

EBC Solid Waste Management Program

Impact of PFAS on Solid Waste Operations



Welcome

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Introduction and Program Overview

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Energy Environment Economy

PFAS in Wastewater, Biosolids, & Residuals and Implications for Solid Waste Management

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Environmental Business Council of New England
Energy Environment Economy



PFAS in Wastewater, Biosolids and Implications for Solid Waste Management

Ned Beecher, MS • NEBRA • Tamworth, NH

November 12, 2019

EBC New England • Framingham, MA



NEBRA...

www.nebiosolids.org



- Founded in 1997
- Non-profit, tax-exempt membership organization
- New England and Eastern Canada
- Mission - *Promoting the environmentally sound recycling of biosolids and other residuals in the greater New England region.*
- Funding from public wastewater agencies, private biosolids management companies, environmental engineers, end users of biosolids, project grants.
- Provides networking information hub (website, newsletters), public education, fosters research

***Acknowledgements & Sources: these PFAS slides**
Inclusion on this list does not imply endorsement. Views expressed are those of Ned Beecher/NEBRA only.

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- Linda Lee and Rooney Kim, Purdue University
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- Shelagh Connelly, RMI
- Jeff McBurnie, Casella Organics
- *And many others (apologies for any omissions):*
 - Sally Brown, Univ. of WA
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 - Mike Person, MI DEQ
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 - Andrew Carpenter, Northern Tilth
 - Ed Topp, Agriculture & Agrifood Canada
 - Charles Neslund, Eurofins
 - Matt Berg & Sherri van der Wege, WEAT

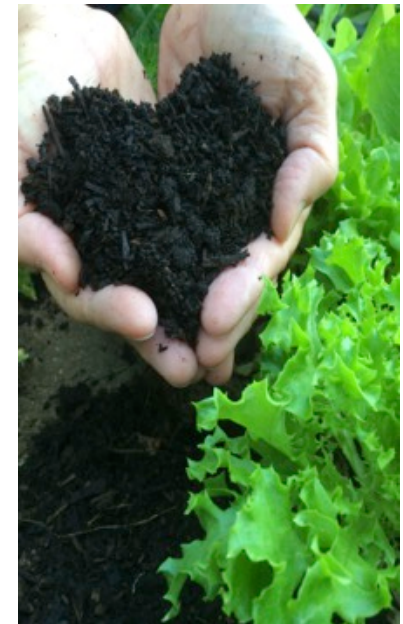
AND organizations across North America who are funding NEBRA's PFAS work in 2019.

THANK YOU!

Recycling organic “wastes” benefits society & the environment.

Wastewater, biosolids, & other organic residuals are treated, tested, regulated, and recycled routinely – and have been for decades. This does amazing things:

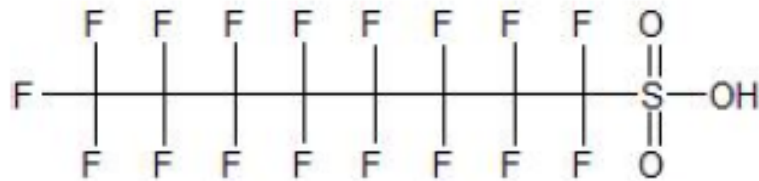
- enhances soil health
- recycles nutrients – macro & micro
- sequesters carbon (mitigating climate change)
- reduces fertilizer & pesticide use
- strengthens farm economies (thousands of farmers choose to use biosolids, because they work)
- restores vitality to degraded lands
- puts to productive use residuals that every community has to manage
- is part of the circular economy



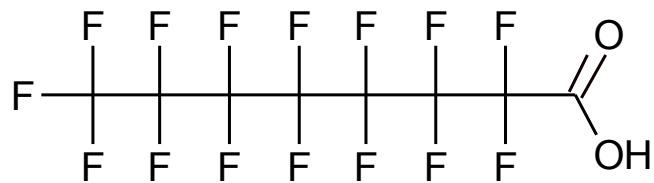
PFAS & any emerging contaminant must be addressed in ways to continue to maximize these known benefits.

perfluorinated:

PFOS



PFOA

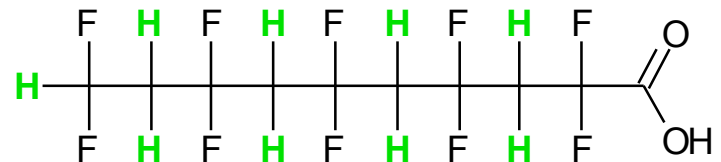


PFAS

an extreme, worst-case CEC

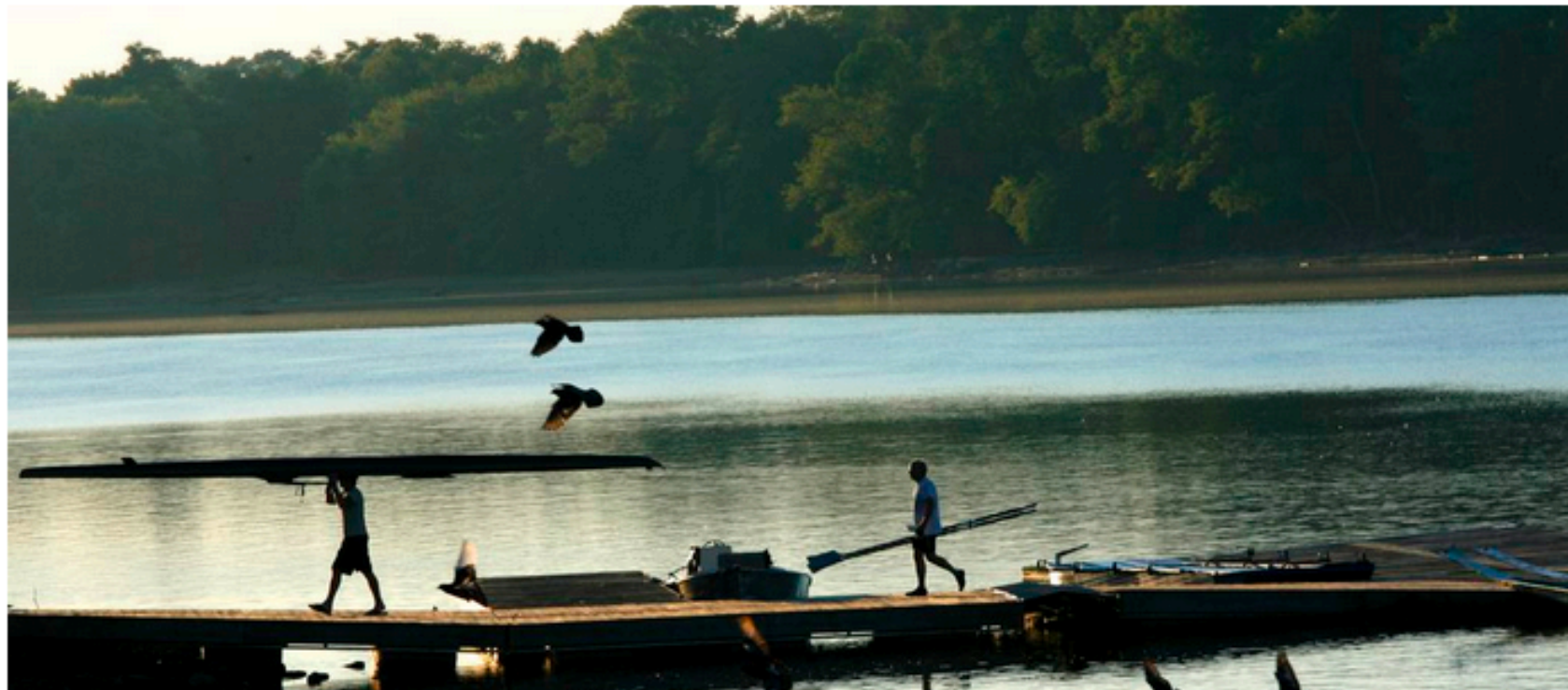
the only *common* trace contaminant of drinking water regulated in low ppt

polyfluorinated:



Toxic chemicals can be dumped into Merrimack River, federal and state officials say

By [David Abel](#) Globe staff, November 5, 2019, 6:41 p.m.



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**Why has it become
so important...**

...for biosolids/residuals and wastewater management?

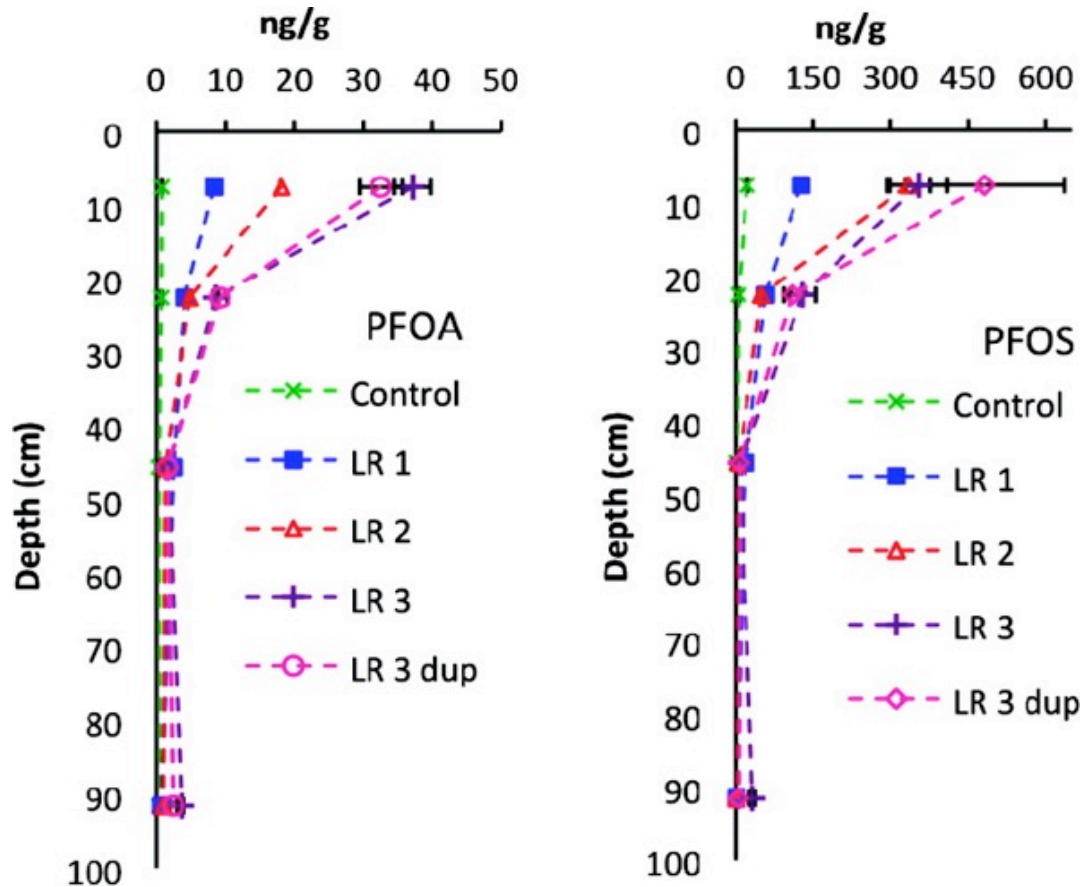
PFAS are in wastewater & biosolids, of course. Wastewater & biosolids mirror modern life.

- Even small-town, purely domestic wastewater has PFAS.
- We are aware because of advances in analytical chemistry: measuring at ppt levels.



Why the concern about PFAS in wastewater & biosolids?

1) PFAS leach in soil some.



Sepulvado et al;
Environ. Sci. Technol. 2011,
45, 8106-8112

Concentrations of PFOA and PFOS with depth in the long-term plots at various loading rates. Control = 0 Mg/ha, LR 1 = 553 Mg/ha, LR 2 = 1109 Mg/ha, and LR 3 and LR 3 dup = 2218 Mg/ha (on dry weight basis).

Why the concern about PFAS in wastewater & biosolids?

2) PFAS are likely emitted to air from sewage sludge incineration.

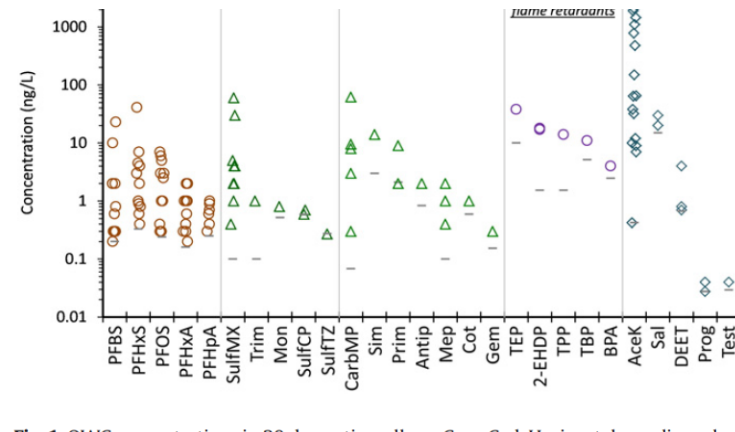
- PFAS destruction requires $>1000^{\circ}$ C.
- PFAS are not found in ash (Manchester, NH testing)
- Do air emissions controls capture it?
- Testing & research needed & are starting
- Some may worry about downwind plumes & deposition & impacts on groundwater – but SSI's are unlikely to be major emitters, but it's uncertain...

Why the concern about PFAS in wastewater & biosolids?

3) Some are regulating at background levels.

NH MCLs & ambient groundwater quality standards:

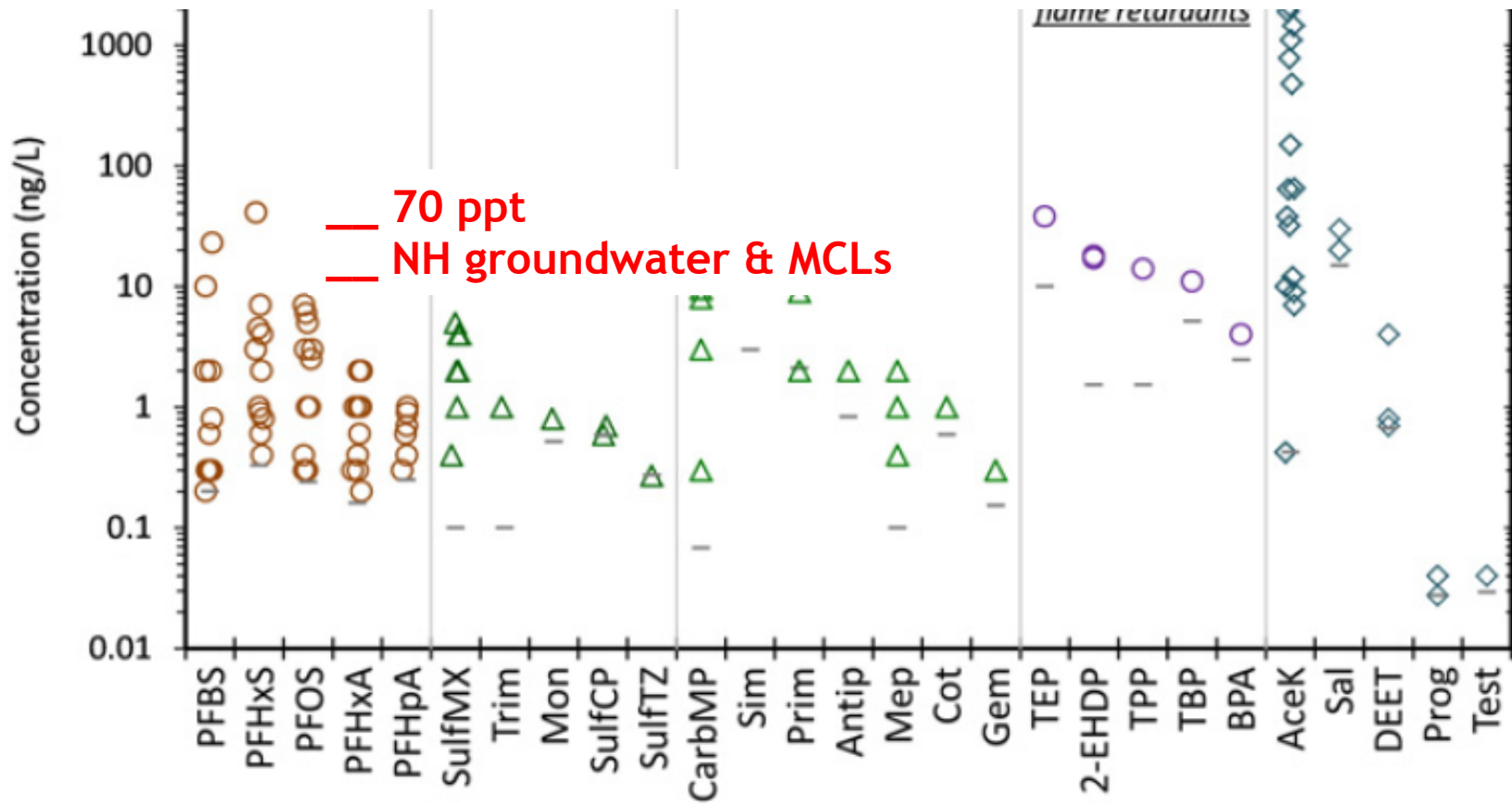
- PFOA 12 ppt
- PFOS 15 ppt
- PFHxS 18 ppt
- PFNA 11 ppt



Effective September 30, 2019.

Estimated cost for 2 years: \$267 million (likely an underestimate); no funding provided for municipalities & utilities.

Regulating at background levels? Cape Cod groundwater & drinking water impacted by septic systems



* Schaider et al., 2016. Septic systems as sources of organic wastewater compounds in domestic drinking water wells in a shallow sand and gravel aquifer. *Sci. Total Environ.*

4) Landfill disposal of sludge/biosolids is the only other option.

- As land application is challenged in NH & ME, more demand for landfill disposal.
 - Sludge/biosolids are wet and organic; landfills cannot manage indefinite quantities.
 - Landfill capacity in this region is limited.
 - Landfill concerns about PFAS-containing materials, and all biosolids have PFAS.
-

Measuring PFAS:

In waters: in ppt

1 ppt = 1 second in ~31,700 years

In soils/solids: in ppb

1 ppb = 1 second in 31.7 years

Analytical methods:

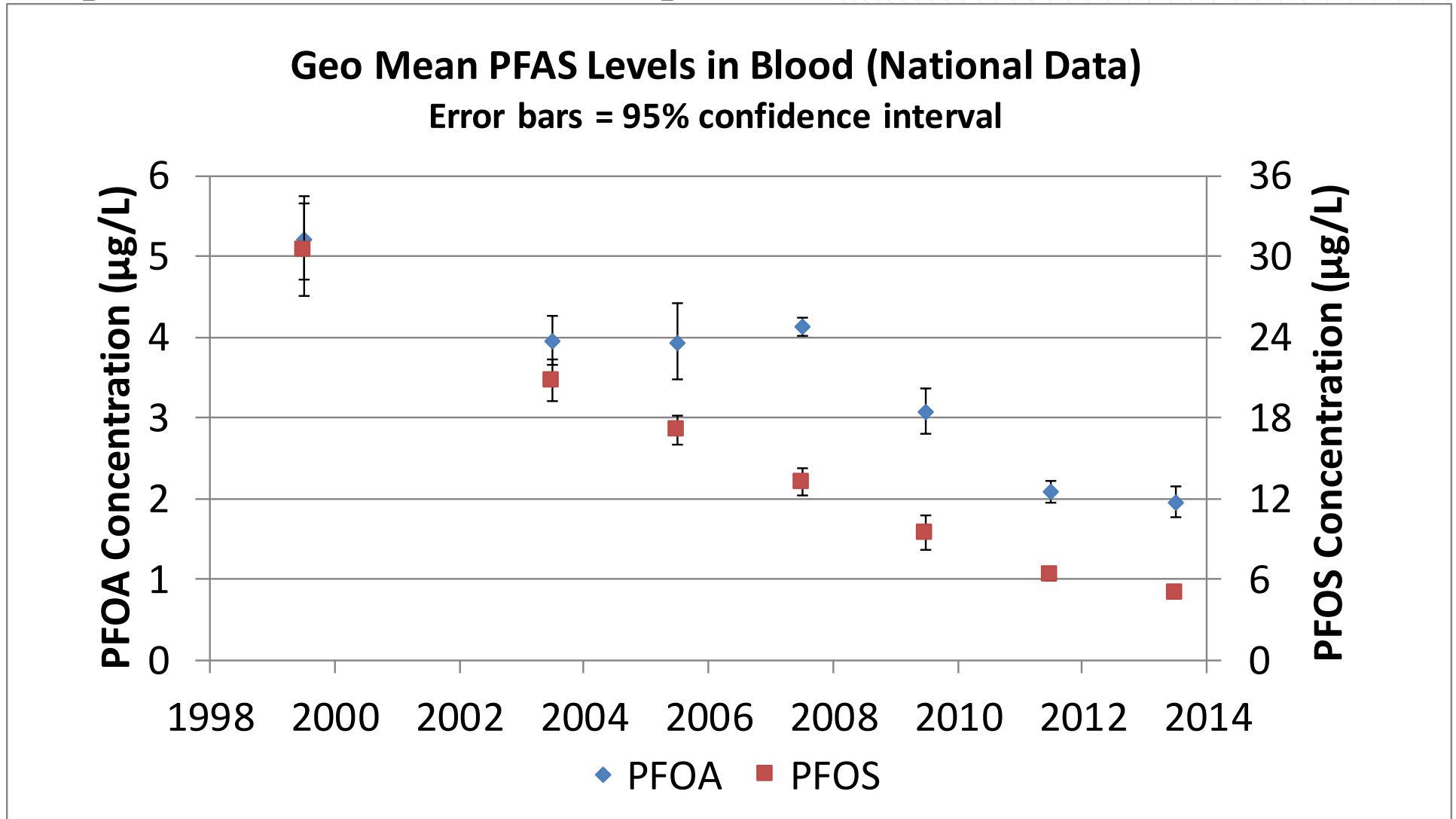
- EPA Method 537.1 (Nov. 2018) – for drinking water only
- DoD guidance for other matrices – is
- Draft EPA SW method for non-drinking
- 2020 draft EPA SW method for solids,

**Be skeptical
of PFAS data.**

the level of PFAS health risk?

There is debate. That is not ours to figure out. But we track & comment to ensure no rush to judgment without good science.

The most cost-effective strategy for persistent & proven toxic CECs is to phase out their use.



There are 2 major sources of PFAS

in the environment:

- industrial discharges
- fire-fighting (including training, e.g. at military sites)

Major sources of PFAS in the environment:

Cottage Grove, MN

Parkersburg, WV

EPA reaches new C8 deal with DuPont

on January 16, 2017 at 4:54 pm



The Washington Works DuPont plant in Parkersburg, West Virginia, on Wednesday, August 5, 2015. Photo: Maddie McGarvey for The Intercept/Investigative Fund

PARKERSBURG, WV — “Less than two weeks before the Obama administration leaves office, the U.S. Environmental Protection Agency on Monday said it had reached a new agreement with DuPont Co. regarding pollution of drinking water in the Mid-Ohio Valley with the toxic chemical C8 from the company’s manufacturing plant near Parkersburg.

EPA said in a [news release](#) that it had amended its 2009 agreement with DuPont to reflect a lower level of C8 exposure recommended in an EPA health advisory issued last year. While more protective than the previous agreement with DuPont, the new number would allow larger

LAWSUITS CHARGE THAT 3M KNEW ABOUT THE DANGERS OF ITS CHEMICALS



Sharon Lerner

April 11 2016, 9:42 a.m.

FOR DECADES, 3M was the primary producer of C8, or [PFOA](#), and was the sole producer of a related chemical known as PFOS. But while DuPont was caught up in a [massive class-action suit](#) over C8, 3M has largely avoided public scrutiny and serious legal or financial consequences for its role in developing and selling these industrial pollutants.

In February, however, a state court in Minnesota, where the company is headquartered, allowed a lawsuit against 3M to move forward. And late last year, lawyers filed a class-action suit in Decatur, Alabama, home to one of 3M’s biggest plants. Both lawsuits charge that 3M knew about the health hazards posed by the perfluorinated chemicals it was manufacturing and using to make carpet coating, Scotchgard, [firefighting foam](#), and other products – and that the company knew the chemicals were spreading beyond its sites. With PFCs cropping up in drinking water around the country and all over the [world](#), the two lawsuits raise the possibility that 3M may finally be held accountable in a court of law.

State Attorney General Lori Swanson first filed the lawsuit against 3M on behalf of the people of Minnesota in 2010, claiming that the company polluted more than 100 square miles of groundwater near its plant in Cottage Grove, Minnesota, as well as four aquifers serving as drinking water for some 125,000 people in the Twin Cities. The suit charges that the company piped PFC-polluted wastewater into a stream that flows into the Mississippi River and disposed of it on land near the river, which allowed it to leach into the river.



Based on the company’s own research, the complaint argues, 3M “knew or should have known” that PFCs harm human health and the environment. [Flip Photo](#) that the chemicals would leach from their disposal site.

Major source of PFAS in the environment: AFFF, Pease AFB, NH

All the white is AFFF
(PFAS-containing foam)



https://www.youtube.com/watch?v=8W_zJfJGhSI&feature=youtu.be

Data: PFAS contamination at industrial sites

EXAMPLE: Wolverine Worldwide Kent County tannery dump sites, Rockford, MI

Date of discovery: 2017

Results (PFOS/ PFOA) or Range above EPA LHAs: House Street Area
Testing Results as of 12/20/18 as reported by Wolverine:

- Wolverine has sampled 689 homes
- 38 homes over 70 PPT (PFOA+PFOS)
- 392 had detection of PFOA/PFOS
- Highest concentration is **76,000 PPT** (PFOA+PFOS)

Suspected source: This area consists of a former licensed disposal facility owned and operated by Wolverine... and several unregulated dump sites across three townships in northern Kent County.

<https://www.ewg.org/research/update-mapping-expanding-pfas-crisis>

*Data: PFAS at firefighting & training sites

EXAMPLE: Battle Creek Air National Guard Base, MI

Date of discovery: 2018

Results (PFOS/ PFOA) or Range above EPA LHAs: On-base groundwater:

-PFOA: **21,500 ppt**

-PFOS: **55,000 ppt**

-PFHxS: **38,400 ppt**

Two contaminated private wells (drinking water): -PFOS+PFOA: high of 411 ppt

Other Results PFAS or Range above EPA LHAs: On-Base water wells show presence of 13 PFAS compounds - Highest results: PFHxS=38,400 ppt

Suspected source: Firefighting foam used at Battle Creek ANGB

EXAMPLE: Travis Air Force Base, CA

Date of discovery: 2018

Results (PFOS/ PFOA) or Range above EPA LHAs:

-PFOA + PFOS = **712,000 ppt**

- PFOA = **88,000 ppt**

- PFOS = **690,000 ppt**

Other Results PFAS or Range above EPA LHAs: PFBS = 140,000 ppt

Suspected source: Firefighting foam

<https://www.ewg.org/research/update-mapping-expanding-pfas-crisis>

PFAS

ambient background:

includes most wastewater & biosolids and other residuals (e.g. compost, paper mill residuals), septic (onsite) systems, solid waste management activities

Typical biosolids are part of “ambient background” levels of PFAS.

There are a few cases of large industrial inputs to solid waste facilities & sewers; those are industry point sources - not typical.



Source: Dr. Bradley Clarke, RMIT, Per- and polyfluoroalkyl substances (PFAS) in Australia, Dec. 2017 slide presentation to Water Research Australia

Data...

PFAS are showing up in various waters & soils:

drinking water

groundwater

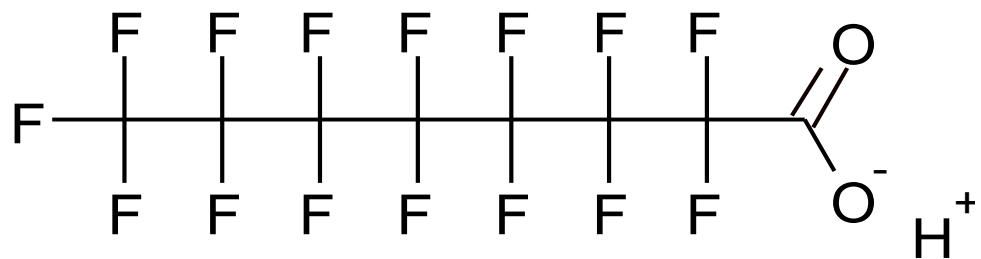
surface water

wastewater

landfill leachate

Compare the following data to the 10,000s of ppt at industrial & fire-fighting sites.

PFOA



Data...

PFAS are showing up in various waters:

drinking water

groundwater

surface water

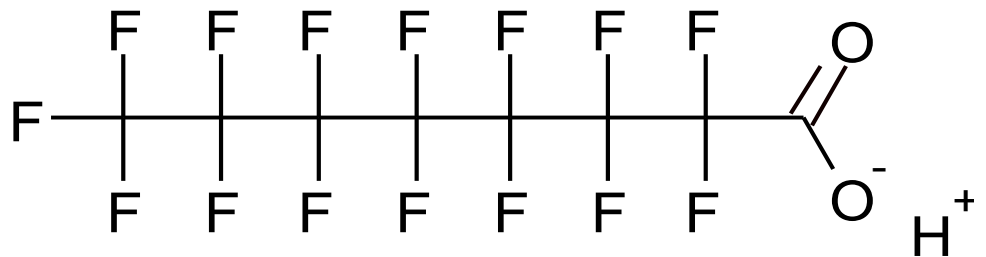
wastewater

landfill leachate

**DATA following are
ng/L (ppt)**

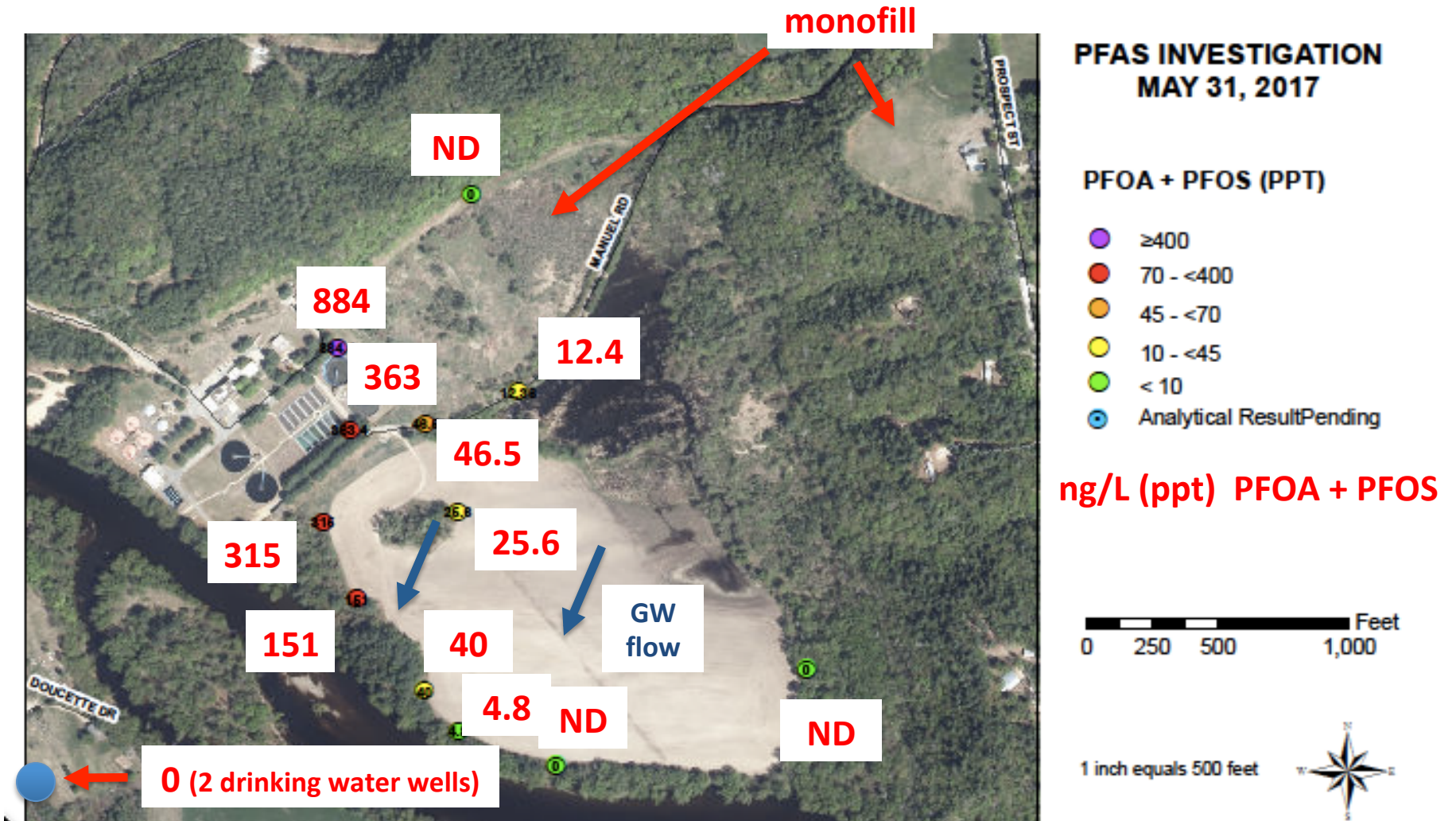
**Compare to 70 ppt
for PFOA + PFOS (EPA PHA)**

PFOA



Monitoring well testing at sludge monofill

- Monofill used in 1980s. Since ~1996, all biosolids from WWTP (11.5 MGD) have been land applied, some on farm field shown.
- Likely a worst-case scenario? But nothing like a firefighting site!



Data...

PFAS are showing up in various waters:

drinking water

groundwater

surface water

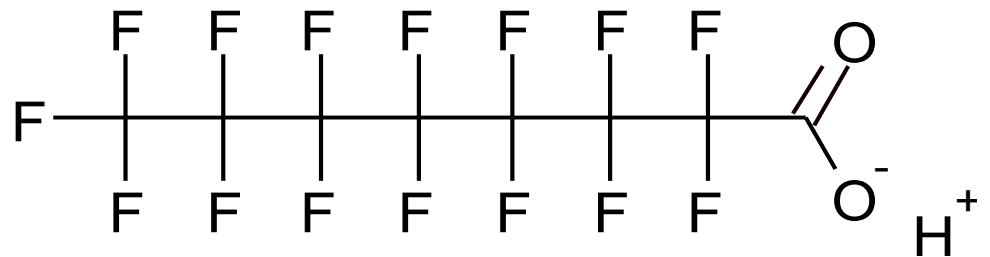
wastewater

landfill leachate

DATA following are
ng/L (ppt)

Compare to 70 ppt
for PFOA + PFOS (EPA PHA)

PFOA



Old landfill / Surface water
Hoosic River, NY
2016

SW-2
9.8 ppt

Hoosic River
sample near
landfill.

MW-2
21000 ppt

MW-1B
150 ppt

SW-3A
1900 ppt

Landfill seep/
leachate sample.

MW-4
1300 ppt

SW-3B
1200 ppt

Sample from pond.

