

# Abiotic Treatment Technologies for In-Site Remediation of Persistent Perfluoroalkyl Acids

Linda S. Lee<sup>1,2\*</sup>, Saerom Park<sup>2,3</sup>, and Jenny Zenobio<sup>2,3</sup>

<sup>1</sup>Professor of Environmental Chemistry, Agronomy

<sup>2</sup>Interdisciplinary Ecological Sci. & Engineering Graduate Program, Program Head

<sup>3</sup>PhD Students

June 26, 2015

NICOLE Workshop

Manchester, UK



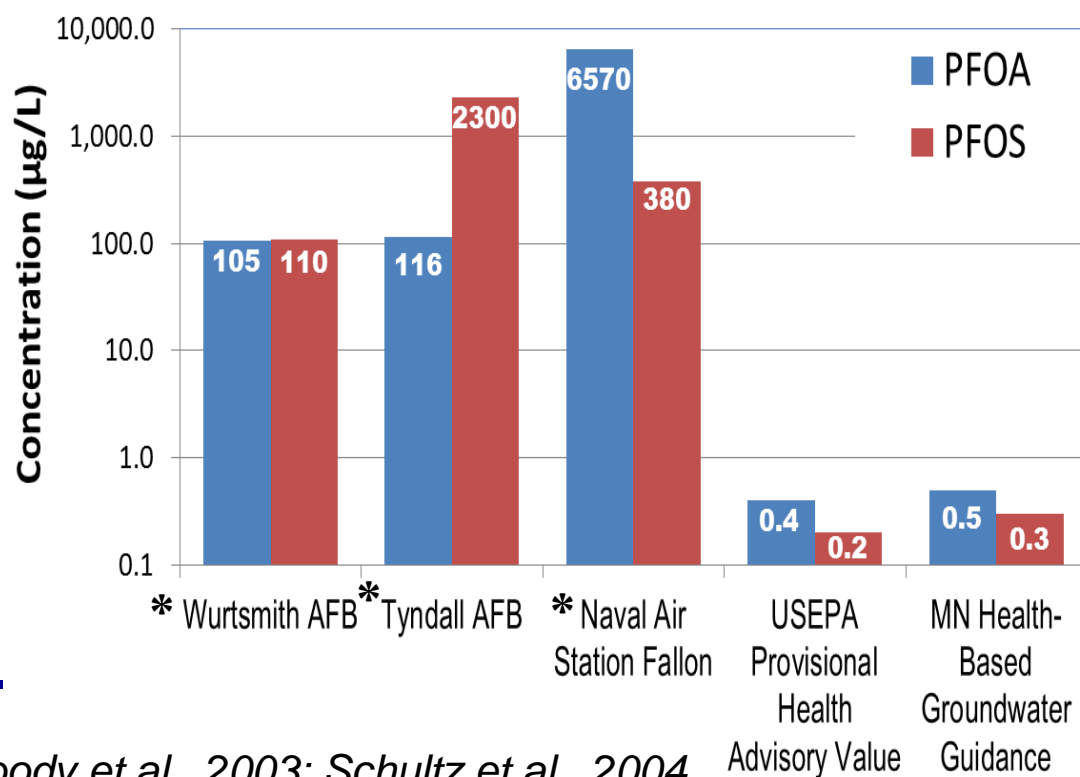
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# Aqueous Film-Forming Foam (AFFF) Sources

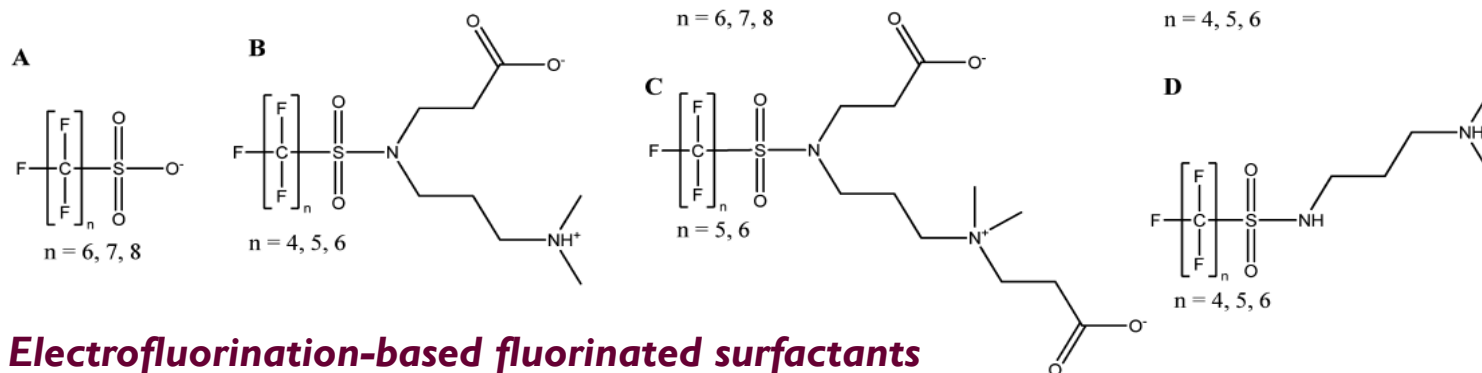
- US Military big user of AFFFs, which are a primary source of PFAAs and likely present at > 550 sites.
- Additional, many other military sites due to use/releases of AFFFs to extinguish hydrocarbon fires or industrial activities, etc.
- PFAAs are persistent, bioaccumulative, and relatively mobile.
- Provisional health advisory levels are well below what is expected at military sites
- **Currently, no viable in-situ technology has been successfully demonstrated for the entire suite of PFASs, particularly linear PFOS, or PFAA precursors.**



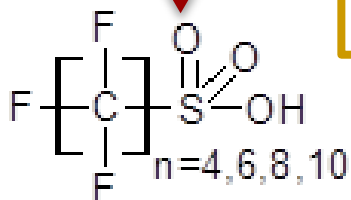
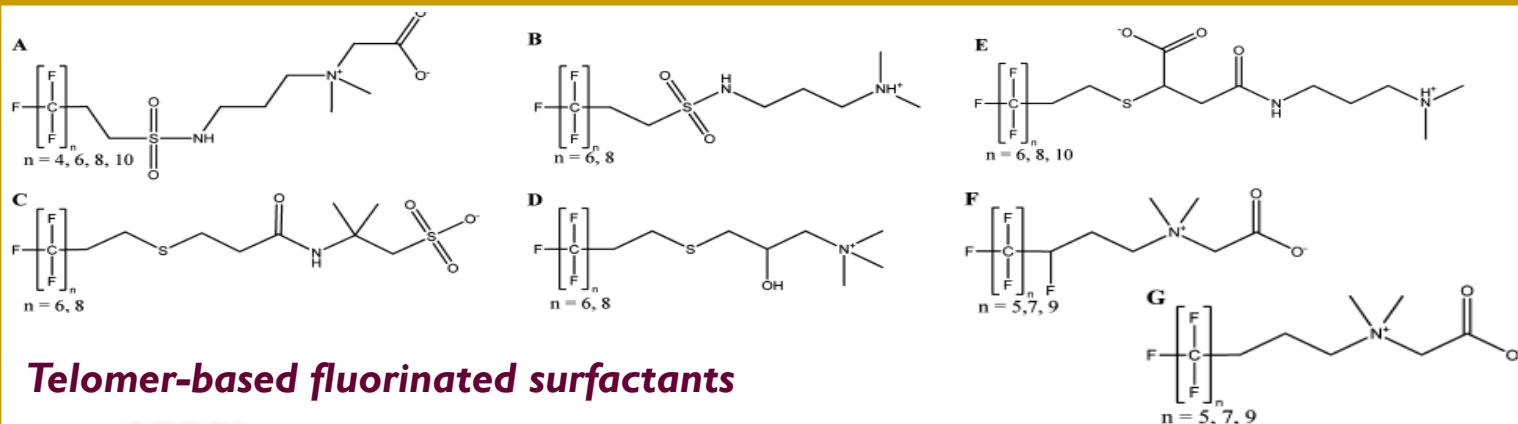
*\*Moody and Field, 1999; Moody et al., 2003; Schultz et al., 2004*

# PFASs in Aqueous Film Forming Foams (AFFFs)

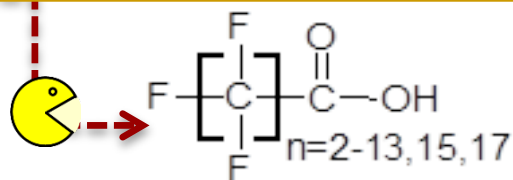
(Place & Field, EST, 2012)



B, C & D



**Perfluorosulfonic acids**  
PFSA (PFOS  $\text{pK}_a < 0$ )




**Perfluorocarboxylic acids**  
PFCAs (PFOA  $\text{pK}_a < 4$ )

**Terminal microbial end products**

$\Sigma = \text{PFAAs} = \text{perfluoro alkyl acids}$

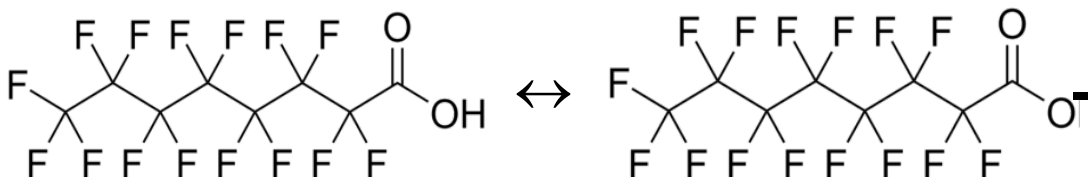
# Initial Approach: Chemical Oxidative Treatment

- **Fenton's Reagent**
  - Thermodynamic studies indicate not effective
  - PFOS not degraded with an aggressive treatment.
- **Ultraviolet reactions**
  - Successful for only PFOA
  - Conditions not applicable in situ
- **Permanganate**
  - some success with PFOS at  $\geq 65$  °C & low pH (*Liu et al, 2012*)
- **Sonolysis**
  - Good results for PFOA and PFOS
  - Not applicable for in situ
- **Persulfate** 
  - UV and heat activation established successful for PFOA (*Hori et al., 2005; Lee et al, 2012; Liu et al., 2013*)

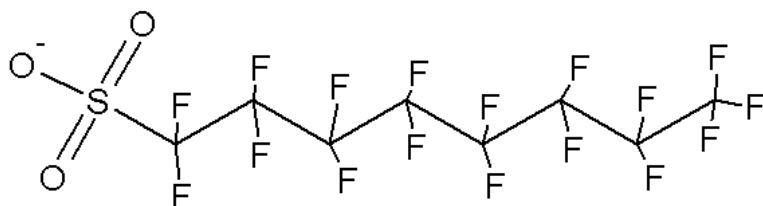
***\*Choice of activation mode dependent on effectiveness and efficiency for a given environment, e.g., in-situ versus ex-situ.***

# Heat-activated Persulfate for 3 Representative PFASs

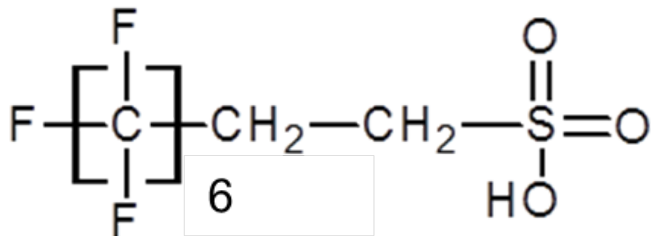
## PFOA/PFOA<sup>-</sup>



## PFOS<sup>-</sup>



## 6:2 FTS (6:2 Fluorotelomer sulfonate)



## Experimental Variables

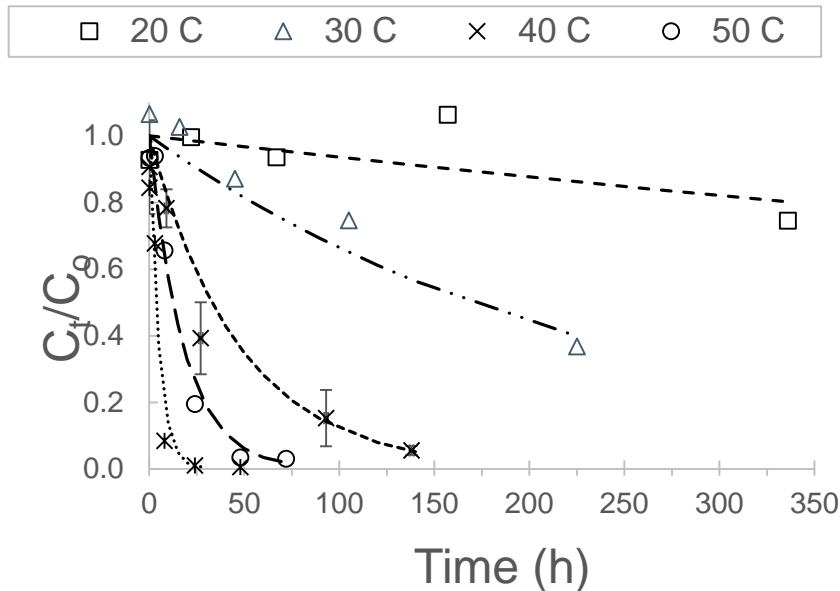
- Temperature (20 ~ 60 °C)
- Unbuffered pH
- Persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) Conc. (0 ~ 20,000 mg/L, 84.00 mM)
- PFACs conc. (50 ~ 2,500 µg/L, 0.12 µM ~ 6 µM)
- Fuel co-contaminants (BTEXs up to 1,000 µg/L)
- Aquifer



