

# Investigation of thermal air degradation and pyrolysis of PFAS and PFAS alternatives in soil

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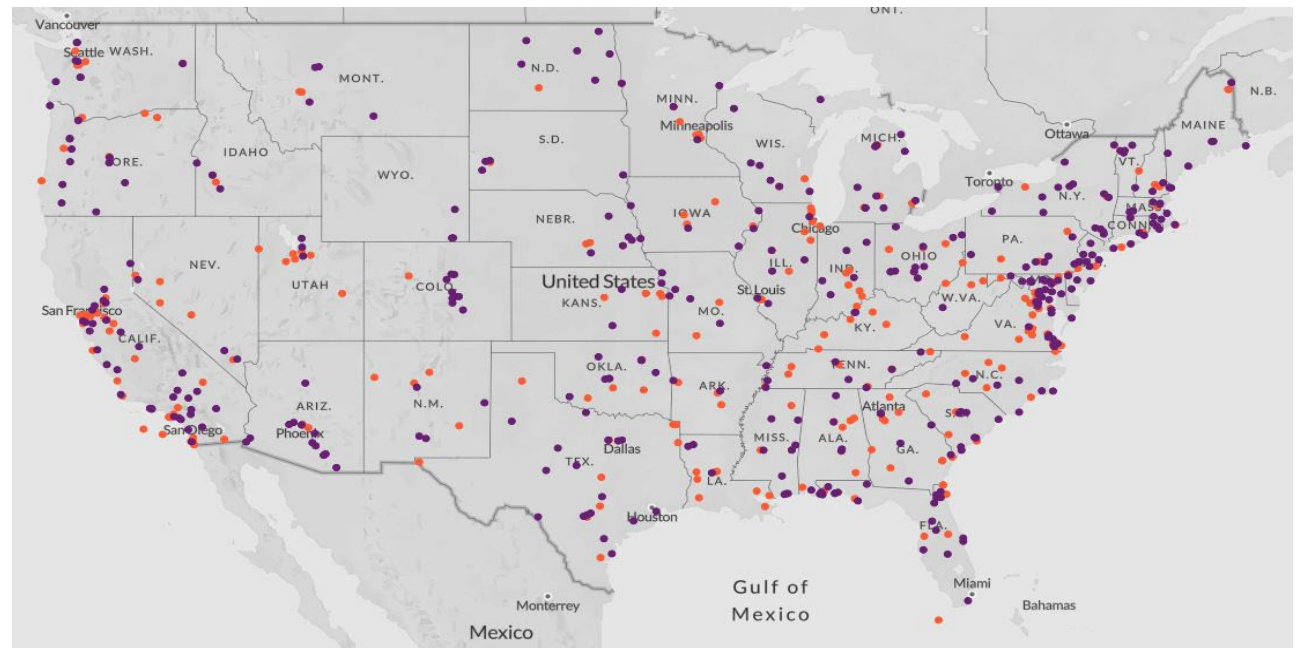
## ***PFAS Contamination in Soil***

### Point contamination

- AFFF-impacted sites
- PFAS manufacturing facilities
- Municipal landfills

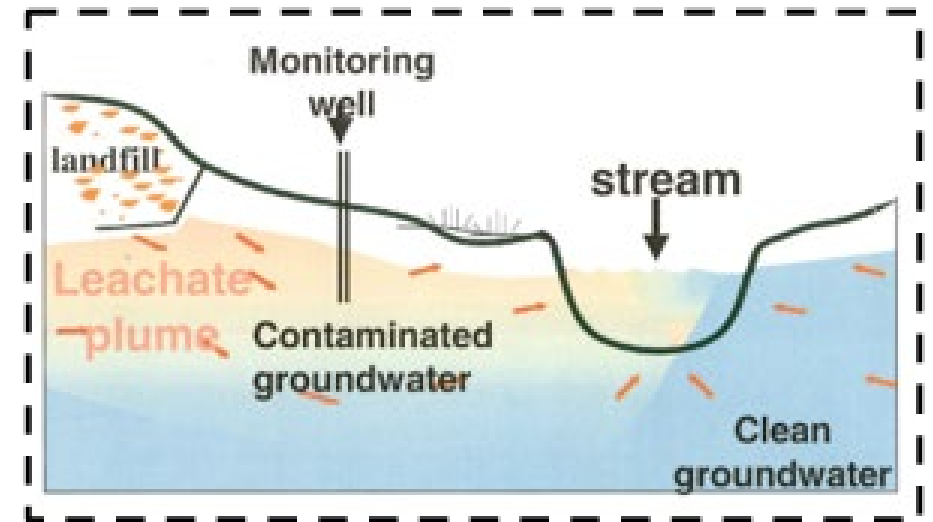
### Non-point contamination

- Land application of PFAS-containing biosolids and reclaimed wastewater



## PFAS Contamination in Soil

- In U.S. and Canada, PFOA was detected in the range of 42 to 5000 ng/L in landfill leachate, whilst PFOS was from 9.5 to 4400 ng/L (**Wei et al., 2019**).
- PFAS contaminated soil will contaminated the surrounding soil and groundwater resources



