PFAS TREATMENT AND REMEDIATION WEBINAR: TREATMENT OPTIONS FOR SOIL & GROUNDWATER

MICHELLE CRIMI, PH.D.

ASSOCIATE PROFESSOR, INSTITUTE FOR A SUSTAINABLE ENVIRONMENT, CLARKSON UNIVERSITY

DECEMBER 14, 2016

Clarkson UNIVERSITY defy convention™

NEWMOA NORTHEAST WASTE MANAGEMENT OFFICIALS' ASSOCIATION

OBJECTIVES:

- **Summarize the challenges associated with treatment of PFAS-contaminated soil and groundwater**
- **Describe potential viable PFAS remediation approaches**

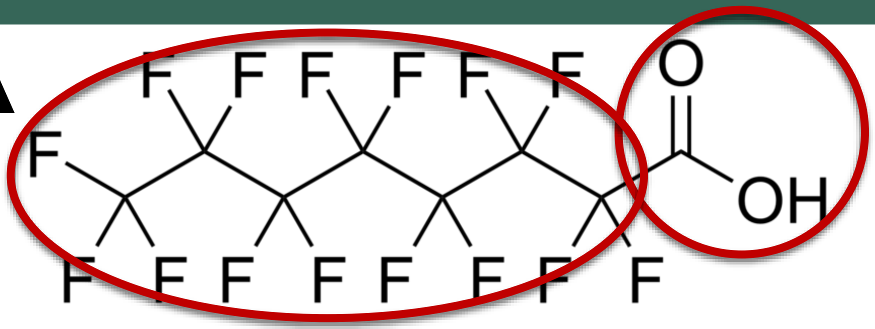
INTRODUCTION

- Perfluorinated Compounds
  - Perfluorinated alkyl acids (PFAAs)
    - PFOA
    - PFOS
    - PFBS
    - PFBA
    - PFHxA
    - PFHxS
  - Intermediates or Precursors
    - N-MeFOSE
    - N-EtFOSE
    - 6:2 FTS

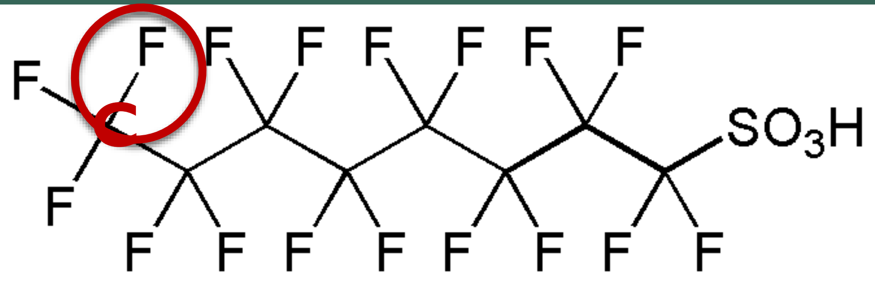
Guidelines (ng/L)					
	PHA	MN	NJ	NC	EPA (2016)
PFOA	400	300	40	2000	70
PFOS	200	200	n/a	n/a	

INTRODUCTION

PFOA



PFOS

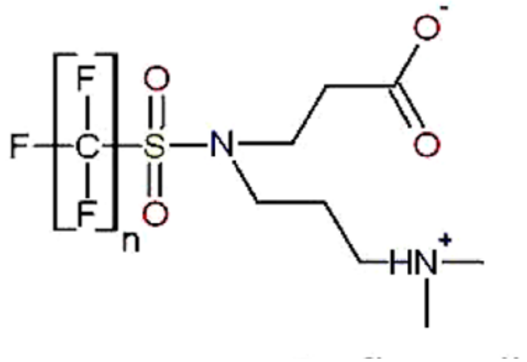


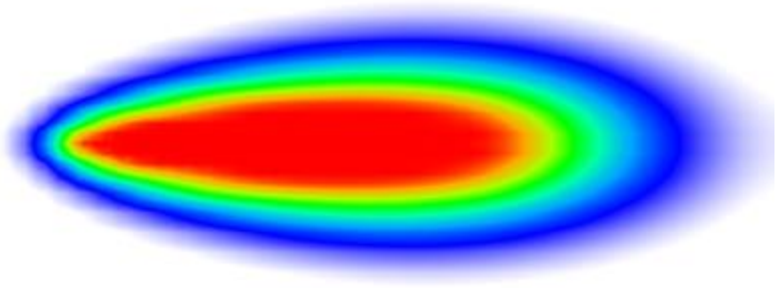
	Formula	Vapor Pressure	Aqueous Solubility	Log K_{oc}	Degradation
PFOA	$C_8HF_{15}O_2$	0.1 kPa (20°C) 10 mm Hg (25°C)	4.1 g/L (22°C) 9.5 g/L (25°C)	2.06	Stable
PFOS	$C_8F_{17}SO_3^-$	3.31 x 10^4 Pa at 20°C	570 mg/L	2.57	Stable
PFHxS	$C_6F_{13}SO_3$	0.61Pa (25°C)^{ES}	6.2 mg/L^{ES} 22 mg/L^{ES}	3.5^{ES}	Stable
PFBS	$C_4F_9SO_3$	0.29 mm Hg at 20°C	8900 mg/L^{ES} 344mg/L^{ES}	2.2^{ES} 1.9^{ES}	Stable
6:2 FTS	$F(CF_2)_6CH_2CH_2SO_3^-$	0.115Pa(25°C)^{ES} 0.00086 mm Hg (25°C)^{ES}	11 mg/L^{ES} 2mg/L^{ES}	4.0^{ES}	Biodegradable under specific conditions

ES = estimated from EPISuite (U.S. EPA http://www.epa.gov/opptintr/exposure/pubs/episuite.htm)

CHALLENGES

- Broad mixture
  - Can't even detect/quantify some of these
  - Range of properties with chain length and function group(s) – hydrophobicity, reactivity
  - Hydrophobic and electrostatic effects
    - Anionic PFAAs
    - Cationic or zwitterionic PFAS
  - Precursors → Compounds of concern
- Recalcitrant
  - Strong C-F bond
- Low volatility
- High solubility
  - Long plumes





REMEDIATION OPTIONS

- Excavation → Incineration
  - Expensive
  - Contaminants must be treated off site
- Immobilization/Stabilization
  - RemBind
    - Powdered reagent added directly to soil
  - matCARE
    - Modified clay
- Filtration
  - Nanofiltration
  - Reverse Osmosis

TREATMENT TRAINS and COMBINED REMEDIES!

- Sorption
  - Granular Activated Carbon (GAC)
  - Carbon nanotubes
  - Biomaterials
- Ion Exchange
  - Resins
  - Mineral materials (e.g., zeolites)
  - Polymers
- Chemical treatment
  - Chemical oxidation – single oxidant and oxidant mixtures
  - Electrochemical, sonochemical, and photochemical
  - Plasma
  - Customized reductants

SORPTION BY GAC

SORPTION – GAC

- SERDP ER-2423

Clarkson University defy convention

ARCADIS

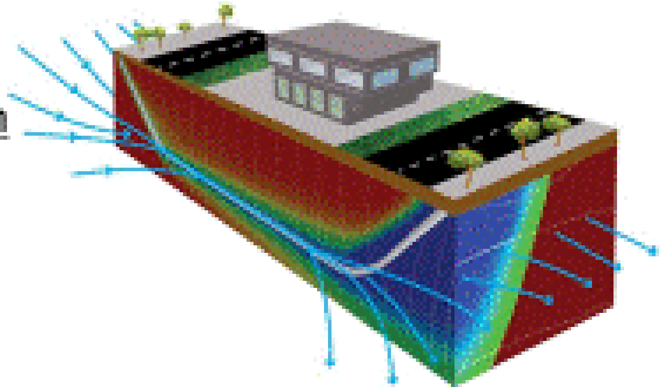
Southern Nevada Water Authority

Technical Objectives

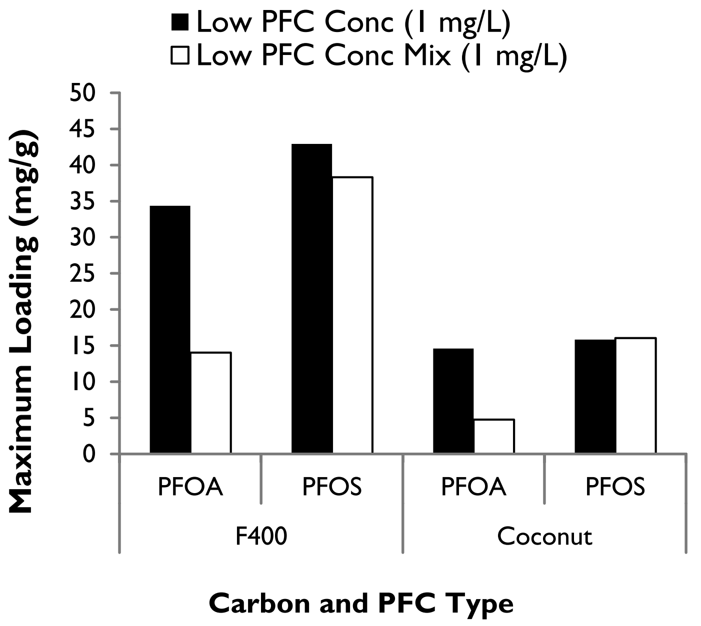
The objective of our research is to evaluate the *feasibility*, *effectiveness*, and *sustainability* of a treatment train approach:

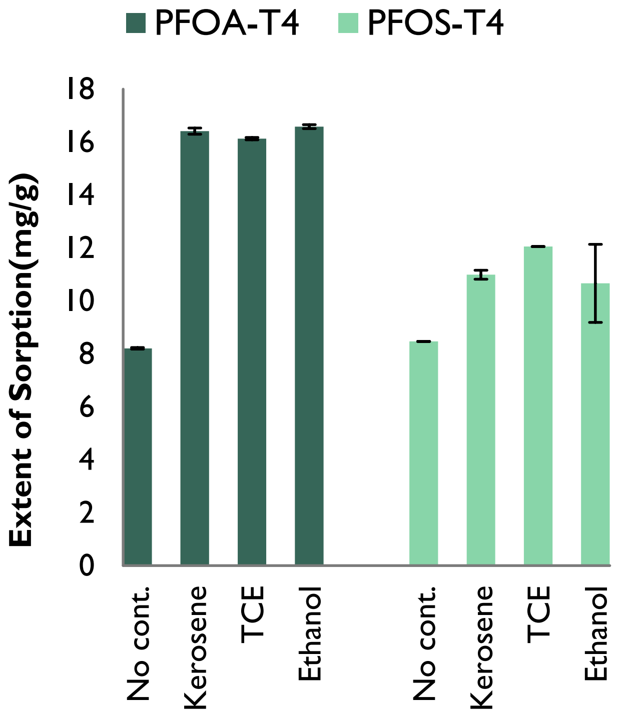
In Situ Chemical Oxidation of Sorbed Contaminants (ISCO-SC)

