QUARTERLY PROGRESS REPORT

[April 01, 2023 – June 30, 2023]

PROJECT TITLE: Fate of PFAS and Other Contaminants During Leachate Evaporation

PRINCIPAL INVESTIGATORS:

Youneng Tang (PI), Ph.D., Associate Professor

Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering

2525 Pottsdamer Street Suite A130, Tallahassee FL 32310; Tel: 850-4106119;

ytang@eng.famu.fsu.edu

Project summary: As more wastewater treatment plants reduce or cease acceptance of landfill leachate, more solid waste facilities have been moving to implementation of leachate evaporation using heat from the combustion of landfill gas and/or heat from the exhaust of landfill gas-to-energy generators. Residuals (*i.e.*, leachate concentrate) from this process are dried and then returned to the landfill. The objective of this project is to answer the following questions:

1) What happens to per- and polyfluoroalkyl substances (PFAS) and other contaminants when the leachate is evaporated? Do they concentrate within the residue? Are they emitted into the atmosphere?
2) What affects the distribution coefficient of PFAS (= PFAS in gas emission due to evaporation/PFAS in leachate residue after evaporation)?
3) What effects are likely on the chemical concentration of future leachate from the reintroduction of the concentrated leachate residuals into the landfill?

The project, if successful, will provide information to landfill managers who plan to move from the discharge-to-sewer method to the leachate evaporation method.

Work Accomplished during this Reporting Period:

The project has three tasks. We have completed ~70% of Task 1, ~50% of Task 2, and ~0% of Task 3. The completed work in each task is described below:

<u>Task 1: Effects of leachate evaporation on the fate of PFAS and contaminants regulated by 40 CFR 445.11</u>

We used a rotary evaporator (see Figure 1) to evaporate landfill leachate sampled from three landfills in Florida. For each landfill, 1.6 liters of leachate was evaporated at a temperature of 77 °C via a water bath and a vacuum pressure of -650 mmHg (relative to the atmospheric pressure of 0). We took samples from the leachate residual and condensate when 0%, 12.5%, 25%, 50%, 75%, and 90% evaporation was completed. We proposed to measure 14 contaminants regulated by 40 CFR 445.11, total dissolved solids (TDS), chemical oxygen demand (COD), total organic carbon (TOC), and per- and polyfluoroalkyl substances (PFAS). The 14 contaminants regulated by 40 CFR 445.11 include five-day biochemical oxygen demand (BOD_5), total suspended solids (TSS), ammonia, α-terpineol, aniline, benzoic acid, naphthalene, p-cresol, phenol, pyridine, arsenic, chromium, zinc, and pH. These contaminants have been classified in four groups, including general parameters, metals, organic contaminants, and PFAS. The contaminants in each group and the methods for measurement are summarized in Table 1. In this quarterly report, we measured pH, TDS, fluorotelomer alcohols (FTOHs), α-terpineol, aniline, benzoic acid, naphthalene, p-cresol, phenol, and pyridine. The results are shown in Figures 2-4. Interestingly, the concentration of each organic contaminant was decreasing in both leachate residual and condensate (Figure 3).

Figure 1. Rotary evaporator for leachate evaporation

Table 1. Methods for characterizing leachate residual and condensate

Category	Parameters	Regulated by 40 CFR 445?	Methods	Equipment	References
A) General parameters	TOC[1]	No	Combustion catalytic oxidation	TOC analyzer (Shimadzu TOC-VCSH)	Opio et al., 2015
	COD[2]	No	Reactor digestion method (HACH method 8000)	Spectrophotometer (DR3900, Hach)	Elnakar and Buchanan, 2020
	TDS[3]	No	Electrometric method	Electrical conductivity meter (HQ440D, Hach)	Rice et al., 2012
	pH	Yes	Electrometric method	Multi-parameter meter (HQ440D, Hach)	Rice et al., 2012
	BOD_5[4]	Yes	5210 B Method	Bottles with a ground-glass stopper	APHA, 2005
	TSS[5]	Yes	5240 D Method	Benchtop Muffle Furnaces (Thermolyne™)	APHA, 2005
	Ammonia	Yes	Salicylate Method	Spectrophotometer (DR3900, Hach)	Adeniyi et al., 2023
B) Metals	zinc, arsenic, chromium,	Yes	EPA[6] method 3050B	4100 MP-AES[7] (Agilent Technology)	U.S. EPA, 1996
C) Organic contaminants	α-terpineol, aniline, benzoic acid, naphthalene, p-cresol, phenol, pyridine,	Yes	Mass spectrometry method	GC-MS[8] (Agilent Technology)	Simões et al., 2007
D) PFAS[9]	FTOHs[10]	No	Mass spectrometry method	GC-MS (Agilent Technology)	Tang et al., 2023
	Other PFAS	No	EPA method (537 modified)	LC-MS/MS[11]	U.S. EPA, 2020

