

QUARTERLY PROGRESS REPORT

[December 01, 2018 – February 28, 2019]

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 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 quarter, we completed part of Task 1 by 1) designing six lab-scale landfills and 2) preliminarily testing one landfill to determine if improvement was needed. In the second quarter (this report), we continued to work on Task 1 by 1) improving the lab-scale landfill design based on the preliminary test, 2) characterizing a real-world leachate injected into the lab-scale landfills at the beginning of the landfill operation as a seed and 3) weekly characterizing the leachate and gas produced from all six lab-scale landfills.

1. Improved the landfill design based on the preliminary test

Five identical lab-scale landfills (L1 – L5) and one control landfill (*i.e.*, without drywall, L0) were operated in parallel. In the preliminary test, the simulated rainwater was continuously distributed to the waste surface at a constant flow rate of 230 mL/week to simulate an annual precipitation of 75 cm/year with 24% infiltration (Holmes 1984, Lang et al. 2017), and the leachate collected was not recirculated back to the landfills. We did not see methane or H₂S production in the first month. To accelerate waste decomposition, we changed to the leachate recirculation mode as most lab-scale landfills do (Šan and Onay 2001, Sadri et al. 2010). Immediately after sampling 230 mL leachate in the leachate collection vessel each week, 230 mL of simulated rainwater was injected into the leachate collection vessel through the same sampling port to keep mass balance. The leachate and simulated rainwater mixture in the leachate collection vessel was recirculated back to landfill at a flow rate (Q_R) of 1,500 mL/week, corresponding to a leachate recirculation rate of four times per week (Equation 1) (Šan and Onay 2001, Sadri et al. 2010). Before the simulated rainwater was injected into the leachate collection vessels, it was degassed with N₂ for 30 minutes to minimize O₂ intrusion into the landfills and then adjusted to pH = 7.0 ± 0.1 by NaOH solutions.

$$Q_R = 4 \frac{\text{times}}{\text{week}} \times V_{\text{Leachate}} \quad \text{Equation 1}$$

where Q_R is the recirculation flow rate (mL/week), V_{Leachate} is the volume of total leachate in the collection vessel (~380 mL for each landfill).

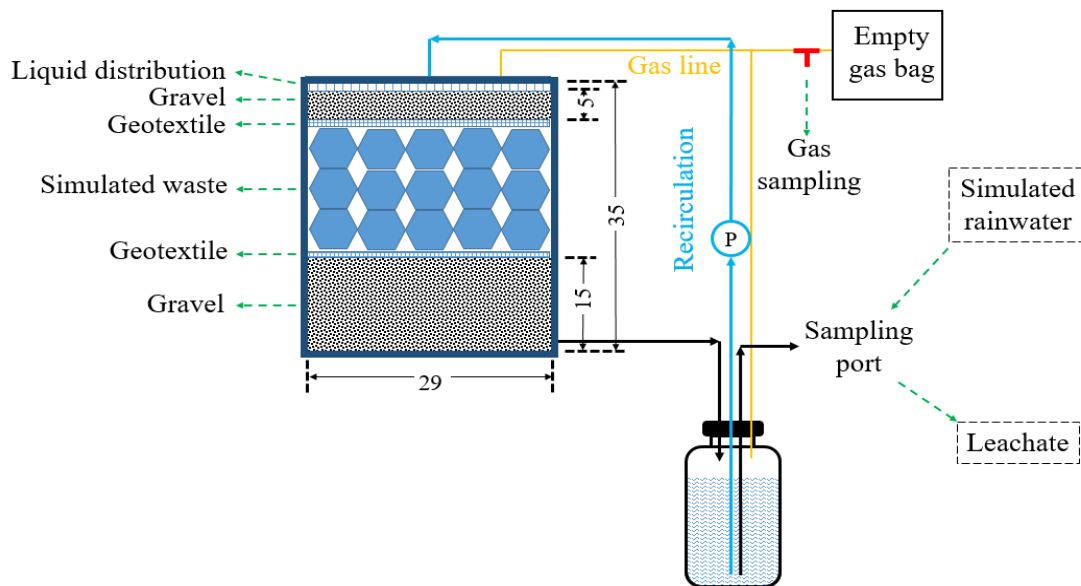


Figure 1. Schematic diagram of the lab-scale landfills (unit of the dimension is cm). P = pump

2. Characterized a real-world leachate injected into the landfills at the beginning of the landfill operation as a seed

To seed the landfill, a real-world leachate (~3.2 L) from a local landfill was injected into each landfill. The seed leachate was characterized. The results are summarized in Table 1.

