

# QUARTERLY PROGRESS REPORT

[May 01, 2021 – July 31, 2021]

**PROJECT TITLE:** Non-Thermal Plasma Degradation of Per- and Polyfluoroalkyl Substances (PFASs) from Landfill Leachate

## **PRINCIPAL INVESTIGATORS:**

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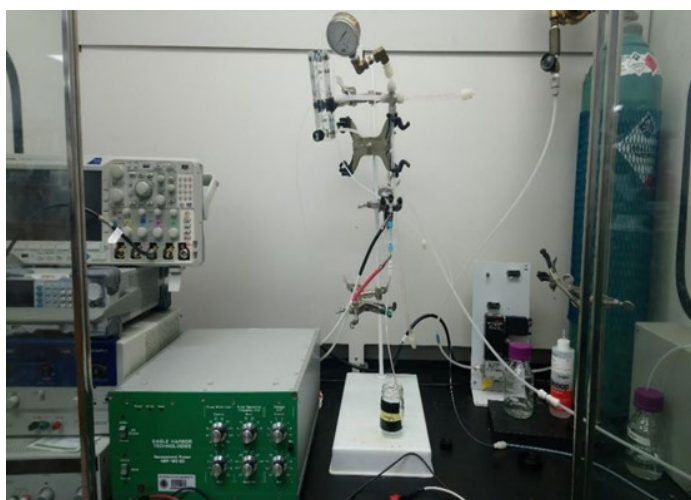
**PROJECT WEBSITE:** [https://web1.eng.famu.fsu.edu/~ytang/PFAS in leachate.html](https://web1.eng.famu.fsu.edu/~ytang/PFAS_in_leachate.html)

### Work Accomplished during this Reporting Period:

The project has four tasks. We have completed ~40% of Task 1, ~60% of Task 2, ~10% of Task 3, and ~50% of Task 4. The completed work for each task during this reporting period is described below:

#### **Task 1: evaluate the removal of five representative PFAS in addition to PFOA at leachate-relevant PFAS concentrations ( $\mu\text{g/L}$ ) by the gas-liquid flowing film plasma reactor**

We used the plasma reactor (photo shown in Figure 1) to treat a real-world landfill leachate sampled from a municipal landfill in Florida. The characteristics of the landfill leachate is shown in Table 1. The power supply settings were 16 kV (input voltage), 40 ns (pulse width), and 5 kHz, and the flow rate was 2 mL/minute.



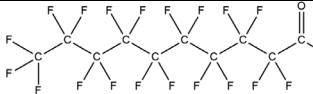
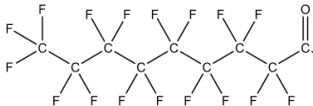
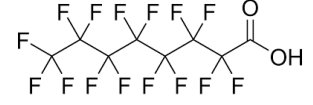


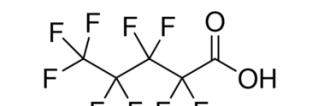
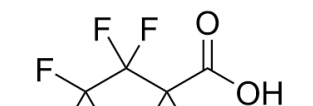
**Figure 1.** The plasma reactor used in this study

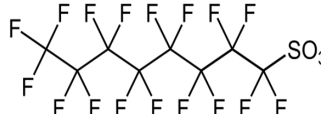



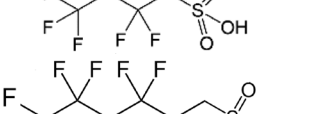
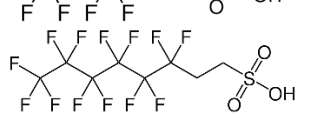
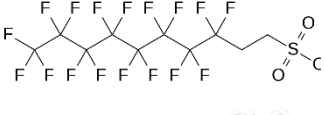
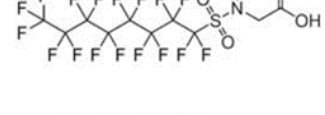
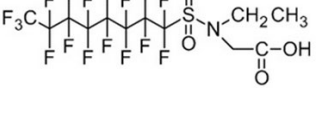