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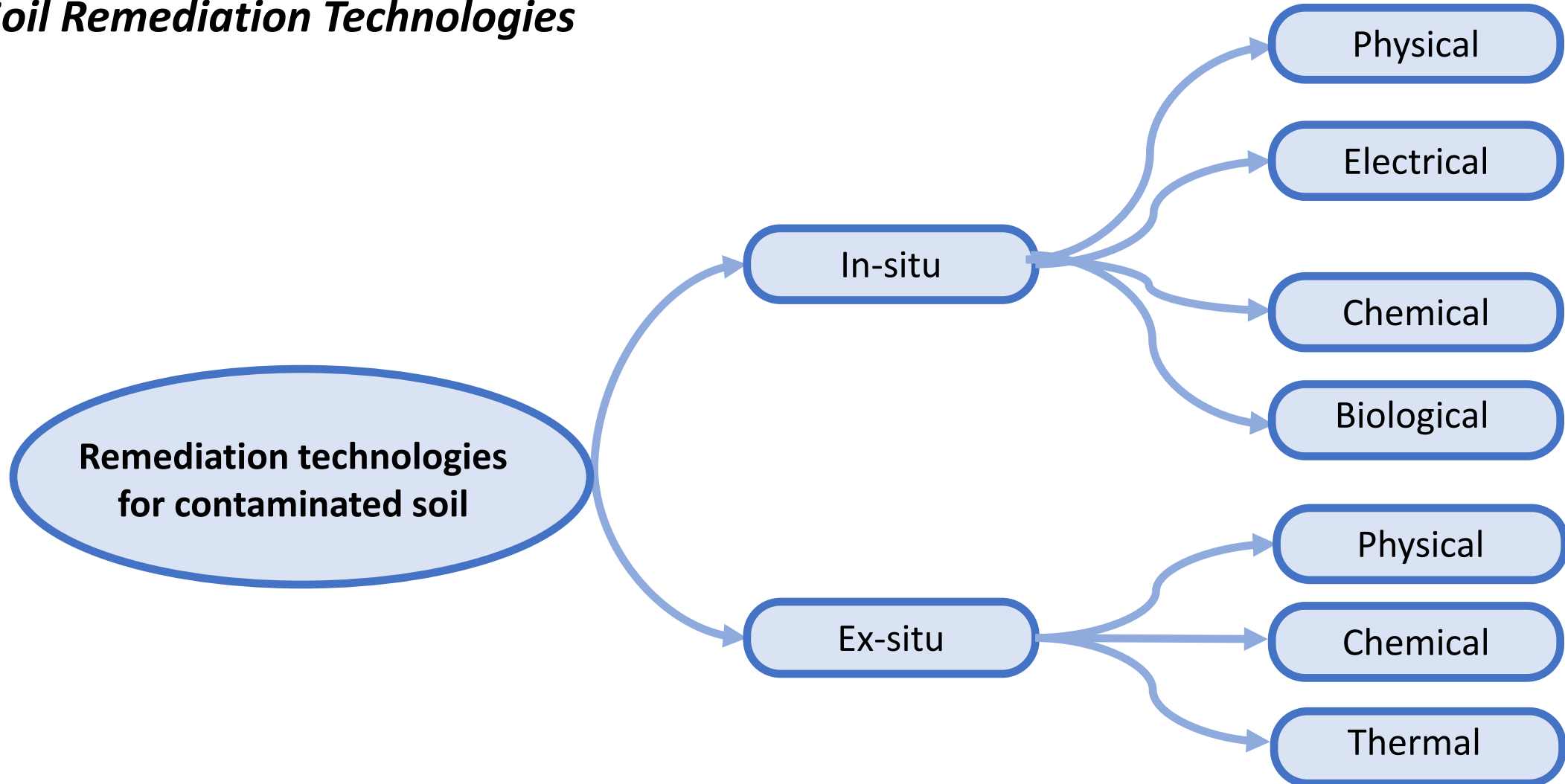
**Toxic "forever chemicals" found in groundwater near more U.S. military bases**

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Contamination with PFAS chemicals has been documented at and around [Cannon Air Force Base](#) near Clovis as well as at Holloman Air Force Base near Alamogordo and other locations in New Mexico. The state [sued the U.S. Air Force in 2019](#), saying the federal government has a responsibility to clean up plumes of toxic chemicals left behind by past military firefighting activities.

