PFAS 101 Applied to the Solid Waste Industry

WDNR Solid Waste
Interested Parties
May 15, 2019

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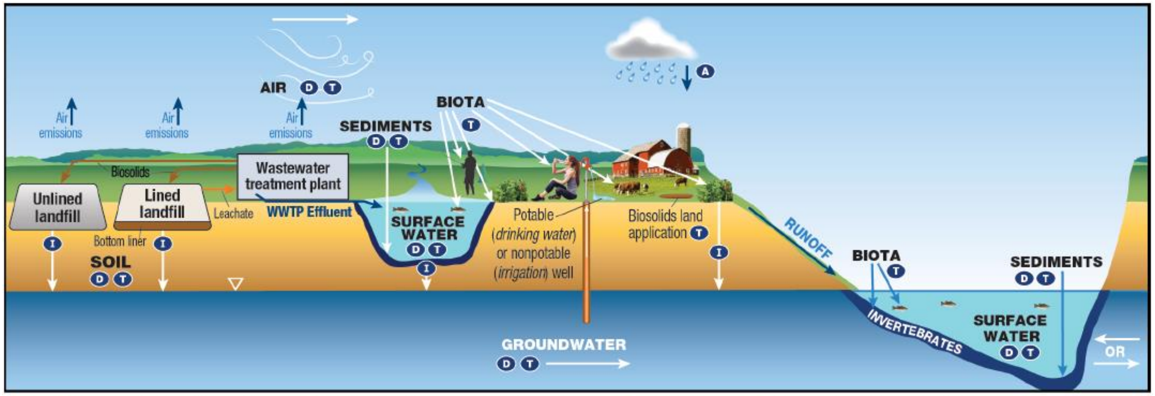
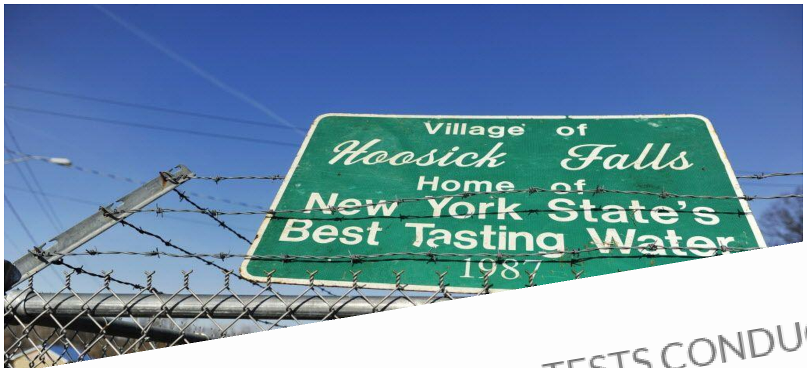
Technical Director
TRC Environmental Corp.



KEY A Atmospheric Deposition D Diffusion/Dispersion/Advection I Infiltration T Transformation of precursors (abiotic/biotic)

Figure 3. Conceptual site model for landfills and WWTPs.
(Source: Adapted from figure by L. Trozzolo, TRC, used with permission)

PFAS in the News



Monday, July 30, 2018

Michigan declares state of emergency for cities pl… water con…

REAKING

MADISON WATER UTILITY | More TESTS CONDUCTED

Traces of two PFAS compounds found in four additional Madison wells

STEVEN VERBURG sverburg@madison.com Apr 10, 2019

PFAS 101 for Solid Waste

- Summary – What's the Big Deal?
- PFAS – What are they – a little chemistry
- PFAS in Manufacturing
- Fate and Transport, and Toxicology,
- Regulatory Status
  - Emerging regs for long chain PFAS
  - Short chain PFAS regs, are they coming?
- PFAS in Landfills
- Treatment and Remediation

PFAS: What's the Big Deal

And Should We Be Concerned?

- **Regulations** – Developing rapidly – (e.g., 8 states added rules in 2018, 19 Total)
- **PFAS are Ubiquitous** – Used in industry and in numerous commercial products since 1960s.
- **Public:** Public concern is growing (e.g., opposition groups using PFAS presence to argue against facilities)
- **Standards in PPT:** Varies by state. Water standards are typically 70 ppt, or less.
- **Highly Mobile:** Migration occurs easily and rapidly in groundwater, surface water and air.
- **Degradation:** No degradation of basic perfluorinated compounds
- **Difficulties with PFAS:**
  - Complicated: Sampling and analytical methods
  - Difficult to treat ($$$$) – especially in leachate

What and Where are PFAS?

PFAS – Per- and Polyfluoroalkyl Substances. A large group of fluorinated compounds used for their stable, unreactive properties.

- Fire Fighting Foams:
  - Type B fire fighting foams – Airports, refineries, etc.
- Textiles and Leather
  - Carpets, clothing, etc.
- Paper Products
  - Food contact materials
- Metal Plating Facilities
- Industrial Surfactants, Resins, Molds, Plastics
- Photolithography, Semiconductor Industry
- Biosolids
  - Paper mill sludge
  - Certain POTW sludge
- Landfills
  - Industrial wastes
  - Leaching from consumer products
  - Landfill fires, depending on whether foam was used.