**Table 1.** Characterization of the Landfill Leachate

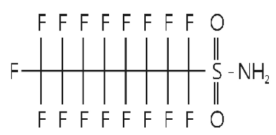
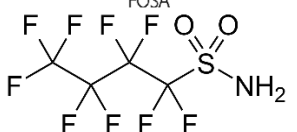
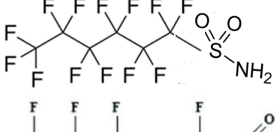
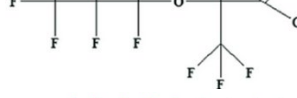
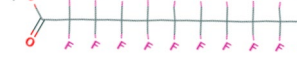



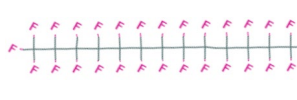
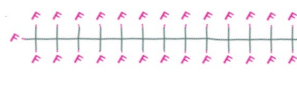
Parameter (units)	Value
pH	7.49
Conductivity (ms/cm)	15.7
Chemical oxygen demand (mg/L)	2,960
Dissolved organic carbon (mg C/L)	1,150
Sulfate (mg S/L)	326
Iron (mg Fe /L)	2
Lead (mg Pb /L)	0.1
Nickel (mg Ni /L)	0.05
Cadmium (mg Cd/L)	Below the quantification limit of 0.005 mg Cd/L
Copper (mg Cu /L)	0.04

The results, given in Table 2, show the high efficiency of the reactor for removing the majority of per- and polyfluoroalkyl substances (PFASs). For example, the removal percentages of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are 76% and 83%, respectively. The names and chemical structures of PFOA, PFOS, and other PFASs are included in Table 2. 30 PFASs were measured at Florida Department of Environmental Protection (FDEP). We divide the 30 PFASs into four categories and discuss each category separately as follows.

**Table 2.** Degradation of PFASs in a real-world landfill leachate treated by the plasma reactor

PFAS Category	PFAS Name	Quantification Limit (ng/L)	Effluent Concentration When Plasma Was Off, control (ng/L)	Effluent Concentration When Plasma was On (ng/L)	Removal Percentage (%)	PFAS Structure
PFCA (perfluorinated carboxylic acids)	PFDA (perfluorodecanoic acid)	4	16	7.3	54.4	
	PFNA (Perfluorononanoic acid)	2	1100	290	73.6	
	PFOA (Perfluorooctanoic acid)	2	1400	340	75.7	
	PFHpA (Perfluoroheptanoic acid)	2	560	240	57.1	
	PFHxA (Perfluorohexanoic acid)	2	2600	1400	46.2	
	PFPeA (Perfluoropentanoic acid)	2	1100	1200	-9.10	
	PFBA (Perfluorobutanoic acid)	4	490	1400	-185.7	

PFSA	PFOS (Perfluorooctanesul- fonic acid)	2	1100	190	82.7		
	PFHpS (Perfluoroheptanesu- lfonic acid)	0.8	22	4.4	80.0		
	PFHxS (Perfluorohexanesul- fonic acid)	0.8	610	190	68.9		
	PFPeS (Perfluoropentanesu- lfonic acid)	0.4	130	60	53.9		
	PFBS (Perfluorobutanesul- fonic acid)	0.4	1400	860	38.6		
	Other PFASs above the quantification limit	4:2 FTS (Fluorotelomer sulphonic acid 4:2)	2	160	82	48.8	
		6:2 FTS (Fluorotelomer sulphonic acid 6:2)	16	3400	920	72.9	
		8:2 FTS (Fluorotelomer sulphonic acid 8:2)	2	67	22	67.2	
		N-MeFOSAA (2-(N- Methylperfluorooct anesulfonamido) acetic acid)	0.8	28	5.4	80.7	
		N-EtFOSAA (2-(N- Ethylperfluorooctan esulfonamido) acetic acid)	0.8	1.8	0	100.0	

PFASs below quantification limit	FOSA (Perfluorooctanesul fonamide)	0.4	1.8	0.71	60.6	
	FBSA (Perfluorobutane sulfonamide)	0.4	24	95	-295.8	
	FHxSA (Perfluorohexane sulfonamide)	0.4	19	23	-21.1	
	HFPO-DA (Hexafluoropropyle ne oxide dimer acid)	4	BQL*	BQL	-	
	PFUnA (Perfluoroundecano ic acid)	2	BQL	BQL	-	
	PFNS (Perfluorononanesu lfonic acid)	0.4	BQL	BQL	-	
	PFDaA (Perfluorododecano ic acid)	2	BQL	BQL	-	
	PFDS (Perfluorodecanesu lfonic acid)	0.4	BQL	BQL	-	
	PFTriA (Perfluorotridecano ic acid)	2	BQL	BQL	-	
	PFTeA (Perfluorotetradeca noic acid)	2	BQL	BQL	-	

