FLORIDAPOLY

PFAS and Landfill Leachate: Treatment Challenges and Opportunities

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PFAS history

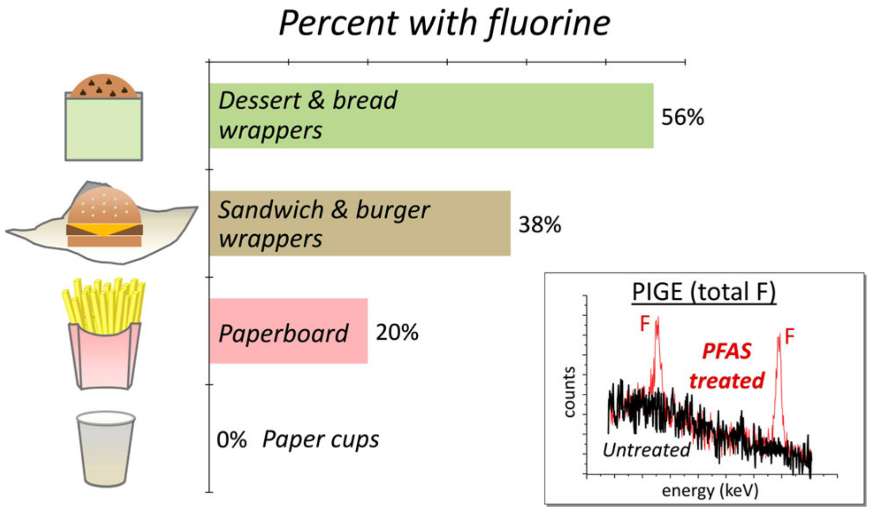
PFAS accidentally invented in 1938 by DuPont chemists as refrigerants

After World War II, marketed perfluorooctanoic acid (PFOA) as “Teflon” to make cookware and water and stain-resistant fabrics

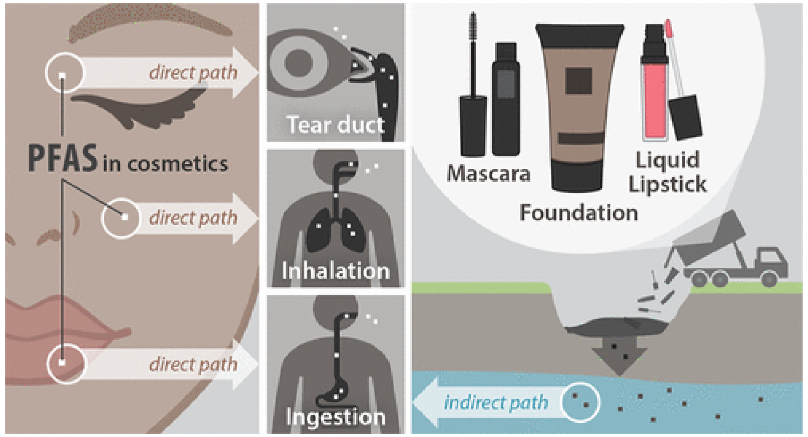
In 1952, 3M discovered perfluorooctanesulfonic acid (PFOS), marketed in 1956 as “Scotchgard”

PFAS-containing firefighting foam, or aqueous film-forming foam (AFFF) — a foam mixture developed to extinguish fire

> 3000 types of PFAS has been on the global markets

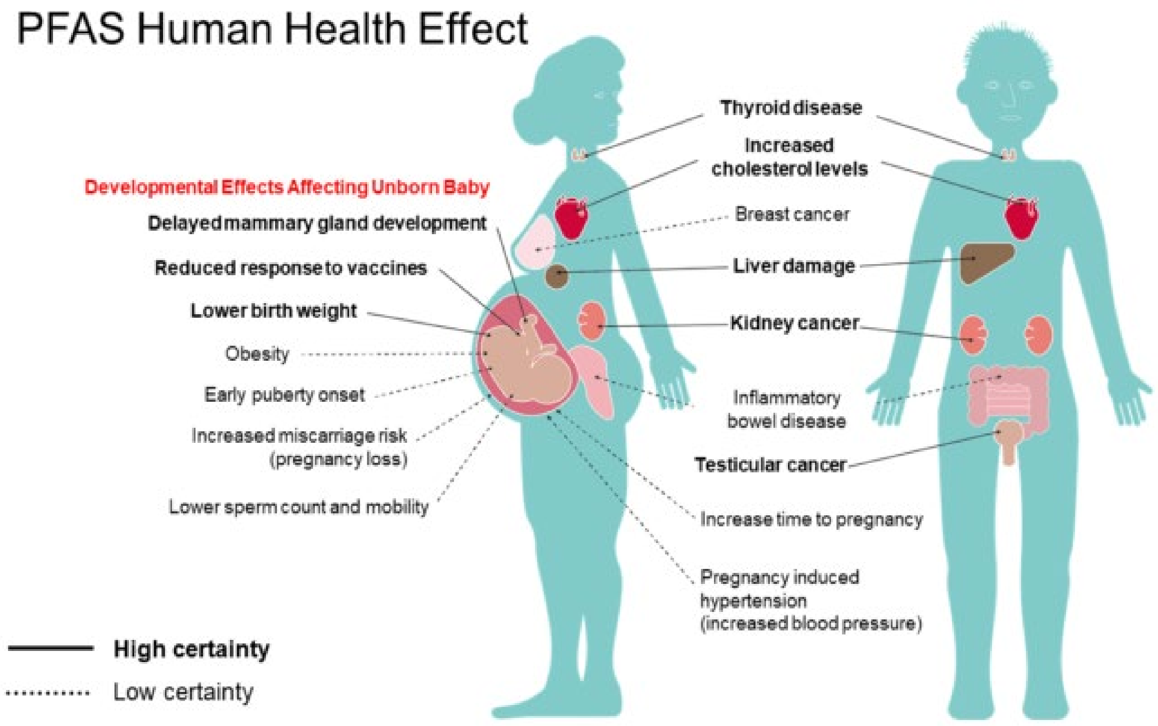


Environ. Sci. Technol. Lett. 2017, 4, 3, 105–111



Environ. Sci. Technol. Lett. 2021, 8, 7, 538–544

What are major concerns of PFAS?



- Pervasive, persistent, and bioaccumulative
- Exposed to PFAS in a variety of Ways
- Measurable level in 98% American bodies
- Associated with adverse health effects
- September 6, 2022, EPA designated PFOA and PFOS as “hazardous substances” under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), aka the Superfund.

PFAS – EPA regulation

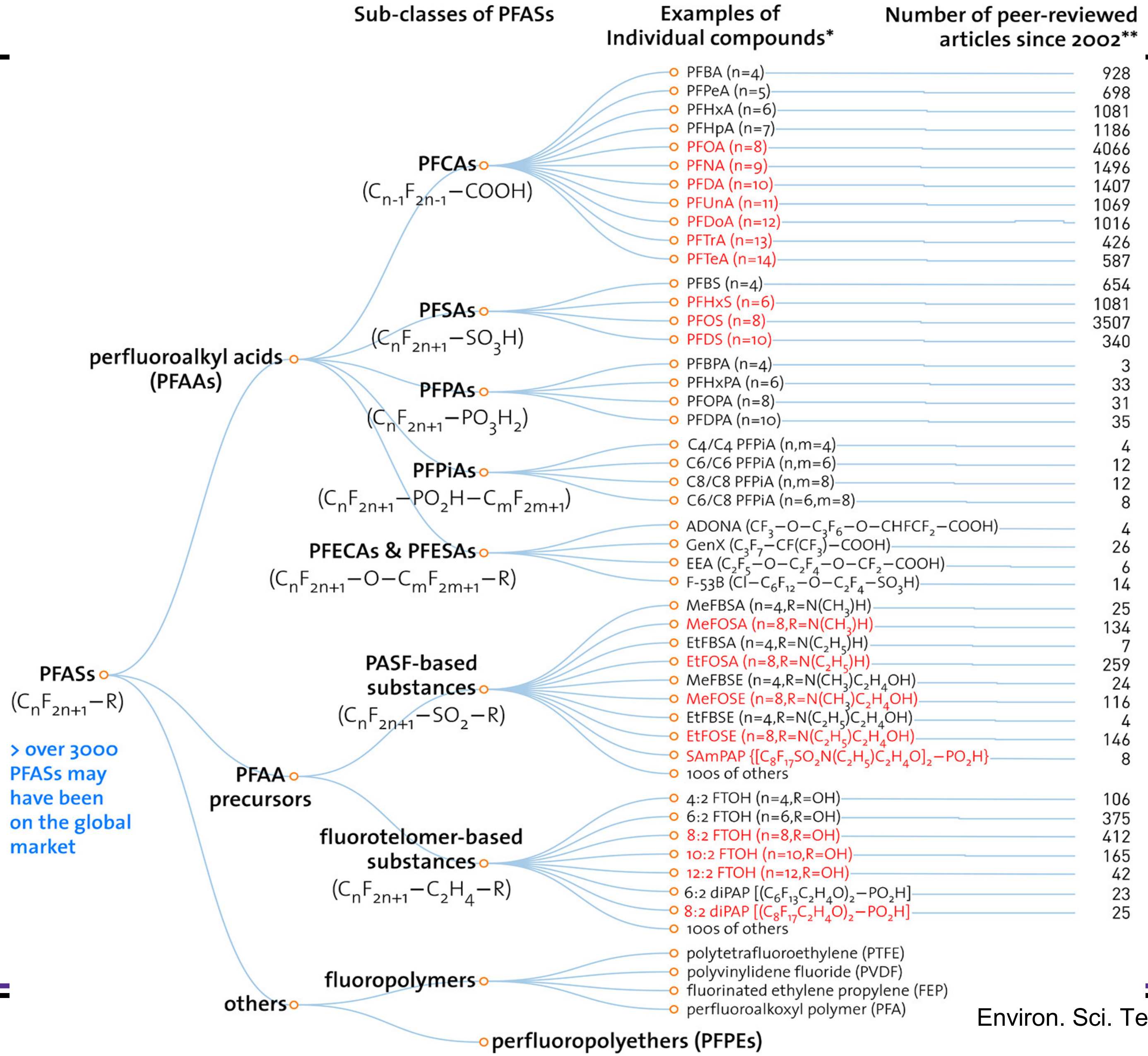
Safe Drinking Water Act (SDWA)

- **April 10, 2024**, EPA establish MCL (enforcement level) for six types of PFAS, include **PFOA and PFOS (4 ppt), and PFHxS, PFNA, HFPO-DA (GenX), PFBS (each 10 ppt)** and mixture of these PFAS (HI is 1).
- March 2021, the EPA announced regulatory determinations for **PFOA and PFOS** but no specific limits.