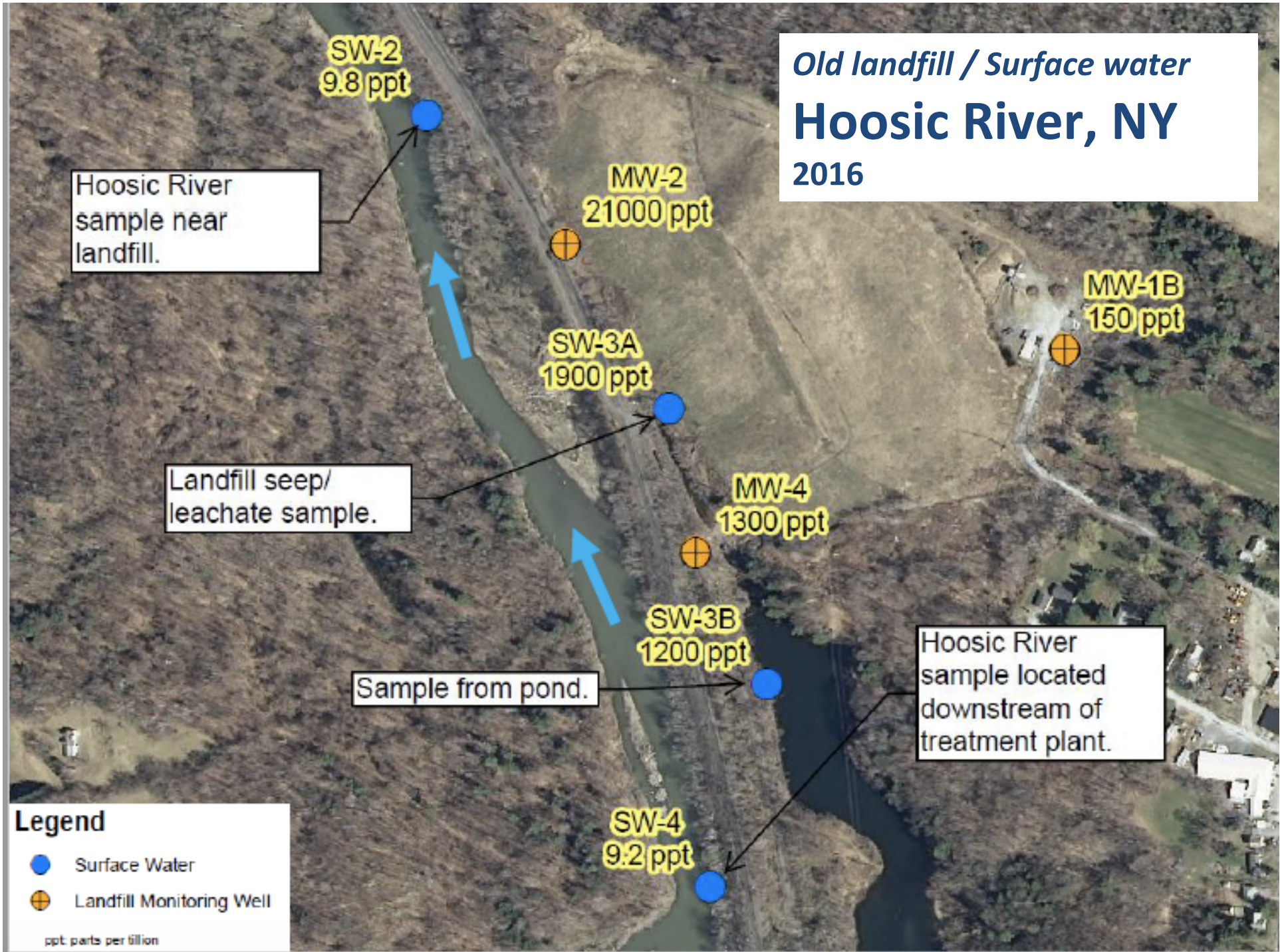
Hoosic River
sample located
downstream of
treatment plant.

SW-4
9.2 ppt

Legend

- Surface Water
- ⊕ Landfill Monitoring Well

ppt: parts per billion



Paper mill residuals composting operation.

Regulatory response in March 2017 drives recycle paper mill residuals to landfill and composting business to laying off workers.



Data...

PFAS are showing up in various waters:

drinking water

groundwater

surface water

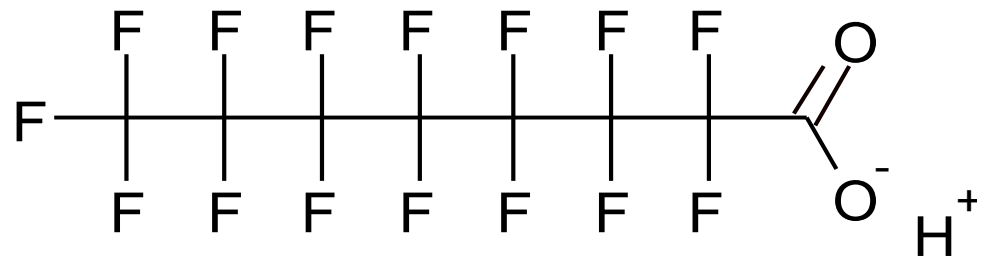
wastewater

landfill leachate

DATA following are
ng/L (ppt)

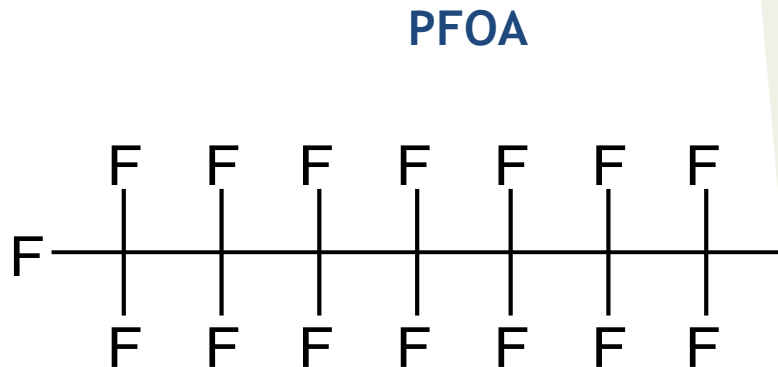
Compare to 70 ppt
for PFOA + PFOS (EPA PHA)

PFOA



Data...

PFAS are present in all biosolids,
some residuals, & soils...



**DATA following are
ng/g (ppb) dry weight**

Compare to:

~72 ppb a NY DEC screening value

2.5 ppb ME PFOA limit*

5.2 ppb ME PFOS limit*

***NEBRA finds these values are
inappropriate for use with biosolids.**

Recent PFAS test results:

Biosolids, Residuals, & Septage (ng/g, ppb)

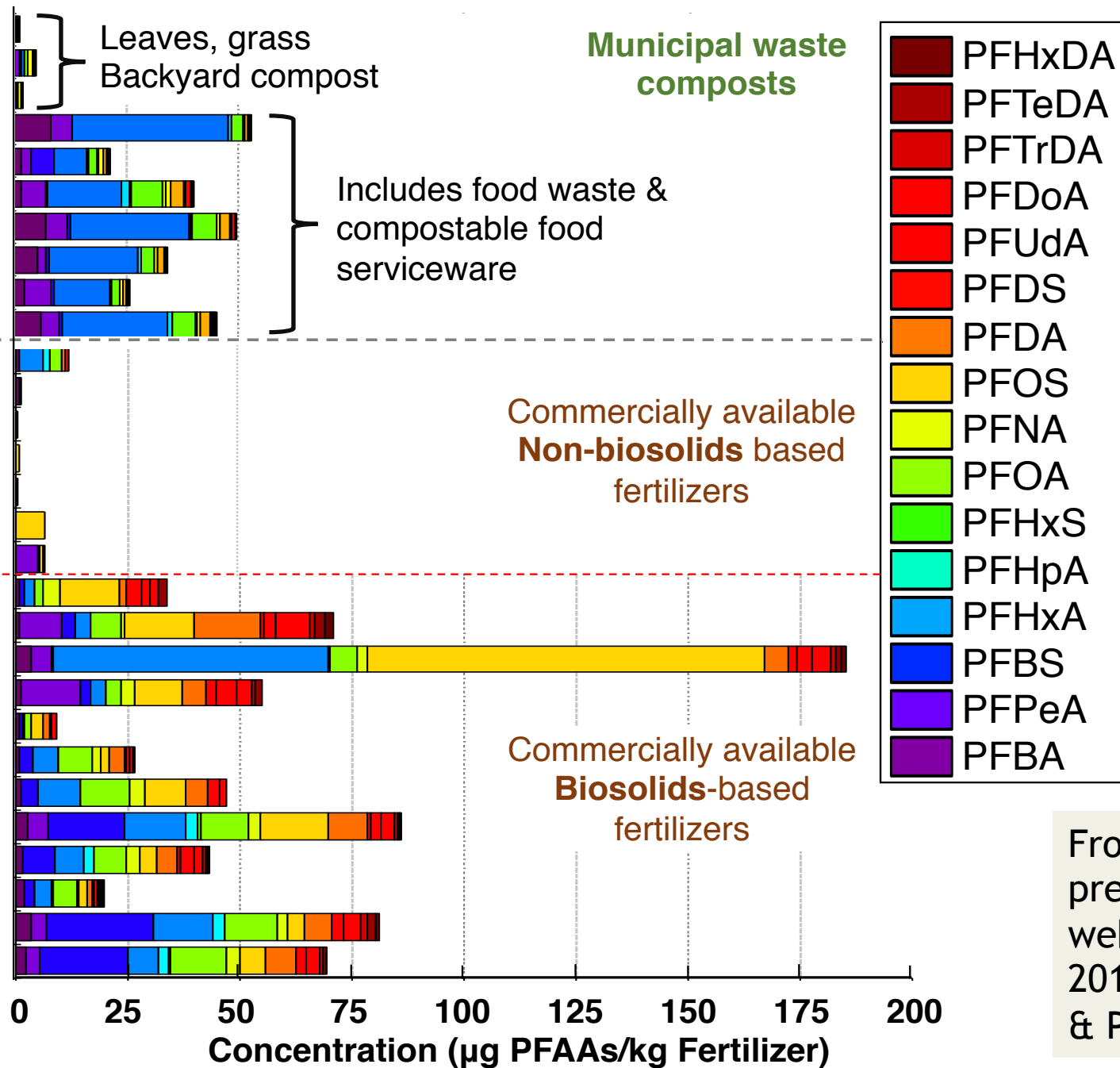
	PFOA*	PFOS*	PFNA*	PFHxS*	PFHpA*	PFDA	Notes
Biosolids products nationwide, 2018	~3 - ~15	~2 - ~ 90	ND - ~4		ND - ~4	< 1 - ~17	7 composts tested by Lazcano, Lee - Purdue
ME biosolids, 2019	0.6 – 46 (mean = 8.5)	3.2 – 120 (mean = 25.4)					55 biosolids sampled, cake & composts
Food waste & compostable foodware compost, 2018	~3 - 12	ND - ~2	ND - ~2	~0.2 - 1	ND - ~3	~1- 3	PFHxA = ~ 9 – 50 7 composts tested by Choi, Lazcano - Purdue
ME septage, 2019	15 – 60	< 10 - 121					7 samples; typical levels > biosolids**
U. S. sewage sludges, 2001	12 – 70 (mean = 34)	308 – 618 (mean = 403)					Venkatesan & Halden, 2013; older sludges = higher PFOA & PFOS
SCREENING							
Modeled PFAS levels in biosolids to avoid impacts to 1 m ground water above 70 ppt (EPA screen)	sum = < 40 – 60: 40 PFOA + 0 PFOS or 0 PFOA + 60 PFOS						Stone Environmental PRZM modeling, 2019, for NEBRA
ME DEP screening level developed for non-agronomic residuals, 2018	2.5	5.2					Applied to biosolids & biosolids soils in 2019

All data are suspect & variable due to there being no approved analytical method other than for drinking water and different lab protocols in use.

* There were 6 PFAS included in the U. S. EPA Unregulated Contaminant Monitoring Rule 3 (UCMR 3) testing of drinking water; the 6th, not shown here, is PFBS.

** Septage may have higher levels than biosolids because it is older, having sat in septic tanks for up to 10 years, reflecting higher uses of PFOA and PFOS prior to the early-2000s phase-out of these 2 PFAS.

ND = not detected



From Kim-Lazcano – presentation for USCC webinar, Jan. 18, 2019. © Kim-Lazcano, & Purdue Univ. data.

A few biosolids are impacted at levels of some concern - when an industry discharges large amounts of PFAS to a sewer:

- Decatur, AL (2000s) – 3M manufacturing facility
- Lapeer, MI (2017) – metal plating industry
- Maine farm (2019) – issue is not municipal biosolids; PFOS is the only concern; paper industry sludge/ash; max soil: 878 ppb PFOS (see NEBRA fact sheet: <https://www.nebiosolids.org/pfas-biosolids>)

Solution:

Apply pretreatment & source control.

Data...

PFAS in...:

drinking water

groundwater

surface water

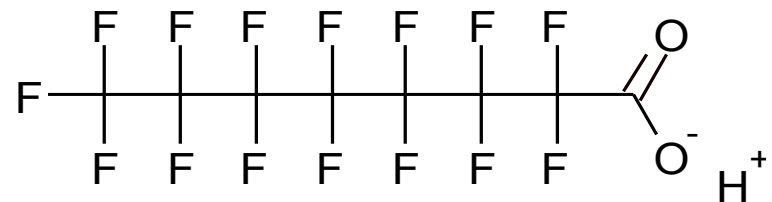
wastewater

landfill leachate

**DATA following are
ng/L (ppt)**

**Compare to 70 ppt
for PFOA + PFOS (EPA PHA)**

PFOA



Sources of PFAS at Landfills (?)

- Consumer products
- Sewage sludge (or treated biosolids)
- Industrial wastes
- Auto shredder residue
- Debris from fire cleanup
- Discarded AFFF
- Other sources



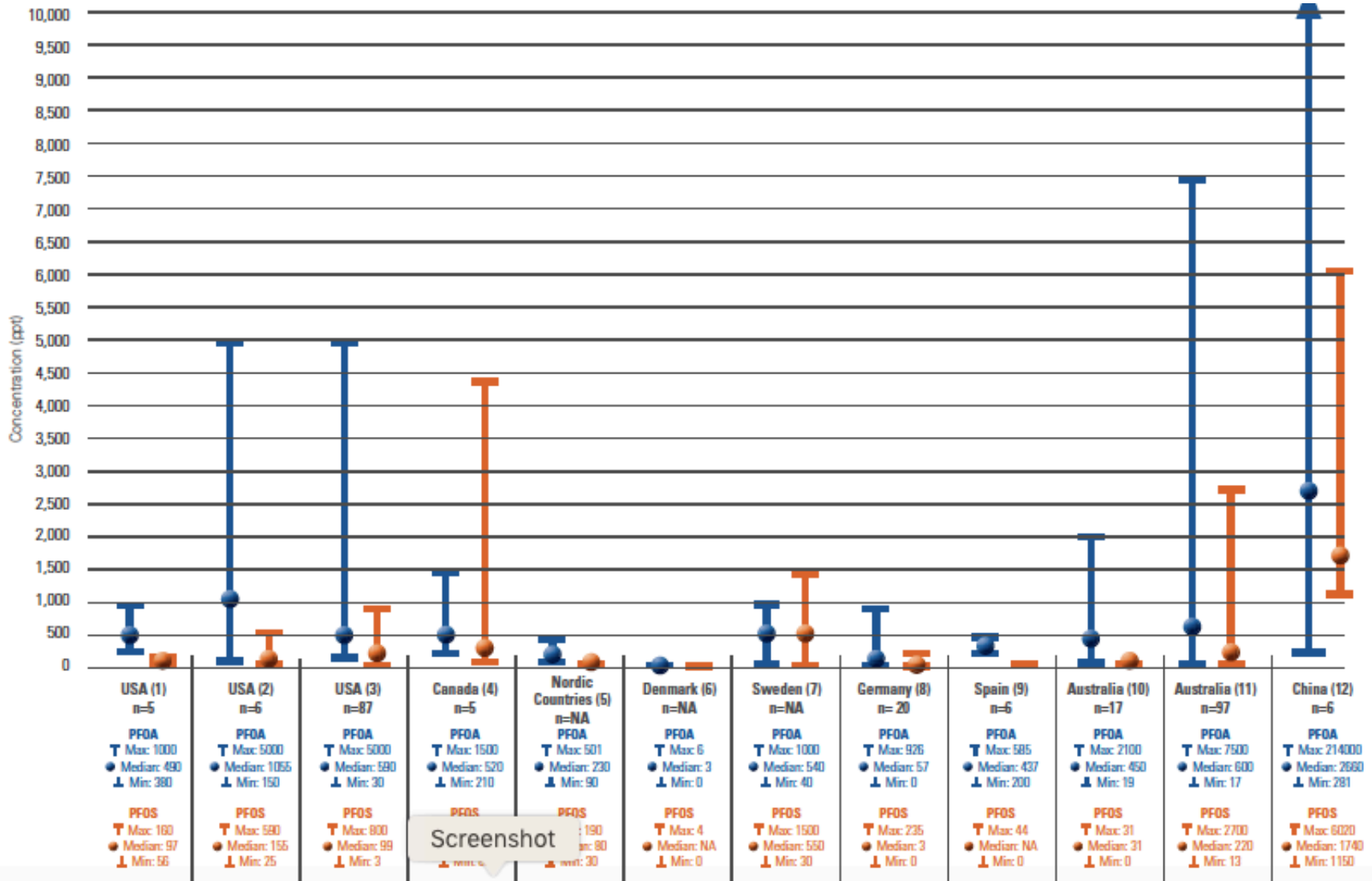
Landfill leachate PFAS concentrations (ng/l or ppt)

(adapted from MI Waste & Recycling Association, Table 4.3, <https://www.michiganwasteandrecyclingassociation.com/>)

Location	PFOA	PFOS	Notes
Michigan	16 – 3,200	9 – 960	32 MI landfills & MiWaters data (see report link above)
Vermont	80 – 2,800	23 - 300	11 analyses of 9 samples in 2018
United States	30 – 5,000	3 – 800	
Europe	ND – 1,000	ND – 1,500	
Australia	17 – 7,500	13 – 2,700	
China	281 – 214,000	1,150 – 6,020	
STANDARDS			guidance only
VT screening levels for landfill leachate, 2018	120,000	1,000	
MI EGLE surface water limit (2015)	420	12	if source of drinking water; limits are being used to screen wastewater effluent
Canada Health (2018) drinking water	200	600	
U.S. EPA drinking water screening value (2016)		70	applies to the sum of 2 PFAS

Landfill leachate PFAS concentrations (ng/l or ppt)

(from MI Waste & Recycling Association, Figure 2.1, <https://www.michiganwasteandrecyclingassociation.com/>)



Conclusions for wastewater utilities

(from MI Waste & Recycling Assoc. <https://www.michiganwasteandrecyclingassociation.com/>)

“a. leachate provides a relatively minor contribution to the overall PFOA and PFOS concentration/mass in most WRRF influent because of the relatively low leachate discharge volumes;

“b. non-leachate sources of PFOA and PFOS significantly contribute to WRRF influent and at higher volumes. It is noteworthy that the WRRF influent that have no landfill leachate contribution show a similar concentration range for PFOA and PFOS as WRRF influent that has leachate contribution; and

“c. although reduction of landfill leachate concentrations of PFOA and PFOS to the WRRF influent could be beneficial to meeting WQS in the WRRF effluent, the impact may be minor in most cases since leachate typically contributes a relatively small volume to the overall WRRF influent.”

Toxic chemicals can be dumped into Merrimack River, federal and state officials say

By [David Abel](#) Globe staff, November 5, 2019, 6:41 p.m.



Leachate levels: ~7000 ppt / ng/L; assume ¼ is PFOA: 1,750
Leachate volume: 25,000 gals. / 94,625 L per day (per EPA letter)
Total PFOA per day to Lowell WRRF: 165 milligrams (mg/d)
Lowell flow: 33.4 MGD / 126,432,360 L per day
Typical PFOA level in wastewater: 60 ppt / ng/L (high end of range)
Total PFOA per day in Lowell influent: 7,586 mg/d
Landfill leachate might be <2% of PFOA in Lowell wastewater.



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Biosolids compost for my raspberries... still using it, even though I know it has PFAS in it. The benefits outweigh the risks :)

Thank you.

Ned Beecher, MS • NEBRA • Tamworth, NH

November 12, 2019

EBC New England • Framingham, MA

Estimating Total Mass of PFAS in Landfill Leachate

- Lang et al (2017) published PFAS measurements in landfill leachate (*Environ. Sci. Technol.* **51**:2197–2205)
 - 70 PFAS / 95 samples / 18 landfills
 - Estimate 563 – 638 kg of PFAS in leachate per year in the U.S.



Ballpark Estimate of PFAS in Sludge & Biosolids



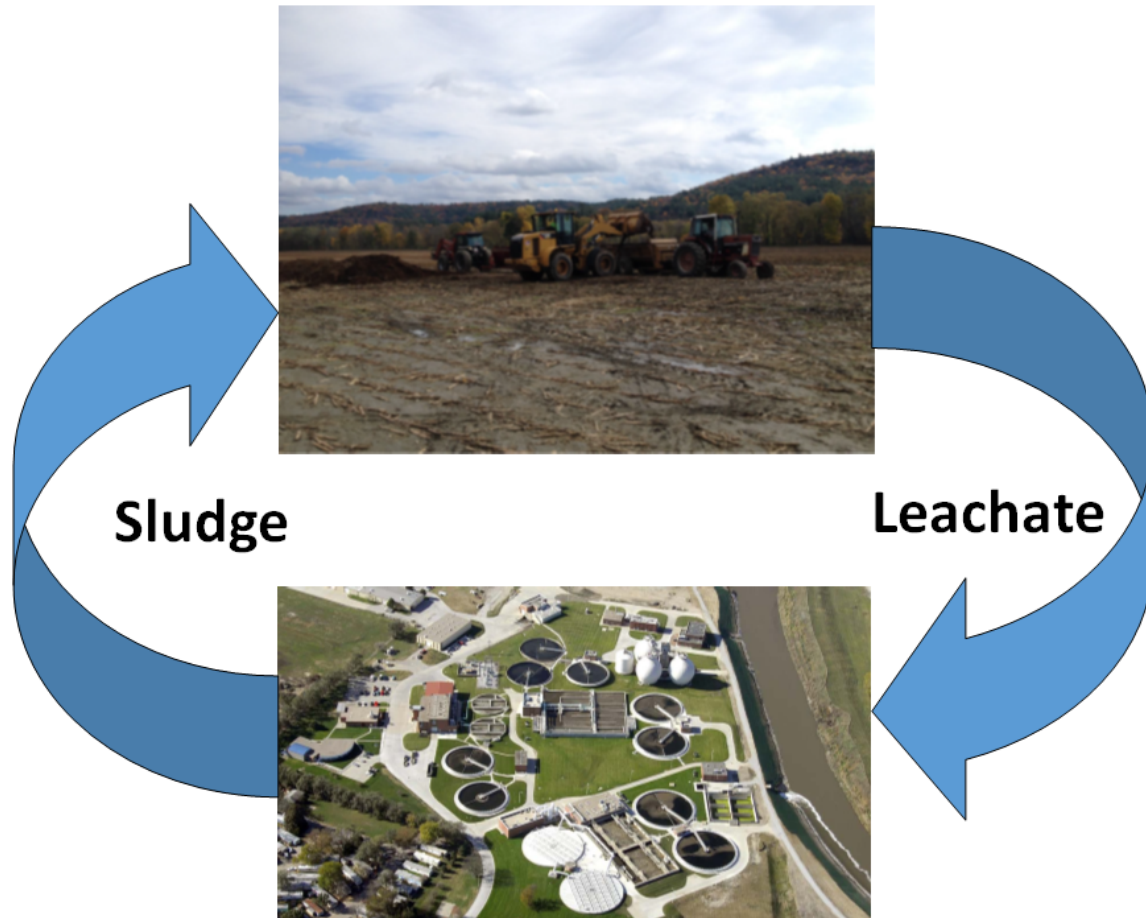
Assume

- 7.2 million dry tons of sewage sludge (NEBRA et al., 2007)
- PFAS content ~100 ppb ($\mu\text{g}/\text{kg}$ summed)

Find

- ~700 kg/year of PFAS in sewage sludge
- Comparable total mass to what's in leachates

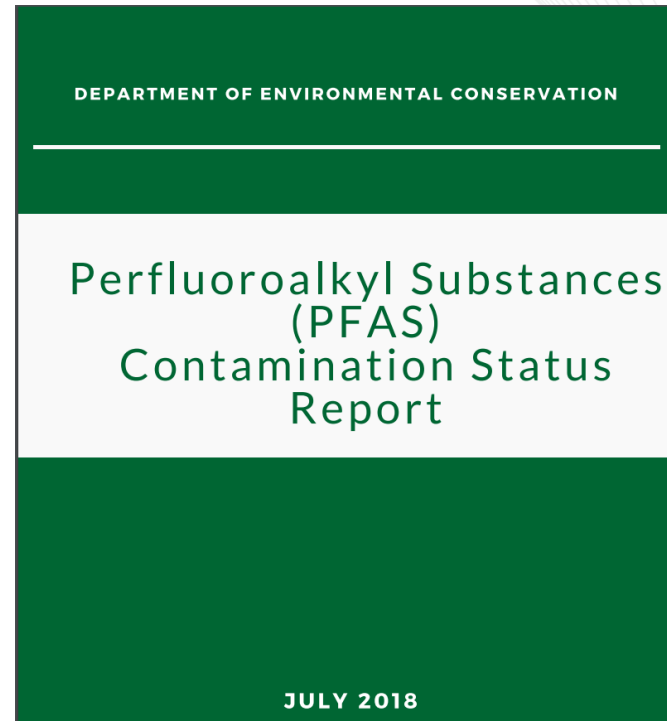
PFAS Relationship Between Landfills and Wastewater Treatment Plants (WWTPs)



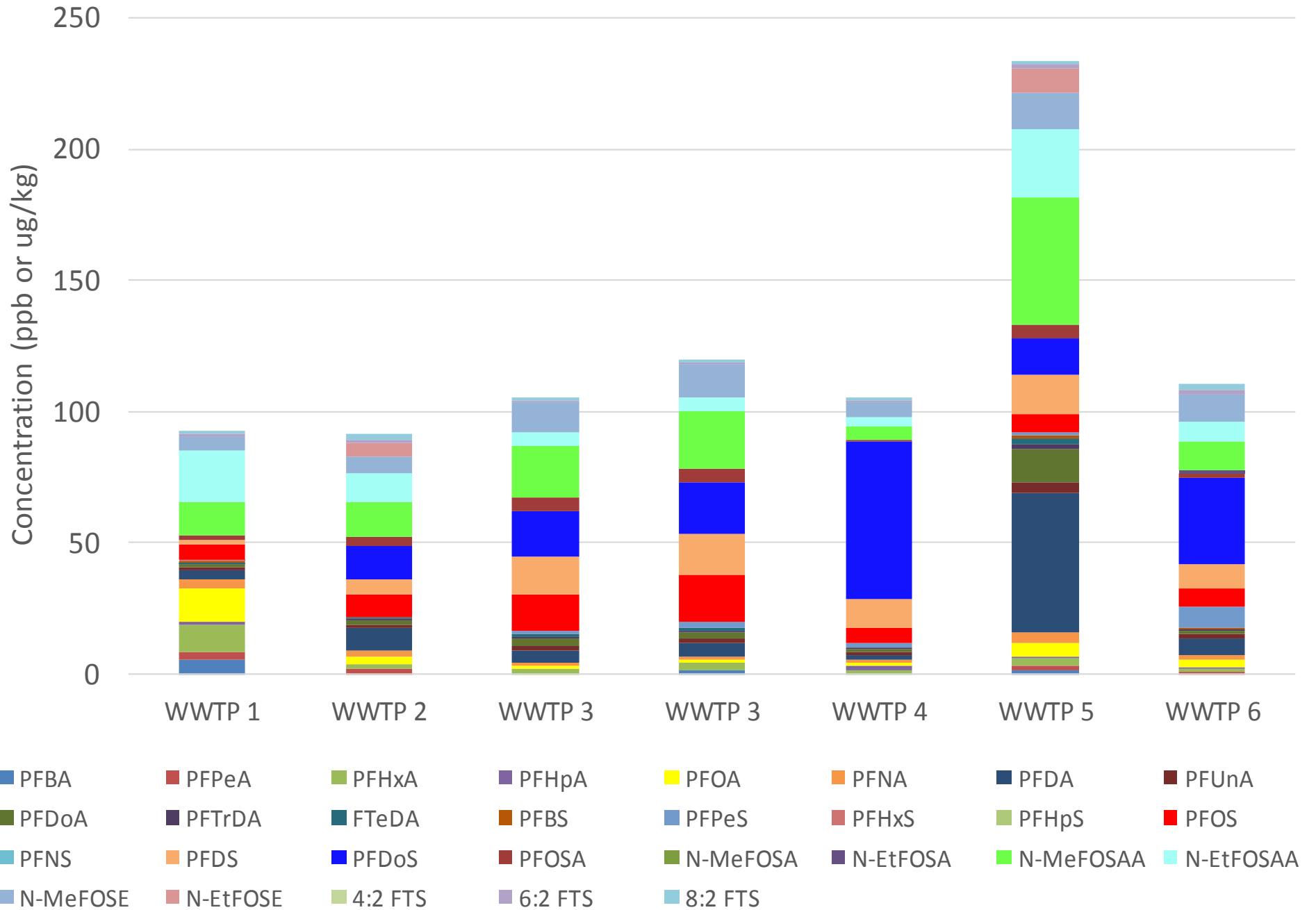
Do PFAS cycle between landfills and WWTPs?

Leachate and Sludge Data

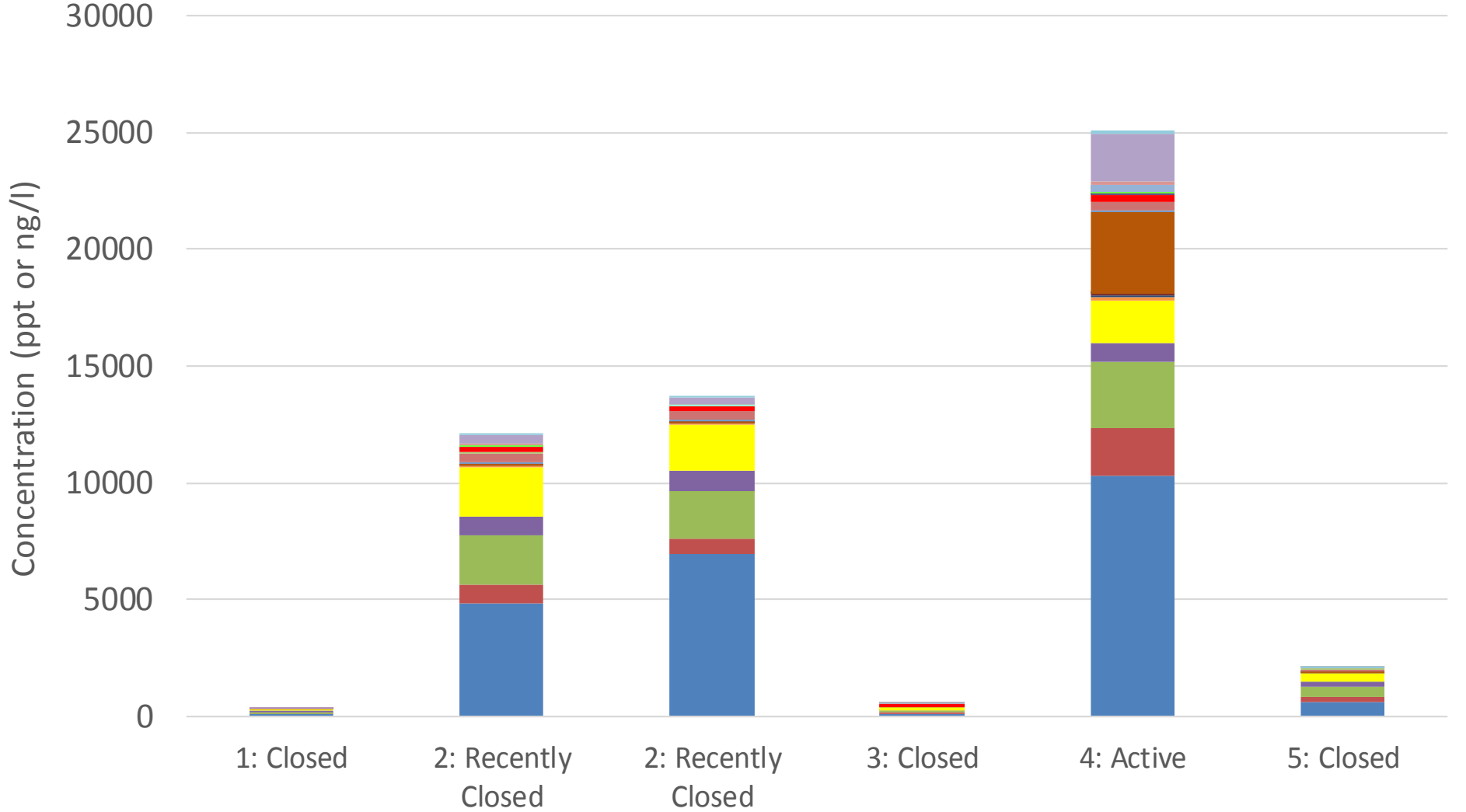
- VT DEC (1) investigated PFAS in landfill leachate and WWTP sludge (and WWTP influent/effluent)
 - 29 PFAS
 - 5 landfills
 - 1 active
 - 4 closed
 - 6 WWTPs



PFAS in VT Sewage Sludges

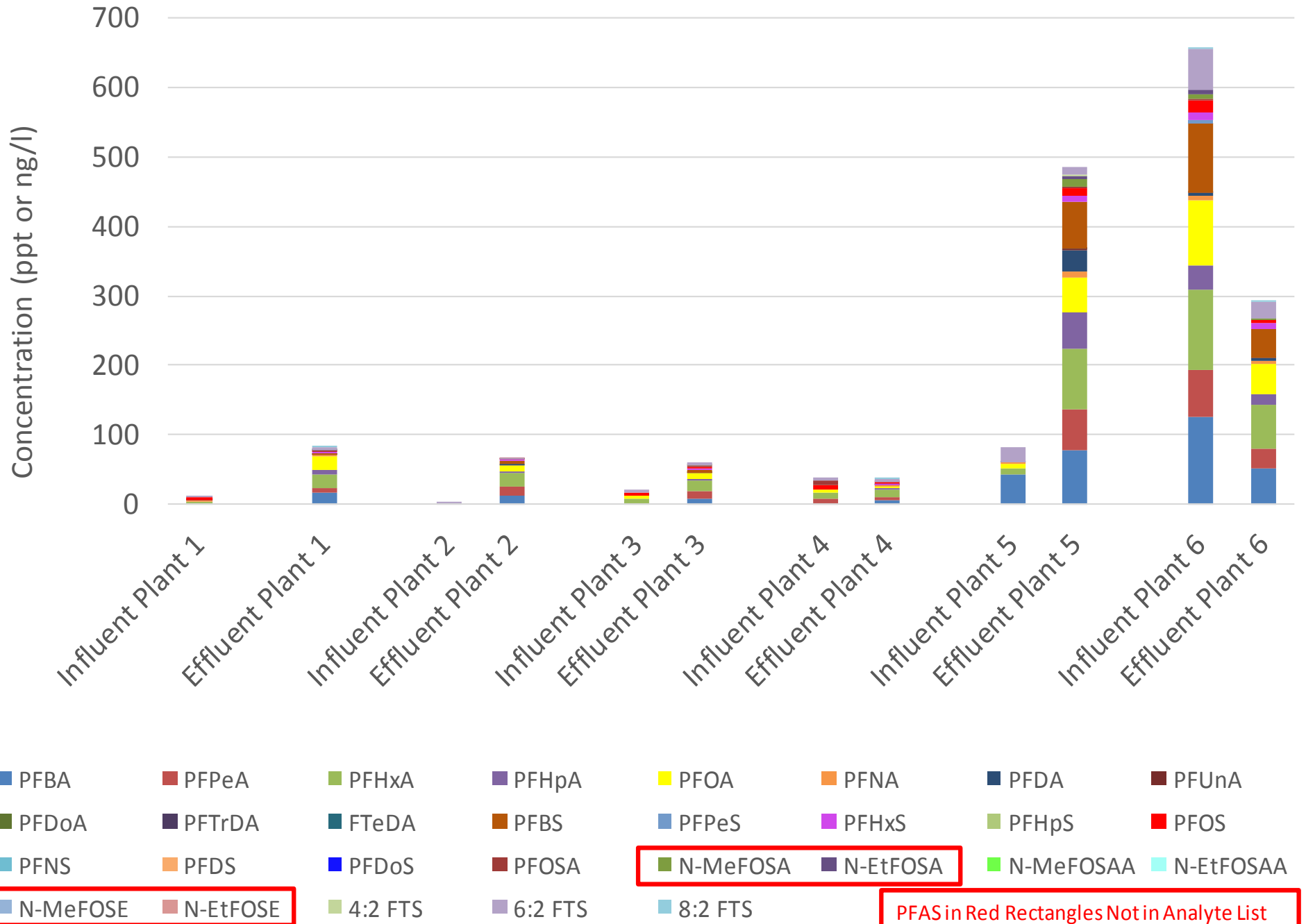


PFAS in VT Landfill Leachate

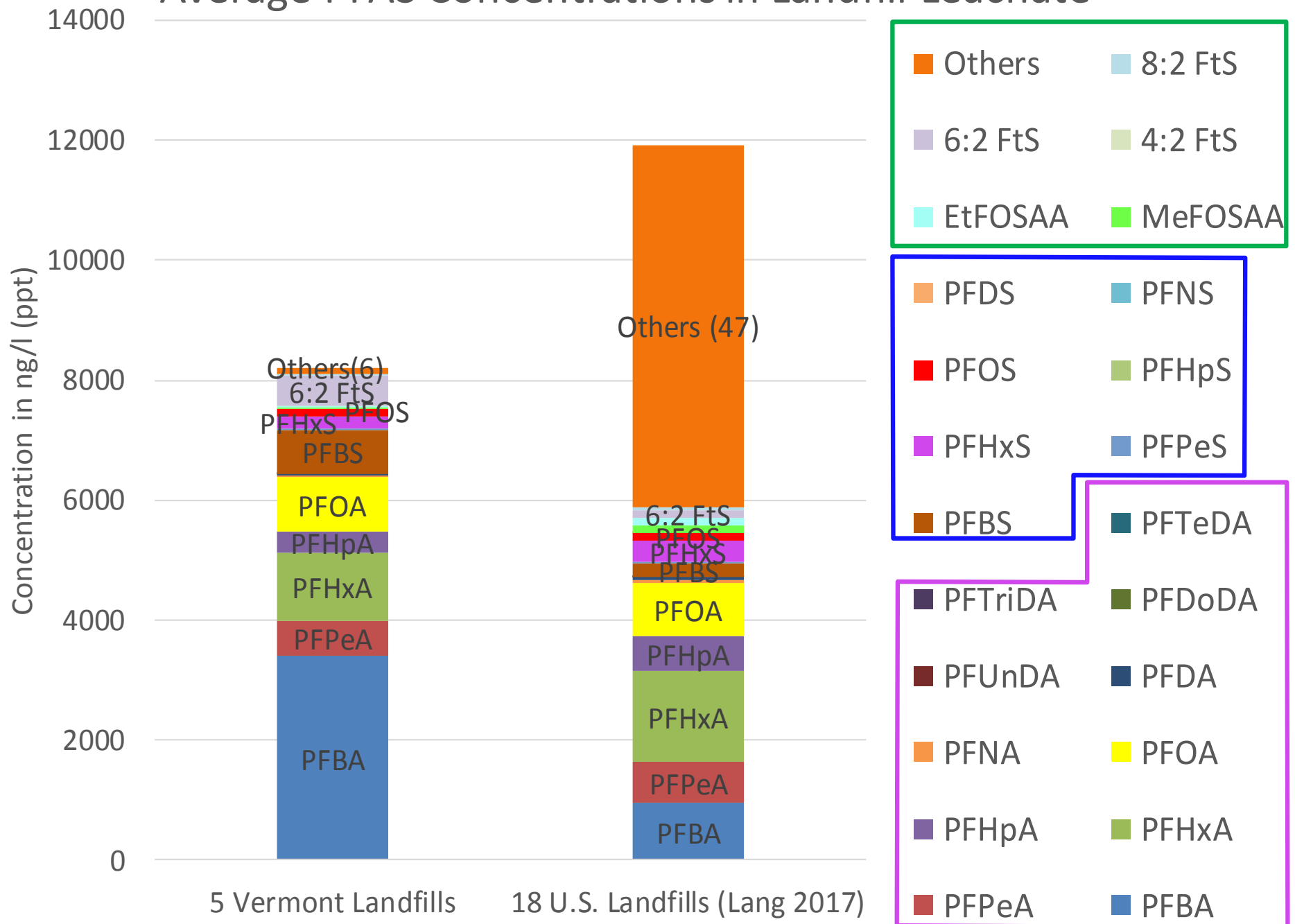


- PFBA
- PFDoA
- PFNS
- N-MeFOSE
- PFPeA
- PFTrDA
- PFDS
- N-EtFOSE
- PFHxA
- FTeDA
- PFDoS
- 4:2 FTS
- PFHxA
- PFBS
- PFOSA
- 6:2 FTS
- PFOA
- PFNA
- PFPeS
- N-MeFOSA
- 8:2 FTS
- PFDA
- PFHxS
- PFHpS
- PFUnA
- PFOS
- N-MeFOSAA
- N-EtFOSAA