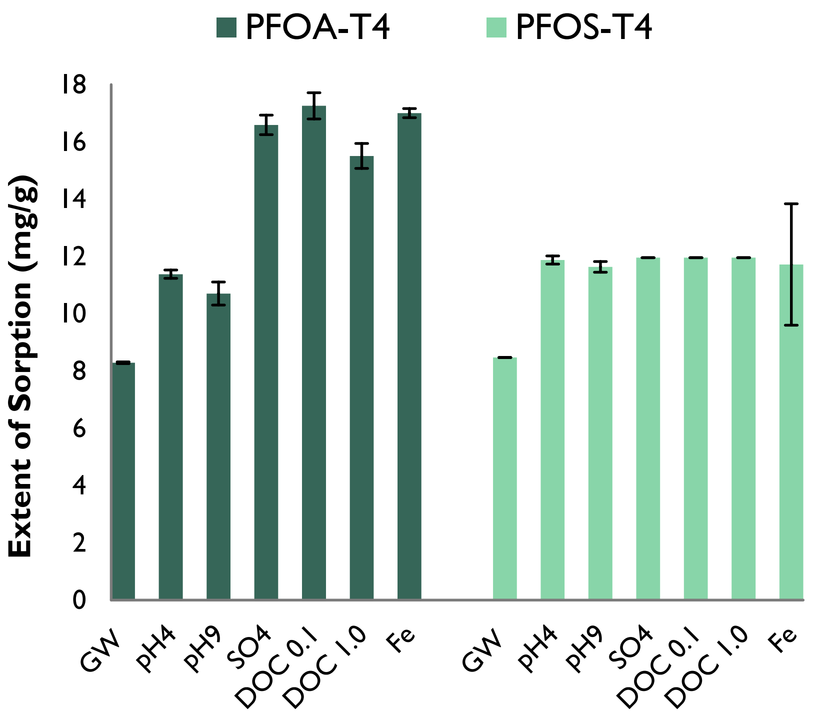
Activated carbon for *in situ* sorption and concentration of PFCs, followed by contaminant destruction and carbon regeneration by *in situ* chemical oxidation using activated persulfate



SORPTION – GAC







Sorption under site-specific conditions…

ION EXCHANGE

Sustainable Removal of Poly- and Perfluorinated Alkyl Substances (PFAS) from Groundwater Using Synthetic Media

Nathan Hagelin, Amec Foster Wheeler; Steve Woodard, ECT

Media Selection

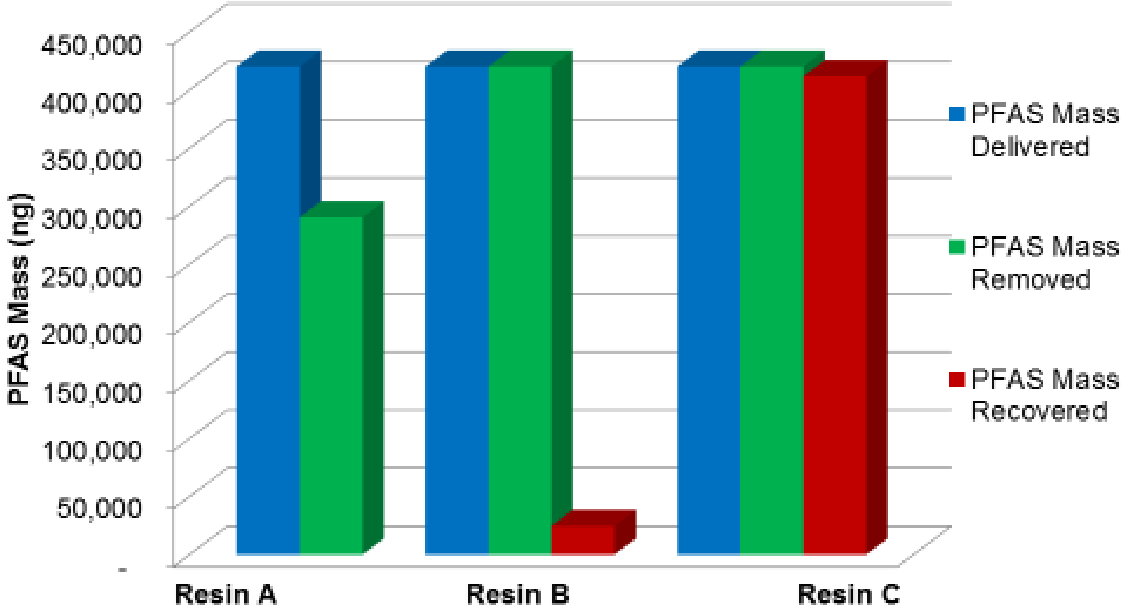
- Synthetic media (resins) removes various contaminants from liquids, vapor or atmospheric streams
- Isotherm testing to identify potentially effective media
- Potential for indefinite reuse via regeneration

Ion Exchange

Polymeric

Carbonaceous

Adsorption and Regeneration of Leading Resins from Column Testing



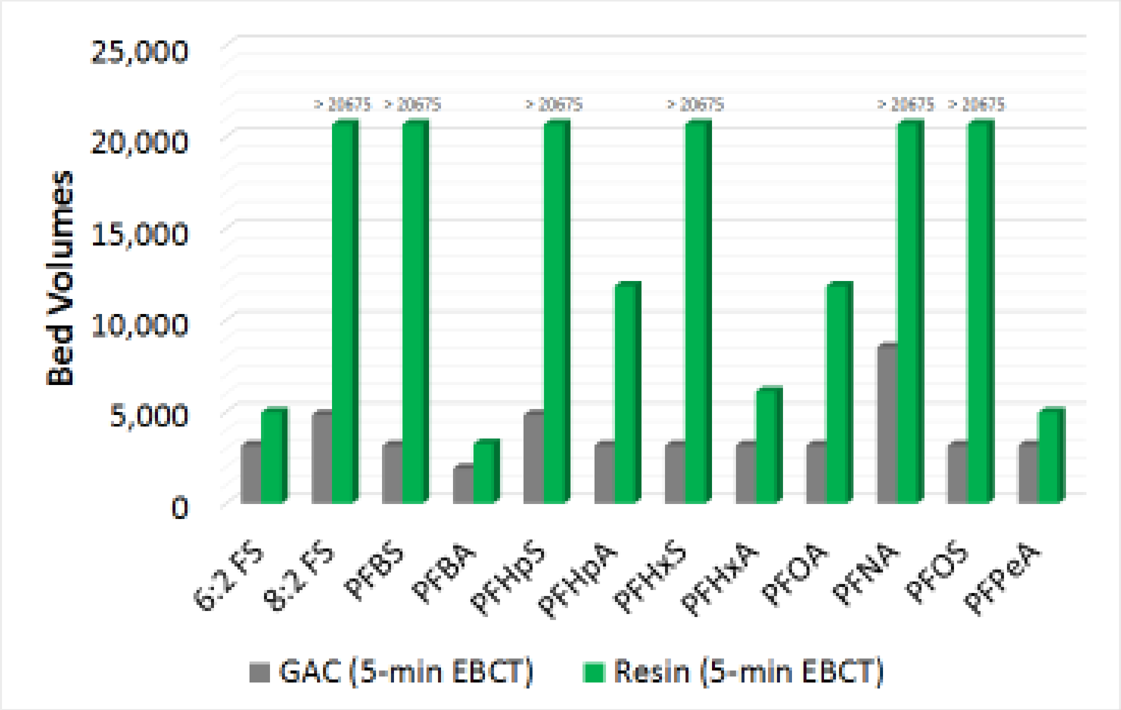
Final Outcome of Bench Test

- Adsorption of PFCs to resin below detection limits
- No breakthrough observed
- >99% regeneration of media with solvent/brine solution
- Success of bench test led to a pilot test for evaluation at the Site

Best Performing Resin

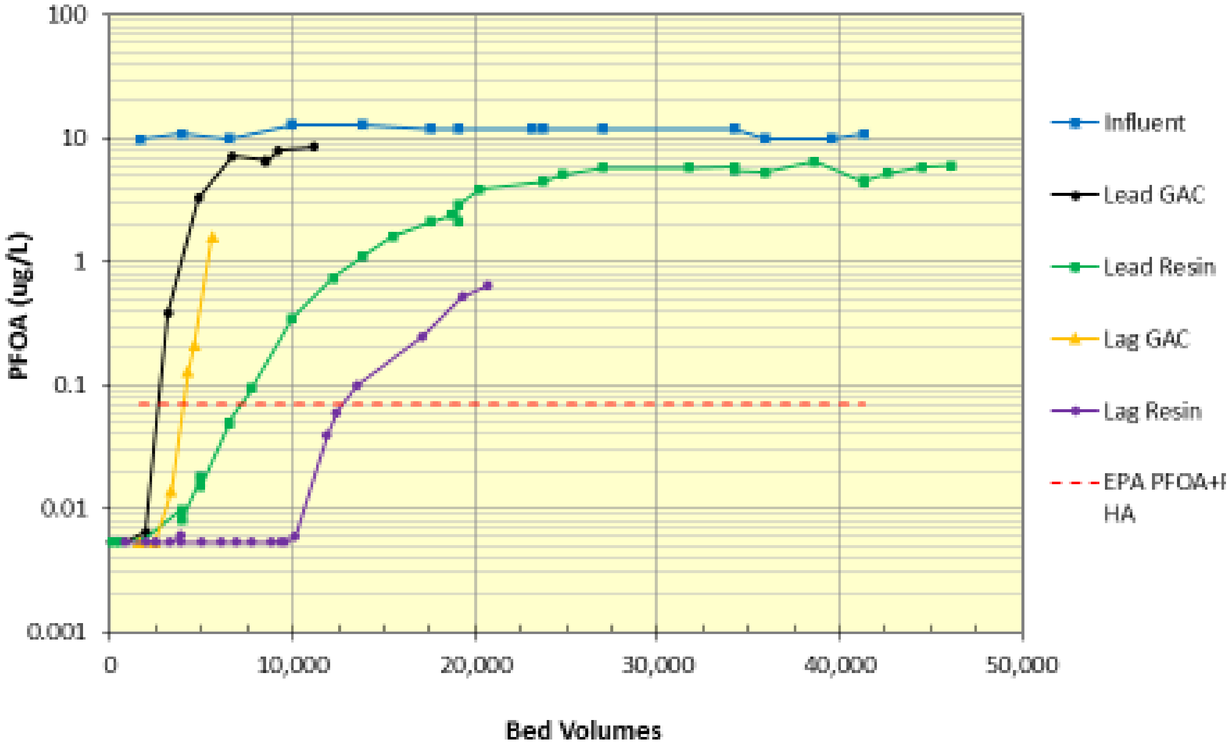
Sorbix A3F
A strong base anion exchange resin