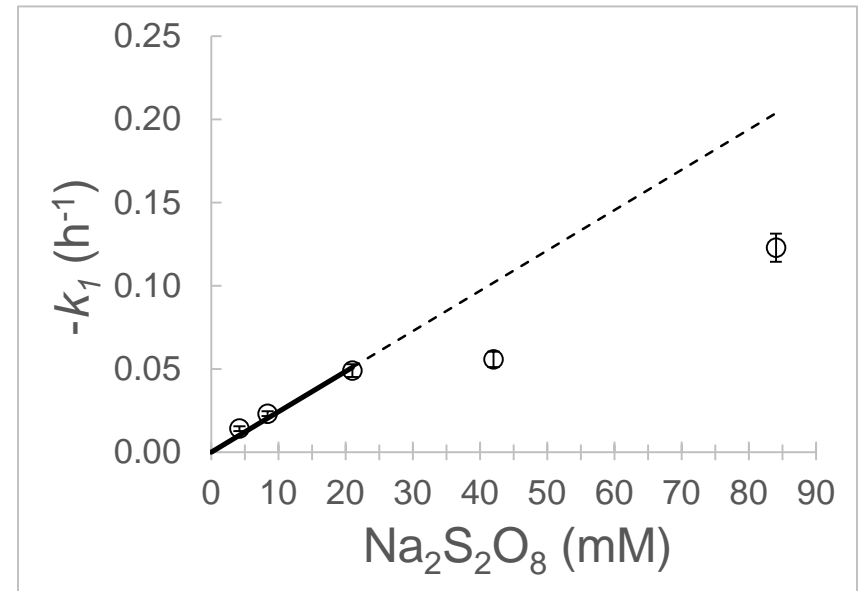
# Heat-Activated Persulfate (100 $\mu\text{g/L}$ PFOA)



**Varying Temperature**  
 **$[\text{Na}_2\text{S}_2\text{O}_8] = 10,000 \text{ mg/L}$**



**Varying  $[\text{Na}_2\text{S}_2\text{O}_8]$ ,  $T = 50^\circ\text{C}$**



- Removal rate  $\uparrow$  with  $\uparrow$  temperature and  $\uparrow [\text{Na}_2\text{S}_2\text{O}_8]$
- Linear Arrhenius Plots (right graph)
- Unbuffered pH (pH decreases with reaction)
- Same for PFCA range tested: 50 ~ 2,500  $\mu\text{g/L}$  (0.12  $\mu\text{M}$  ~ 6  $\mu\text{M}$ )

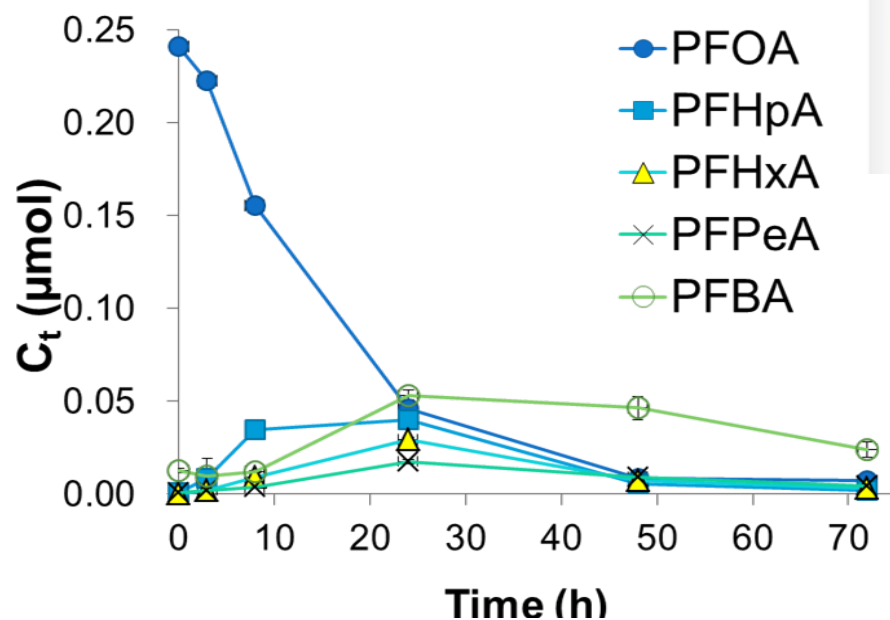


# Heat (50 °C) - Activated Persulfate

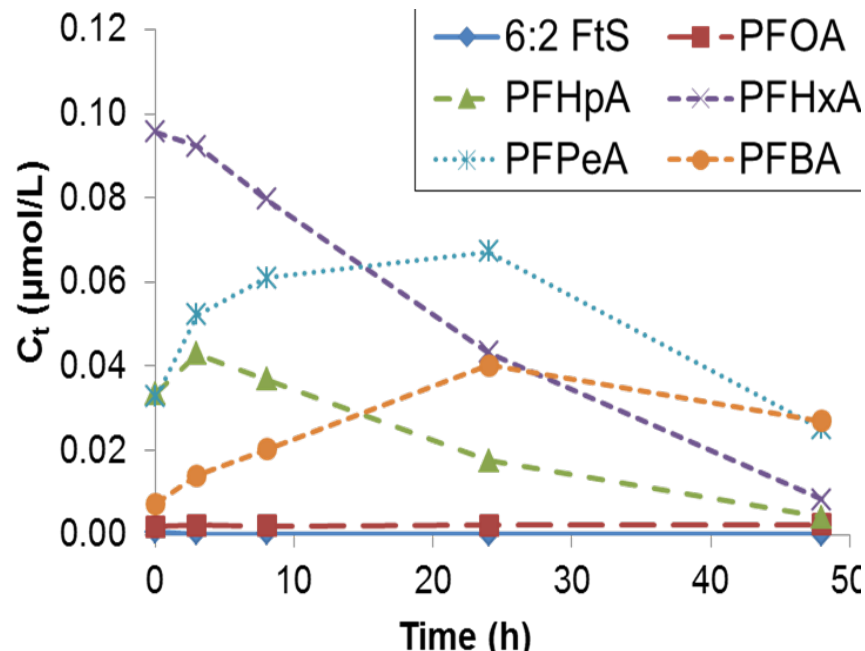
$[\text{Na}_2\text{S}_2\text{O}_8] - 10,000 \text{ mg/L}, 50 \text{ }^\circ\text{C}$



~100  $\mu\text{g/L}$  M) (0.241  $\mu\text{M}$ ) PFOA



~100  $\mu\text{g/L}$  (0.215  $\mu\text{M}$ ) 6:2 FTS

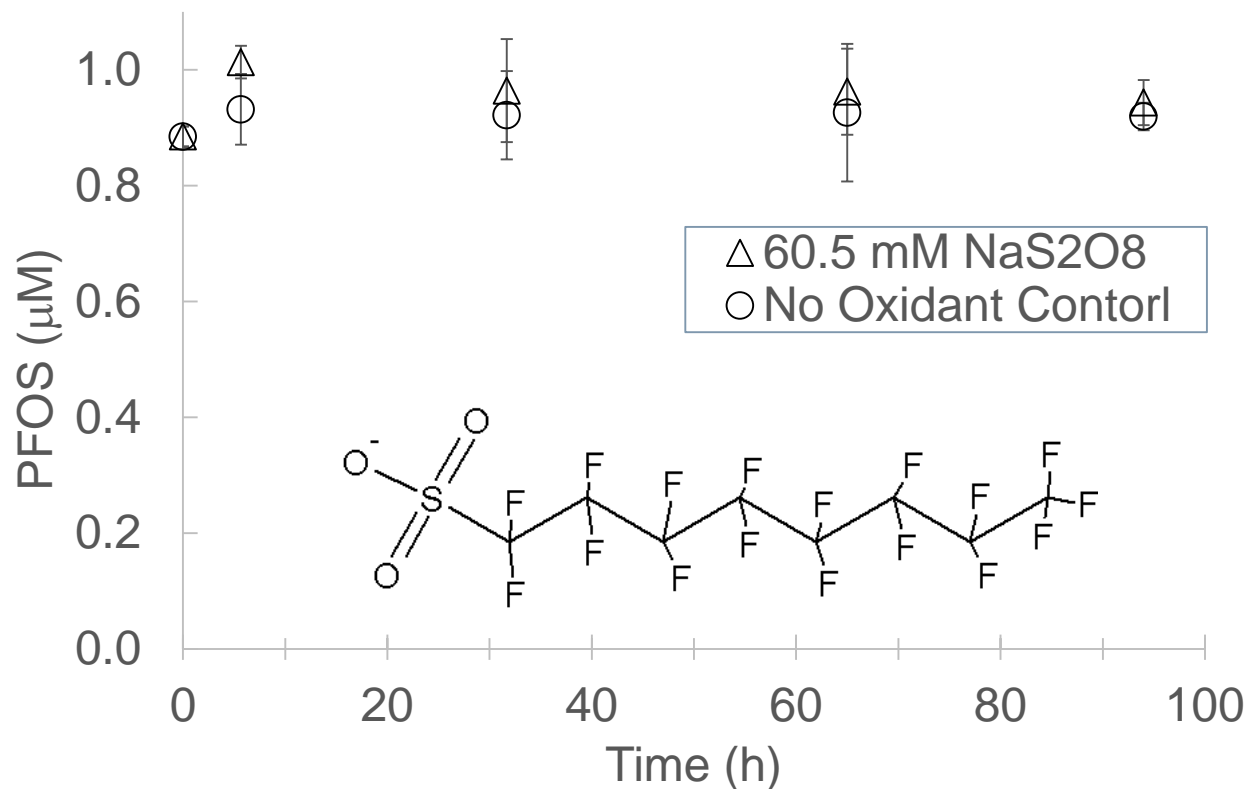
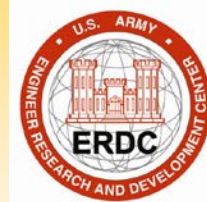


- PFOA and 6:2 FTS unzipped to smaller PFCAs
- Eventually complete abiotic mineralization ( $\text{F}^-$  and  $\text{CO}_2$ )
- Co-contaminants (@ 1000 mg/L) - PFAS degradation NOT affected



