

ADVANCES IN PFC INVESTIGATION AND REMEDIATION

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Presentation Outline

Lessons learned (to date) from PFAS (Per- and poly-fluorinated alkyl substances) experience with respect to :

- sampling considerations
- analytical methods
- remedial approaches

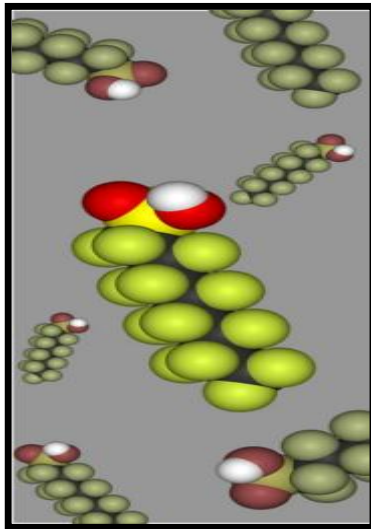
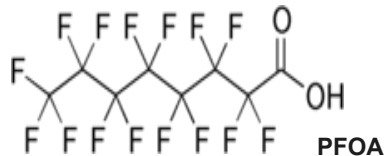
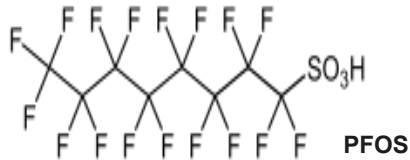
Arcadis PFAS Experience

- Site investigation
 - Analytical Chemistry
 - Risk assessment
 - Soil treatment
 - *In Situ* groundwater treatment studies
 - Biological
 - Chemical oxidation
 - Other
 - Due diligence
 - Emergency response
 - Litigation
- International Team working on PFA issues
 - Engineers, hydrogeologists, toxicologists, chemists, and others
 - Consortium involvement: CONCAWE, NICOLE working group, University of Waterloo (lab, field trials)
 - Primary Sectors
 - Federal Defense Departments (Canada, US, EU)
 - Airports (Canada , US , EU, Australia)
 - Refineries (US, GER)



What are PFAS?

Per/poly fluorinated alkyl substances



- Perfluorinated sulfonic acids (PFSA) with carbon chain lengths from C2 to C16. Perfluorooctane sulfonate (PFOS) with 8 carbons (C8) is the most studied PFSA.
- Perfluorinated carboxylic acid (PFCAs) with carbon chain lengths from C2 to C16. Perfluorooctanoic acid (PFOA) with 8 Carbons (C8) is the most studied PFCA.
- PFCA's and PFSA's are collectively termed PFAA's (perfluorinated alkyl acids)
- Precursor Compounds –that biotransform to produce long chain PFCA's or PFSA's including:
 - Fluorotelomers (polyfluorinated compounds), with a $\text{CH}_2\text{-CH}_2$ -group between the fluorocarbon chain and the functional group
 - Per/polyfluorinated compounds with higher molecular weight functional groups - polyfluorinated sulphonamides, phosphates, amines etc.

Apart from PFOS and PFOA, there are 100s of additional C2-C16 and other precursors to consider

PFAS: fate, transport, transformation

- Fate and transport of PFAS differ from many other common contaminants
- Precursors have the potential to biotransform/degrade into long chain perfluoroalkyl compounds (PFAA's –generally PFCA's but also PFSA's) as dead end products
- There are potentially hundreds of compounds in AFFF formulations which can degrade to form perfluorinated compounds
- Carbon-fluorine bond is the strongest organic bonds in chemistry so difficult to cleave- non-reactive, stable, persistent
- Surfactant properties, but both hydrophobic and lipophobic, prefers to adhere to surfaces or phase boundaries (air-water interface), binding to glass, filters, stratify in solution
- Water solubility covers a wide range (depending on chain length)
- Sorption is dependent on charge and carbon chain length (and silt and clay content of soils) , plumes are generally long as no biodegradation of perfluorinated sulphonates (e.g. PFOS) or perfluorinated carboxylates (PFOA) have been reported

Physicochemical properties vary significantly between the different precursor compounds. Still an area of active research

Sampling Considerations

- Detection limits are low (ng/L) so avoid use of fluorinated polymers which can release PFAS (e.g. Teflon) in sampling / analytical methodologies
- Avoid use of glass sampling vessels or metals as PFAS adhere to the surface of glass/metals
- Samples should be collected in polypropylene or polyethylene (HDPE) bottles fitted with an unlined (no Teflon), polypropylene screw cap.
- Avoid any filtering during sample preparation as PFAS adhere to filter matrices
- PFAS stratify in solution as they collect at the air / water interface so consider that:
 - sampling from groundwater wells should ideally be from the surface of the water table (USAF protocols)
 - protocols for working with water samples must include a vigorous shake of the solution before subsampling
- Microbes can degrade precursor molecules making more PFOS / PFOA