AFFF; firefighting foam

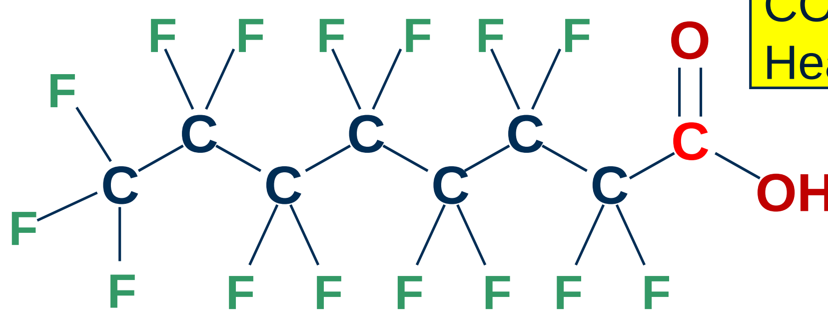
Photos: Charles Hutchins, Yossi Gurvitz, Windell Oskay, Jean-Pierre, White93, Shawn Campbell, Jack W. Reid

A Little PFAS Chemistry

Quick Chemistry Lesson #1

- PFAS are **Per** and **Poly**fluoroalkyl substances
- **Per-fluoroalkyl substances**: can't be degraded, the fully fluorinated tail is very stable.
- **Examples of Per-fluorinated compounds**

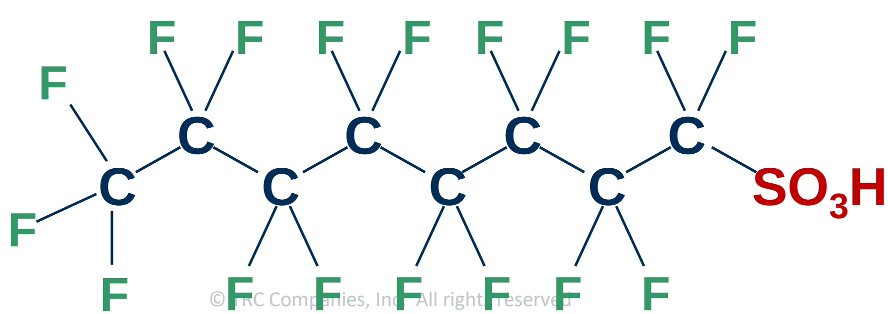
PFOA
Perfluorooctanic Acid



COOH = Carboxylic Head

Alkyl tail, fully fluorinated

PFOS
Perfluorooctanic Sulfonic Acid

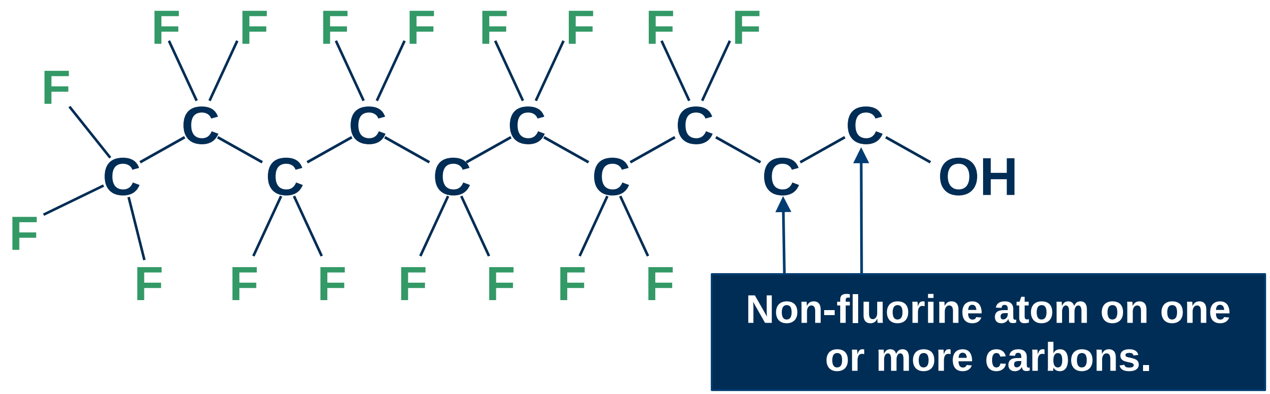


SO_3H = Head

Quick Chemistry Lesson #2

- **Examples of Poly-fluorinated compounds**
- **Poly-fluoroalkyl substances**: non-fluorine atom (typically hydrogen or oxygen) attached to at least one carbon atom

8:2 Fluorotelomer Alcohol (8:2 FTOH)



Polyfluoroalkyl substances may also be degraded to perfluoralkyl substances (e.g. PFOS or PFOA, etc.)

