Laboratory Treatability Studies for PFAS-impacted Water

Ryan Thomas, PhD

April 18, 2019

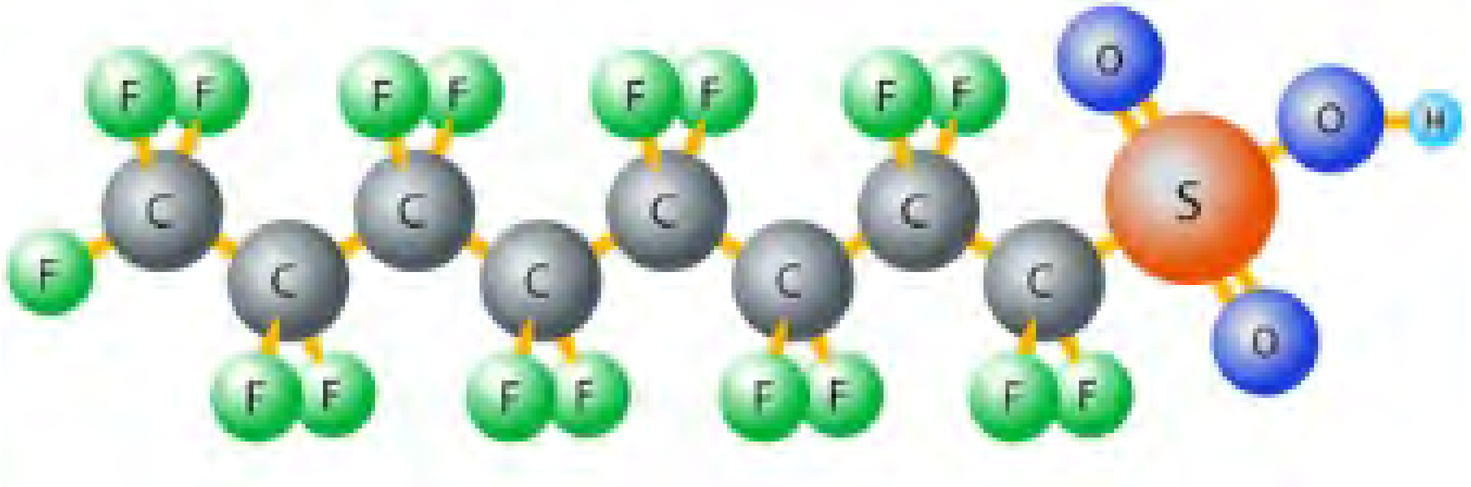
Agenda for Today

- What are PFAS
- Remediation Challenges
- Preliminary Treatability Studies

What are PFAS?

PFAS

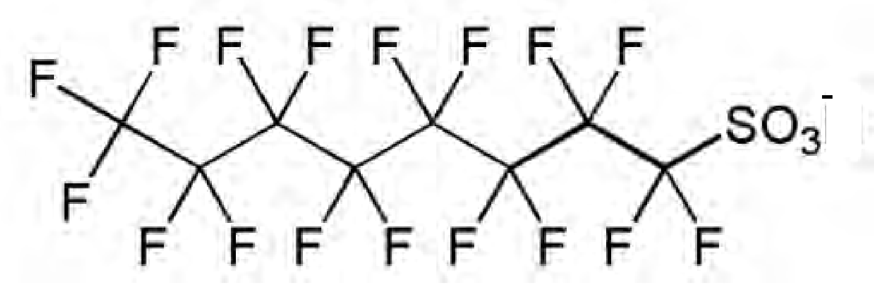
- PFAS – Per- and Polyfluoroalkyl substances
- Large class (5,000+) of anthropogenic compounds
- Commercial analytical methods detect ~24 PFAS
- Tail - carbon chain with fluorine substituting some/all of the hydrogens on the chain (hydrophobic and oleophobic)
- Head – Polar functional group (hydrophilic)
- Unique surface active properties – leads to partitioning at interfaces (e.g., soil/water, water/air, and water/NAPL)



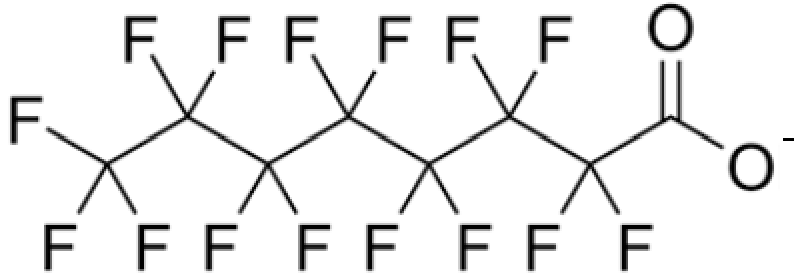
Per-PFAS versus Poly-PFAS

- Per-PFAS are fully fluorinated PFAS
- Carbon-fluorine bond very strong
- Per-PFAS very recalcitrant to degradation or destruction
- Most commonly used per-PFAS: Perfluorooctane sulfonate (PFOS) and Perfluorooctanoate (PFOA)