ADONA (4,8-dioxo-3H  
perfluorononanoic  
acid)

0.4

BQL

BQL

-



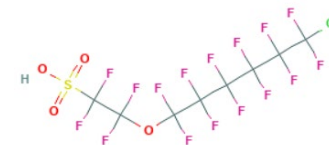
9Cl-PF3ONS (9-  
chlorohexadecafluoro-3-oxanone-1-  
sulfonic acid)

2

BQL

BQL

-



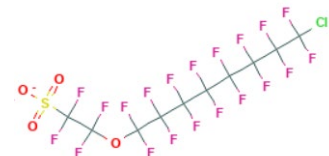
11Cl-PF3OUdS (11-  
chloroeicosafluoro-3-oxaundecane-1-  
sulfonic acid)

2

BQL

BQL

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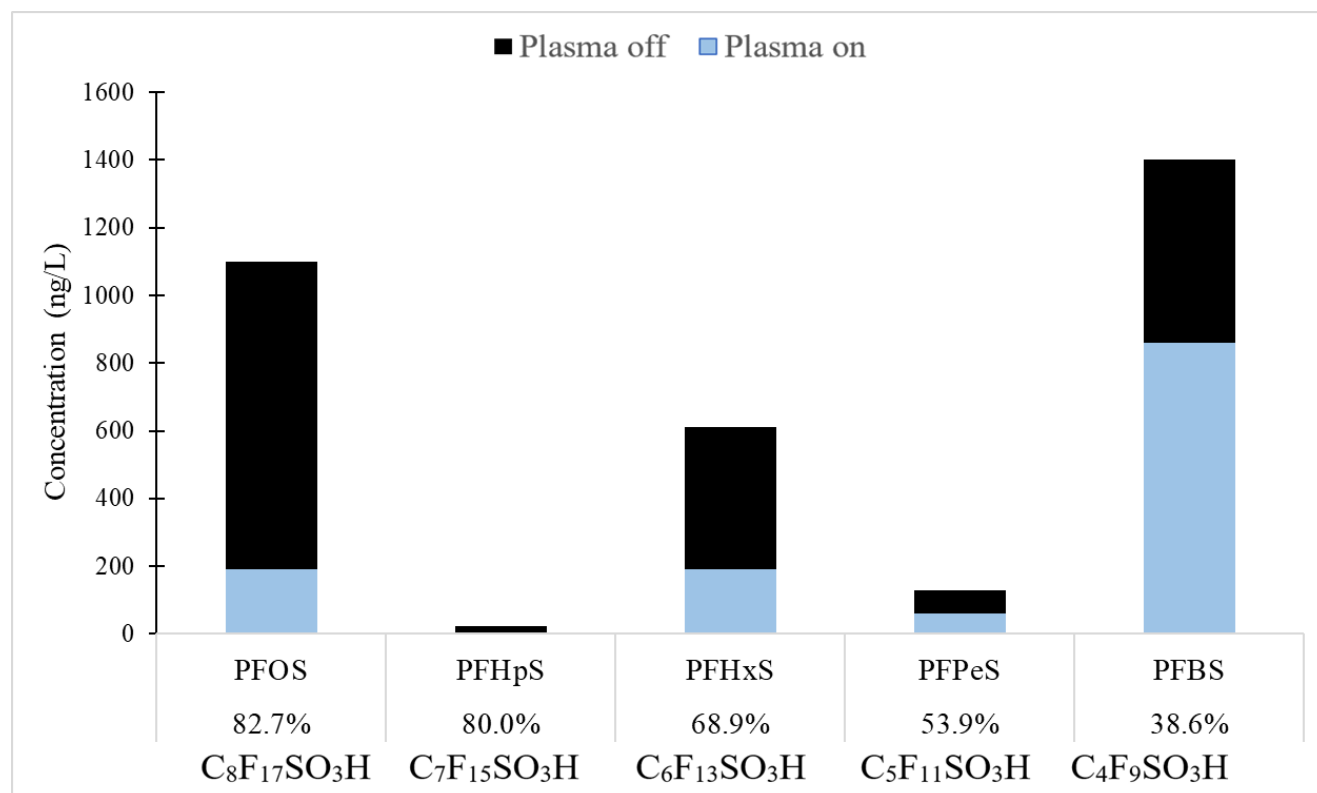


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Note: \*BQL = Below quantification limit.