Toxic Substances Control Act (TSCA)

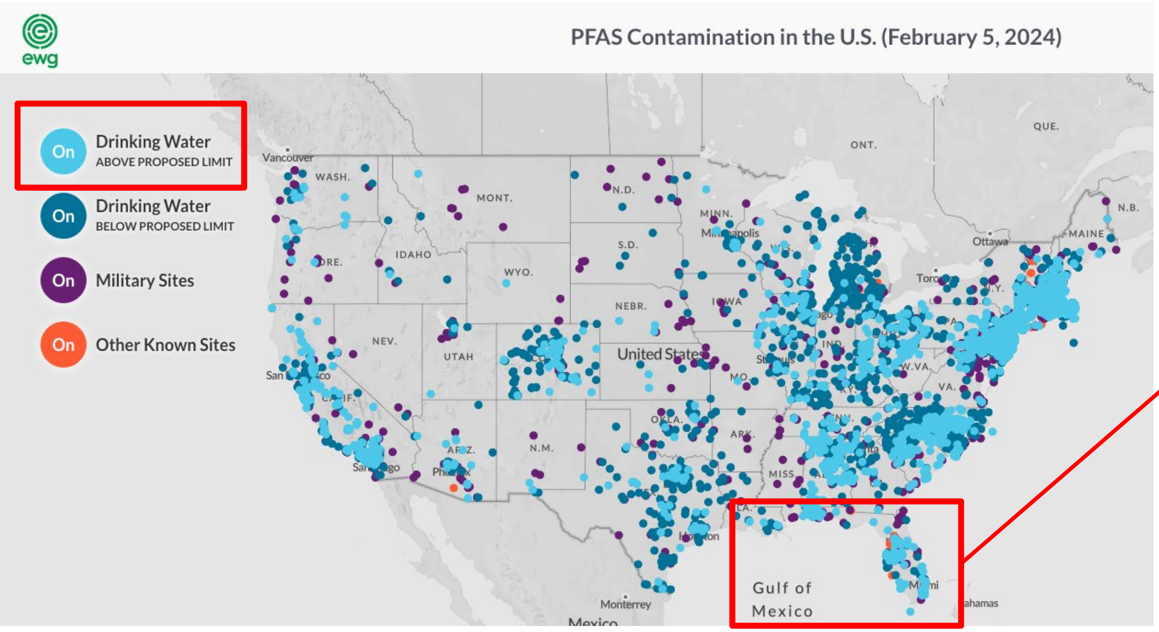
- In January 2024, the number is increased to **329**.
- EPA took regulatory actions to limit any future manufacture or importation of **271** PFSA chemicals on the U.S. market under the by 2007.

Different types of PFASs

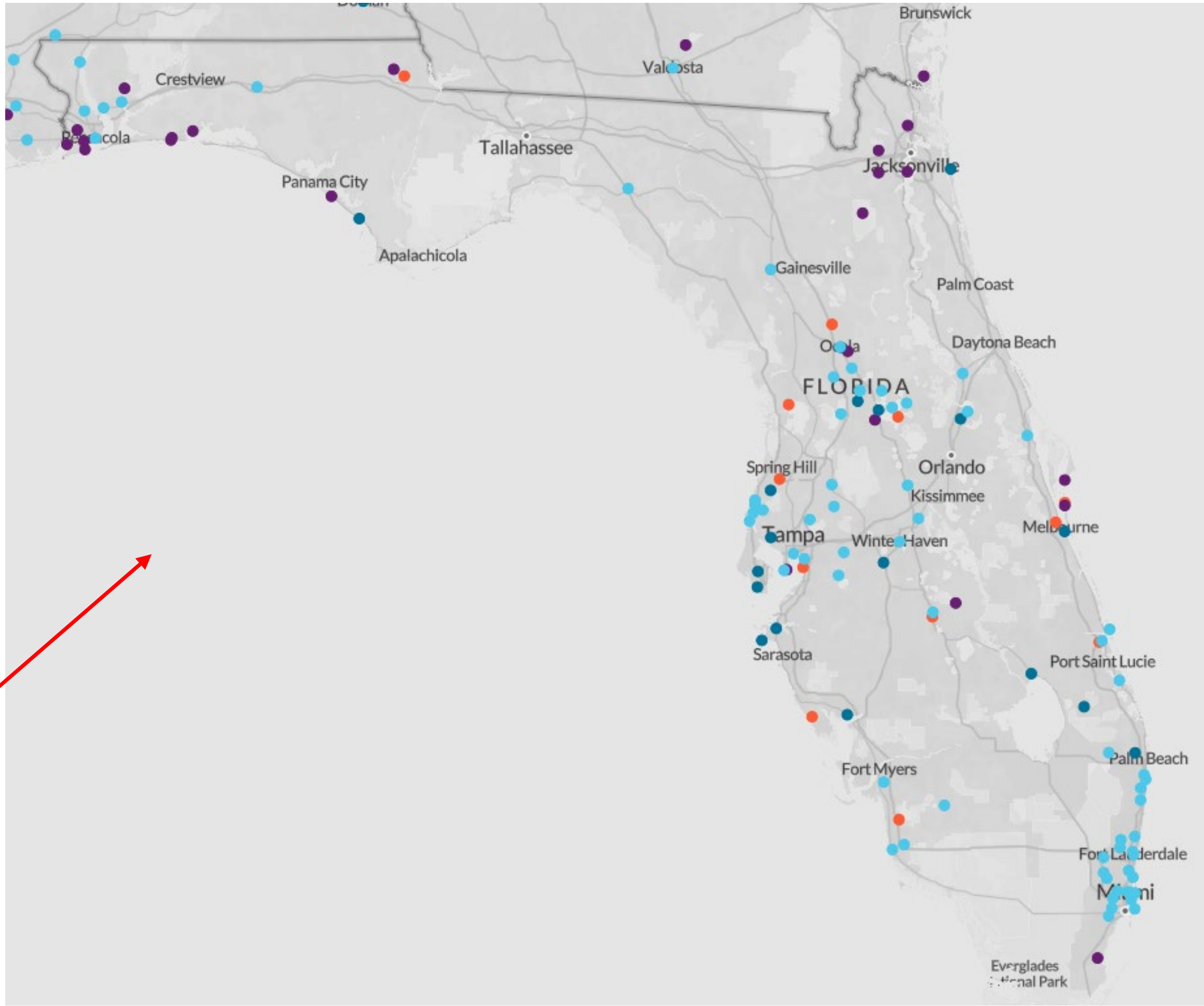


Environ. Sci. Technol. 2018, 52, 5, 3325

PFAS in drinking water

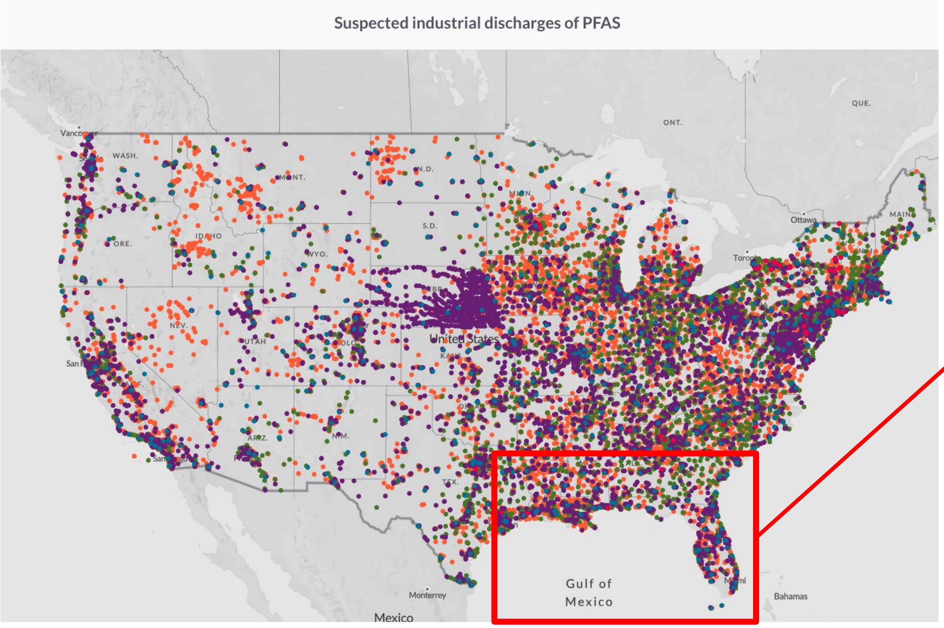


2024, Environmental Working Group.