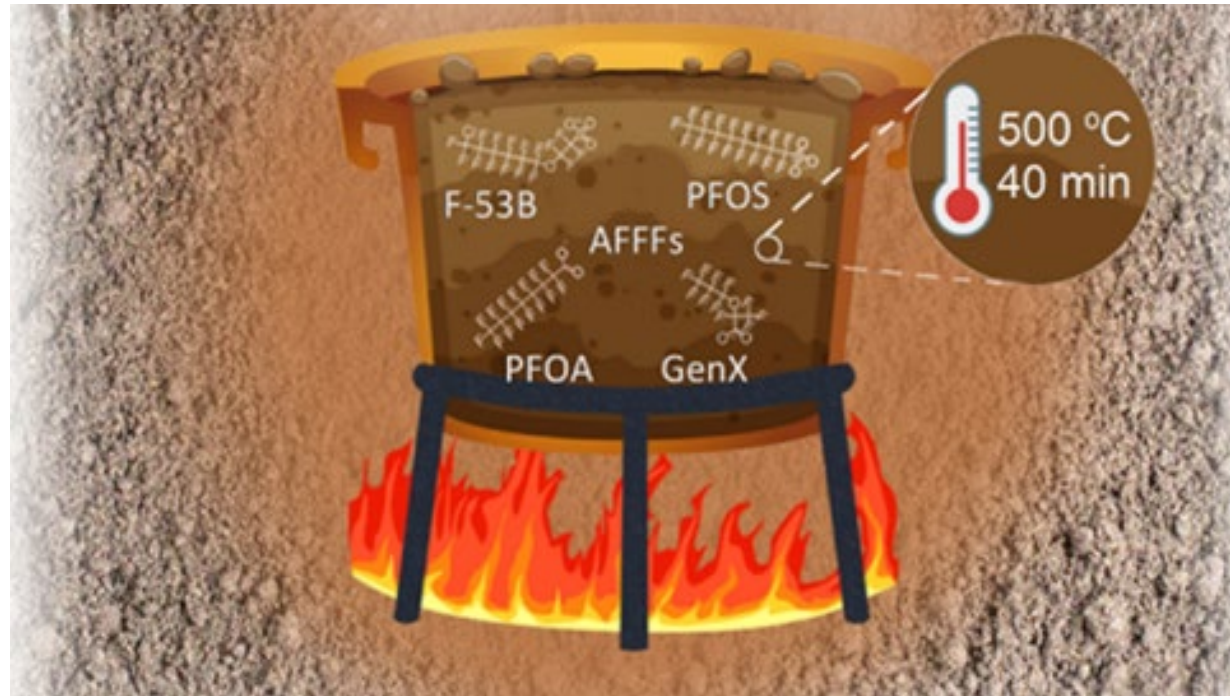
## *Soil Remediation Technologies*



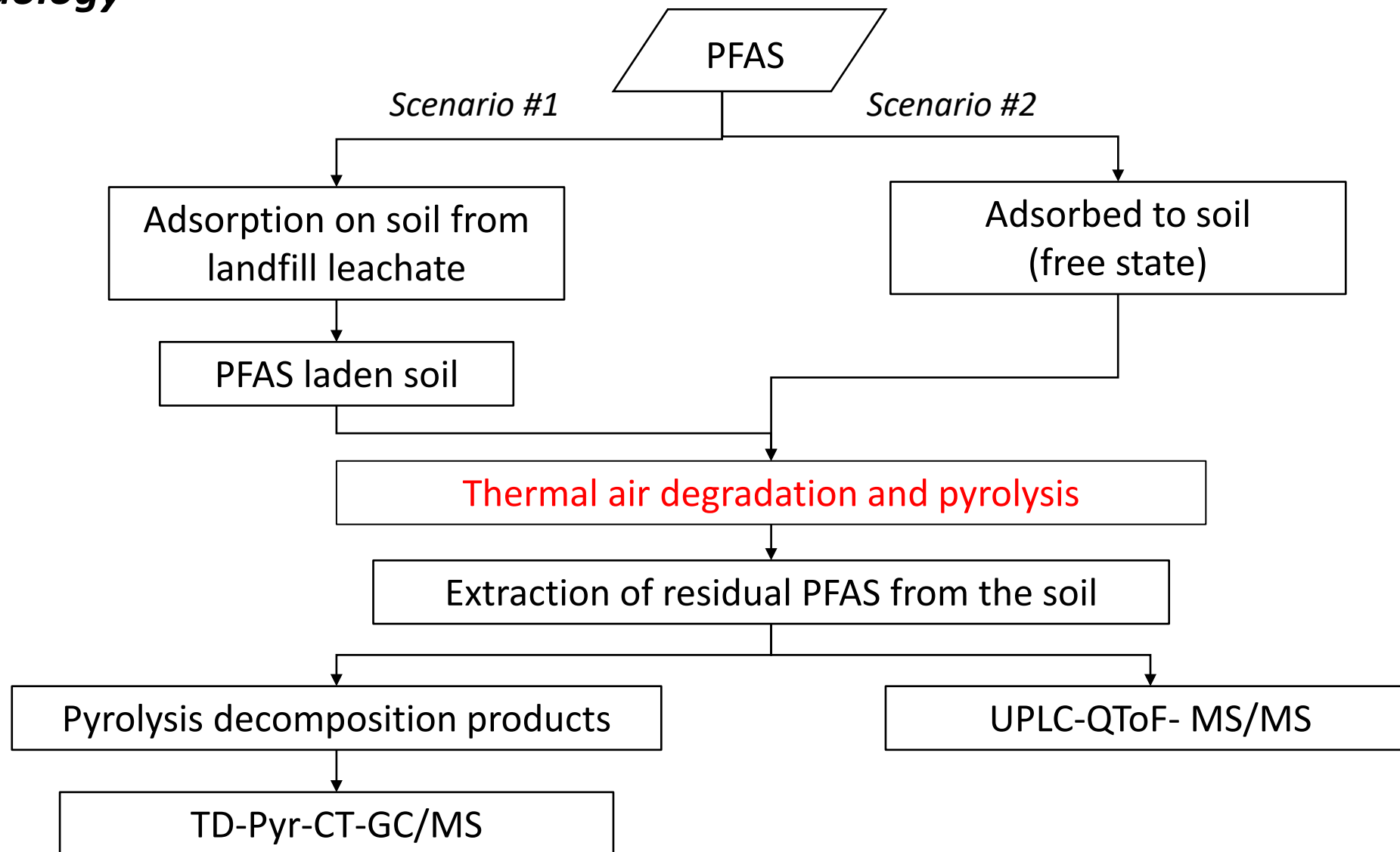
## *Remediation of PFAS-contaminated soil*

- A few treatment and remediation approaches have been investigated for removing PFAS from contaminated water and soil, including solvent flushing, photocatalytic degradation, sequestration, ball milling, electrochemical approaches, and hydrothermal methods.
- In an interim guideline, US EPA has identified **thermal treatment** as one of the technological solutions that is commercially available and has the capacity to degrade or manage the migration of PFAS in contaminated materials ([EPA, 2020](#)).

- This study was carried out to delineate factors that impact the fate of PFAS in soil during thermal treatment and influence the selection and operation of thermal technologies for the remediation of PFAS-contaminated sites.



## Methodology



## PFAS Chemicals and AFFFs

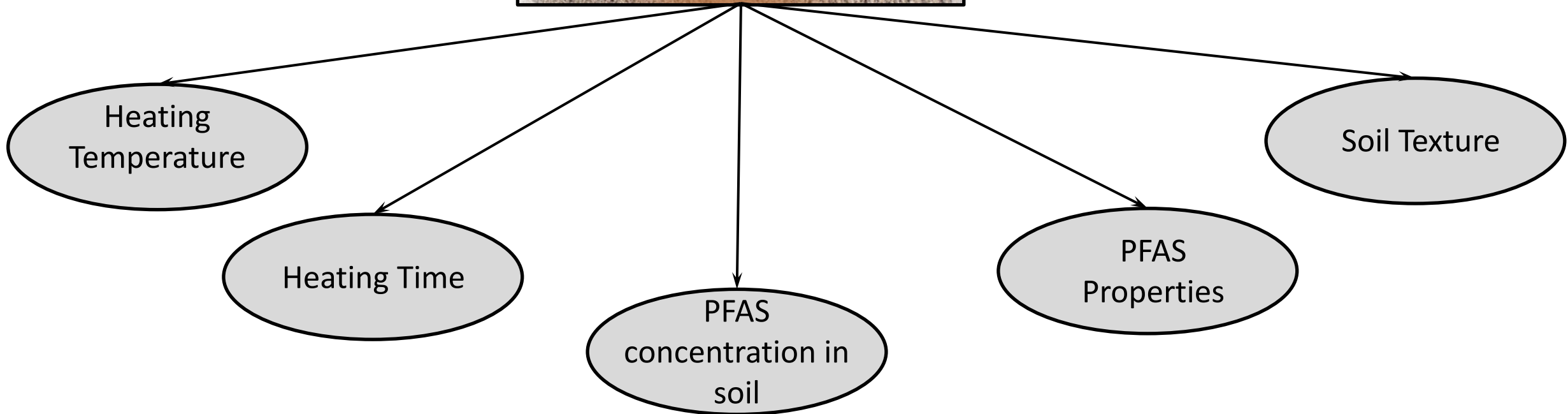
### PFAS

1. PFCAs (PFBA, PFPeA, PFHpA, PFOA, PFNA, PFDA, PFUnDA)
2. PFSAs (PFBS, PFHxS, PFOS)
3. Cationic and Zwitterionic (PFOAAmS, PFOSAmS, PFOAB, PFOSB)
4. Anionic PFAS (N-MeFOSAA, 8:2 FTS, HFPO-DA, 6:2 Cl-PFAES)
5. Two 3M AFFF samples