The Evolution of PFAS
As Shown in Fire Fighting Foams (AFFF)

1st Generation
Long Chain
PFOS AFFF
1960-2002

- PFOS based (80%)
- Developed in 1960s
- Production ended in 2002

2nd Generation
Long Chain Fluorotelomer AFFF
1970s-2016

- Sold from 1970s - 2016
- **Long-chain fluorotelomers (8:2 FTS) can breakdown to PFOA**

Modern
Short Chain Fluorotelomer AFFF

- Most foam mfrs transitioned to this
- **No PFOS and no breakdown to PFOS**
- **Short-chain fluorotelomers (6:2 and 4:2 FTS)**
- **May contain trace amts of PFOA and PFOA precursors**
- Considered lower in toxicity and reduced BAP

Similar evolution in other industrial uses

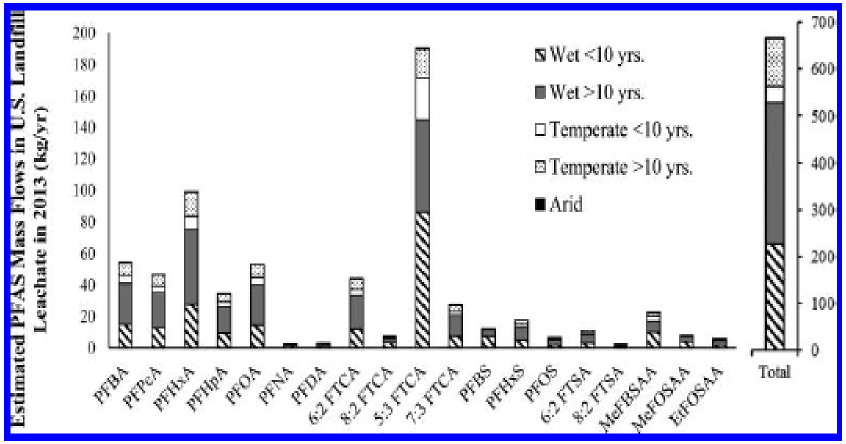
PFAS in Landfills, Leachate, and Gas

PFAS in Landfill Leachate

- US Landfill Study (Lang et al., 2017) – 95 samples from 18 landfills
  - ➢ 70 PFAS measured, 19 PFAS detected in >50% of samples
  - ➢ PFOS: 3 to 200 ppt
  - ➢ PFOA: 100 to 1,000 ppt
  - ➢ Total PFAS: 2,000 to 29,000 ppt
  - ➢ 5:3 FTCA (precursor) dominant in most leachates: 400 to 15,000 ppt

National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate ES&T 2017

J. R. Lang, B. McKay Allred, J.A. Field, J.W. Levis, & Morton A. Barlaz



- Canadian Landfill Study (Li, 2012) samples for 28 landfills
  - ➢ PFAS detections in all 28 samples
  - ➢ PFOA detected in all samples, mean concentration of 439 ppt

- German Landfill Study (Busch, 2009) – 22 German landfills
  - ➢ 38 PFAS detected
  - ➢ Total PFAS: 30.5 ppt to 13,000 ppt

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Michigan PFAS in Leachate & Effects on POTWs

Michigan Waste & Recycling Association/MDEQ (3/1/2019)

https://docs.wixstatic.com/ugd/6f7f77_9b845fefde8b4fd3b42e6a7bd321e21f.pdf

- 30 Mich. LFs, leachate analysis of PFOA & PFOS
  - PFOA – range 3 to 800 ppt vs. MDEQ SW criterion 420 ppt
  - PFOS – range 100 to 710 ppt vs. MDEQ SW criterion 11 ppt
- Landfills as PFOA/PFOS sources to WWTP are relatively minor
- Non-leachate sources contribute greater mass to WWTP influent than leachate.
- Study limitation: Analyzed for PFOA & PFOS only
  - No precursor analyses.
  - Precursors can be present in anaerobic conditions (i.e., in leachate), with degradation to PFOA and PFOS in aerobic treatment system.

Landfill Gas

- PFAS detected in:
  - Landfill Gas
  - Landfill gas condensate
  - Ambient air around landfill (and waste water treatment plants)

Compound	Vapor Pressure (at 25-C)
2,3,7,8-TCDD	2E-07
Dieldrin	7E-04
PFOA	1.3
Naphthalene	10.6
8:2-FTOH	212
PCE	2550
TCE	9900
Benzene	12800

- Volatile Precursors
  - Some PFAS (e.g. fluorotelomer alcohols like 8:2-FTOH) have moderate volatility
  - These compounds can break down to form regulated PFAS in the environment
  - Significant PFAS (mostly FTOH) emissions (>1000 g/year) have been calculated from WWTPs and landfills (Ahrens et al, 2011)