# Heat-Activated Persulfate

## PFOS (100 $\mu\text{g/L}$ )

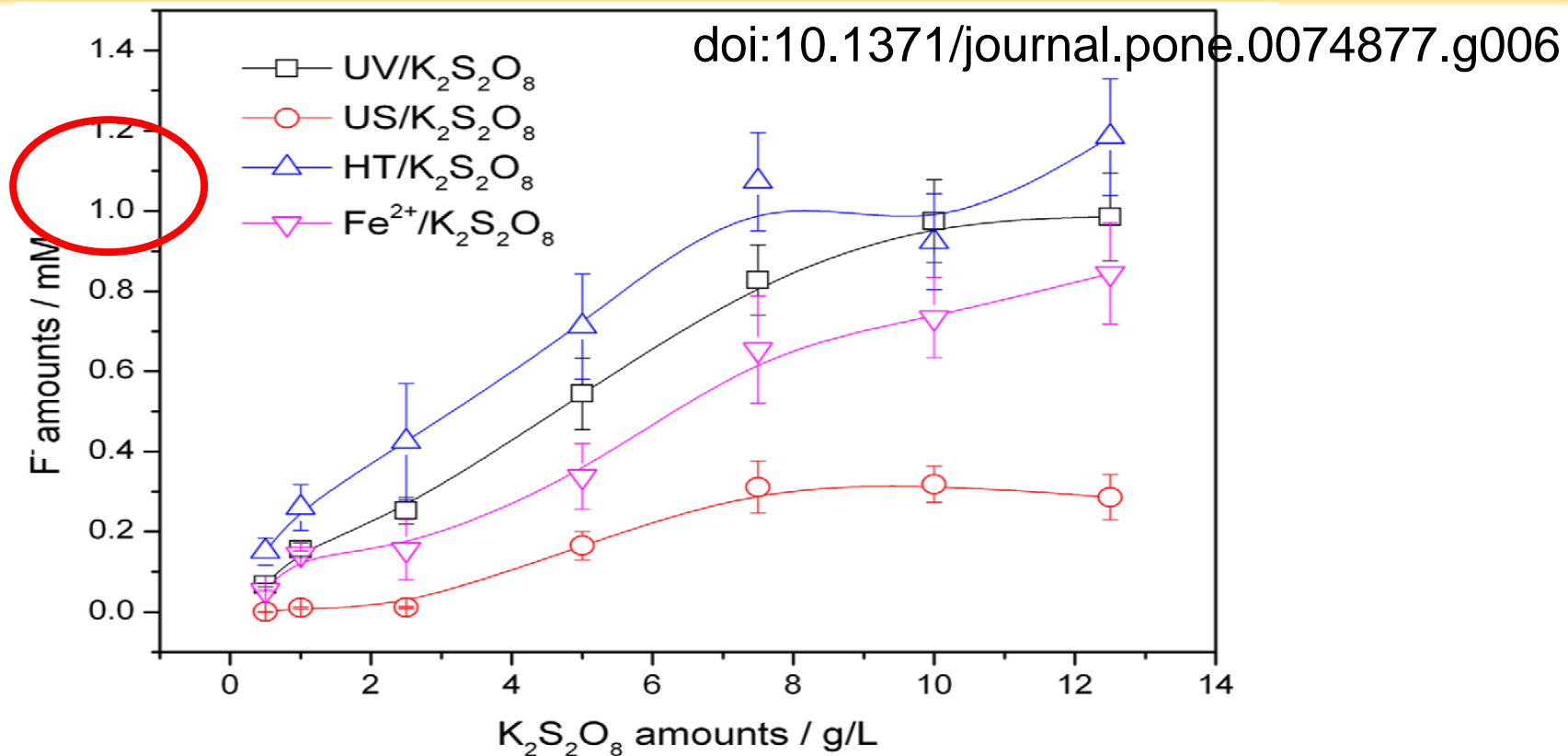


- PFOS unaltered at 90 C with 60.5 mM  $\text{Na}_2\text{S}_2\text{O}_8$  as well as at 90 C with 84 mM  $\text{Na}_2\text{S}_2\text{O}_8$
- PFOA & PFOS will coexist in groundwater, thus technologies that can remediate both are needed



# Persulfate Oxidation - Yang et al. (2013)

## 100,000 $\mu\text{g/L}$ PFOS (0.2 mM)



- High PFOS concentration (0.2 mM PFOS = 3.4 mM Fluoride)
- High persulfate concentration and no controls presented
- Hydrothermal (HT) – high temperature and pressure
- Other literature: Kingshott (2008) Thesis – probing using reactant concentrations approaching solubility limits



# Method Development

## Approach for successful exploration requires:

- Accurately quantify target parent PFAS (and isomers)
  - High extraction efficiencies of all phases
  - Reliable chromatographic separation and detection
- Accurately quantify fluoride and sulfonate metabolites
  - Above background noise
  - Optimize nanocomposite synthesis to minimize background
  - Minimize analytical matrix effects
  - High extraction efficiencies and appropriate analytical methods
- Identify organic metabolites and quantify if possible
  - TOF, MS/MS probing of aqueous and extractants
  - Headspace sampling (requires airtight reaction vessel)

**Analytical methods are treatment technique dependent**

# Reductive Approaches: Literature

- ❖ **UV (254 nm) photolysis**- generated aquated electrons ( $e_{aq}^-$ ) from iodide ( $E_o = -2.9$  V) (*Park et al., 2009*)
  - PFOS degraded faster than PFOA (under argon atmosphere)
  - Not applicable for in situ
- ❖ **Vitamin B<sub>12</sub>** (*Ochoa-Herrera et al., 2008*) 
  - Successful for only branched PFOS isomers, but not linear chain
- ❖ **Boron Doped Diamond Electrode** (*Carter and Ferrell, 2008*)
  - Some success for PFOS
  - Very expensive
  - Not applicable for in-situ
- ❖ **Zero Valent Iron (ZVI)** ( $E_o = -0.447$  V) (*Hori et al., 2005; 2008*) 
  - Degraded PFOS at high T & high pressure (→ near supercritical)
- ❖ **Electrochemical** (*Schaefer et al., 2015, J Hax. Materials*)

**Theoretical and experimental evidence: PFOS is amenable to reduction. Need: Enhance reactivity and delivery**

# Our Current Research Questions

- What **extent** of reductive transformation especially of linear PFOS can be achieved with the primary reductive techniques proposed?
- What are the **intermediates** of PFCAs and PFSA's defluorination using the proposed reductive techniques?
- How is reductive transformation affected by various **solution parameters** (pH, electrolyte composition, redox potential) and co-contaminants likely to be associated with AFFF-contaminated groundwater at military sites?
- How does the presence of **porous media** affect defluorination potential and reductant reactivity?
- How amenable are intermediates to other remediation processes (**treatment train potential**)?

# Reductive Approaches Probed to Date

- Metals

- nZVI – *not successful by itself*
- nZVI/Pd as a function of % Pd, initial pH, temperature
- nZVI/Pd/Al
- nZVI/Ni with GO or GAC
- Mg/Pd

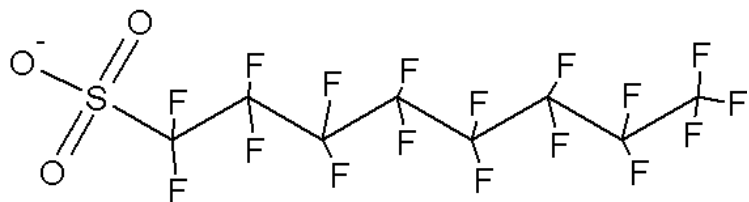
- Enhanced delivery

- Fe<sub>3</sub>O<sub>4</sub> composites
- Deposit reactive metals within clay layers
- Organo-bentonite

- Vitamin B12 with

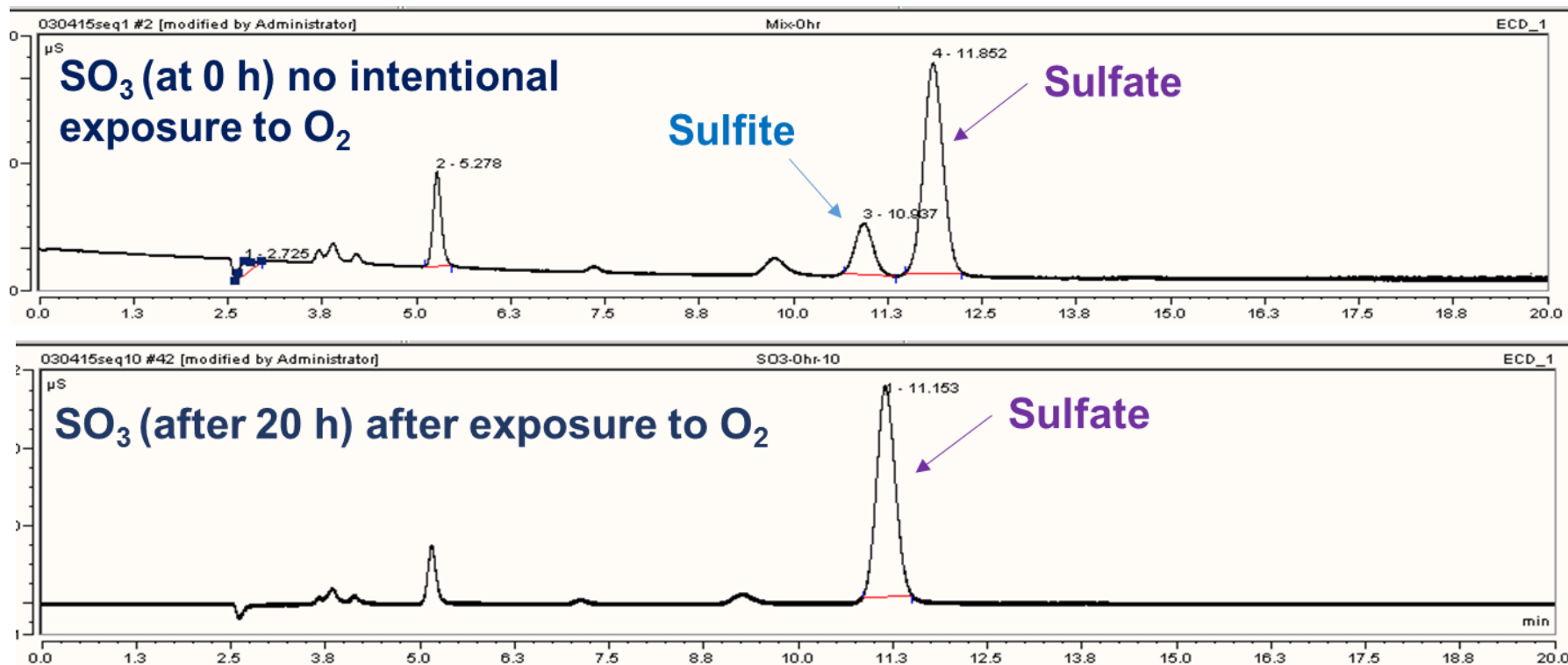
- Ti-citrate
- Cu
- n-ZVI
- n-ZVI/Pd

# Expected Inorganic Metabolites



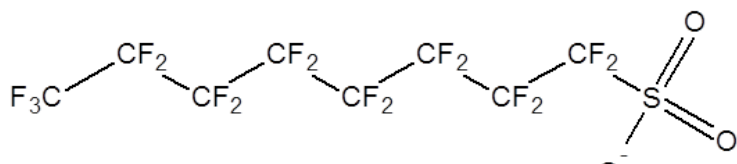
$\text{F}^- + \text{SO}_3^{2-} +$   
*per/poly*-fluoroalkanes +  
*Poly*-fluoroalkyl sulfonates

❖ Any sulfite generated expected to rapidly convert to sulfate:

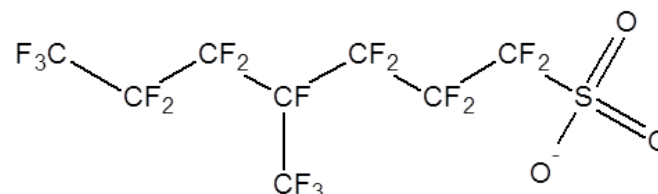


Consistent with Literature: Sulfite oxidation rate = 0.009 /h (Shizuo Tsunogai, 1971)

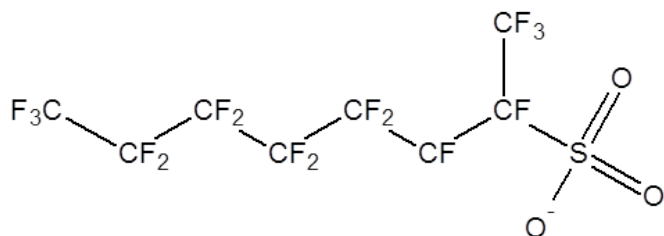
# PFOS Isomers in Technical Grade PFOS & Formulations