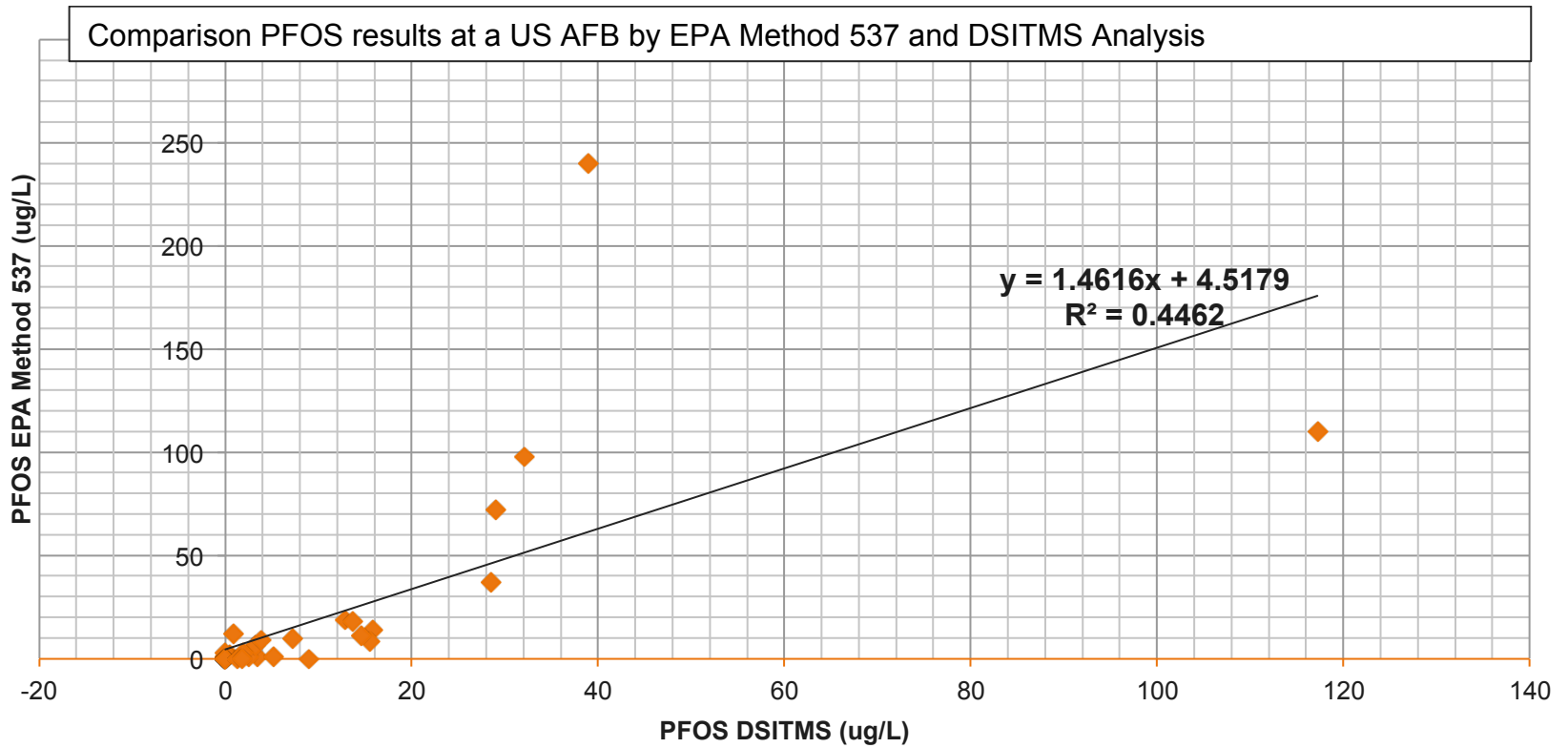
Specific specialized sampling protocols required

Mobile sampling for PFAs

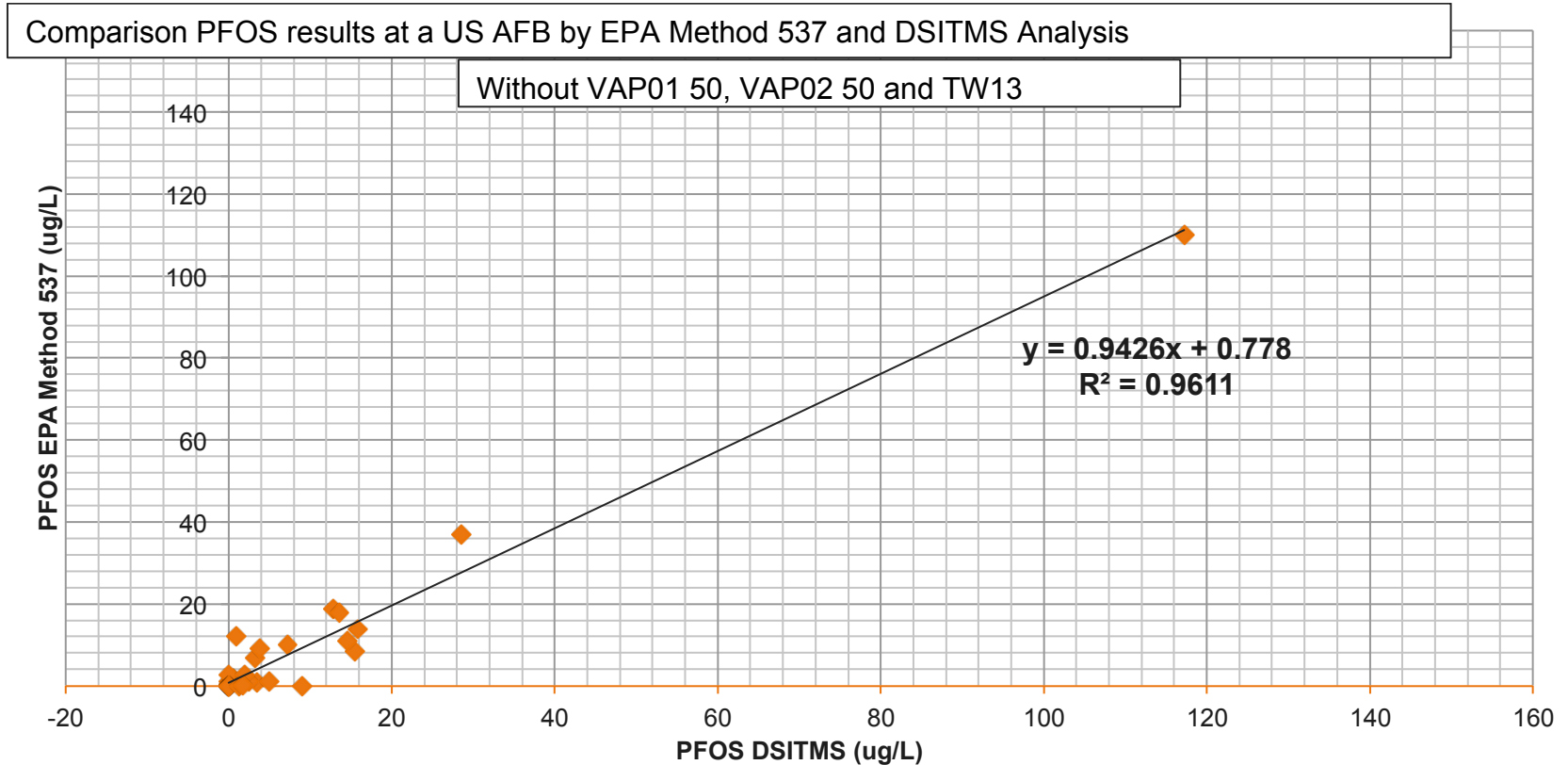
- Working with Triad Environmental Solutions to develop mobile based sampling method based on DSITMS (direct sampling ion trap mass spectrometer)
- Analogous to method used for DNAPL sampling and mapping – real time delineation and site characterization - Triad Environmental has been used at sites in Alberta and Ontario for on-site rapid accurate chlorinated solvent analyses
- Current fixed based methods (EPA 537) are slow and expensive – mobile lab based method has potential to achieve 30-40 samples per day
- extraction method from EPA 537 is used to concentrate PFAs from groundwater
- 537 uses liquid chromatography (LC) followed by negative ion electro-spray mass spectrometry ((-)ESI MS)
- Field method will use (-)ESI MS in a multiple MS mode- skipping the LC step
- initial tests have yielded promising results
- Goal is to modify other analytical methods so they can be used in the field