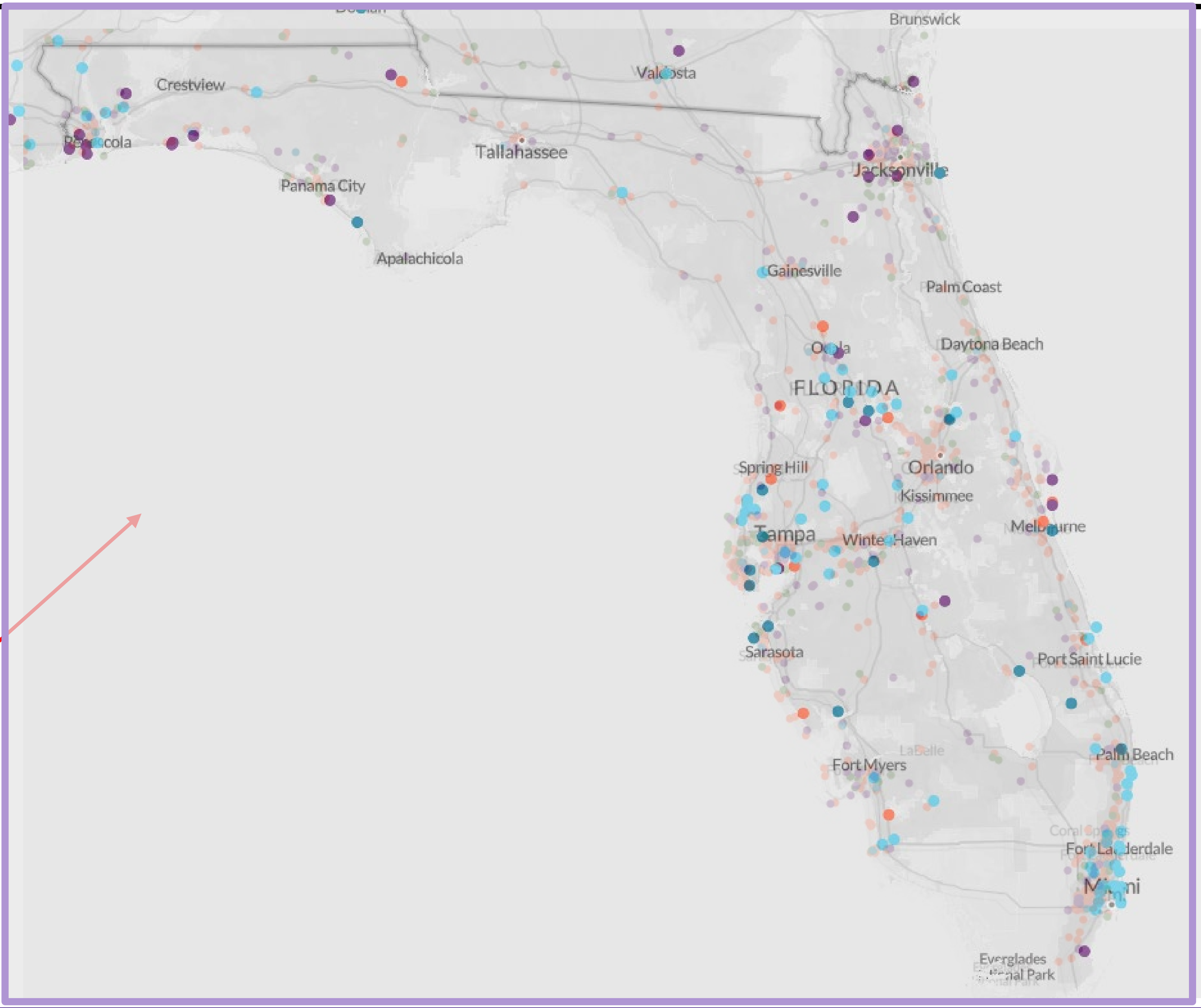


PFAS in discharge

- Known users of PFAS
- Suspected users of PFAS
- Airports previously required to use AFFF
- Landfills and waste disposal facilities
- Sewage and waste treatment plants



2024, Environmental Working Group.

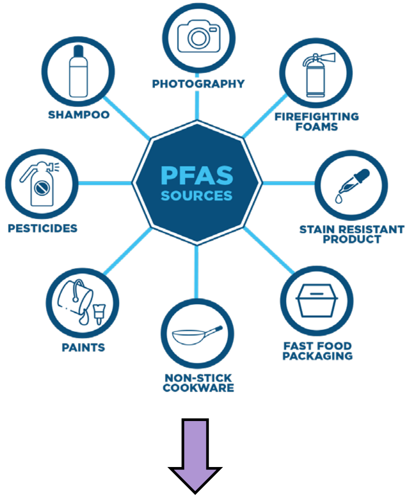


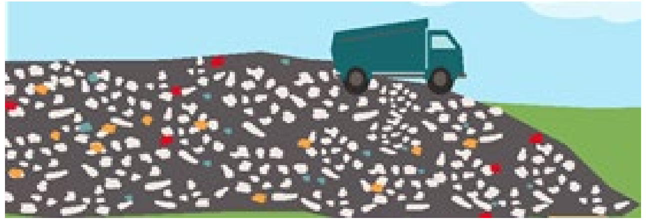
PFAS in landfill

Landfill leachate	PFOA (nmol/L)	PFOS (nmol/L)
US[1]	2.42	0.20
Florida[2,3]	3.63 (600 ng/L)	1.13 (550 ng/L)
Michigan[4]	2.87	0.57
North Carolina[5]	2.01	0.48

Total PFAS concentration in the leachate is 31000* ng/L

*averaged number from three selected Florida landfill





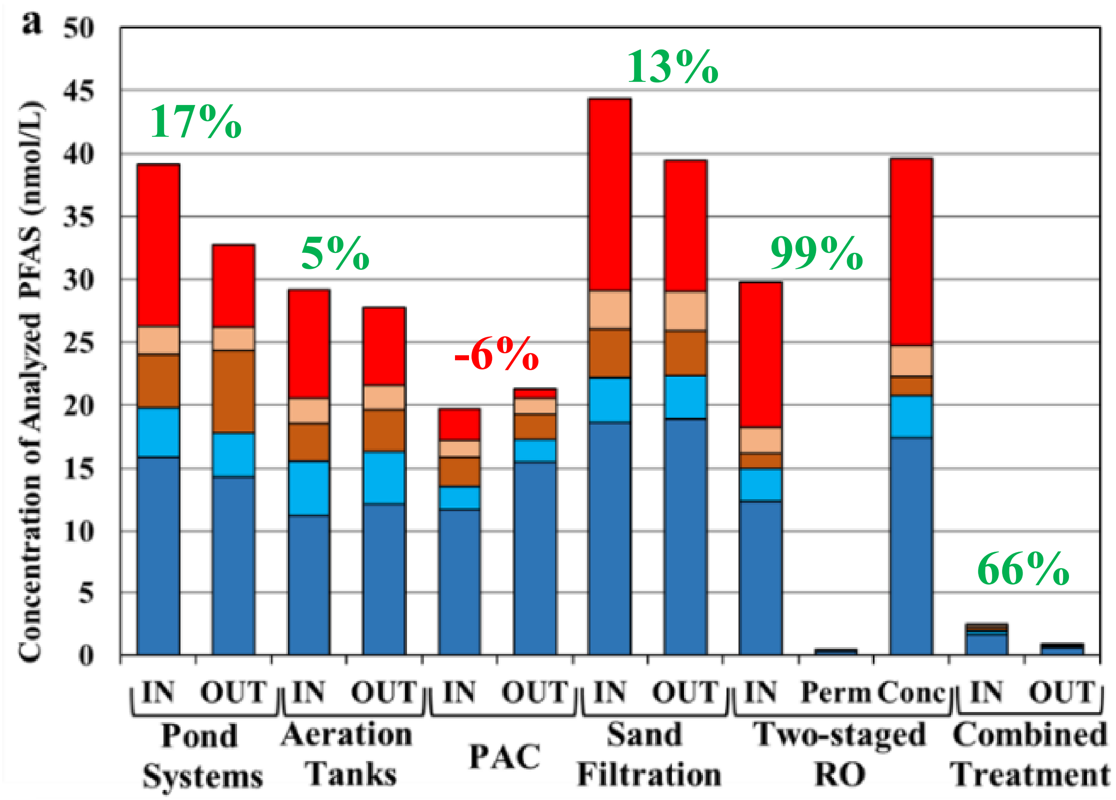
- Widely spread in **closed (31 ng/L)** and **active** landfills (**up to 12,800 ng/L**).
- Estimated mass flux of $\sum_{26}$PFAS released from landfills was **36.8 g/ha-yr**[1].
- **97%** of PFAS was found in leachate[1].
- PFAS from landfill will be leased for **over 40 years**[1].
- Highly concentrated: **more than 10 times** than the paired WWTP influent

[1]Data by March 2024

Waste Management, 2024, 175, 348-359
Environ. Sci.: Water Res. Technol., 2020,6, 1300-1311

PFAS in landfill

Current on-site treatment is ineffective



Journal of Hazardous Materials
Volume 402, 15 January 2021, 123453

Laboratory-scale and pilot-scale stabilization and solidification (S/S) remediation of soil contaminated with per- and polyfluoroalkyl substances (PFASs)

Mattias Sörengård [a], Pablo Gago-Ferrero [b], Dan B. Kleja [c d], Lutz Ahrens [a]

Feasible PFAS treatment in landfill is limited

ACS ES&T Water

Pilot-Scale Continuous Foam Fractionation for the Removal of Per- and Polyfluoroalkyl Substances (PFAS) from Landfill Leachate

Sanne J. Smith*, Karin Wiberg, Philip McCleaf, and Lutz Ahrens

Waste Management
Volume 161, 15 April 2023, Pages 187-192

Behavior of Per- and polyfluoroalkyl substances (PFAS) in Pilot-Scale vertical flow constructed wetlands treating landfill leachate

Dreyton J. Lott [a], Nicole M. Robey [a], Rachel Fonseca [a], John A. Bowden [a b], Timothy G. Townsend [a]

Show more

PFAS – Hinkley center efforts

FLORIDAPOLY

Occurrence and quantification

Investigation efforts*

PFAS in **Biosolids** (2022), **E-Waste** (2022)
PFAS **Releases** from Landfills in Florida (2019)
Preliminary Evaluation of **Leachate Treatment Processes** (**2017**)

Fate and transport

Impact of the **Perfluoroalkyl Chain Length** (2023)
Bench-Scale Municipal Solid Waste Landfills (2023)
During **Leachate Evaporation** (2022), **Gas Emissions** (2021)

Remediation

via **Solar Photocatalysis** (2019, 2022), **Advanced Oxidation/Reduction** (2019)
Aqueous PFAS Destruction or Solid Thermal **Incineration** (2020)
Non-Thermal Plasma Degradation (2020)

Management

PFAS Remediation **Residuals** (2020)

*Simplified title with highlights

*Estimated by published data

PFAS – What are current issues

Feasible and effective PFAS treatment in landfill?

- Cost-effective?
- Large volume?
- PFAS precursor?
- Remediation residual?
- Complicated water matrix?
- Short-chain PFAS?