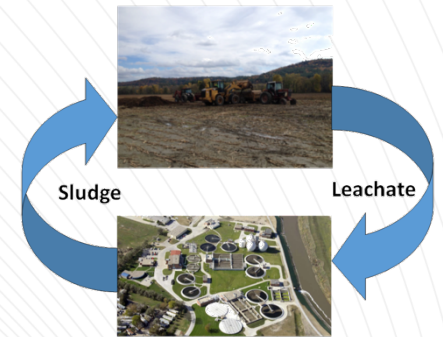
PFAS in VT WWTP Influent and Effluent



Average PFAS Concentrations in Landfill Leachate

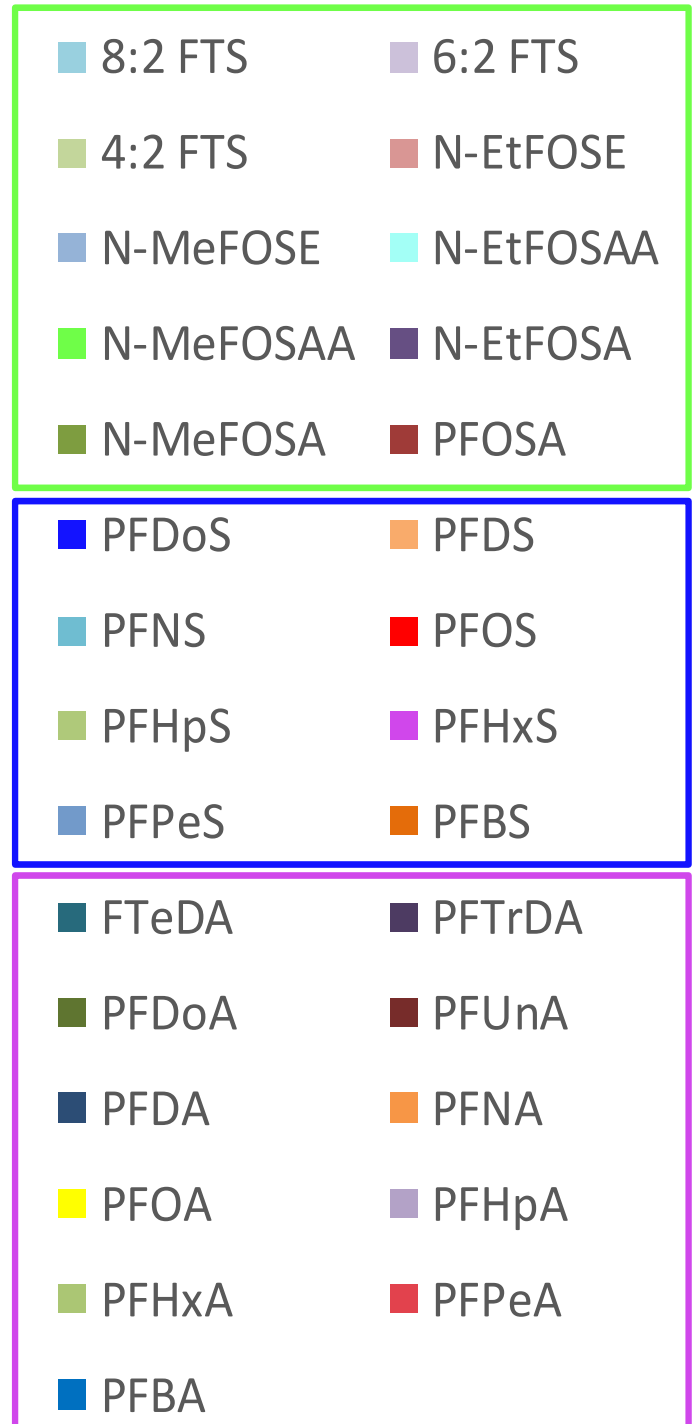
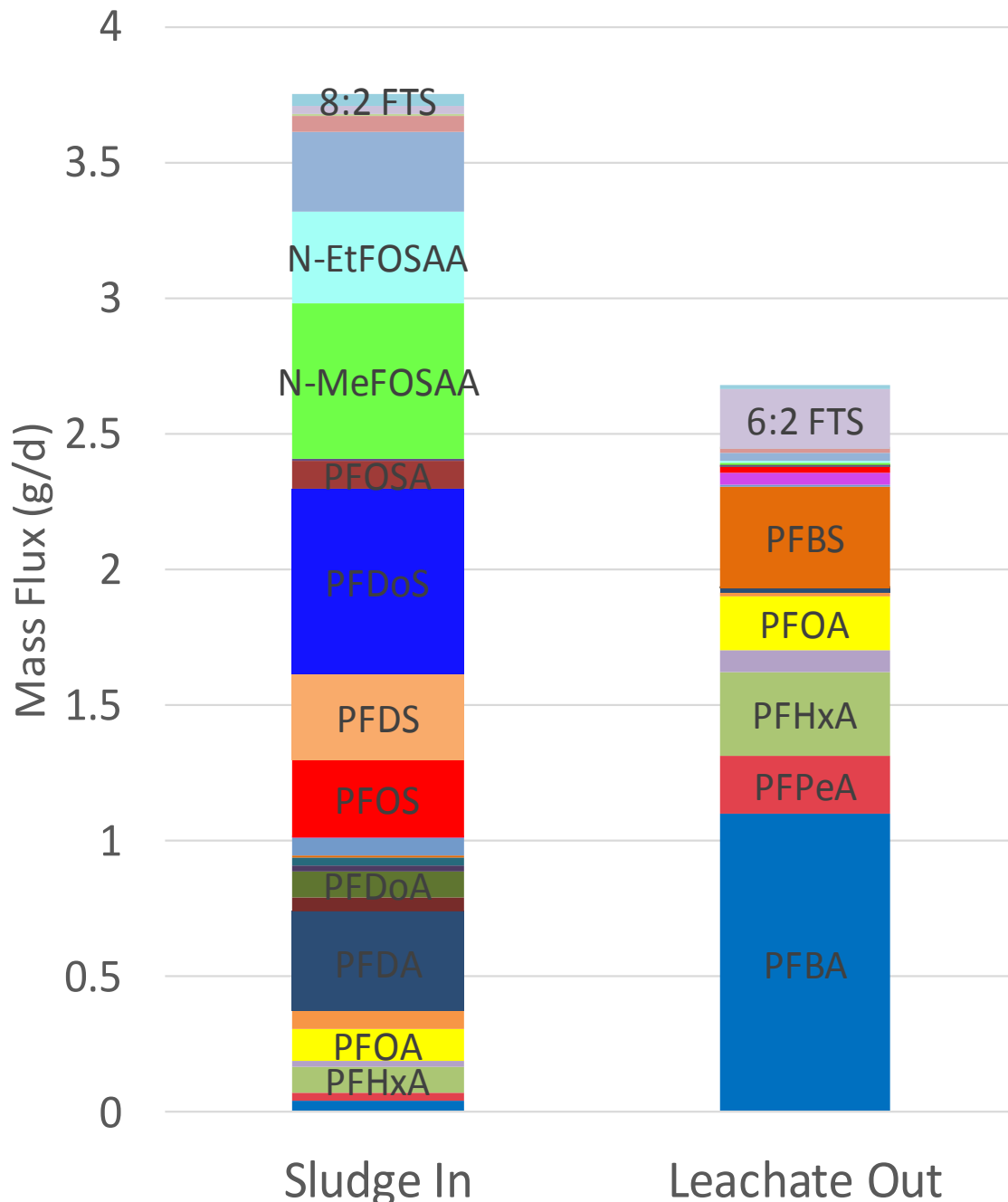


PFAS Cycle/Comparison



- Case study very rough examination of an active landfill
 - Leachate generation ~ 30,000 gal/d
 - Sludge acceptance ~ 270,000 lb/day (wet)
 - Sludge water content 75%
 - Average PFAS concentration in sludge
 - Landfill-specific PFAS concentration in leachate

PFAS Cycle / Mass Flux Comparison



Observations

- Estimates of PFAS fluxes into (sludge) and out of (leachate) the landfill are similar in magnitude, but the PFAS distributions differ markedly
 - Long-chain PFAS, especially sulfonic acids, may sequester in the landfill
 - Short-chain compounds are prevalent in leachate, and appear to come from sources other than sludge
- PFAS cycling may not be significant at the compound level, and the overall PFAS balance appears to be much more complex
- Comparing PFAS data can be challenging due to varying analyte lists and lack of consistent analytical methods, data quality.



Additional Questions

- What fraction of WWTP loading comes from landfill leachate? (Mostly minimal, as discussed above.)
- What are the specific sources of PFAS found in leachate?
- What fractions of the PFAS in leachate are due to landfill gas condensate?
- Can leachate be treated in a cost-effective manner?
- Are air emissions of PFAS important?





Biosolids compost for my raspberries... still using it, even though I know it has PFAS in it. The benefits outweigh the risks :)



Thank you.

Ned Beecher, MS • NEBRA • Tamworth, NH

November 12, 2019

EBC New England • Framingham, MA



An Overview of PFAS Occurrence at Landfills

Arie Kremen, Ph.D.

Client Manager

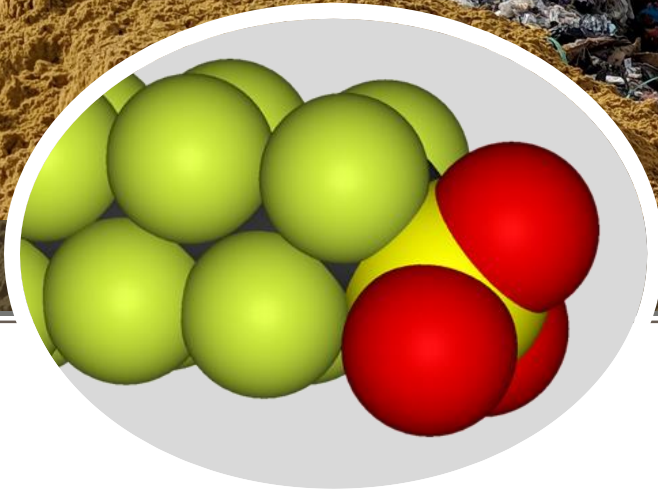
Tetra Tech



Environmental Business Council of New England

Energy Environment Economy

An Overview of PFAS Occurrences at Landfills



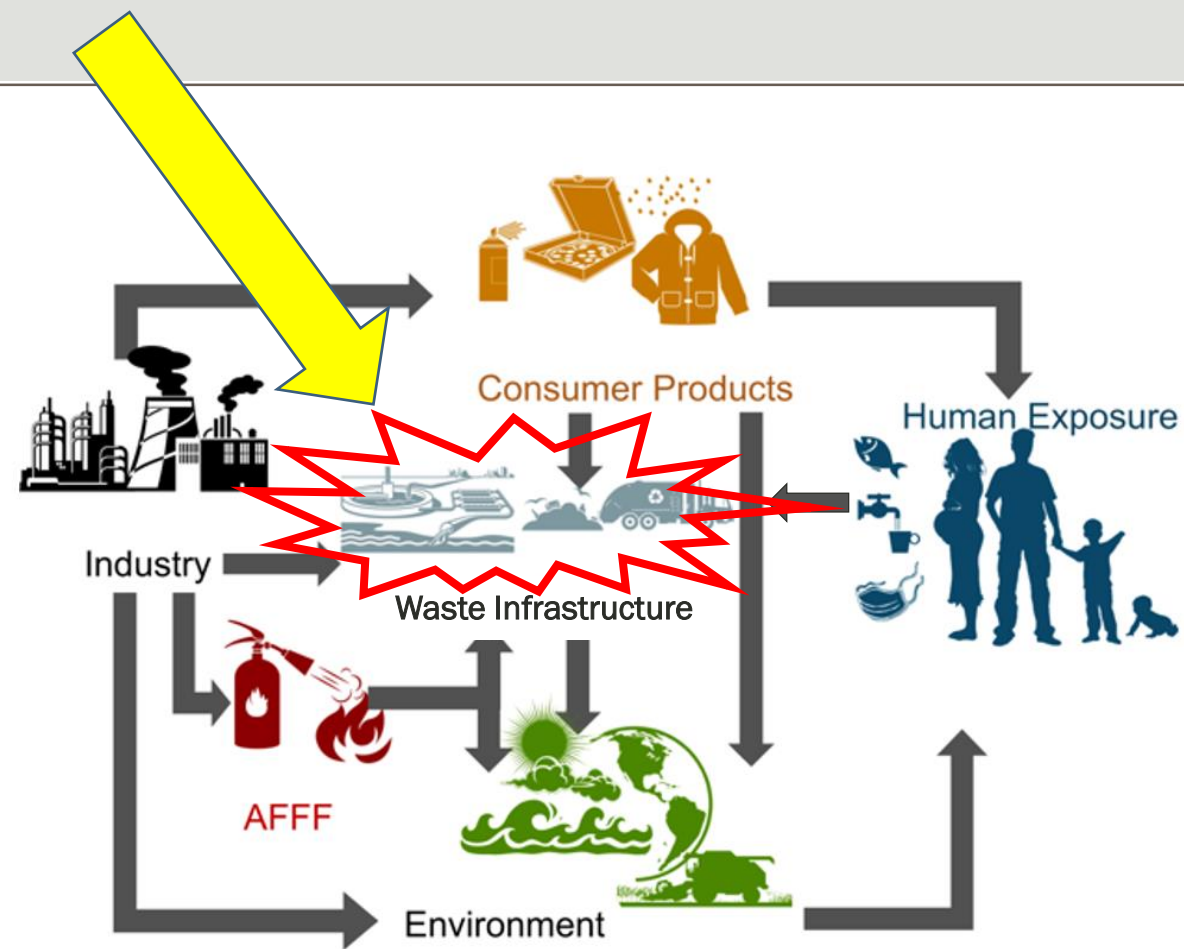
EBC Solid Waste Management Program – Impact of PFAS on Solid Waste Operations

Overview of PFAS Occurrences at Landfills

Environment	Materials	Equipment
Groundwater	Solid Waste	Operations equipment
Surface water	Leachate	Hand and stationary tools
Stormwater	Landfill Gas	Personal Protective Equipment
Ambient air	Cover Material	Sampling equipment
Soil	Construction Materials	Food packaging

PFAS are ubiquitous and are present in all aspects of landfill operations.

Potential Major Exposure Pathways



Source: Sunderland et al. (2019)

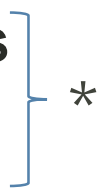
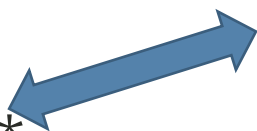
Attempts at a PFAS Mass Balance

Inputs

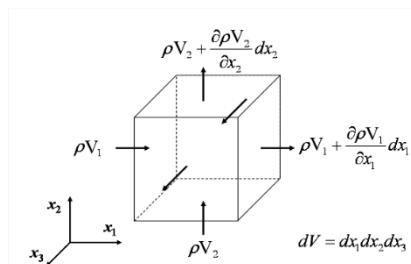
- Waste*
- Biosolids*
- Cover material*

Outputs

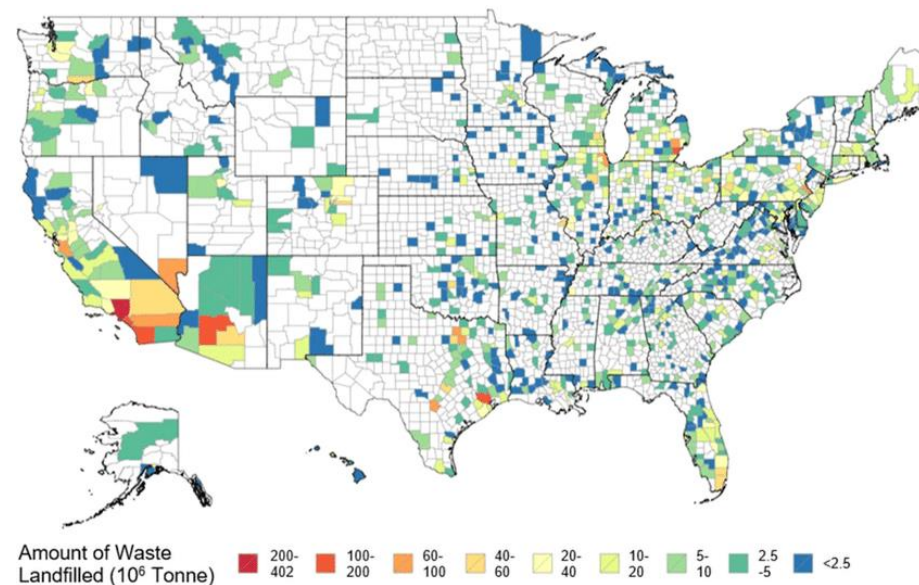
- Leachate*
- ~~Surface water~~
- Surface emissions
- Landfill gas



$$\left[\text{Rate of Accumulation} \right] = \left[\text{Rate}_{in} \right] - \left[\text{Rate}_{out} \right] + \left[\text{Rate of Generation} \right]$$



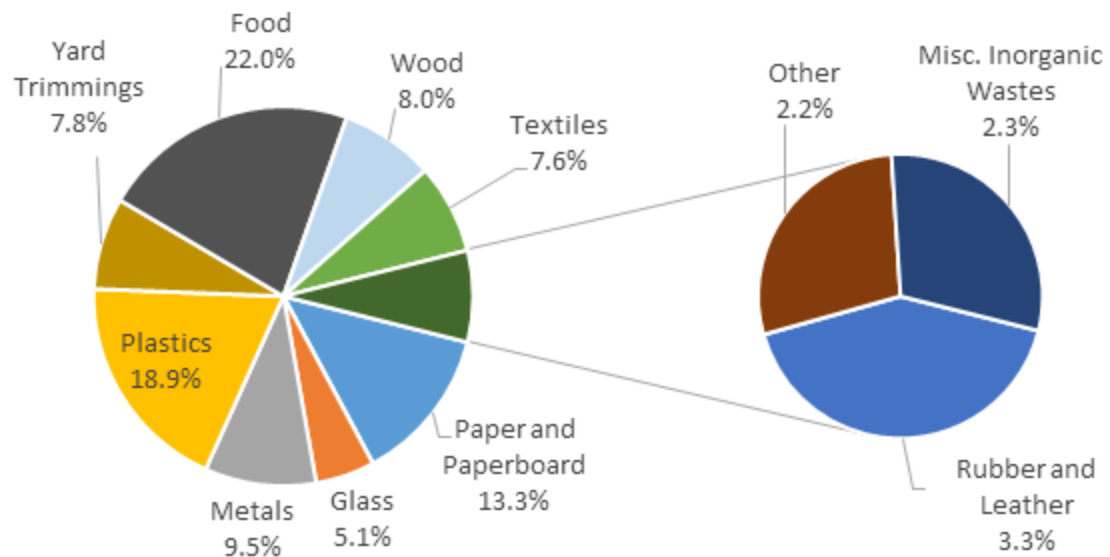
Control Volume: US MSW Landfills



Source: Powell et al. (2016)

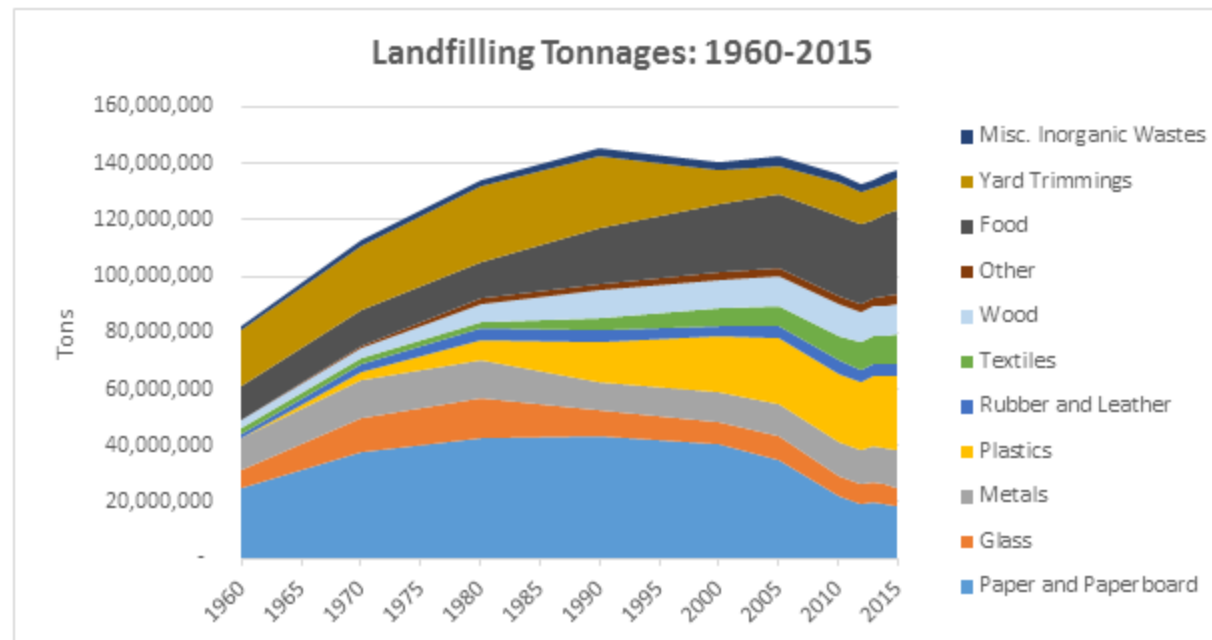
Landfilled MSW Composition & Tonnage

Total MSW Landfill by Material, 2015
(137.7 million tons)



Source: USEPA (2018)

Landfilling Tonnages: 1960-2015



Main Source Quantification: MSW

MSW Component	PFAS Content
Compost w/o packaging material	2.4-7.6 ng/kg
Compost w/packaging material	28.7-75.9 ng/kg
Bulky Waste	500 ng/g
C&D waste	800 ng/g
ASSUME ('Fermi Approximation')	1, 10, 100, and 1,000 ng/g

Based on annual amount of landfilled waste of 137.7 million tons:

MSW PFAS content	Estimated Amount PFAS landfilled
1 ng/g	124.9 kg/yr
10 ng/g	1,249.2 kg/yr
100 ng/g	12,492 kg/yr
1,000 ng/g	124,920 kg/yr



Challenging sampling and analysis matrix

Release Potential from Landfill Leachate

National Release Potential (Lang et al., 2017)

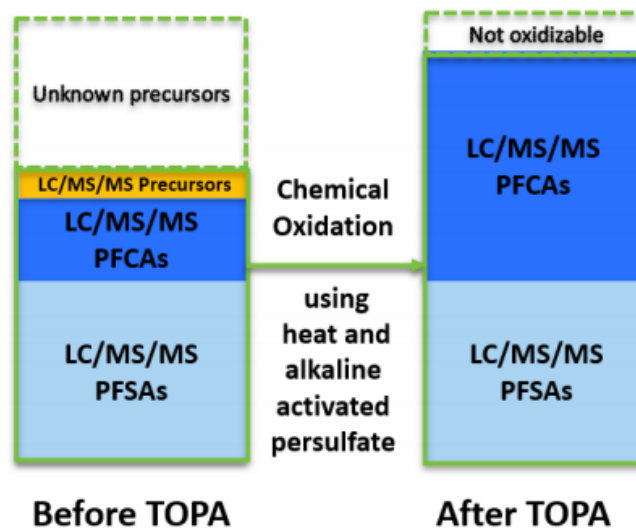
Climate	Wet		Temperate		Arid		Total (kg/yr)
Landfill Age	<10 yr (n=14)	>10 yr (n=12)	<10 yr (n=2)	>10 yr (n=6)	<10 yr (n=2)	>10 yr (n=4)	
PFAS (ng/l)	15,000	11,000	7,000	11,000	29,000	15,000	
	±16,000	±12,000	±1,000	±9,000	±1,000	±16,000	
Leachate	12,700 Mgal/yr		3,450 Mgal/yr		30 Mgal/yr		
Loading (kg/yr)	625.0		117.5		2.5		745.0

Note:

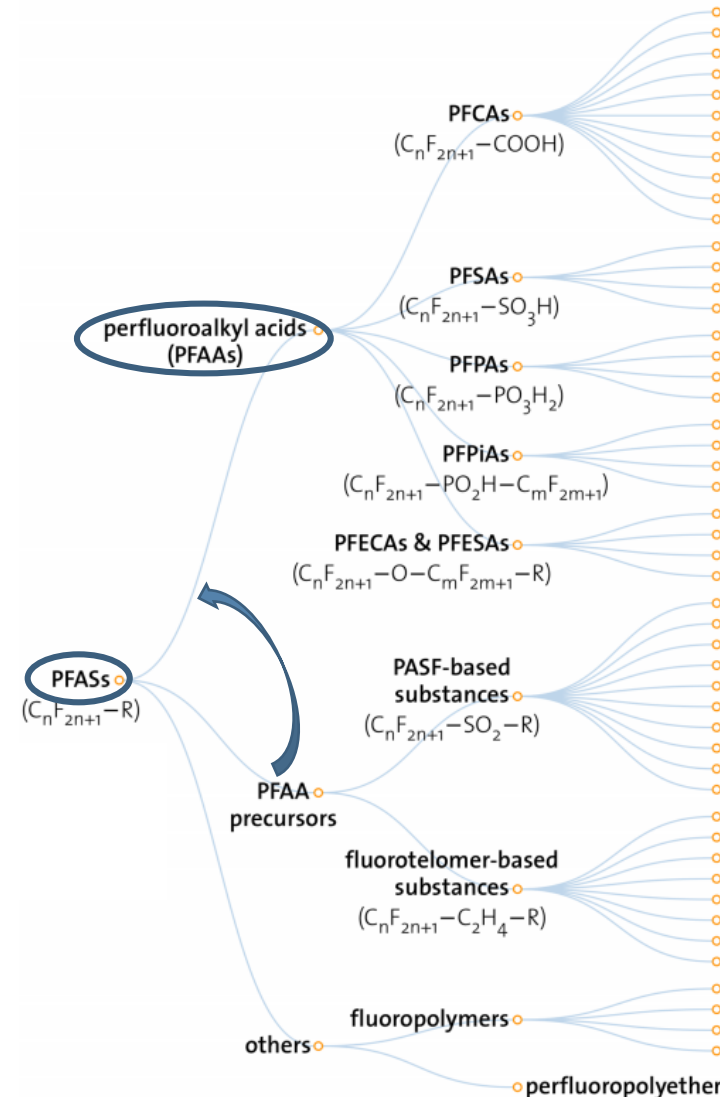
- Total of 70 quantifiable PFAS (Σ PFAS)
- Excludes oxidizable precursors
- Relied on averages, as standard deviations are too large

Precursors of Perfluoroalkyl Acids (PFAA)

- The PFAS group consists of
 - PFAA precursors
 - PFAA, including PFOS and PFOA
 - Others
- PFAA are non-degradable, and are considered ‘terminal PFAS’;
- PFAA precursor quantification is limited due to a lack of analytical standards;
- Total Oxidizable Precursor Assay (TOPA) is used to determine the presence of PFAA precursors in a sample (not commercial);



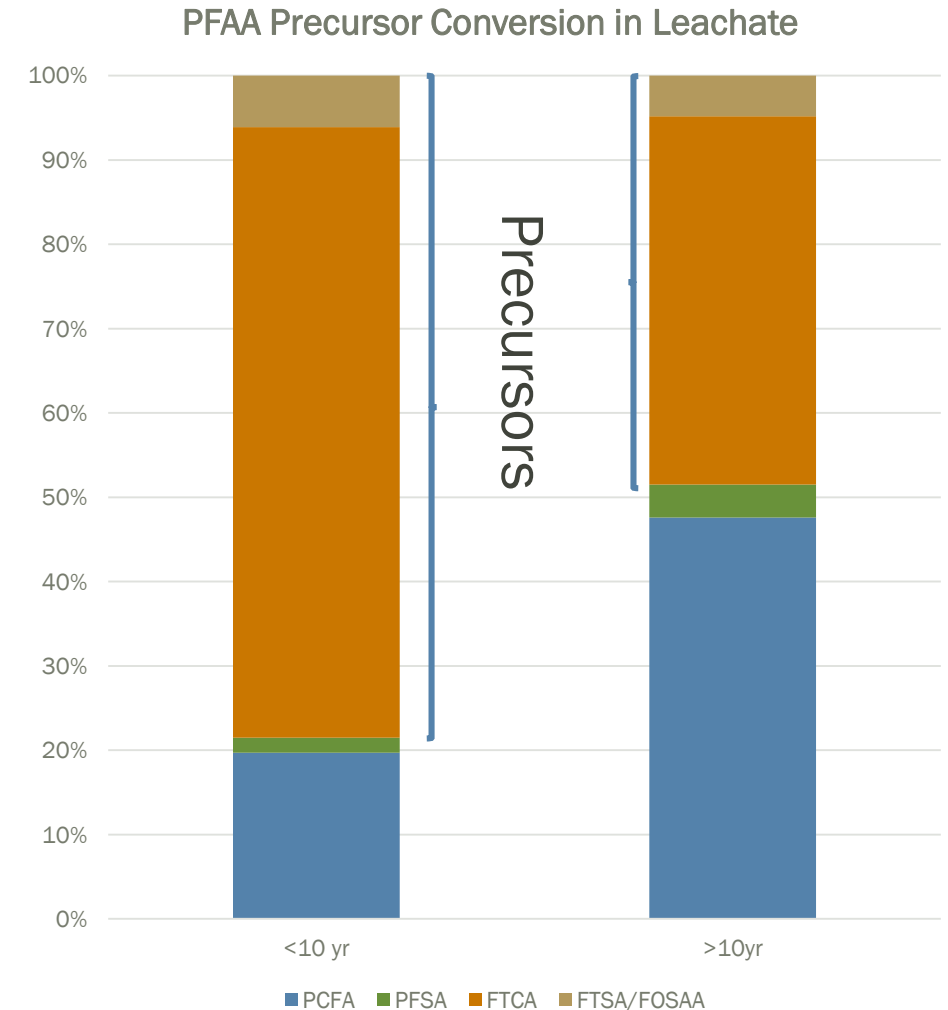
Source: Chiang (n.d.)