Potential in- field PFA analyses

Mobile Sampling -Example results



Mobile sampling – Example Results



AFFF contained many thousands of PFAS compounds including precursors

Current analysis only examines a small fraction of the compounds present (16 - 39 compounds)

Microbes attack the non perfluorinated parts of the PFAS precursor molecules making PFAA's as dead-end products- so PFAS precursors biotransform to PFAA's which do not biotransform further and are non-biodegradable

There are potentially hundreds of PFAS compounds to assess (C2 – C16, straight chain, branched chain, cyclic, telomers, betaines, sulphonamide, amino etc.)

The analytical costs to assess the concentration of all of these PFAS individually will be substantial

Analytical Techniques

Expanding analytical tool box to deal with precursors and cost:

LCMSMS Alcontrol Laboratories, UK

- Most common tool is LC-MSMS –Liquid Chromatography with tandem mass spectrometers (US EPA 537)
- Can detect C4 to C12 perfluorinated carboxylates & sulphonates (including PFOS & PFOA)
- Detection limits to approx. 0.1 ng/L

Total Oxidisable Precursors (TOP) Assay Alcontrol Laboratories, UK

- Pre-treatment of samples using conventional chemical oxidation which converts precursors to perfluorinated carboxylates (PFCA's) & sulphonates (PFSA's) which can be detected using LCMSMS;
- Shows sum of precursors which are converted to PFCA's & PFSA's - Done in addition to LCMSMS to provide difference between precursor and free PFCA & PFSA concentrations
- Detection limits as for LC-MSMS

Quadrupole Time of Flight (QTOF) MS Sheffield Hallam University, UK

- Identifies multiple precursors via mass ion capture and accurate mass estimation to give likely empirical formulae
- Semi quantitative

Particle Induced Gamma Emission (PIGE) Spectroscopy Hope College, USA

- Separation of organofluorine compounds by SPE cartridge then analysis of total fluorine content to give a sum of fluorinated species (analogous to TPH for hydrocarbons)
- Detection limits to 2.2 ug/L F

Adsorbable Organo Fluorine (AOF) Water Technology Centre (TZW), Germany

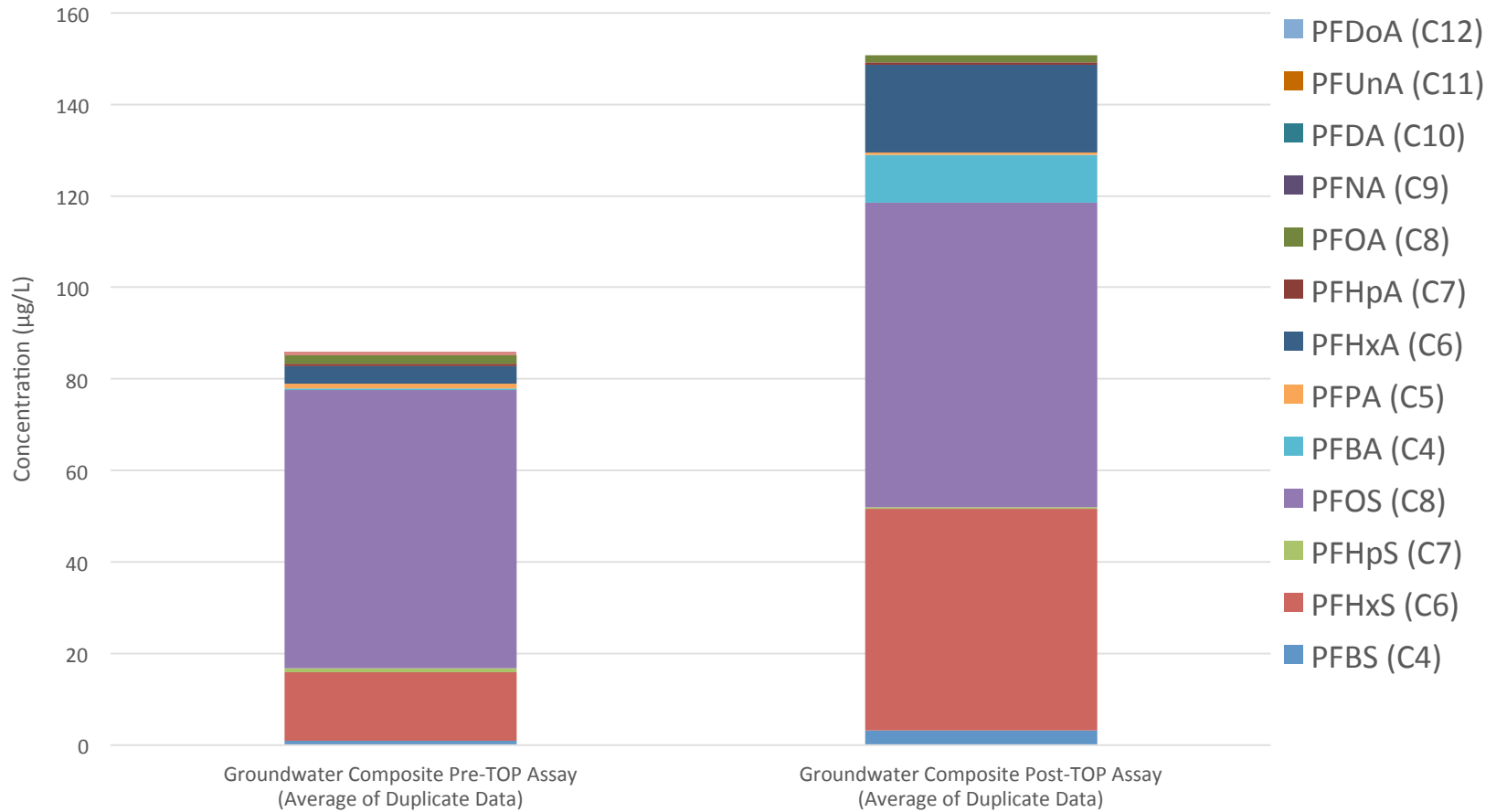
- Separation of organofluorines by synthetic Activated Carbon (AC) & subsequent analysis by combustion ion chromatography (CIC) – sum of organofluorine (analogous to TPH for hydrocarbons)
- Detection limits 1 ug/L F