Remediation

via **Solar Photocatalysis** (2019, 2022), **Advanced Oxidation/Reduction** (2019)
Aqueous PFAS Destruction or Solid Thermal **Incineration** (2020)
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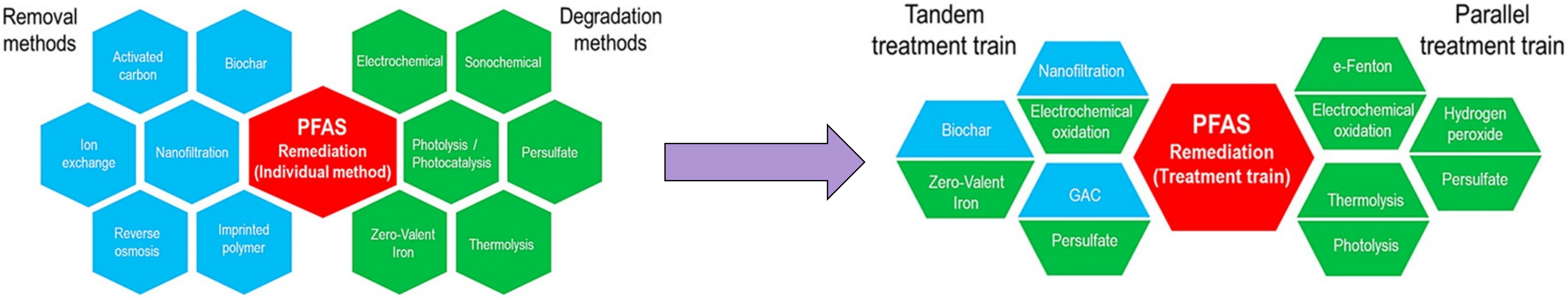
Management

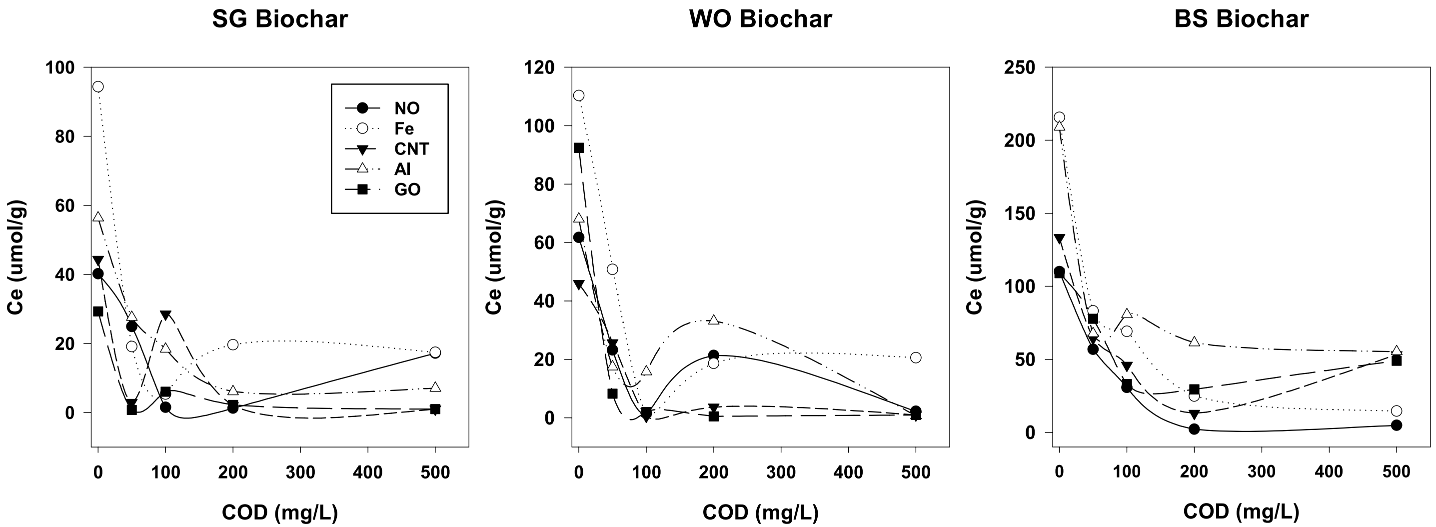
PFAS Remediation **Residuals** (2020)

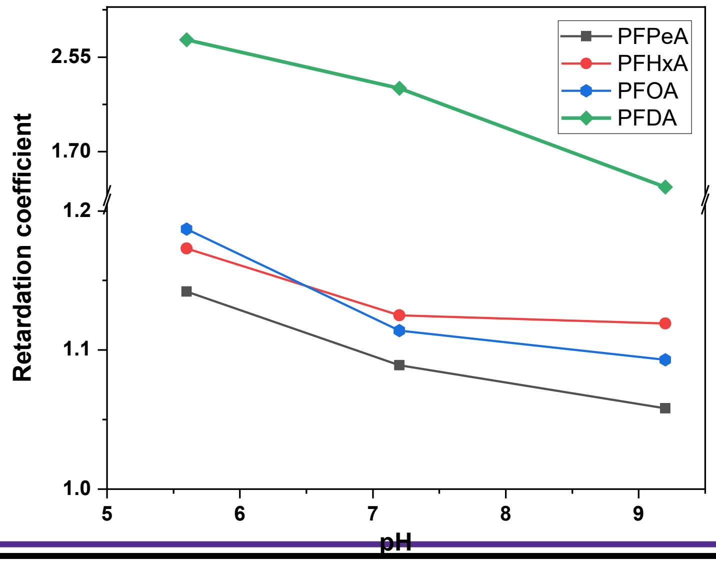
PFAS – Management with Treatment Train

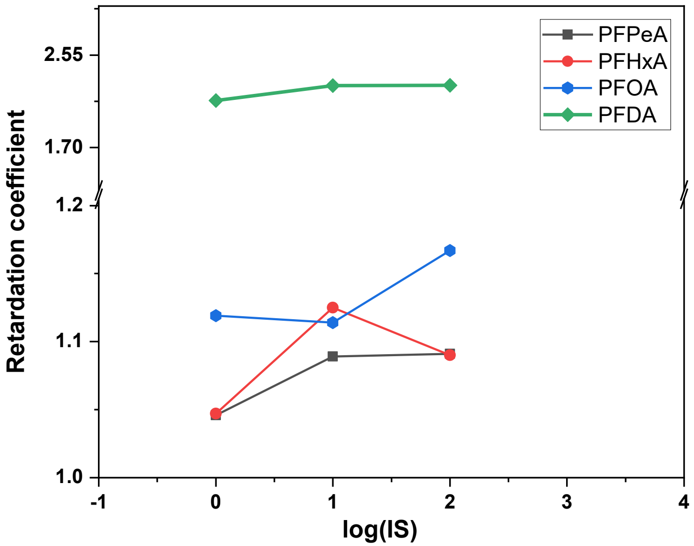


Journal of Hazardous Materials, 2020, 386, 121963

PFAS – What we found is current issues





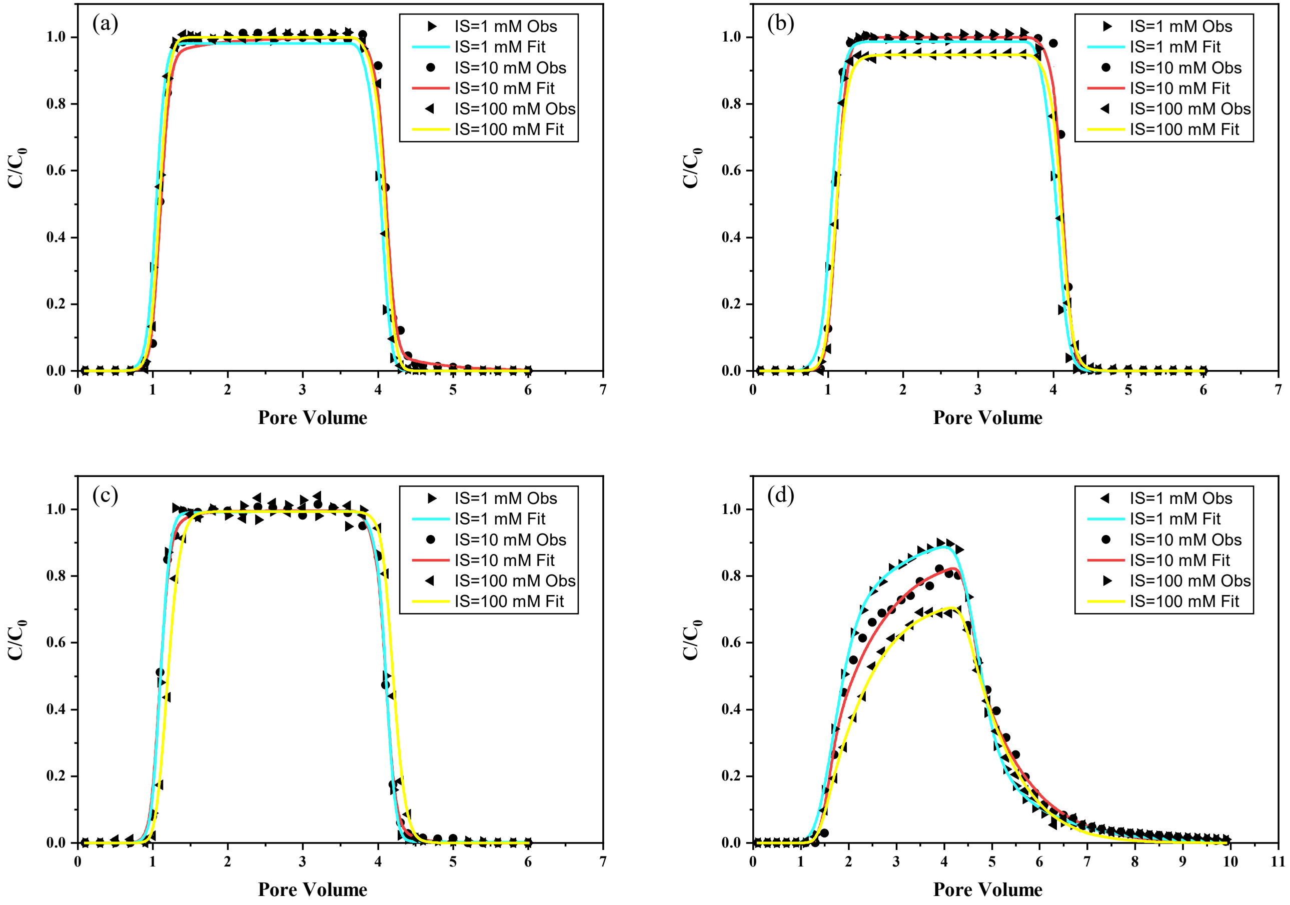


PFAS – What we found is current issues

Observed (dots) and Fitted (lines) Breakthrough Curves of PFPeA, PFHxA, PFOA, and PFDA