Fate and Transport and Toxicology

Fate and Transport of PFAS

Landfills and WWTPs

Source Example

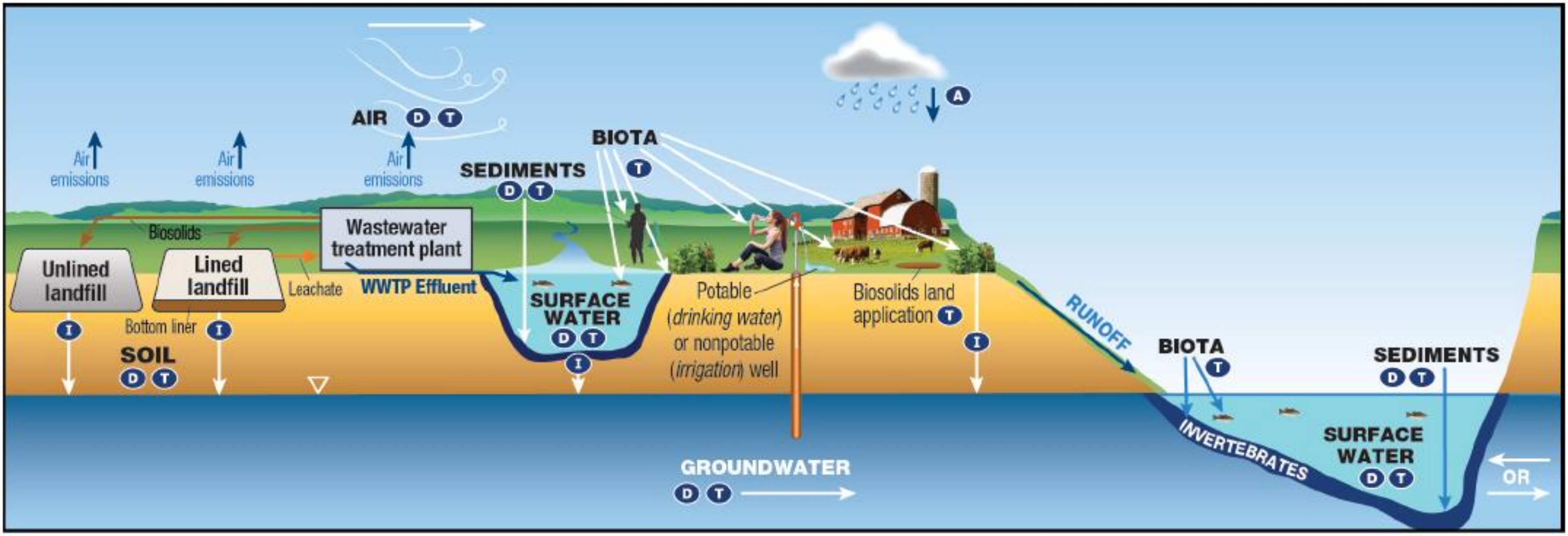
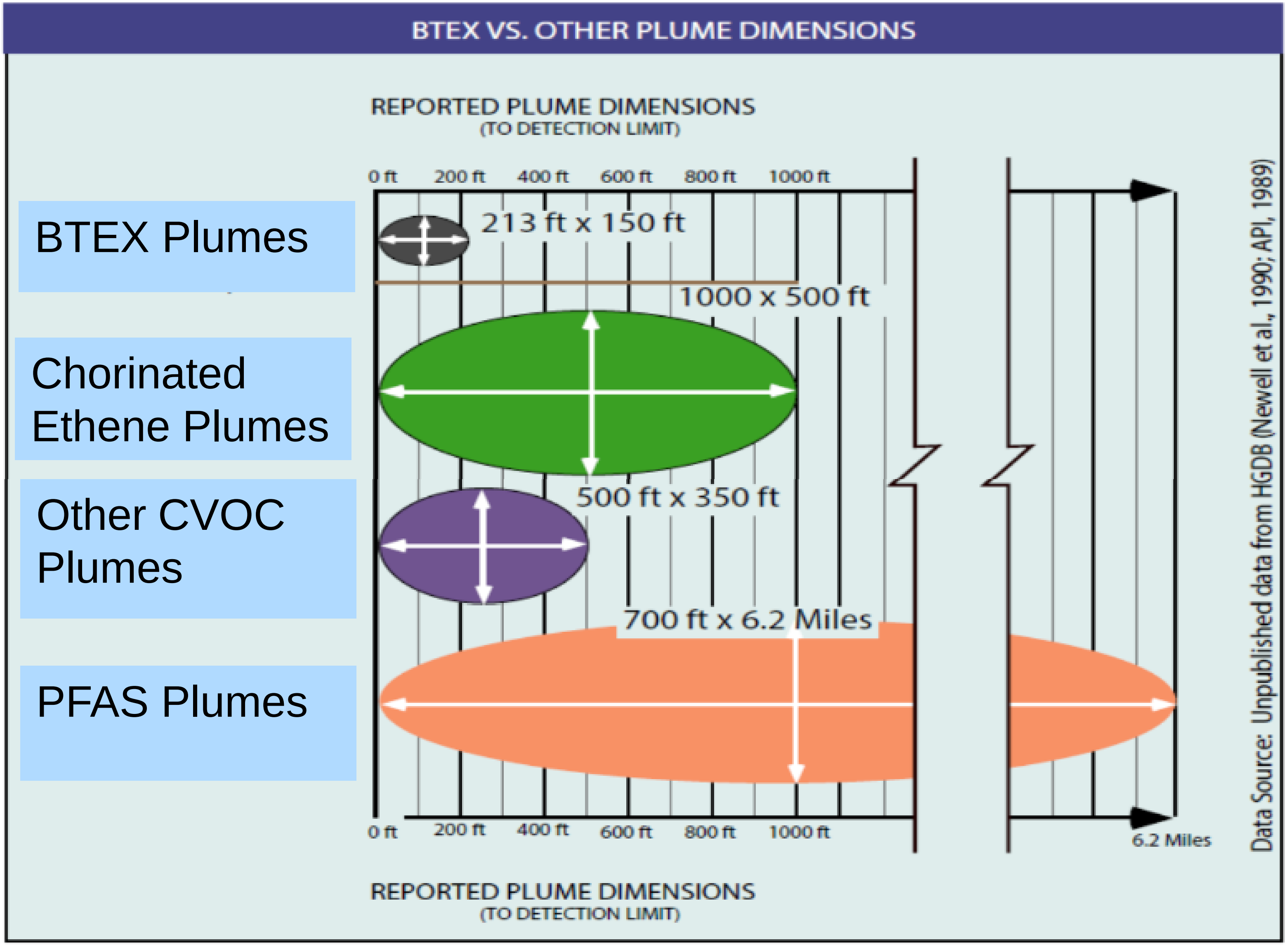


Figure 3. Conceptual site model for landfills and WWTPs.