## *Thermal decomposition*



## *Soils*



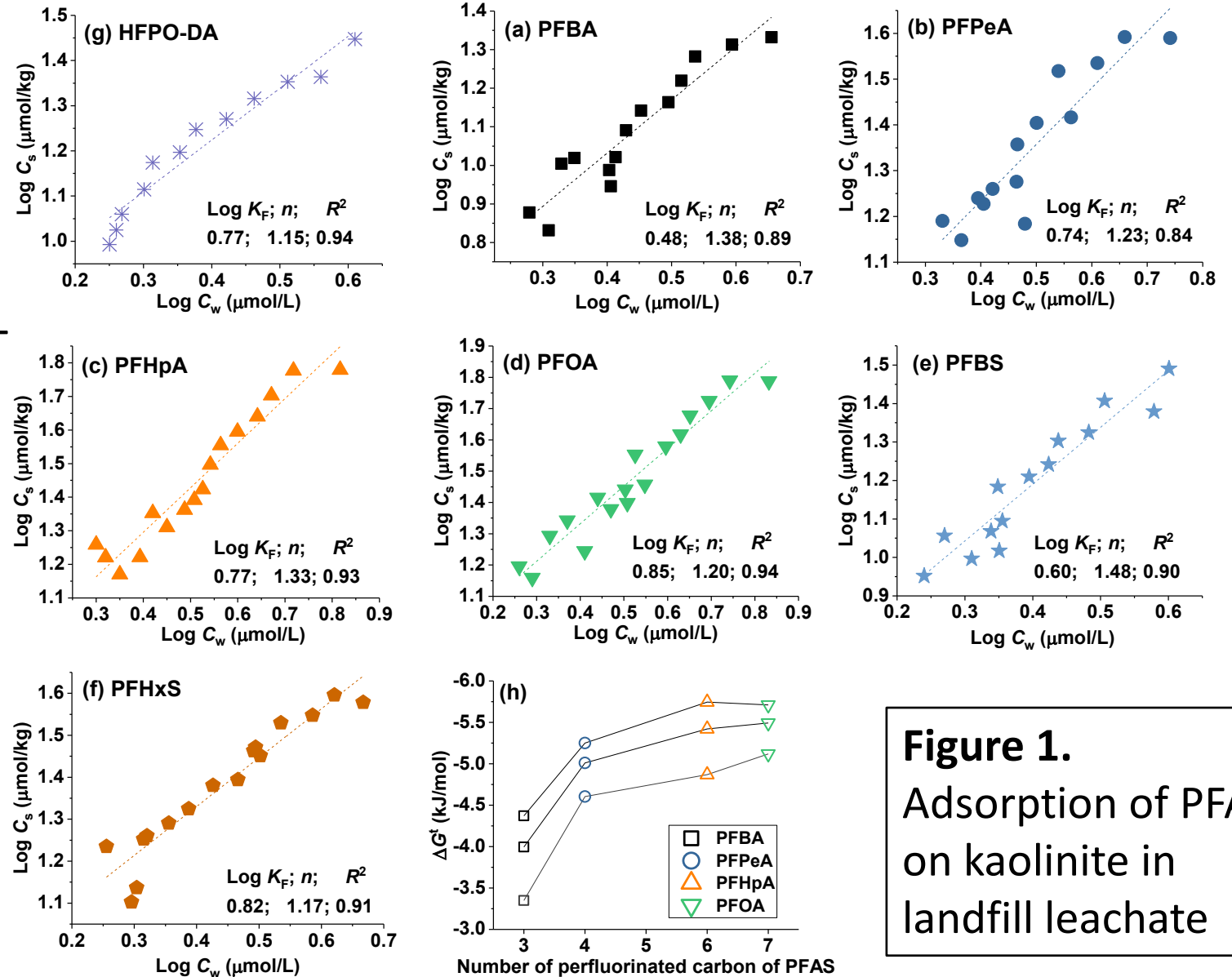
Natural soil  
(clay loam with soil organic matter of 9.8%)