Table 1. Characterization of seed leachate

Sample	Parameters	Concentrations
Seed Leachate	Acetate	30.4±0.2 mg C/L
	Chemical oxygen demand (COD)	2667±115 mg/L
	Dissolved organic carbon (DOC)	880±17 mg C/L
	SO ₄ ²⁻	92.9±0.4 mg S/L
	SO ₃ ²⁻	BDL ¹
	[S ²⁻] _{total}	BDL ²
	NH ₄ ⁺	93.2±0.6 mg N/L
	NO ₃ ⁻	0.34±0.02 mg N/L
	NO ₂ ⁻	BDL ³
	Dissolved organic nitrogen (DON)	206±1 mg N/L
	pH	7.77±0.02

Notes:

1. BDL: Below Detection Limit = 0.02 mg S/L.
2. BDL = 0.1 mg S/L.
3. BDL = 0.01 mg N/L.

3. Weekly characterized the leachate and gas produced from all six landfills

The solid waste decomposition occurred after we added the seed leachate. Four steps, including hydrolysis, acidogenesis, acetogenesis and methanogenesis, usually occur during anaerobic degradation of solid waste (Yang et al., 2013; Staszewska and Pawlowska, 2011). The leachate and gas characterization results suggested that hydrolysis, acidogenesis, acetogenesis started to occur in the first week and methanogenesis started to occur in Week 5. Sulfate reduction to sulfide (*i.e.*, odor production) started to occur in Week 7.

3.1 Leachate characterization

Ammonium and DON. The hydrolysis and acidogenesis processes were known through the accumulation of ammonium and the trend of DON in the leachate of all landfills (Figure 2) (Price et al., 2003). The ammonium concentration increased from 93.2 at the beginning to 287 - 432 mg N/L (depending on the landfills) at Week 8. The concentration of dissolved organic nitrogen (DON) increased in the first month (Figure 2b), which was probably caused by the decomposition of organic matters via hydrolysis and acidogenesis. The decreasing trend of DON concentration in the second month corresponded to the rapid increasing trend of ammonium concentration (comparison of Figure 2a and 2b), suggesting conversion of DON to ammonium via hydrolysis and acidogenesis in the second month.

Acetate, COD, and DOC. Acetogenesis was known through the significant generation of acetate (increased from 30 (in seed leachate) to ~5,000 mg C/L), COD (increased from 2,667 to ~35,000 mg/L), and DOC (increased from 880 to ~10,000 mg C/L) in leachate in the first week (Figure 3). The decreasing trend for all these three parameters in the second month can be explained by biological degradation combined with rainwater dilution. The acetate and COD decreased by approximately 9% each week. Out of the 9%, 7% was due to the leachate dilution by the simulated rainwater, and 2% was due to biological removal.

Sulfate. Sulfate concentrations in landfills L1 to L5 were much higher than that in the control landfill (L0) (Figure 4a). The decomposition and dissolution of gypsum released sulfate into the leachate, especially under a condition of $\text{pH} < 7$ (Table 2, a summary for parameters that remained stable so far) due to the generation of protons in acidogenesis and acetogenesis. The sulfate in the

control landfill (L0) leachate came from two sources, the seed leachate (93 mg S/L) and residuals in the solid waste. Sulfate reduction to sulfide began at the 7th week (Figure 4b). We expect that this process will accelerate in the near future due to the recent steep increase of H₂S (Figure 4b).

Other parameters. Other parameters did not significantly change in the first eight weeks. They are summarized in Table 2.