- Data from recent comparative studies :
 - Precursors may make up a significant portion of total fluorinated mass in sample – PFOS, PFOA analyses not enough
 - Large variability in total PFAs between conventional laboratory and QTOF analyses - some higher, some lower- suspect sample handling and preparation procedures deployed at different laboratories strongly influenced results
 - Remediation technology testing- awareness of ‘splitting’ samples for different laboratories - where the sample is collected in the common test reservoir could also influence results (vertical stratification of sample)
 - Swedish site- analyses of soil and groundwater by TOP Assay showed total PFA concentration orders of magnitude higher than conventional analytical results

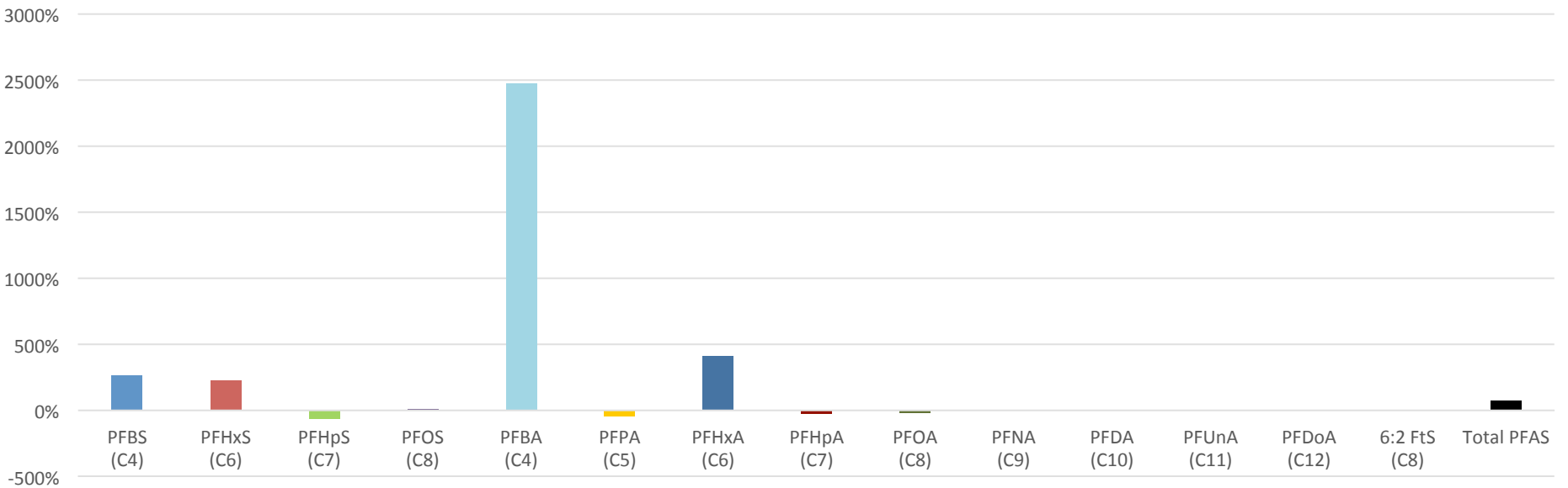


TOP Analysis -Groundwater

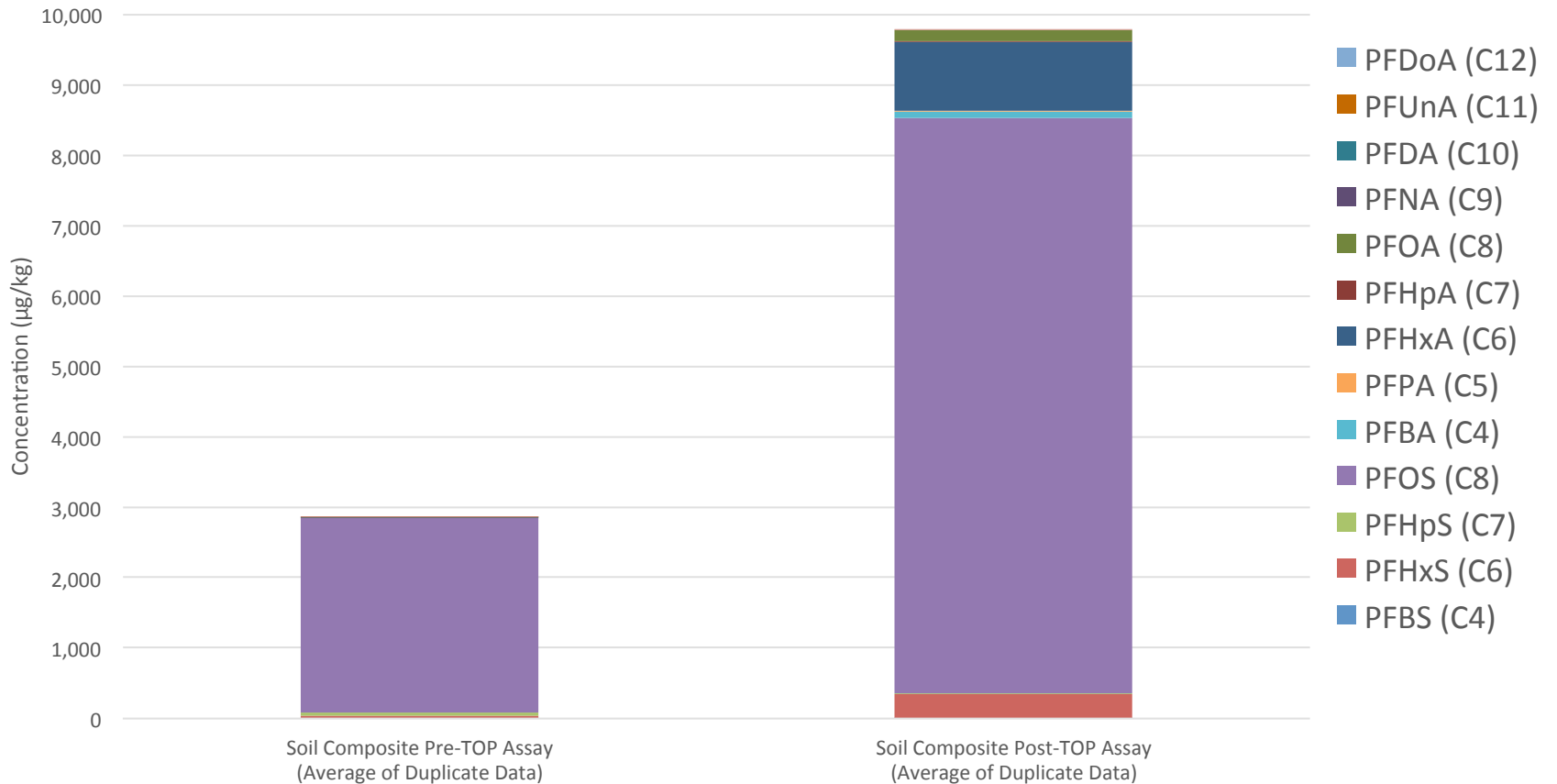


Percentage Increase in PFAS via TOP assay