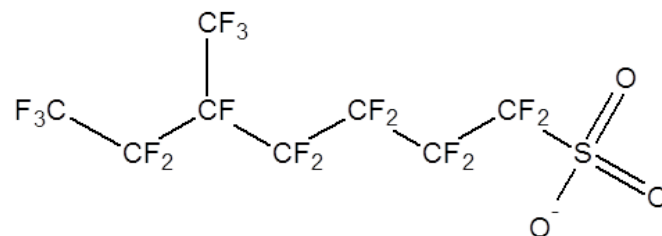
**Linear 65-75%**



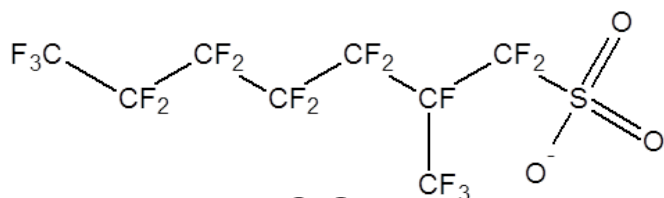
**4-PFOS**



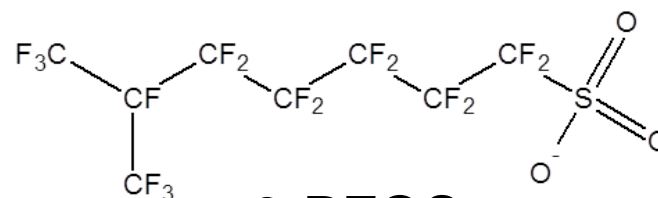
**1-PFOS**



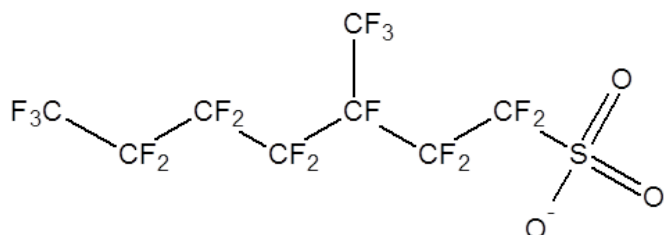
**5-PFOS**



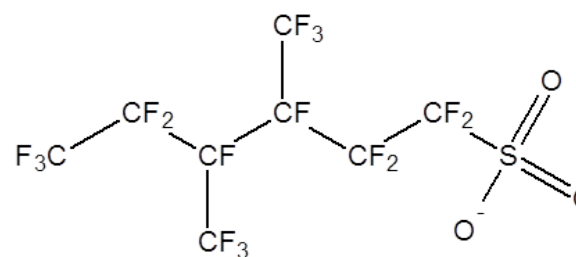
**2-PFOS**



**6-PFOS**

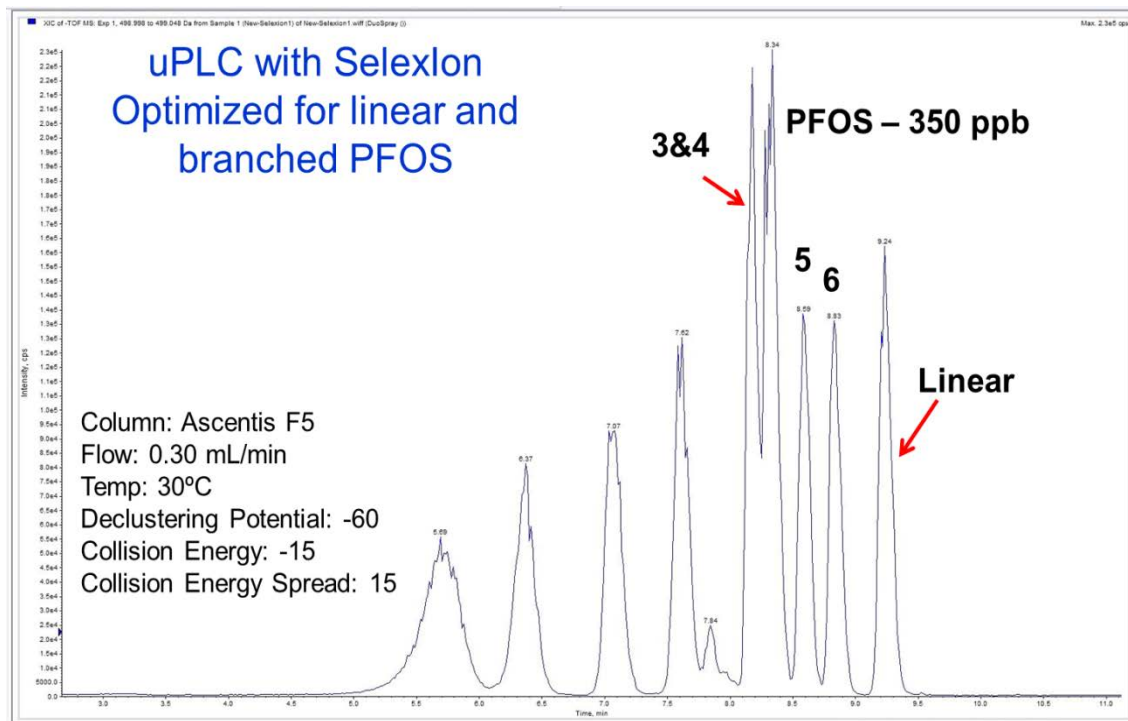
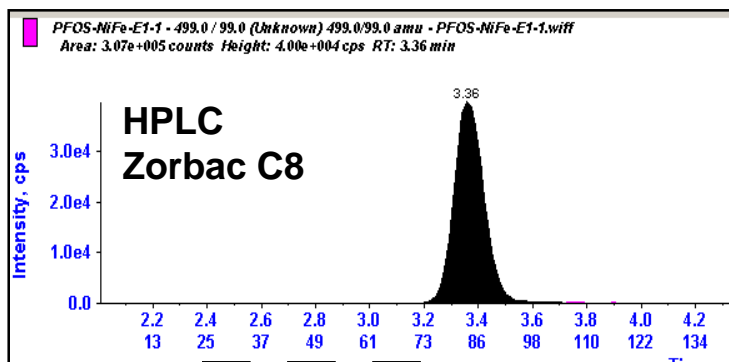


**3-PFOS**



**dm-PFOS**

# Isomer Separation and Response Optimization



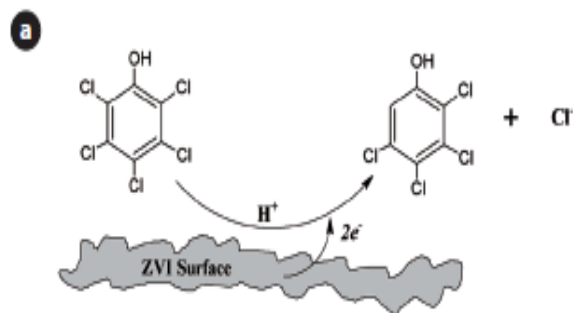
- Standard analyses – all isomers elute in one peak
- Ascentis F5 allows for isomer separation
- Selexion allows for enhanced response to each isomer



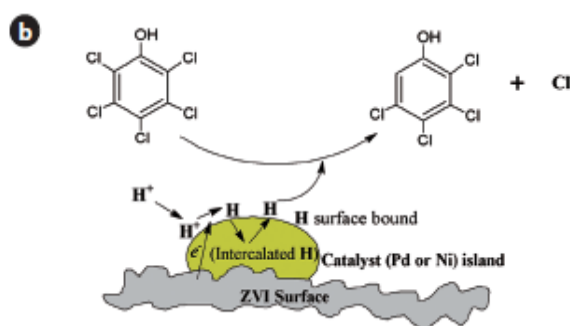
# Why nZVI Systems?

- ZVI is a potent reductant ( $E_o = -0.447 \text{ eV}$ )
- Nano-sized ZVI (nZVI) - high surface area (40~60 m<sup>2</sup>/g)
- Cost-effective (low installation and operation cost)
- Low environmental impact and low toxicity
- nZVI can be doped with a catalyst such as Pd, Pt, Cu, Ni and Ag to improve the reactivity.
- Successful for dehalogenation of chlorinated alkenes, alkanes, and PCBs

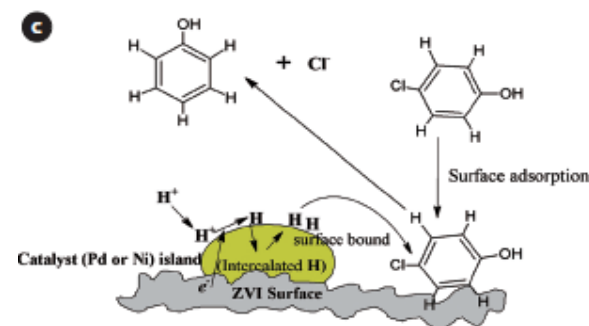
## ❖ Mechanisms of contaminants (e.g. chlorinated solvent) removal



a) Direct electron transfer

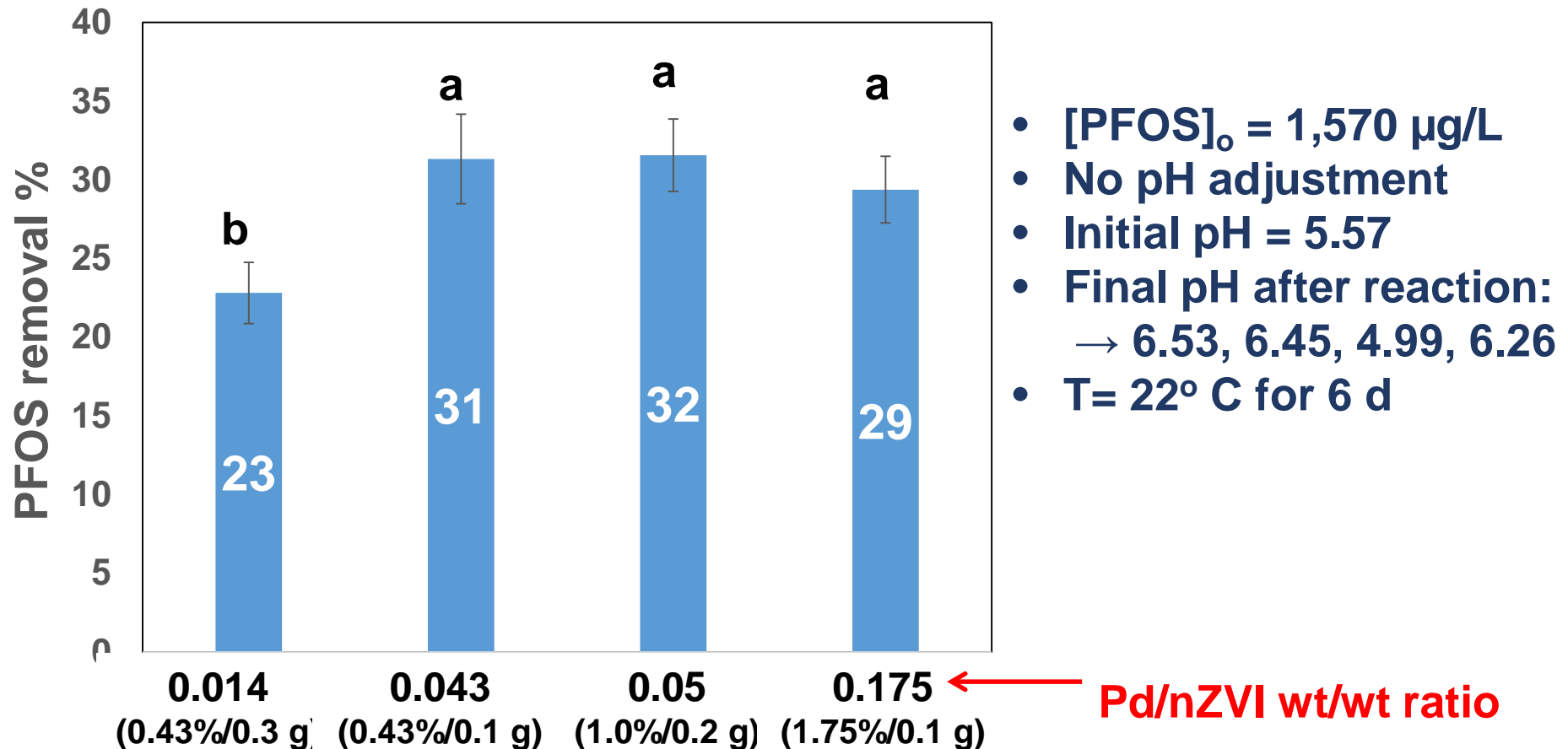


b) Hydro-defluorination onto the catalyst surface



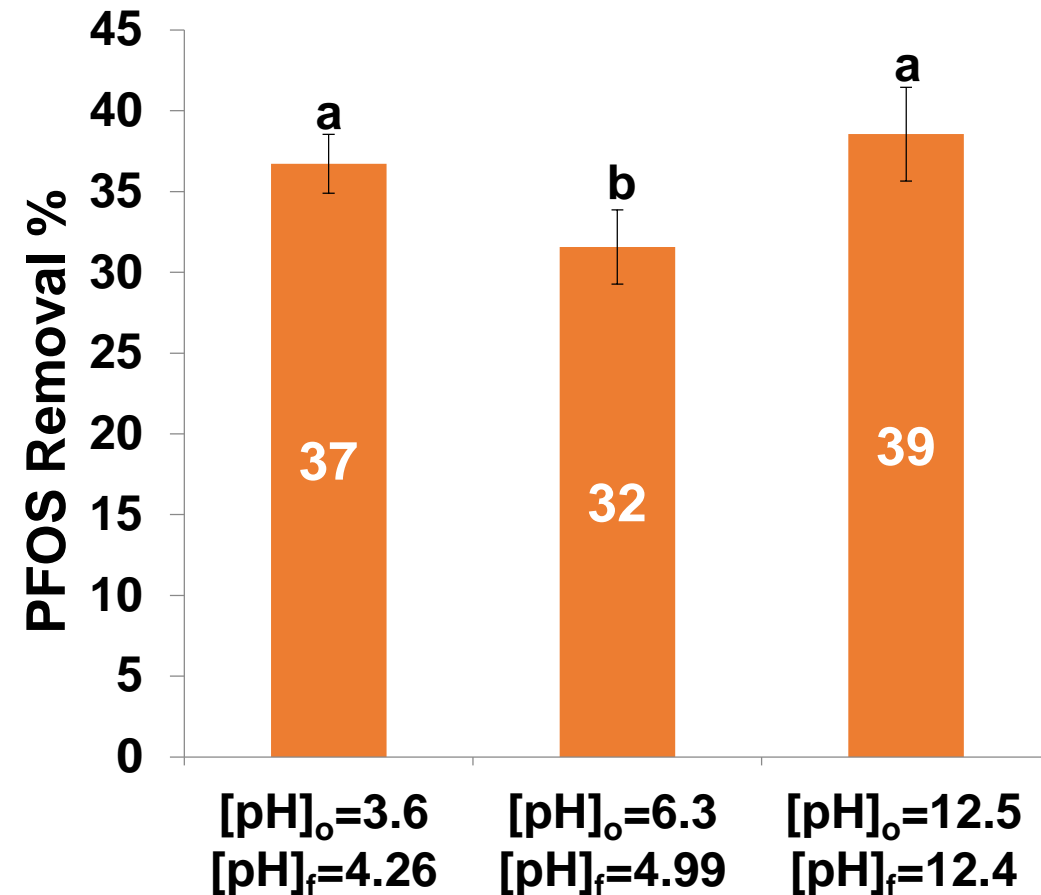
c) Hydro-defluorination onto the nZVI surface

# Effect of %Pd and Mass of Bimetal



- For  $\text{Pd/Fe} \geq 0.043$ , no significant difference on PFOS removal.