Notes:
[1] TOC = Total organic carbon
[2] COD = Chemical oxygen demand
[3] TDS = Total dissolved solids
[4] BOD_5 = Five-day biochemical oxygen demand
[5] TSS = Total suspended solids
[6] EPA = Environmental Protection Agency
[7] MP-AES= Microwave plasma-atomic emission system
[8] GC/MS = Gas chromatography mass spectrometry
[9] PFAS = Per- and polyfluoroalkyl substances
[10] FTOHs= Fluorotelomer alcohol
[11] LC-MS/MS = Liquid chromatography with mass spectrometry in tandem

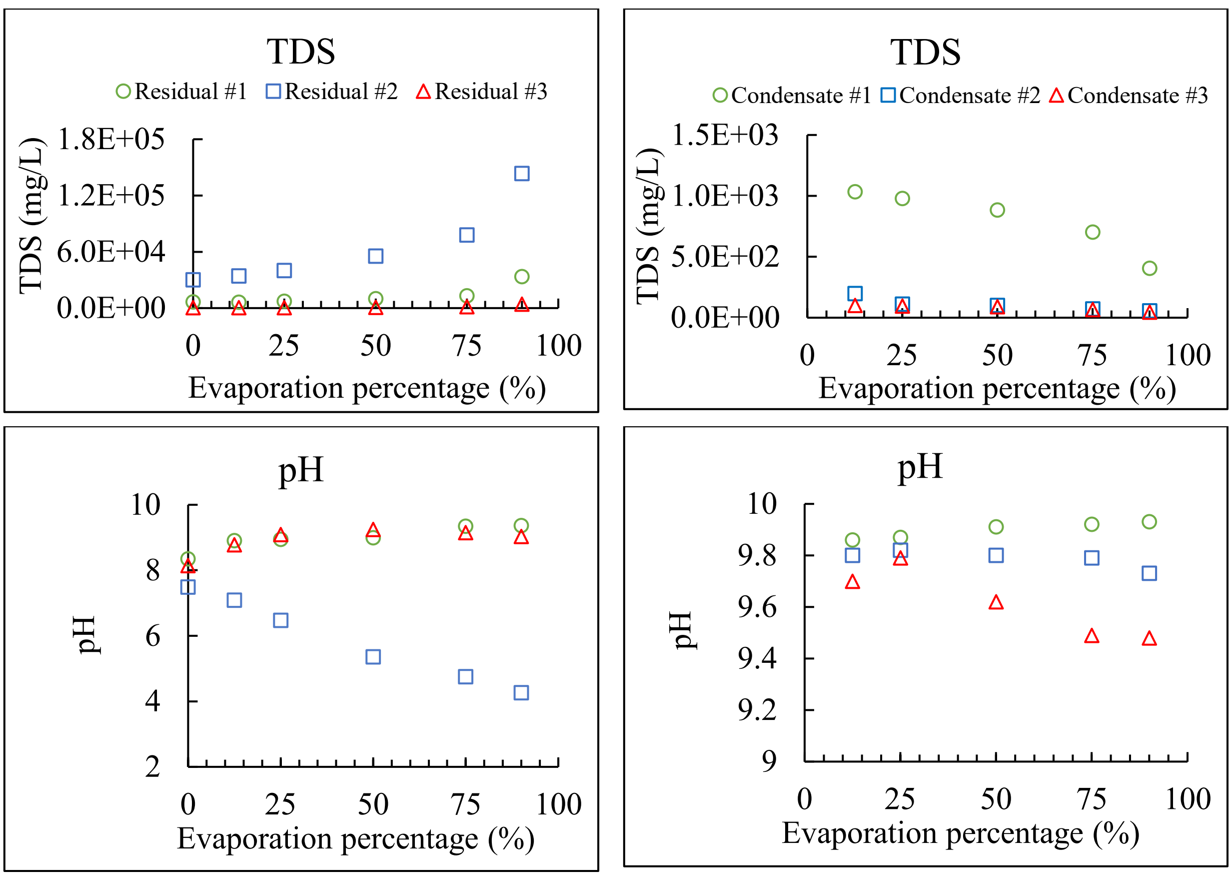

Figure 2. General parameters in the leachate residual (left) and condensate (right)