Leachate PFAA Precursor Estimate

- Precursor content decreased from 78.5% to 48.5% in LFs > 10 yrs
 - PFAS content is underestimated
 - Treatment to increase PFAS content
- PFAA precursor oxidation increases leachate PFAS content
- Additional oxidation during leachate treatment
- PFAA conversion estimate:

$$745.0 \text{ kg/yr} \times 2 = 1,490 \text{ kg/yr}$$



Source: Lang et al. (2017)

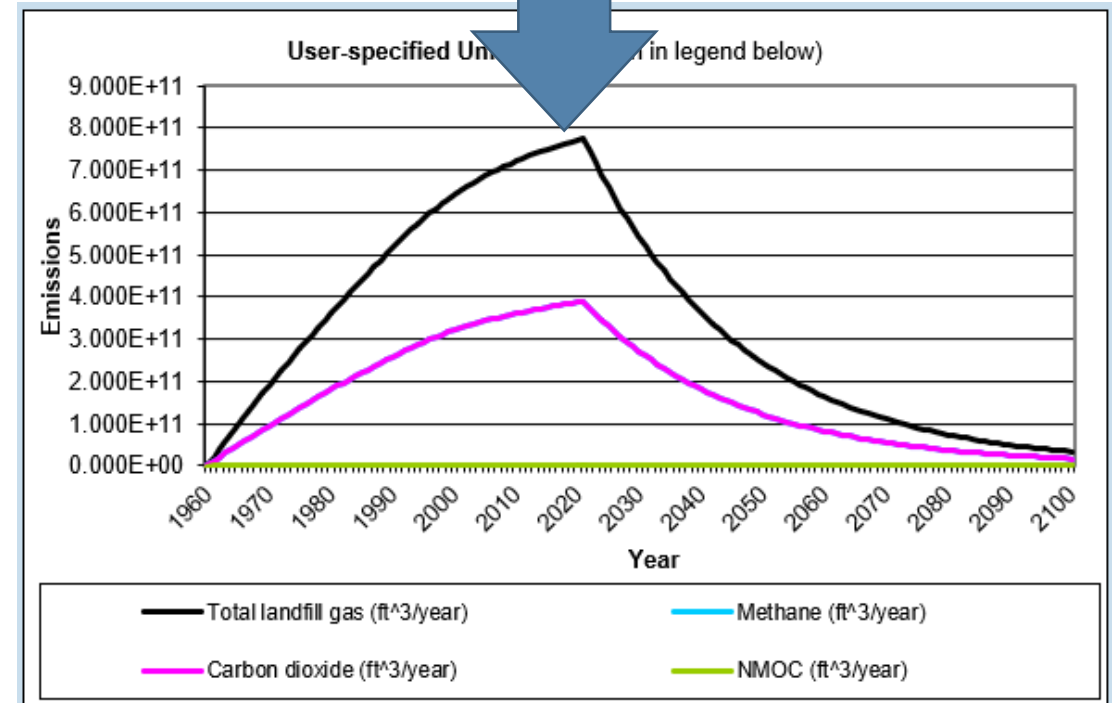
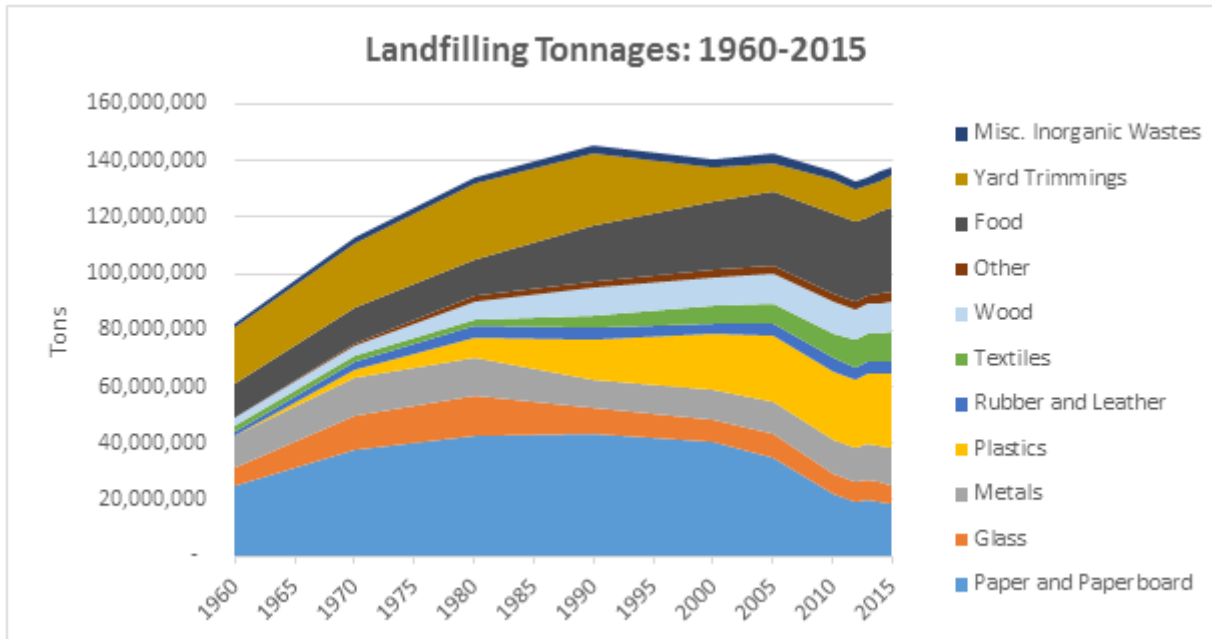
National Inventory of PFAS in US Biosolids (2001 EPA Survey)

Compound	Concentration (ng/g-dw)	Detection Frequency	Estimated Annual Load (kg/year)				%landfilled
			Biosolids Production	Land Application	Landfill	Incineration	
PFBA	2.0 (1.2-3.2)	80%	10.0-12.5	5.0-7.5	1.7-2.1	2.0-2.5	
PFPeA	3.5 (1.8-6.7)	100%	17.7-22.2	8.8-13.3	3.0-3.8	3.5-4.4	
PFHxA	6.2 (2.5-11.7)	100%	31.8-39.9	15.9-23.9	5.4-6.8	6.4-8.0	
PFHpA	3.4 (1.2-5.4)	80%	17.4-21.8	8.7-13.1	3.0-3.7	3.5-4.4	
PFOA	34.0 (11.8-70.3)	100%	172-215	85.8-129	29.3-36.6	34.3-43.1	6.3%
PFNA	9.2 (3.2-21.1)	100%	47.2-59.1	23.5-35.5	8.0-10.0	9.4-11.8	
PFDA	26.1 (6.9-59.1)	100%	133.0-167.0	66.6-100.0	22.7-28.4	26.7-33.4	
PFUnDA	11.7 (2.8-38.7)	100%	59.9-69.7	29.9-45.1	10.2-12.8	12.0-15.0	
PFDoDA	10.9 (4.5-26.0)	100%	55.6-69.7	27.8-41.8	9.4-11.9	11.1-13.9	
PFBS	3.4 (2.5-4.8)	60%	17.6-22.0	8.8-13.2	3.0-3.7	3.5-4.4	
PFHxS	5.9 (5.3-6.6)	100%	29.9-37.5	15.0-22.5	5.1-6.4	6.0-7.5	
PFOS	403 (308-618)	100%	2,052-2,575	1,026-1,545	349-438	410-515	74.6%
PFOSA	20.7 (2.2-68.1)	100%	105-132	52.7-79.3	17.9-22.5	21.1-26.4	
Source: Venkatesan and Halden (2013)			2,749-3,443		467.7-586.7		17.0%

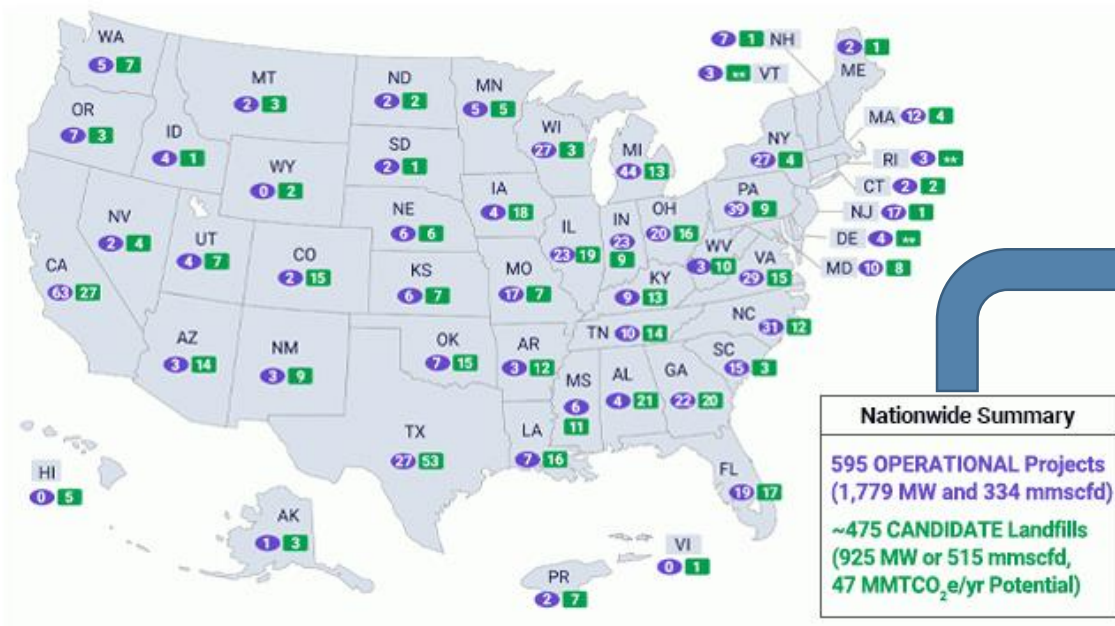
LFG Generation (not Recovery) Potential Estimate

LandGEM, using 'Inventory Conventional' settings:

- Methane generation rate: $k=0.05 \text{ yr}^{-1}$
- Specific methane generation capacity: $L_0=100 \text{ m}^3/\text{Mg}$



PFAS Emission Potential with LFG



LMOP data

- Recoverable LFG potential:
 - Operational: 334 mmscfd
 - Candidates: 515 mmscfd
 - Total: 849 mmscfd
- Assume 60% collection efficiency
 - Generation: 1,415 mmscfd
 - 5.165 × 10¹¹ ft³/yr

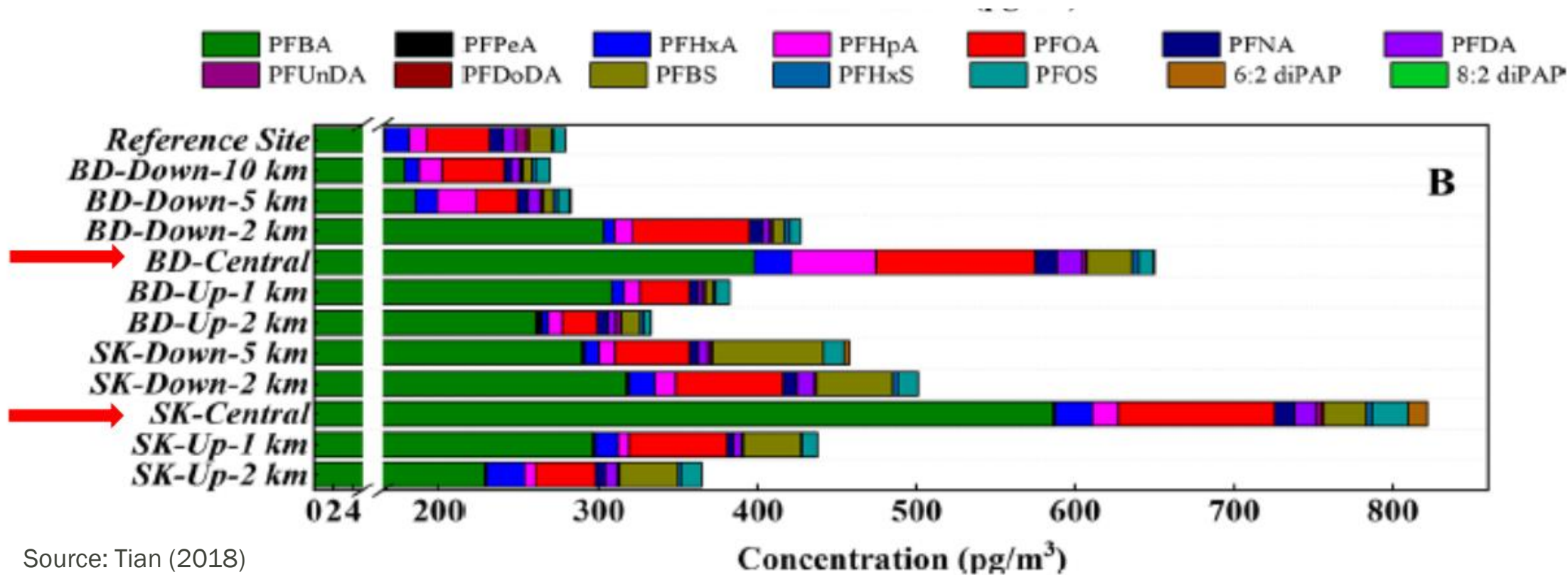
Source/Model	ft ³ /yr	m ³ /yr	Average
LandGEM	7.719 × 10 ¹¹	0.219 × 10 ¹¹	0.183 × 10 ¹¹
LMOP	5.165 × 10 ¹¹	0.146 × 10 ¹¹	

PFAS Potential to Emit with LFG

ΣPFAS in LFG: 650-850 pg/m³, assume 1,000 pg/m³

NEGLIGIBLE

Annual Emission Potential: $0.185 \times 10^{11} \text{ m}^3/\text{yr} \times 1,000 \times 10^{-15} \text{ kg/m}^3 = 0.02 \text{ kg/yr}$



Source: Tian (2018)

PFAS Input with Cover Material

Input with Cover Material

- Estimate cover as 20% of landfilled MSW

$$\Sigma\text{PFAS} = 25 \text{ ng}_{\text{PFOA}}/\text{g}_{\text{soil}} + 200 \text{ ng}_{\text{PFOS}}/\text{g}_{\text{soil}}$$

$$= 225 \text{ ng/g}$$

$$M_{\text{PFAS}} = 0.2 \times 140 \times 10^6 \text{ ton/yr} \times 225 \text{ ng/g}$$

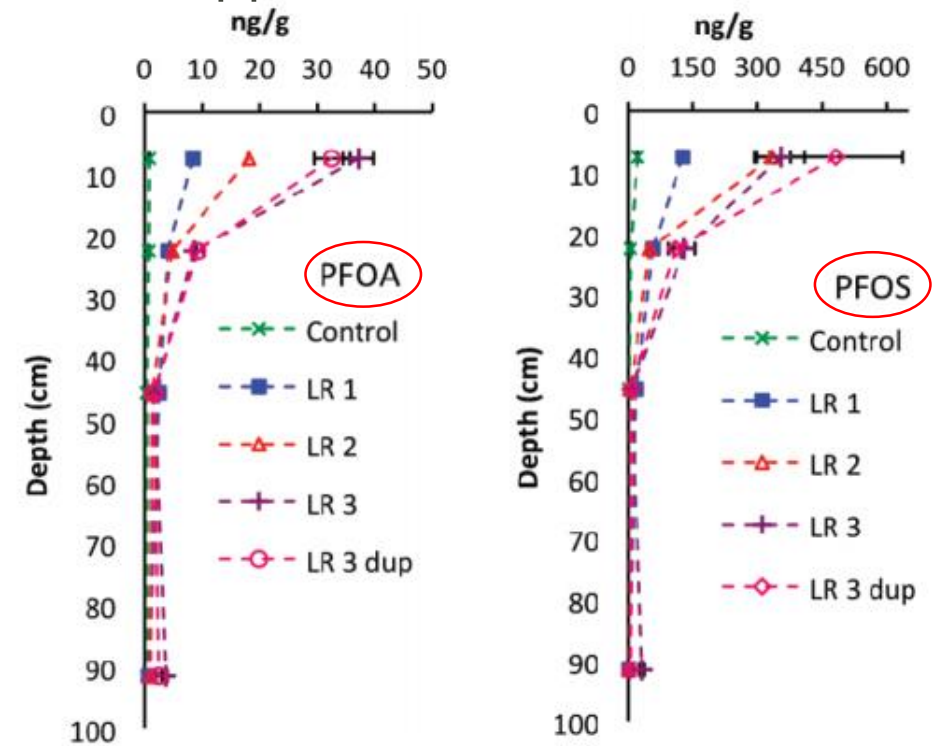
$$= \dots$$

$$= 40.7 \text{ kg/yr}$$

PFAS leaching from Soils (Source: McLachlan et al., 2019)

- PFAS leaching occurred within 49-120 days
- Soil/water partitioning $k_d \approx 0.5$
 - Leached – 20.3 kg/yr (→ leachate)
 - Adsorbed – 20.3 kg/yr (immobilized)

PFOA and PFOS in Soils from Land Application of Biosolids



Source: Sepulvado et al. (2011)

Annual Flux Summary by Stream (kg/yr)

			Input	Output	
Waste	1 ng/g	124.9			
	10 ng/g	1,249.2	1,249.2		
	100 ng/g	12,492.0			
	1,000 ng/g	124,920.0			
Biosolids	467.7 - 586.7		527.2		
Cover			20.3		
Leachate				745.0	
Precursors			745.0		
Landfill Gas				0.02	
Total Fluxes			2,541.7	745.0	29.3%
Net Flux			1,796.7		

Summary & Conclusions

- On a national basis, landfills appear to sequester PFAS
- The largest inputs of PFAS are
 - Solid waste
 - Biosolids
 - Precursors (internal source)
- Leachate is the predominant pathway for PFAS removal, about 30%
- LFG recovery and emissions appear to have little-to-no impact
- Review of additional data and papers to validate the finding
- Use of impacted cover soil – by itself – appears to be net neutral
- Role of precursors requires greater focus
- Need for larger sample size, better spatial and temporal resolution
- Need for standardizing sampling and analytical techniques

Questions? Comments?

Thank you!

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Treatment Technologies for PFAS in Landfill Leachate

Ivan Cooper

Principal

Civil & Environmental Consultants, Inc.



Environmental Business Council of New England
Energy Environment Economy



Civil & Environmental Consultants, Inc.

Leachate Treatment for PFAS

ENVIRONMENTAL BUSINESS COUNCIL

FRAMINGHAM, MASSACHUSETTS

NOVEMBER 12, 2019

Ivan A. Cooper, PE, BCEE
Civil & Environmental Consultants, Inc.
Charlotte NC

Agenda

▶ Emerging Contaminants –

- PFAS

▶ Treatment Technologies

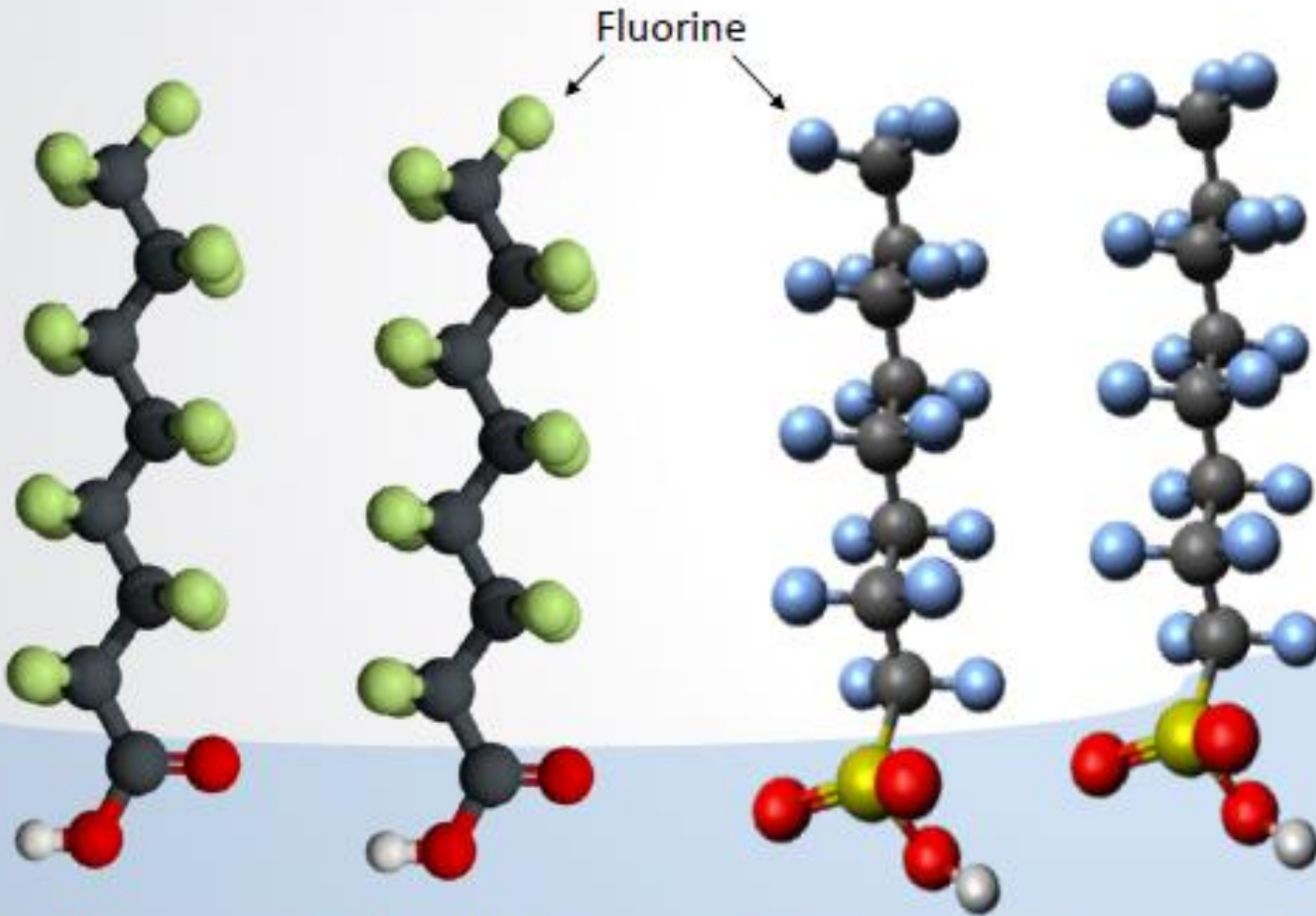
- Activated Carbon
- Ion Exchange
- Reverse Osmosis
- Innovative Technologies
 - Advanced Remediation Catalysis (ARC)
 - Advanced Reduction Processes (ARP)
 - Non-Thermal Plasma Reduction
 - Advanced Oxidation – Persulfate; Nano-ZVI
 - Electro-Oxidation/Transmembrane Systems
 - Others?

▶ Summary

Per- and Polyfluoroalkyl Substances (PFAS) - What Are They?

➤ A class of man-made chemicals

- Chains of carbon (C) atoms surrounded by fluorine (F) atoms
 - Water-repellent (hydrophobic)
 - Stable C-F bond
- Some PFAS include oxygen, hydrogen, sulfur and/or nitrogen atoms, creating a polar end



Perfluorooctanoic acid (PFOA)

Perfluorooctanesulfonic acid (PFOS)


PFAS –Why Important?

- ▶ **Thousands of Fluorinated Compounds in class**
- ▶ **Short-chained (C₄-C₇) carboxylates or sulfonates are present at greater abundance relative to longer-chain homologs (≥C₈).¹**
 - Leachate tests showed Perfluoroalkyl carboxylates (2,800 ng/L max) followed by Perfluoroalkyl sulfonates (2,300 ng/L max).
 - Water soluble responsible for presence in leachate and potential release to the environment.
- ▶ **Linked to many health impacts, linked to cancer**
 - Example – 50,000 people sued DuPont in Parkersburg WV for PFOA in drinking water from plant making Teflon²
 - Current estimates are 15 million people have contaminated drinking water in US
 - Found in virtually every persons blood, US and worldwide

1.Huset et al., 2011

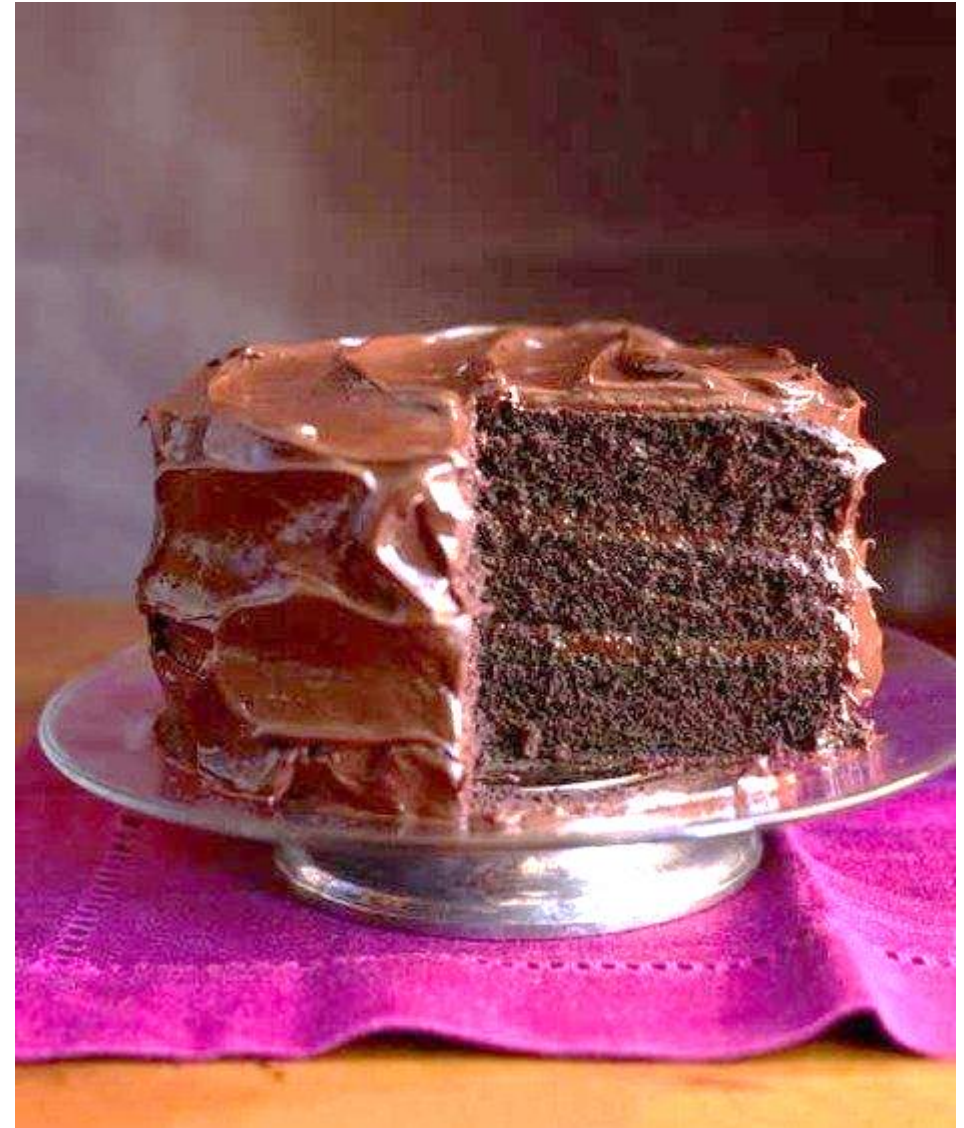
2. Environmental Working Group, 2018

Where PFAS is Used?

	Product Uses/Sources
<p>Fluoropolymer coatings</p> <ul style="list-style-type: none"><input type="checkbox"/> Plastics/polymers<ul style="list-style-type: none"><input type="checkbox"/> Oil, stain, water repellent (, Stainmaster® carpets, Scotch Gard™ and Gore-Tex®)<input type="checkbox"/> Surfactants used in firefighting foams<input type="checkbox"/> Mist suppressants for metal plating operations<input type="checkbox"/> Photomicroolithography process to produce semiconductors<input type="checkbox"/> Photography and film products 	<ul style="list-style-type: none"><input type="checkbox"/> Some grease-resistant paper<input type="checkbox"/> Fast food containers/wrappers (27 fast food chains)<ul style="list-style-type: none"><input type="checkbox"/> Microwave popcorn bags<input type="checkbox"/> Pizza boxes<input type="checkbox"/> Candy wrappers<input type="checkbox"/> Non-stick cookware such as Teflon™-coated pots/pans<ul style="list-style-type: none"><input type="checkbox"/> Used on carpets, upholstery, and other fabrics<input type="checkbox"/> Water-resistant clothing - Hush Puppy Shoes (Wolverine Worldwide)<input type="checkbox"/> Adhesives<input type="checkbox"/> Aviation hydraulic fluids<input type="checkbox"/> Cleaning products<ul style="list-style-type: none"><input type="checkbox"/> Personal care products such as shampoo, dental floss, and cosmetics (nail polish, eye makeup)<input type="checkbox"/> Paints, varnishes and sealants

PFAS Found in Food 20 years ago!

- ▶ **3M Commissioned Study reported in 2001 – PFOA and PFOS in beef, pork, chicken, milk, green beans, eggs, bread, and others in 6 cities in US southeast**
 - Levels from 500 to 14,700 ppt
- ▶ **FDA study 2019 – PFAS in meat, seafood, dairy, sweet potatoes, pineapples, leafy greens, chocolate cake with icing –**
 - **17,640 parts per trillion (ppt) of perfluoro-n-pentanoic acid (PFPeA) in chocolate cake with icing.**
 - If regulated at same level as proposed NY drinking water guidelines of 10 ppt, cake would contaminate thousands of gallons of water.



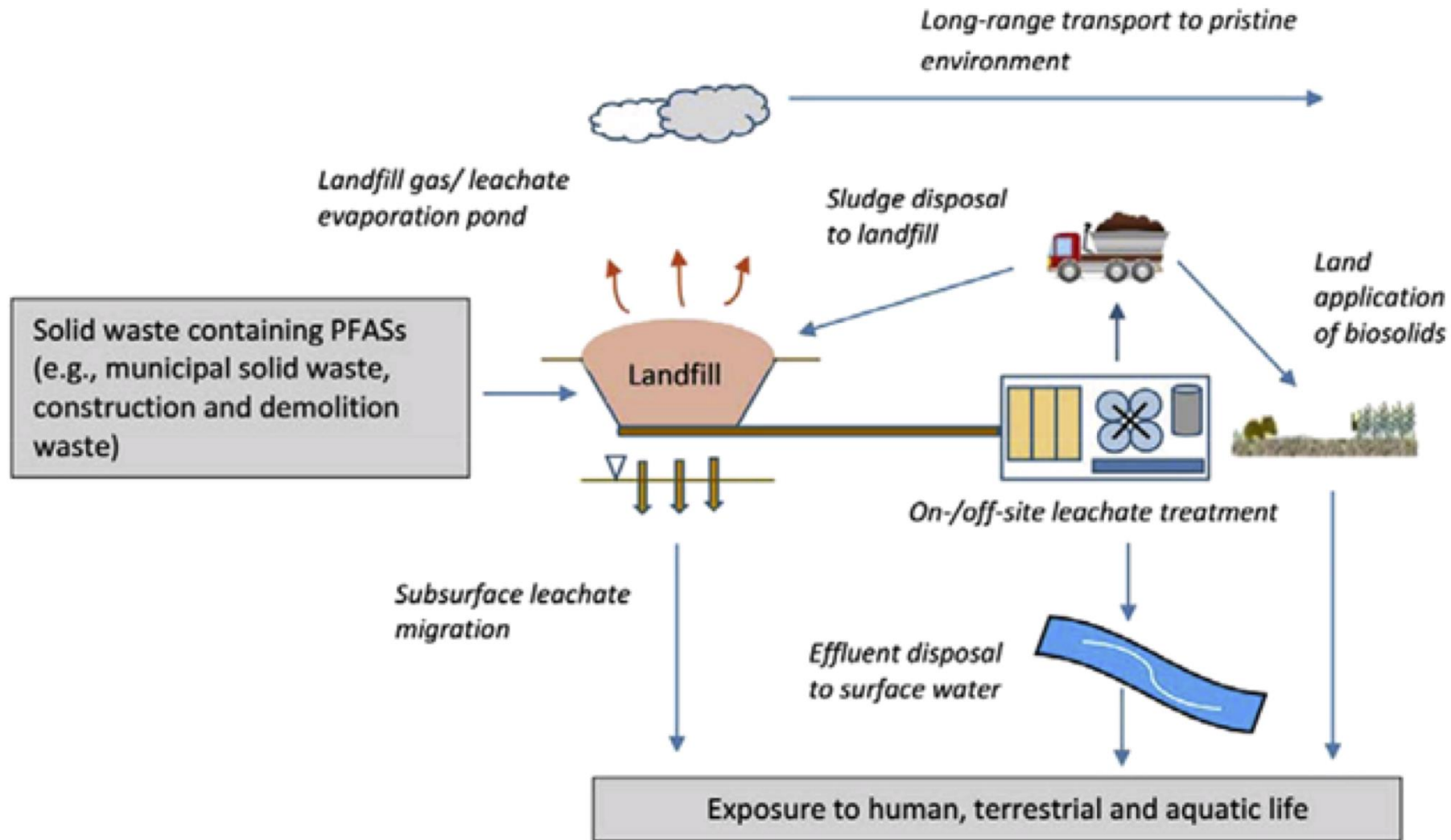
Drinking Water Standards

Parts per Trillion - As of October 2019		PFOS	PFOA	PFNA	PFHxS	PFHpA	PFBS	PFDA	PFHxA	GenX
USEPA	Health Advisory	70 sum		NA	NA	NA	NA	NA	NA	NA
ATSDR	Tox Values	7	11	10	70	NA	NA	NA	NA	NA
NY	Recommended MCL	10	10	NA	NA	NA	NA	NA	NA	NA
NJ	MCL or Proposed	13	14	13	NA	NA	NA	NA	NA	NA
VT	Health Advisory/ Emergency Rules	20 sum of five				NA	NA	NA	NA	NA
MA	Current ORSG	20 proposed sum of six				NA	NA	NA	NA	NA
CT	Water Board Notification Levels	70 sum of five				NA	NA	NA	NA	NA
CA	Regulatory Standard	6.5	5.1	NA	NA	NA	NA	NA	NA	NA
MI	Health Based	16	8	6	51	NA	420	NA	400,000	370
MN	Drinking Water Guidelines	70	38	NA	47	NA	NA	NA	NA	NA
NH	Regulatory Standards	12	15	23	85	NA	NA	NA	NA	NA
NC	Guidance/Goals	70 sum		NA	NA	NA	NA	NA	NA	140
Other States	EPA Values	70 sum		NA	NA	NA	NA	NA	NA	NA

PFAS

- ▶ **Lined landfills = leachate; unlined C&D landfills = groundwater; Soluble in water**
- ▶ **Readily bind to solids, but hard to predict**
- ▶ **Very Stable and persistent (3M in Minnesota, DuPont primary suppliers – now banned)**
- ▶ **Not treatable by conventional technology**
- ▶ **In 1/3 drinking water supplies in US, dust/ambient air, food**
- ▶ **High human toxicity, possibly human carcinogen, bioaccumulative**
- ▶ **Found in many landfill leachates (Canada study on 28 landfills– found in all leachates)**
- ▶ **Lab data difficult – Sampling protocol, Lab techniques, high variability, poor confidence?**

PFAS Landfill Cycle



PFAS Impacts on Landfills

- ▶ **POTW – Plants may put limits on leachate; likely during re-permitting**
- ▶ **PFAS found in all waste types and hard to limit amount entering landfills**
- ▶ **PFAS will be discharged in leachate**
- ▶ **Low levels make analysis difficult and expensive**
- ▶ **Low level limits likely, but unclear at this time**
- ▶ **Cost of sampling, analysis, and leachate management will go up**
- ▶ **Start seeing in state and local permits**
 - VT, MI, others?