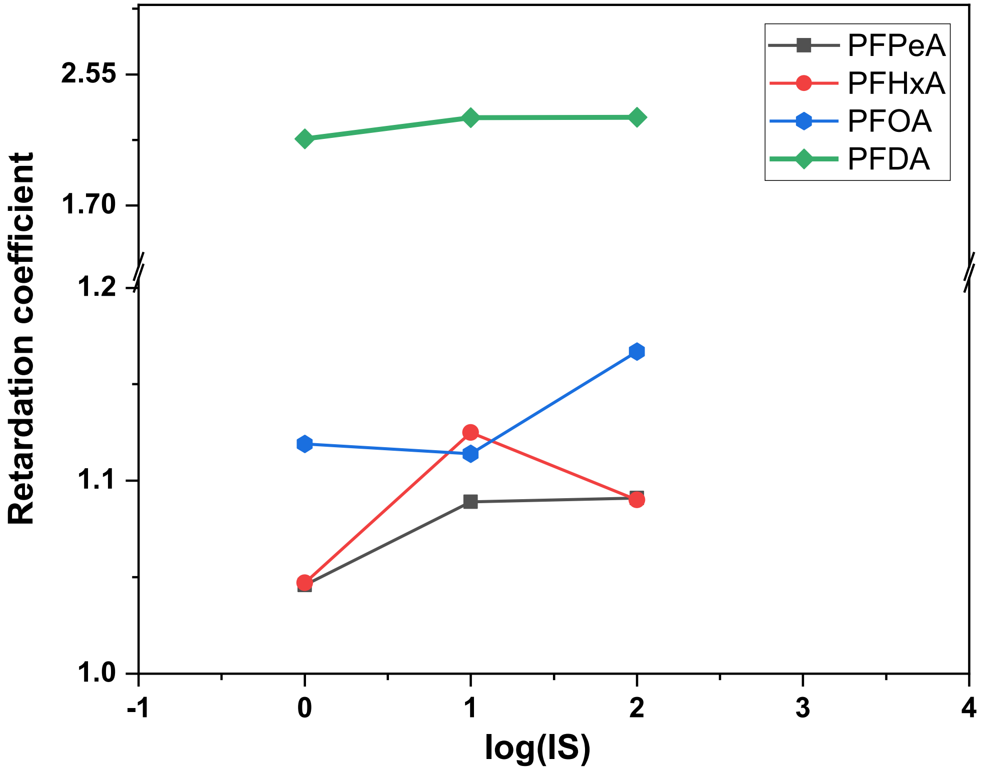
PFPeA

PFHxA

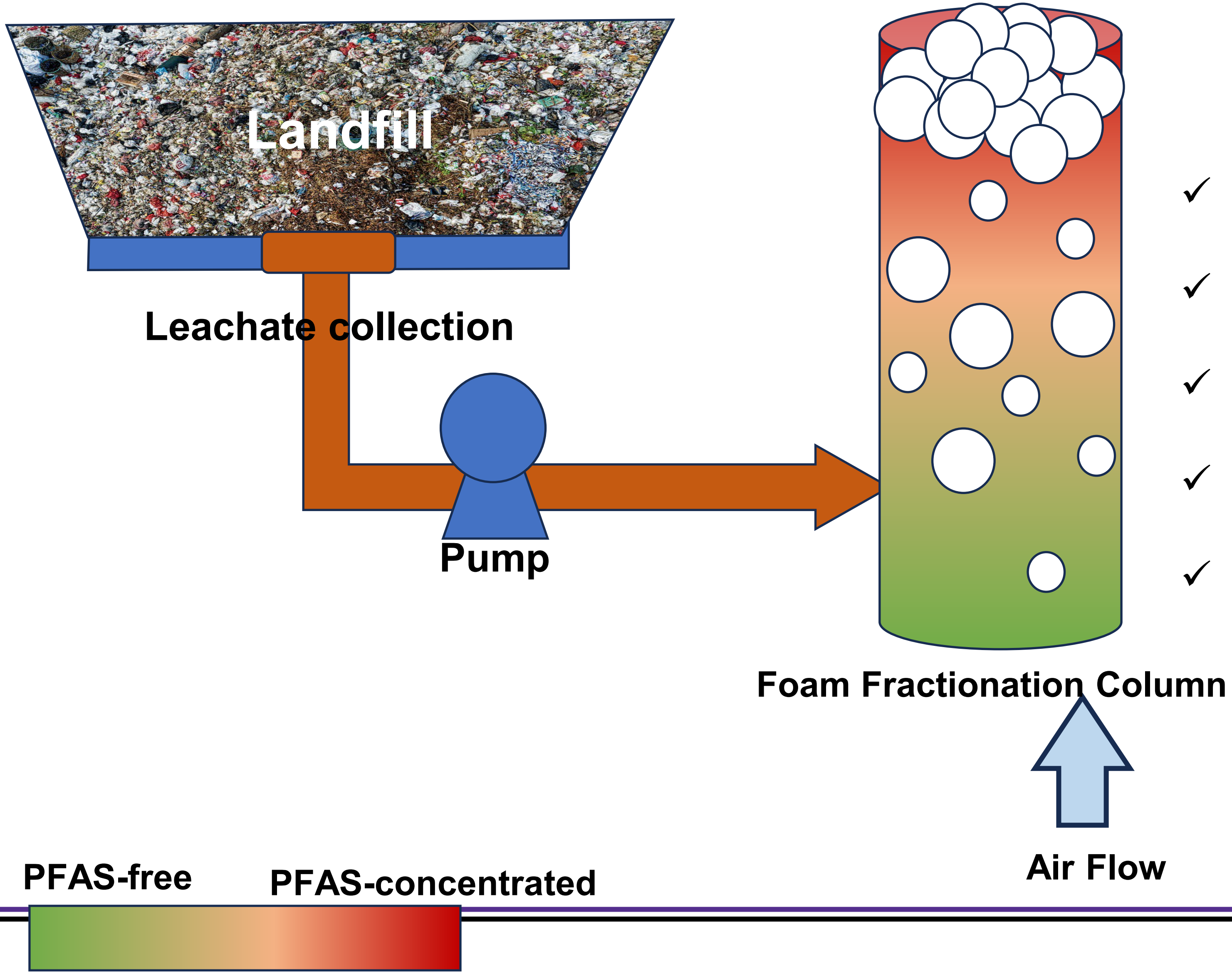


PFOA

PFDA

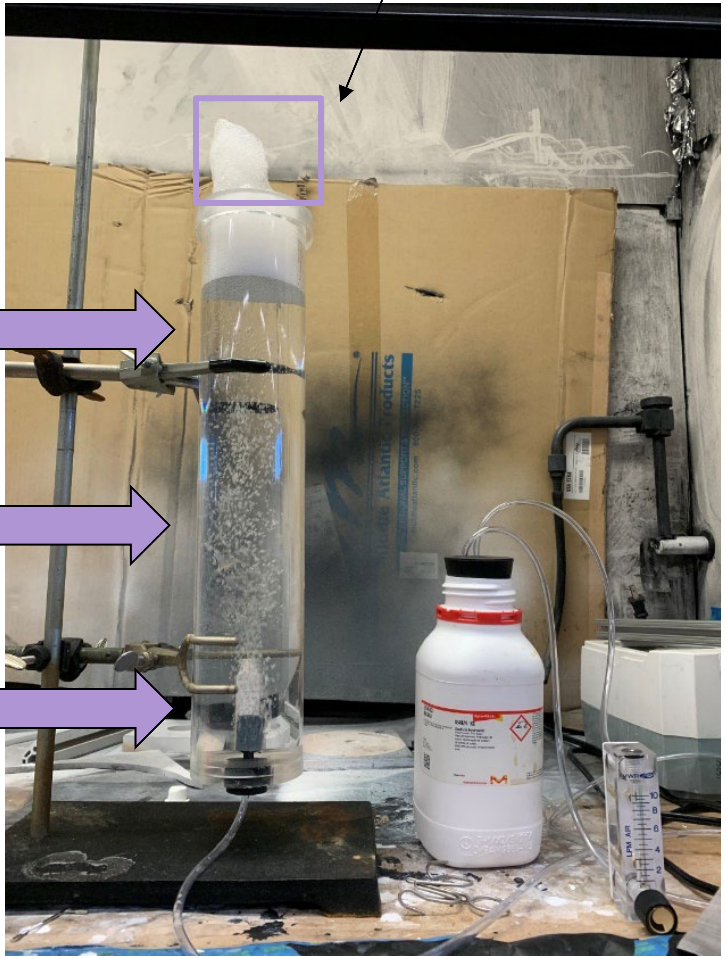


PFAS – What could be the solution



- ✓ Utilize built-in technology
- ✓ Based on the surfactant characteristic of PFAS
- ✓ Green technology
- ✓ Concentrating PFAS stream
- ✓ Eliminating competition of dissolved organic matter