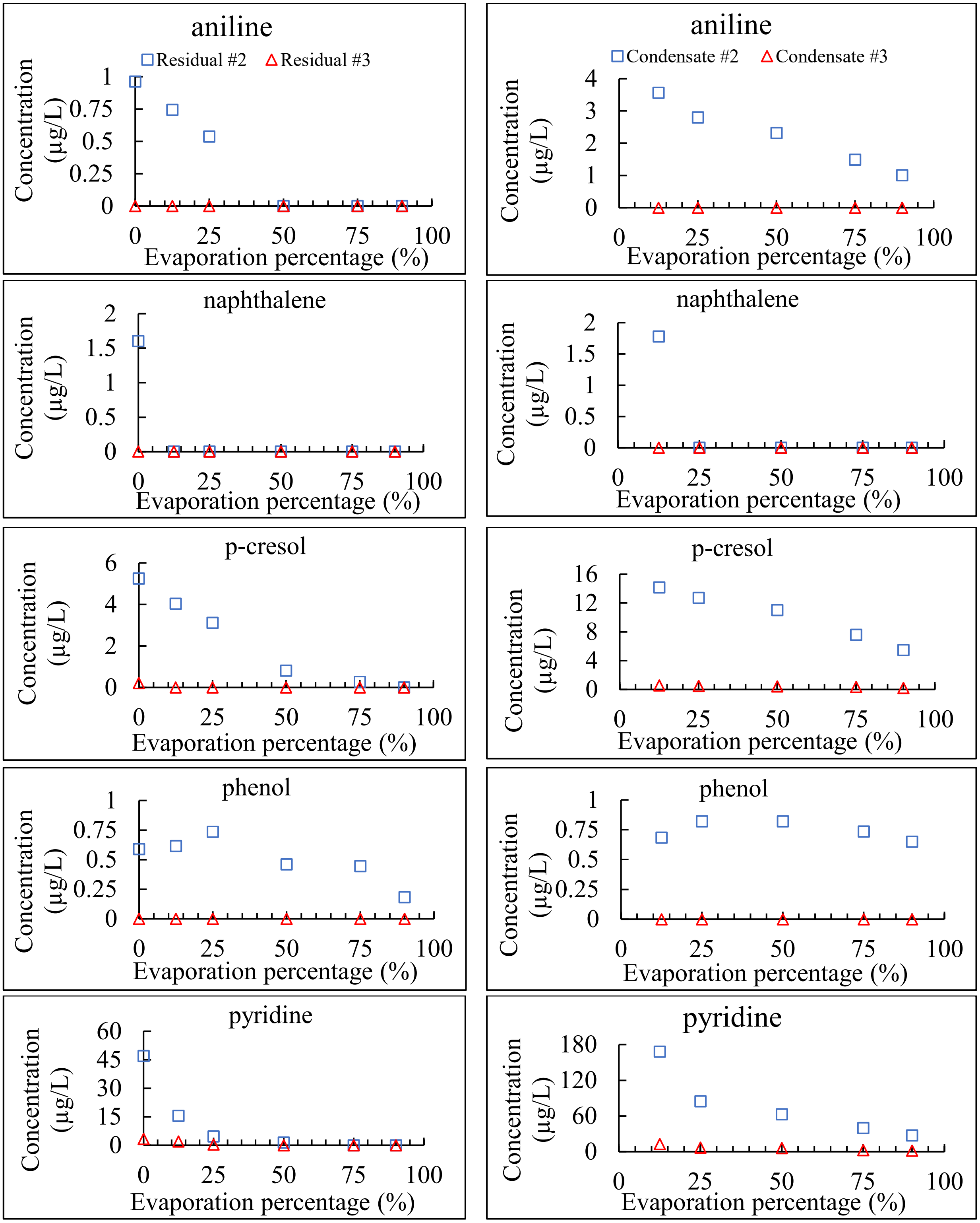

Figure 3. Organic contaminants in leachate residual (left) and condensate (right). Note: The concentrations of α-terpineol and benzoic acid were below the quantification limits.