Reference Kaolinite clay

## Results

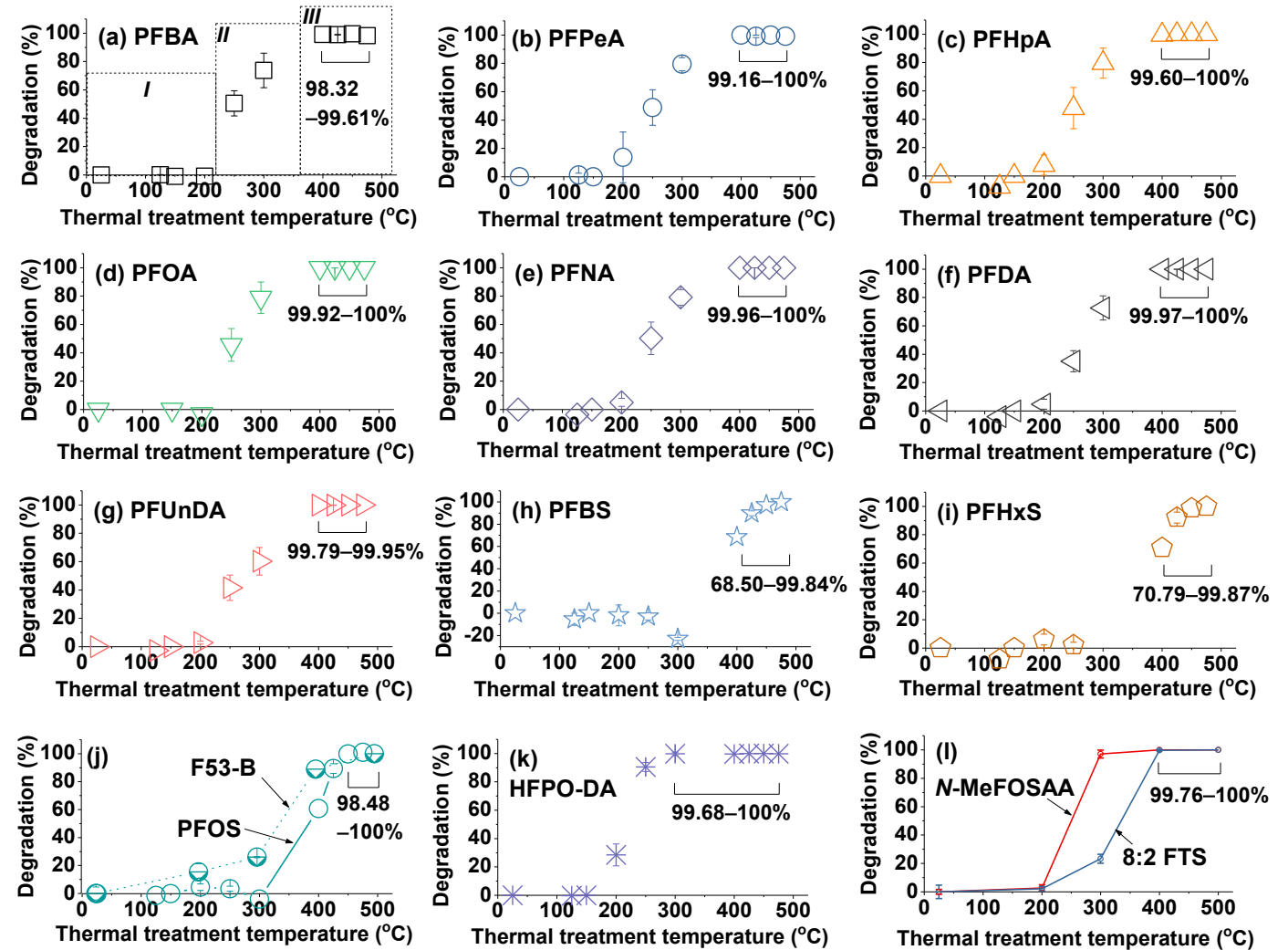
- Dashed line represents fitted data by Freundlich model
- The Freundlich coefficient is 1.15-1.48
- The value of  $(-\Delta G^t)$  follows the order, PFBA < PFPeA < PFHpA  $\leq$  PFOA, the same order as in the number of perfluorinated carbons, suggesting that the hydrophobic effect is a major driving force.



**Figure 1.**  
Adsorption of PFAS  
on kaolinite in  
landfill leachate

## Heating Temperature

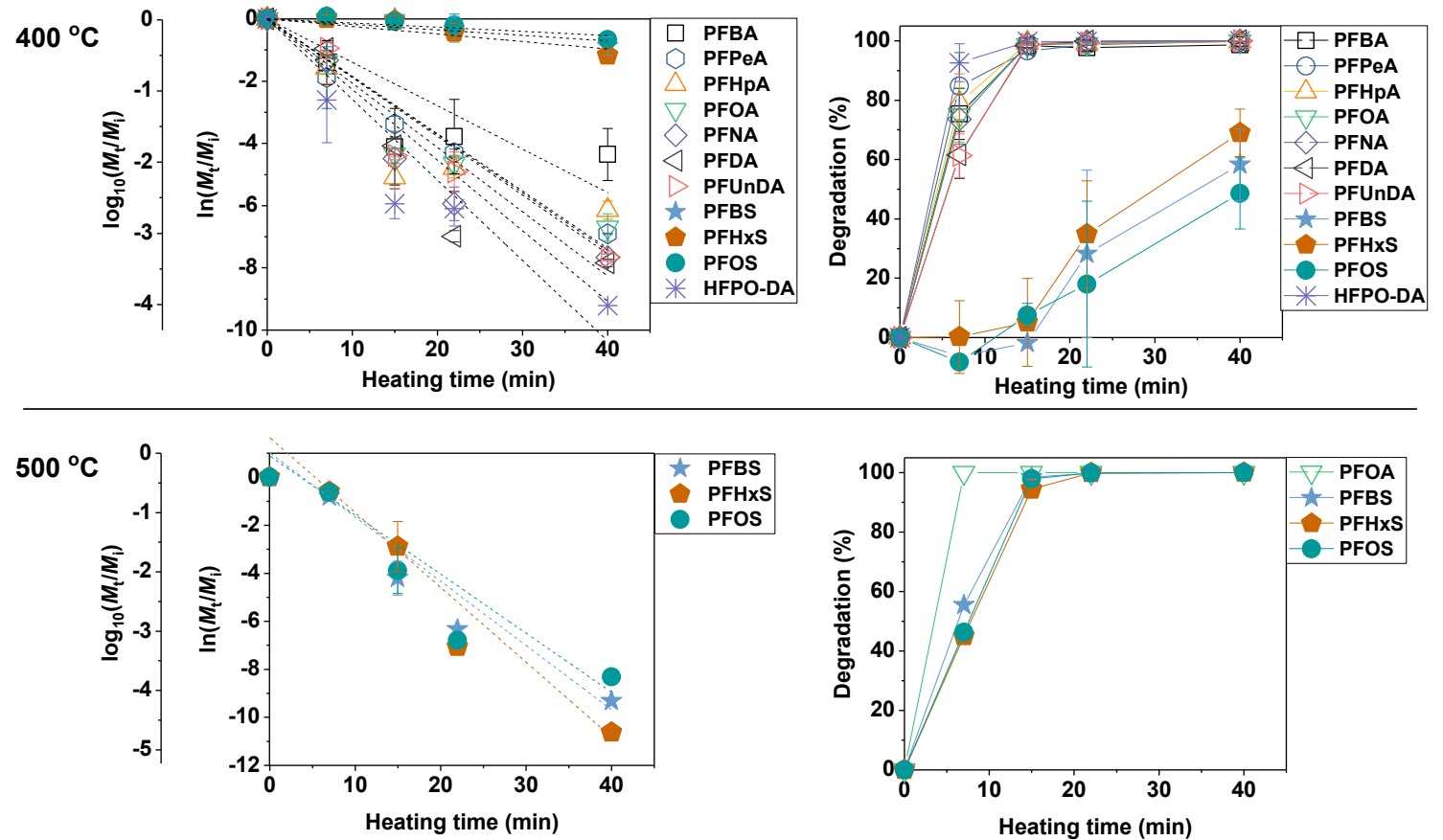
- The thermal stability followed the order: PFSAs > 6:2 Cl-PFAES  $\approx$  8:2 FTS  $\approx$  PFCAs > N-MeFOSAA > HFPO-DA.
- PFCAs started to decompose at 200-400 °C and decomposed almost completely in 30 min at >400 °C
- PFSAs require higher temperature to decompose.
- Polyfluorinated ether sulfonate (6:2 Cl-PFAES; the major component of F-53B) appears to be more thermally stable than the perfluorinated ether carboxylic acid (HFPO-DA that is the conjugate acid of GenX).
- Near-complete degradation in soil for Polyfluorinated compounds at >400 °C.