PFAS – What could be the solution



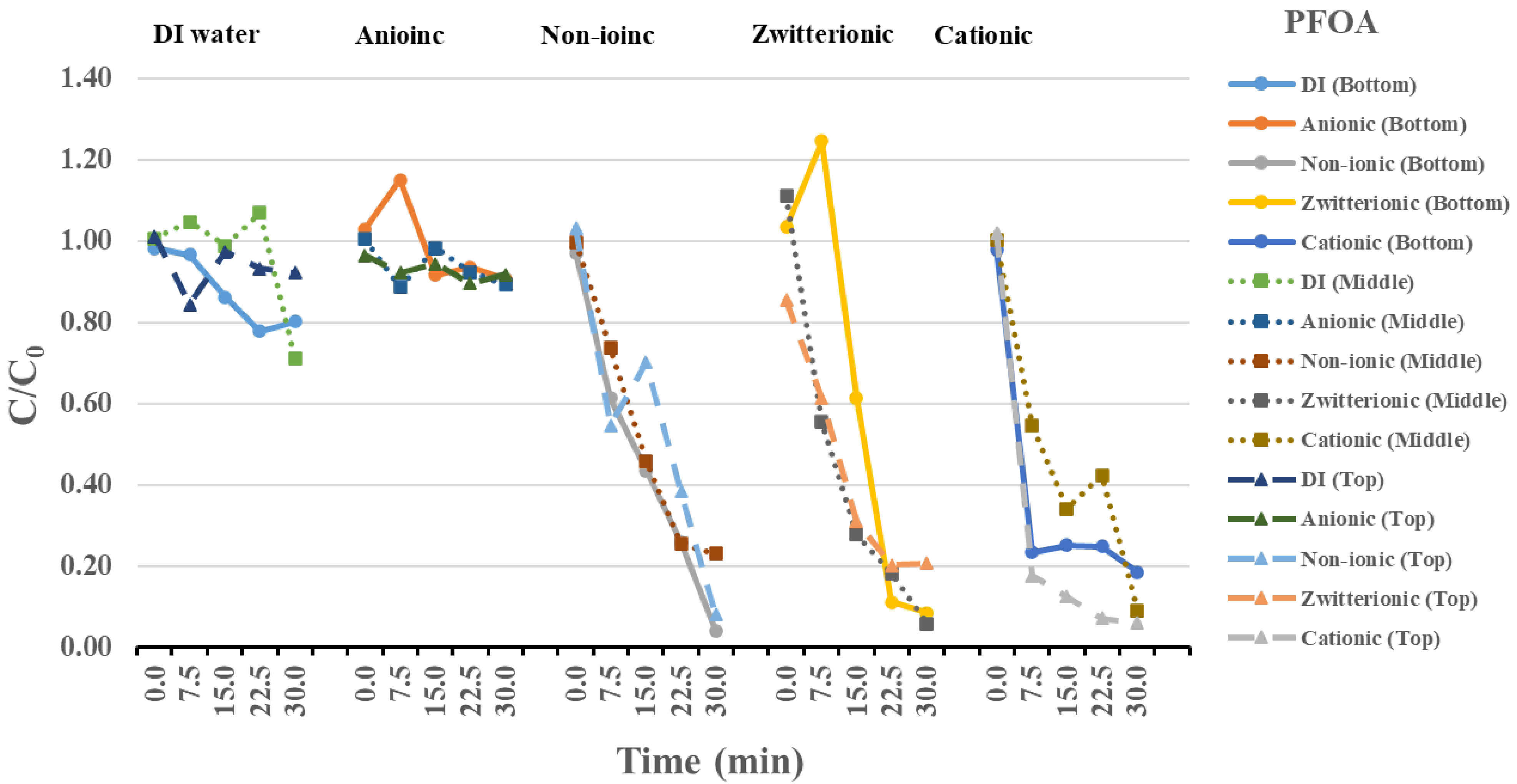
$$Normalized\ concentration = \frac{C_t}{C_0}$$

- Column dimension: 7.0-cm ID × 40.0-cm length
- PFAS: **Mixture** of six types of PFAS, 100 ppb/PFAS type
- Co-surfactant: four types, 20 mg/L
- Air purging rate: 0.5 L/minute
- Sampling location: top, middle and bottom part
- Sampling time: 0, 7.5, 15, 22.5, and 30 minutes
- All samples are in liquid

This part of experiment is credited to Lin Qi, Ph.D. Candidate

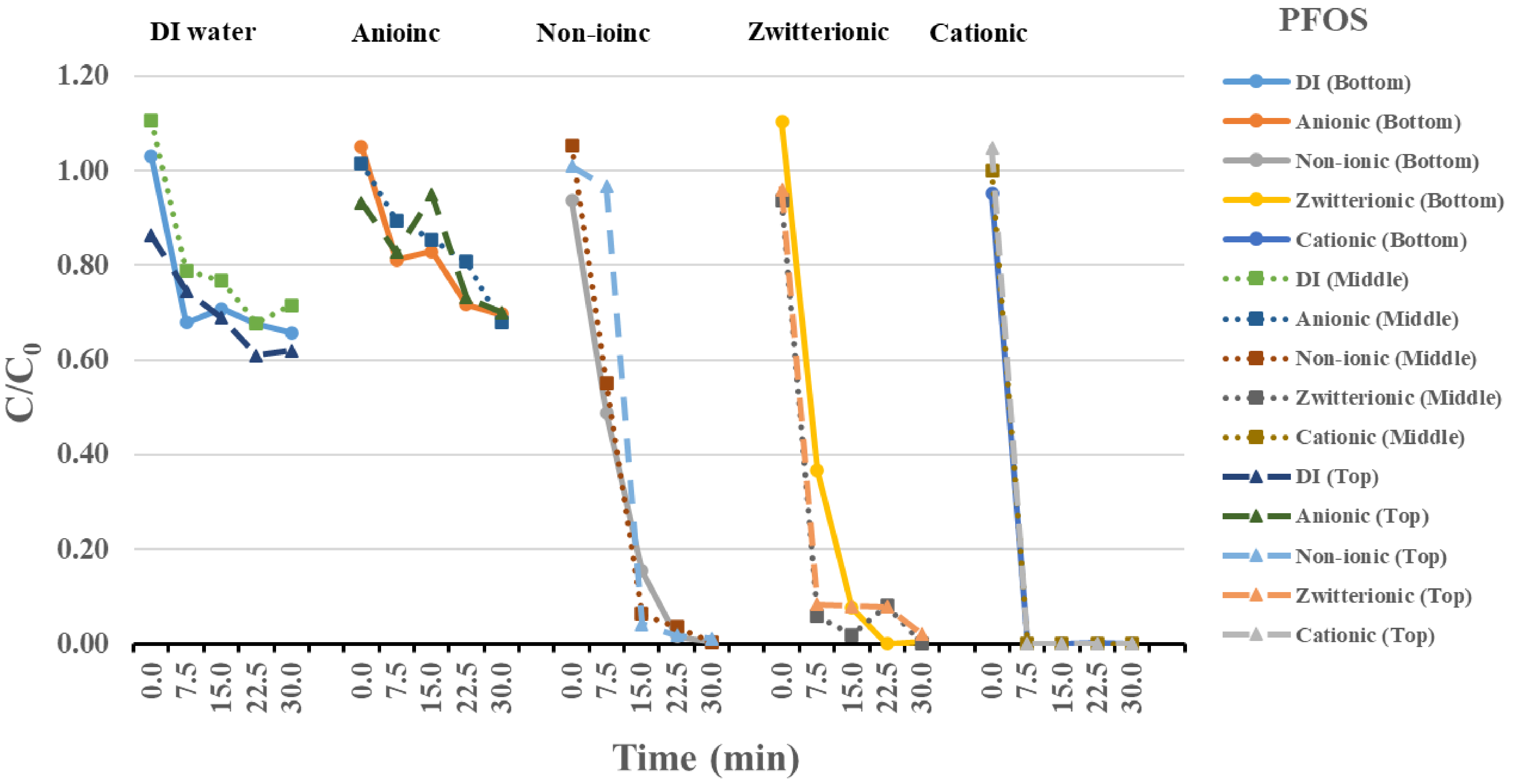
Foam fractionation results (selected): PFOA

PFOA	C8 HF15O2	PFCA



Foam fractionation results (selected): PFOS

PFOS	C8 HF17O3S	PFSA



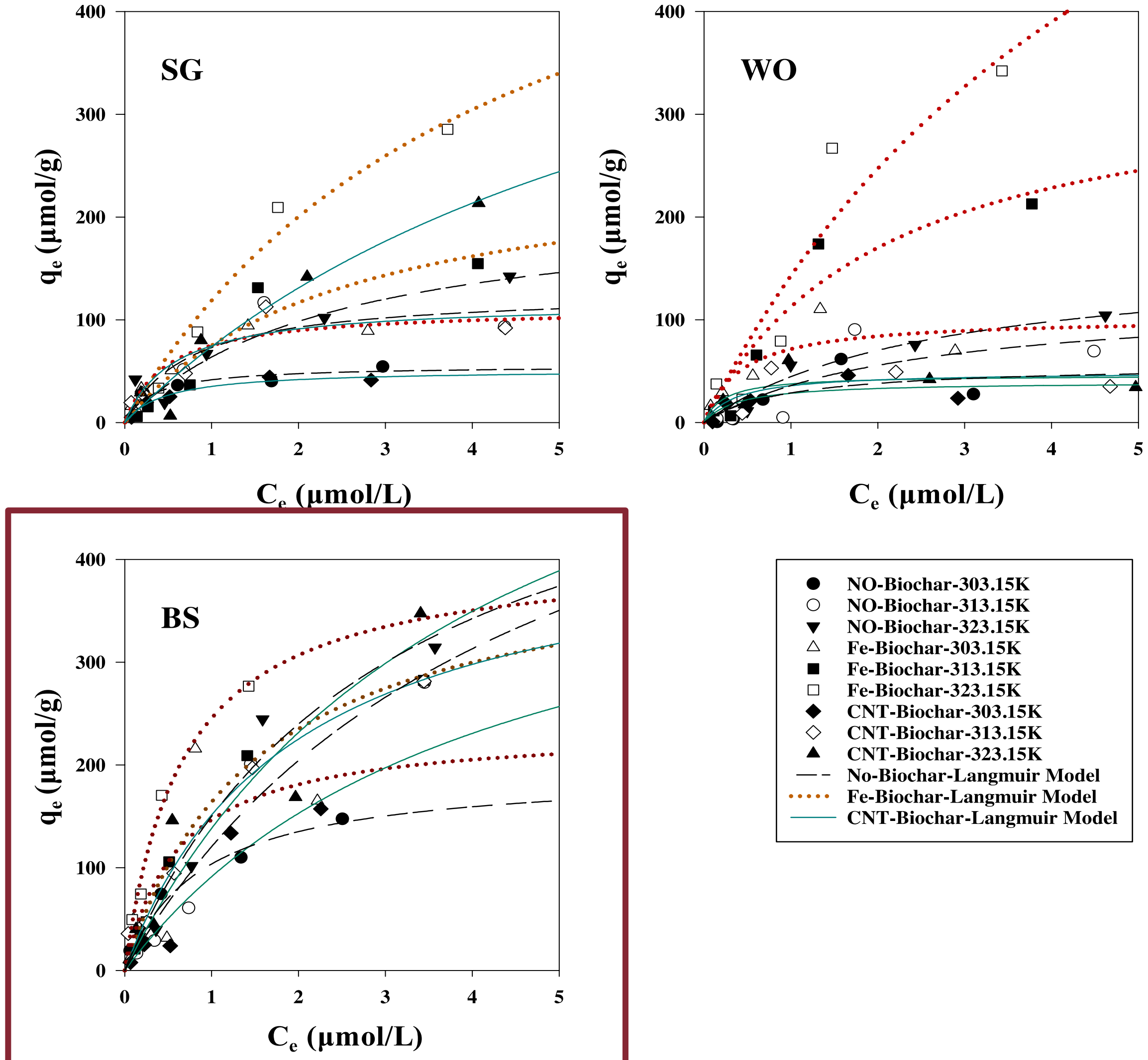
Biosolid biochar-PFAS adsorption

- Sewage sludge
- Three types of biosolid: **class A, AA and B**
- **Two-third** of biosolid produced in Florida are treated to Class B
- Class B biosolid has limited land application and other beneficial usages