Volume Treated Before Breakthrough: All Observed PFAS



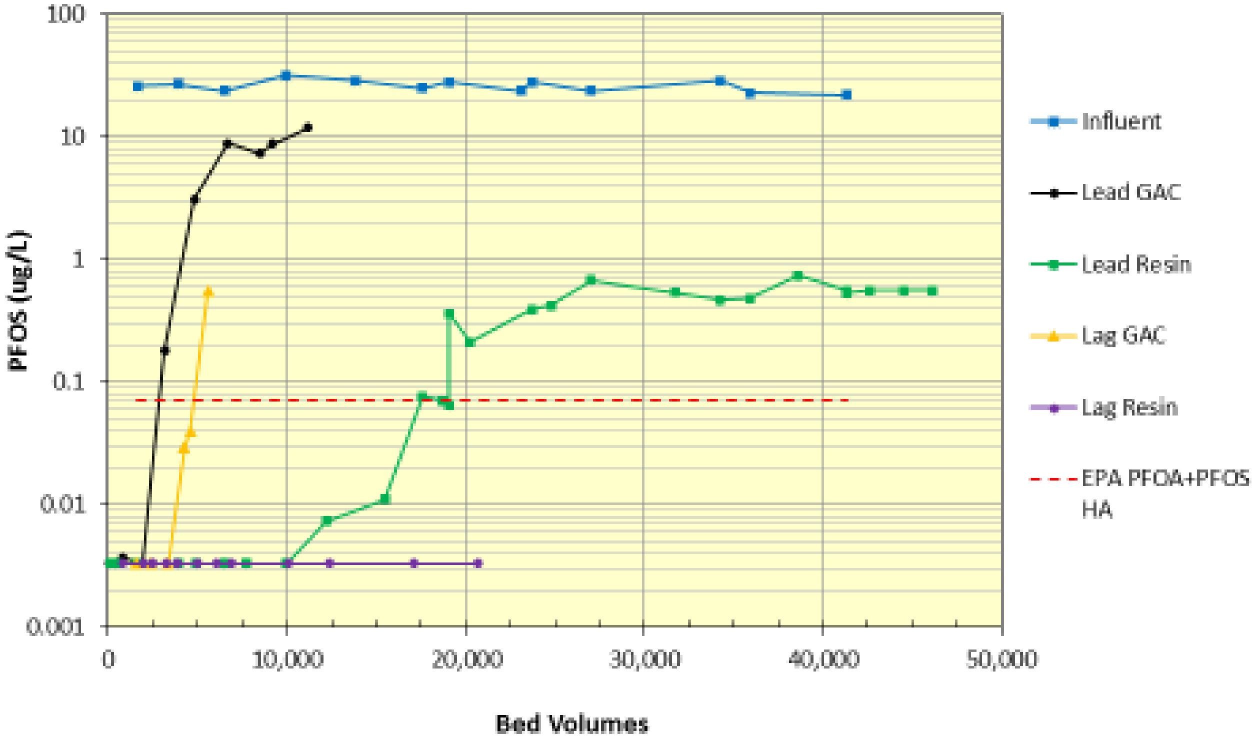
Courtesy of Nathan Hagelin, Amec Foster Wheeler and Steve Woodard, ECT_2

PFOA Breakthrough Results



BLACK	=	Lead GAC
YELLOW	=	Lag GAC
GREEN	=	Lead Resin
PURPLE	=	Lag Resin

PFOS Breakthrough Results



Courtesy of Nathan Hagelin, Amec Foster Wheeler and Steve Woodard, ECT_2

CHEMICAL TREATMENT

- **Activated Persulfate**
- **Electrochemical**
- **Chemical Reduction**
- **Plasma**
- **Combinations…**

Oxidation Approach	Intermediates and Byproducts
Persulfate	F^-, PFPrA, PFHpA, PFHxA, PFPA PFPeA , PFBA, TFA
Permanganate	F^-, SO_4^{2-}
UV-Fenton	F^-, Formic acid, PFPrA, PFHpA, PFHeA, PFPeA , PFBA
Fe(III)	F^-, PFPrA, PFHpA, PFHeA, PFPeA
Ferrates	No observed F^-
Fe(III) and Oxalate	F^-, PFPrA , PFBA, PFPeA, PFHxA, PFHpA
Catalyzed H_2O_2	N/A
Plasma	F^-, TFA PFPrA , PFBA, PFPeA, PFHxA, PFHpA, PFBS
UV-Pb-modified TiO_2	PFHpA , PFHeA, PFPrA, TFA PFPeA, PFBA
Sonolysis	PFHpA, PFHxA, PFPA, TFA and F^- ,PFHpS, PFHxS, PFOA
Photocatalysis with Inidium oxide	F^- ,PFHpA , PFHeA, PFPrA, PFPeA, PFBA
TiO_2 photocatalysis	PFHpA, PFHpA, PFPeA, PFBA
Environmental photolysis	PFBA, PFBS, PFOA
Electrochemical oxidation	F^-, TFA, PFPA, PFBA, PFPeA, PFHxA, PFHpA
Photolysis with persulfate	F^-, CO_2, SO_4^{2-} PFBA, PFPeA, PFHxA, PFHpA
Microwave hydrothermal decomp.	F^-, CO_2, PFBA, PFPeA, PFHxA, PFHpA, PFHeA

Reduction Approach	Intermediates and Byproducts
Mg-aminoclay coated nanoscale ZVI	F^-
Sub critical elemental iron	F^- SO_4^{2-}, CF_3H, CO_2
UV-KI	F^-, formic acid, acetic acid, PFCAs (C1–C6). CF_3H, C_2F_6
UV photolysis of alkaline 2-propanol	F^- SO_4^{2-} CF_4, C_2F_6, C_3F_8, C_7F_{16}
Vitamin B_{12} with Ti(III)-citrate	F^-
Photocatalysis with B-Ga_2O_3	F^-, PFPrA, PFHpA, PFHxA, PFPA PFPeA , PFBA, TFA