(Source: Adapted from figure by L. Trozzolo, TRC, used with permission)

Source: March 2018 ITRC Factsheet: Environmental Fate & Transport for PFAS, used with permission

PFAS Mobility



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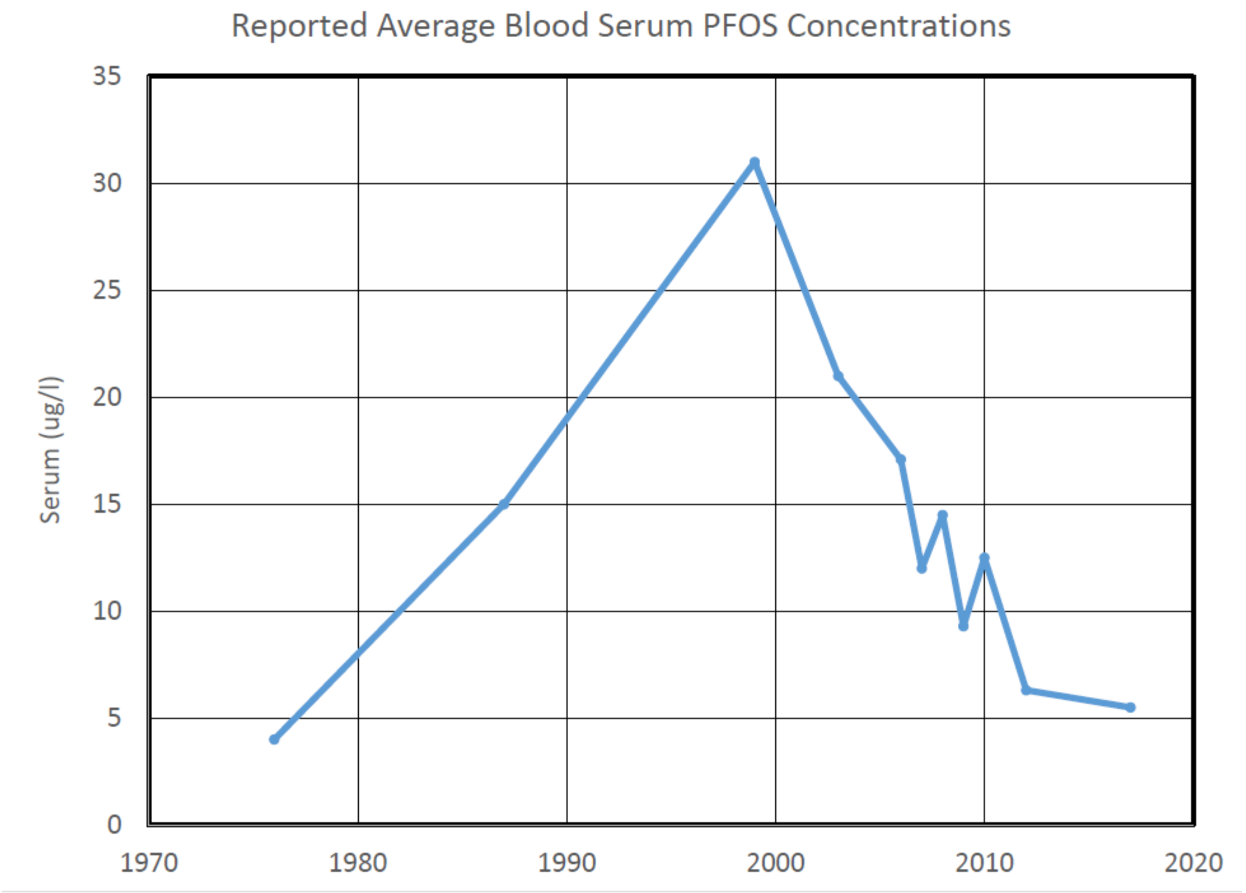
Exposure in Humans

- Majority of US population exposed to PFAS
- Half-life = 2 - 10 years (humans)
- Prevalent in blood and urine samples – baseline exists
- Can cross placental barrier – exposure to developing fetus
- C8 Health project, 70,000 residents with drinking water exposure linked to serum-PFOA concentrations and variety of health outcomes

High cholesterol	Ulcerative colitis	Thyroid disease	Pregnancy-induced hypertension	Cancer (testicular, kidney)