% Change in PFAS compounds Following TOP Assay
Site Groundwater

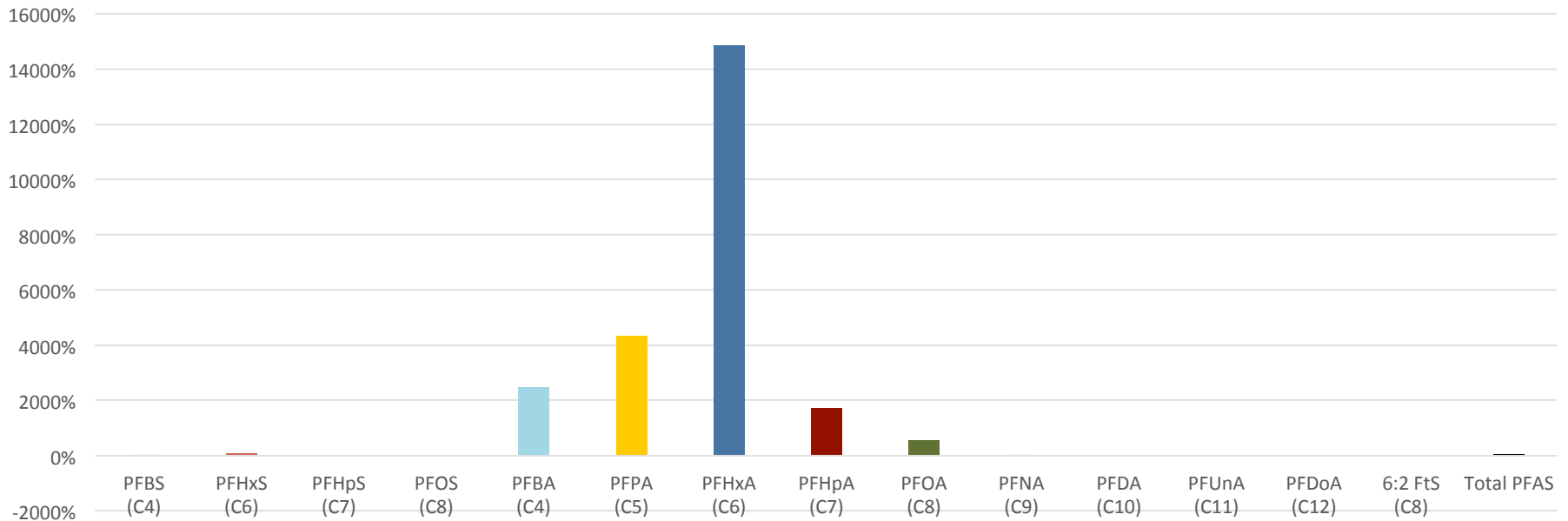


TOP Analysis -Soils

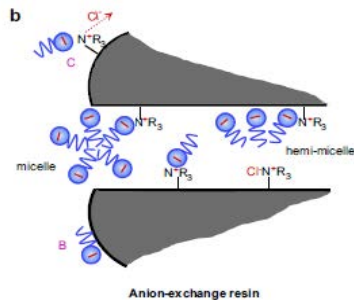
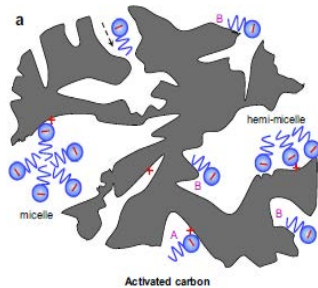


Percentage Increase in PFAS via TOP assay

% Change in PFAS compounds Following TOP Assay
Individual Site Soils



PFAS Groundwater Remediation



- Currently the only viable commercial option is P&T
- Granulated activated carbon can be effective in removing PFOS/PFOA, however sorption is low and competition occurs (higher costs than conventional contaminants)
- Ion exchange resins or polymers with a large surface area are suitable for low concentrations and high volumes, regeneration with NaCl, ethanol or hot water
- Other potential techniques are nano filtration and reverse osmosis
- Oxidation is difficult due to strength of the C-F bond and may lead to higher PFCA / PFSA levels as a result of precursor breakdown