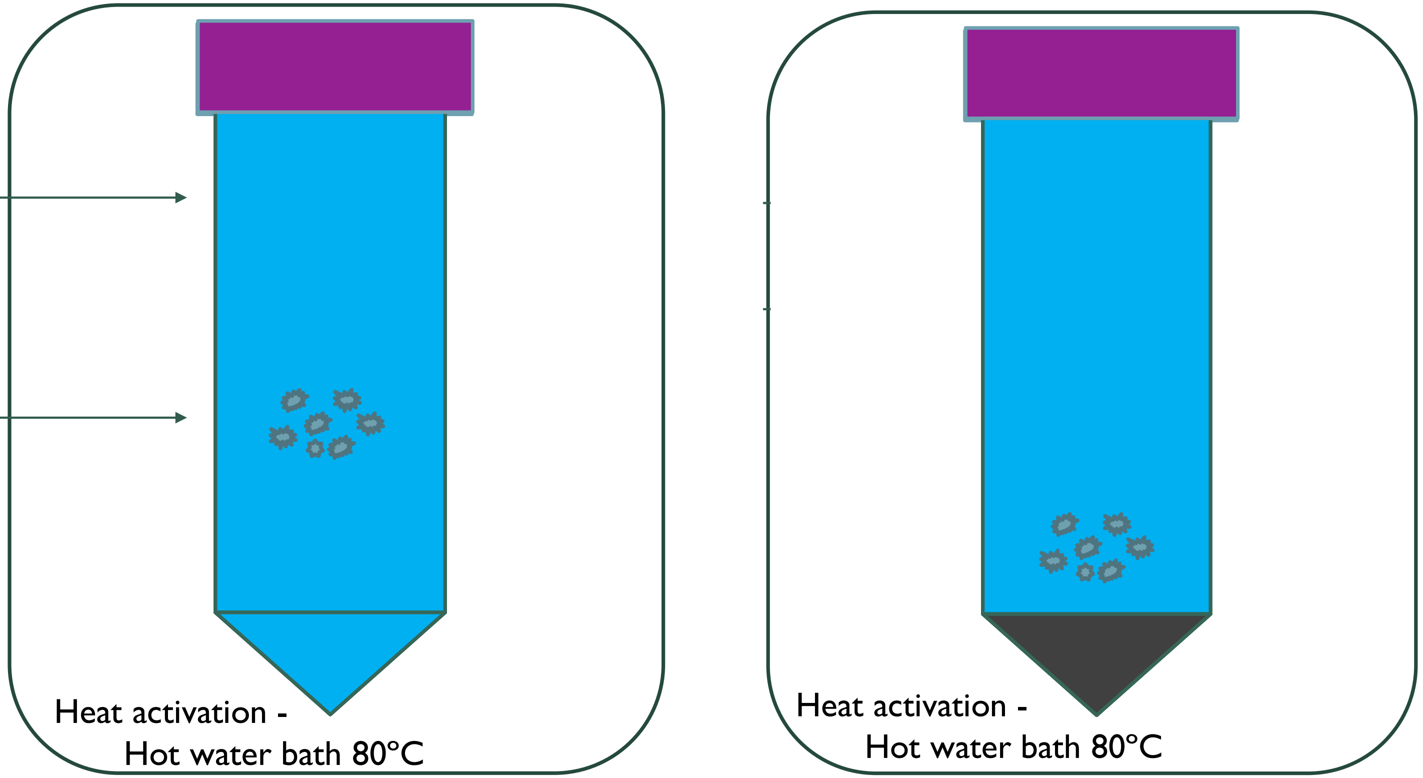
ACTIVATED PERSULFATE

50 mL polypropylene centrifuge

PFOA and PFOS solution

Powder sodium persulfate

Single dose=10 g/L
Multiple dose = 2g/L × 5

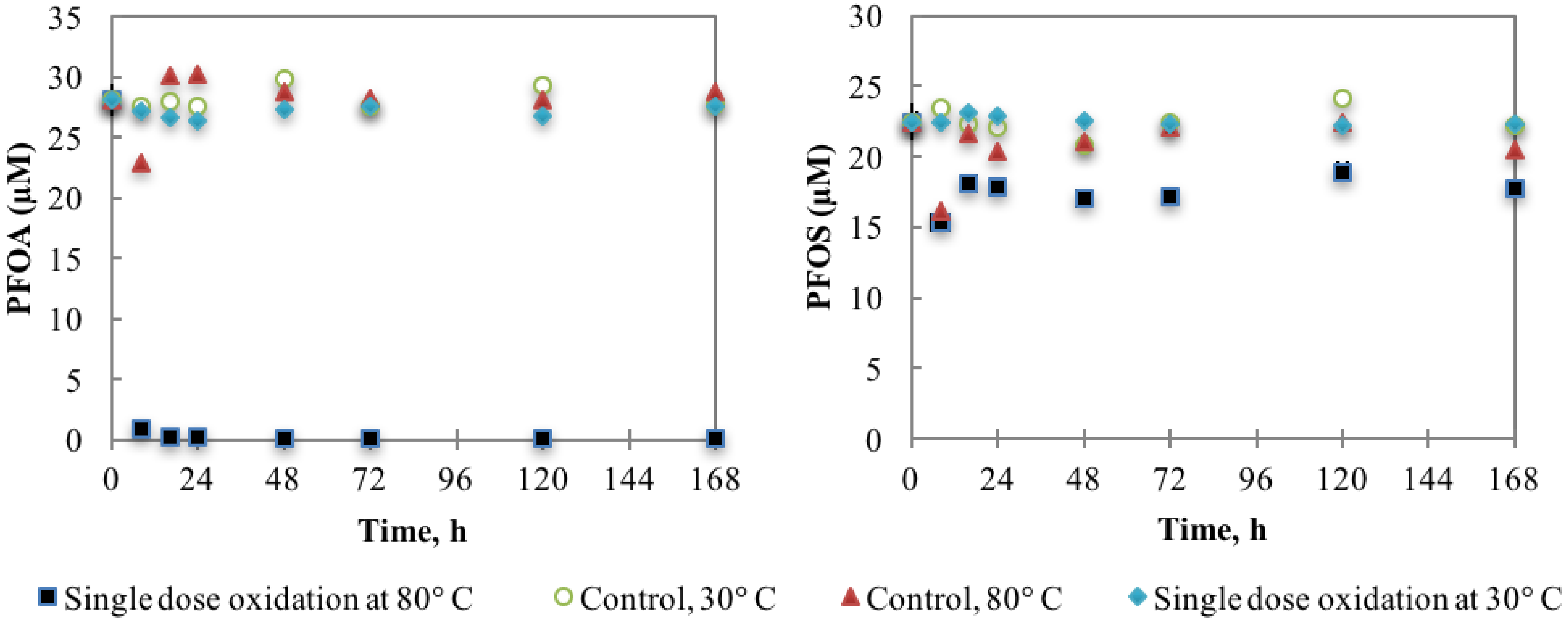


Aqueous

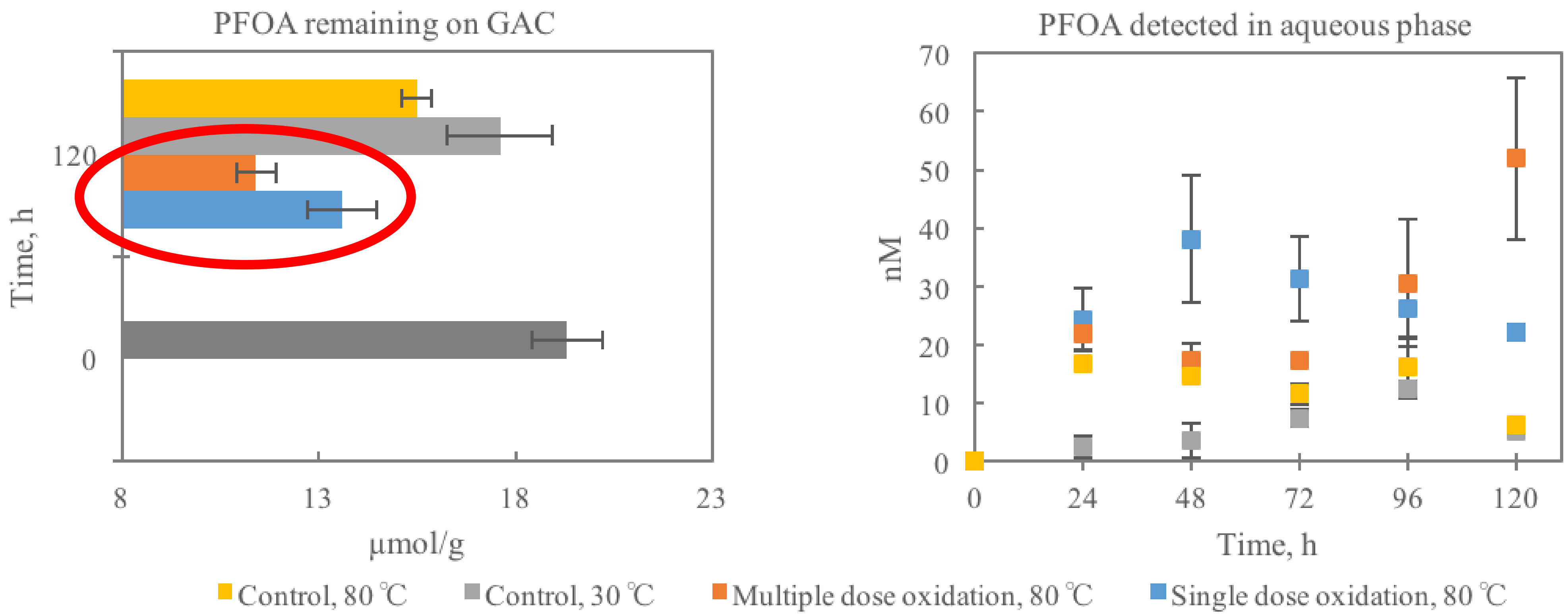
Sorbed

Clarkson UNIVERSITY defy convention™

ACTIVATED PERSULFATE – AQUEOUS PHASE



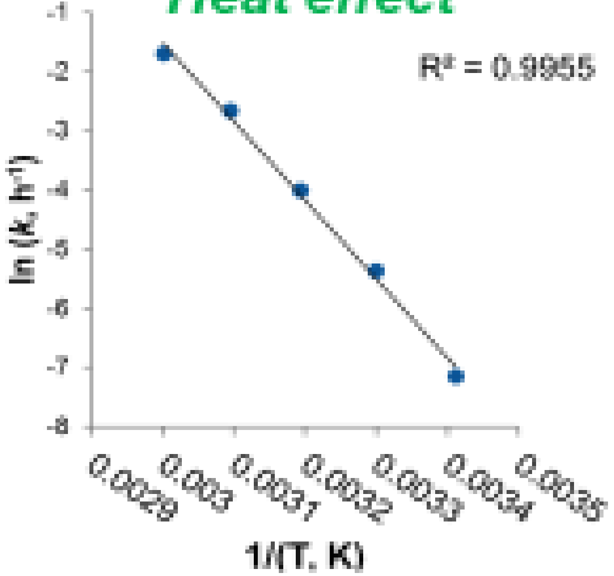
ACTIVATED PERSULFATE – SORBED



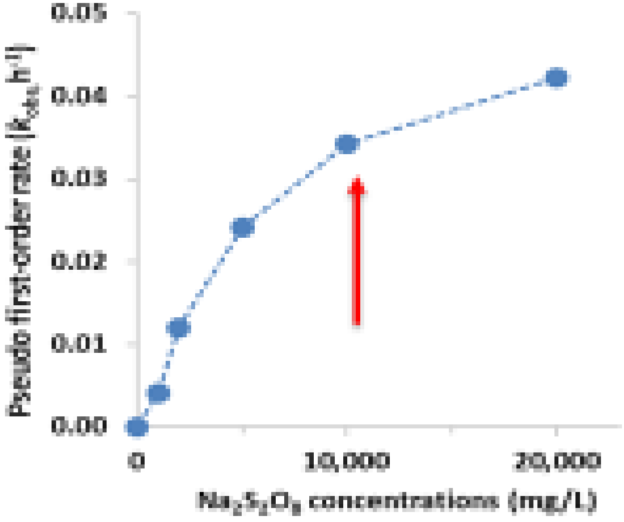
5) Heat-activate persulfate technique for PFOA transformation

Courtesy of Linda Lee, Professor, Purdue University

Heat effect

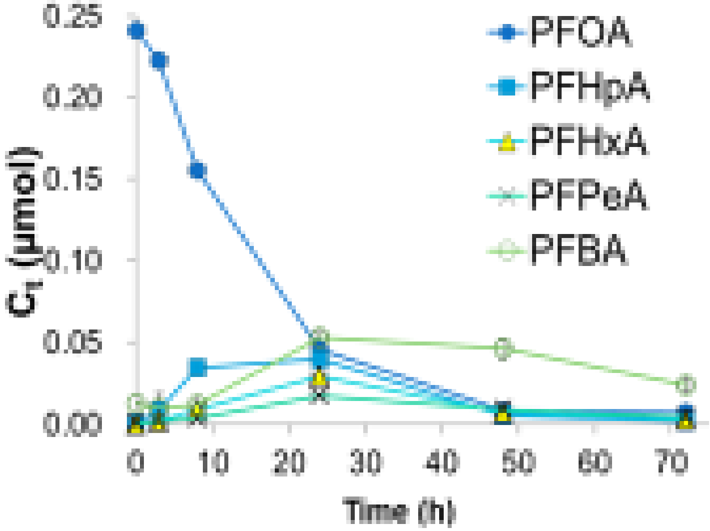


Persulfate conc. effect

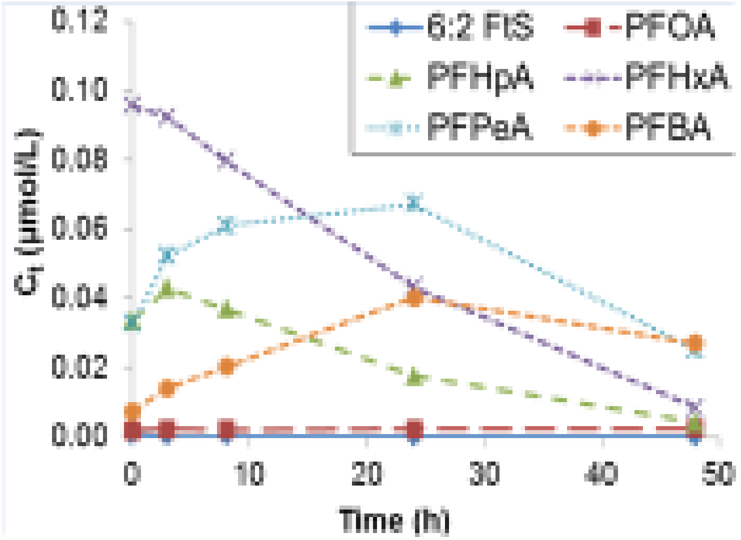


- As T increased, the first order rate of PFOA transformation was increased as well (22~60 °C).
- Higher persulfate dosing results in faster; but sulfate radicals become self-scavenging when > 10000 mg/L of $Na_2S_2O_8$