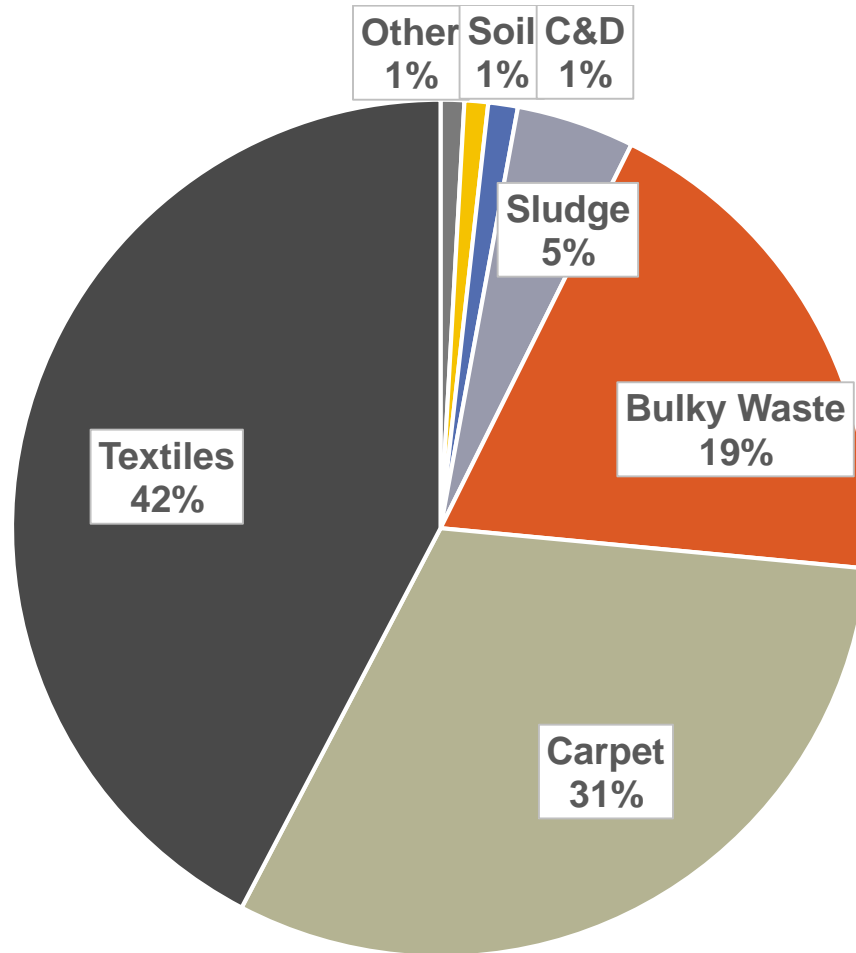
Usage	Aqueous film-forming foams (AFFF)	Military installations, airports, hangars, fire training areas, refineries
	Metal plating (mist suppressants)	Industrial facilities, water discharges
	Photolithographic chemicals	Manufacturing and processing
	Coatings that resist heat, oil grease, stains: Scotchgard, Gore-Tex, Teflon, food packaging, fabrics, carpet	Households and production facilities



US Military had largest stockpile of AFFF: 11 million L, 29% of US stocks in 2004



PFAS Mass Loading

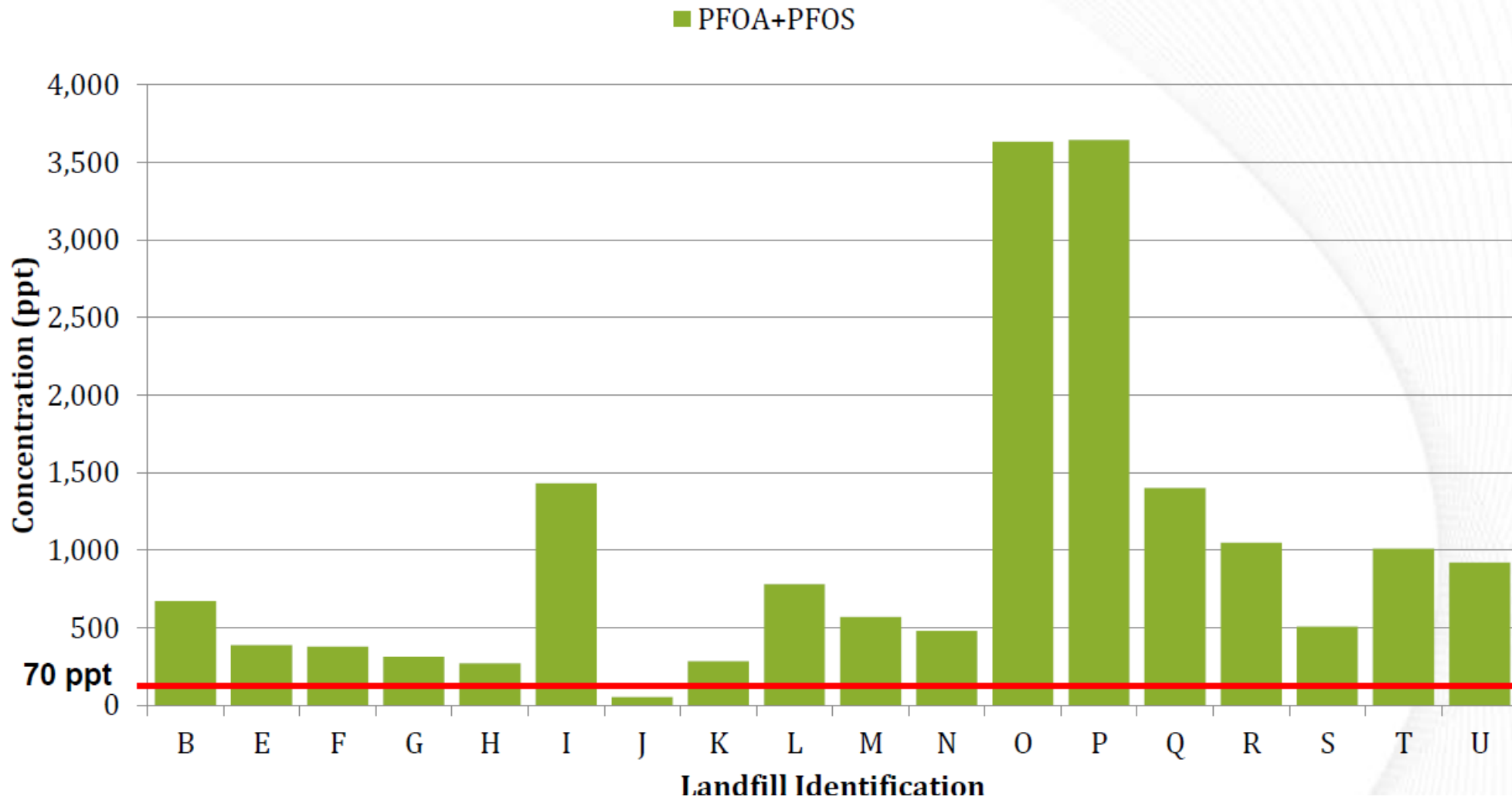


Recent LF Waste Study (Biased)

95% of tested waste contained PFAS

Excluded MSW

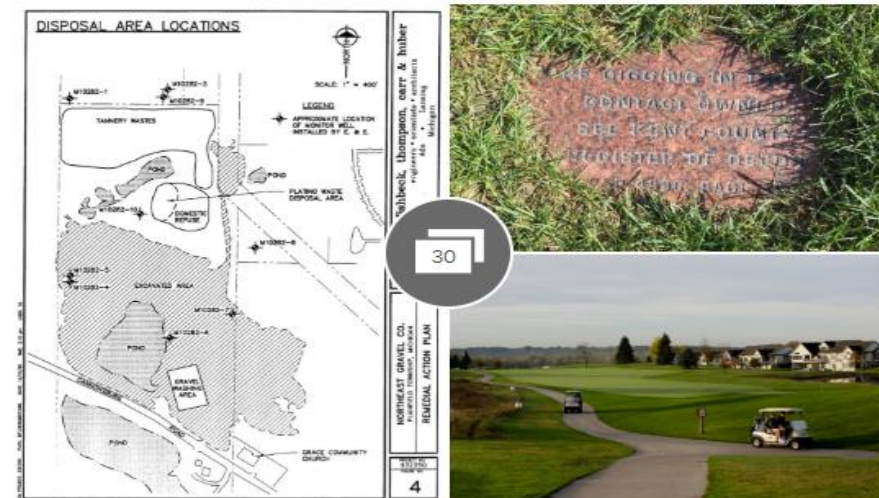
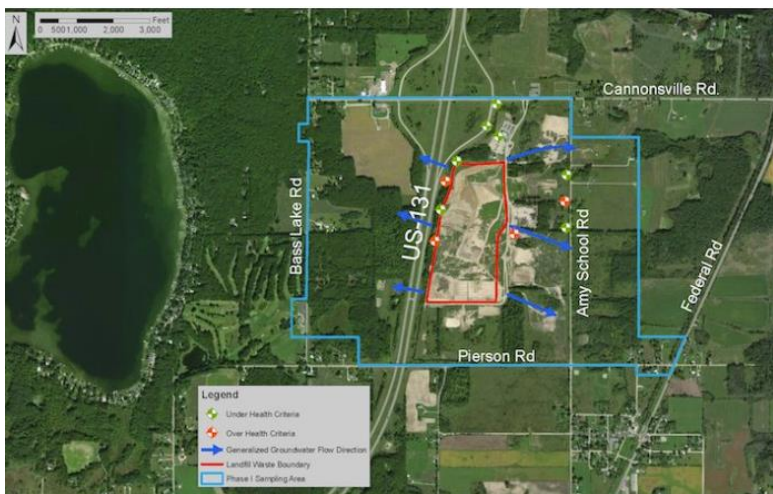
PFAS in Landfill Leachate



Lang et al, National Estimate PFAS Release to US Municipal Landfill Leachate, 2017

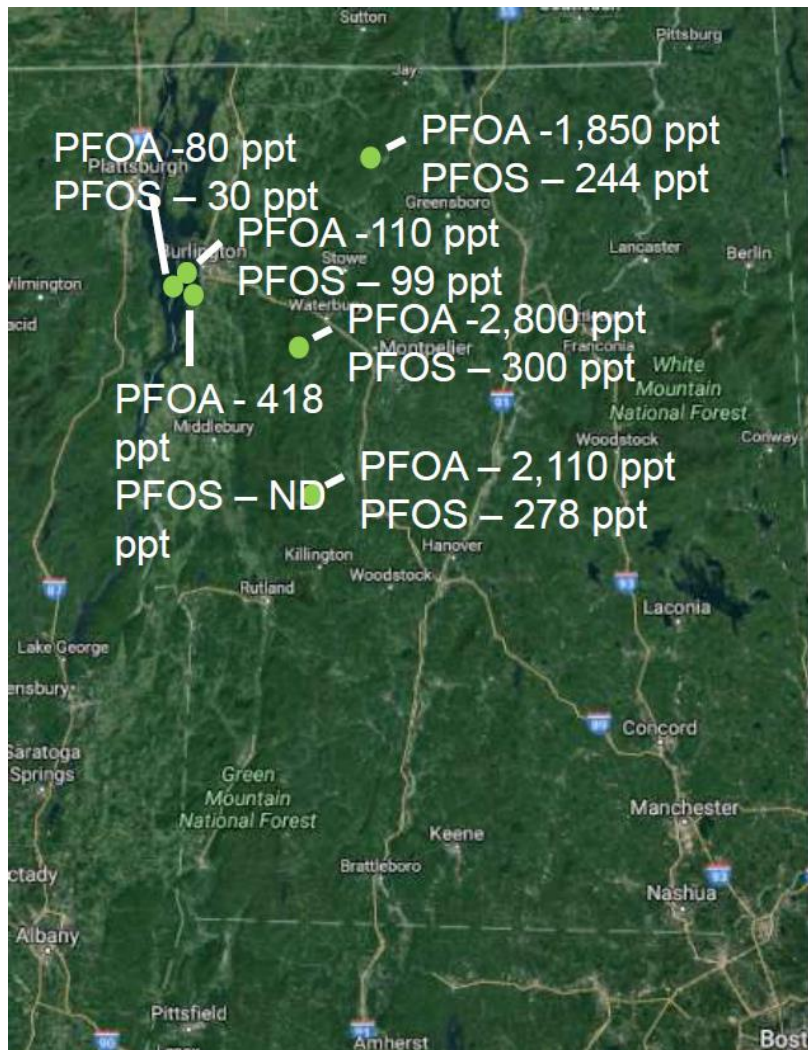
Site Example – Wolverine Dump Sites, Michigan

- ▶ Wolverine Worldwide dumped PFAS wastes in several Michigan landfills
- ▶ Wolverine World Wide tannery waste dumped into Northeast Gravel mine and landfill daily between 1970 and 1979. Keeler Brass also dumped electroplating wastes.
- ▶ A well near the Wolverine Gravel dump less than 10 miles away has almost 59,000 ppt PFAS, now a Superfund site
- ▶ Central Sanitary landfill, located in the Montcalm County village of Pierson, recently tested at concentrations above 70 parts-per-trillion.
- ▶ Kent County MI Landfill also has high concentrations PFAS
- ▶ Michigan very active in landfill identification and leachate for PFAS



Vermont Landfill Leachate

(Vermont DEC, May 2018)



PFOA
 High – 2,800 ppt
 Low – 80 ppt

PFOS
 High – 300 ppt
 Low – Non-detect

Transborder implication – data and evaluations to the Gouvernement du Quebec Ministere de l’Environnement.

1,000 feet to Lake Memphremagog – water supply to Quebec.

Vermont Guidelines, May 2018

PFAS Analyte:	Landfill Leachate concentration requiring no restrictions	Landfill Leachate concentration which may require restrictions	Landfill Leachate concentration requiring pretreatment
PFOA	0.120 mg/L (120,000 ppt)	0.120 mg/L to 1.2 mg/L	>1.2 mg/L
PFOS	0.001 mg/L (1,000 ppt)	0.001 mg/L to 0.010 mg/L	>0.010 mg/L

Vermont PFAS in Closed Landfills

(Vermont DEC, May 2018)

ppt	MSW LF 1	MSW LF 2	MSW LF 3	MSW LF 4	MSW LF 5	MSW LF 6	Paper Sludge LF	C&D LF
Sample Date	10/17	10/17	9/16	9/16	10/16	12/16	10/16	10/16
PFOA	11.3	44.9	8.43	14	2	8.99	18	900
PFOS	ND	37	4.98	5	ND	ND	11	140
TOTAL	11.3	81.9	13.41	19	2	8.99	29	1040

PFAS in NH Landfills

PFAS Concentrations in NH Landfill Leachate					
	Concentration in ng/L				
Criteria	PFOA	PFOS	PFBA	PFPEA	PFHPA
Min	0.5	0.44	0.55	1.0	0.89
Max	2200	1560	493	260	410
Mean	12.9	18.0	13.7	14.0	8.0
Median	9.0	17.1	21.7	18.5	10.8

PFAS in Landfill Leachate

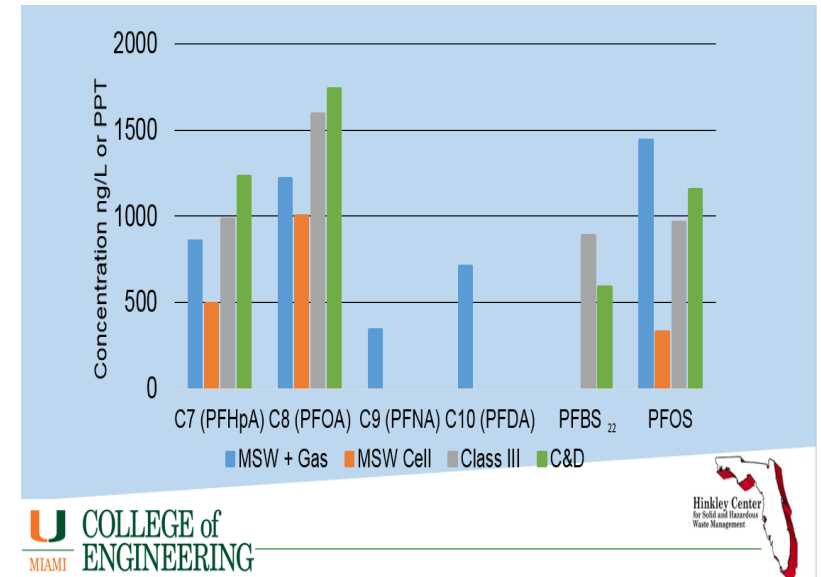
Nationwide - 20 Billion Gals/yr - 1900 Landfills *

▶ Main Typical PFAS*:

- ▶ Typical Concentrations: 0.1 to 10 ppb *
- ▶ PFOA perfluorooctanoic acid
- ▶ PFHxA perfluorohexanoic acid
- ▶ 5:3 FTCA fluorotelomer carboxylic acids

▶ Other PFAS:

- ▶ Typical Concentrations: 0.2 to 1.5 ppb
- ▶ PFOS
- ▶ PFBS
- ▶ PFHpA
- ▶ PFNA
- ▶ PFDA



* Ref. Lang, Johnsie PFAS in MSW Landfill Leachate 2016 Thesis UNC

Primary Source: Carpets and Clothing

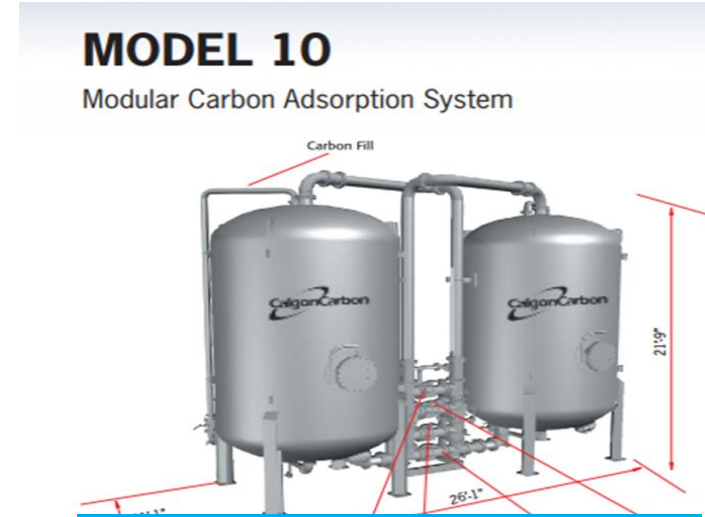
PFAS Treatment Technologies

- Activated Carbon
- Ion Exchange
- Reverse Osmosis
- Deep Well Injection
- Innovative Technologies
 - Advanced Remediation Catalysis (ARC)
 - Advanced Reduction Processes (ARP)
 - Non-Thermal Plasma Reduction
 - Advanced Oxidation – Persulfate; Nano-ZVI
 - Plasma Arc
 - Etc
 - Etc
 - Etc

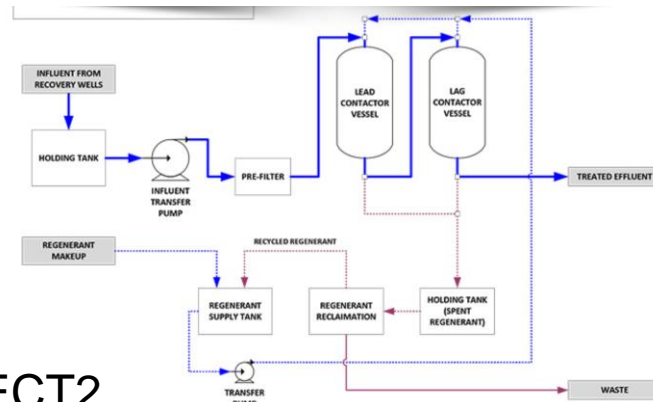
PFAS Remediation Options for Pump & Treat



Membrane Filtration



Carbon Adsorption



ECT2

Methanol/Brine
Regenerable Resin



Single-Use Resin

Types/Forms of Activated Carbon

Raw Materials

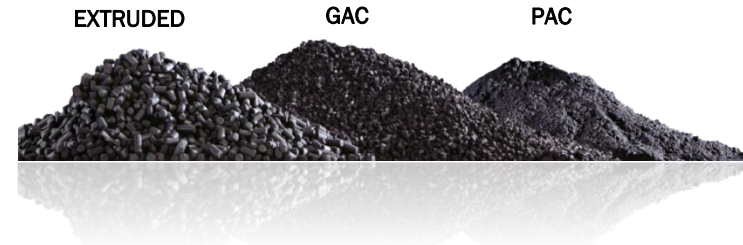


Raw Material dictates:

- Ash impurities
- Density
- Hardness
- Transport pore structure
- Adsorption kinetics

Wood ≠ Coconut ≠ Lignite ≠ Bit. Coal

Forms of Activated Carbon



Extruded: Typically, vapor phase
Low Pressure Drop /Slow Kinetics
Usually, 3 or 4 mm diameter

GAC: Liquid Phase (12x40, 8x30)
Vapor Phase (4x8, 4x10)

PAC: Typically, Liquid Phase 65-85% < 325 U.S. Mesh
(0.045 mm) or finer
(Smaller particles have faster kinetics, but are more challenging to remove)

GAC Adsorption

- ▶ **With GAC, adsorption occurs on the surface of the interior graphite platelets which are the solid part of the porous structure of the granules**
- ▶ **Adsorption is an equilibrium process and capacity is concentration dependent**
- ▶ **Exhausted GAC can often be sent to a reactivation furnace to destroy the adsorbates and produce a reusable product – air emissions?**

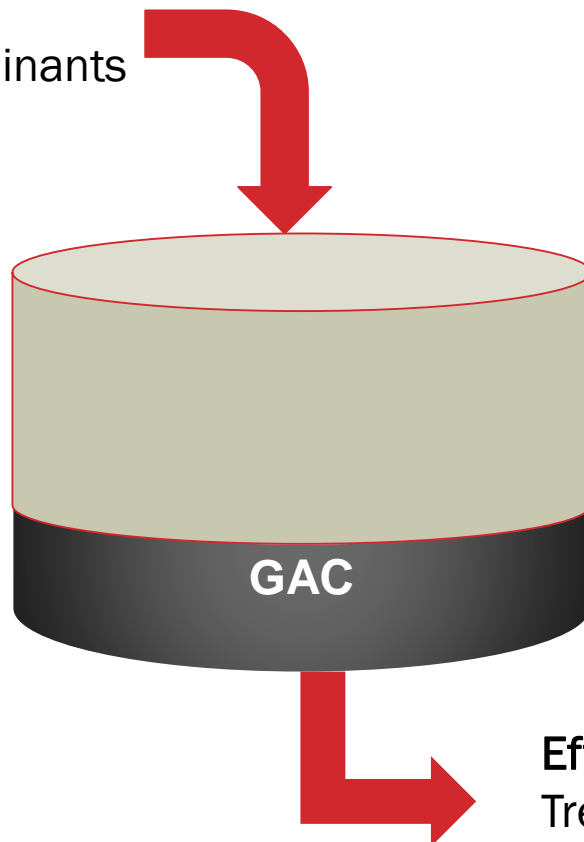


Activated Carbon

▶ Granular Activated Carbon (GAC) Well Demonstrated

- Bituminous GAC – increasing full scale installations
- Competing Organics fill absorption sites
- Needs high quality leachate treatment before GAC

Influent
Bulk solution + Contaminants



Effluent
Treated Solution

General Comments:

Typically operate downflow

Typically Empty Bed Contact Time (EBCT) is in **minutes**

Typical Superficial Velocities:
2-5 gpm/ft²

Isotherm testing initially done for feasibility

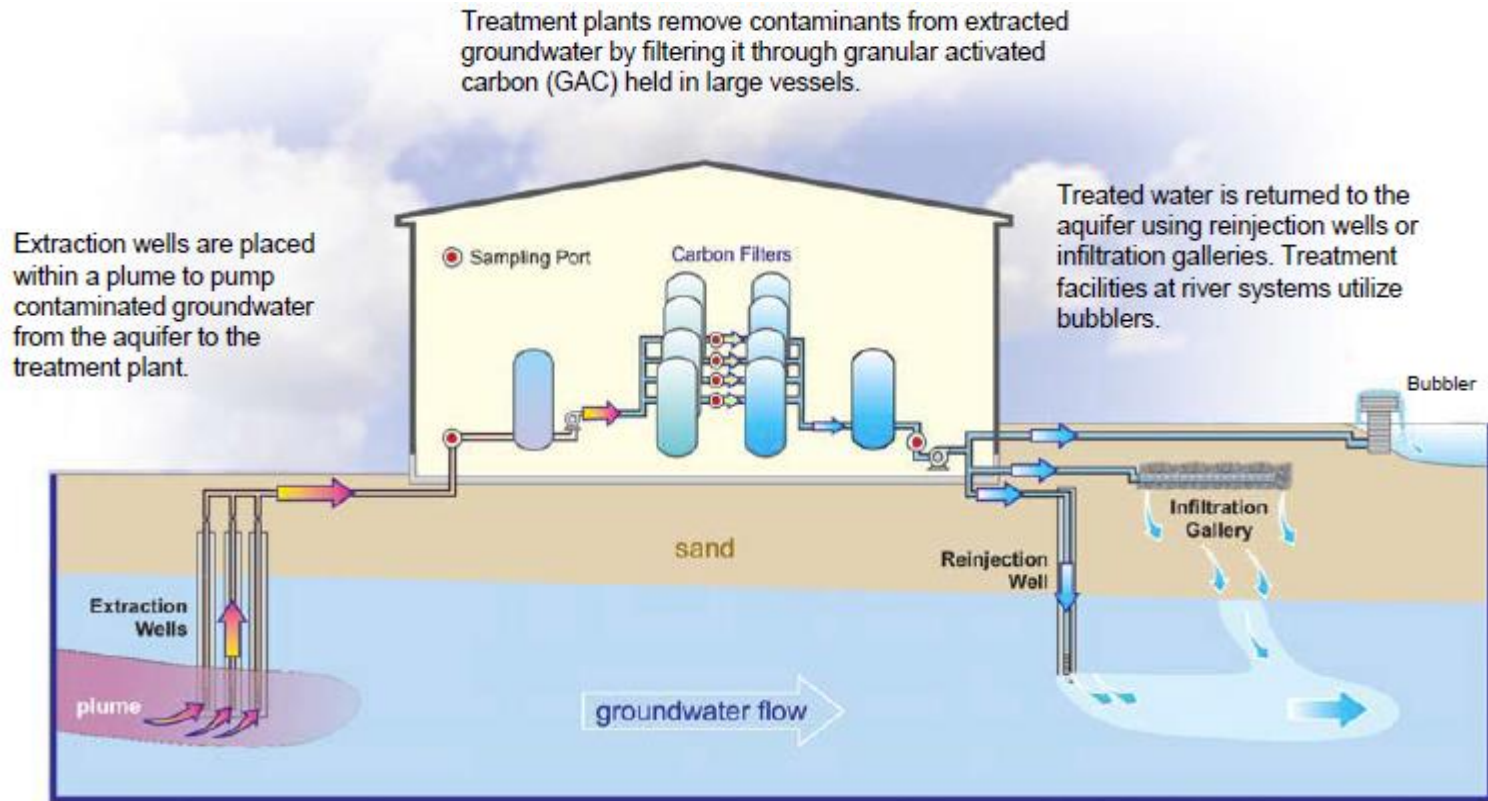
Accelerated Column Test (ACT)/Rapid Small Scale Column Test (RSSCT) or pilot performed to validate system design

Some usage rates/performance can be computer modeled in water

GAC can be reactivated once it has been used

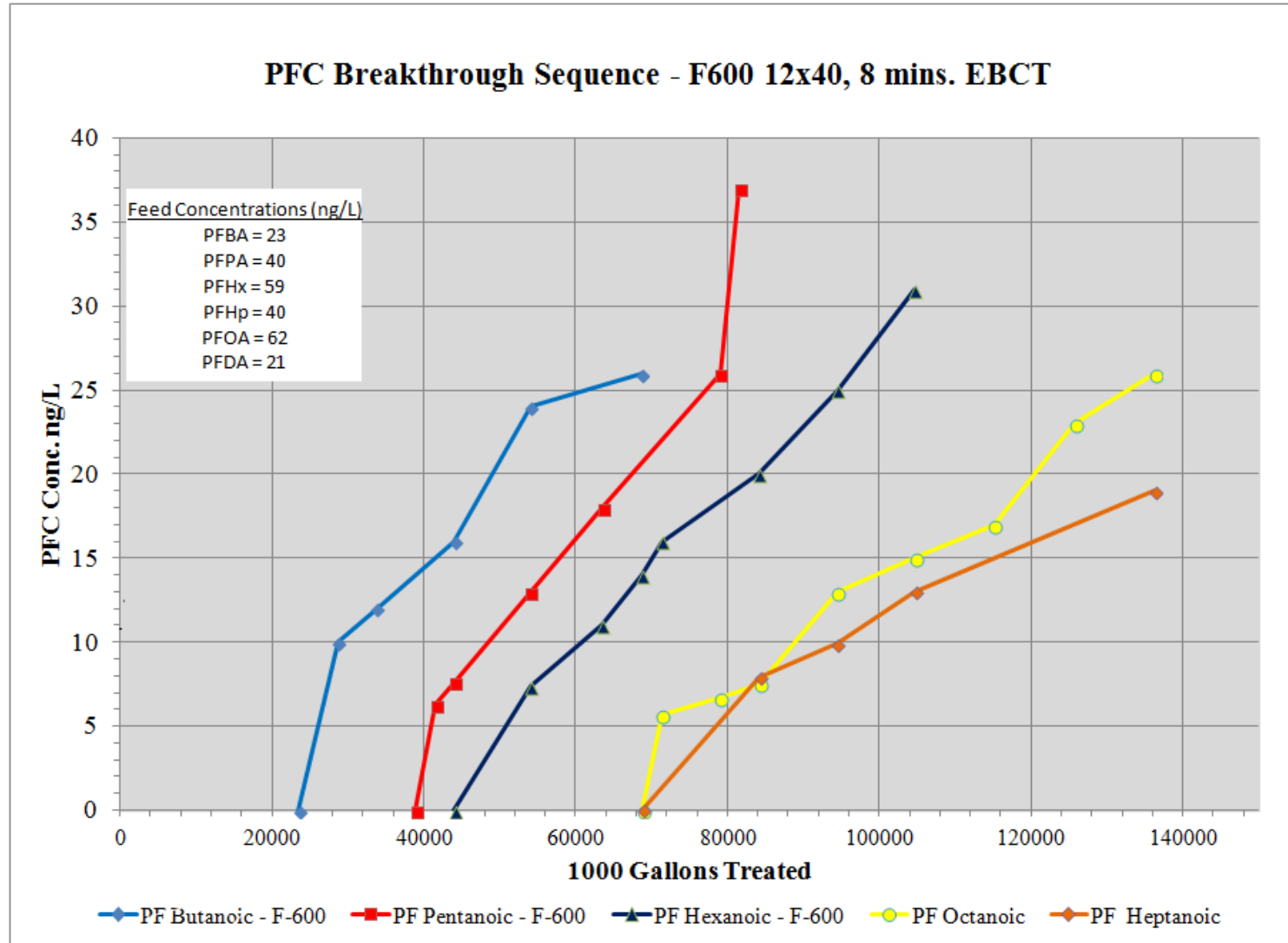
GAC Perfluorinated Compound Adsorption

- ▶ GAC has been in use at Minnesota sites for groundwater treatment for many years in this service
- ▶ Spent GAC can be successfully reactivated from this service for a minimum of waste generation
- ▶ As is typical of GAC adsorption, smaller and lower formula weight compounds tend to adsorb less strongly than larger, heavier compounds with similar structures.



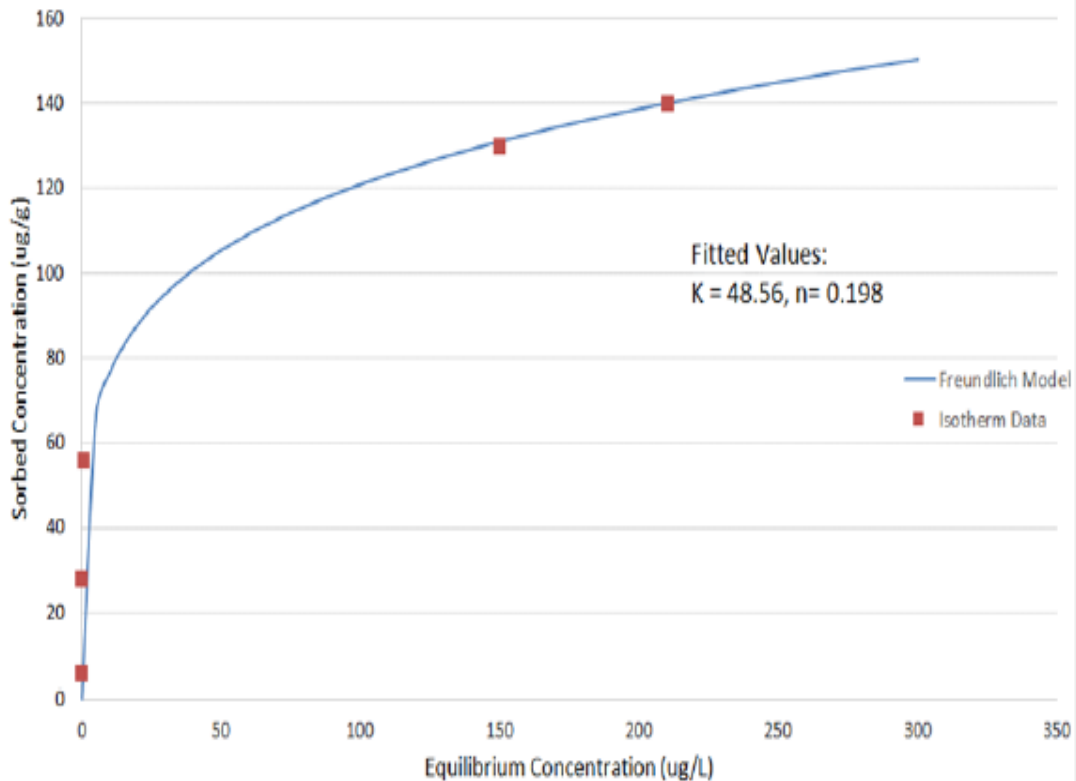
Courtesy USAF – Jt. Base Cape Cod

GAC Perfluorinated Compound Relative Activated Carbon Breakthrough Time versus PFAS congeners

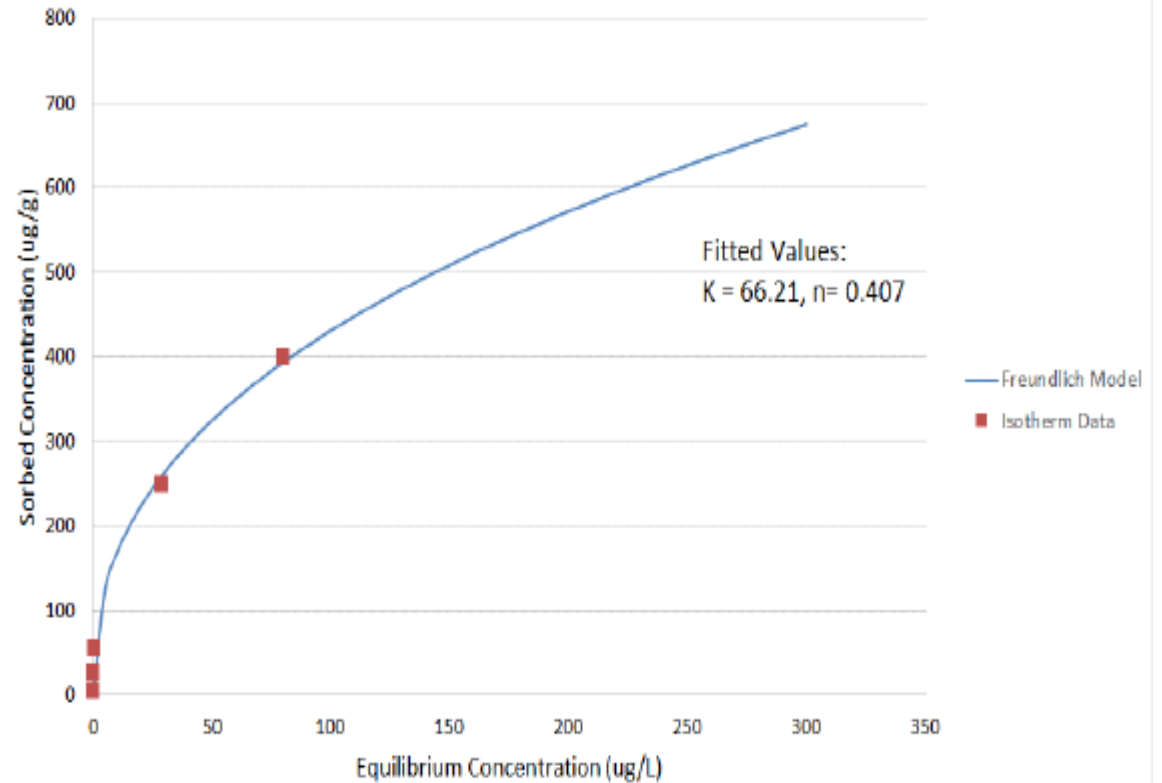


GAC PFAS Adsorption

Activated Carbon - PFOA Adsorption



Activated Carbon - PFOS Adsorption

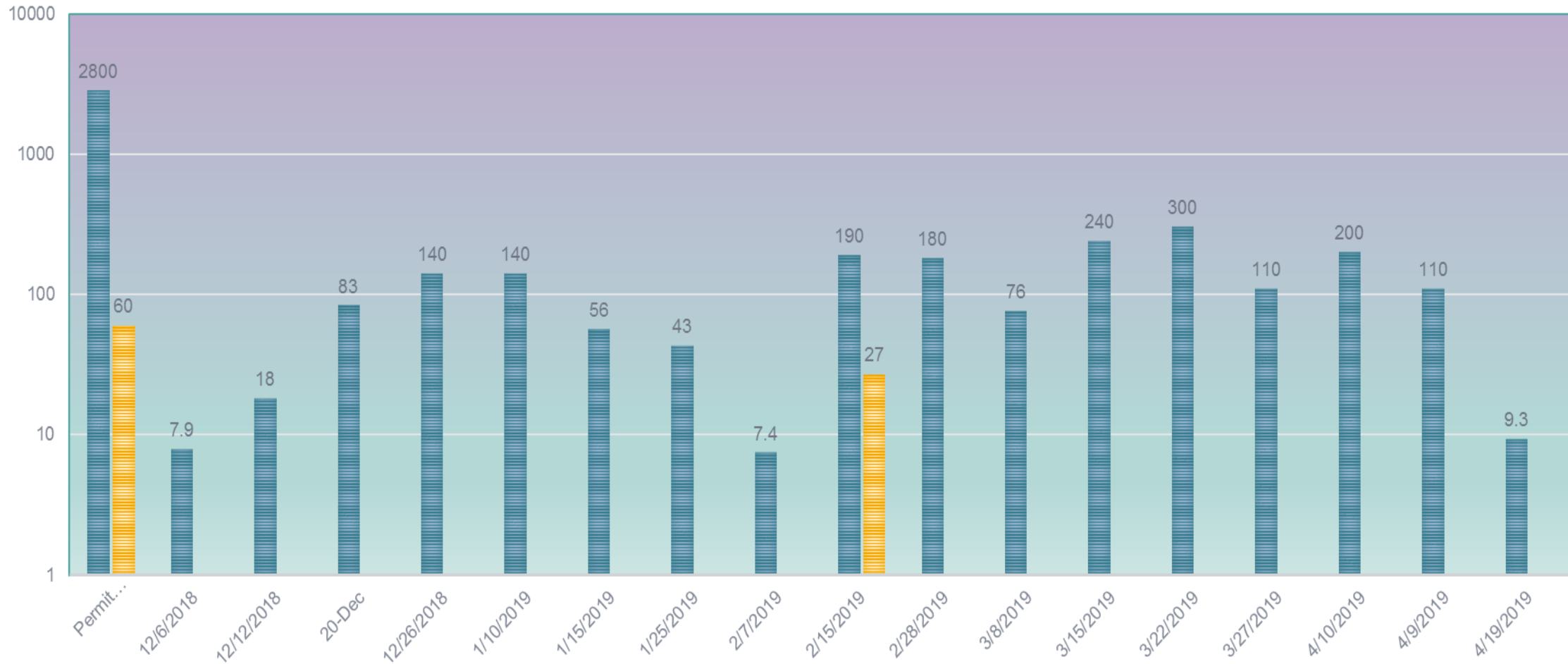


So absorption characteristics depend on type of PFAS!! – See vertical scale on both graphs.