**Figure 2.** Decomposition of PFAS after 30 min heating at different temperatures

## Heating Time

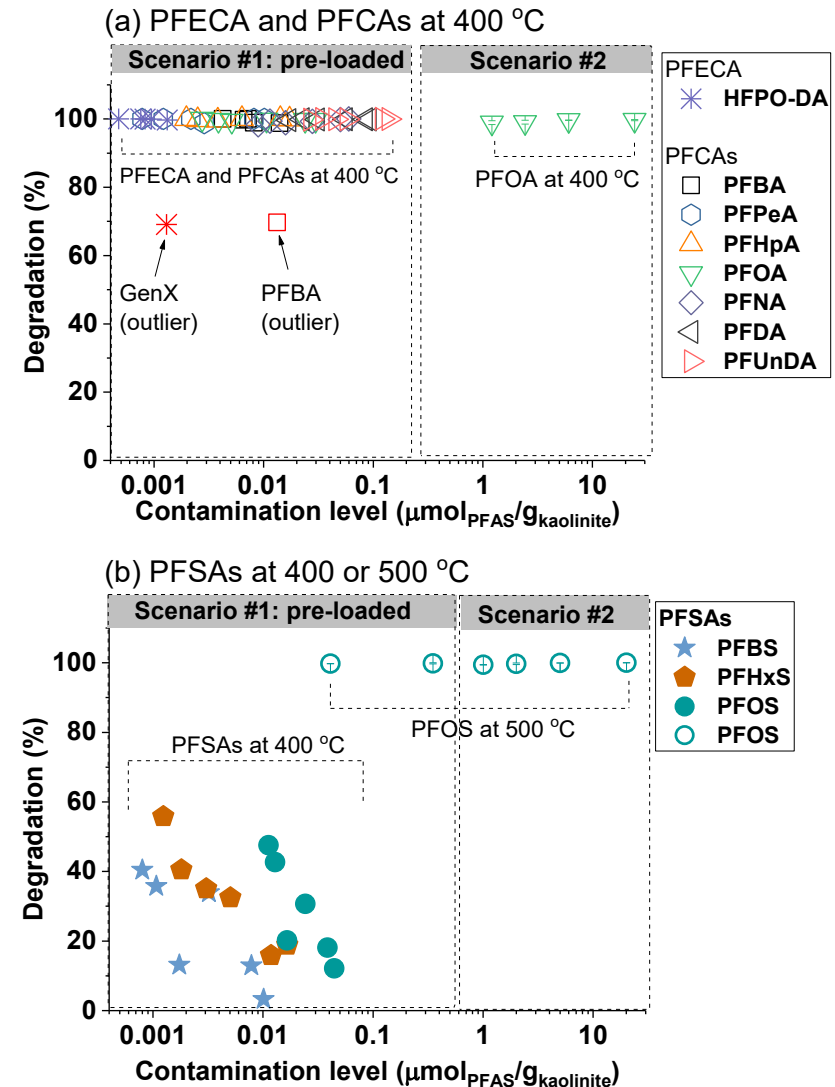
- PFCAs mass dropped dramatically after 7 minutes (400 °C)
- 99.99% degradation for PFOA at 500 °C after 7 minutes
- Up to 99.9976% degradation in PFSAs (including PFOS) at 500 °C for 40 minutes
- The apparent thermal decomposition half-lives ( $t_{1/2, \text{thermal}}$ ) of HFPO-DA, PFCAs, and PFSAs in soil at 400 °C were 2.7 min, 3.1–5.0 min, and 28.7–51.8 min, respectively
- The apparent thermal decomposition half-lives of PFSAs in soil were determined to be 2.4–3.1 min at 500 °C.