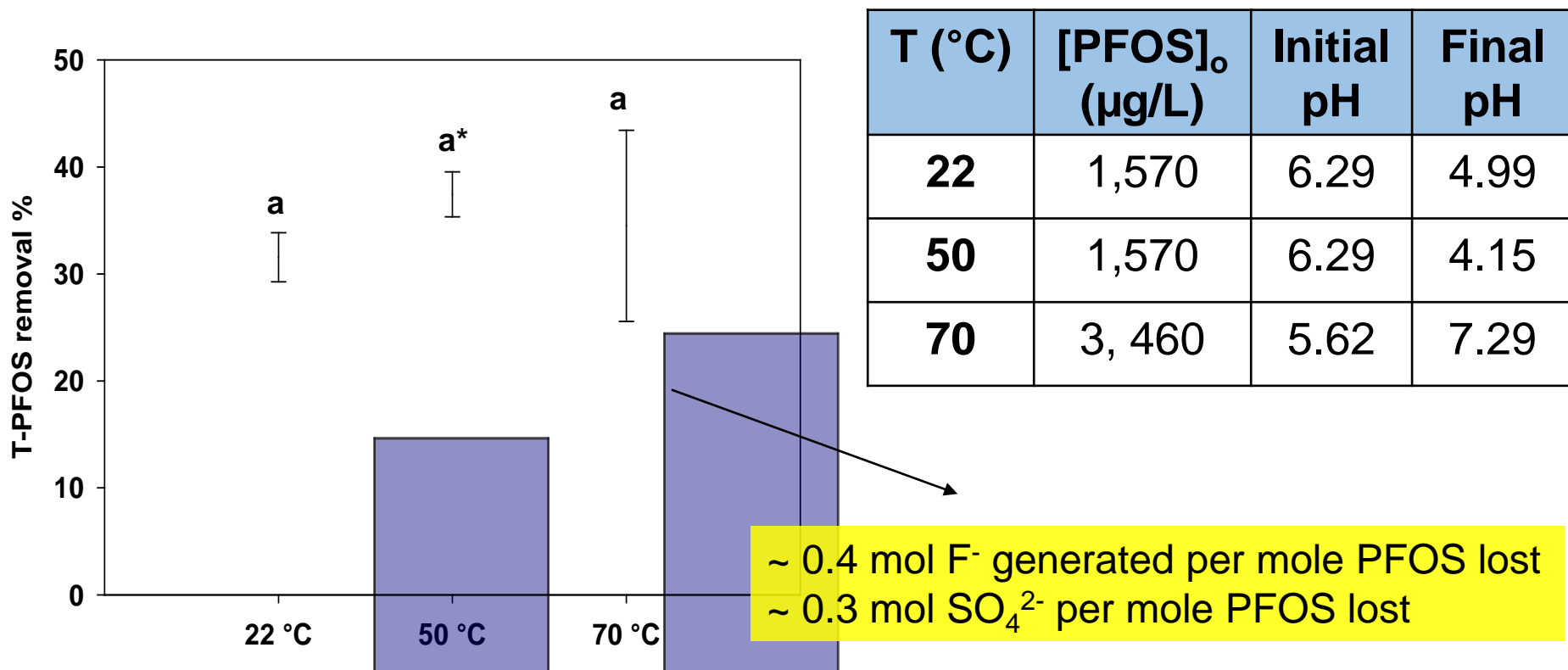
# Effect of Initial pH with Pd/nZVI



- [PFOS]<sub>o</sub> = 1,570 µg/L
- 1% Pd/0.2 g nZVI
- pH adjusted with HCl or NaOH
- T= 22 °C for 6 d

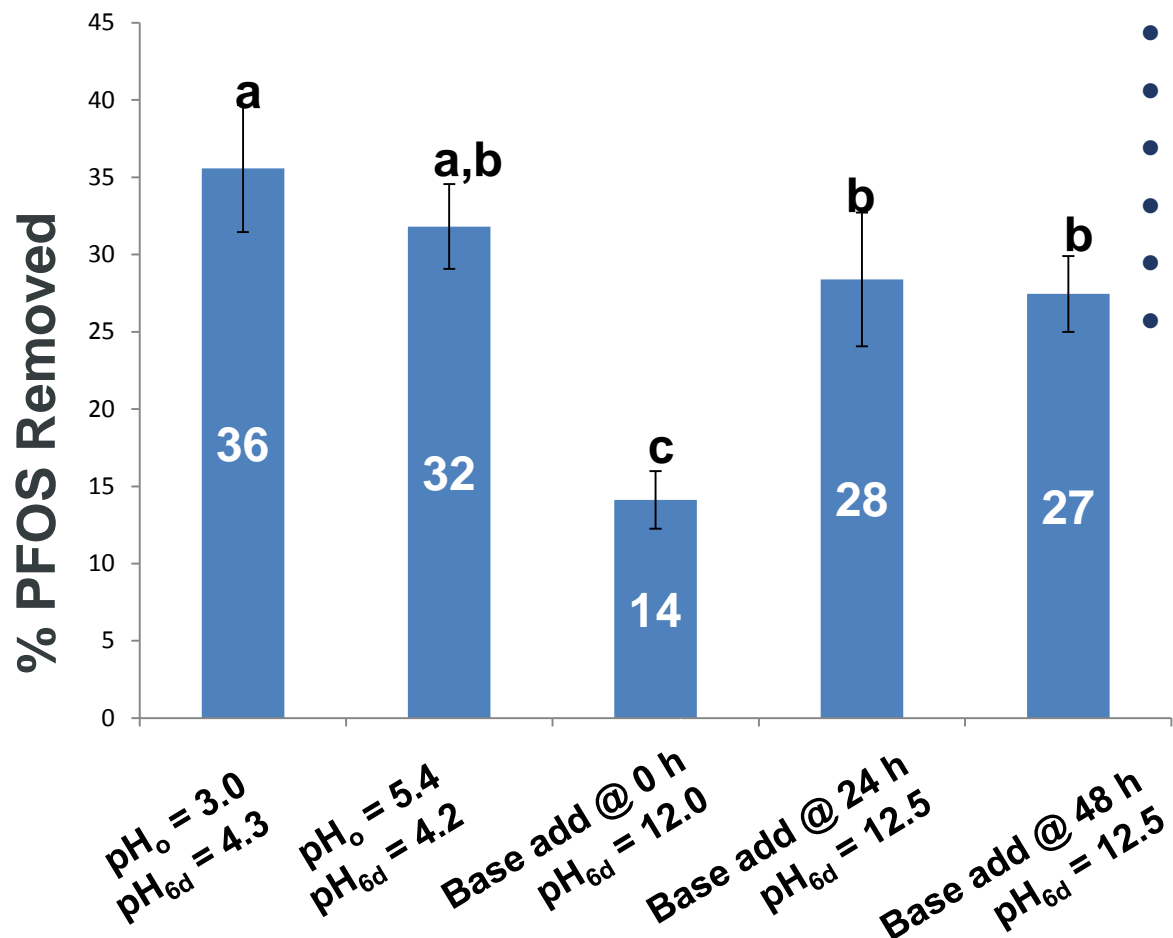
- Acidic and basic initial pH had highest and similar PFOS removal.
- Removal lowest at near neutral pH condition.

# Temperature Effect with Pd(1%)/nZVI (0.2 g)



Role of temperature not clear

# pH Effect with Pd/Fe/Al Trimetal



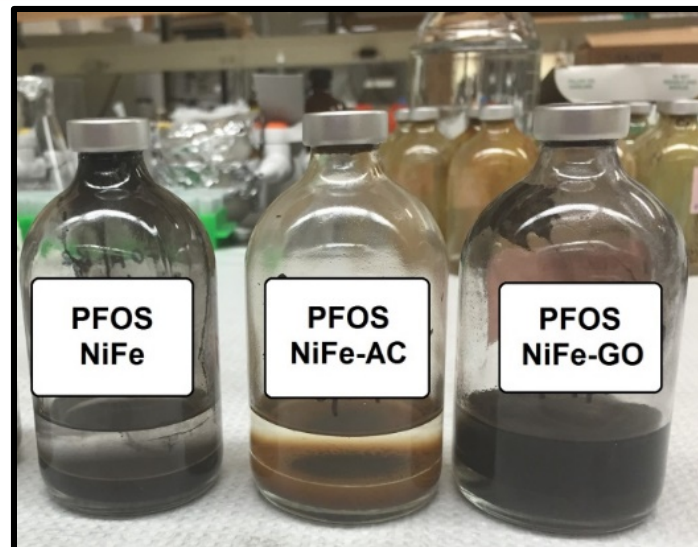
- [PFOS]<sub>0</sub> = 880 µg/L
- 1% Pd/0.5g of Fe/Al
- pH adjusted with HCl/NaOH
- Base added at 0, 24, and 48 h
- T = 22 °C
- Reacted for 6 d

- Initial high pH slowed/reduced PFOS removal likely due to  $\text{Al}(\text{OH})_4^-$  formation
- Reaction appeared complete by 24 h

# Ni-nZVI

## Method

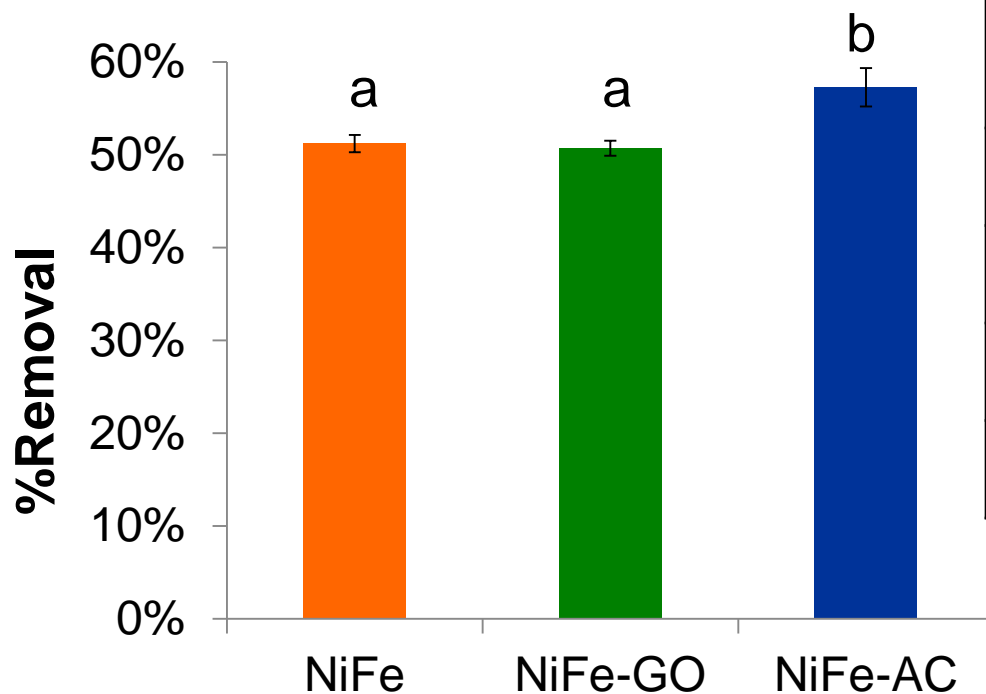
- Ni content over  $\text{Fe}^0$  was 1.8 wt%.
- Batch experiments were carried out in triplicates for:
  - ✓ Ni/Fe
  - ✓ Ni/Fe-Graphene (NiFe-GO)
  - ✓ Ni/Fe-Activated Carbon (NiFe-AC)
- 0.2 gr was added to each replicate and matrix. Both were mixed for 3 days.
- A blank containing 10 mL of PFOS (2 ppm) was carrying out together with all the samples.
- 4 extractions using ethyl acetate.