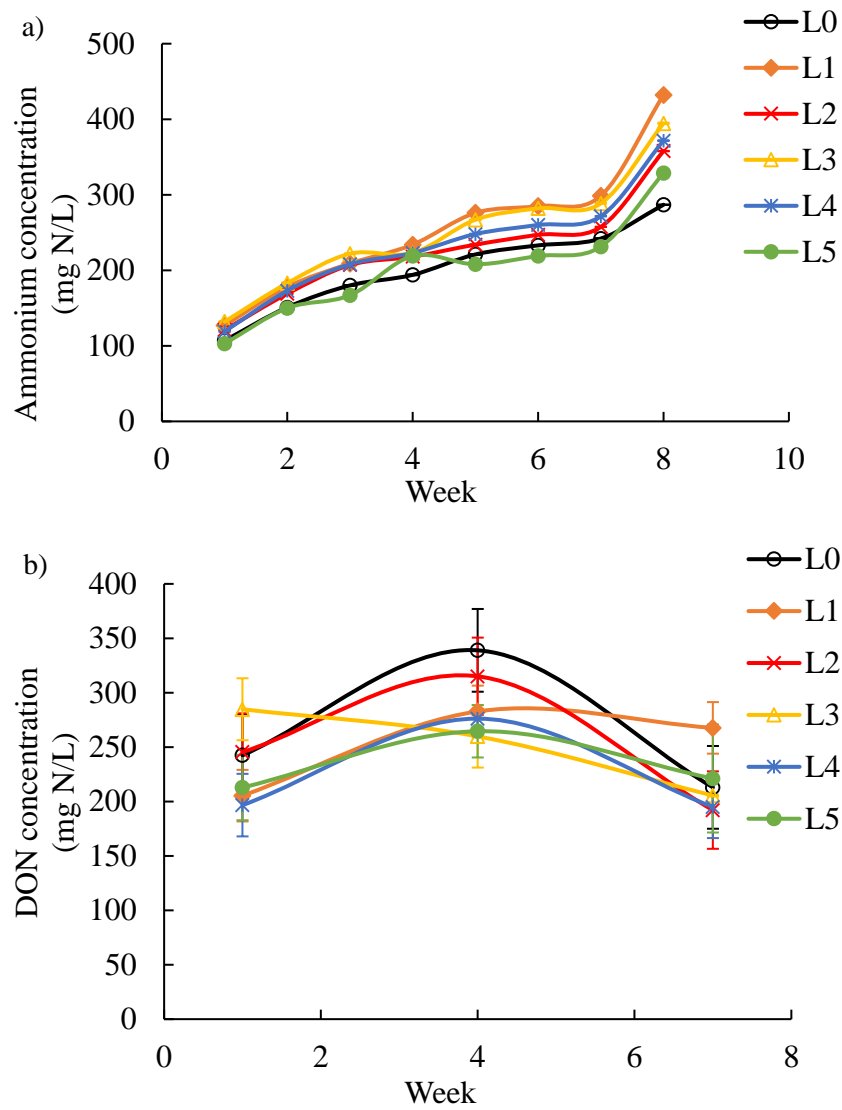


Figure 2. Concentrations of nitrogen species in the leachate

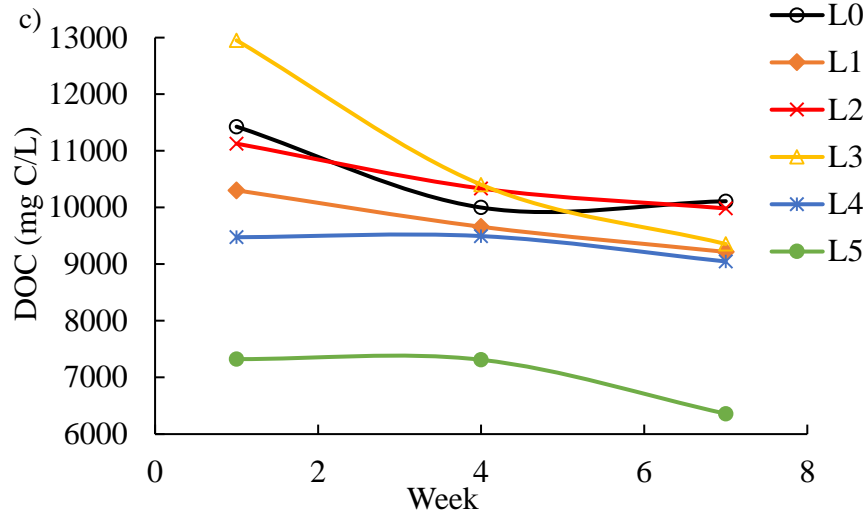
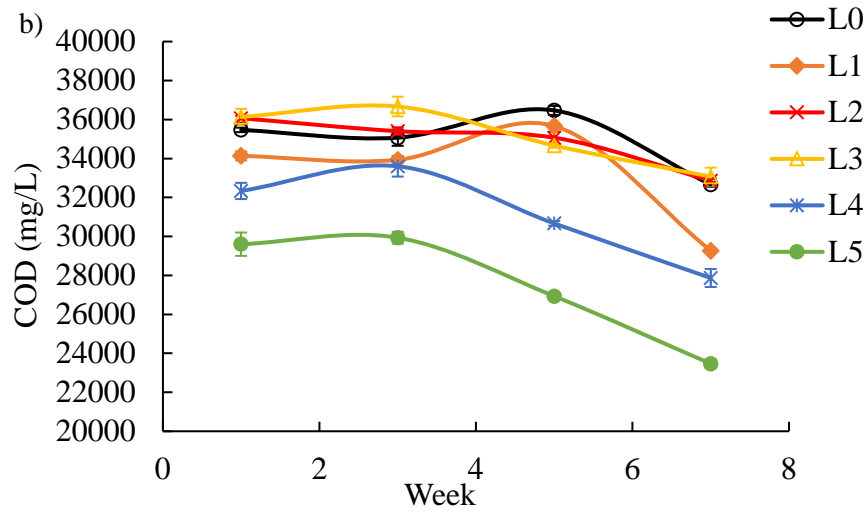
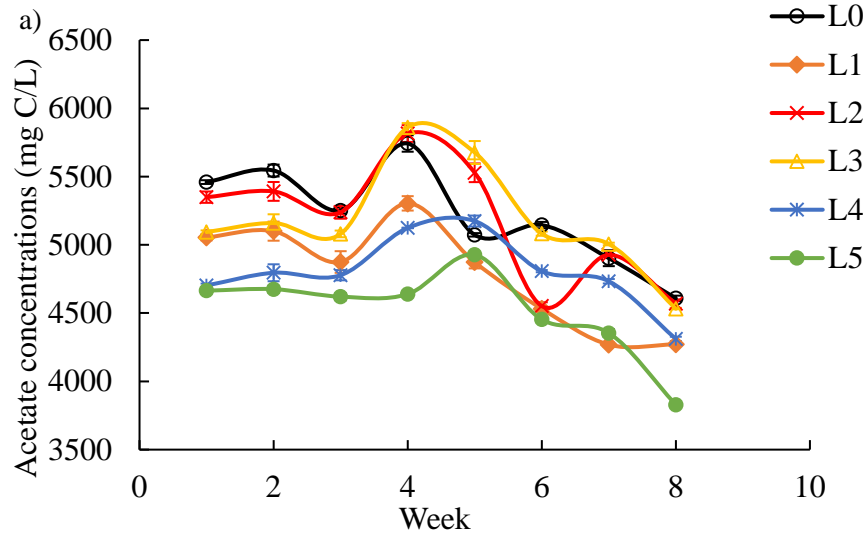


Figure 3. Concentrations of carbon species in the leachate

Table 2. Parameters with stable values for all landfills

Parameters	Concentrations
NO ₃ ⁻	<1 mg N/L
NO ₂ ⁻	BDL
SO ₃ ²⁻	BDL
pH	5.1-5.6
O ₂	BDL ¹
N ₂	60-90%
CO ₂	10-40%
Gas volume	<20 mL/day

Notes:

1. Detection limit of O₂ is 0.1 mg/L.

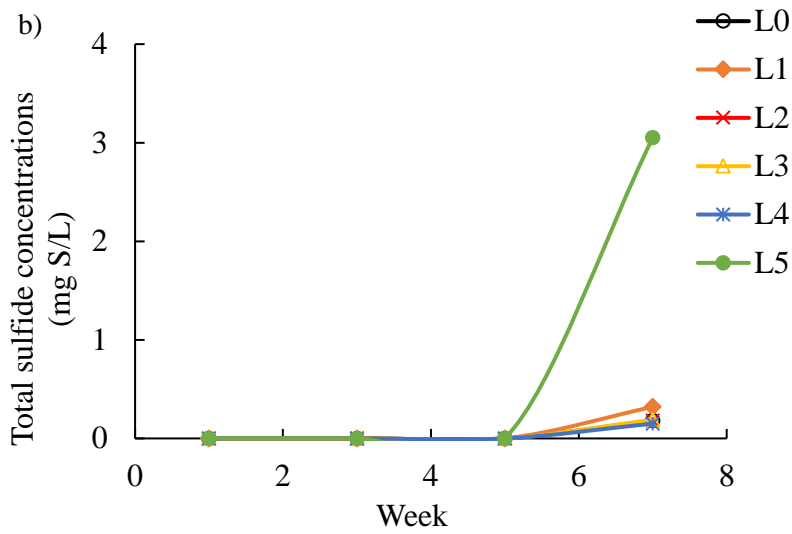
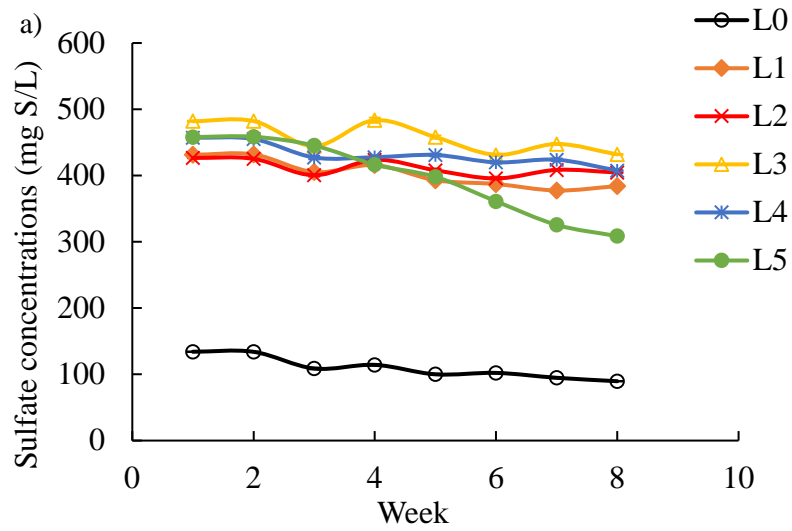


Figure 4. Concentrations of sulfur species in the leachate

3.2 Gas characterization

Methane. The CH₄ percentage at headspace of the leachate collection vessels is shown in Figure 5a. To compare the CH₄ concentration to other carbon species (*e.g.*, DOC and acetate) on the same basis for understanding of carbon conversion, an assumed CH₄ concentration ($C_{methane-assumed}$ = total methane mass in leachate and headspace divided by the leachate volume) is shown in Figure 5b. The CH₄ percentage started to increase at the beginning of the second month, reaching 1.7% at the headspace in Week 8. The assumed CH₄ concentration (~20 mg C/L in Week 8) was orders of magnitude smaller than the DOC concentration in the leachate (~10,000 mg/L), suggesting that only a very small fraction of the DOC was converted to methane.

The methane percentage ($C_{percent}$) in the headspace was measured using a gas chromatography (GC) system (SRI Instruments), and the gas volume in the gas bag (V_{gasbag}) was measured by a 140 mL syringe. The gas volume and methane percentage in headspace were then used to calculate the methane concentration in the headspace ($C_{methane-headspace}$, mg C/L), the methane concentration in the leachate ($C_{methane-leachate}$, mg C/L), and the assumed CH₄ concentration ($C_{methane-assumed}$, mg C/L) in Equations 2 - 4, respectively.

$$C_{methane-headspace} = \frac{(C_{percent} \times MW_{carbon} \times 10^3)}{(22.4L / mol)} \quad \text{Equation 2}$$

$$C_{methane-leachate} = C_{methane-headspace} \times K_{H-CH_4} \quad \text{Equation 3}$$

$$C_{methane-assumed} = \frac{[C_{methane-headspace} \times (V_{vessel-headspace} + V_{gasbag}) + C_{methane-leachate} \times V_{leachate}]}{V_{leachate}} \quad \text{Equation 4}$$

where MW_{carbon} is the molar mass of carbon (12 g/mol), K_{H-CH_4} is the dimensionless Henry' Law Constant for methane (0.035) (Sander, 2015), $V_{leachate}$ is the leachate volume in the collection vessel (mL), $V_{vessel-headspace}$ is the headspace of a leachate collection vessel (820 mL).