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**Category 1 -- Perfluorosulfonic acids (PFSAs):** In general, the degradation percentages of PFSAs decreased with decreasing chain length: PFOS (C8; 83%) > PFHpS (C7; 80%) > PFHxS (C6; 69%) > PFPeS (C5; 54%) > PFBS (C4; 39%) (See Figure 2). Lower surface activity of short-chain PFSAs than longer chain PFASs leads to a smaller removal rate of the short-chain compounds. These results are consistent with previous studies (Singh et al., 2021).

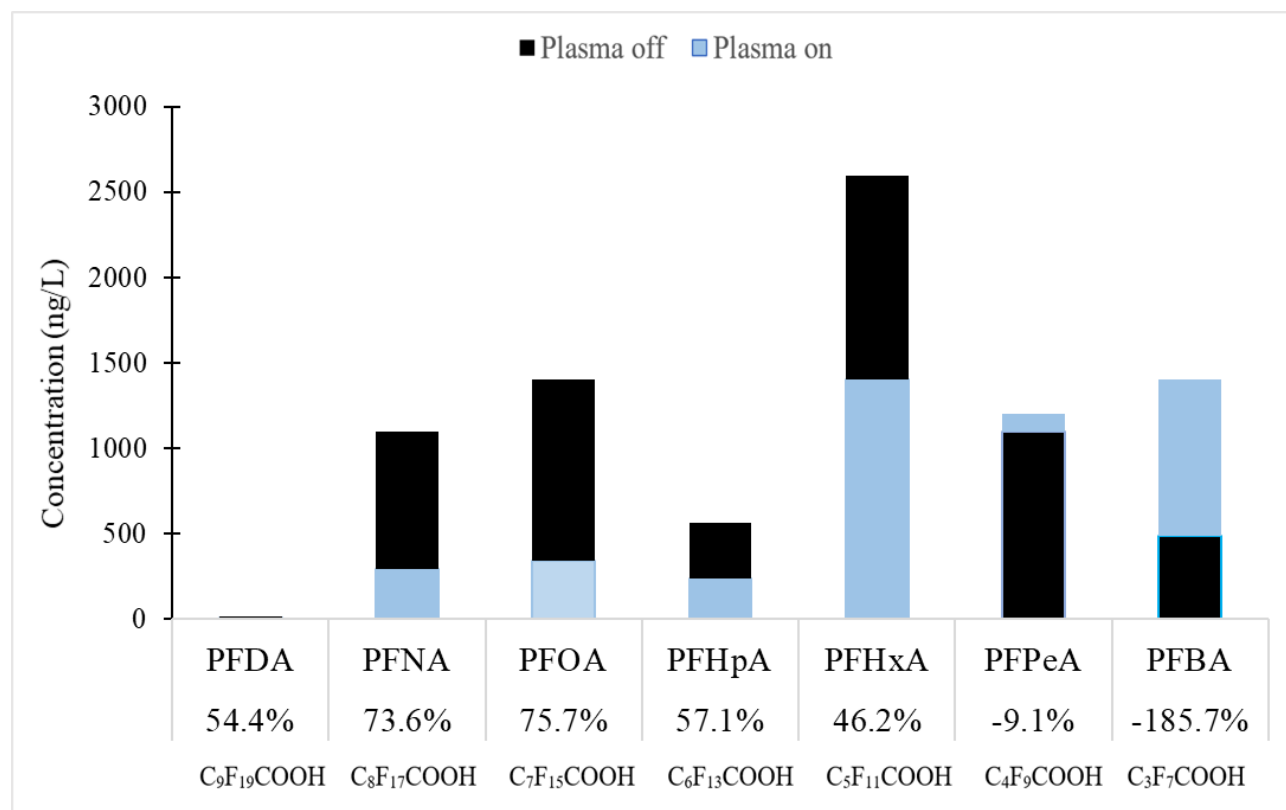


**Figure 2.** Concentration of PFSAs with plasma turned off and on in the effluent of the plasma reactor. Note: the percentage refers to the removal.