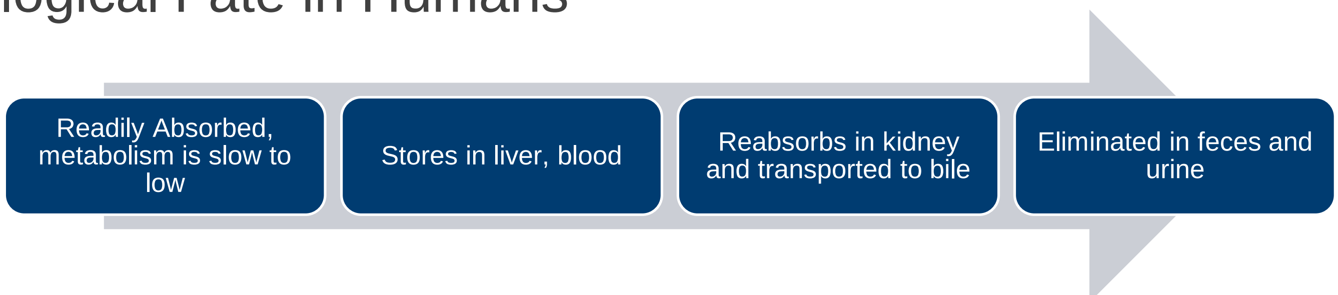
Average blood Serum Concentrations US



trcsolutions.com

Toxicology of PFOA and PFOS

- Most toxicology studies have focused on PFOA and PFOS
  - Conflicting study results in literature
- Has a low affinity to lipids and preferentially binds to proteins
  - Liver, kidney, muscle and blood
- Biological Fate in Humans



- Dec 2018 USEPA IRIS announced 5 PFAS (PFNA, PFBA, PFHxA, PFHxS, PFDA) will be reviewed for toxicity assessment
  - Some of these are the short chain PFAS compounds that form the bases for Modern AFFF

Regulatory Status

What is Occurring? – What to Expect?

U.S. EPA's Recent Actions

EPA PFAS Action Plan: An Overview

- PFOA & PFOS proposed to be listed as hazardous substances under CERCLA
- Development of MCLs for PFOA & PFOS
- Expand monitoring of PFAS in UCMR5
- Consider PFAS for Toxics Release Inventory
- Develop risk communication toolbox
- Develop toxicity standards for select PFAS
- Develop new analytical methods for PFAS
- Evaluate treatment options for PFAS
- PFOA & PFOS groundwater cleanup recommendations

EPA wants to close gaps on PFAS science ASAP.

EPA Announces Most Comprehensive Cross-Agency Action Plan in History of EPA for PFAS

- April 25, 2019 Draft Groundwater Remediation Standards for public comment
  - 40 ng/L for a screening level
  - 70 ng/L for the preliminary remediation goal (PRG)

EPA Action Plan Identifies CERCLA as the Likely Federal Cleanup Program to Address Releases of PFAS

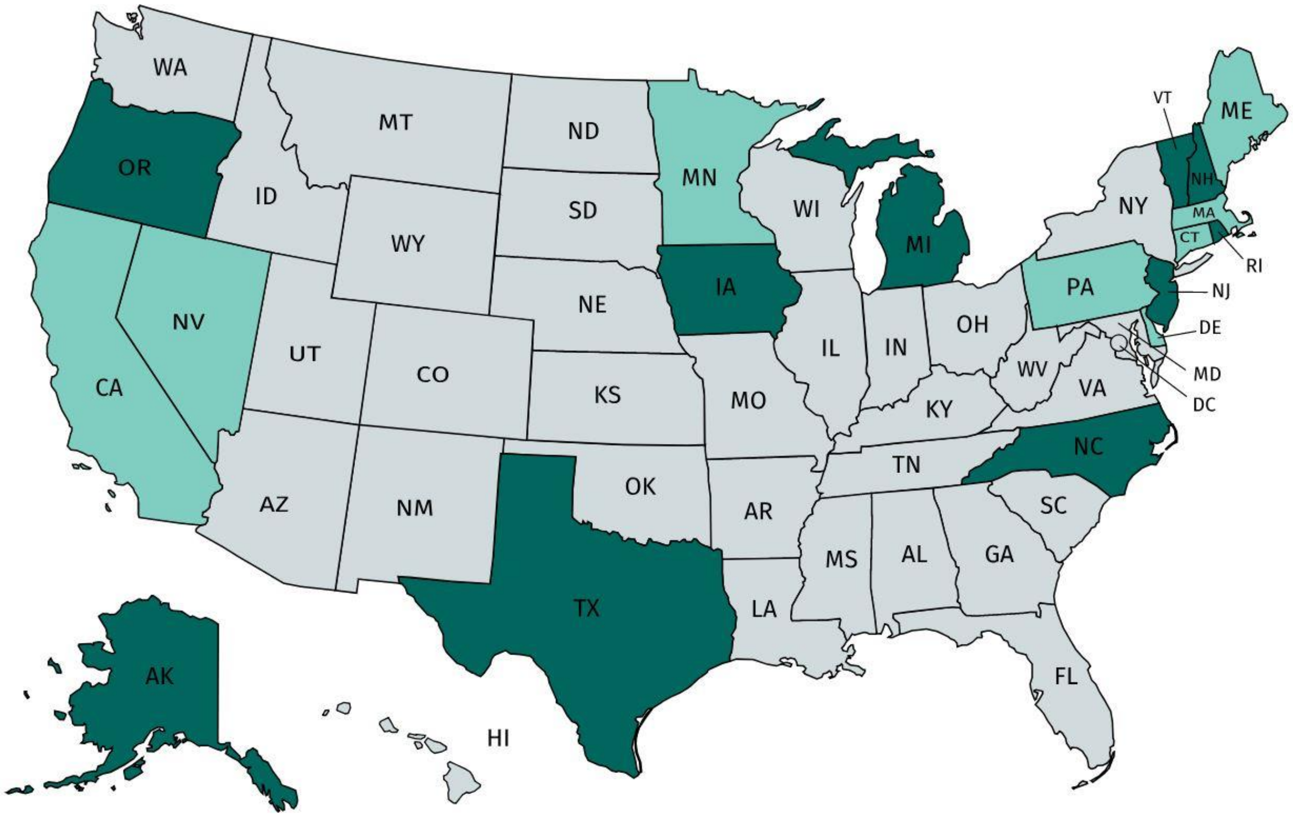
Comprehensive Environmental Response, Compensation, and Liability Act
Provides broad authority to federal government (including natural resource trustees) to respond directly to releases or threatened releases of ***hazardous substances*** that may endanger public health or the environment.