Metabolites for PFOA



Metabolites for 6:2 FTSA

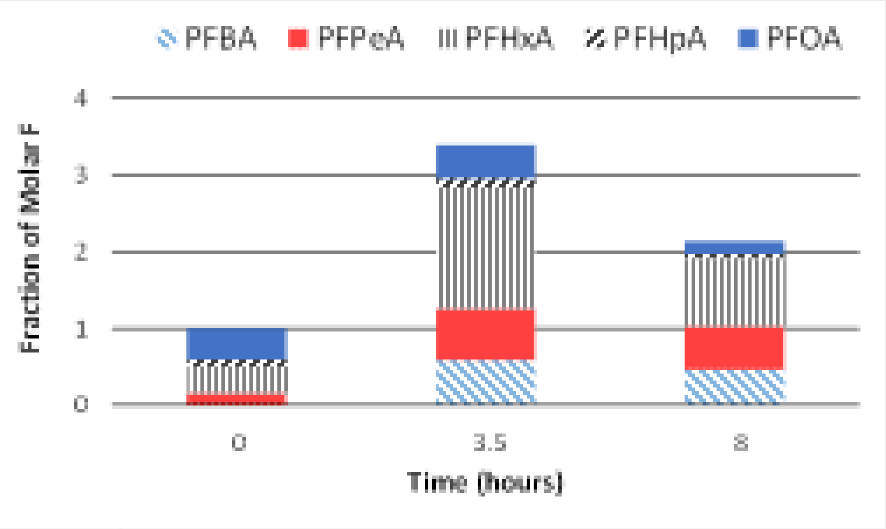


UNZIPPING…

Park, Lee et al. (2016) Chemosphere 145:376-383
Funding: AFCEE. BA715, E-3

Boron Doped Diamond Electrochemical Treatment

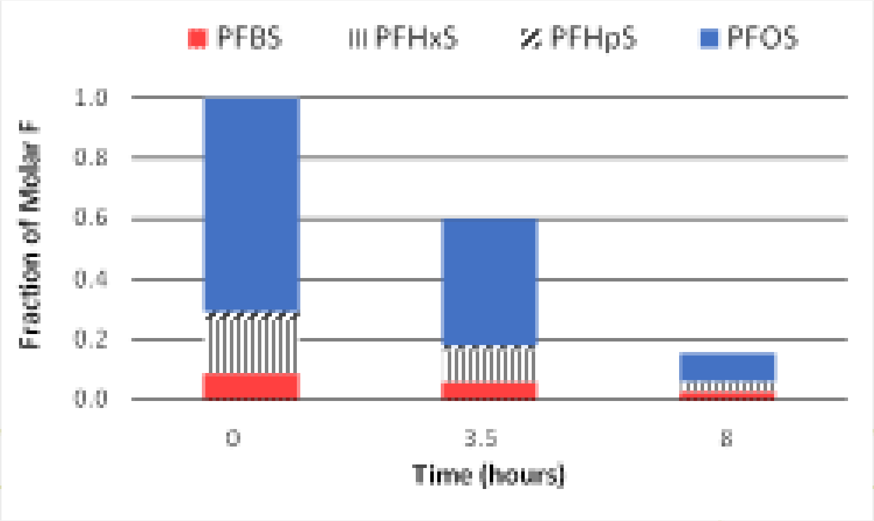
3M AFFF spiked into natural groundwater



Carboxylates

SERDP
DOD • EPA • DOE
Project No. ER-2424
CDM Smith, CB&I, CSM, UC

Sulfonates



Perchlorate formed during electrochemical treatment can be biologically removed

Schaefer et al., under review in *Chemical Engineering J.*

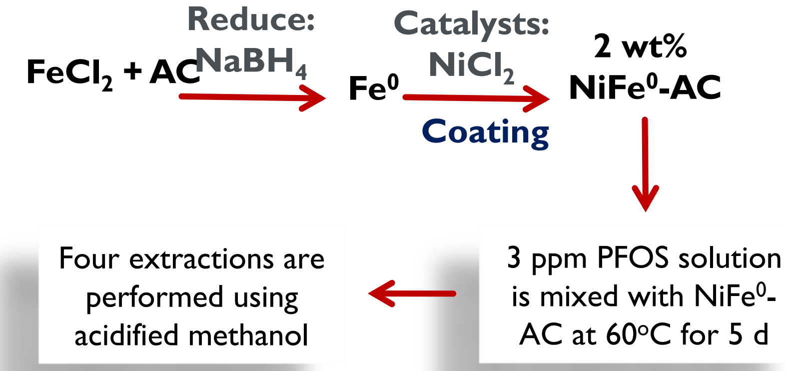
CDM Smith

Courtesy of Charles Schaefer, Principal, CDM Smith

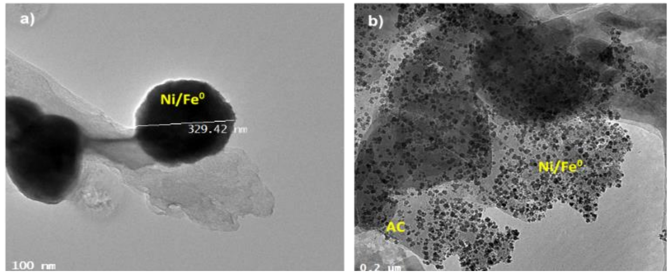
PFOS reduction by synthesized activated carbon (AC)-supported nano-bimetals

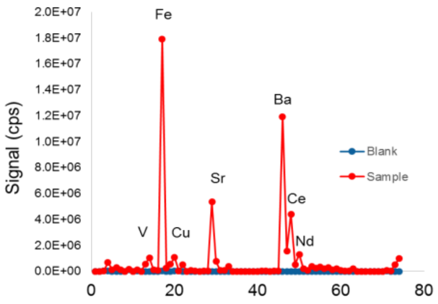
Courtesy of Linda Lee, Professor, Purdue University

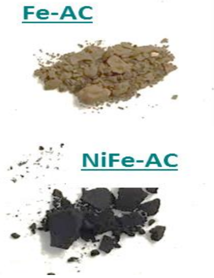
Synthesis



Particle Characterization

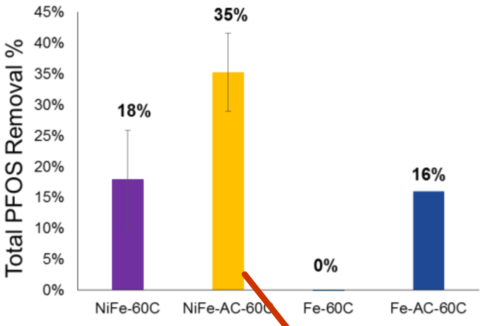




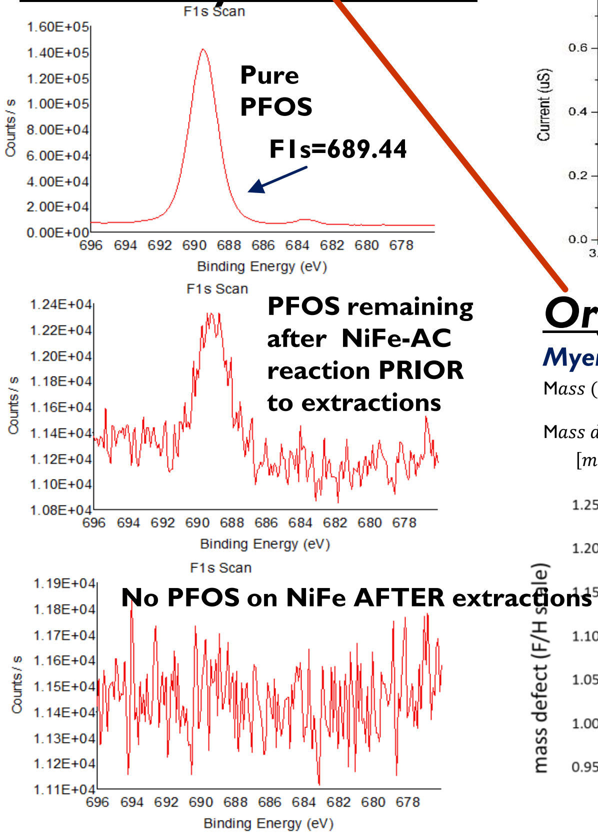


Zenobio and Lee (2016) SERDP-ER-2426

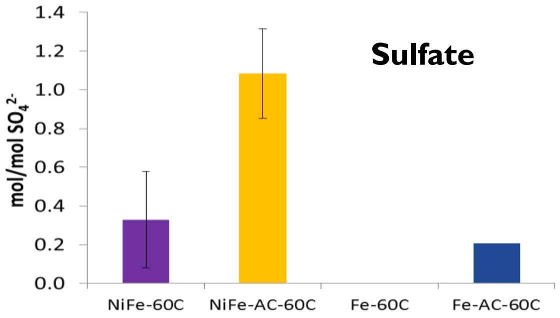
PFOS mass removal

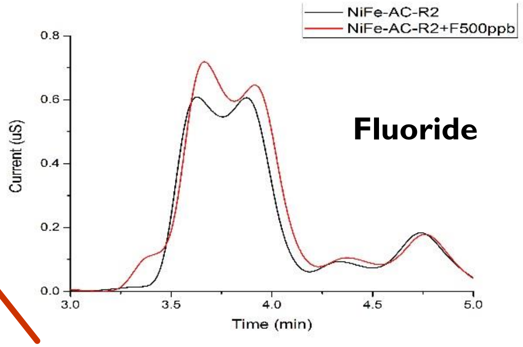


PFOS Fully Extractable



Inorganic metabolites (F^- & SO_4^{2-})