**Category 2 -- Perfluorinated carboxylic acid (PFCAs):** For PFCAs, we observed similar trends to PFSAs: The degradation rate of PFCAs decreased with decreasing chain length: PFNA (C8; 74%) ~ PFOA (C7; 76%) > PFHpA (C6; 57%) > PFHxA (C5; 46%) > PFPeA (C4; -9%) > PFBA (C4; -186%) (See Figure 3). The only exception is PFDA (C9; 54%). The low degradation efficiency of this contaminant may be attributed to its low initial concentration and the possible high measurement error (plasma off). Moreover, we observed that two short-chain PFCAs (PFPeA and PFBA) had negative degradation percentages. This may be explained by two reasons. First, the long-chain perfluoroalkyl acids (PFAAs) and some PFASs precursors can



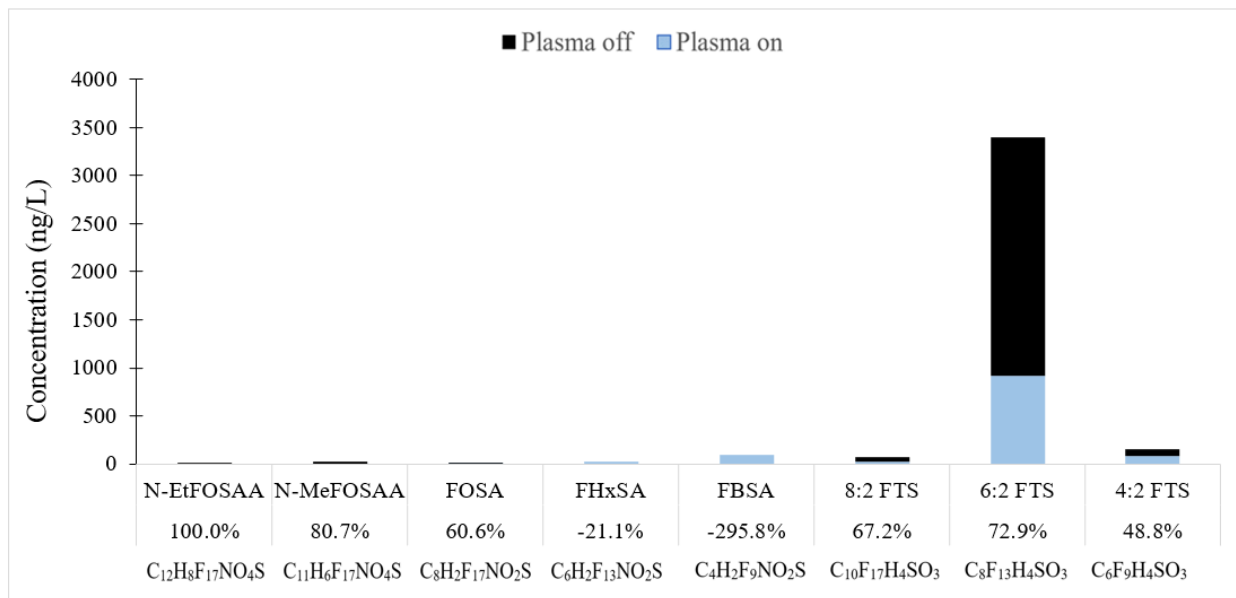
be degraded into short-chain PFCAs such as PFPeA and PFBA. Second, as mentioned earlier the removal efficiency of short-chain PFCAs is low.



**Figure 3.** Concentration of PFCAs with plasma turned off and on in the effluent of the plasma reactor. Note: the percentage refers to the removal.

### Category 3 – Other PFASs above the quantification limit (mainly PFASs precursors):

Among precursors, 8:2 FTS, N-MeFOSAA and N-EtFOSAA (fluorinated carbon chain length = 8) had high degradation rates. However short-chain precursors had lower removal percentages because of their lower surface activity. As shown in Figure 4, the fluorinated carbon chain length of fluoroalkyl sulfonamides (FASAs) had a significant effect on the degradation rate: N-EtFOSAA (C8; 100%) > N-MeFOSAA (C8; 81%) > FOSA (C8; 61%) > FHxSA (C6; -21%) > FBSA (C4; -296%).