GAC Actual Performance on Wastewater/Leachate

Leachate/Industrial Waste Pretreatment Effluent, PPT

■ PFOA ■ PFOS



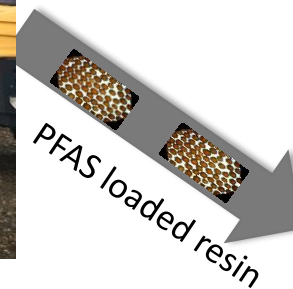
Note: Limited information on design, influent, operating conditions,

IX - Single-Use Selective Resin + Incineration

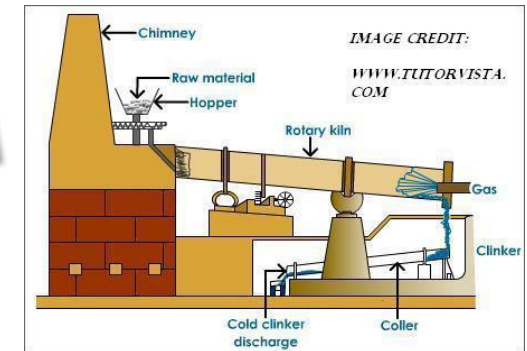
PFAS in water



PFAS-free water



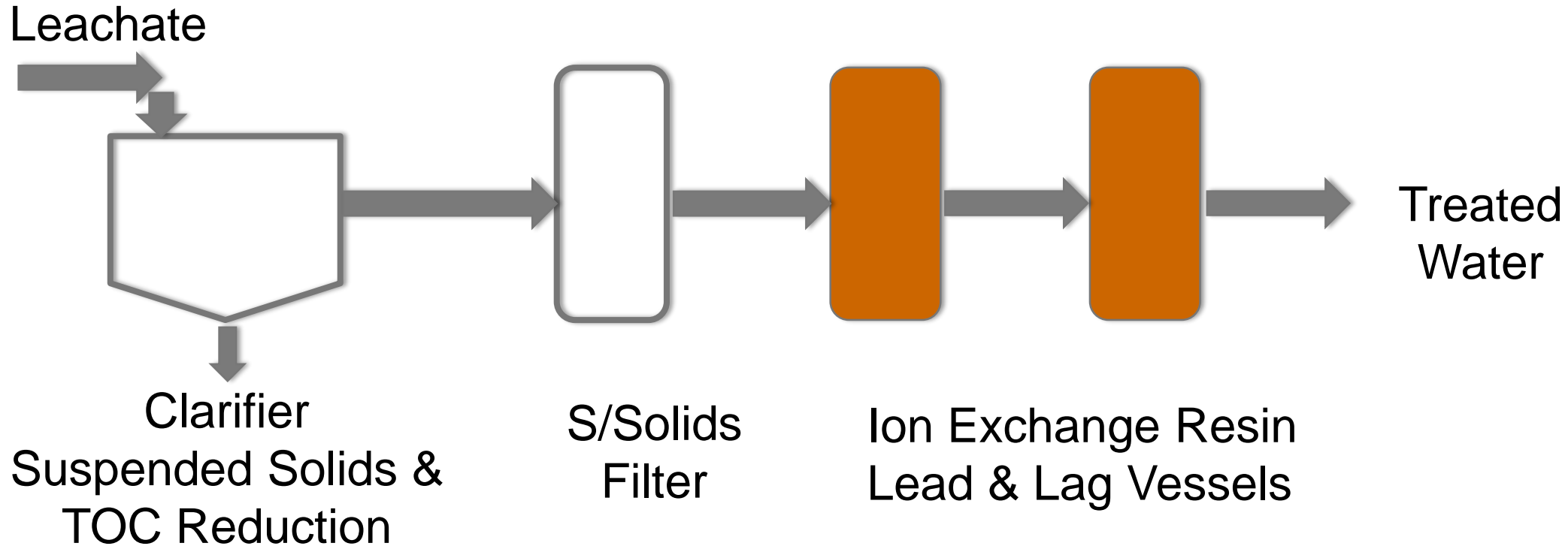
Cement Kiln Incineration
1400°C to 2000°C



Short Contact Time ~3 mins
Simple & Effective - Operator Preferred.

Complete Destruction of PFAS

General Process Flow Scheme Using Ion Exchange



Selective IX Capacity in leachate : Expect 10,000 to 20,000 BV

IX - Ion Adsorption

▶ Many competing constituents

- Constituent slows transport kinetics (speed that constituent adsorbs)
- Limits adsorption capacity (how much PFAS can be adsorbed)
- Background organics
- Anions (chlorides, sulfates)
- May be restricted to batch treatment given limitations

Must Consider Negative Impact of Leachate Chemistry on GAC & IX

Table 1 The chemical composition of leachate.

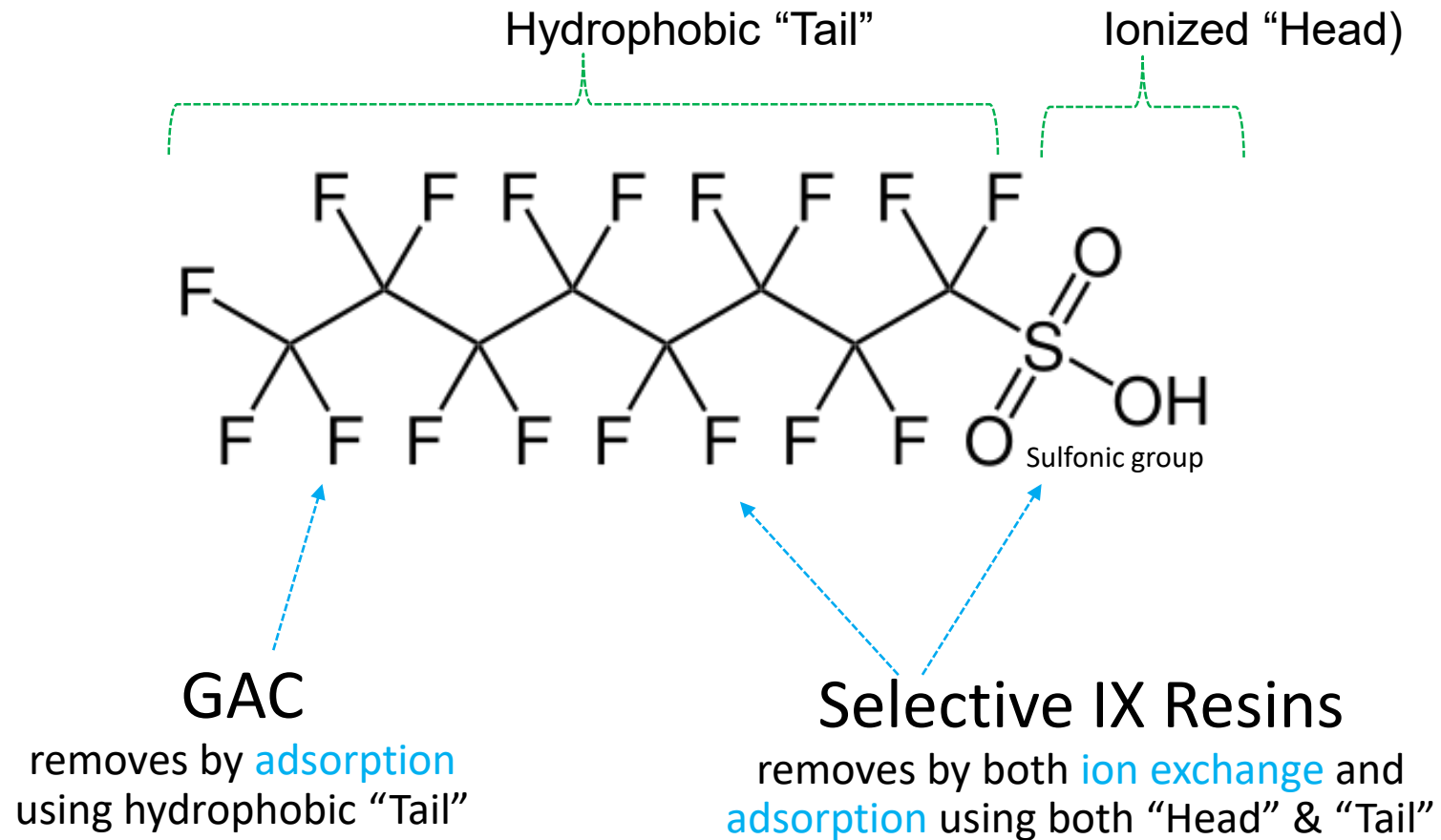
Parameter	Measured characteristic
BOD5	3400 PPM ←
COD	8250 PPM ←
pH	8.24
Turbidity	1400 NTU ←
TS	29942 PPM ←
TDS	26612 PPM ←
Conductivity	59400 ←
SO ₄	34712 PPM ←
Cl ⁻	6365 PPM ←
P ₂ O ₅	1308 PPM ←
NO ₃	3.95 PPM
NH ₄	3745 PPM

Some constituents interfere more than others!!

Ref. Raghab,Safaa, Treatment of Municipal Solid Waste Landfill HBRC Journal 2013 Vol 9 187-192

Superior Dual Removal Mechanisms for IX vs GAC

PFOS – Perfluoroalkyl Sulfonic Acid



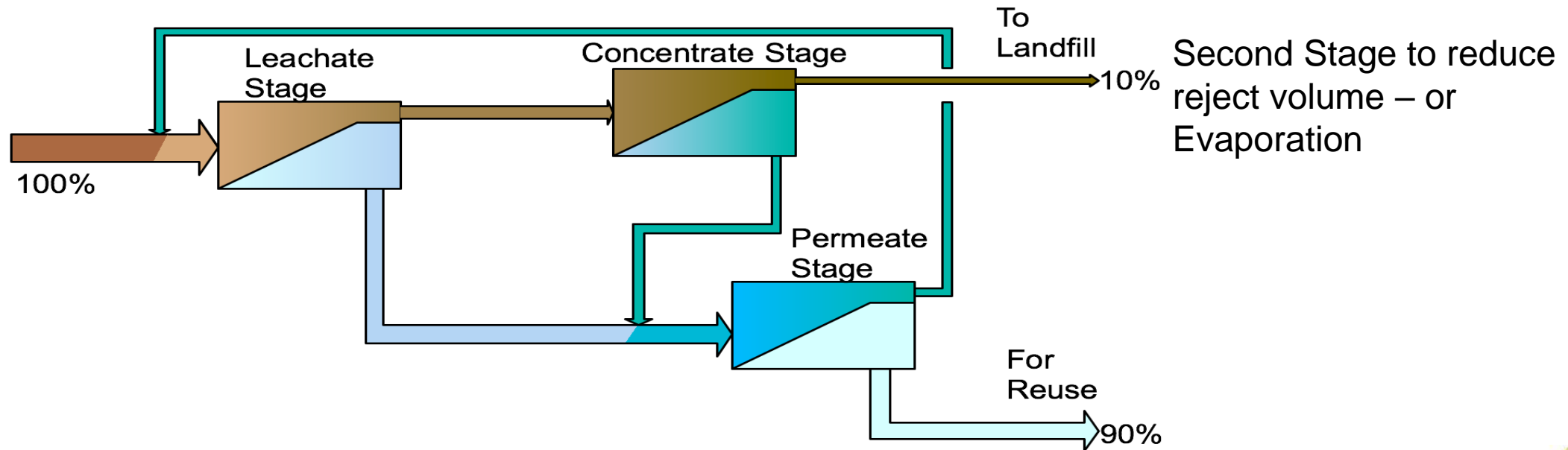
Reverse Osmosis

- ▶ Should work effectively
- ▶ Membrane Based Separation Process.
- ▶ Separates Water from Organic and Inorganic Compounds.
- ▶ Effluent for reuse or disposal.
- ▶ What to do with Reject???
- ▶ If recirculation is allowed, returns the contaminants to the landfill where they were originally deposited.
- ▶ Solidification – Lime, others?
- ▶ Evaporation – Crystallization
 - Heat needed
 - Air Emissions



Reverse Osmosis

- ▶ Membrane Based Separation Process.
- ▶ Separates Water from Organic and Inorganic Compounds.
- ▶ If recirculation is allowed, returns the contaminants to the landfill where they were originally deposited.
- ▶ Effluent for reuse or disposal.



Reverse Osmosis - PFAS Expected Removal from Leachate (µg/l concentrations) - Additional Information

Compound (ng/l)	Leachate	RO 1 Permeate	RO 2 Permeate	Rejection
Perfluorobutanesulfonic acid (PFBS)	280	<2	<1.9	>99.3%
Perfluorobutanoic acid (PFBA)	1100	5	<1.9	>99.8%
Perfluoroheptanoic acid (PFHpA)	480	<2	<1.9	>99.6%
Perfluorohexanesulfonic acid (PFHxS)	690	<2	<1.9	>99.7%
Perfluorohexanoic acid (PFHxA)	2100	7.8	<1.9	>99.9%
Perfluorooctanesulfonic acid (PFOS)	200	<2	<1.9	>99.1%
Perfluorooctanoic acid (PFOA)	820	2.5	<1.9	>99.8%
Perfluoropentanoic acid (PFPeA)	880	2.7	<1.9	>99.8%
Total	6550	18	0	>99.9%

Source, Rochem 2018

Treatment Technology Status

Field Implemented	Limited Application	Developing
<ul style="list-style-type: none">• Full Scale Operation• Multiple Sites• Multiple Designers• Well Document by Peers	<ul style="list-style-type: none">• Limited Sites• Limited Number of Designers• No Peer Review Literature	<ul style="list-style-type: none">• Laboratory research• Bench Scale Studies• No Field Demonstrations

Limited Application and Developing Technologies

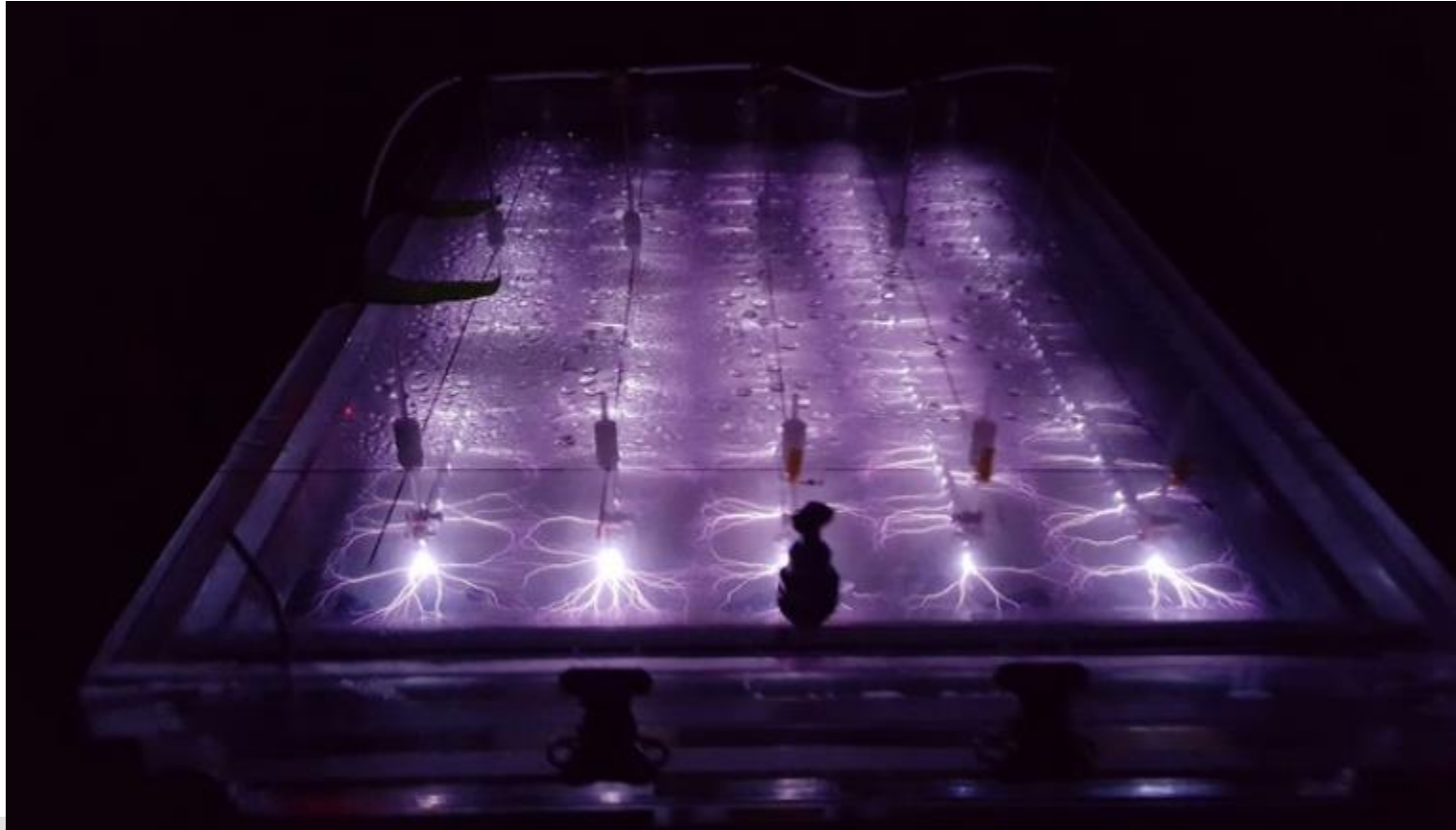
Developing Technologies

- PerfluorAd (Cornelsen) – Liquid PerfluorAd changes solubility of PFAS for adsorption and removal
- Chemical Oxidation
 - Ozone
 - Perozone
 - Heat-Activated Persulfate
 - Cavitation Oxidation
 - Hydrated Ion (ARC)
- Thermal Decomposition
- Solvated Electron Reduction
- Electron Beam
- Absorbents – Protein-Based – Waste Oil based (Flinders Univ – Australia) or Polymer Based, Cationic Hydrophobic
- Boron Doped Diamond Electro-Oxidation- MSU
- Nanoporous Nets - metal organic frameworks or MOFs

Limited Application Technologies

- Electrochemical Oxidation
Converted into PFAAs during bio or chemical oxidation processes?
- Electrochemical + Membrane Concentration or Bio
- Deep Well Injection
- Plasma (several in Australia)
- Advance Oxidation (AOP)
- Zero Valent Iron (ZVI) reduction + Bio Treatment
- Chemical Oxidation + Bio Treatment
- Non-Thermal Plasma
- Hydrothermal
- ScisoR® – Smart Combined In-situ oxidation and reduction
- PRB – Funnel & Gate + Additional treatment

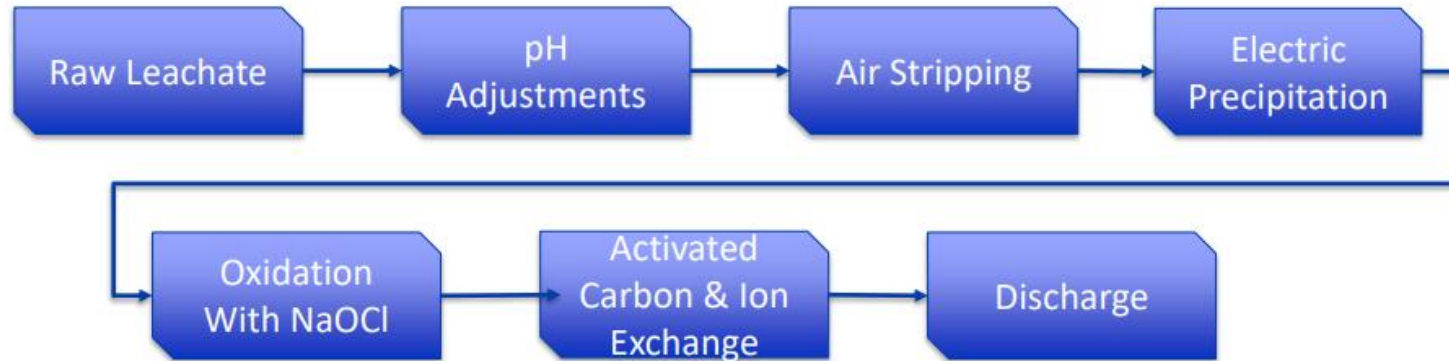
Enhanced Contact Plasma Reactor



A plasma reactor is demonstrated at Wright-Patterson Air Force Base, Ohio, Sept. 25, 2019 to degrade and destroy perfluorooctane sulfonate and perfluorooctanoic acid, better known as PFOS and PFOA, in sample groundwater. The test was the first field demonstration of the Enhanced Contact Plasma Reactor, conducted under an Air Force Civil Engineer Center contract with primary contractor, Clarkson University and teaming partner, GSI Environmental. (U.S. Air Force courtesy photo by Clarkson University)

Electro Coagulation – HTX Technology as a service

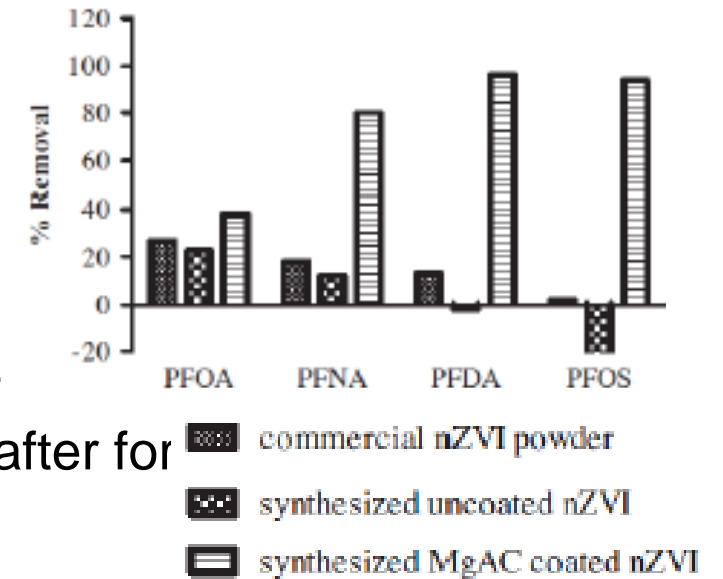
Electro-Coagulation Demonstration



Ref. Michael Cook, Burns & McDonnell,
RAM/SWANA Conf Oct 2018

Other Innovative Technologies

- ▶ **Various studies of advanced oxidation / reduction: all on bench scale**
 - Ozone, perozone, heat-activated persulfate, cavitation oxidation, non-thermal plasma, electrochemical oxidation, solvated electron reduction, zero valent iron (ZVI) reduction
- ▶ **Advanced Reduction Processes (ARP)**
 - Catalytic generation of reductants using sulfite
- ▶ **Electro-Oxidation –**
 - Reported 96 - 99% removal for Perfluorooctanoic acid (PFOA), Per sulfonate (PFOS), Perfluorononanoic acid (PFNA) - RO before or after for polishing?
- ▶ **Plasma – Limited sites - application in Australia**
- ▶ **Most Have Limited Bench-Scale Evaluations**

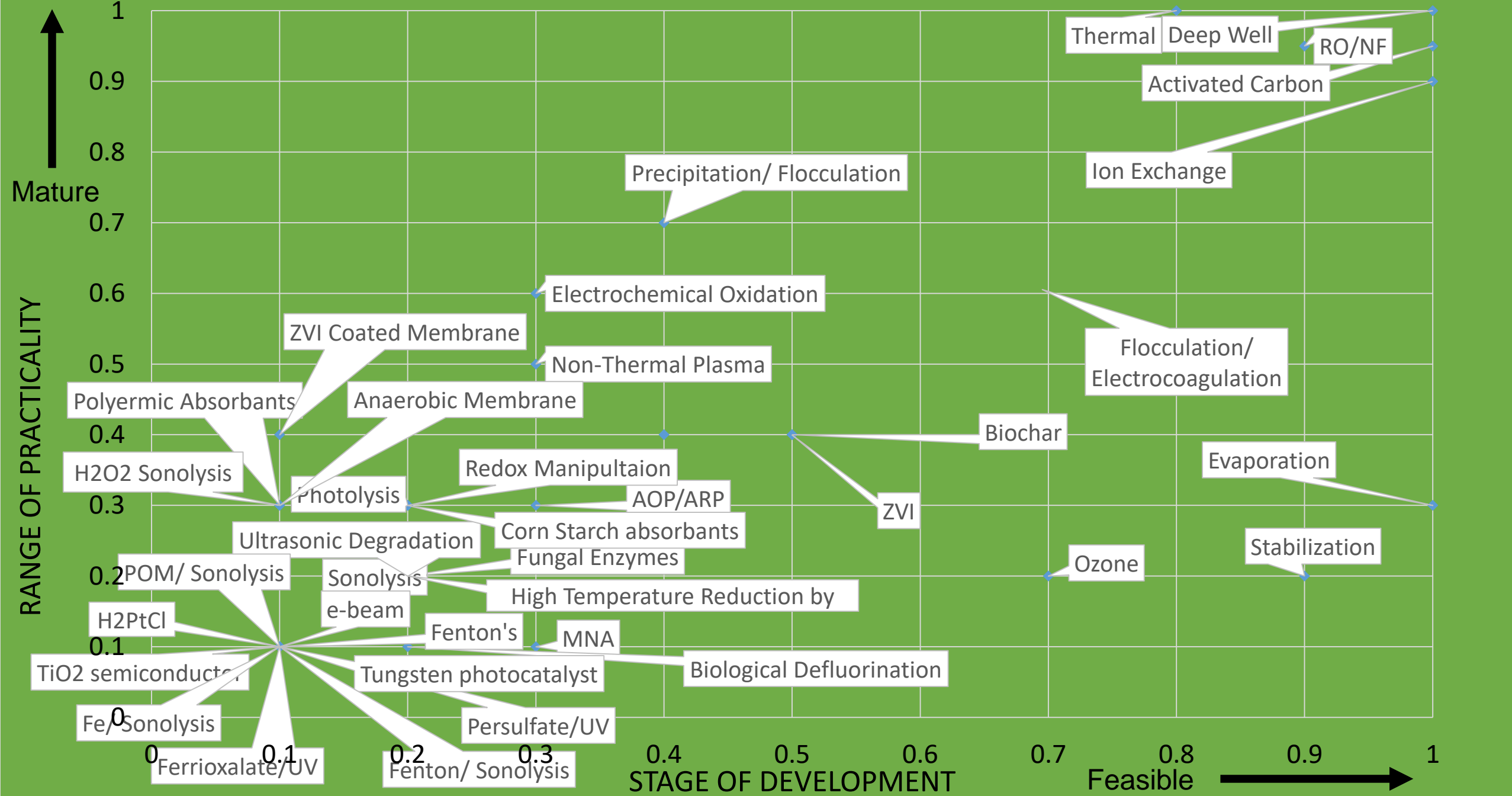


Summary of Water Treatment Options for Various PFAS Compounds

Compound	Acronym	Molecular Weight (g/mole)	Aeration	Coagulation Dissolved Air Flootation	Coagulation Flocculation Sedimentation Filtration	Conventional Oxidation (MnO ₂ , O ₃ , ClO ₂ , CLM, UV-AOP)	Anion Exchange (Select Resins Tested)	Granular Activated Carbon	Nano Filtration	Reverse Osmosis
Perfluorobutanesulfonic Acid	PFBS	300								
Perfluoroheptanoic Acid	PFHpA	364								
Perfluorohexanesulfonic Acid	PFHxS	400								
Perfluorooctanoic Acid	PFOA	414								
Perfluorononanoic Acid	PFNA	464		unknown			assumed	assumed		
Perfluorooctane Sulfonate	PFOS	500								
<i>Table modified from E. Dickenson and C. Higgins 2016</i>										
		> 90% removal			>10%, < 90% removal					< 10% removal

E. Dickenson and C. Higgins, "Treatment Mitigation Strategies for Poly- and Perfluoroalkyl Substances," Water Research Foundation, 2016.

DEVELOPMENT AND PRACTICALITY OF TREATMENT TECHNOLOGIES



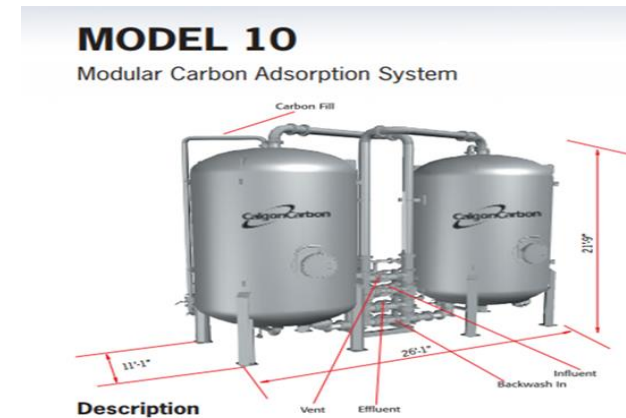
Treatment Technologies – Pretreatment?

Contaminant	Biological Treatment	Activated Carbon ¹	Ion Exchange ₁	Reverse Osmosis ²	Electro Oxidation	AOP	ARC
COD/Ammonia	Yes	Possible	Possible	Possible – Reject	Yes	Possible	Possible
I,4 Dioxane	Possible	OK	OK	OK – Reject	OK	OK	OK
DON and rDON	Possible	OK	Possible	OK – Reject	Possible	Possible	Possible
PPCP	Possible	OK	OK	OK – Reject	OK	OK	OK
Nanoparticles /Microplastics	No	No	No	Yes – Reject	No	No	No
UV Absorbing	No	Possible	No	Yes <500 nm, Reject	Possible	No	Possible
PFAS	No	OK	OK	OK – Reject	Possible	Possible	OK

1. Residuals from spent activated carbon or ion exchange requires replacement and disposal
2. RO reject flow requires management by concentration, evaporation, solidification, deep well injection, or other means.

Thank You !!!

- ▶ Ivan A. Cooper, PE, BCEE
- ▶ Civil and Environmental Consultants, Inc.
- ▶ icooper@cecinc.com
- ▶ Direct: (980) 260-2110
- ▶ Mobile: (980) 238-0373



The Impact of PFOAs in Landfill Leachate on POTWs in Michigan

Richard Burns

*Senior Vice President
NTH Consultants, Ltd.*



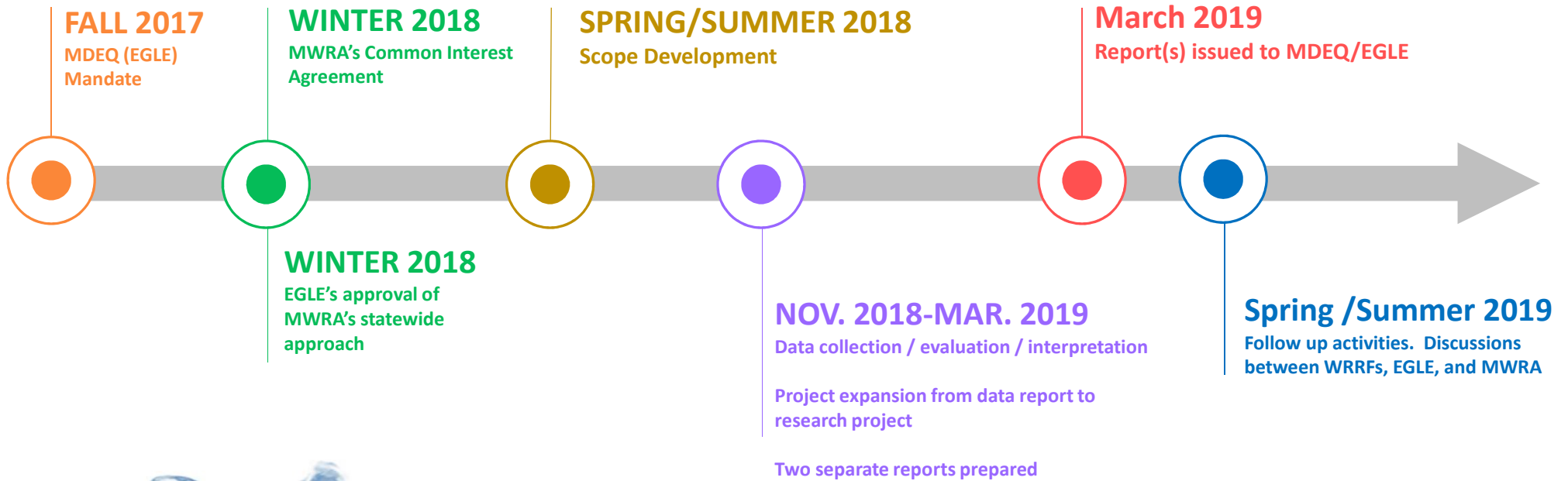
Environmental Business Council of New England
Energy Environment Economy



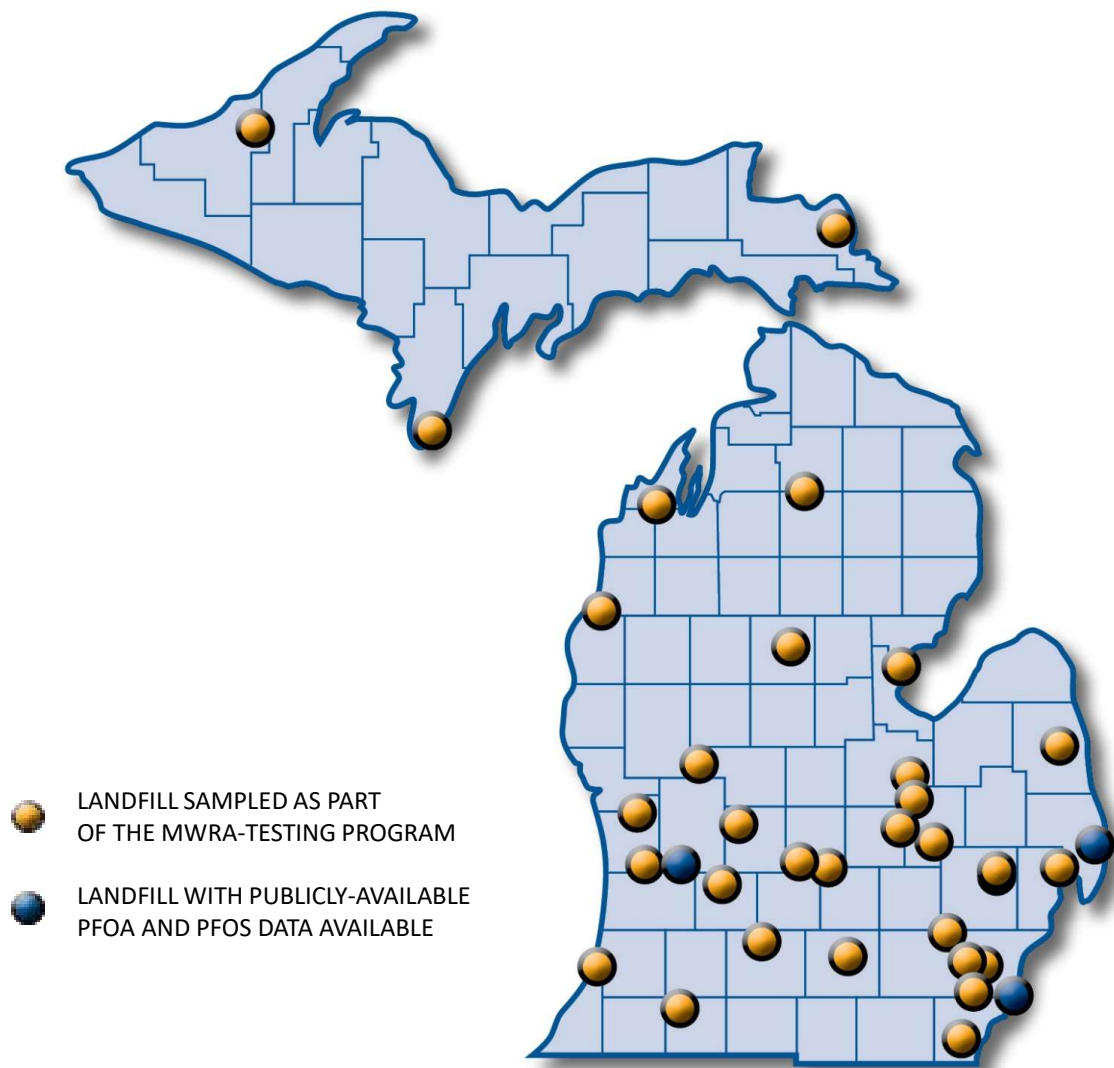
Michigan Landfill Leachate PFAS Impact on WWTP Influent