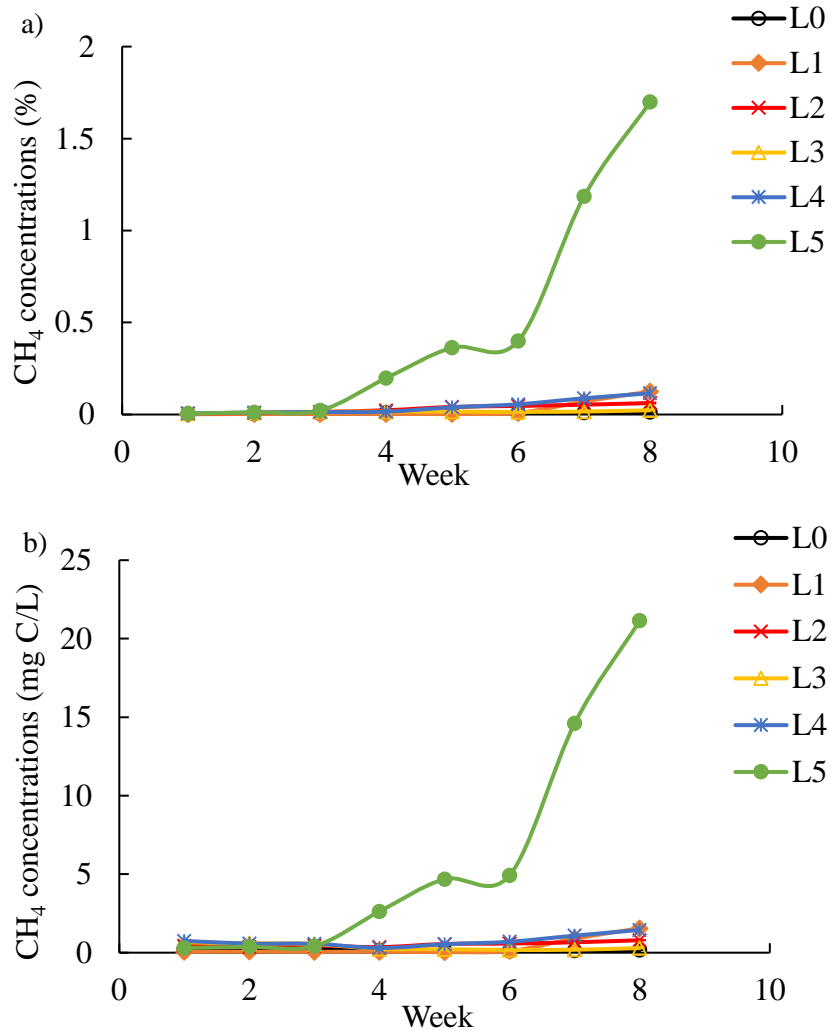


Figure 5. CH₄ percentage in headspace (a) and assumed concentration in leachate (b) of the landfills. Note: Assumed concentration in leachate = total methane mass in leachate and headspace divided by the leachate volume.

Hydrogen sulfide. The H₂S concentration in the headspace ($C_{H_2S-headspace}$) is shown in Figure 6a with ppmv as unit which is consistent with the odor threshold unit (Ko et al., 2015). To compare sulfide to other sulfur species (e.g., sulfate) on the same basis for understanding sulfur conversion, the concentration of aqueous hydrogen sulfide was estimated in two ways. First, it was converted from $C_{H_2S-headspace}$ assuming there is an equilibrium between the head space and the leachate (Equation 5), and the results are shown in Figure 6b as $C_{H_2S-leachate\ from\ headspace}$.

$$C_{H_2S-leachate\ from\ headspace} = \frac{(C_{H_2S-headspace} \times MW_{sulfur})}{(22.4L/mol \times 10^3)} \times K_{H-H_2S} \quad \text{Equation 5}$$

where MW_{sulfur} is the molar mass of sulfur (32 g/mol), K_{H-H_2S} is the dimensionless Henry' Law Constant for hydrogen sulfide (0.41) (Prata et al., 2016; Andrear et al., 1991).

The concentration of aqueous hydrogen sulfide can also be calculated in Equation 6 based on the measured concentration of total sulfide species ($C_{S^{2-}total}$, Figure 4b) and expressed as

$C_{H_2S-leachate\ from\ total\ sulfide}$:

$$C_{H_2S-leachate\ from\ total\ sulfide} = C_{S^{2-}total} \times \frac{1}{1 + \frac{K_{a1}}{10^{-pH}} + \frac{K_{a1} \times K_{a2}}{(10^{-pH})^2}} \quad \text{Equation 6}$$

where K_{a1} ($= 10^{-7.1}$) and K_{a2} ($=10^{-17}$) are the acid dissociation constants for H_2S and HS^- , respectively (Hughes et al., 2009; Stumm and Morgan, 1996). At the typical pH of 5.3 in the leachate, H_2S was the dominant sulfide species in the leachate (~98%).

The concentration of aqueous hydrogen sulfide estimated in the two ways are compared in Figure 7 for Landfill L5. $C_{H_2S-leachate\ from\ headspace}$ was lower than $C_{H_2S-leachate\ from\ total\ sulfide}$, suggesting that the leachate and headspace did not reach a complete equilibrium.