PFOS



PFOA

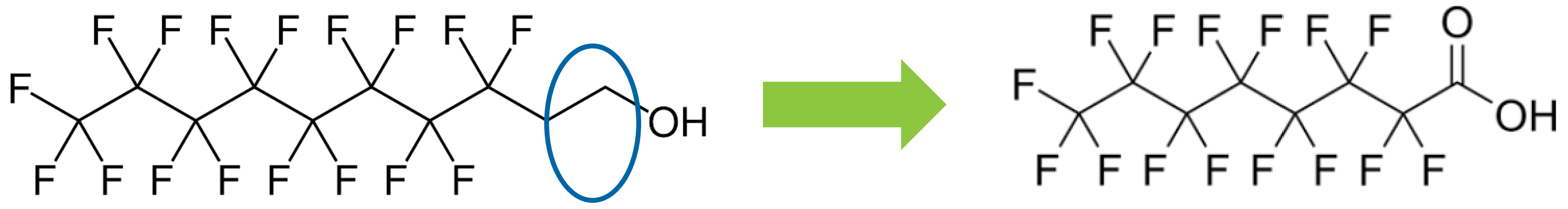


Per-PFAS versus Poly-PFAS

- Poly-PFAS are not fully fluorinated
- Creates a “weak-link”
- Can be transformed into Per-PFAS

8:2-FTOH

PFOA



PFAS – Uses and Sources

Example uses:

- Chrome plating historically used PFOS as a fume suppressant (e.g., in automobile industry)
- Textiles and leather
- Class B fire fighting foams (AFFF)
  - Flammable liquids and gases, petroleum greases, tars, oils and gasoline, solvents, alcohols and other flammable liquids
- Industrial surfactants
- Photolithography/semiconductor industry
- Paper and packaging
- Wire manufacturing
- Sealants and finishings (floors and furniture)

No natural sources

Waste sector important

Potential Exposure Pathways – Commercial and Consumer Products

Commercial and Consumer Products Containing PFAS:

- paper and packaging
- clothing and carpets
- outdoor textiles and sporting equipment
- ski and snowboard waxes
- non-stick cookware
- cleaning agents and fabric softeners
- polishes and waxes, and latex paints
- pesticides and herbicides
- hydraulic fluids
- windshield wipers
- paints, varnishes, dyes, and inks
- adhesives
- medical products
- personal care products (for example, shampoo, hair conditioners, sunscreen, cosmetics, toothpaste, dental floss)

SOURCE: www.atsdr.cdc.gov/pfas

SOURCE: ITRC – History and Use of PFAS Fact Sheet 2017

PFAS timeline

2019 USEPA releases PFAS Action Plan

2018 USEPA issues draft toxicity criteria for GenX PFAS compounds

2018 ATSDR releases draft Toxicological Profile for Perfluoroalkyls

2010

2016 USEPA issues Drinking Water Health Advisories for PFOA and PFOS)

2010 Health Canada issues provisional drinking water guidance values for PFOS and PFOA

2009 PFOS added to Annex B of the Stockholm Convention on persistent organic pollutants

2009 USEPA Preliminary Drinking Water Health Advisory for PFOA/PFOS

2000

2006 McDonald's phases out fluorotelomers in packaging

2006 USEPA PFOA Stewardship Program established

2003 China and Brazil scale-up production

2001 3M ceases production of PFOS and related compounds

1990

Late 1990s Widespread occurrence of PFOS/PFOA in blood of the general population

Late 1990s Improved analytical capabilities for detecting low concentrations

1960

1961 DuPont research suggest negative health effects on mice fed PFOA

1950

1951 DuPont begins using PFOA to make Teflon; first use of PFAS as a wetting agent and fume suppressant in chrome plating industry