**Figure 3.** Thermal decomposition of PFAS in soil as a function of heating time

## Initial PFAS loading in Soil

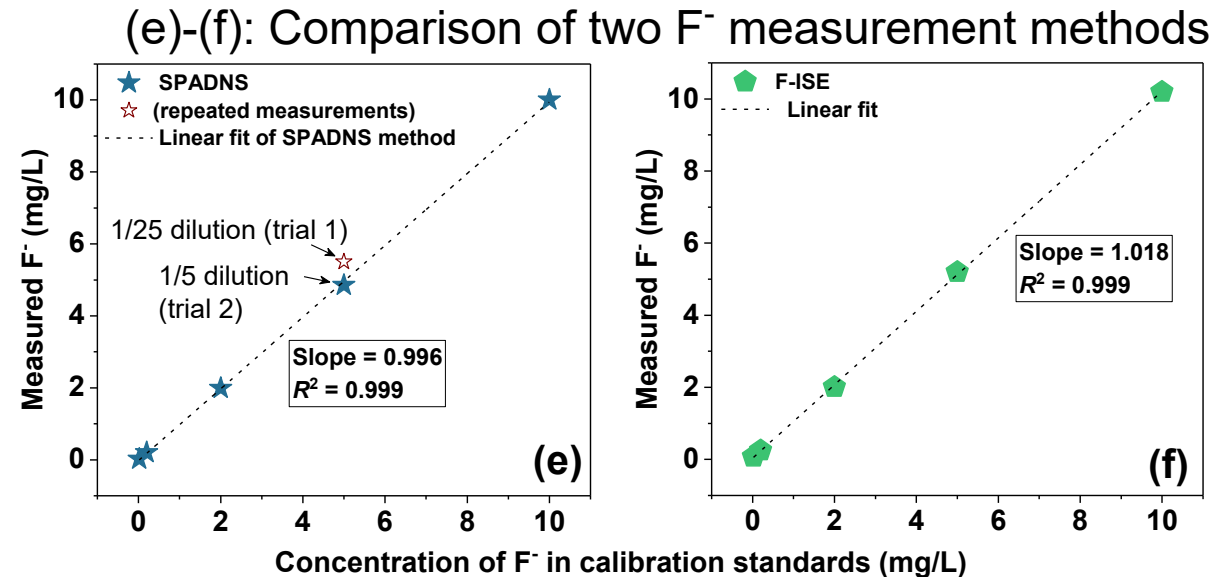
- At 400 °C, a consistently high decomposition rate (>98%) of PFCAs and HFPO-DA was observed over four orders of magnitude in concentration ranging from 0.00077 to  $\sim 24.2 \mu\text{mol}_{\text{PFCA}}/\text{g}_{\text{clay}}$
- Heating at 400 °C was insufficient to degrade PFSA in 30 min, therefore an increase in PFSA loading led to an apparent decline in the thermal decomposition rate
- Insignificant effects of initial PFAS loading for PFSA at 500 °C
- Reduction of residual PFSA mass to less than 0.6% of the initial mass within 30 min at 500 °C



**Figure 4.** PFAS decomposition in kaolinite heated for 30 min as a function of initial loading

## Yield of Fluoride

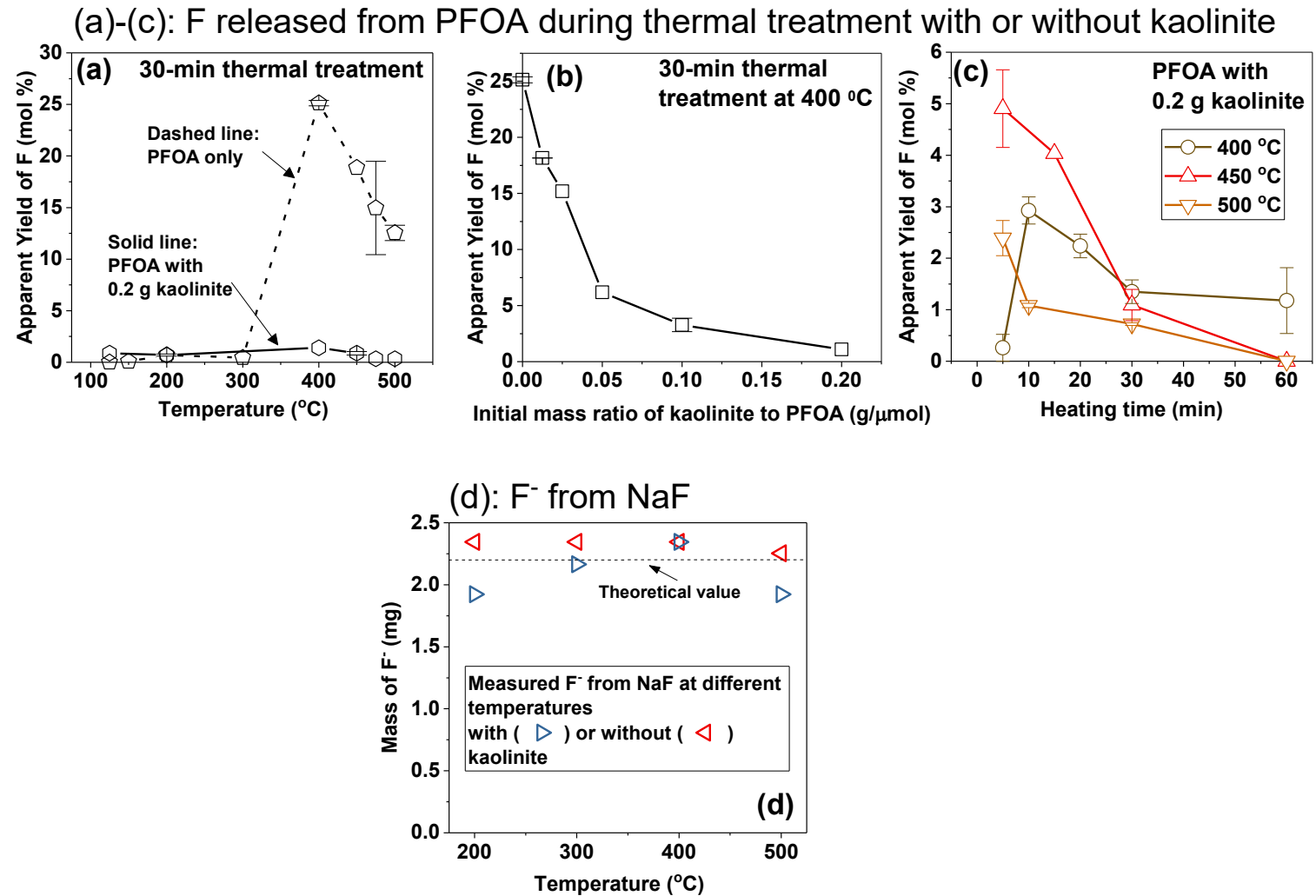
- The quantification of F was conducted with US EPA SPADNS method and ISE method in this study
- The measurement of F<sup>-</sup> by ion chromatography can be hampered by the overlap of peaks of F<sup>-</sup> and other anions, such as formate and acetate.
- Both SPADNS and ISE yielded reliable results over a wide concentration range of F<sup>-</sup>
- However, the detection limit of the SPADNS method is only 2 mg F<sup>-</sup> /L; a substantial dilution of a sample may cause dilution errors