Other gases. The concentrations of the methane and hydrogen sulfide are expected to increase significantly in the near future based on the current trend. The O_2 was below the detection limit, indicating an anaerobic condition in the landfills (Table 2). CO_2 generated due to solid decomposition only slightly increased. N_2 was the major gas, since the system was flushed with N_2 at the beginning of experiment to eliminate O_2 .

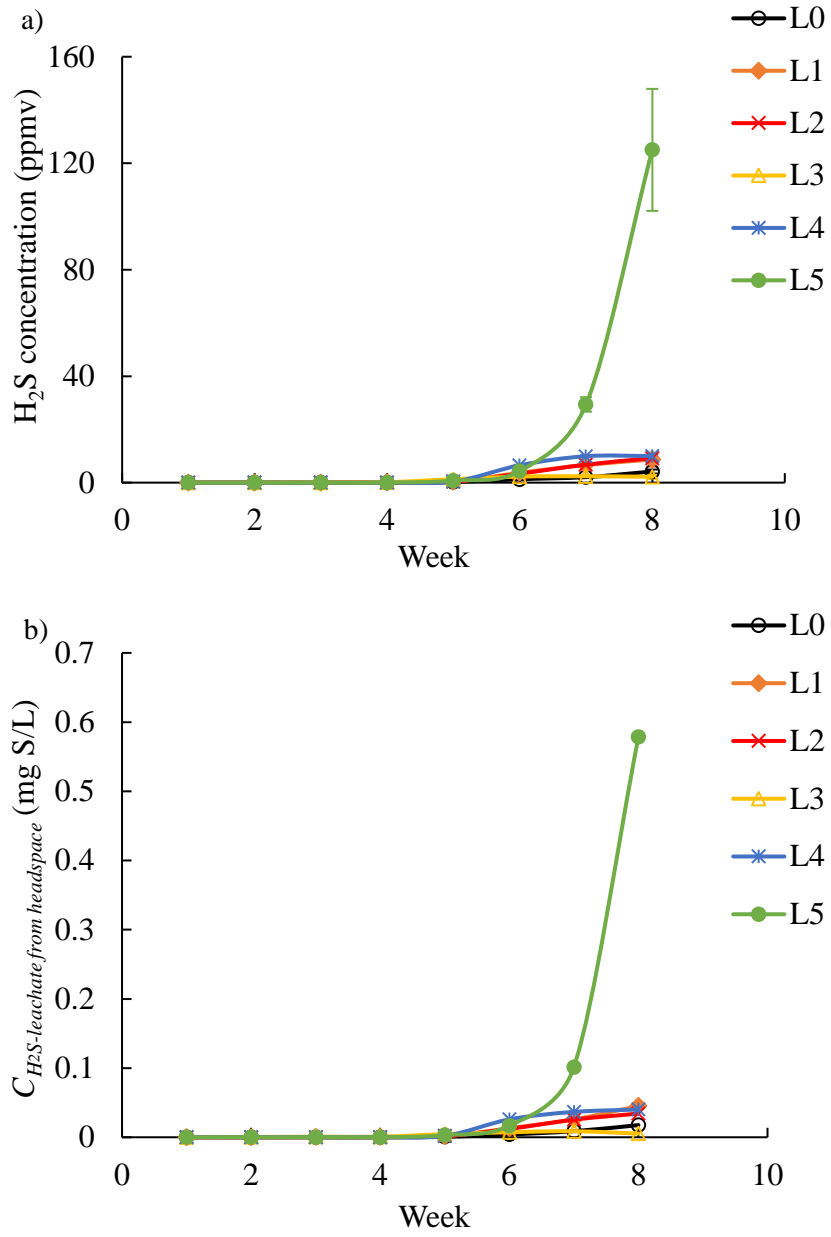


Figure 6. H₂S concentration in headspace (a) and aqueous H₂S concentration (b) converted from its headspace concentration based on Henry's Law