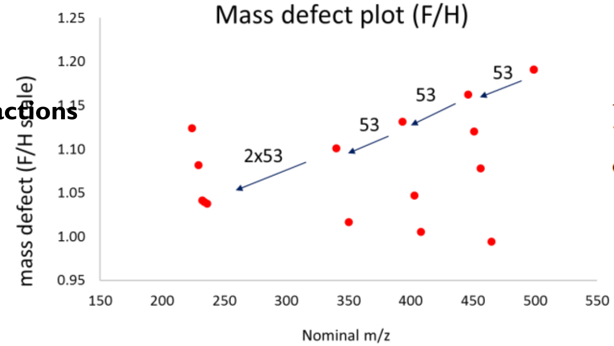


Organic metabolites

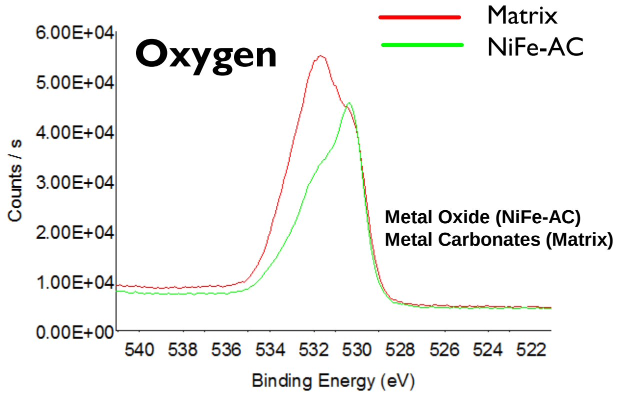
Myers et al. 2014

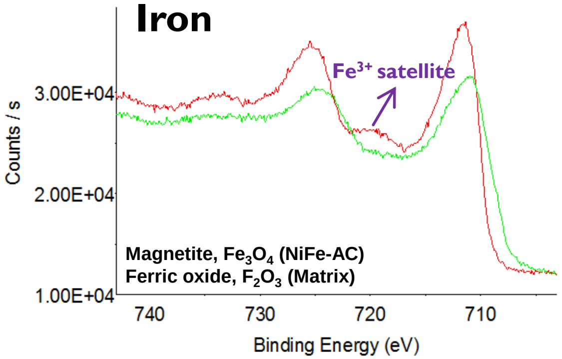
$$Mass\ (F/Hscale) = \left[mass\ (IUPAC\ scale) x\ \frac{18}{17.9905782}\right]$$

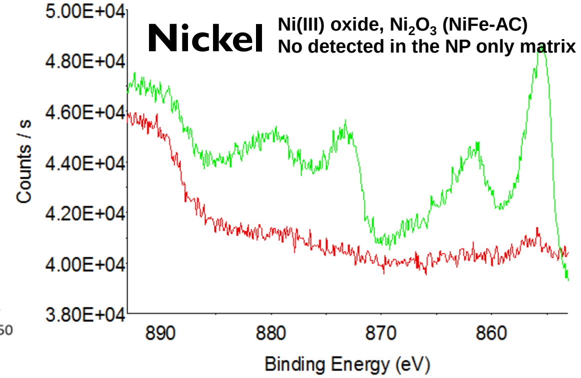
$$Mass\ defect\ \left(\frac{F}{Hscale}\right) = [mass\ (F/H\ scale)\ - nominal\ mass\ (rounded\ down, F/H\ scale)]$$



Oxidation state pre/post reaction

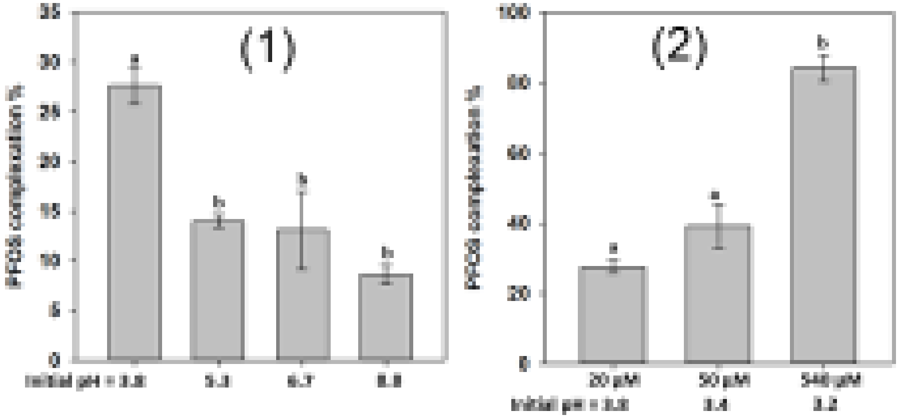


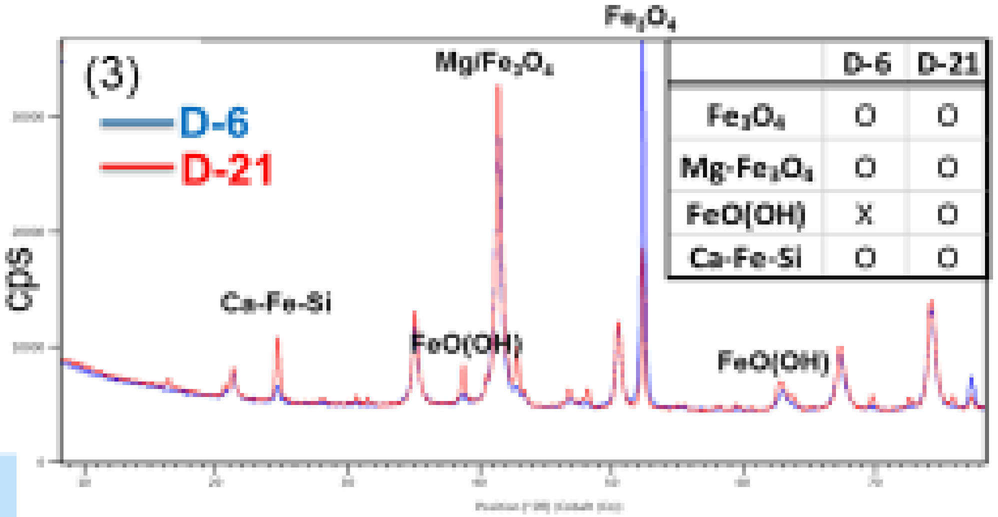




Nanosized Pd^0/nFe^0 Potential for PFOS transformaton

- Initial work indicated that acidic initial pH resulted in the highest PFOS removal (~30%) as defined by the least PFOS recovered. However, no F^- or SO_4^{2-} was detected.
- Further assessment revealed that ***Fe-PFOS complexation*** caused a negative in PFOS concentrations, thus an overestimation of PFOS 'loss'.
- Complexation increased with decreasing pH (1) and increasing Fe concentrations (2).
- PFOS-Fe complexes were broken when sample aliquots adjusted to pH > 10 with NaOH and equilibrated or 24 h.
- PFOS still not recovered at early times is due to ***'strong' adsorption*** to the Pd^0/nFe^0 surface, which transforms to less sorptive oxides over time, releasing PFOS.



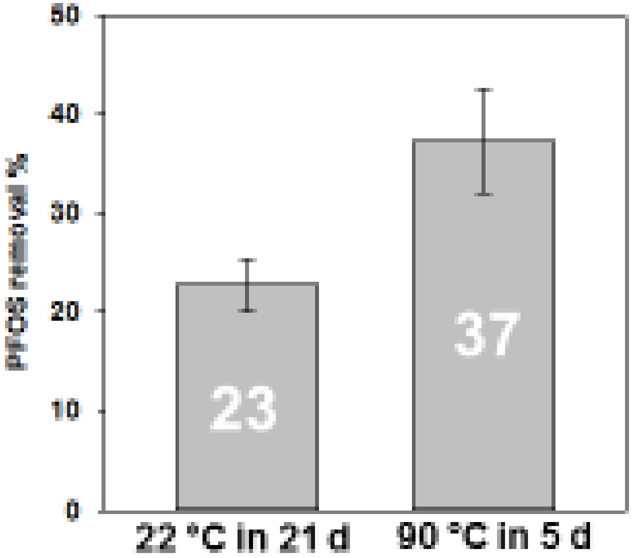


Park and Lee (2016) SERDP-ER-2426

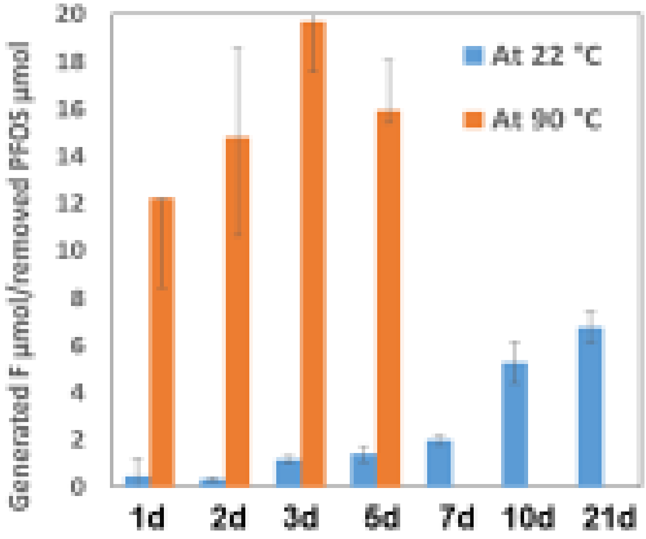
Courtesy of Linda Lee, Professor, Purdue University

Vitamin B12 technique for PFOS transformation

PFOS removal % in VB12+nZn^0

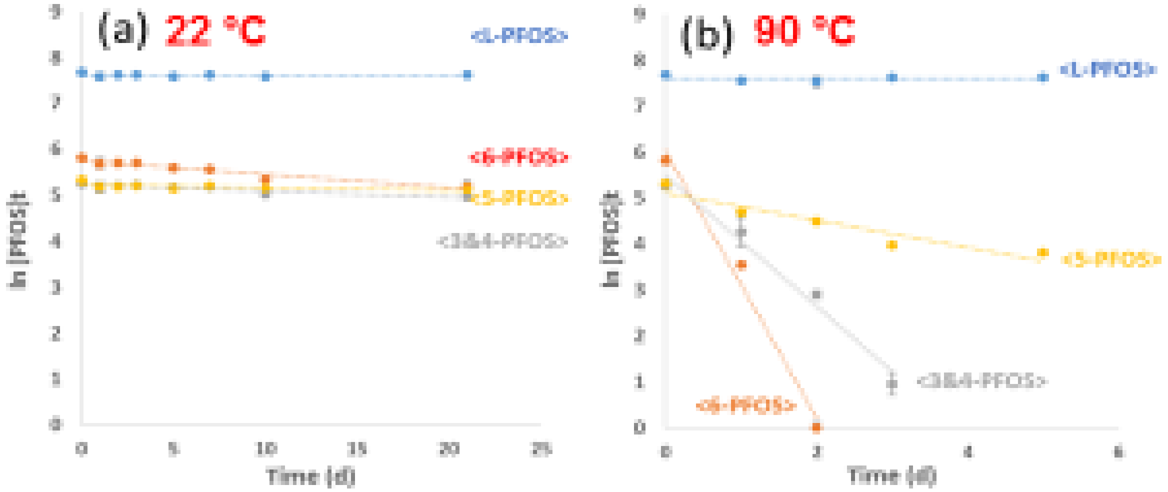


F$^-$ generation per mole of PFOS lost



- Complete PFOS defluorination was observed at 90 °C in 5-d with 19 ± 2 of F$^-$ mole generated per mole of PFOS lost.