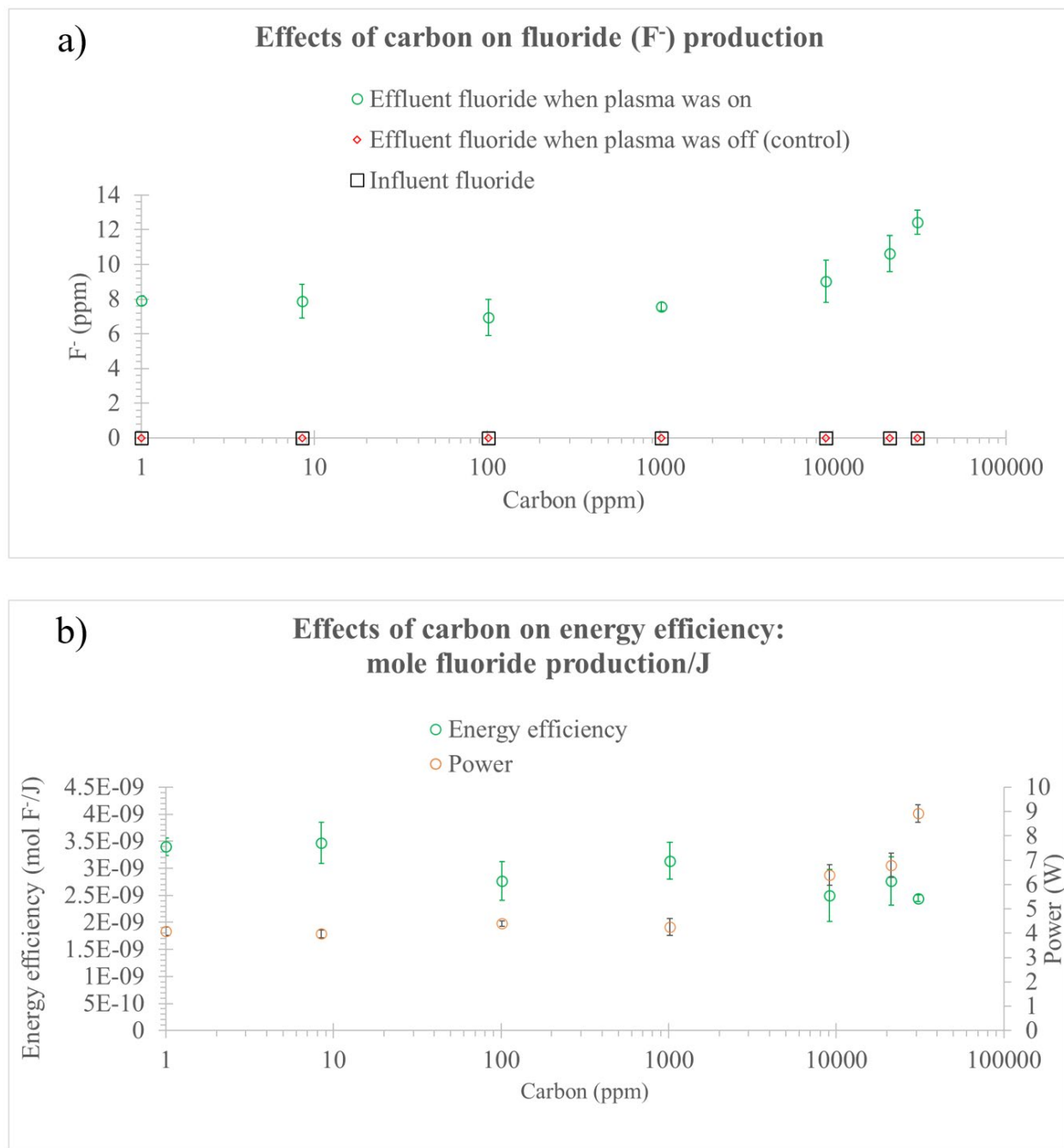
**Figure 4.** Concentration of PFAS precursors with plasma turned off and on in the effluent of the plasma reactor. Note: the percentage refers to the removal.

**Category 4 – PFASs below quantification limits:** As shown in Table 3, the concentration of ten PFASs was below the quantification limit. These PFASs belong to different groups. For example, PFTeA ( $C_{13}F_{27}COOH$ ), PFTriA ( $C_{12}F_{25}COOH$ ), PFD<sub>o</sub>A ( $C_{11}F_{23}COOH$ ) and PFUnA ( $C_{10}F_{21}COOH$ ) are members of PFCAs; PFDS ( $C_{10}F_{21}SO_3H$ ) and PFNS ( $C_9F_{19}SO_3H$ ) are members of PFSAs; and ADONA, 9Cl-PF3ONS, and 11Cl-PF3OUdS are PFAS precursors. Interestingly, all of these PFASs are long-chain PFASs.