1940

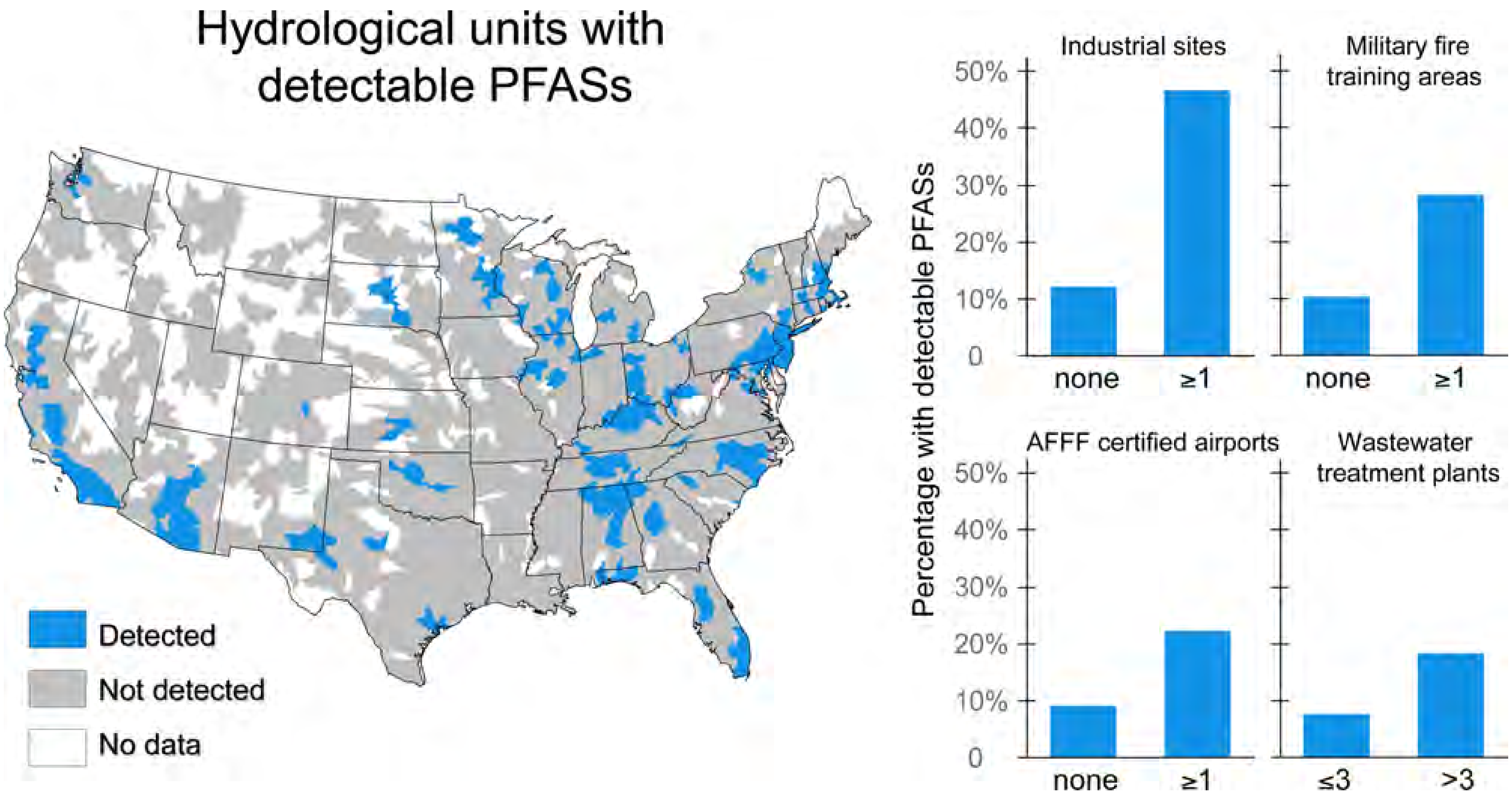
1947 3M begins production of PFOS and PFOA

EPA PFAS Action Plan - 2019

On February 14, 2019, the EPA unveiled their comprehensive **PFAS action plan**. This action plan involves:

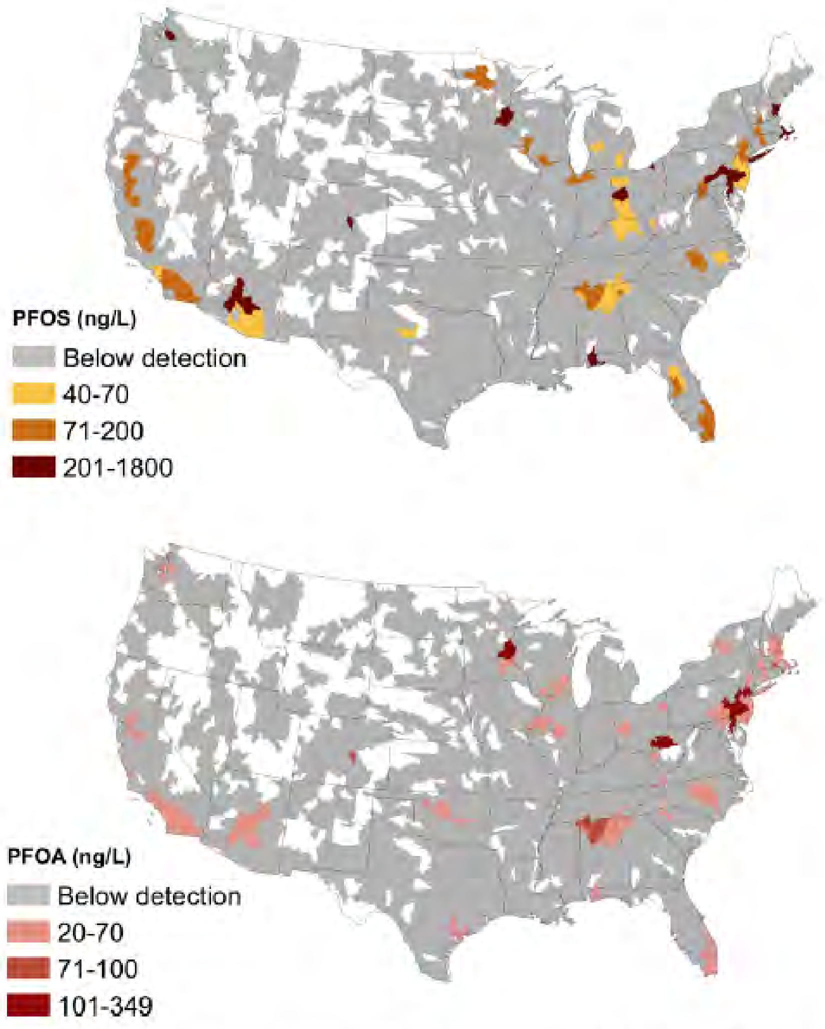
- Moving forward with the Maximum Contaminant Level (MCL) process outlined in the Safe Drinking Water Act (SDWA) for PFOA and PFOS
- Continue strengthening enforcement authorities and clarifying cleanup strategies through actions such as designating PFOA and PFOS as hazardous substances and developing interim groundwater cleanup recommendations
- Considering the addition of PFAS chemicals to the Toxics Release Inventory (TRI) and rules to prohibit the uses of certain PFAS
- Enhancing the way in which agencies communicate about PFAS and potential human health risks, including convening a federal interagency PFAS risk communication workgroup and developing a Risk Communication toolbox.

Why are PFAS a concern?



SOURCE: Hu, Xindi C., et al. "Detection of poly-and perfluoroalkyl substances (PFASs) in US drinking water linked to industrial sites, military fire training areas, and wastewater treatment plants." *Environmental science & technology letters* 3.10 (2016): 344.

Evaluation of Risk – PFAS in drinking water



US EPA's Health Advisory is 70 ng/L

Figure 1. Hydrologic unit codes (eight-digit HUCs) used as a proxy for watersheds with detectable PFOA and PFOS in drinking water measured in the US EPA's UCMR3 program (2013–2015). Blank areas represent regions where no data are available.

SOURCE: Hu, Xindi C., et al. "Detection of poly-and perfluoroalkyl substances (PFASs) in US drinking water linked to industrial sites, military fire training areas, and wastewater treatment plants." *Environmental science & technology letters* 3.10 (2016): 344.

Toxicity assessment of PFAS

USEPA has developed toxicity criteria for PFOA, PFOS, and several GenX chemicals

- Validated but not yet approved for IRIS toxicity database
- Legacy C8 compounds better studied than C6 GenX chemicals

Animal studies serve as the basis for toxicity criteria

- Adverse effects from PFOA and PFOS include elevated serum cholesterol and liver enzymes, decreased immune response, and reproduction/development impacts

Similar effects seen in highly exposed human populations

Some epidemiology data links PFAS exposure to cancer (testicular, kidney, bladder) but these studies are not definitive

Which PFAS to regulate?