- pH shifts during reaction:

ID	NiFe	NiFe-GO	NiFe-AC
Matrix Day 0	7.21	7.71	7.70
Matrix Day 3	8.62	8.90	8.65
Day 0	7.39	7.17	7.95
Day 3	10.18	10.61	10.28

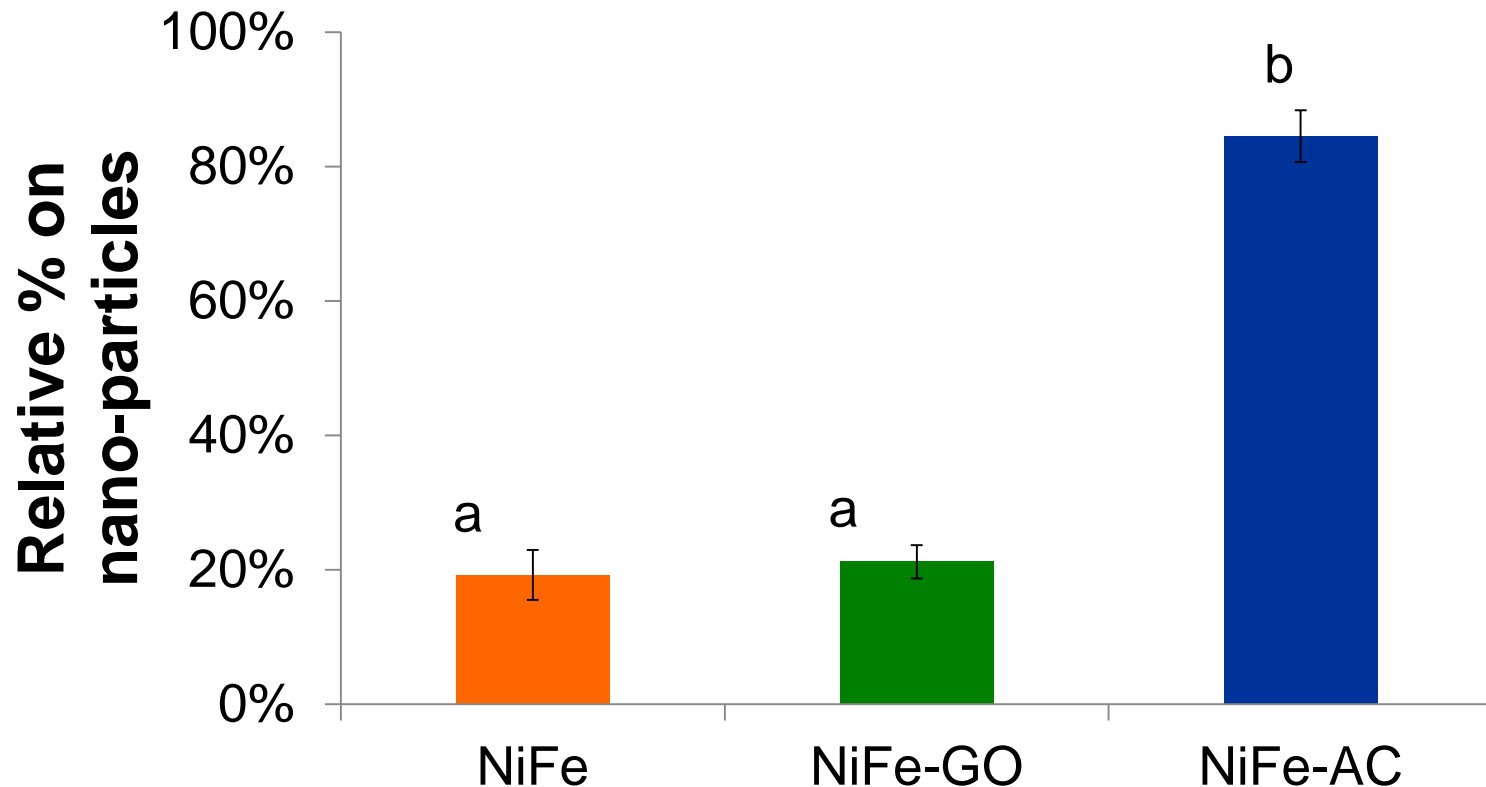
# Ni-nZVI



ID-Extract#	% relative to Sum recovered
NiFe-AC-E1	86
NiFe-AC-E2	9.7
NiFe-AC-E3	2.8
NiFe-AC-E4	1.6

- 51% to 57% PFOS not recovered so assume 'transformed'
- Four extractions was found sufficient for PFOS from nZVI particles
- Apparent higher loss for Ni-nZVI on activated carbon may be extraction efficiency issue – now using 5 extractions

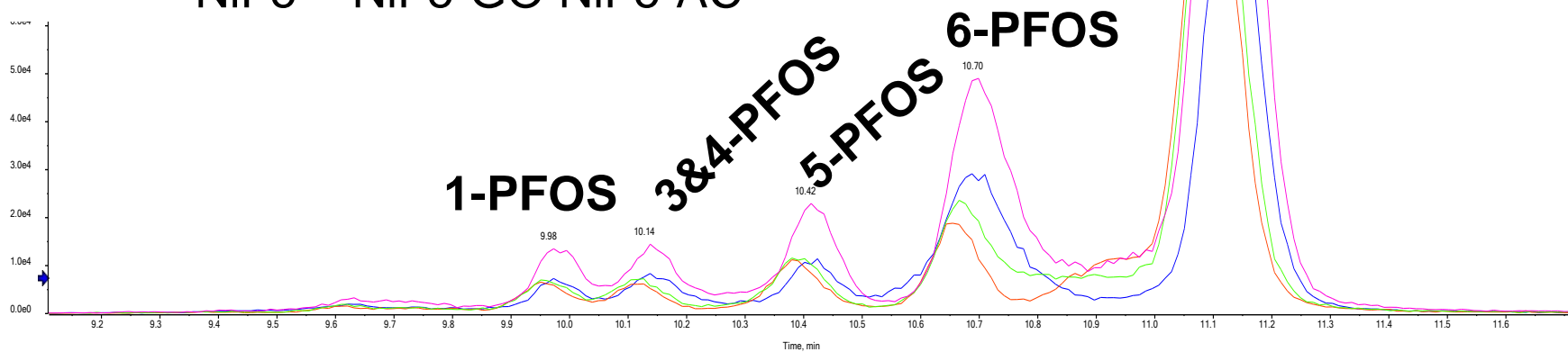
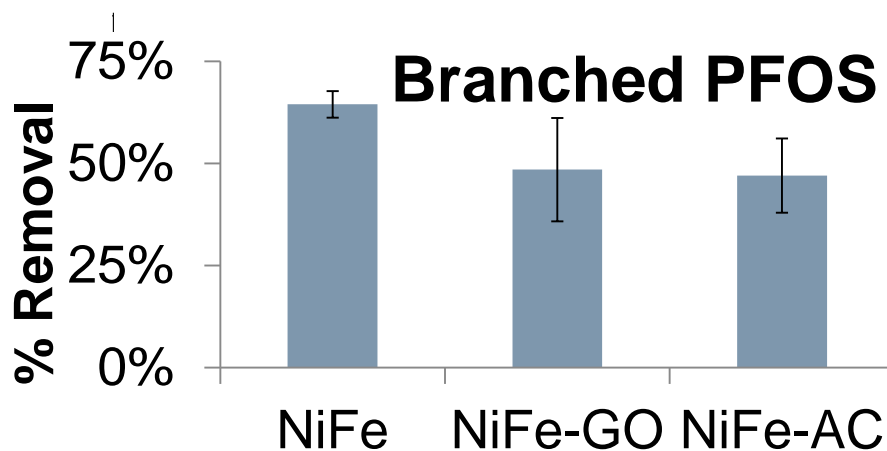
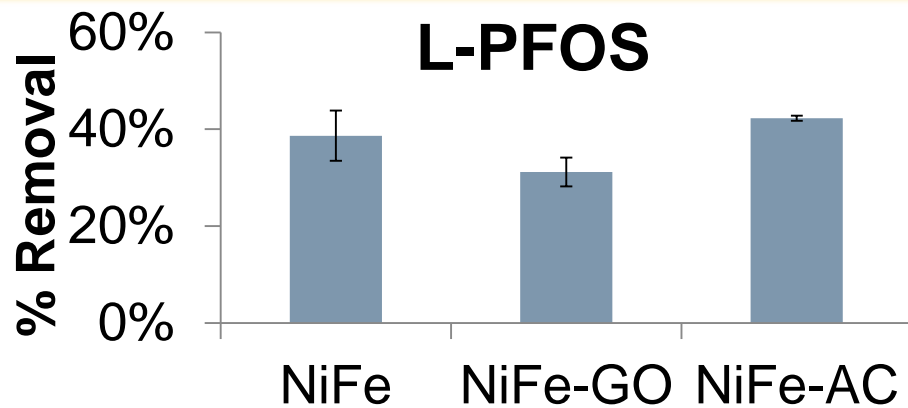
## **% Extracted from Ni/nZVI particles versus in Aqueous Phase**



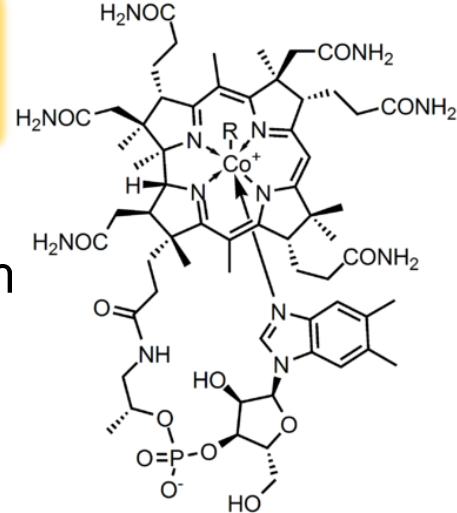
- More associated with NiFe-AC particles (~85%).
- Significant differences were observed on NiFe-AC compared to NiFe ( $P < 0.0001$ ) and NiFe-GO ( $P < 0.0001$ )