Project Timeline (Fall 2017 to Summer 2019)



Solid Waste Disposal Facilities Included



- Advanced Disposal Services Arbor Hills Landfill, Inc.
- Autumn Hills Recycling and Disposal Facility
- Brent Run Landfill
- C&C Expanded Sanitary Landfill
- C&C Expanded Sanitary Landfill
- Carleton Farms Landfill
- Central Sanitary Landfill, Inc.
- Citizens Disposal
- Dafter Sanitary Landfill
- Eagle Valley Recycle and Disposal Facility
- Glens Sanitary Landfill
- Granger Grand River Landfill
- Granger Grand River Landfill
- K&W Landfill
- Manistee County Landfill, Inc.
- Michigan Environs Inc.
- Northern Oaks
- Oakland Heights Development, Inc.
- Orchard Hill Sanitary Landfill
- Ottawa County Farms Landfill
- Peoples Landfill, Inc.
- Pine Tree Acres, Inc.
- Pitsch Sanitary Landfill
- Recycling and Disposal Facility
- Republic Services of Pinconning (Whitefeather)
- Riverview Land Preserve
- Sauk Trail Hills Landfill
- SC Holdings
- Smith's Creek Landfill
- South Kent Landfill
- Tri-City Recycling and Disposal Facility
- Venice Park Recycling and Disposal Facility
- Vienna Junction Industrial Park Sanitary Landfill
- Waters Landfill
- Westside Recycling and Disposal Facility
- Woodland Meadows RDF - Van Buren

Leachate Sampling and Laboratory Testing Program

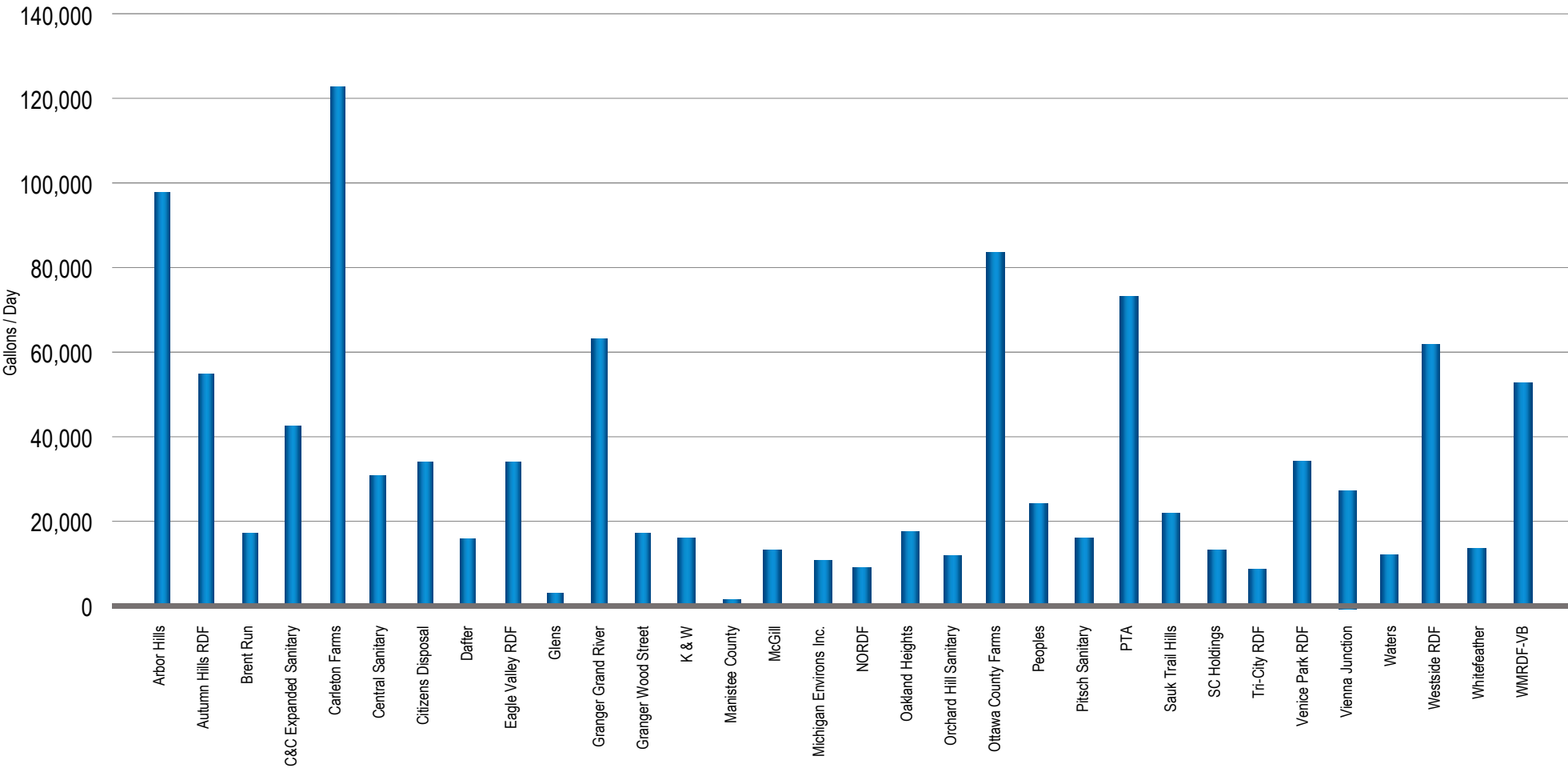


Sample Shipment – Sealed Cooler Prepared for Shipment

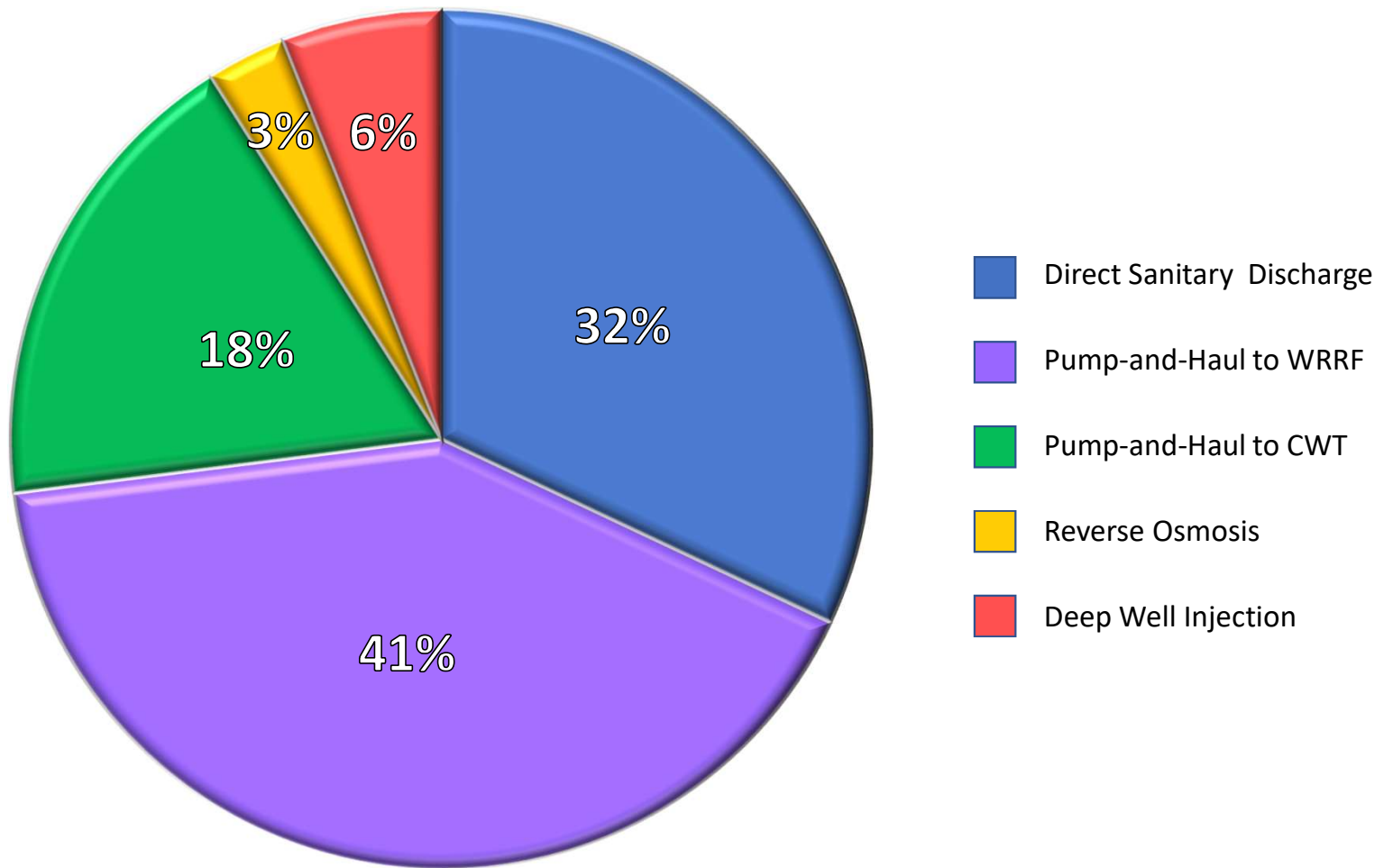
- Samples collected using MDEQ/EGLE draft PFAS protocol
- Test America-San Francisco completed analyses per Method 537 (modified)
- All results provided by mid-January 2019
- No statistical outliers present in data set



Leachate Volumes Per MWRA Landfill



Leachate Disposal Methods

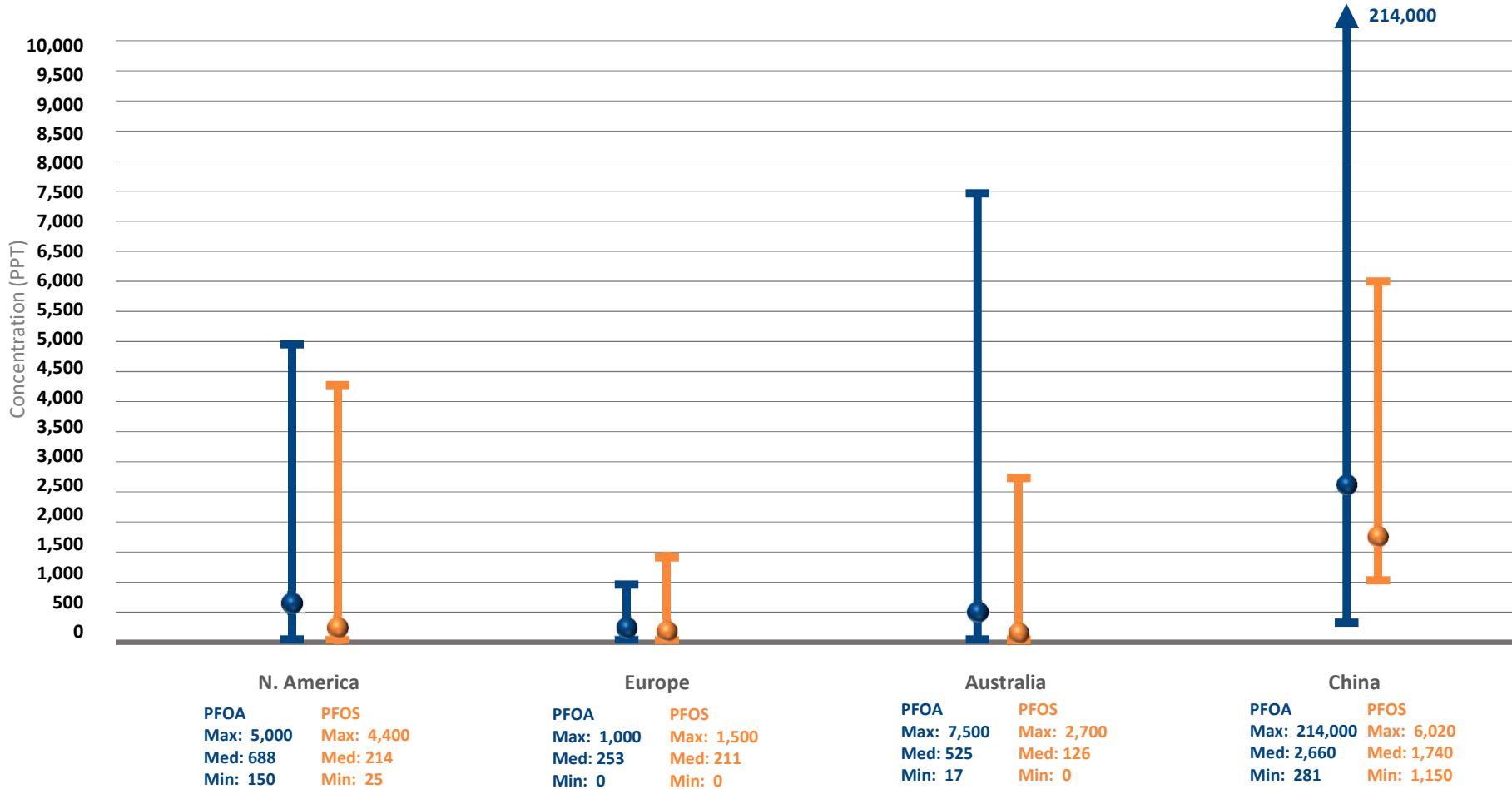


WATER RESOURCE RECOVERY FACILITY (WRRF) SUMMARY

Summary of WRRF PFOA/PFOS With Influent Data Evaluated in This Study			
WRRFs with PFOA/PFOS data that manage MWRA-member landfill leachate	Total WRRFs with PFOA/PFOS data that manage leachate from other active Type II Landfills	WRRFs with PFOA/PFOS data that do not manage Leachate from active Type II Landfills	Total WRRFs with PFOA/PFOS data included in this Study
11	7	16	34



WORLD-WIDE LEACHATE PFOA & PFOS CONCENTRATIONS



**STATEWIDE PFOA AND PFOS
MWRA TYPE II LANDFILL LEACHATE CONCENTRATIONS (abbreviated)**

MWRA Participating Landfill Designation	Average Leachate Volume GPD	PFOA (ppt)	PFOS (ppt)	"PFOA Daily Mass (lb/day)"	"PFOS Daily Mass (lb/day)"
Arbor Hills Landfill	98,400	3200	220	0.0026	0.00018
Autumn Hills RDF	54,800	1300	380	0.0006	0.00017
Brent Run Landfill	16,400	540	110	0.0001	0.00002
C&C Expanded Sanitary Landfill	42,000	1300	450	0.0004	0.00015
Carleton Farms Landfill	123,300	1800	250	0.0018	0.00026
Central Sanitary Landfill	30,100	2500	470	0.0006	0.00012
Citizen's Disposal Inc.	32,900	1100	180	0.0003	0.00005
Dafter Sanitary Landfill	16,500	680	130	0.0001	0.00002
Eagle Valley RDF	32,900	490	170	0.0001	0.00005
Glens Sanitary Landfill	3,800	770	210	0.00002	0.00001
Summary Statistics	minimum	16	9	0.000016	0.000007
	maximum	3200	960	0.003	0.0004
	median	1000	220	0.0001	0.00005
	average	1186	287	0.0004	0.0001
	n	39	39	33	33

Michigan Compared to Other Regions

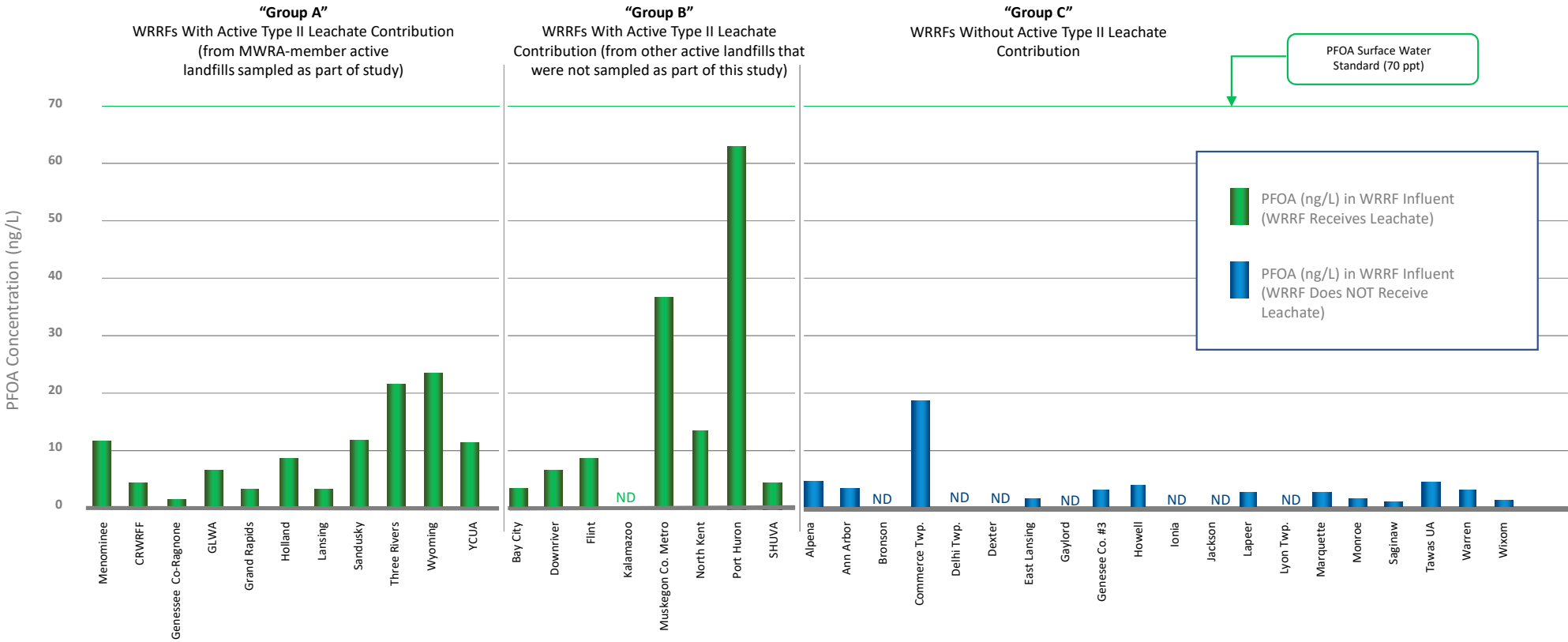
Region	PFOA (ppt)	PFOS (ppt)
Michigan	16 to 3,200	9 to 960
United States	30 to 5,000	3 to 800
Europe	ND to 1,000	ND to 1,500
Australia	17 to 7,500	13 to 2,700
China	281 to 214,000	1,150 to 6,020
Worldwide Range	ND to 214,000	ND to 6,020

Current EGLE/EPA PFOA & PFOS Criteria

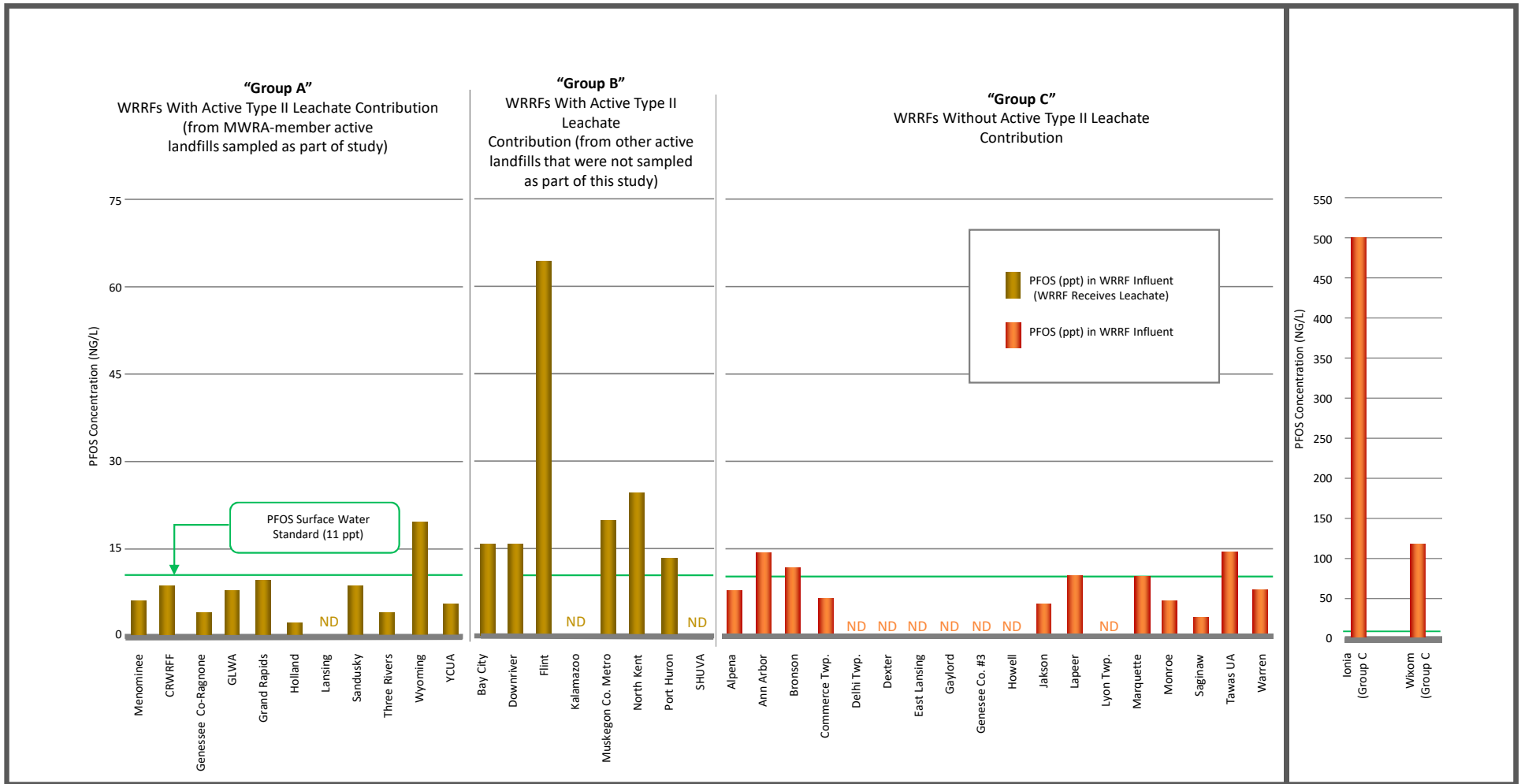
Chemicals	Human Non-Cancer Value (Non-Drinking Water)	Human Non-Cancer Value (Drinking Water)
PFOS	12 ppt	11 ppt
PFOA	12,000 ppt	420 ppt

Note: USEPA Health Advisory (HA) = 70 ppt (PFOA+PFOS)

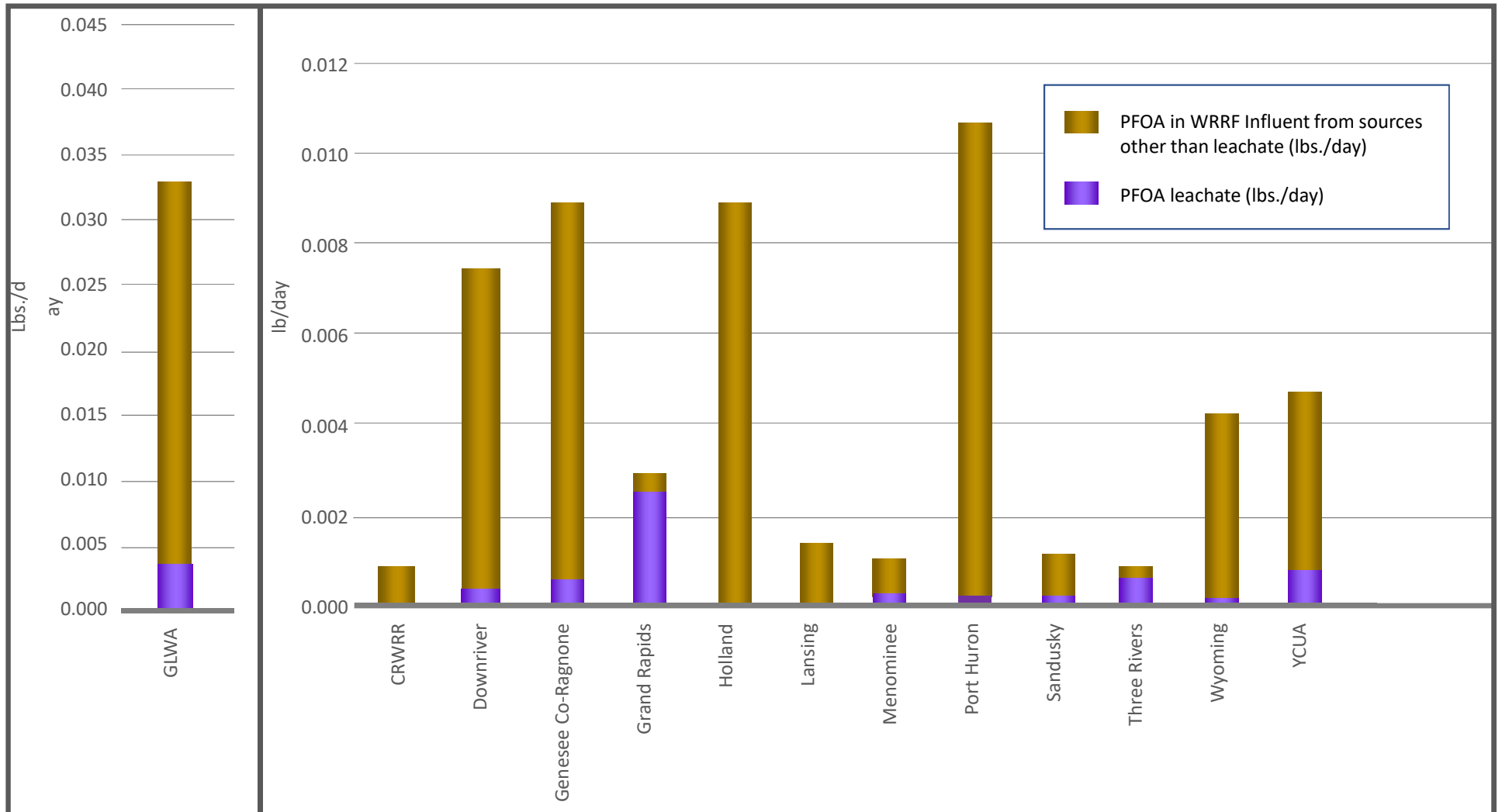
WRRF Overall Influent PFOA Concentrations



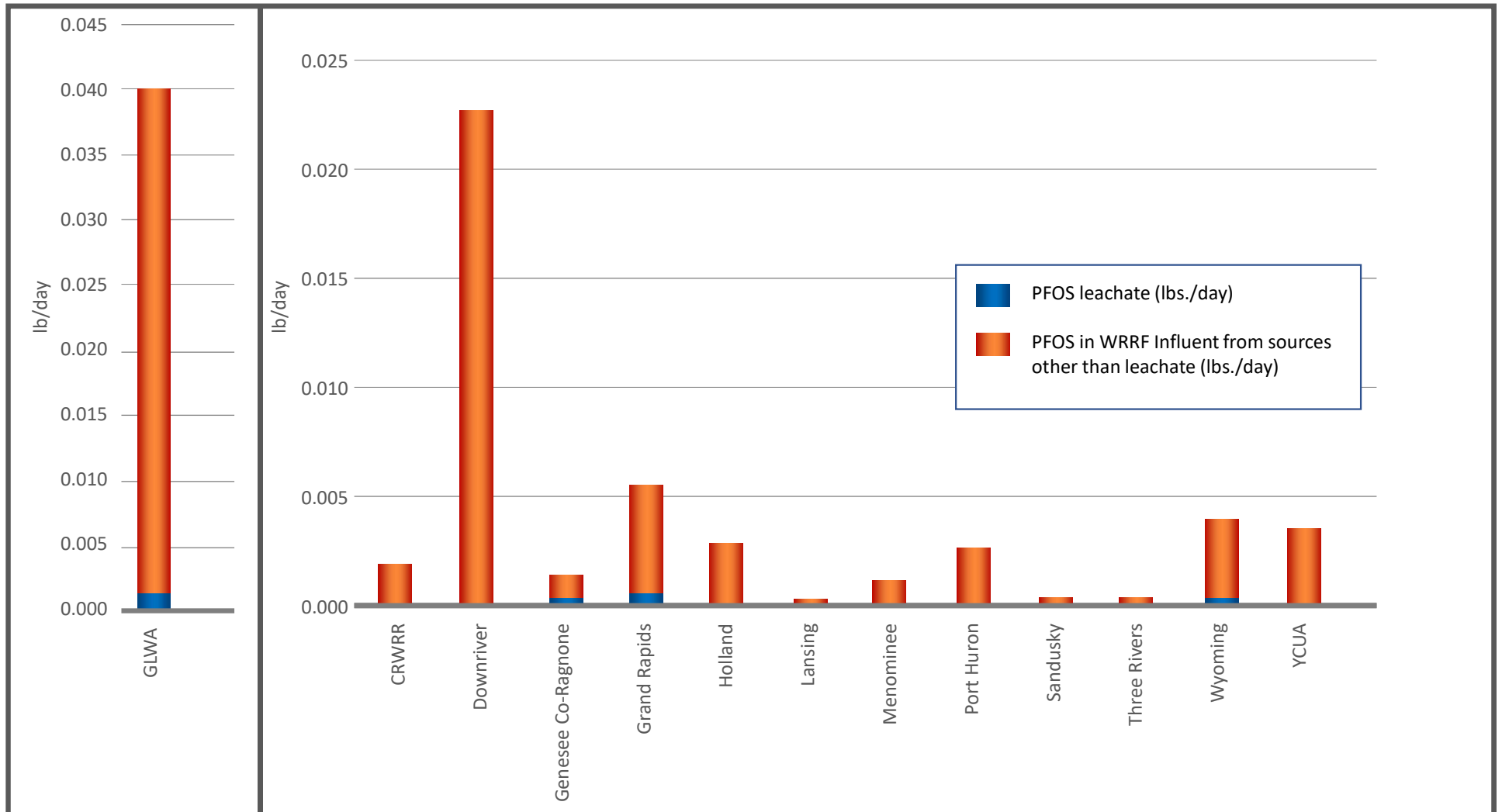
WRRF Overall Influent PFOS Concentrations



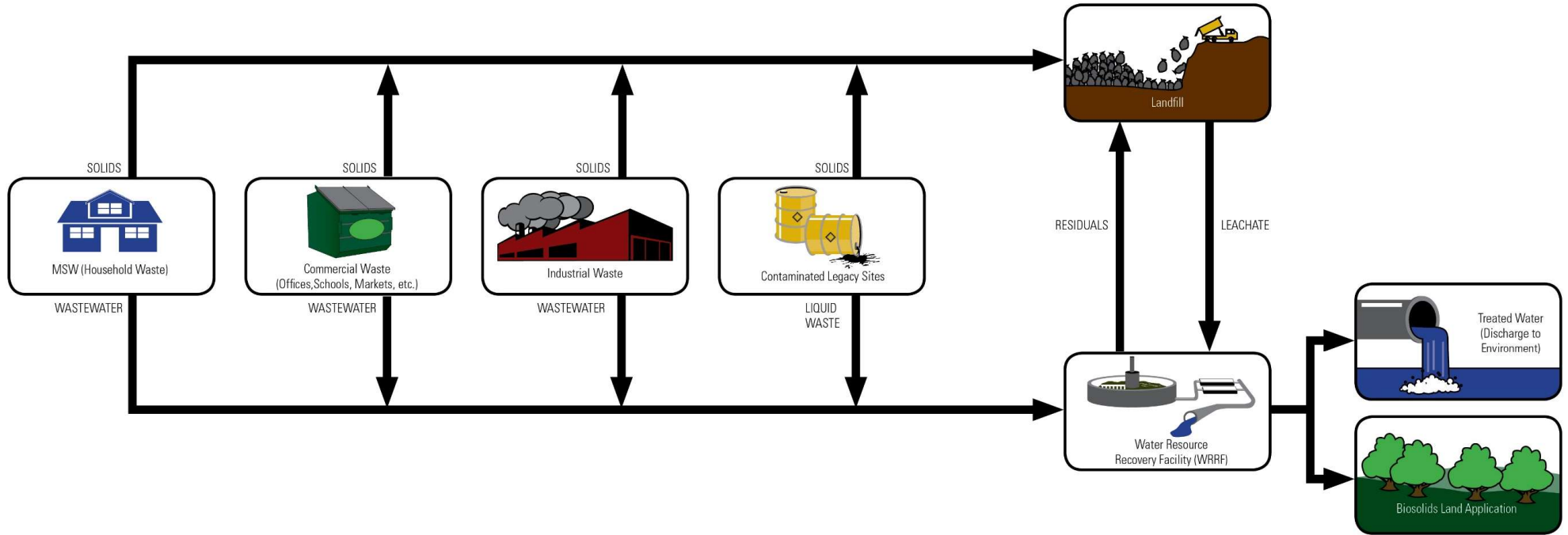
PFOA Mass: Influent Leachate vs. Overall WRRF Influent



PFOS Mass: Influent Leachate vs. Overall WRRF Influent



PFOA & PFOS "CYCLING" WITHIN THE "WASTE ECONOMY"



OVERALL SUMMARY

- **Unsurprisingly, PFOA and PFOS detected in all landfill leachate**
 - Varying concentrations
- **USA and Michigan landfill leachate PFOA and PFOS concentrations similar to other Western countries**
 - China leads all industrial nations.
- **Participating Michigan landfills discharge 1 MGD to WRRFs**
 - Contributing approximately 0.01 lbs./day PFOA and 0.003 lbs./day PFOS
- **WRRF influent approximately 1.4 BGD**
 - With ~ 0.09 lbs./day PFOA and 0.15 lbs./day PFOS



OVERALL SUMMARY (continued)

- **State-wide WRRF influent PFOA concentration were below EGLE's 420 ppt DW WQS**
- **Approximately two-thirds of WRRF influent PFOS concentrations were below EGLE's 11 ppt DW WQS**
- **Landfill leachate appears a relatively minor source of PFOA & PFOS to WRRF influent statewide**
- **Total mass balance and fate-and-transport not fully-understood**
- **PFAS management is a societal problem**



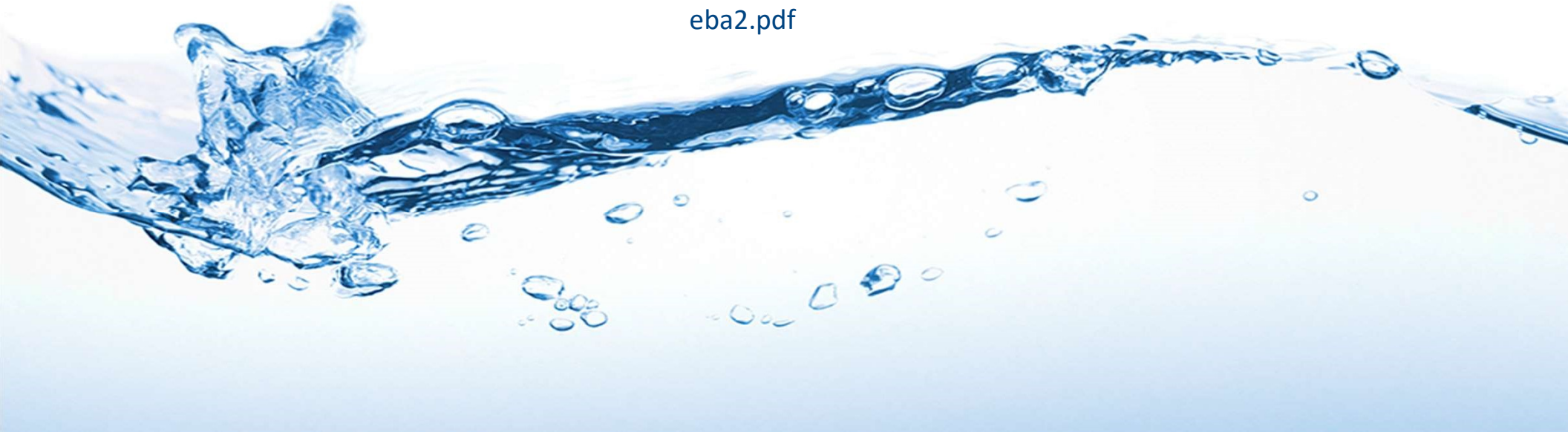
QUESTIONS?