Region	PFOA	PFOS	PFNA	PFBA	PFBS	PFHxS	PFOSA	PFHpA
USEPA	Yes	Yes						
PA	Yes	Yes						
AK	Yes	Yes				Yes		Yes
CA	Yes	Yes						
MI	Yes	Yes						
MN	Yes	Yes		Yes	Yes	Yes		
CT	Yes	Yes	Yes			Yes		Yes
Australia	Yes	Yes				Yes		

Remediation Challenges

Treatment Options - Water

Field Demonstrated	Emerging – Pilot / Bench Scale
• Granular Activated Carbon (GAC) • Ion Exchange • Nanofiltration • Reverse Osmosis • Ozone fractionation	• Coagulation • Electrochemical • Advanced Oxidation/Reduction • Sonochemical • Plasma • Biodegradation

Treatment Options – Soil / Infrastructure

Excavation and incineration

- High temperatures and off gas treatment required to destroy PFAS
- Requires high temperature incinerators
- Approach is very high cost and ‘less than environmentally sustainable’

On-site stabilization

- e.g., stabilization with products such as Rembind or Activated Carbon
- Does not destroy PFAS

On-site containment

- On-site landfill construction
- Does not destroy PFAS

Remediation Challenges – PFAS

Biodegradation

- Very limited research to date showing biodegradation of Per-PFAS
- Evidence of transformations of Poly-PFAS
- Ability to treat to the proposed standards?

Oxidative / Reductive Technologies

- Requires high energy and/or diverse reactive species – complex chemistry
- Several bench studies and few pilots performed showing destruction of PFAS
- Research is ongoing to treat precursors

SOURCE: XDD Environmental – PFAS Remediation Webinar – Part 1

Preliminary Treatability Studies

Why these Studies?

- So GHD can continue to innovate with our Innovative Technology Group and stay on the leading edge of PFAS remedial technologies in North America and globally

- Identify treatment technologies for industrial wastewater/groundwater/landfill leachate from client sites that will advance the science and benefit our clients.

- Identify treatment technologies for drinking water from a client site that will advance the science and benefit our clients

- Based on literature and project site review we selected ultraviolet and chemical oxidation (groundwater/leachate) to be tested at ITG
- Natural absorbents (drinking water) and electrochemical treatment will be tested at XDD and Fraunhofer
- These technologies have a reasonable likelihood of successful treatment and commercial viability compared to other technologies (e.g., carbon)
- The study scopes have been fully developed and GHD/partners are implementing the work
- Estimated 6 month schedule to completion (including reports)

Who are our Partners?

- XDD, reputable remedial technology company with a treatability lab in NH

XDD ENVIRONMENTAL

- Test America, US national commercial laboratory that we have partnered with for decades. They are currently doing 1,000s of PFAS analyses/week and are recognized PFAS analytical experts

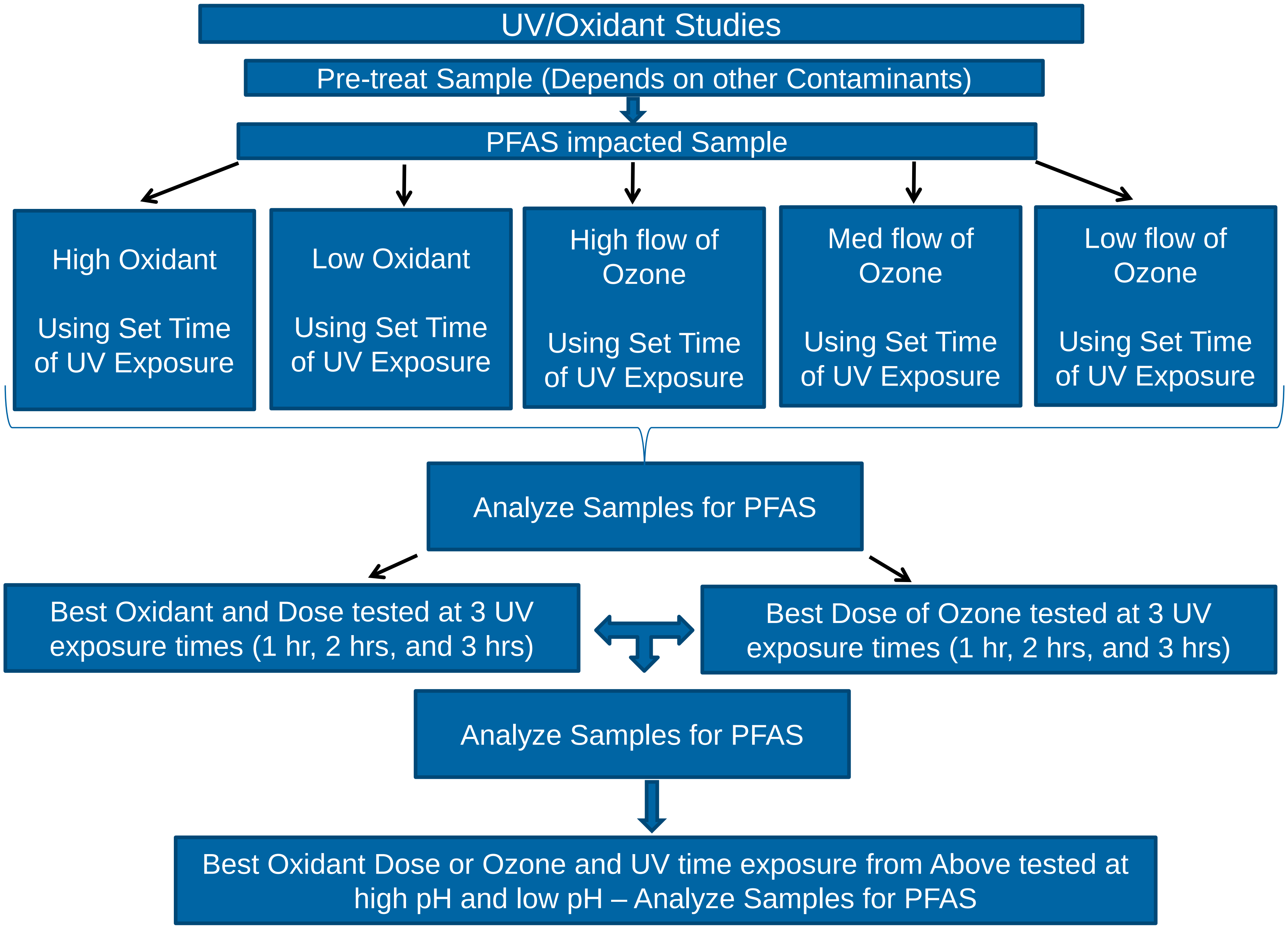
TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