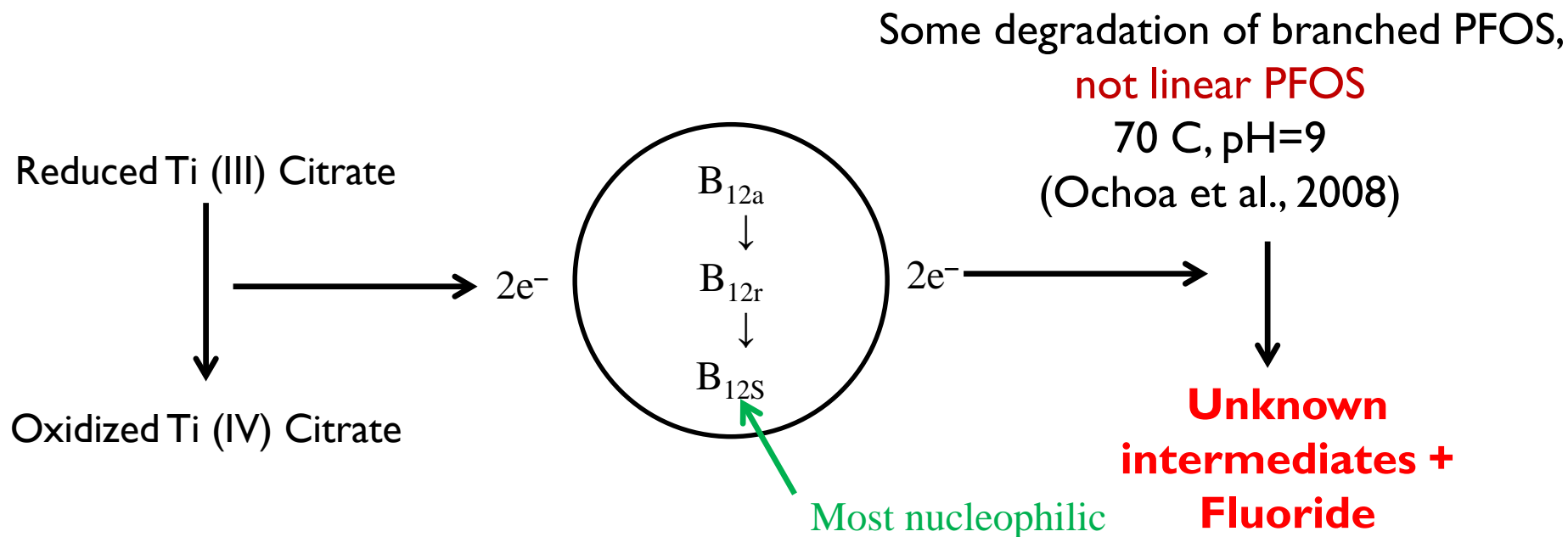
# Isomer-specific Removal



# Why Vitamin B<sub>12</sub> Systems?

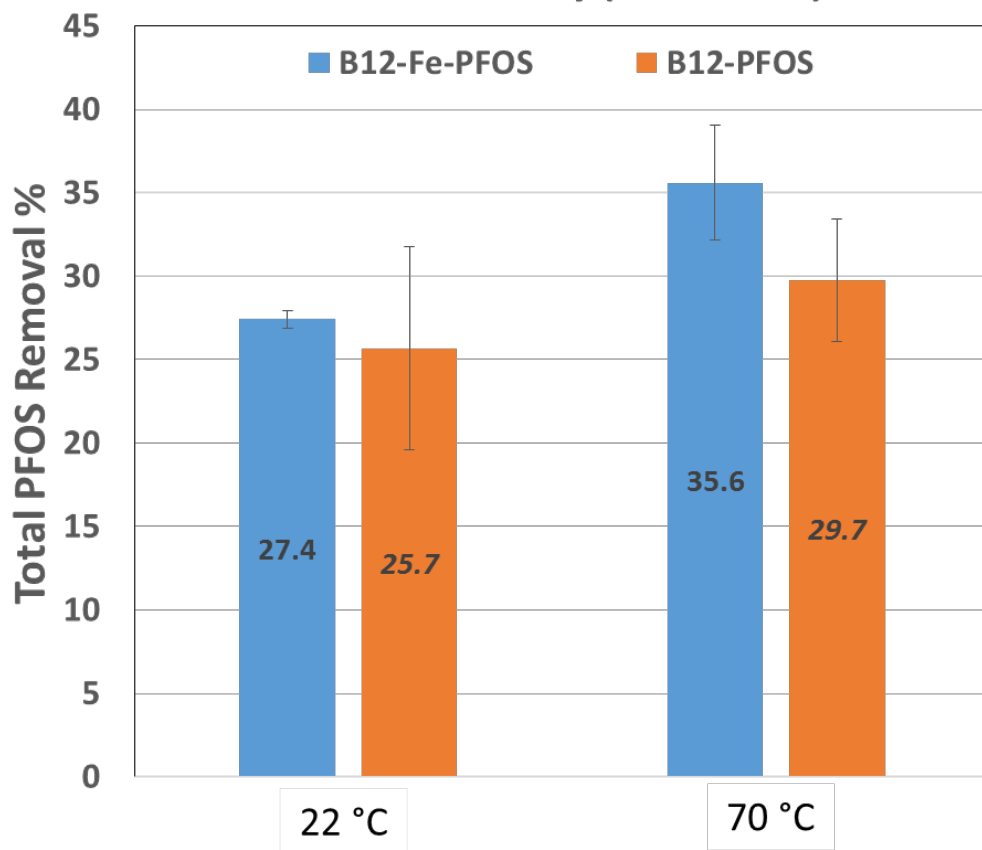


- Vitamin B<sub>12</sub> (cyanocobalamin) is produced by anaerobic bacteria contains a corrin ring that coordinates a cobalt atom
- Cobalt center of V-B<sub>12</sub> can exist in 3 oxidation states (B<sub>12a</sub>, B<sub>12r</sub>, B<sub>12s</sub>)
- Electrons transferred from reduced metal (Ti exemplified below but also assessed with other metals) to the contaminant

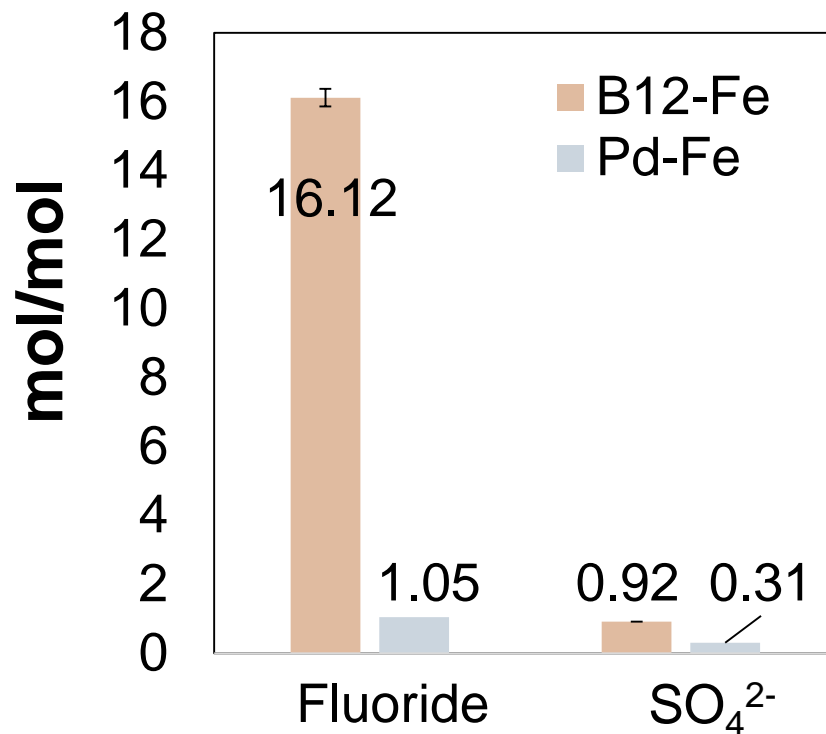


# Vitamin B12 (0.4 mM) + n-ZVI (0.2 g)

B12-Fe kinetic study (22 & 70 °C) data

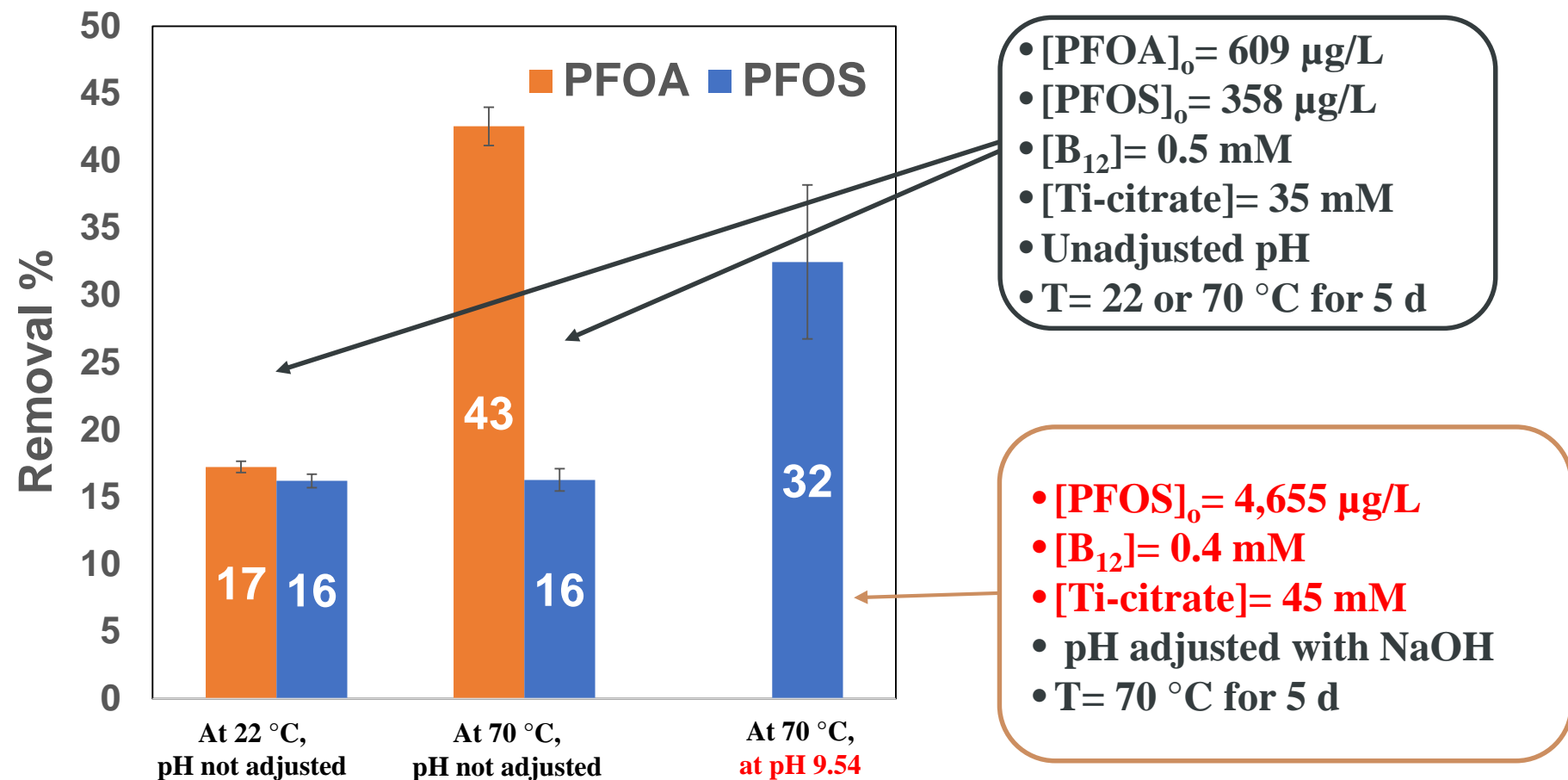


F<sup>-</sup> or SO<sub>4</sub><sup>2-</sup> / PFOS removed (Comparing 2 systems)



- Similar PFOS removal in both systems
- Inorganic metabolite production varies
- Organic metabolites also appear different

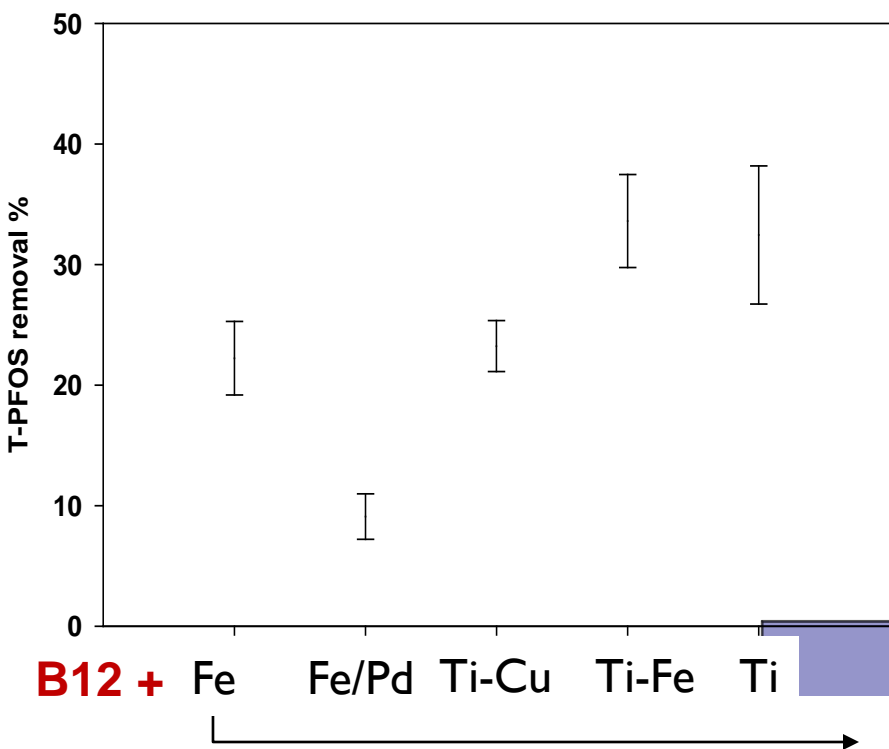
# Effect of Temperature and Initial pH for B<sub>12</sub>+ Ti System



- Heat enhanced only PFOA removal
- At T=70 °C, PFOS removal increased with increase in initial pH

# Effect of $\text{Cu}^\circ$ , $\text{Pd}^\circ$ or $\text{Fe}^\circ$ in $\text{B}_{12}$ - Ti system

$[\text{PFOS}]_0 = 4,655 \mu\text{g/L}$ ,  $T = 70^\circ\text{C}$ , Reaction = 5 d