Summary Report

https://docs.wixstatic.com/ugd/6f7f77_b3c62cab66454fea9a66ce6986887da7.pdf

Technical Report

https://docs.wixstatic.com/ugd/6f7f77_5be8751a1f754474ac6e27fc8247eba2.pdf



Removing the Handle from the PFAS Pump

Tiffany Skogstrom, MPH

Outreach & Policy Analyst

Massachusetts Office of Technical Assistance (OTA)

Executive Office of Energy & Environmental Affairs



Environmental Business Council of New England

Energy Environment Economy

REMOVING THE HANDLE



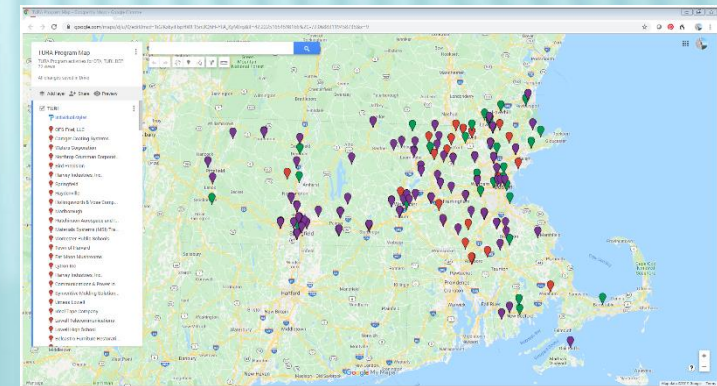
FROM THE PFAS PUMP

Tiffany Skogstrom, MPH
tiffany.skogstrom@mass.gov, 617-626-1086



OFFICE OF TECHNICAL ASSISTANCE (OTA)

- Non-regulatory agency within Executive Office of Energy and Environmental Affairs (EOEEA)
- Provides confidential onsite technical and compliance assistance to manufacturers, businesses, and institutions
- All OTA services are available free of charge to any Massachusetts toxics user
- Some statistics –
 - × More than 3,500 site visits to about 1,500 facilities
 - × Helped in reducing the use of millions of pounds of toxic chemicals, and saving companies millions of dollars in operating costs



TRACKING CHOLERA

NOTICE.

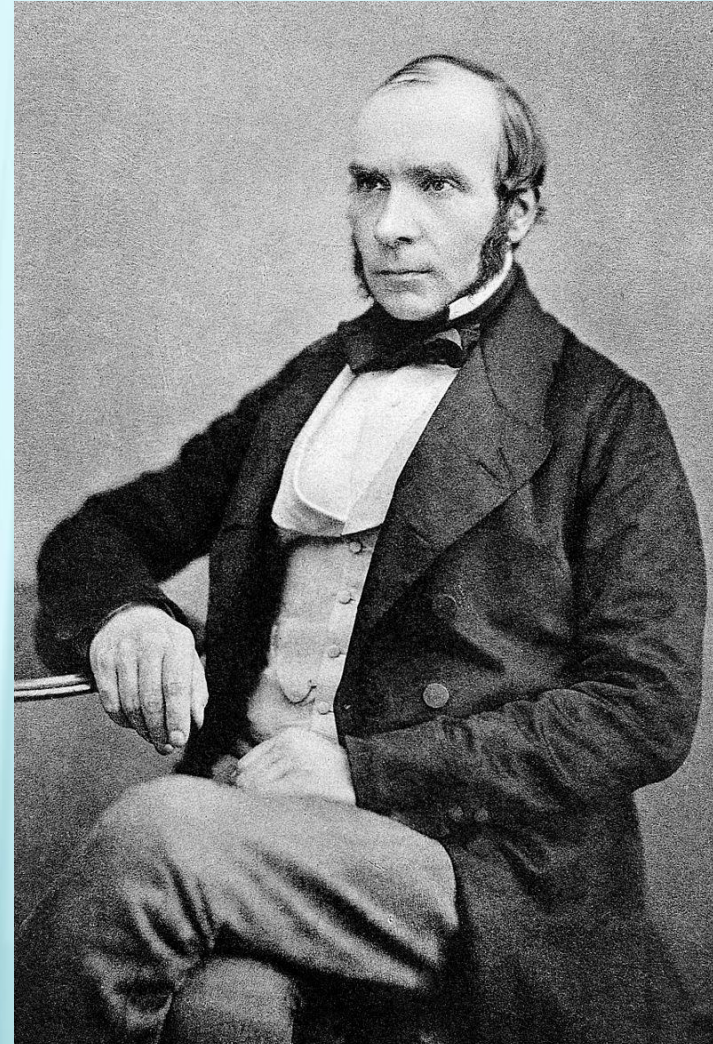
PREVENTIVES OF

CHOLERA!

Published by order of the Sanatory Committee, under the sanction of the Medical Council.

BE TEMPERATE IN EATING & DRINKING!
Avoid Raw Vegetables and Unripe Fruit!

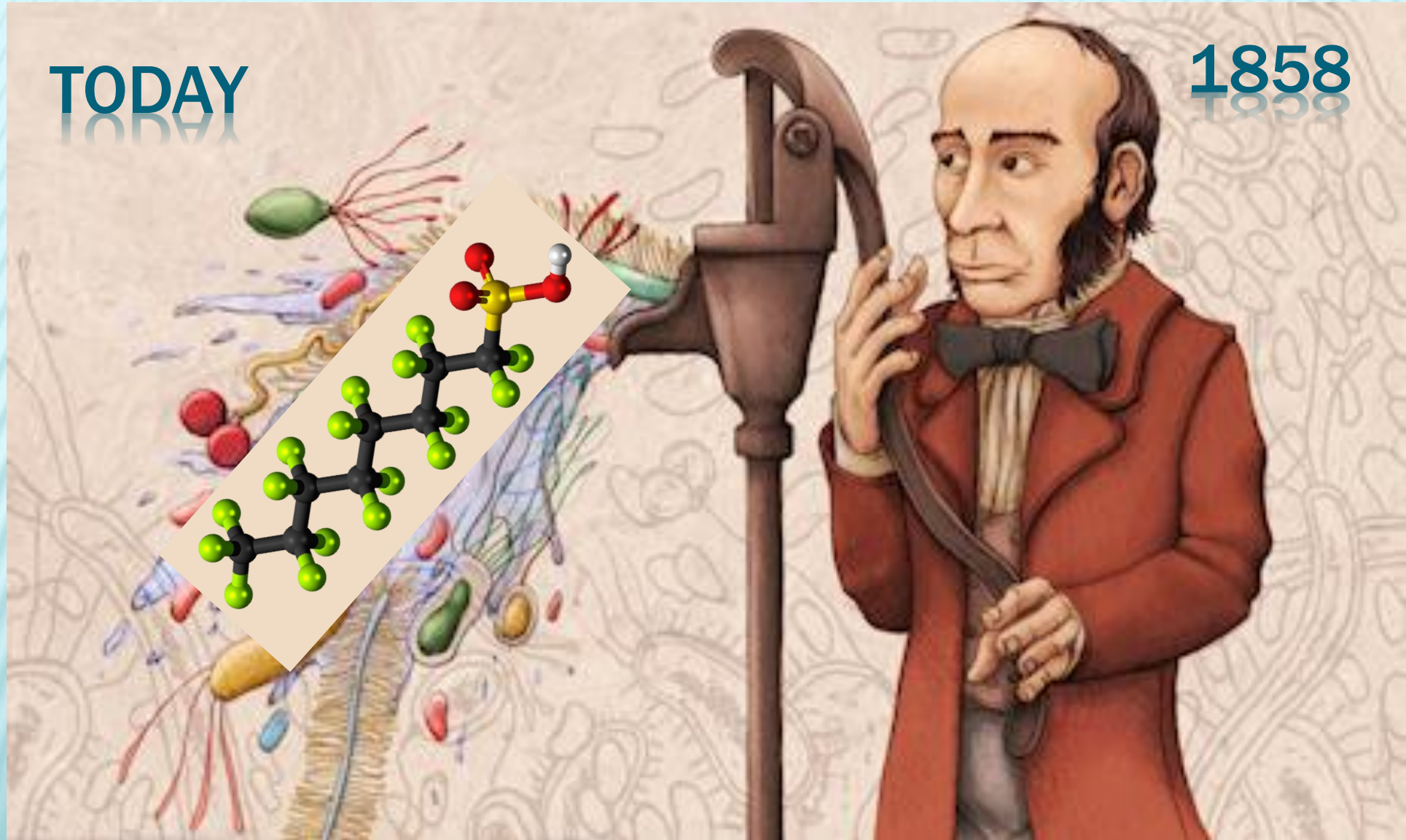
Abstain from **COLD WATER**, when heated, and above all from *Ardent Spirits*, and if habit have rendered them indispensable, take much less than usual.

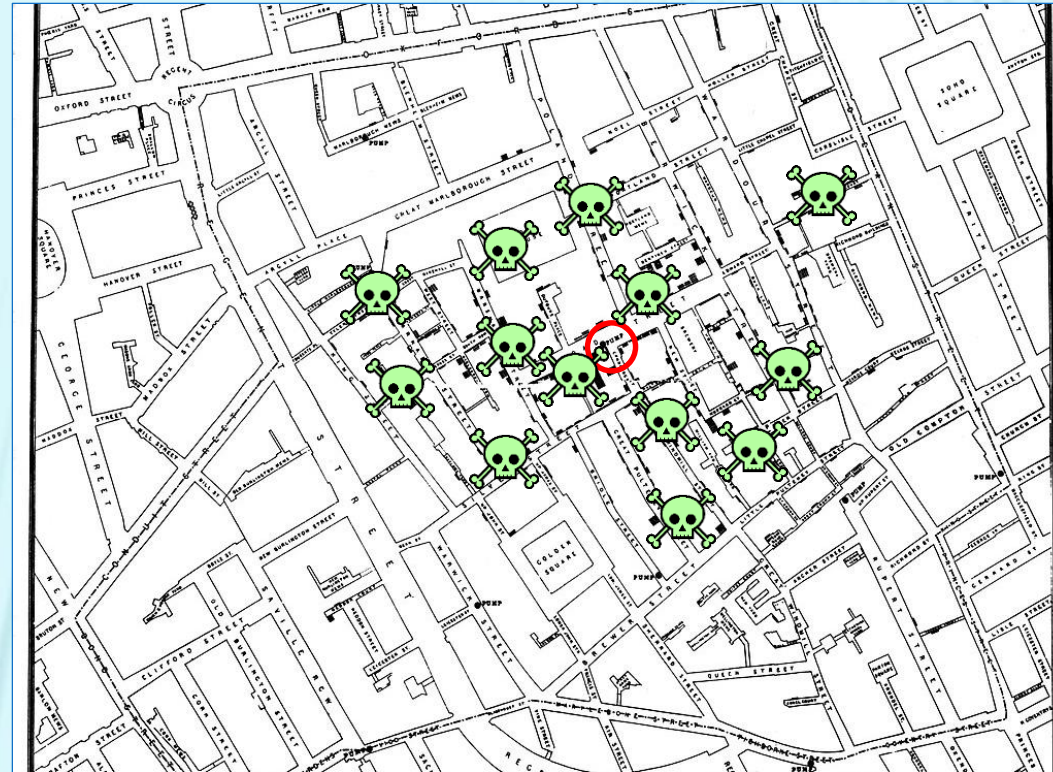
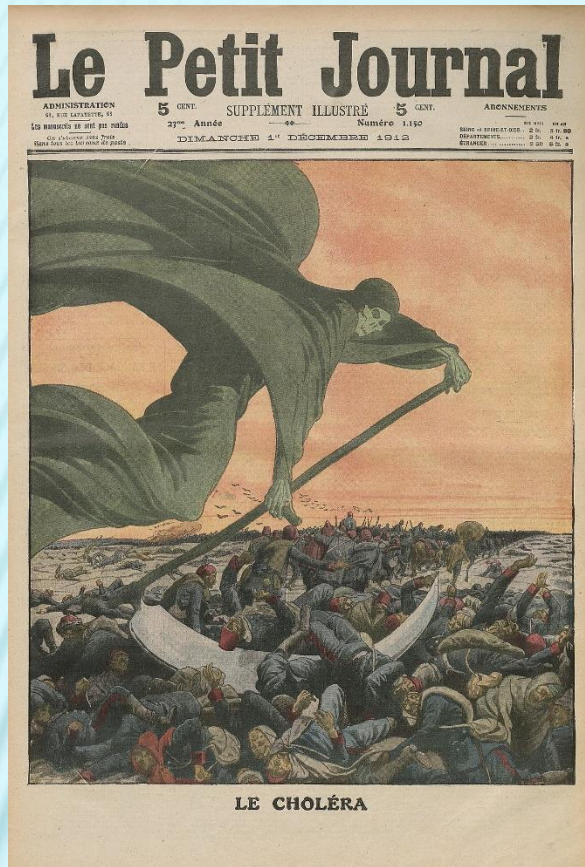


John Snow

TODAY

1858





1858 – MAP THE CHOLERA CASES

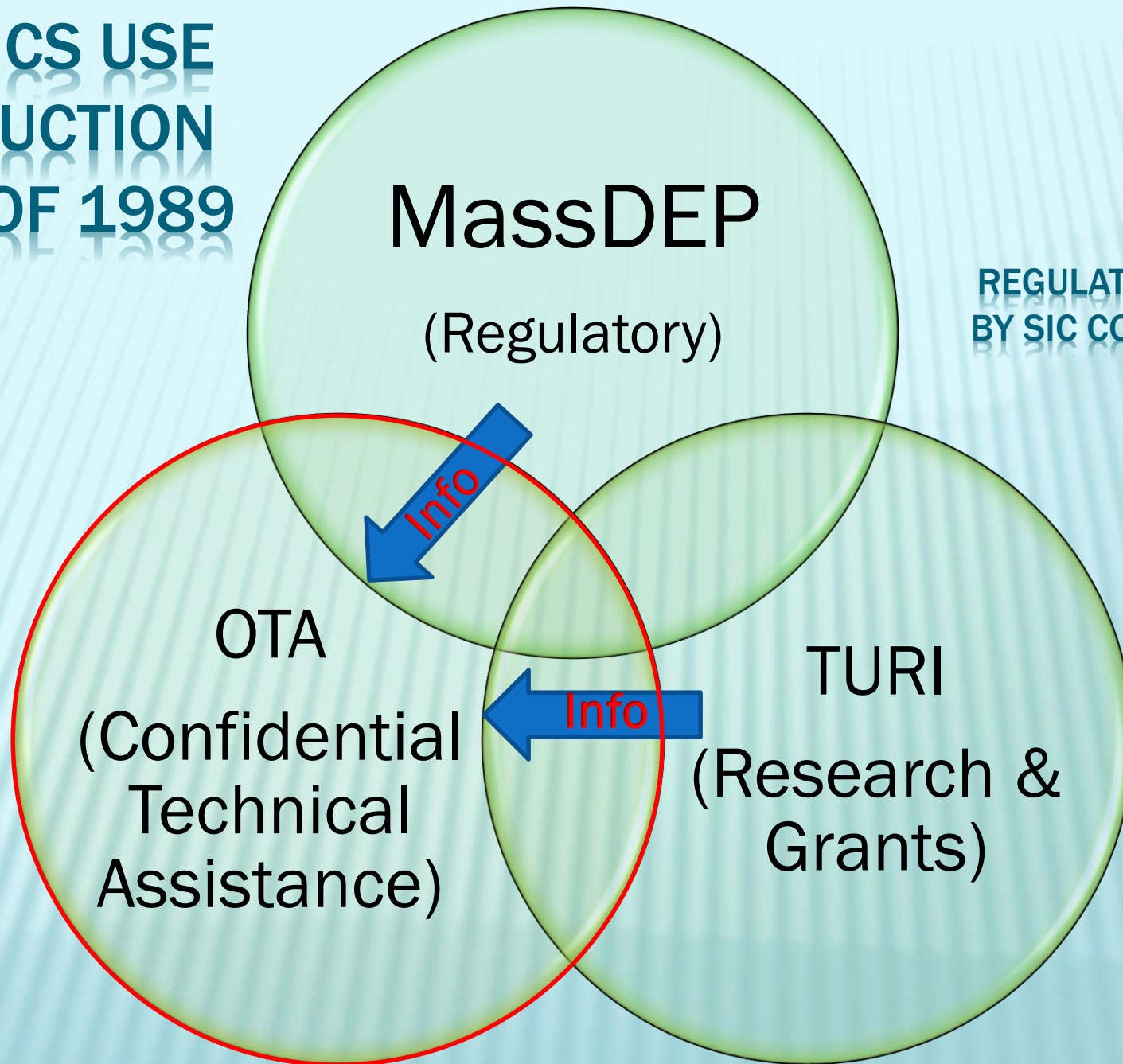
TODAY - MAP THE SOURCES

- ✘ Fire Training Facilities
- ✘ Rug Manufacturers
- ✘ Clothing Manufacturers
- ✘ Airports
- ✘ Etc





**TOXICS USE
REDUCTION
ACT OF 1989**



**REGULATED
BY SIC CODE**

MassDEP

(Regulatory)

OTA

(Confidential
Technical
Assistance)

TURI

(Research &
Grants)

Info

Info

PROCESS FOR IDENTIFYING COMPANIES



Search Online Libraries for SICs / NAICS



Visit Company Websites



Company Familiarity with TURA Program



Follow the Hottest Trail

IDENTIFY THE INDUSTRIES

SIC Code	Industry
2821	Plastics Materials & Synthetic Resins
3479	Metal Coating & Allied Services
3999	Manufacturing Industries
2295	Coated Fabrics, Not Rubberized
5172	Petroleum Products

NAICS Code	Industry
322220	Paper Bag & Coated & Treated Paper Manufacturing
334419	Other Electronic Component Manufacturing
33599	All Other Miscellaneous Electrical Equipment & Component Manufacturing
335929	Other Communication & Energy Wire Manufacturing

PFAS & TOXICS RELEASE INVENTORY

View Rule

View EO 12888 Metadata External Friendly Version Download RIN Data as XML

EPA/OCSPD RIN: 2019-AK51 Publication ID: Spring 2019

Title: Addition of Certain Per- and Polyfluoroalkyl Substances (PFAS) to the Toxic Release Inventory

Abstract:
 Section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA) created the Toxic Release Inventory (TRI) Program. The TRI Program is a tool EPA may use to understand the releases of Per- and Polyfluoroalkyl Substances (PFAS) by industrial and federal facilities. This information may be helpful to inform decision-making by communities, government agencies, companies and others. Currently, no PFAS chemicals are included on the list of chemicals required to report to TRI; however, the EPA is considering whether to add certain PFAS chemicals. In considering listing, the EPA must determine whether data and information are available to fulfil the statutory listing criteria and the extent and utility of the data that would be gathered. In addition, in considering if TRI will provide useful information to stakeholders, the EPA also will consider if those PFAS are still active in commerce. The process for listing includes notice and comment rulemaking to list PFAS chemicals for reporting year to adding these chemicals to the TRI for annual reporting.

Agency: Environmental Protection Agency (EPA) **Priority:** Substantive, Non-significant
RIN Status: First time published in the Unified Agenda **Agency Stage of Rulemaking:** Pretitle Stage
Major: No **Unfunded Mandates:** No
EO 13771 Designation: Not subject to, not significant
CFR Citation: [40 CFR 372](#)
Legal Authority: [21 U.S.C. 11963 et seq.](#)
Legal Deadline: None
Timetable:

Action	Date	FR Cit.
AMPRM	10/09/2019	

**Advance Notice of
 Proposed Rulemaking
 Expected to be Published
 in November 2019**

NAICS Code	Impacted Industry
31311	Fiber, Yarn, & Thread Mills
314110	Carpet & Rug Mills
324110	Petroleum Refineries
325	Chemical Manufacturing
423220	Home Furnishing Merchant Wholesalers
561740	Carpet & Upholstery Cleaning Services

ONLINE LIBRARIES

- × A to Z Database
- × Mergent Online
- × D & B Hoovers

Other Available Databases:

- × EPA's Enforcement & Compliance History Online (ECHO)
- × Toxics Release Inventory (TRI)



ECHO BY SIC & NAIC CODES

The screenshot shows the EPA ECHO Facility Search Results page. The page title is "Facility Search Results" and it displays a map of Massachusetts with green markers indicating facility locations. A yellow box with a red border contains the text "Quarterly Webinars!". In the bottom left corner of the map area, a red circle highlights the "Download Data" button. The right sidebar shows search criteria: "714 Facilities Found", "Selected Criteria" (Search Type: All Data, State: Massachusetts, Active/Operating: Yes, 4-digit SIC: 2821, 3479, 3999, 2295, 5172 OR, NAICS: 322220, 334419, 33599, 335929, 31311, 314110, 324110, 325, 42320, 561740), and "Explore Enforcement and Compliance Criteria" (63 Facilities with Current Violations, 22 Facilities with Significant Violations, 123 Facilities with Violations (3 years), 51 Facilities with Formal Enforcement Actions (5 years), 121 Facilities with Informal Enforcement Actions (5 years)).

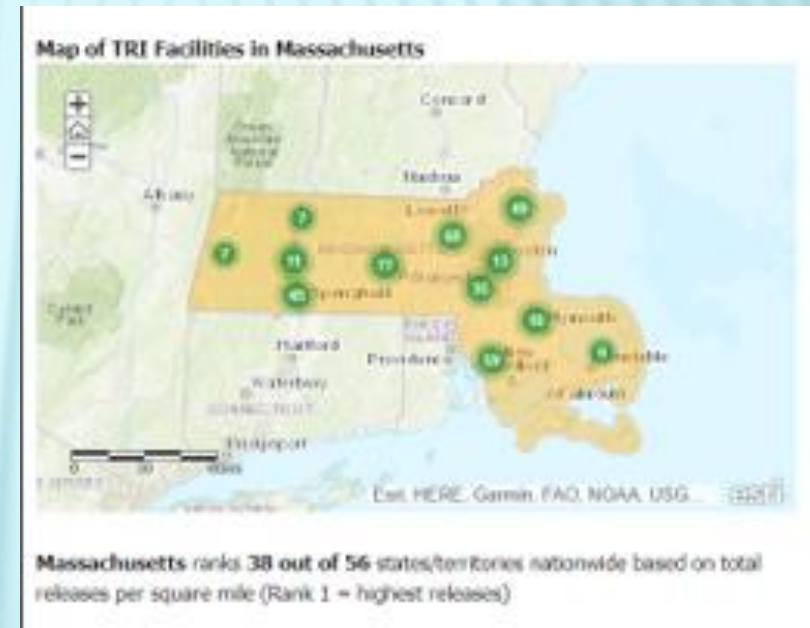
Downloadable Into Excel Files

TOXICS RELEASE INVENTORY TOOLS

Facility Search by State & NAICS

The screenshot shows the EPA TRI Explorer interface. At the top, it says "EPA United States Environmental Protection Agency" and "LEARN THE ISSUES | LAWS & REGULATIONS | ABOUT EPA". Below that is the "TRI Explorer" header. The main content area is titled "Release Reports" and has tabs for "Facility", "Federal Facility", "Trends", "Geography", and "Industry". The "Facility" tab is selected. Below the tabs, there are filters for "Year of Data" (set to 2018), "Geographic Location" (set to Massachusetts), "Chemical" (set to All chemicals), and "Industry" (set to Change selected industry/industries). There are also checkboxes for "Data Set" (2018, 2017, 2016, 2015). A "Generate Report" button is at the bottom left.

All TRI Facilities in State



Both Downloadable Into Excel Files

PROCESS FOR IDENTIFYING COMPANIES



Search Online Libraries for SICs / NAICS



Visit Company Websites



Company Familiarity with TURA Program



Follow the Hottest Trail

Facility Criteria



Manufactures in MA



Process qualifies as non-stick coating, waterproofing, etc

PROCESS FOR IDENTIFYING COMPANIES



Search Online Libraries for SICs / NAICS



Visit Company Websites

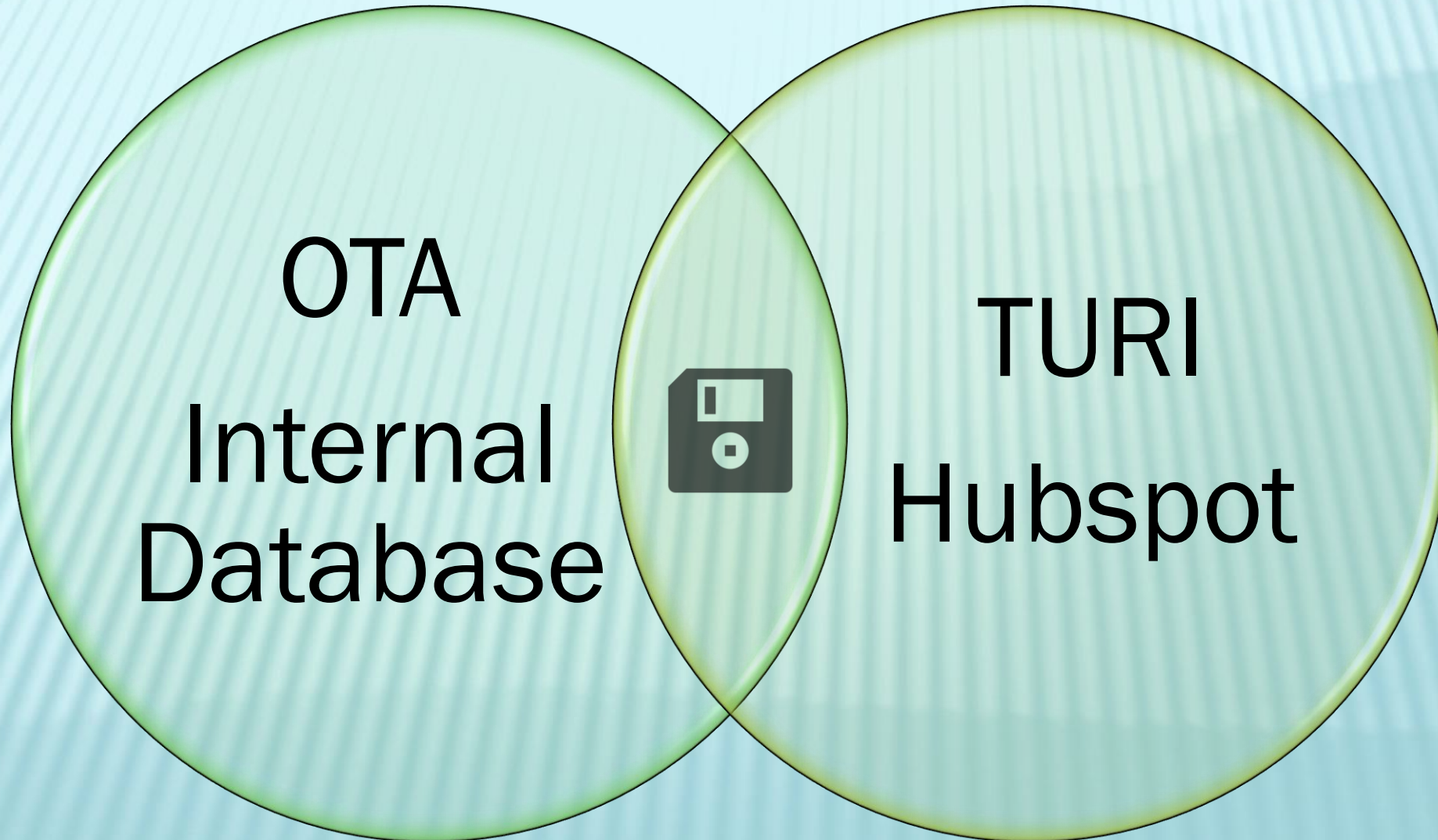


Company Familiarity with TURA Program



Follow the Hottest Trail

FAMILIARITY WITH TURA PROGRAM



FAMILIARITY WITH TURA PROGRAM

OTA

Last Date Worked
with OTA

TURI

Last Date Worked
with TURI



PROCESS FOR IDENTIFYING COMPANIES



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Company Familiarity with TURA Program



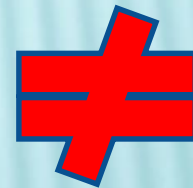
Follow the Hottest Trail

OBSTACLES

- × Lack of Awareness
- × No SDS Listing
- × Tainted Incoming Feedstock
- × Regrettable Substitution
 - + 'Shorter Chain' is Still a '**Forever Chemical**'
- × Fear of Liability
 - + Other PFAS Sources = Misplaced Liability
- × No Existing Regulations

No Health

Data



Safe

FOLLOW THE HOTTEST TRAIL

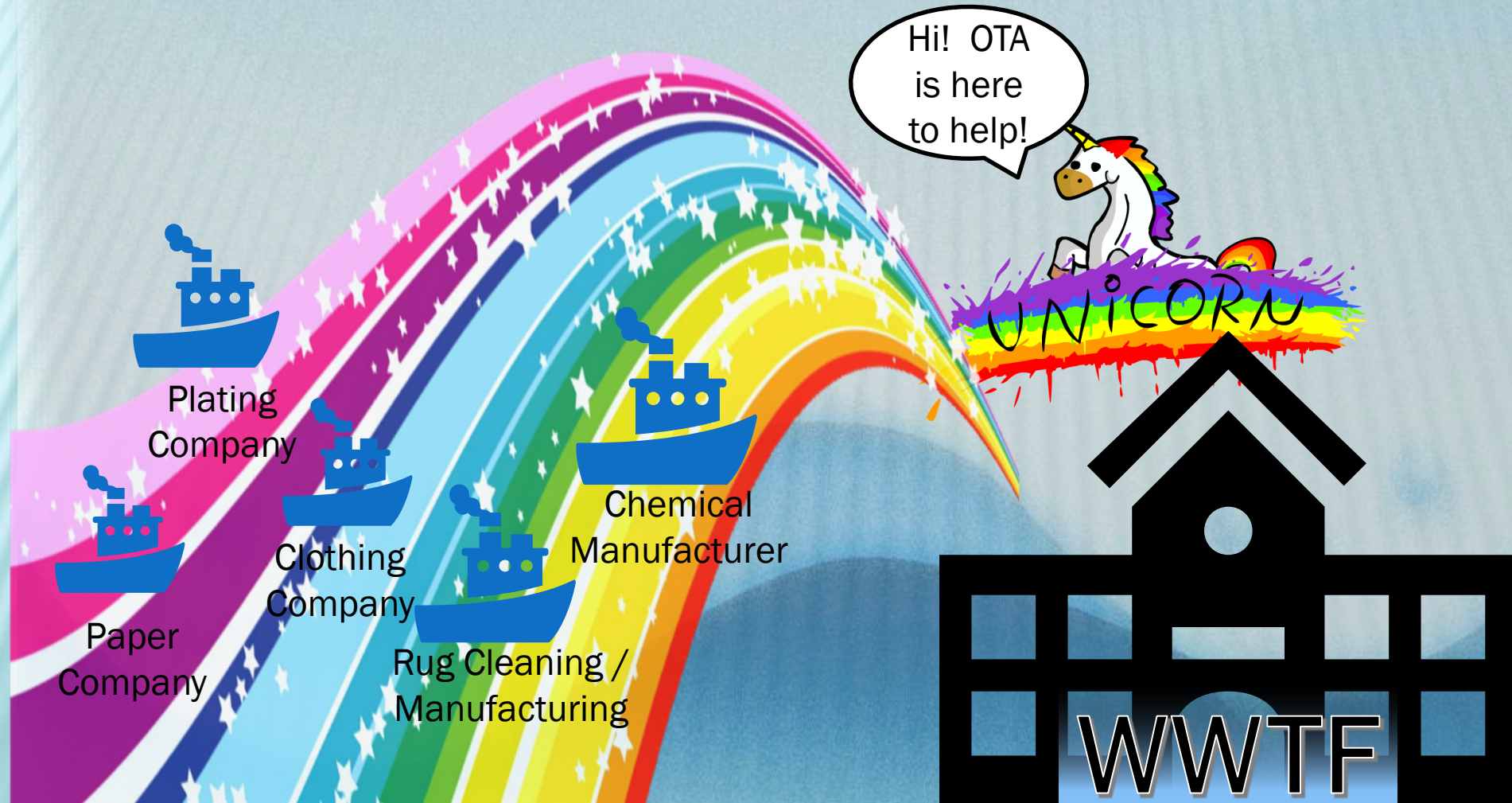
Remind company of positive TURA
Program experience / OTA
confidentiality

Questions to ask:

- ✘ Are you following the PFAS issue?
- ✘ Do you believe you are using PFAS?
- ✘ Are you seeking out safer alternatives?
- ✘ How can we help you?

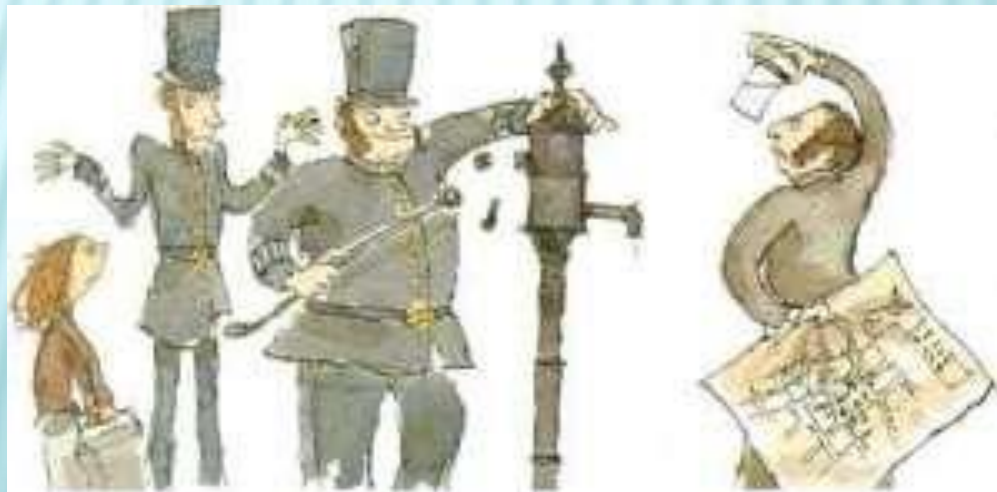


HOW OTA HELPS UPSTREAM



REMOVING THE HANDLE FROM THE PFAS PUMP

- ✘ Offering Free & Confidential Site Technical Assistance
- ✘ Referrals to TURI grants / research / lab
- ✘ Identifying Safer Alternatives



USEFUL WEBSITES

- × OTA – The MA Office of Technical Assistance
www.mass.gov/eea/ota
- × TURI – The Toxics Use Reduction Institute
www.turi.org
- × EPA Enforcement & Compliance History Online (ECHO)
<https://echo.epa.gov/>
- × EPA Toxics Release Inventory (TRI) Facility Release Reports
https://enviro.epa.gov/triexplorer/tri_release.facility
- × EPA Toxics Release Inventory (TRI) Analysis Where You Live
<https://www.epa.gov/trinationalanalysis/where-you-live>
 - × TURA Data
www.turadata.turi.org
 - × Tier II Data

UPCOMING PFAS EVENT!

NORTHEAST CONFERENCE
THE SCIENCE OF PFAS:
Public Health & The Environment

Tuesday, March 31, 2020 - Wednesday, April 1, 2020

**Sheraton Framingham Hotel & Conference Center
Framingham, MA**

WWW.NEWMOA.ORG

THANK YOU!



FOR MORE INFORMATION:

Tiffany Skogstrom, MPH
tiffany.skogstrom@mass.gov, 617-626-1086



Moderated Discussion

Moderator: Debra Darby, *Darby Marketing*

Panelists:

- **Ivan Cooper, *CEC***
- **Arie Kremen, *Tetra Tech***
- **Tiffany Skogstrom, *Massachusetts OTA***



Environmental Business Council of New England
Energy Environment Economy