- Alpha Analytical, NE regional, reputable laboratory already doing PFAS studies

ALPHA ANALYTICAL, INC

GHD

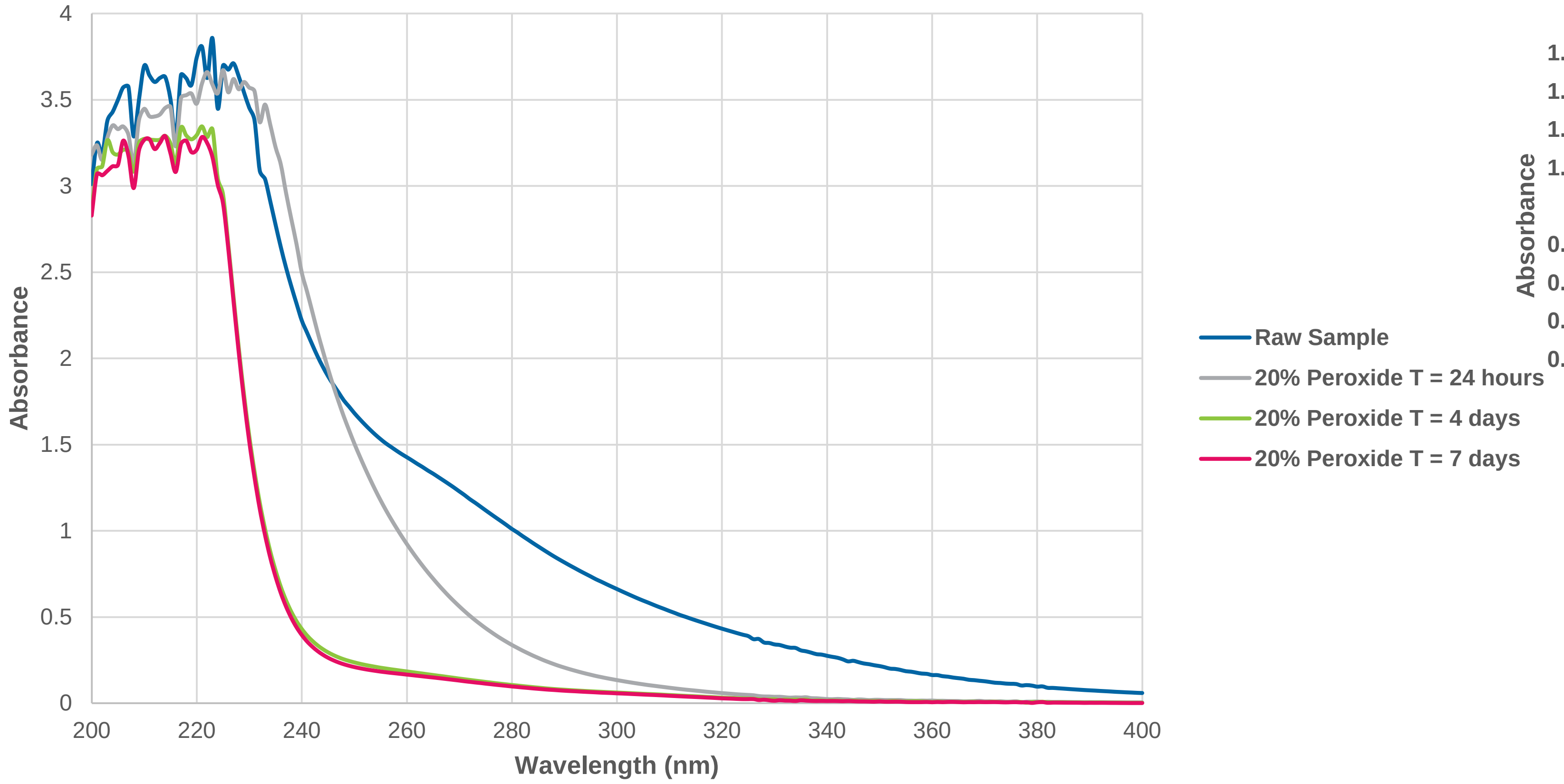

UV/Oxidant Studies
Pre-treat Sample (Depends on other Contaminants)
PFAS impacted Sample
High Oxidant
Using Set Time of UV Exposure
Low Oxidant
Using Set Time of UV Exposure
High flow of Ozone
Using Set Time of UV Exposure
Med flow of Ozone
Using Set Time of UV Exposure
Low flow of Ozone
Using Set Time of UV Exposure
Analyze Samples for PFAS
Best Oxidant and Dose tested at 3 UV exposure times (1 hr, 2 hrs, and 3 hrs)
Best Dose of Ozone tested at 3 UV exposure times (1 hr, 2 hrs, and 3 hrs)
Analyze Samples for PFAS
Best Oxidant Dose or Ozone and UV time exposure from Above tested at high pH and low pH – Analyze Samples for PFAS

