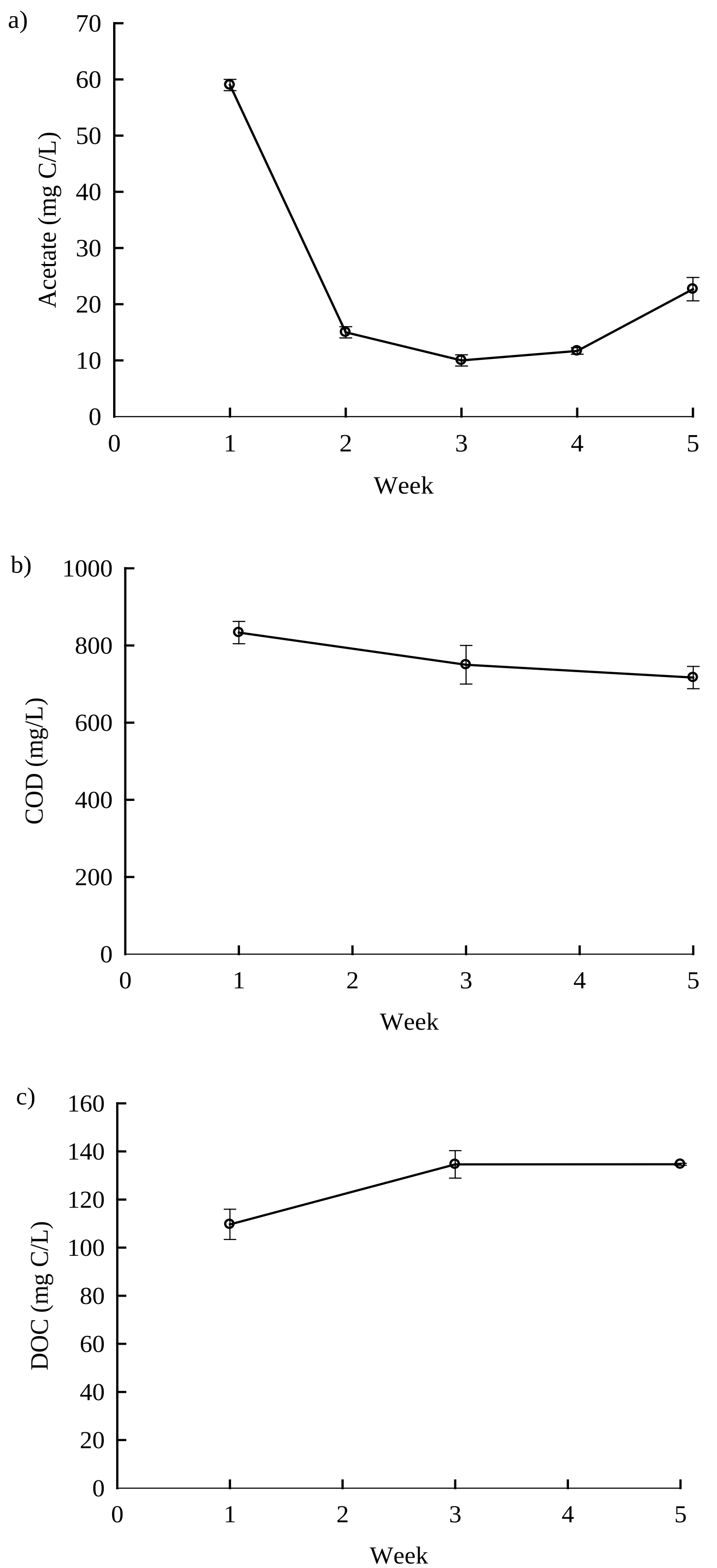


Figure 9. Concentrations of carbon species in the leachate in Task 2

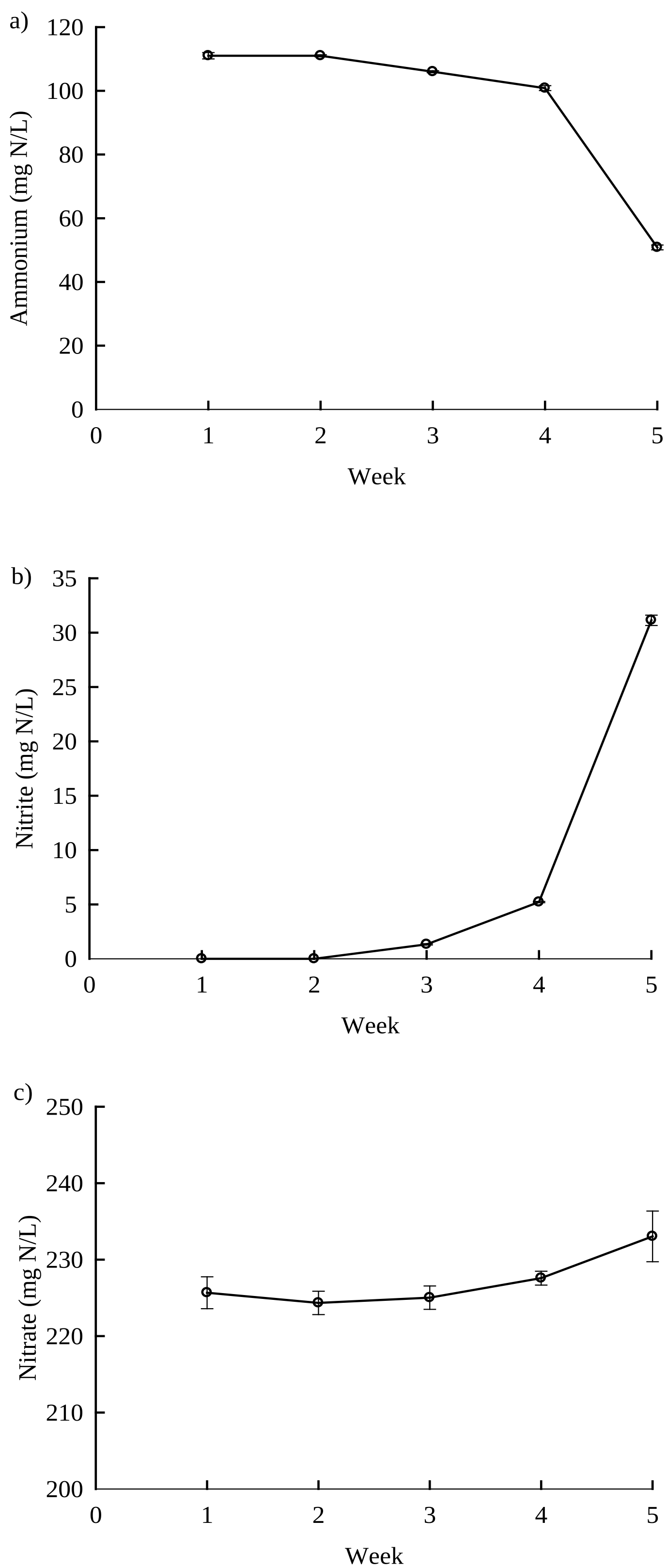


Figure 10. Concentrations of nitrogen species in the leachate in Task 2

***Other parameters*:** Other parameters are summarized in Table 3. They did not significantly change.

Table 3. Parameters that did not significantly change

Parameters	**Concentrations**
DON	110 mg N/L
SO_4^{2-}	120 mg S/L
SO_3^{2-}	BDL
$[S^{2-}]_{total}$	< 1 mg S/L
pH	~7.5

References:

Agency for Toxic Substances and Disease Registry. Health consultation, exposure investigation report for airborne exposures to hydrogen sulfide. 2008.

Hach. Method 8000 USEPA Reactor Digestion Method. 2014. https://www.hach.com/asset-get.download.jsa?id=7639983816

Hach. Method 10208 Persulfate digestion method. 2015a. http://www.hach.com/asset-get.download-en.jsa?id=7639983807

Hach. Method 10001 Direct ISE method. 2017. https://www.hach.com/asset-get.download-en.jsa?id=7639984150

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Mora-Naranjo, N.; Meima, J. A.; Haarstrick, A.; Hempel, D. C. Modelling and experimental investigation of environmental influences on the acetate and methane formation in solid waste. *Waste Management*, 2004, 24 (8), 763-773.

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Reynolds, T. D.; Richards, P. A. *Unit Operations and Processes in Environmental Engineering*, 2nd Edition, PWS Publishing Company, 1996.

Staszewska, E.; Pawlowska, M. Characteristics of emissions from municipal waste landfills. *Environment Protection Engineering*, 2011, 37 (4), 119-130.

Toerien, D. F.; Hattingh, W. H. J. 1969. *The Microbiology of Anaerobic Digestion*, Pergamon Press, Great Britain.

Metrics:

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

None.

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

Youneng Tang. Using Nitrate Produced from Leachate to Control Landfill Odors Project Technical Awareness Group (TAG) Meeting No. 1, October 26 2018, Tallahassee FL.

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?

Brown and Caldwell, in Collaboration with Miami-Dade Water and Sewer Department, Washington Suburban Sanitary Committee, VCS-Denmark, FAMU-FSU College of Engineering, Hampton Roads Sanitation District. Biogas Harvester Pilot Test, June 2019-June 2020, Funded by Water Research Foundation. Total budget $70,000.

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

See No. 4 above.

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) The lab-scale leachate treatment reactor for biological conversion of ammonium to nitrate in Task 2.

2) Karam Eeso, an undergraduate student (freshman) majoring in Chemical Engineering, was measuring CH_4 with Zhiming Zhang, a graduate student majoring in Environmental Engineering.