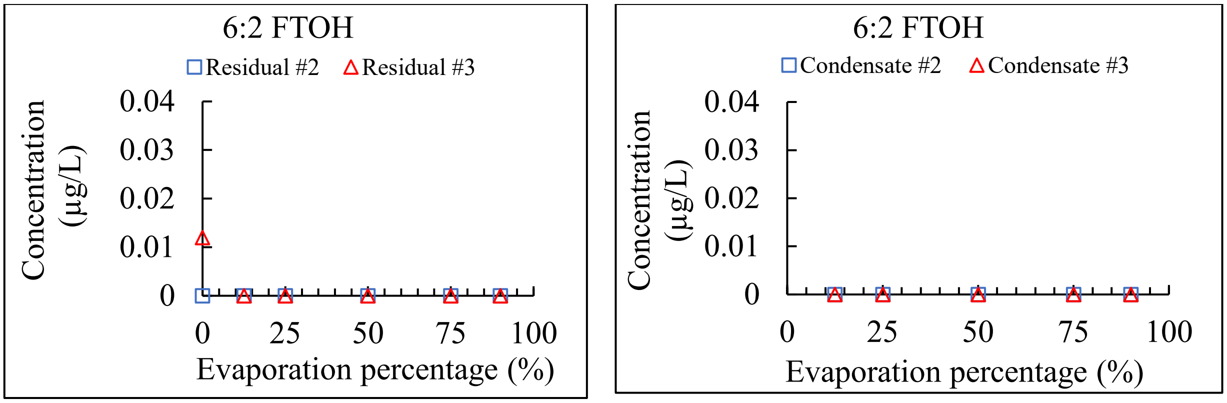

Figure 4. Fluorotelomer alcohols (FTOHs) in leachate residual (left) and condensate (right). Note: The concentration of 4:2 FTOH, 8:2 FTOH, and 10:2 FTOH were below their quantification limits.

Task #2: Distribution coefficients of PFAS

Task 2 extends on Task 1, but focuses on PFAS only. In this Task, we used a synthetic leachate. The synthetic leachate contains 1,000 mg/L of humic acid and 1,500 mg/L of NH_4Cl. We spiked the synthetic leachate with 4:2 fluorotelomer alcohol (4:2 FTOH), 6:2 fluorotelomer alcohol (6:2 FTOH), and 8:2 fluorotelomer alcohol (8:2 FTOH) at 100 µg/L. We evaporated the synthetic leachate and took a sample from the leachate residual and a sample from the condensate when 1.5, 3, 6, 12.5, 25, 50, 75, and 90% evaporation was completed. Figure 5 and Figure 6 show the concentrations of FTOHs in the leachate residual and the condensate, respectively. Similar to the trends of the three Florida landfills in Figure 4, the concentrations of FTOHs quickly decreased in the leachate residual at the beginning of the experiment: The concentration of FTOHs reached below the quantification limits before 12.5% of evaporation (Figure 5). The concentrations of FTOHs in the condensate first increased due to input from the leachate and then decreased due to the vacuum-caused evaporation and dilution in the condensate collector. FTOHs are highly volatile; therefore, they could escape from the condensate. In the next quarterly report, we will add 10:2 fluorotelomer alcohol (10:2 FTOH) and spike all FTOHs at 500 µg/L to confirm the trend at a higher concentration.

To observe the fate of perfluoroalkyl carboxylic acids (PFCAs) during leachate evaporation, we spiked the synthetic leachate with perfluorodecanoic acid (PFDA, C10), perfluorononanoic acid (PFNA, C9), perfluorooctanoic acid (PFOA, C8), perfluoroheptanoic acid (PFHpA, C7), PFHxA perfluorohexanoic acid (PFHpA, C6), perfluoropentanoic acid (PFPeA, C5), and

Perfluorobutanoic acid (PFBA, C4) at 500 μg/L. We took samples from the leachate residual and the condensate when 0% and 90% evaporation was completed. The samples will be measured in a commercial lab by liquid chromatography with tandem mass spectrometry (LC-MS-MS). We also did the same experiment without adding PFCAs as a control.