P&T with GAC treatment is the most commonly applied technology

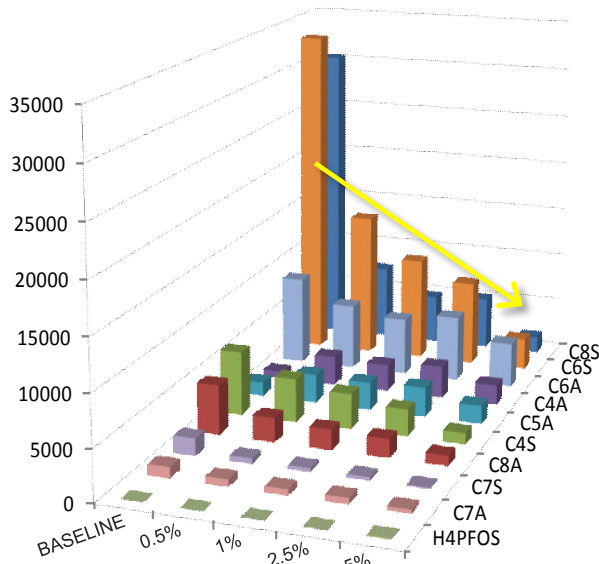
Cost of PFOS Groundwater Treatment with GAC

Low sorption of PFCs → higher GAC consumption, cost

At influent concentrations 3 to 20 µg/L; effluent 0.1 µg/L:

Parameter	Charge capacity (% wt)	Annual GAC Costs (\$/Year)			
		75 Lpm	166 Lpm	832 Lpm	1,665 Lpm
PFOS	0.002 to 0.005	3,932	7,865	39,322	78,643
Chlorinated hydrocarbons	0.02 to 0.4	256	512	2,555	5,112
BTEX	0.1 to 2.0	52	102	512	1,022
PAH	1.3 to 2.5	29	57	284	568

Arcadis ScisoR technology



- Destruction of PFAS by chemical oxidation
- Effective at ambient temperature
- Reagents can be injected or mixed with impacted soil and groundwater
- In situ remediation of AFFF (aqueous fire fighting foam) impacted source areas
- Potential for wastewater, soil wash effluent treatment
- Potential for regeneration of support media (like ion exchange resins and other absorptive media) to destroy PFAS on site
- Patent granted in NL. Patent Cooperation Treaty (PCT) procedure pending for worldwide patent rights

Novel chemical oxidation method to degrade PFAS

Airport Schiphol

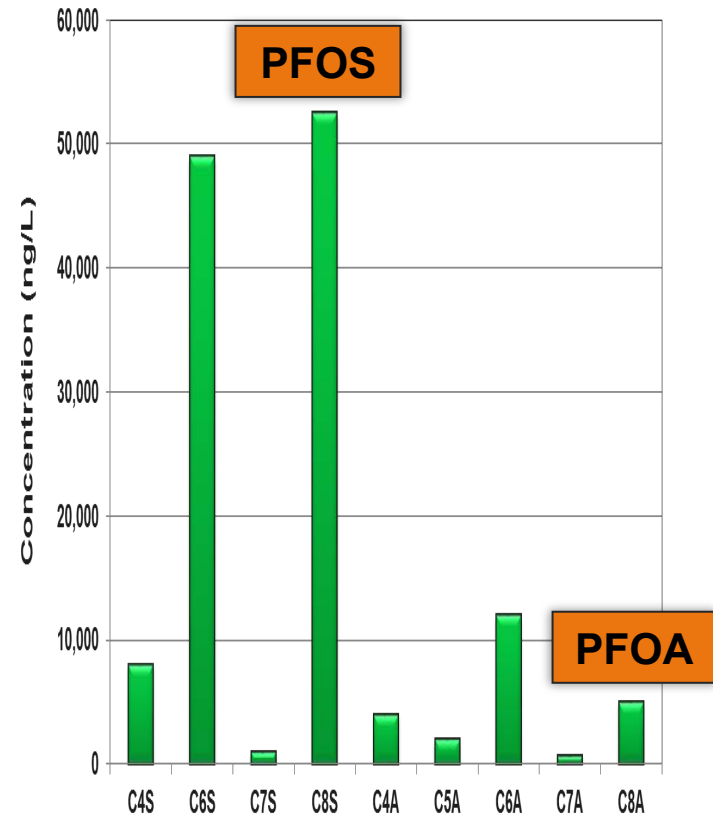
Evaluate initial treatability results and complete sensitivity analysis:

Screened soil and groundwater for ScisoR™:

- Soil suitability for oxidation
- Geochemistry (elevated carbonates)