**Task 2: evaluate the effects of leachate components (e.g., inorganic substances, complex organic substances, simple organic substances, pH, and surfactants) on the removal of one representative PFAS: PFOA.**

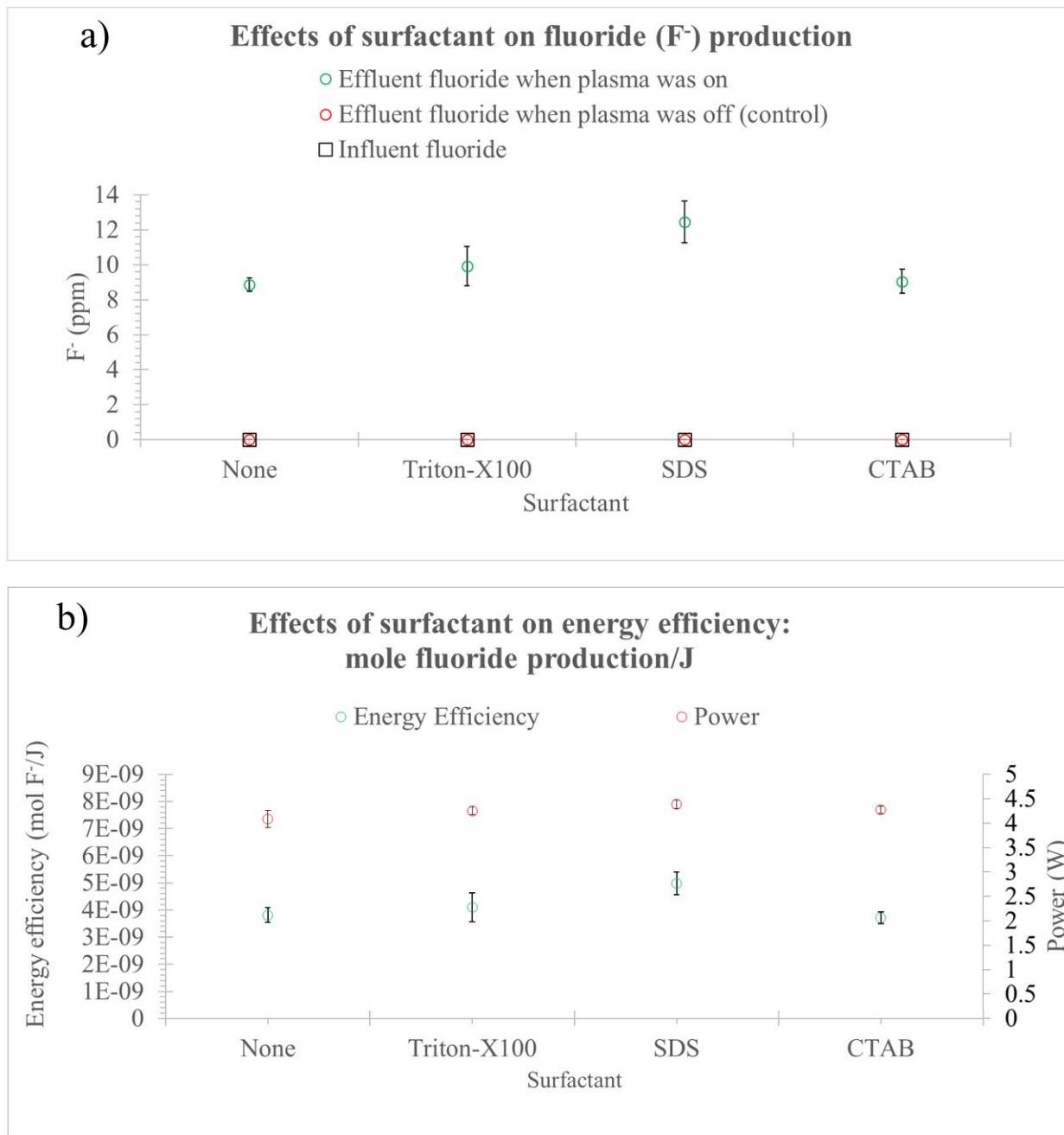
In the first quarter, we determined the effects of salinity on fluoride production when PFOA was treated by the plasma reactor. In this reporting period, we evaluated the effects of acetate, as a simple organic substance, and surfactants on fluoride production and energy efficiency. The reactor operating conditions were the same as those in Task 1. We used a high PFOA concentration of ~50 ppm so that we could measure the fluoride production in the reactor effluent.