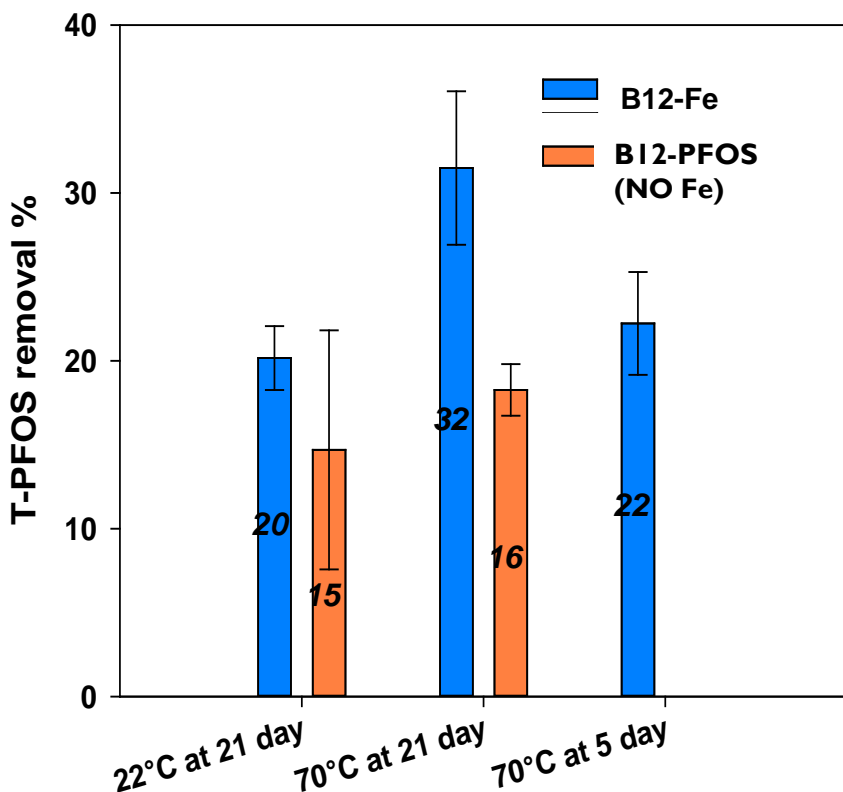


Treatment	[pH] <sub>o</sub>	[pH] <sub>f</sub>
B12-Fe	10.41	8.03
B12-Pd/Fe	10.41	7.61
B12-Ti-Cu	9.54	6.86
B12-Ti-Fe	9.54	9.23
B12-Ti	9.54	6.03

10-14 mol  $\text{F}^-$  generated per mole PFOS lost  
~ 0.7 mol  $\text{SO}_4^{2-}$  per mole PFOS lost

- Addition of  $\text{Fe}^\circ$  (as an electron donor) to  $\text{B}_{12}+\text{Ti}$  systemt did not enhance PFOS removal.
- Addition of  $\text{Cu}^\circ$  or  $\text{Pd}^\circ$ (as a catalyst) to  $\text{B}_{12}$ -Ti-citrate system decreased PFOS removal.
- In Ti-system, high  $\text{Cl}^-$  concentration interfered with  $\text{F}^-$  quantitation.
- $\text{B}_{12}+\text{Fe}$  system,  $\text{F}^-$  and  $\text{SO}_4^{2-}$  were detected indicating partial reduction.

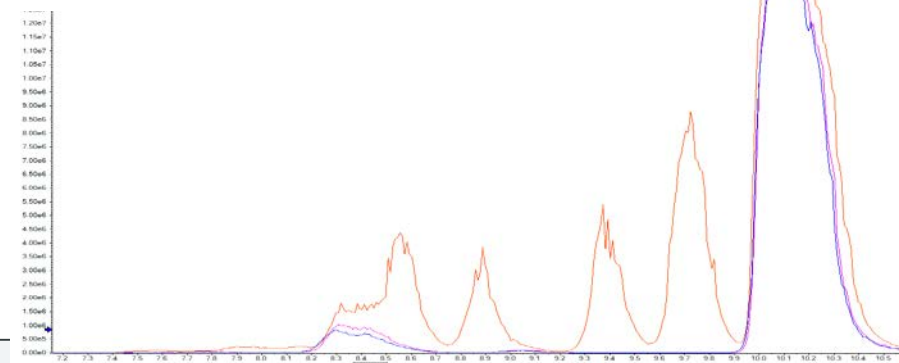
# Effect of Temp. in B<sub>12</sub> (0.4 mM) + nZVI (0.2 g) System



Sample ID	[pH] <sub>o</sub>	[pH] <sub>f</sub>
22 °C at 21 d	10.51	9.89
70 °C at 21 d	10.51	6.67
70 °C at 5 d	10.41	8.03
B12-PFOS (no Fe)	10.51	9.14 (22 °C) 7.52 (70 °C)

PFOS isomers Chromatographs in B<sub>12</sub>-Fe at 70 °C (in Aqueous phase)

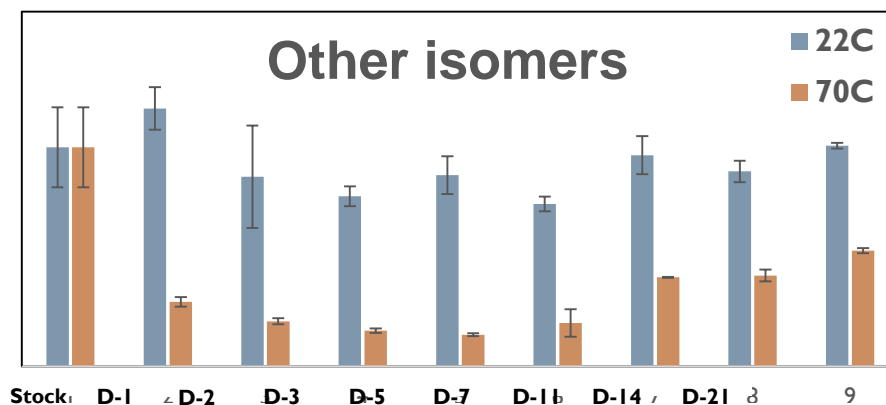
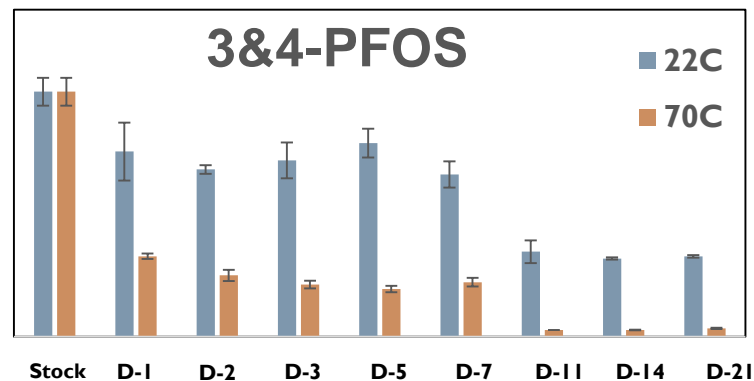
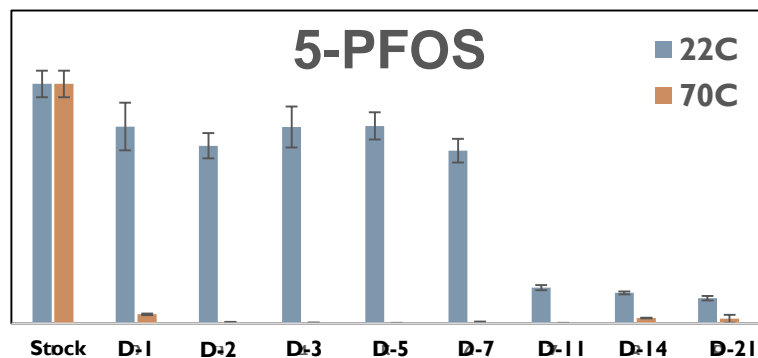
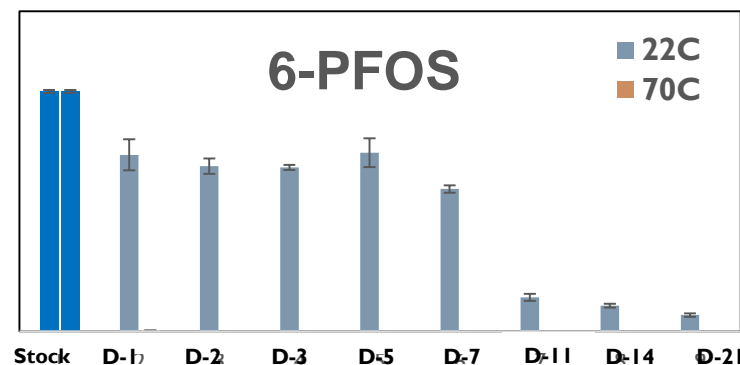
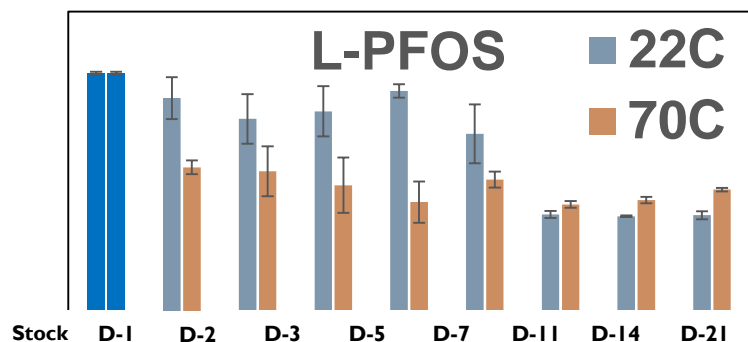
→ Stock, D-14, and D-21



- PFOS removal increased with temperature .
- At 70 °C, PFOS removal continued to increase from 5 to 21 days.
- Most degraded PFOS is branch-PFOS.
- PFOS removal in only Vitamin B12 (no metals to enhance electron shuttle) unexpected.

# Isomer-Specific Peak Comparison for B12-nZVI

RELATIVE to STOCK



TIME (d)

# Organic Metabolites

- **LC/MS-ESI/TOF (and GC/MS Orbitrap forthcoming)**
- Several metabolites produced not in controls
- Expect some perfluoroalkyl alkane/alkenes
- Currently using a mass defect approach to identify metabolite
- **Example: Peaks in Ni/nZVI Treatment Systems:**
  - **Positive Mode**
    - 4 similar peaks observed in all systems
    - One additional peak in graphene oxide (GO) system
  - **Negative Mode**
    - 1 peak observed in all
    - Peak was different in activated carbon (AC) system



# Treatment Train Potential

- Many combinations have been used in field applications
  - ZVI-type treatment zone coupled to natural or enhanced anaerobic treatment zone
  - ISCO treatment zone coupled to enhanced or natural aerobic degradation
  - Aerobic degradation treatment zone coupled to an anaerobic abiotic (ZVI) or bioremediation (biowall) treatment zone
- One treatment can 'soften' a compound to be amenable to natural anaerobic or aerobic degradation and/or to a subsequent chemical treatment.
- At many of the sites where PFASs exist, redox conditions may already be depleted in  $O_2$  (redox range -100 to -250 mV) due to degradation of fuel and other easily biodegradable contaminants.
- Order and placement of treatment train for PFASs depends on proximity to source and contaminants present – precursor oxidation will lead to increased concentration of PFAAs.

# Current Use of Reductive Technologies in the Field

- ❖ Used for Cl-methanes, ethanes, and ethenes, chlorinated phenols, *PCBs*, *hexachlorocyclohexanes*, munitions, metals, nitrates, *perchlorate*
- ❖ *Permeable Reactive Barriers (PRBs)*
- ❖ *Reductions in the target zone of typically 50 to 90 percent*
  - *Treatment Trains*
  - *In-situ Injection*

Barrier Media	Superfund	Industrial	US Gov.	International	Total
ZVI	5	36	26	16	83
Non-Fe reactive materials	1	6	1	1	9
Bio-barrier	0	6	5	4	15
Combo/Sequenced (* ZVI)	0	4	2	0	6 (5*)

- ❖ Enhancing ZVI-based techniques
  - ◆ Nano-ZVI (nZVI) - *pilot & full-scale tests with nZVI1 shows 50-90% conc. reduction*
  - ◆ Surface coated/encapsulated nZVI-type particles (enhanced for in-situ injection)
  - ◆ Carbon/ZVI, C-rich organic/iron combinations (PRBs)
  - ◆ Emulsified ZVI, ZVI-clays, organophilic-ZVI clays (PRBs, in-situ injection)

# Take Home Messages

- **No magic bullet!**
- PFOS is the big challenge - more about steric hindrances
- Reductive approaches showing some promise for 'softening' PFOS (partial transformation)
- Linear PFOS remains the primary challenge – energetically the most stable and ~75% of what is in the environment
- Many published studies lack sufficient recovery efficiencies and background issues
- **We are not ready for any field-scale attempts for in-situ remediation due to**
  - Increasing PFAAs due to aerobic transformation of precursors – increased mobility
  - Unknown metabolites
  - Toxicity potential unknown or unclear for metabolites

# Co-investigators



## **Dr. Linda S. Lee (PI)**

Purdue University



ER-2426

Environmental Chemist; per/polyfluoro alkyl chemical fate expertise

## **Dr. Loring Nies**

Purdue University

Environmental engineering, biodegradation, nanoparticle

## **Dr. Victor Medina**

U.S. Army Engineering Research & Development Center

Chemical/metal remediation experience with military



## **Drs. Marc Mills & Kavitha Dasu\***

U.S. EPA, NRMRL



Fate/remediation expertise; \* PFAS fate/ analytical expertise (with PI)

## **Dr. Hongtao Yu**

Jackson State University

Chemistry/biochemistry; NSF-funded NMR Center



**Beneficial  
Technologies**

**Our challenge**

**Environmental  
Stewardship**



**Quality  
of Life**