The pseudo-first order rate constants and half-lives of PFOS isomers decomposition



- Branched PFOS isomers defluorinated, not L-PFOS.
- K_{deg} (d^{-1})

6-PFOS > 3&4-PFOS > 5-PFOS

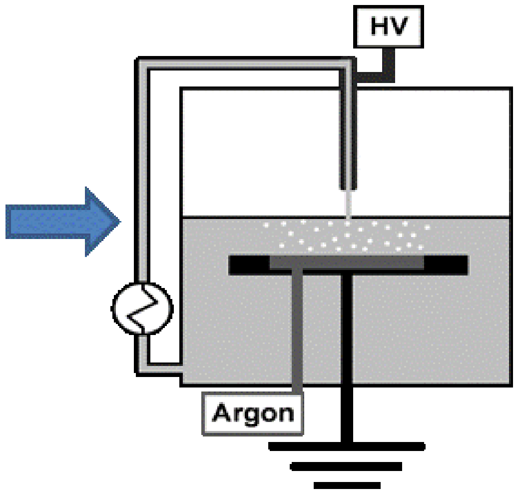
Park and Lee (2016)
SERDP-ER-2426

Courtesy of Linda Lee, Professor, Purdue University

Plasma-based water treatment: Efficient transformation of perfluoroalkyl substances (PFASs) in prepared solutions and contaminated groundwater

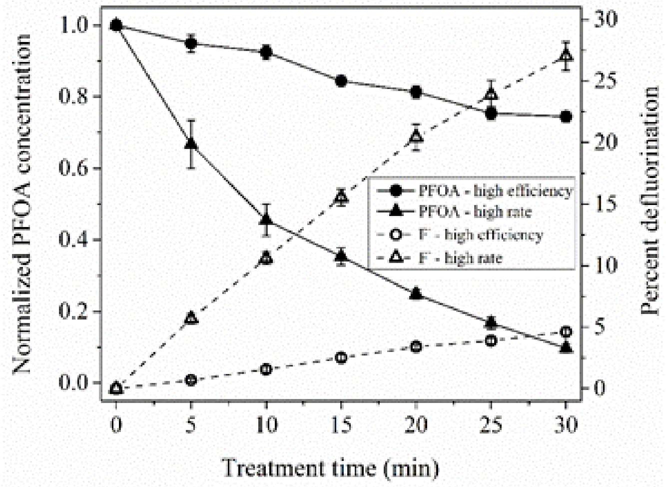
Clarkson UNIVERSITY defy convention™

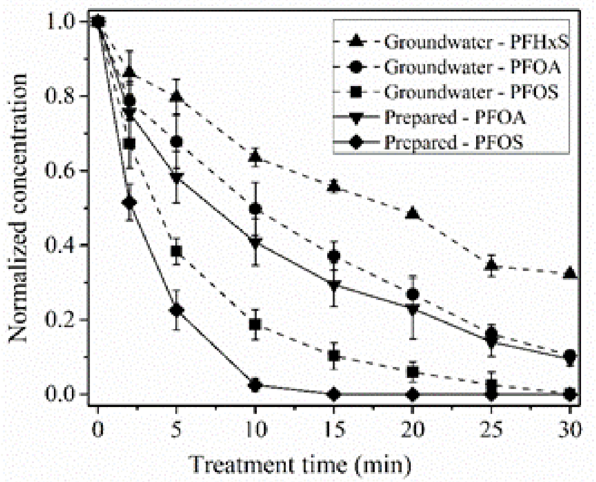
Bench-scale enhanced contact plasma reactor



Plasma produces aqueous electrons and H radicals which are capable of chemically degrading PFASs

G. R. Stratton, F. Dai, C. L. Bellona, T. M. Holsen, E. R. V. Dickenson and S. Mededovic Thagard, "**Plasma-based water treatment: Demonstration of efficient perfluorooctanoic acid (PFOA) degradation and identification of key reactants**" Environmental Science & Technology, 2016, accepted.

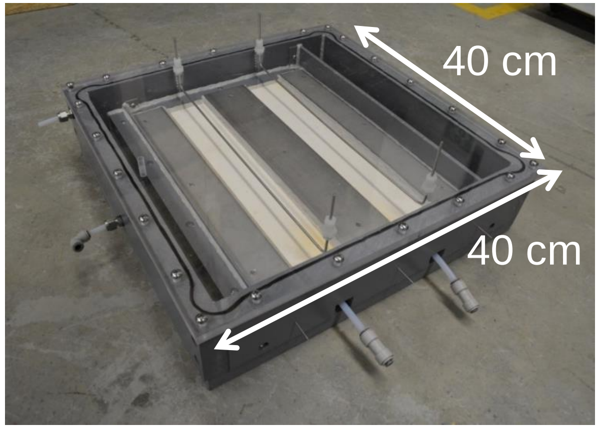


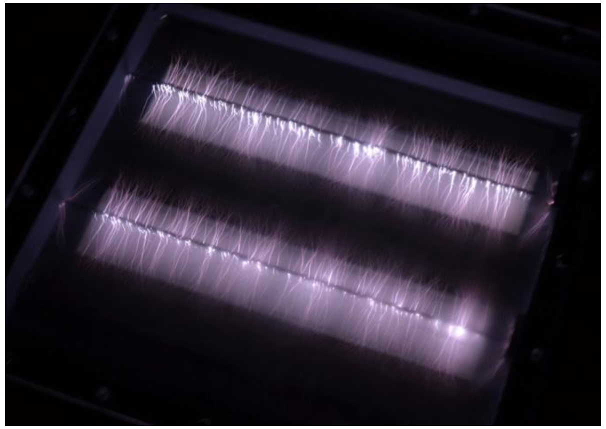


Major byproducts: fluoride ions, fluorinated gases and shorter-chain PFAAs

Courtesy of Selma Mededovic Thagard, Clarkson University

Scaled-up enhanced contact plasma reactor





Treatment efficiency is 15 times greater than in the bench-scale reactor. The overall treatment efficiency is significantly higher compared to leading alternative treatment technologies.

Treatment of contaminated groundwater (naval research site, Warminster, PA)

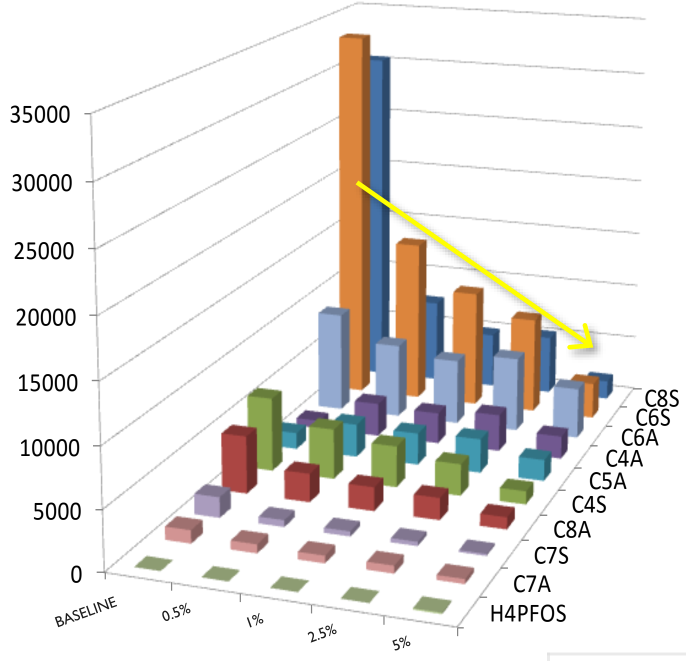
Solid-phase extraction			
Compound	$C_{0\ min}$ (µg/L)	$C_{60\ min}$ (µg/L)	Removal (%)
Perfluorooctanoic acid (PFOA)*	0.89	0.0035	99.6
Perfluorooctane sulfonate (PFOS)*	0.18	0.0026	98.5
Perfluoroheptanoic acid (PFHpA)	0.11	0.0002	99.8
Perfluorohexane sulfonate (PFHxS)	0.32	0.0041	98.7
Perfluorohexanoic acid (PFHxA)	0.27	0.024	91.1
Perfluoropentanoic acid (PFPnA)	0.22	0.16	26.4

PFOA & PFOS concentration was reduced by at least 75% within one minute of treatment