Interestingly, a higher concentration of acetate led to increased fluoride production (Figure 5a)). However, the energy efficiency decreased when the acetate concentration increased (Figure 5b)).



**Figure 5.** The effects of organic substances, represented by acetate, on a) fluoride production and b) energy efficiency. Note: The 1 on the x-axis is actually 0 ppm of carbon. 0 ppm cannot be plotted in the logarithmic X axis.

The effects of three types of surfactants are shown in Figure 6. We used a cationic surfactant (hexadecyl trimethyl ammonium bromide [CTAB, 50 ppm]), a nonionic surfactant (octyl phenol ethoxylate [Triton-X100, 50 ppm]), and an anionic surfactant (sodium dodecyl sulfate [SDS, 50 ppm]). SDS as an anionic surfactant increased the fluoride production (Figure 6a)) and the energy efficiency (Figure 6b)), but the other two surfactants did not show any effect.



**Figure 6.** The effects of surfactants on a) fluoride production and b) energy efficiency

**Task 3: determine the degradation intermediates found in the liquid and gas phases from PFOA**

We are currently developing methods for measuring the degradation intermediates in both gas and liquid phases.

**Task 4: determine the toxicity of the degradation intermediates of PFOA by an EPA recommended method**

The degradation of PFOA may generate intermediates ranging from PFHpA (C6) to trifluoroacetic acid (TFA) (C2). We used a commercial Microtox bioassay to assess the toxicity of the degradation intermediates. In our first experiment, we tested a set of samples that included a raw leachate (S1), a treated leachate (S2), a raw leachate spiked with PFOA at 50 ppm (S3), a treated leachate that was spiked with PFOA at 50 ppm before the treatment (S4), a deionized water spiked with PFOA at 50 ppm (S5), and a treated deionized water that was spiked with PFOA at 50 ppm before the treatment (S6). After assessing toxicity by Microtox bioassay, we found that PFOA at 50 ppm (S5) did not show acute toxicity, and it was consistent with a previous study that used a similar method for measuring toxicity (Trojanowicz et al., 2019). We plan to redo the experiment with a higher PFOA concentration in the near future. The results of other samples are shown in Table 3.

**Table 3.** The acute toxicity of the landfill leachates, before and after plasma treatment

Samples	EC50 Concentration (%) 5	EC50 Concentration (%) 15
	mins	mins
Sample 1: raw leachate	19.8%	17.3%
Sample 2: treated leachate	17.6%	13.0%
Sample 3: raw leachate spiked with PFOA at 50 ppm	19.5%	16.3%
Sample 4: treated leachate spiked with PFOA at 50 ppm	13.2%	11.3%
Sample 5: deionized water spiked with PFOA at 50 ppm	Nontoxic	Nontoxic
Sample 6: treated deionized water spiked with PFOA at 50 ppm	11.9%	9.90%

\*EC50: the effective concentration of a toxic sample causing light to be reduced by 50%

The results of Table 3 show that the toxicity increased after the plasma treatment. The increased toxicity could have been caused by the oxidant and reductive species generated in the reactor such as hydrogen peroxide. They may not be caused by the PFASs intermediates. The next set of experiments will investigate the cause of the increased toxicity.

**TAG Meetings #2:**

- Date of the meeting – to be scheduled between August 10 and August 16.

**References:**

- Singh, R. K., Brown, E., Thagard, S. M., & Holsen, T. M. (2021). Treatment of PFAS-containing landfill leachate using an enhanced contact plasma reactor. *Journal of Hazardous Materials*, 408, 124452.
- Trojanowicz, M., Bartosiewicz, I., Bojanowska-Czajka, A., Kulisa, K., Szreder, T., Bobrowski, K., . . . Kisała, J. (2019). Application of ionizing radiation in decomposition of perfluorooctanoate (PFOA) in waters. *Chemical engineering journal*, 357, 698-714.

**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?

*None in this reporting period.*

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

*FDEP* helped to measure PFAS samples in this reporting period. We highly appreciate this support and collaboration.

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.*

**Pictures:**

- The plasma reactor (See Figure 1 in the report)
- Microtox bioassay that was used in the Task 4



- Treated leachate samples (plasma on) and controls (plasma off)