- At present, CERCLA lists ~ **800** hazardous substances
- EPA has initiated the regulatory development process for listing PFOA & PFOS as CERCLA hazardous substances. This would allow:
  - ✓ EPA to require responsible parties to carry out and/or pay for response actions
  - ✓ Private parties to seek cost recovery for their response actions

Potential for CERCLA reopeners at 5-year review

Potential impacts to existing state cleanup programs for PFAS

Regulatory Status – The States



- **Enforceable limits**
- **Non-enforceable advisories, notification levels, etc.**
- **No standards**

PFAS: The Rapidly Changing Regulatory Landscape

Follow ITRC for updates

https://pfas1.itrcweb.org/fact-sheets/.

State	Year First Listed	Type	Promulgated ?	PFOA	PFOS	PFNA	Other PFAS
Alaska	2016	GW	Y	0.400	0.400		N
	2018	DW GW/SW	N	0.070	0.070	0.070	Y
California	2018	DW	N	0.014	0.013		N
Colorado	2018	GW	Y	0.070	0.070		N
Connecticut	2016	DW/GW	N	0.070	0.070	0.070	Y
Delaware	2016	GW	N	0.070	0.070		N
Delaware	2016	GW	N	0.070	0.070		Y
Iowa	2016	Protected GW	Y	0.070	0.070		N
	2016	Non-protected GW	Y		1		
Maine	2016	DW	N	0.070	0.070		N
	2018	GW	N	0.400	0.400		Y
	2016	GW	N	0.120	0.120		Y
	2016	SW/RW	N	0.170	0.300		Y
Massachusetts	2018	DW	O	0.070	0.070	0.070	Y
Michigan	2015	SW	Y	0.420	0.011		N
	2018	DW/GW	Y	0.070	0.070		N
Minnesota	2017	DW/GW	O/N	0.035	0.027		Y
	2017	DW/GW	O/N	0.035	0.027		Y
	2017	DW/GW	O/N	0.035	0.027		Y
Nevada	2015	DW	N	0.667	0.667		Y

PFAS: The Rapidly Changing Regulatory Landscape

State	Year First Listed	Type	Promulgated ?	PFOA	PFOS	PFNA	Other PFAS
New Hampshire	2016	GW	Y	0.070	0.070		N
New Jersey	2018	GW	Y			0.013	N
	2018	DW	Y			0.013	N
	2017	DW	O	0.014			N
	2018	DW	O		0.013		N
North Carolina	2006	GW	Y	2			N
	2017	DW	N				Y
Oregon	2011	SW	Y	24	300	1	Y
Pennsylvania	2016	GW	N	0.070	0.070		N
Rhode Island	2017	DW/GW	Y	0.070	0.070		N
Texas	2016	GW	Y	0.290	0.560	0.290	Y
Vermont	2018	DW/GW	Y	0.020	0.020	0.020	Y
	2016	GW	Y	0.010	0.010	0.010	Y