Tested groundwater for a suite of 22 PFCs

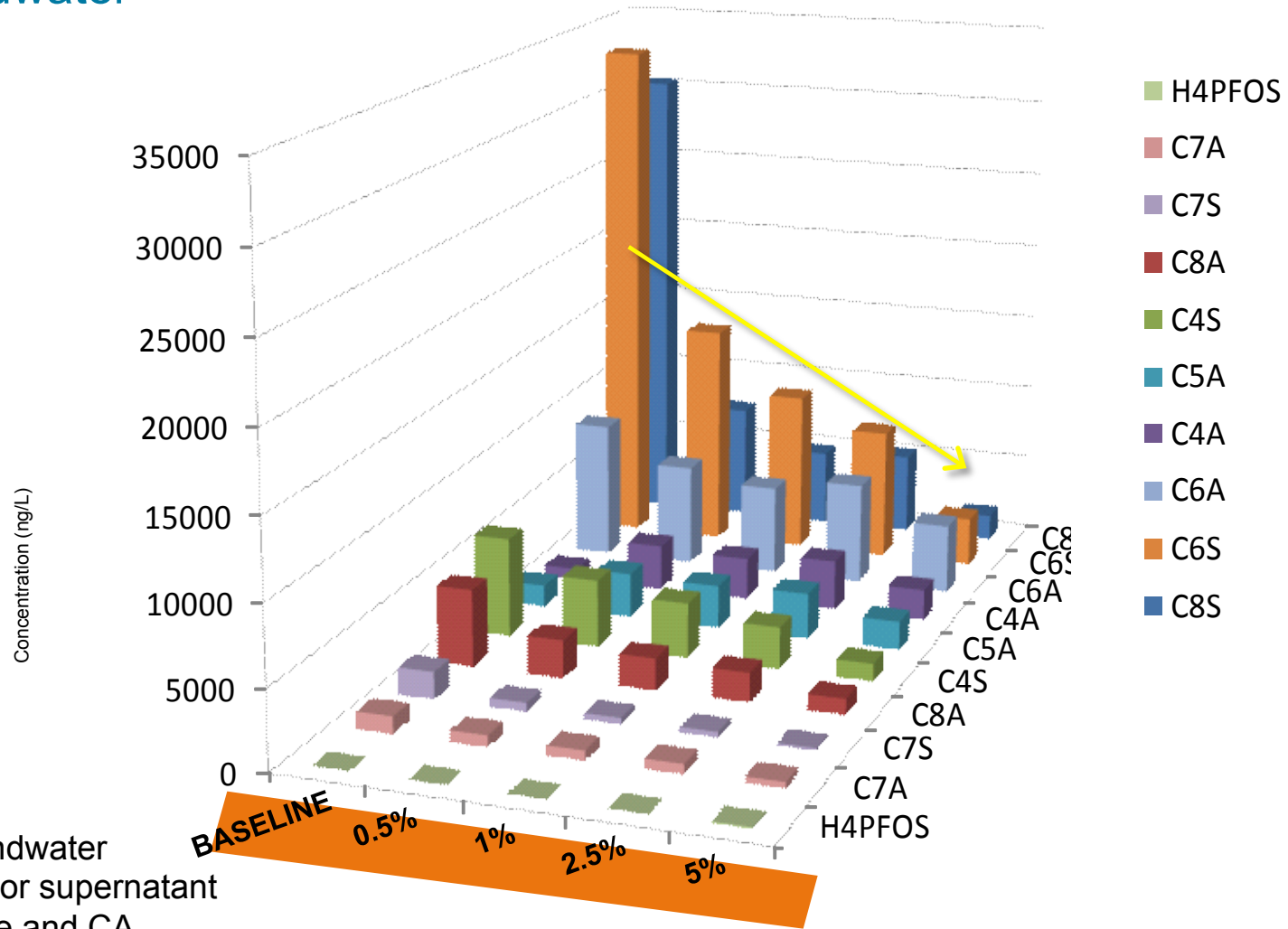
- Other PFCs present, including PFHxA in high concentrations



- C4S:** perfluorobutane sulfonate
- C6S:** perfluorohexane sulfonate
- C7S:** perfluoroheptane sulfonate
- C8S:** perfluorooctane sulfonate (PFOS)
- C4A:** perfluorobutanoic acid
- C5A:** perfluoropentanoic acid
- C6A:** perfluorohexanoic acid
- C7A:** perfluoroheptanoic acid
- C8A:** perfluorooctanoic acid (PFOA)

Phase 2 results: ScisoR™

Soil and Groundwater



- 300 g soil, 300 mL groundwater
- PFCs monitored in reactor supernatant
- All samples contained Fe and CA
- Percentages represent peroxide / persulfate dosing ratio

Swedish site study

Screened groundwater for ScisoR™:

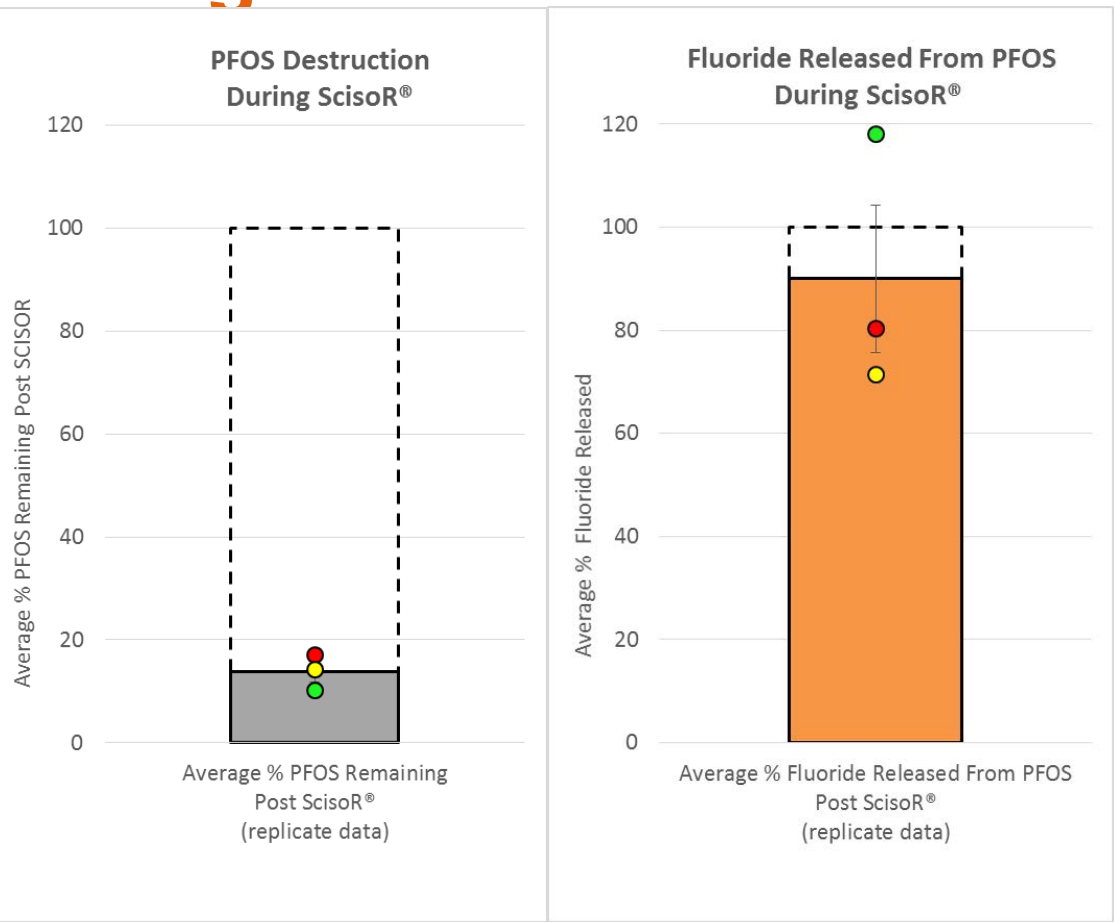
- Mixture of site groundwater with mixtures of persulphate and permanganate
- Decrease in PFOS from >400,000 ng/L to 51,400 ng/L (90% reduction)
- TOP analyses showed much higher concentrations than conventional GC/MS results
- Field pilot scheduled for summer 2016