Courtesy of Selma Mededovic Thagard, Clarkson University

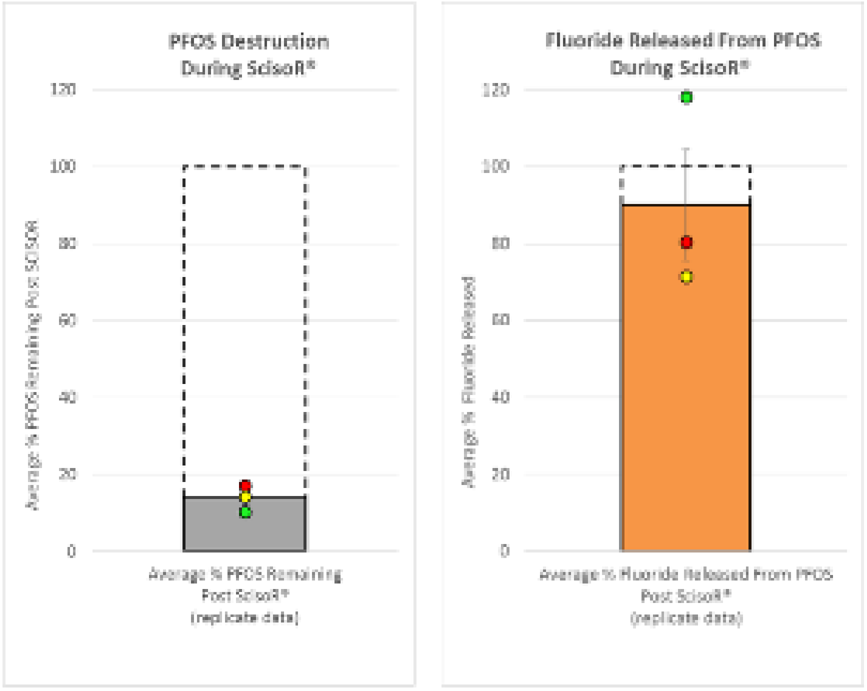
OXIDANT COMBINATIONS

- ScisoR® – ARCADIS
- OxyZone® - EnChem



SCISOR®

- ScisoR ® –Smart Combined *In Situ* Oxidation and Reduction
- Developed, tested and patented and by ARCADIS NL lead by Tessa Pancras
- Initial lab test have show removal of PFAS
  - Effective at ambient temperature
  - Soluble reagents can be injected or mixed with impacted soil and groundwater
  - Comprises a specifically activated persulfate
- Potential for *in situ* / on site remediation of PFAS

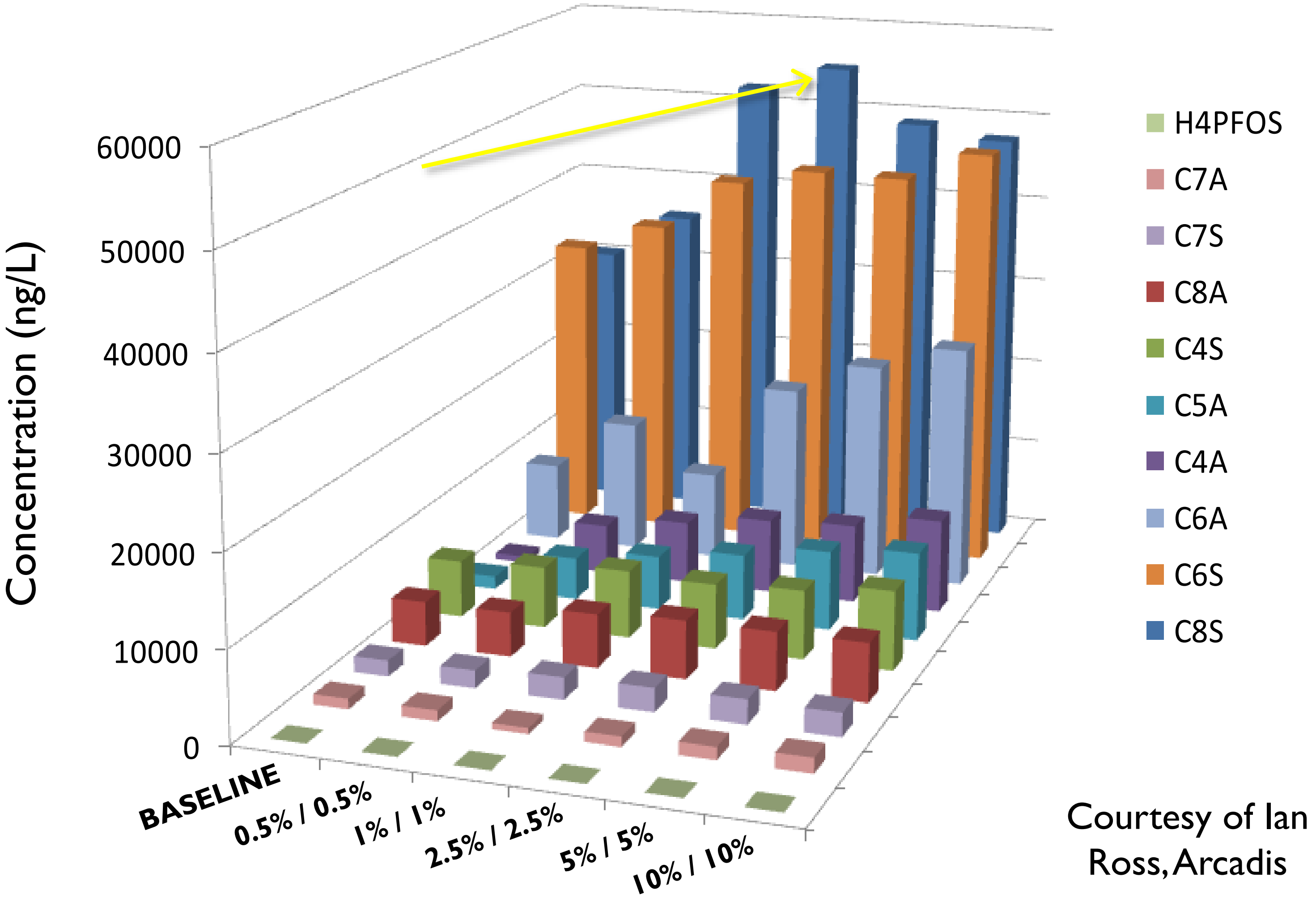


Replicate Data. Error bars are % Standard Error of Measurement (SEM)

Courtesy of Ian Ross, Arcadis

RESULTS: PEROXIDE ACTIVATED PERSULFATE

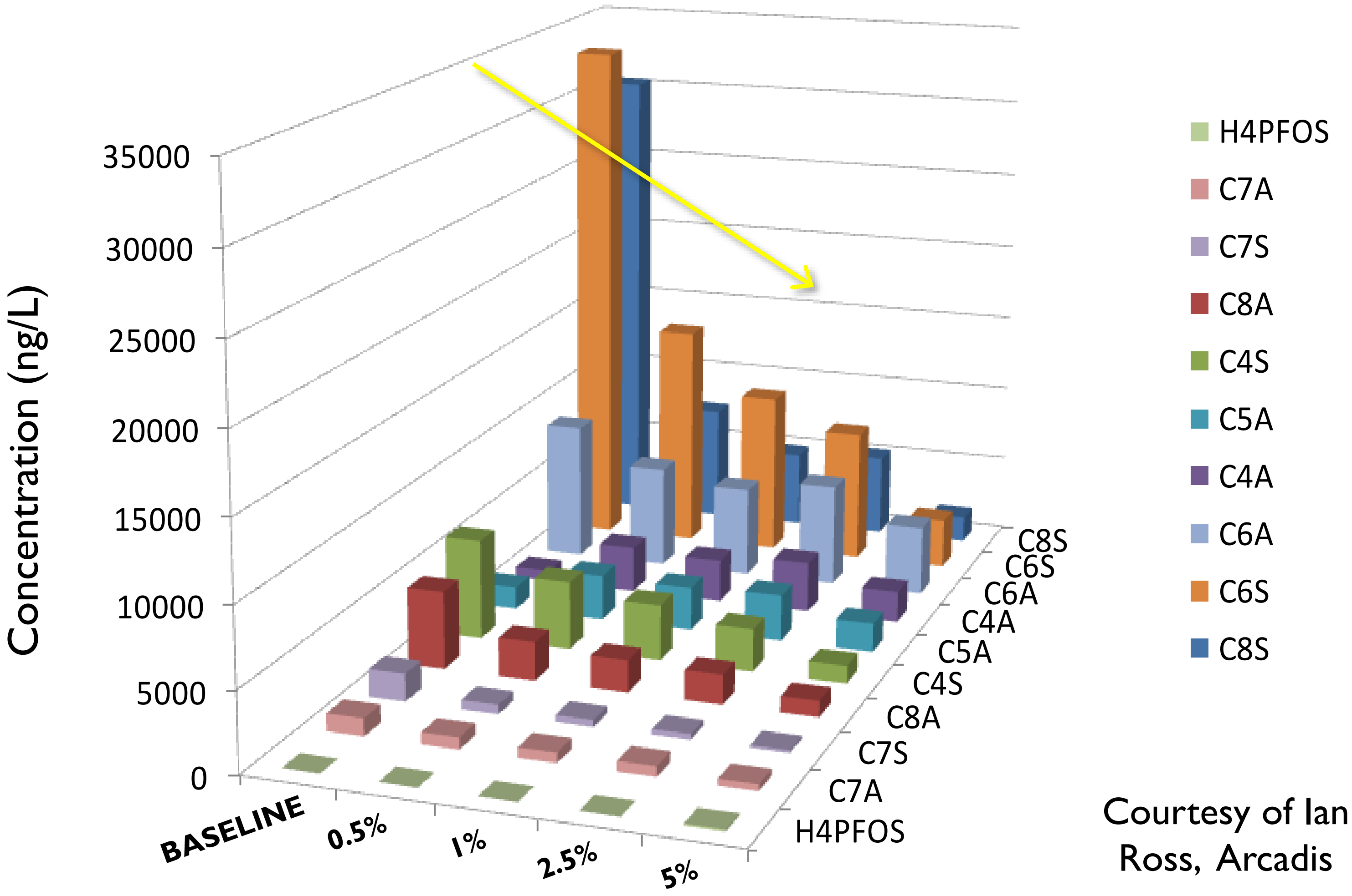
SOIL AND GROUNDWATER



- 300 g soil, 300 mL groundwater
- PFAS monitored in reactor supernatant

Courtesy of Ian Ross, Arcadis

RESULTS: SCISOR®
SOIL AND GROUNDWATER



- 300 g soil, 300 mL groundwater
- PFAS monitored in reactor supernatant

Courtesy of Ian Ross, Arcadis

Contacts

Ian Ross Ph.D.
Global PFAS Lead
Arcadis UK
ian.ross@arcadis.com

Jeff Burdick
North America PFAS Lead
Arcadis US
jeff.burdick@arcadis.com

Tessa Pancras
European PFAS Lead
Arcadis NL
tessa.pancras@arcadis.com

Download at:
https://www.concawe.eu/publications/558/40/Environmental-fate-and-effects-of-poly-and-perfluoroalkyl-substances-PFAS-report-no-8-16

Courtesy of Ian Ross, Arcadis

CHALLENGES AND LIMITATIONS

- Mixtures, precursors, co-contaminants
- Incomplete mineralization
- Managing materials
- Energy intensity
- Technical challenges to *in situ* treatment
- Limited field-scale examples