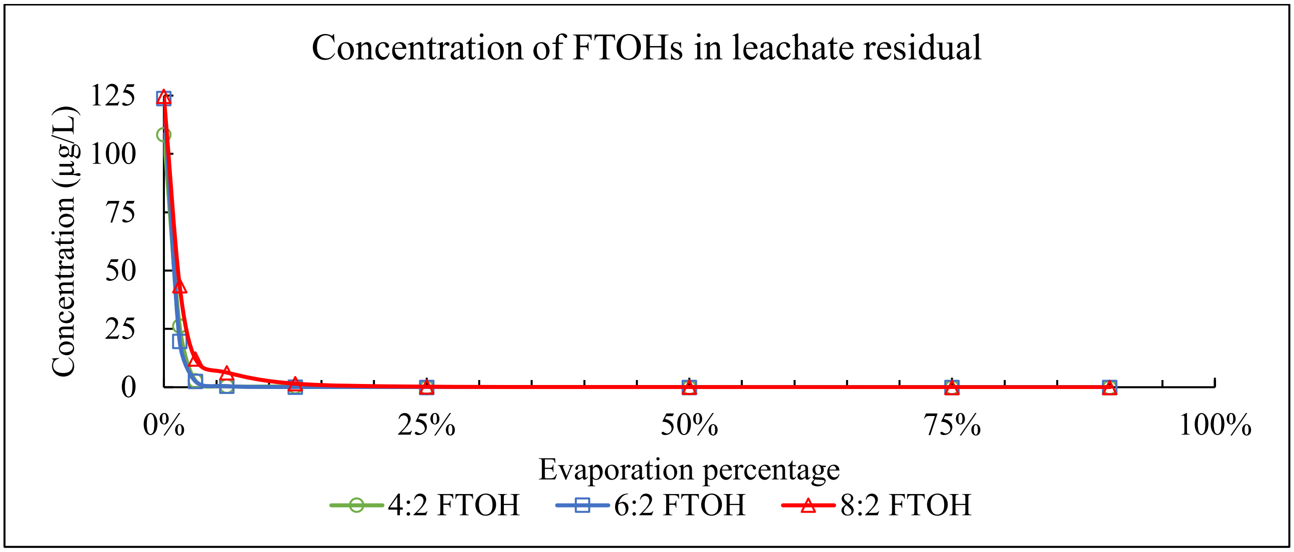

Figure 5. The concentrations of FTOHs in the leachate residual during evaporation