Common practices of biosolid disposal

- **Land application**
- **Surface disposal**
- **Incineration**

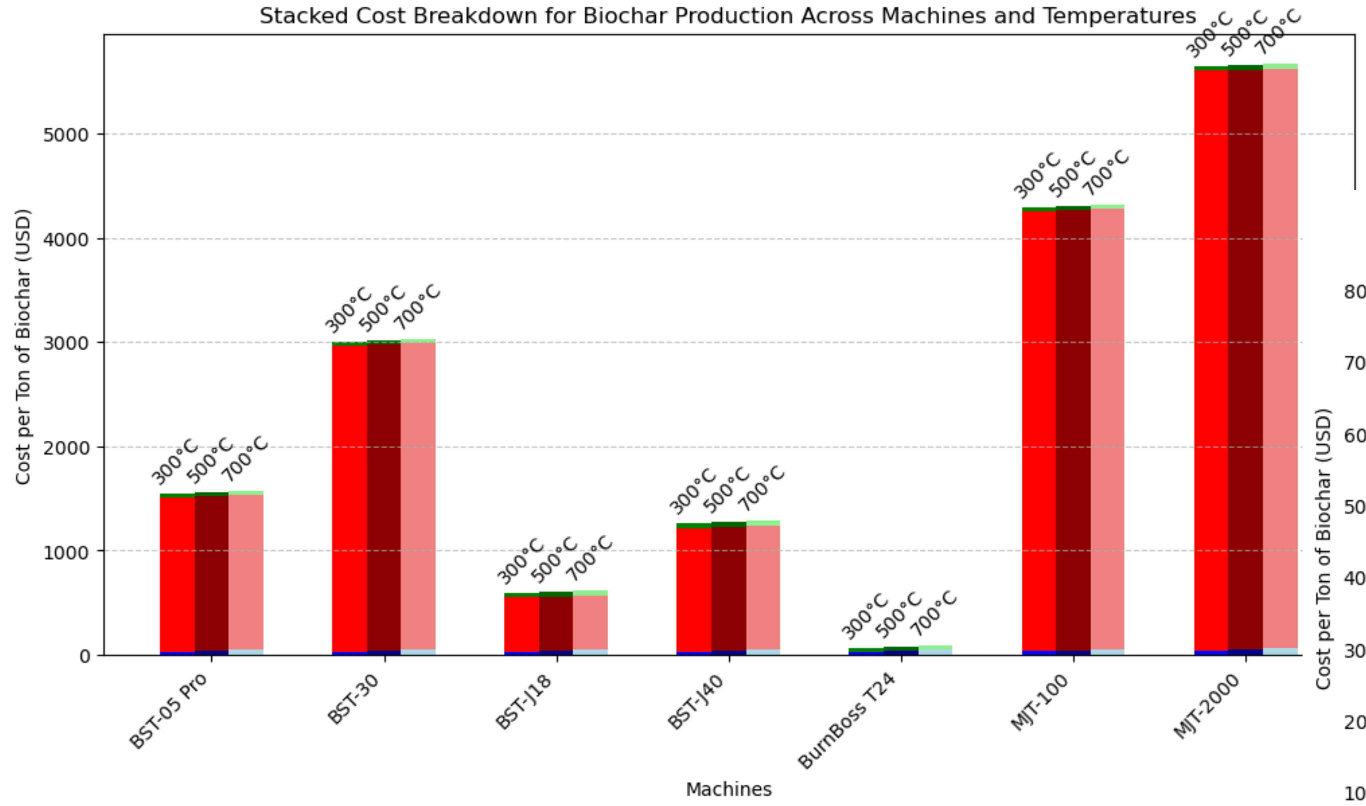
Biosolid biochar-PFAS adsorption

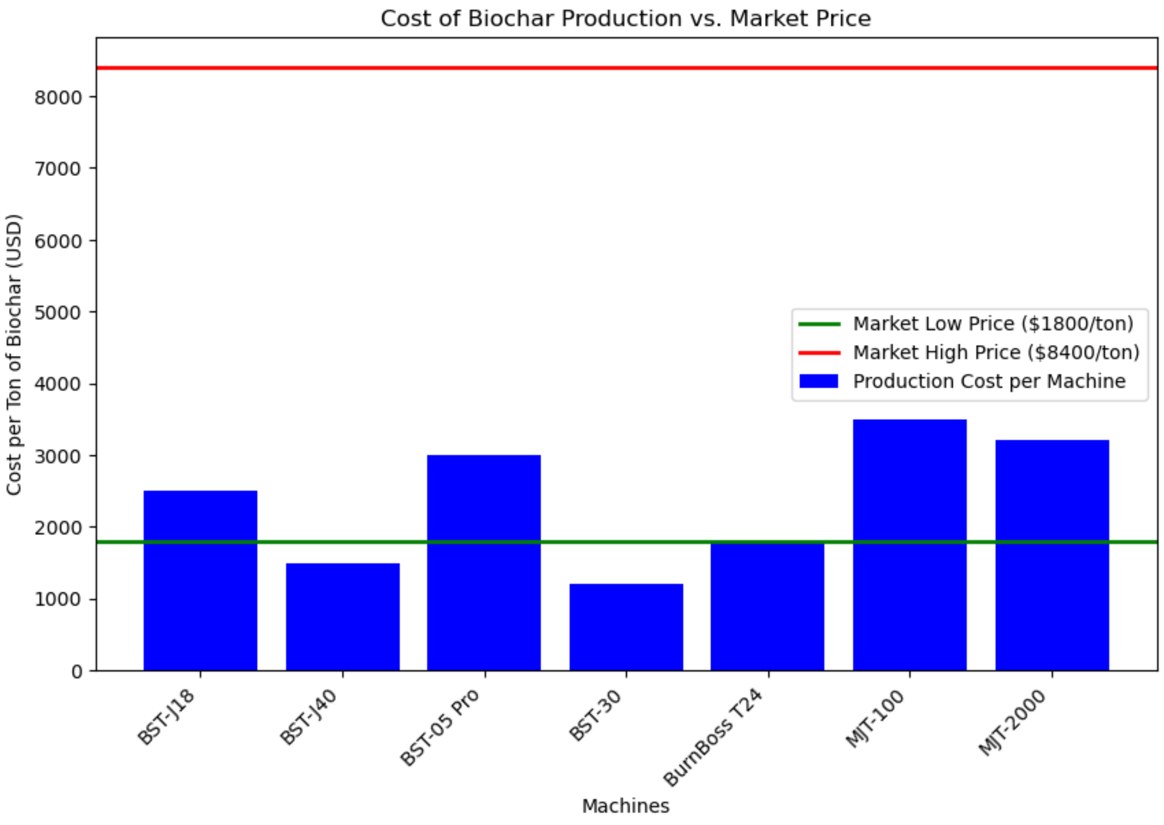


Biochar	Isotherm parameter		
	Q_m (µmol/g)	K (L/µmol)	R^2
SG-No	55.47	3.05	0.87
SG-Fe	111.64	2.05	0.95
SG-CNT	51.58	2.15	0.96
WO-No	56.43	1.05	0.53
WO-Fe	101.98	2.35	0.71
WO-CNT	39.54	2.57	0.96
BS-No	194.00	1.15	0.97
BS-Fe	469.65	1.63	0.61
BS-CNT	236.40	0.24	0.92

Sorbent Type	Maximum Adsorption Capacity (q_e)	Reference
Powered Activated Carbon	39.85 µmol/g	Qu et al. (2009)
Powered Activated Carbon	390 µmol/g	Yu et al. (2008)
Granular Activated Carbon	670 µmol/g	Qu et al. (2009)
Anion-Exchange Resin	2920 µmol/g	Qu et al. (2009)