Sampling and Evaluation

PFAS Sampling Dos and Don'ts

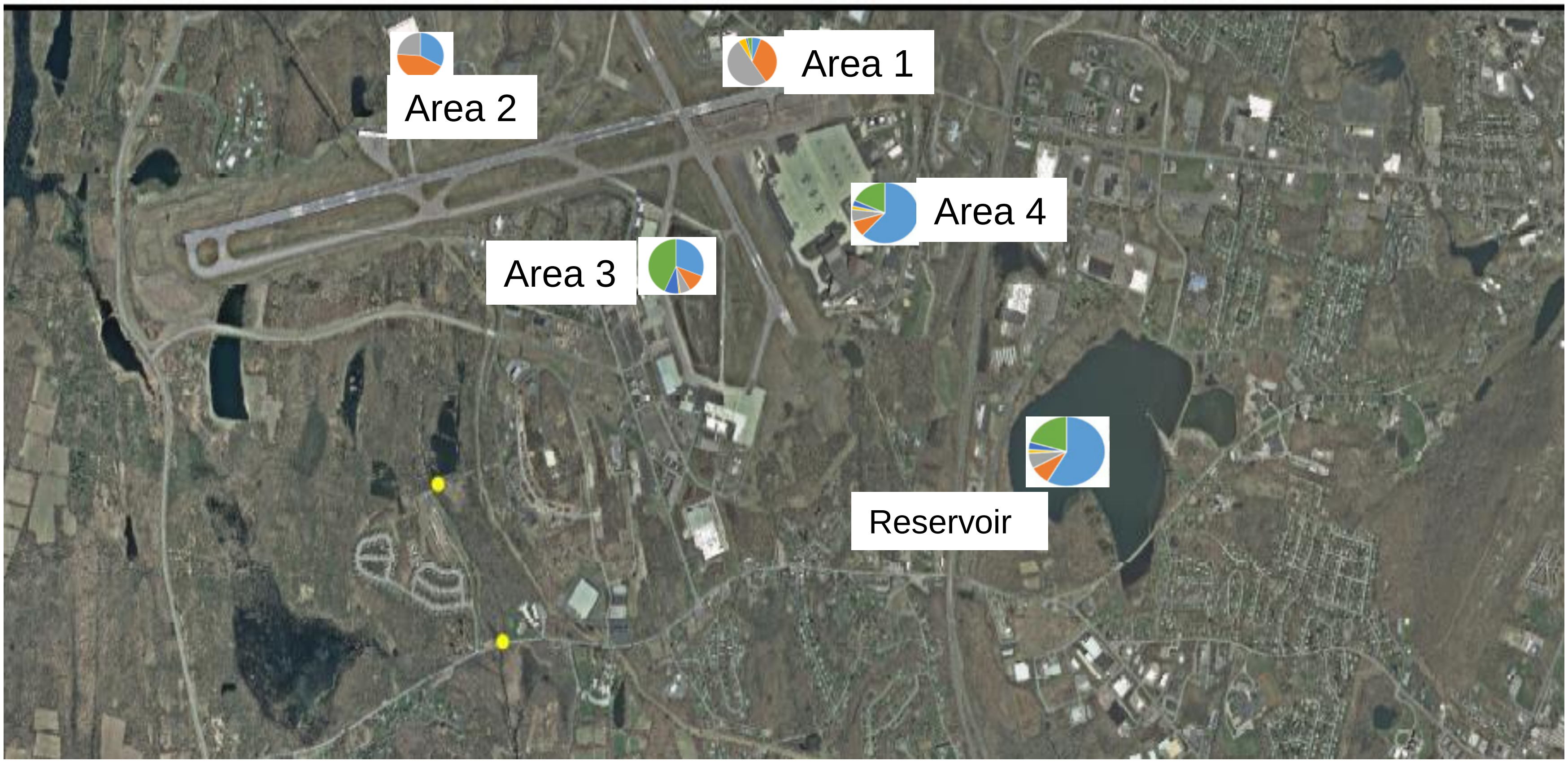
A few examples from TRC's SOP

WHAT SHOULD I AVOID?	USE INSTEAD
Equipment with **Teflon®** (e.g., bailers, tubing, parts in pump) during sample handling or mobilization/demobilization	✓ High density polyethylene (HDPE) or silicone tubing/materials in lieu of Teflon®
Low-density polyethylene (LDPE) or glass sample containers or containers with Teflon-lined lids	✓ HDPE or polypropylene containers for sample storage ✓ HDPE or polypropylene caps
Tyvek® suits and waterproof boots	✓ Clothing made of cotton preferred ✓ Boots made with polyurethane and polyvinyl chloride (PVC)
Waterproof labels for sample bottles	✓ Paper labels with clear tape
Sunscreens, insect repellants	✓ Products that are 100% natural, DEET
Sharpies	✓ Ballpoint pens
Aluminum foil	✓ Thin HDPE sheeting

A few examples only. A complete list available in the TRC SOP for PFAS Sampling.

Separating Impacts

Example: Fingerprinting Multiple Sources of Fire Fighting Foam



Blue – PFOS *Green- PFHxS* *Orange PFOA*
Grey PFHxA

Treatment and Remediation

PFAS Waste Water Treatment

PFAS Remediation Challenges

- Low Volatility (rules out stripping)
- Moderate solubility
- Strength of C-F Bond
- Treatment efficiency must be very high because of low (ppt) remediation objectives

Water Treatment Technologies

- Sorption/Ion Exchange
  - Carbon (can be effective for some PFAS, but can be inefficient)
  - Ion Exchange Resins (costly)
  - Need to remove all other organics before PFAS treatment

PFAS Remediation Alternatives

Ex-Situ Technologies

- Sorption/Ion Exchange
  - Carbon (can be effective for some PFAS, but can be inefficient)
  - Ion Exchange Resins (costly)
- Emerging technologies:
  - Reverse Osmosis
  - Membrane filtration
  - Thermal Treatment
  - SAFF – Surface Activation Foam Fractionation

In Situ Technologies

- Emerging(?) technologies:
  - Carbon injection
    - PRB or Source Area
  - Electro-Chemical Oxidation
  - ART In-Well Circulation System

Thank you

Questions?

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