Environment Canada study

Screened soil and groundwater for ScisoR™ and other oxidant combinations

- Groundwater and simulated soil wash effluent
- Variety of oxidant combinations (persulphate/permanganate, catalyzed H₂O₂)
- ScisoR effective in treating PFOS, only observed early time treatment of PFOA
- Mixed results with H₂O₂
- Variability in laboratory results
- Final results presented at AMOP conference in June (Yao et al)

PFOS Destruction & Fluoride Mass Balance During ScisoR®



- 10 mg/L PFOS starting concentration
- 3 replicate data sets
- 83 to 90% PFOS destruction after 14 days
- 71% to 118% fluoride released from PFOS during SCISOR
- Overall fluoride mass balance (remaining fluoride in PFOS + fluoride released to solution)
 - 86% to 126% of theoretical
- All treated samples were blind spiked with 10 mg/L fluoride
 - 80% to 99% spike recovery
- Spike analyses demonstrate ion measured is fluoride, results are quantitative

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

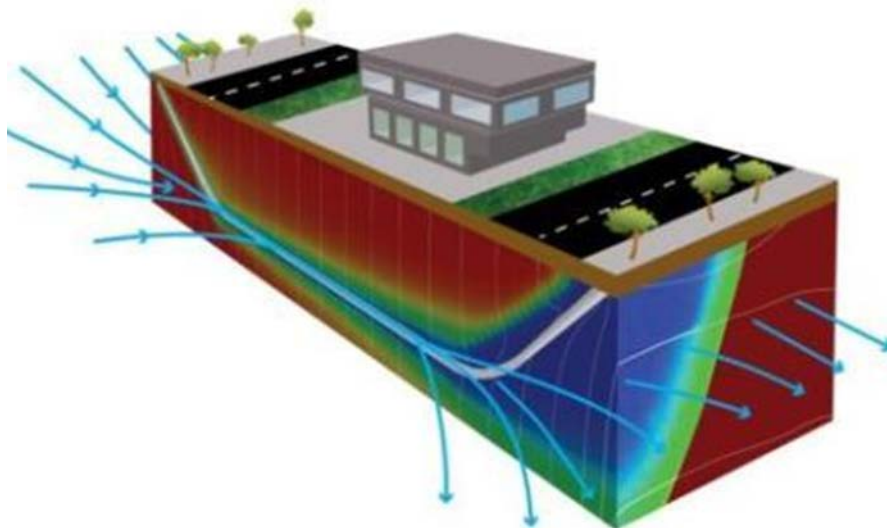
Other treatment options

3-year SERDP funding grant (\$1.2M)

ARCADIS, Clarkson University, Southern Nevada Water Authority

Integrated use of persulfate-based oxidation into the PFC GAC treatment train

Evaluation of other alternative PFC treatment strategies – horizontal well-based capture systems for in situ GAC treatment



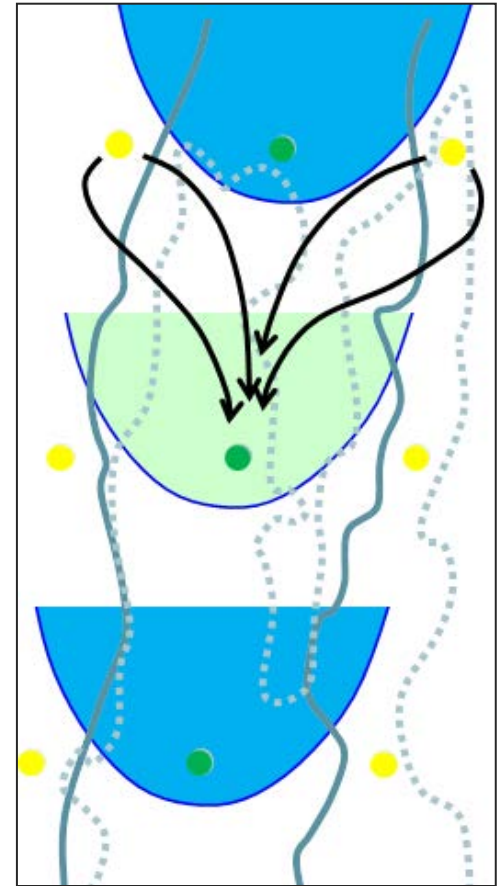
Other treatment Options

Targeted source zone remediation via ScisoR[®]

- Not a plume-wide treatment remedy
- Cost advantage comes in addressing elevated mass to eliminate mass flux to dilute plume

Easily coupled with existing containment remedies such as Directed Groundwater Recirculation (DGR)

- Many PFAS plumes are very long
- Ion Exchange resins and other absorptive media are being tested for commercial use to replace GAC, with the objective of using ScisoR[®] to regenerate the support media (destroy PFAS) on site



PFAS Research & Development

Three current focus areas:

1. Analytical chemistry –fast turnaround, comprehensive and cost effective analytical method (ideally able to be deployed in the field- TOP as a screening tool?)
2. In-situ remediation (ScisoR development) –understand kinetics, dosing and mechanisms
3. Water treatment – what sorbent or water treatment technologies are most promising

Conclusions

- PFAS comprise a complex mixture of perfluorinated and polyfluorinated organic compounds
- Many PFAS are not detected by conventional commercial analytical testing methods
- PFAS compounds including precursors biotransform to produce PFAA's as persistent dead end products
- therefore awareness of total PFAS in sample is key (precursor contribution and degradation)- TOP assay shows considerable promise
- sampling protocols and handling, and analytical methods can significantly influence results, especially in laboratory studies of remedial methods
- ScisoR based oxidation methods show considerable promise as a remedial approach for potential in-situ groundwater treatment

Imagine the Result