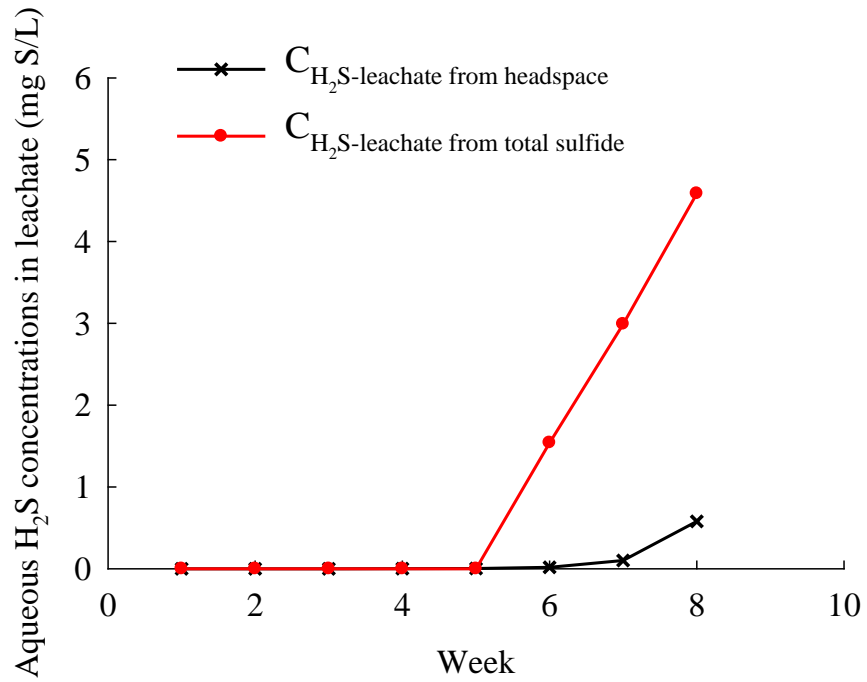


Figure 7. Comparison of the aqueous H₂S concentrations calculated from 1) its headspace H₂S concentration and 2) total sulfide concentration in leachate.

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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?

See Number 5 below.

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

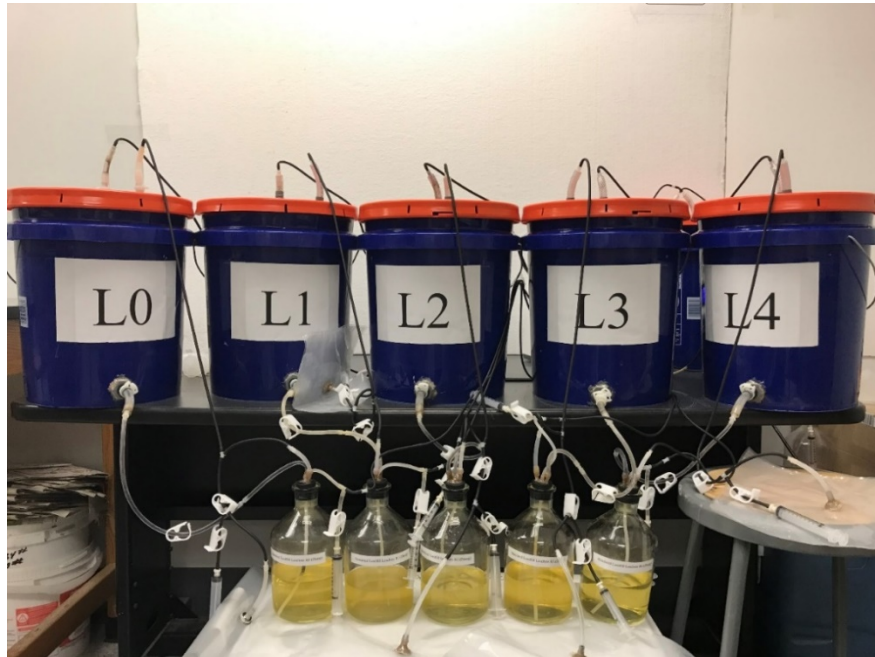
After knowing the PI (Tang)'s ability to characterize materials used in civil engineering (i.e., drywall) and their degradation in the environment through this project, a colleague of the PI (i.e., Dr. Raphael Kampmann at the FAMU-FSU College of Engineering with expertise in structures) initiated collaboration 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 aggressive environments. The project is now funded with a total cost of \$241,457 and project duration of 01/18/2019-07/31/2021.

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) Six lab-scale landfills (L1 – L5 = landfills with mixture of drywall and municipal solid waste, L0 = no drywall control)



2) Karam Eeso, an undergraduate student (freshman) majoring in Chemical Engineering, was measuring CH₄ in the headspace of the leachate collection vessels.