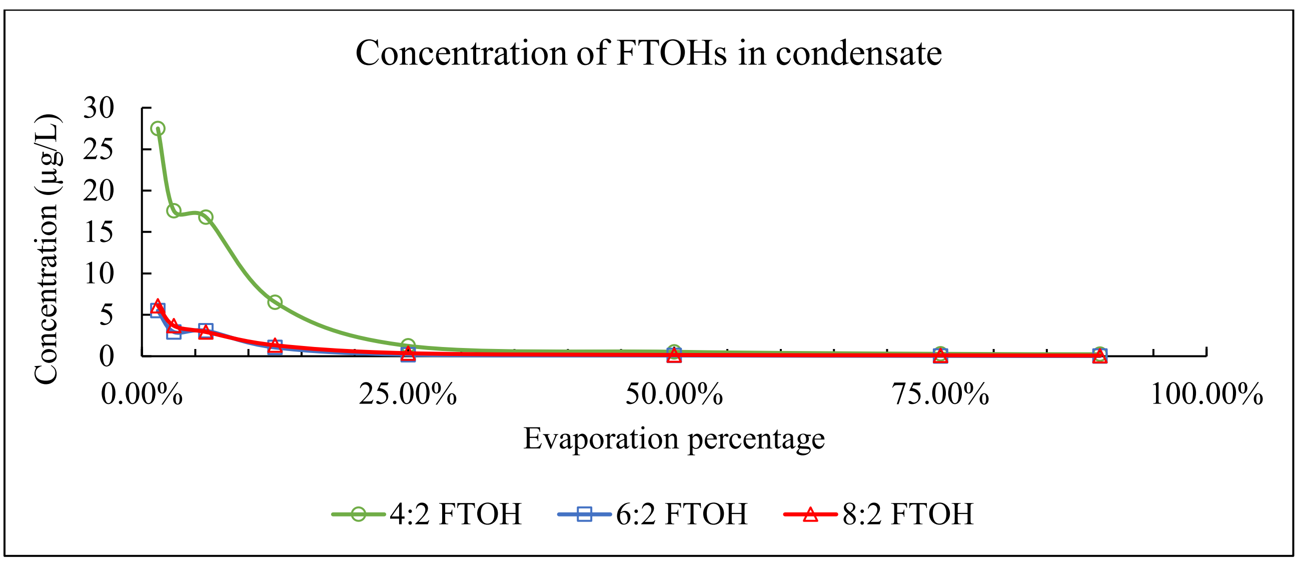

Figure 6. The concentrations of FTOHs in the condensate during evaporation

Task #3: Effects of reintroduction of the concentrated leachate residuals on the fate of PFAS and other contaminants

No work was done during this reporting period.

References:

Adeniyi, Adewale, Ibrahim Bello, Taofeek Mukaila, Ewumbua Monono, and Ademola Hammed. "Developing rumen mimicry process for biological ammonia synthesis." *Bioprocess and Biosystems Engineering* 46, no. 7 (2023): 1011-1020.

Adeniyi, Adewale, Ibrahim Bello, Taofeek Mukaila, Ewumbua Monono, and Ademola Hammed. "Developing rumen mimicry process for biological ammonia synthesis." *Bioprocess and Biosystems Engineering* (2023): 1-10.

American Public Health Association. "APHA standard methods for the examination of water and wastewater." *Standard methods for the examination of water & wastewater. Washington, DC: American Public Health Association* (2005).

Elnakar, Haitham, and Ian Buchanan. "Treatment of bypass wastewater using novel integrated potassium ferrate (VI) and iron electrocoagulation system." *Journal of environmental engineering* 146, no. 8 (2020): 04020075.

Opio, Alfonse, Mike B. Jones, Frank Kansiime, and Tom Otiti. "Dissolved organic carbon in a tropical wetland dominated by Cyperus papyrus." *Wetlands ecology and management* 23, no. 6 (2015): 1033-1038.

Qiu, Y., Frear, C., Chen, S., Ndegwa, P., Harrison, J., Yao, Y., & Ma, J. (2020). Accumulation of long-chain fatty acids from Nannochloropsis salina enhanced by breaking microalgae cell wall under alkaline digestion. *Renewable energy*, *149*, 691-700.

Rice, E.W., Baird, R.B., Eaton, A.D. and Clesceri, L.S., 2012. Standard Methods for the Examination of Water and Wastewater, 22nd Edition. American Public Health Association, American Water Works Association, Water Environment Federation.

Simões, N. G., Cardoso, V. V., Ferreira, E., Benoliel, M. J., & Almeida, C. M. (2007). Experimental and statistical validation of SPME-GC–MS analysis of phenol and chlorophenols in raw and treated water. *Chemosphere*, *68*(3), 501-510.

Tang, Y., Goukeh, M.N., Eeso, K., 2023. Per- and Polyfluoroalkyl Substances (PFAS) in Landfill Gas Emissions.

U.S. Environmental Protection Agency (USEPA) (2020).Method 537.1—Determination of select per-and polyfluorinated alkyl substances indrinking water by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC-MS-MS).

U.S. Environmental Protection Agency, 1996. Method 3050B: Acid digestion of sediments, sludges, and soils. https://www.epa.gov/sites/production/files/2015-06/documents/epa-3050b.pdf.

Metrics:

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

   None in this reporting period.

2. List research presentations resulting from (or about) THIS Hinkley Center project.

   None in this reporting period.

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

   None in this reporting period.

4. How have the research results from THIS Hinkley Center project been leveraged to secure additional research funding? What additional sources of funding are you seeking or have you sought?

   We are preparing a PFAS research proposal to National Science Foundation. The fate of PFAS in landfill leachate is a key component in this proposal.

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

   None in this reporting period.

6. How have the results from THIS Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders?

   None in this reporting period.