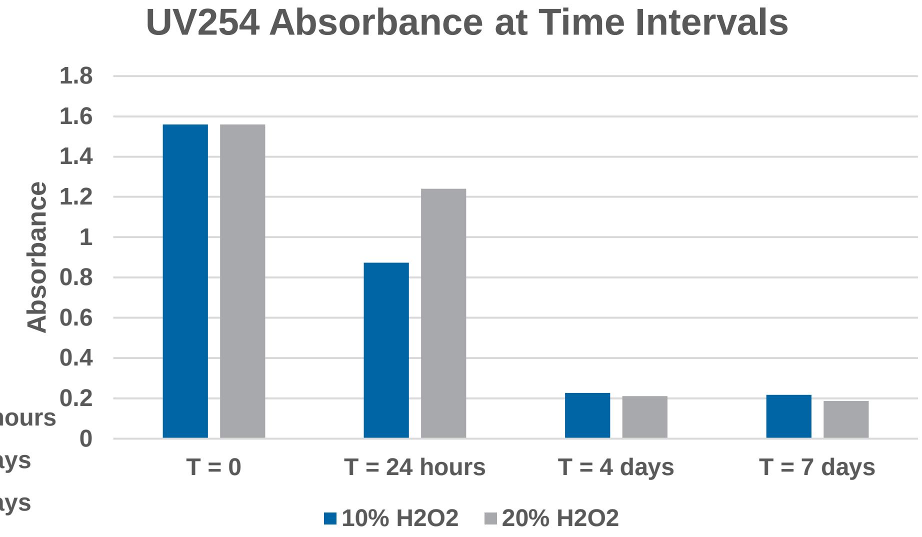
Initial Landfill PFAS results

		Municipal	Municipal	Industrial
8:2-FTS (8:2 Fluorotelomer Sulfonic Acid)	ng/L	32	110	ND (4.6)
NEtFOSAA	ng/L	68	310	ND (2.3)
NMeFOSAA	ng/L	57	110	ND (2.3)
PFBS (Perfluorobutanesulfonic Acid)	ng/L	6300	6900	130
PFHpS (Perfluoroheptanesulfonic Acid)	ng/L	ND (4)	ND (20)	80
PFHxS (Perfluorohexanesulfonic Acid)	ng/L	440	1200	570
PFOS (Perfluorooctanesulfonic Acid)	ng/L	190	340	5,500
PFPeS (Perfluoropentanesulfonic Acid)	ng/L	ND (4)	ND (20)	270
PFBA (Perfluorobutanoic Acid)	ng/L	2800	530	200
PFDA (Perfluorodecanoic Acid)	ng/L	75	100	ND (2.1)
PFHpA (Perfluoroheptanoic Acid)	ng/L	490	850	30
PFHxA (Perfluorohexanoic Acid)	ng/L	2100	4800	60
PFNA (Perfluorononanoic Acid)	ng/L	110	91	ND (0.92)
PFOA (Perfluorooctanoic Acid)	ng/L	1600	4100	100
PFPeA (Perfluoropentanoic Acid)	ng/L	660	760	ND (4.6)

Pretreatment for UV Advanced Oxidation/Reduction Studies

- Pre-treatment of Landfill Leachate samples is required to test UV AOP/RP
- Calgon suggests UV254 absorbance below 0.07





- Fenton's reagent alone significantly reduced UV254 absorbance, but not below 0.07
- PAC is being tested before Fenton's reagent to further reduce absorbance

Pretreatment for UV Advanced Oxidation/Reduction Studies

		Initial	Fenton's Reagent	
Parameters	Units	Industrial	Industrial	Net Change from Initial
PFBS (Perfluorobutanesulfonic Acid)	ng/L	130	120	-10
PFDS (Perfluorodecanesulfonic Acid)	ng/L	ND (1.4)	0.5	0.5
PFHpS (Perfluoroheptanesulfonic Acid)	ng/L	80	94	14
PFHxS (Perfluorohexanesulfonic Acid)	ng/L	570	560	-10
PFNS (Perfluorononanesulfonic Acid)	ng/L	3	2.2	-0.8
PFOS (Perfluorooctanesulfonic Acid)	ng/L	5,500	5,600	100
PFPeS (Perfluoropentanesulfonic Acid)	ng/L	270	230	-40
PFBA (Perfluorobutanoic Acid)	ng/L	200	70	-130
PFHpA (Perfluoroheptanoic Acid)	ng/L	30	37	7