**Figure 5.** comparison of F yield measurement

## Yield of Fluoride

- Our research group previously found a significant increase in the yield of F (up to 92 mol%) when PFOA or PFOS was heated at 700–900 °C.
- At 400 °C, the yield of F from PFOA is less than 25 mol%.
- Sharp reduction of F yield with the presence of kaolinite
- No significant loss of F after heating sodium fluoride with kaolinite (reaction between kaolinite particles and F radicals)
- Further studies are needed on thermal reaction mechanisms between F radicals and kaolinite

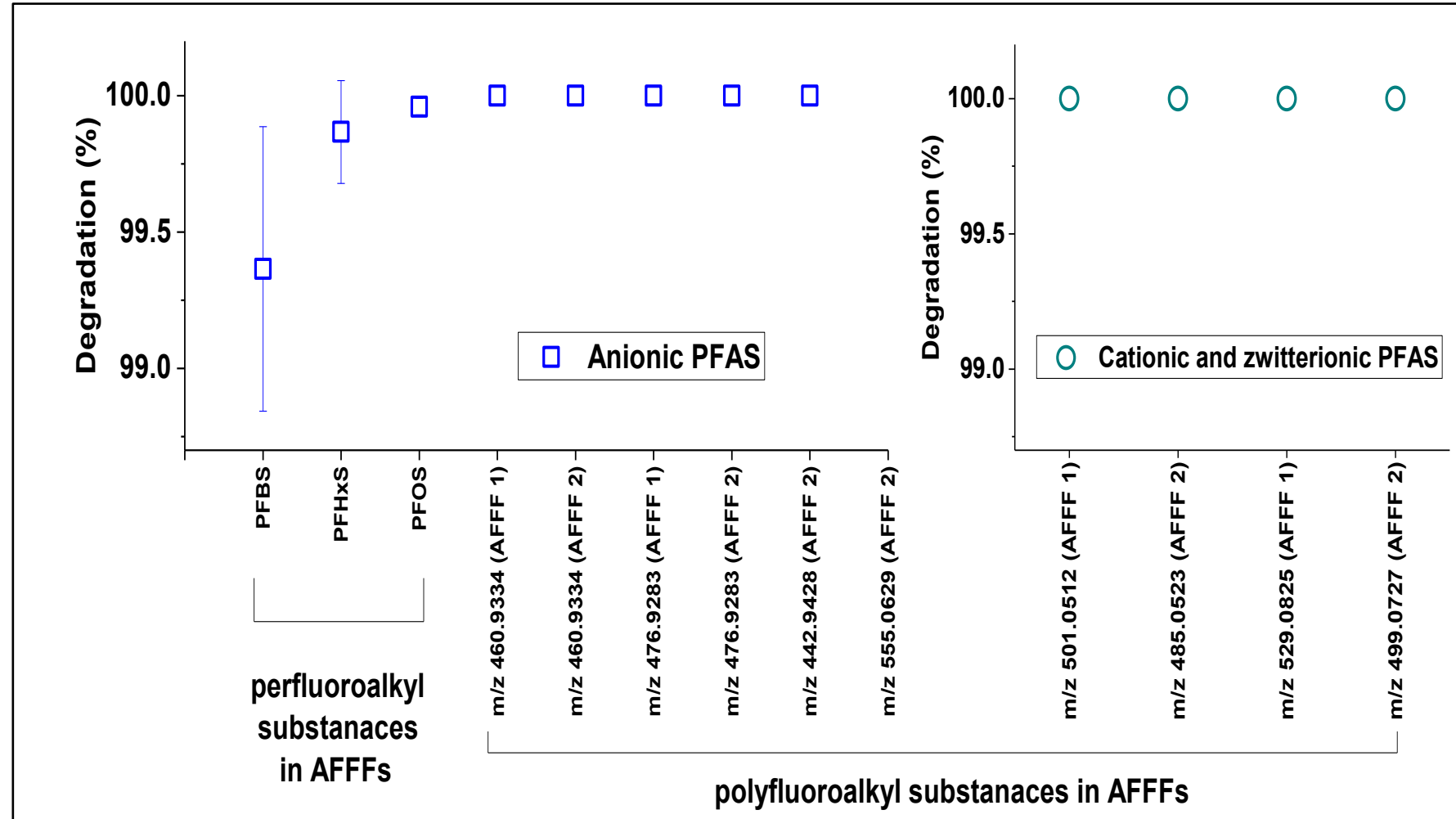


**Figure 6.** yield of F from PFOA during thermal treatment



### 3M AFFF samples

- Near-complete degradation of Polyfluorinated compounds in the soil at temperature  $>400\text{ C}$
- Polyfluorinated compounds are less thermally stable than perfluoroalkyl counterpart



**Figure 7.** Decomposition of PFASs and polyfluoroalkyl substances after 30-min treatment in soil at 500 °C.

## ***Conclusions***

- Different factors such as heating temperature, thermal treatment time, PFAS chemistry, and the initial contamination level play a key role in PFAS degradation in the contaminated soil.
- thermal treatment at moderate temperatures (e.g., ~500 °C during natural wildfires) is highly effective in removing and decomposing a variety of PFAS in soil and is highly suggested.
- The combination of appropriate temperature ( $\geq 500$  °C) and time ( $\geq 30$  min) lead to a near complete decomposition of various PFAS compounds in the soil.
- Emission of F radicals (technological challenge in thermal treatment of PFAS due to the formation of corrosive hydrogen fluoride) can be significantly reduced with the presence of kaolinite.

## For more information,

- **Alinezhad, A.,** Challa Sasi, P., Zhang, P., Yao, B., Kubátová, A., Golovko, S. A., & Xiao, F. (2022). An Investigation of Thermal Air Degradation and Pyrolysis of Per- and Polyfluoroalkyl Substances and Aqueous Film-Forming Foams in Soil. *ACS ES&T Engineering*.

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