Cost breakdown vs market price



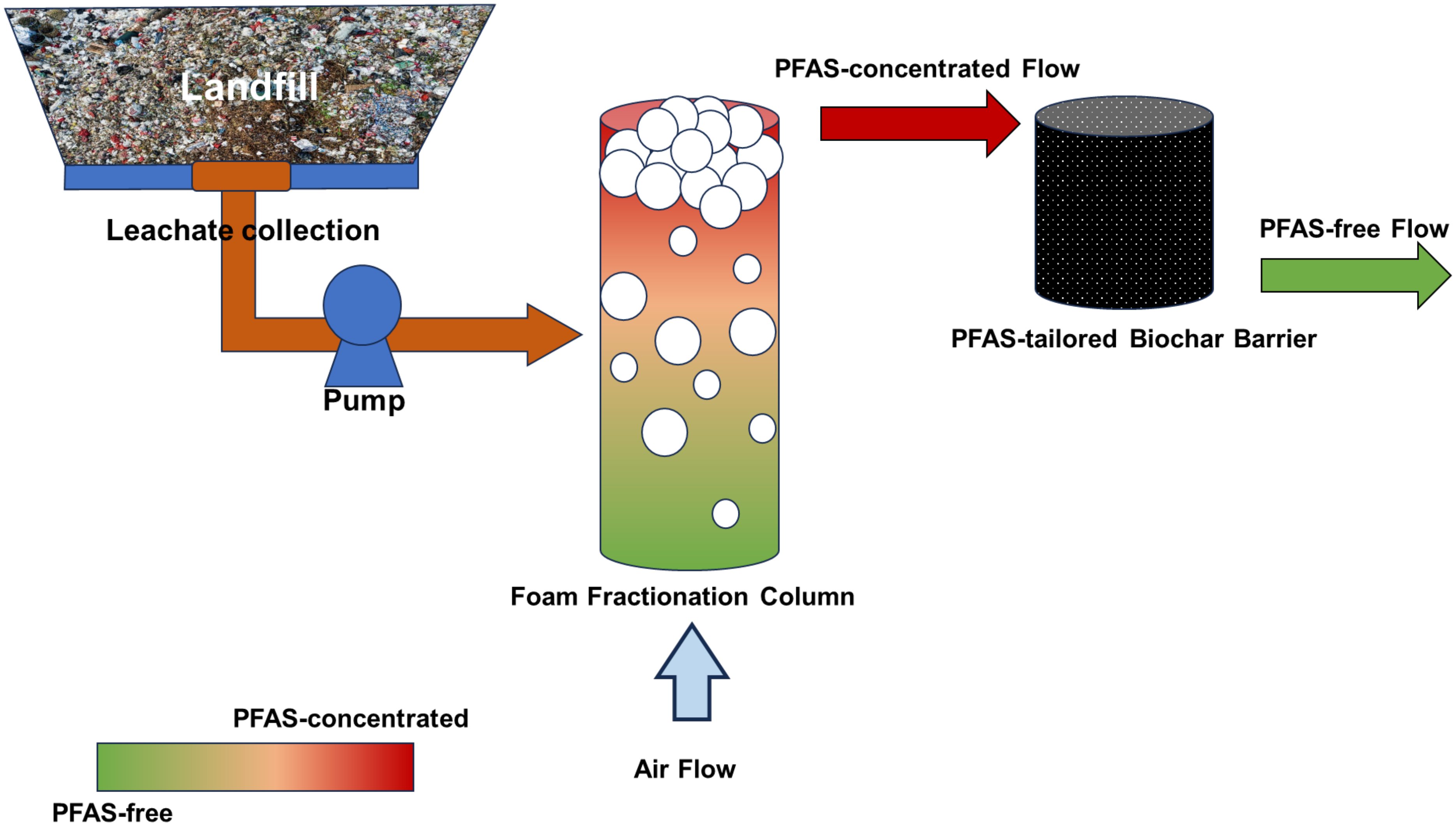


$$\text{Total cost} = \frac{P_{T=60^\circ C}\times\Delta t_{\text{dry}} + \sum P_{T=i}\Delta t_{\text{ramp}} + P_{T=\text{desired}}\times\Delta t_{\text{pyr}}}{M_{\text{biochar}}} + \frac{C_{\text{feedstock}}}{Y_{\text{biochar}}\theta_{\text{feedstock}}}$$

Moving forward: Feedstock contamination: PFAS ?

PFAS Type	Concentration (ng/g)	Method
Biosolid		
Perfluoropentanoic acid (PFPeA)	0.71	1633
Perfluorooctanoic acid (PFOA)	2.7	1633
Perfluorodecanoic acid (PFDA)	6.5	1633
Perfluorooctanesulfonic acid (PFOS)	15	1633
N-Methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	4.0	1633
3-Perfluoropentylpropanoic acid (5:3 FTCA)	95	1633
3-Perfluoroheptylpropanoic acid (7:3 FTCA)	42	1633
Extractable Organic Fluorine (EOF)	**ND**	**ELLE SOP**
Biosolid Compost		
Perfluorobutanoic acid (PFBA)	0.71	1633
Perfluorohexanoic acid (PFHxA)	5.7	1633
Perfluoroheptanoic acid (PFHpA)	0.35	1633
Perfluorononanoic acid (PFNA)	0.39	1633
Perfluorobutanesulfonic acid (PFBS)	0.54	1633
Extractable Organic Fluorine (EOF)	**480**	**ELLE SOP**

Moving forward: “Complete the puzzle”

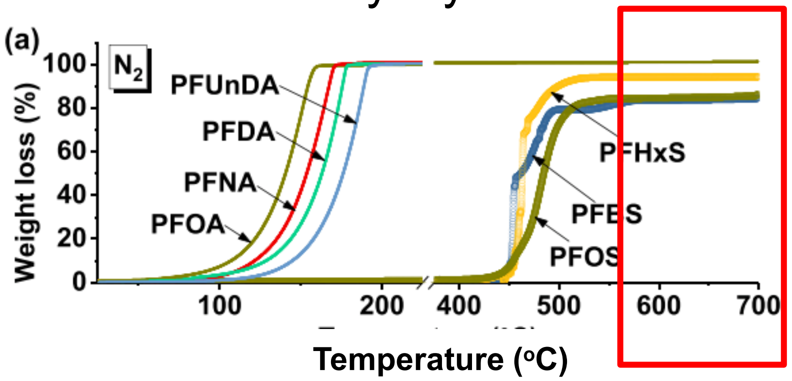


Moving forward: Zero waste of PFAS destruction

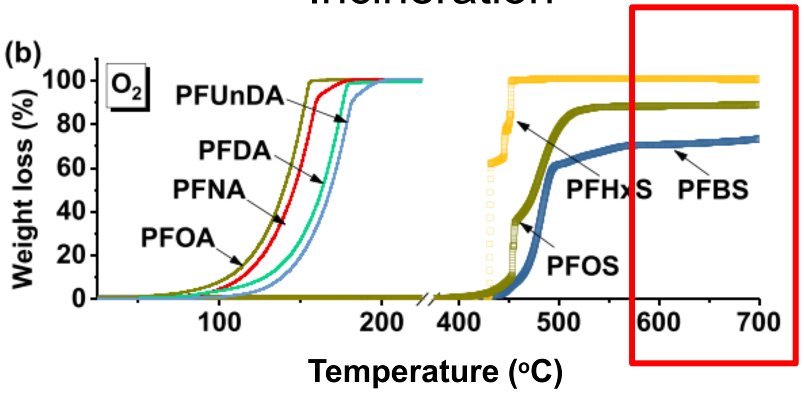
✗ Recycling PFAS-saturated adsorbent back to landfill cannot solve problem

☑ Destructing PFAS-saturated adsorbent and possibly regenerate adsorbent

Pyrolysis



Incineration



TGA analysis of PFAS destruction on Spent Granular Activated Carbon

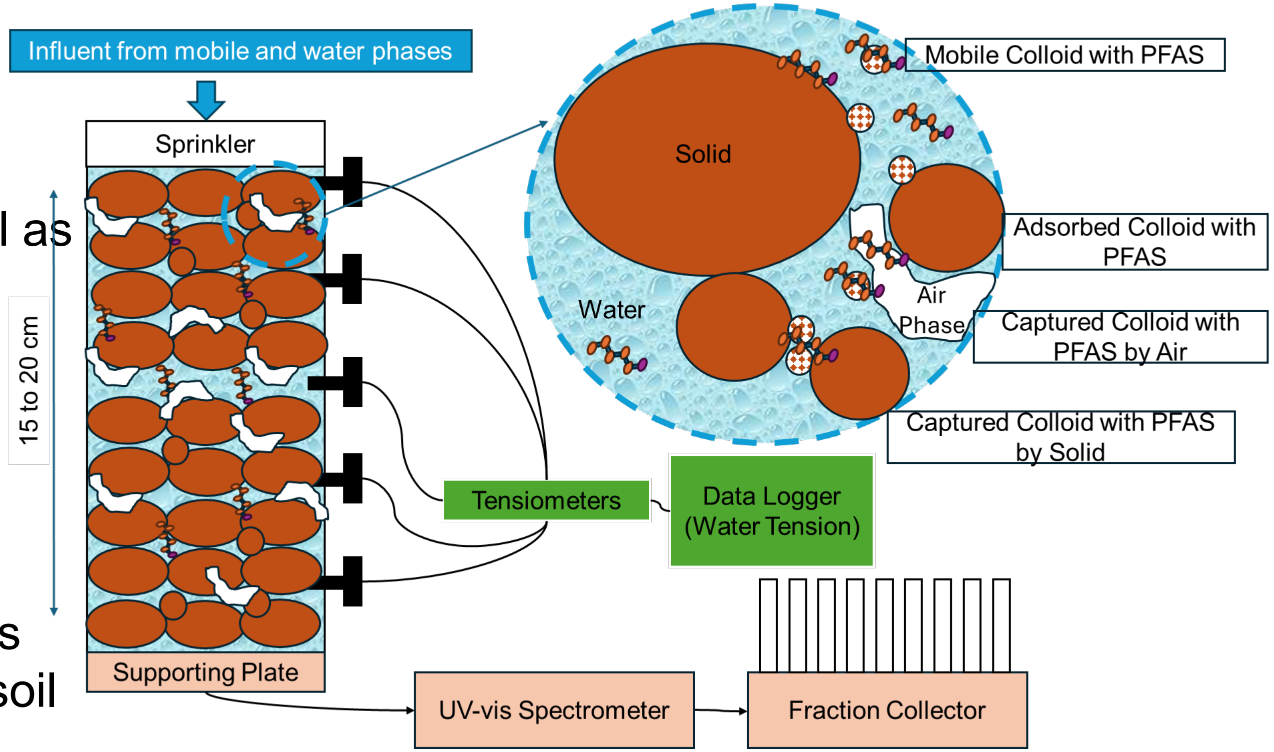
Environ. Sci. Technol. Lett. 2020, 7, 5, 343–350

❗ **Energy intensive**

Rotary kiln at 650-850 °C	1336 (kWh/m^3)
Circulating bed combustion chamber at 750 °C	1099
Hydrothermal treatment at 350 °C	**317**

Moving forward: PFAS contamination of groundwater

- PFASs accumulate in superficial soil layers, where PFASs are discarded.
- Physicochemical processes influence sorption, biotransformation, and plant uptake of PFASs in soil as well as distribution and speciation of PFASs in unsaturated zone.
- Adsorption at air-water interface retards PFAS transport in unsaturated zone.
- Various physical, chemical, and biological processes influence the fate and transport of PFASs from the soil to groundwater.



Moving forward: Data management of PFAS contaminants

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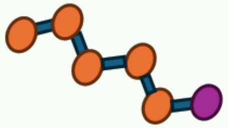
Input

MP

- Structure
- Size
- SSA
- C%
- Function Groups
- Charge Density

PFAS



- Structure
- Low
- Functional Groups
- Chain Length

Model

Data Processing
(Feature reduction, Outliner selection, Data normalization)

↓

Data Arrangement
(Training-Test-Validation Sets)

↓

Model Selection
(RF, SVM, XGB, GPR, MLR)

Output

Output
C_m = Mass of Sorbate/Sorbent
K_d = Adsorption Coefficient

+

Model Evaluation
(Indicator: R^2, RMSE, MSE
+
Data comparison from Task 1 and Task 2)

+

Interpretation and Feedback

Acknowledgement

Hinkley Center for Solid and Hazardous Waste Management