PFHxA (Perfluorohexanoic Acid)	ng/L	60	92	32
PFNA (Perfluorononanoic Acid)	ng/L	ND (0.92)	2.4	2.4
PFOA (Perfluorooctanoic Acid)	ng/L	100	86	-14
PFPeA (Perfluoropentanoic Acid)	ng/L	ND (4.6)	47	47

- After Fenton's reagent, the largest changes was a decrease in PFBA and increase in PFOS.

Adsorption / Ion Exchange (IX) Studies

PFAS impacted Sample: 48-Hr Screening (Batch Reactors)

- GAC
- Organically Modified Media
- Surfactant Modified Media #1
- Surfactant Modified Media #2
- IX Blend #1
- IX Blend #2
- Commercial IX Media
- Chemical Pre-Treatment

Analyze 10 Samples for PFAS

Column Flushing: GAC, Best Media #1 and #2

- GAC at 3 Bed Volumes (1,000 BV, 5,000 BV, 15,000 BV)
- Best Media #1 at 3 Bed Volumes (1,000 BV, 5,000 BV, 15,000 BV)
- Best Media #2 at 3 Bed Volumes (1,000 BV, 5,000 BV, 15,000 BV)

Analyze 13 Samples for PFAS

Regeneration of Best Media (#1 or #2)

Regeneration A and B – Analyze 5 Samples for PFAS

Destruction (Electrochemical [EC]) Studies

PFAS impacted Sample:
1 Time Point (Batch Reactors)

↓ ↓

EC Only

EC with Pre-Treatment (oxidant or other)

Analyze 4 Samples for PFAS

Additional GHD Research

- Testing drinking water source with UV Advanced Oxidant/Reductant technology

- Evaluation of permeability of landfill liners to PFAS migration

- Evaluation of concrete coatings to mitigate PFAS from leaching

- PFAS Soil Washing Approach (with GHD Australia)

- Soil/sediment/waste stabilization to bind PFAS without future leaching

- Partnering with universities as an industrial partner for research grants (eg. US DoD) for forensic evaluations and using machine learning

Special Thanks to:

<u>GHD's Innovative Technology Group</u>

Dr. Sophia Dore
Fred Taylor
Donald Pope
Jennifer Wasielewski

<u>XDD Environmental</u>
Scott Crawford
Michael Marley

www.ghd.com