CLEANTECH ALLIANCE
BREAKFAST SERIES
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# EMERGING CONTAMINANTS PRIMER

CleanTech Alliance, September 9, 2020

# Today's Presenter

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North American Emerging Contaminants Lead

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29 years of experience

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# Today's Presenter

## Erika Houtz, PhD

Senior Environmental Engineer, PFAS Expert

- 12 years of experience
- BS, Chemical Engineer, MS/PhD Environmental Engineering
- Published on the analysis, fate and transport of PFAS in natural and engineered systems, with a particular emphasis on the fate of PFASs found in aqueous film forming foams

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# Emerging Contaminants?

- Impacts to drinking water supplies are driving public awareness
  - Poly and perfluoroalkyl substances (PFAS)
  - 1,4-dioxane
- Changing regulatory standards or debate on toxicity
  - Hexavalent chromium
  - Perchlorate
  - TCE in vapor intrusion
- Evolving understanding of impacts and usage
  - Nanoparticles, pharmaceuticals, pesticides, trichloropropane, flame retardants

# PFAS: Poly and Perfluoroalkyl Substances

# PFAS Introduction

PFAS occur in consumer, industrial, and technical products

Some PFAS are **bioaccumulative** and potentially toxic; data for most are unavailable

**Potential drinking water** impacts drive most investigation and treatment efforts

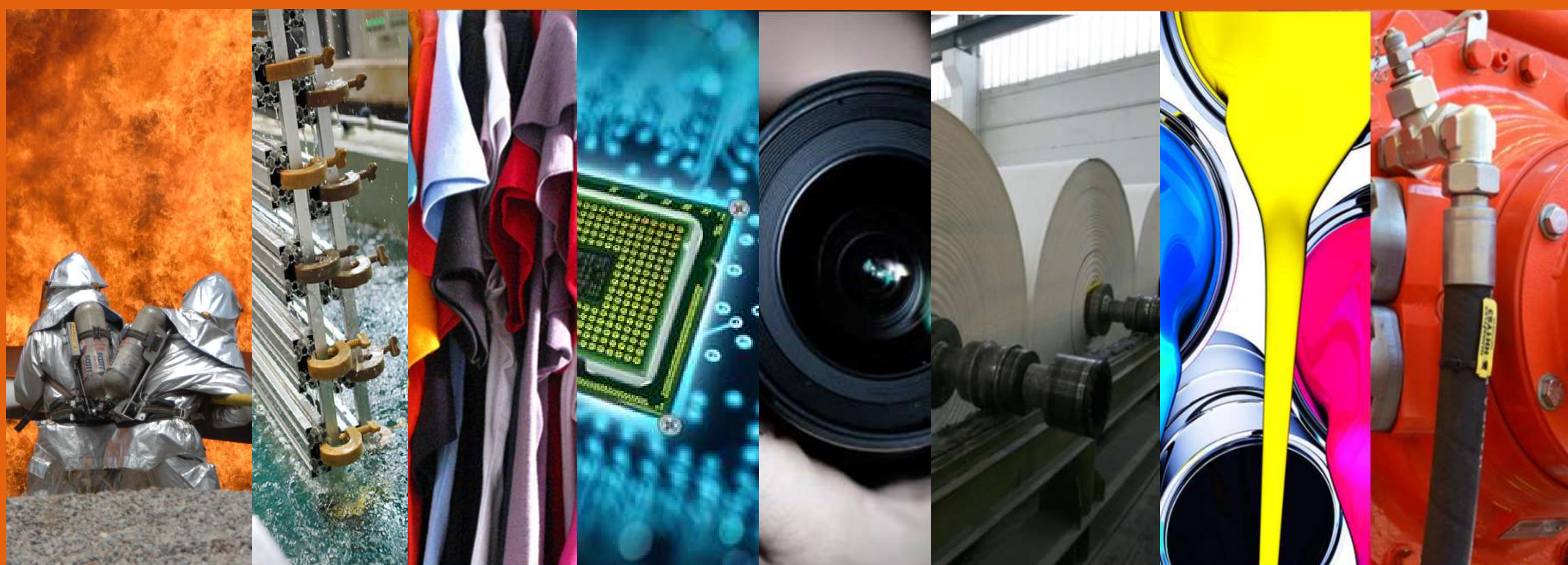
Analytical methods for PFAS are widely available but **not** always standardized

All PFAS are environmentally **stable** or form stable end products

PFAS regulatory targets are becoming more widespread and are on a **downward** trajectory

# PFAS Uses

## Where We Find Them and How They've Evolved



Firefighting Foams | Metal Plating | Textiles | Electronics | Photography | Paper Coatings | Paints | Hydraulic Fluids

# Specific Characteristics of PFAS

- **Mobility**
  High aqueous solubility, moderate sorption
- **Extreme Persistence**
  Perfluoroalkyl compounds don't naturally degrade; polyfluorinated compounds form perfluoroalkyl compounds
- **Surfactant Nature**
  Assemble at surfaces, especially air water interfaces
- **Bioaccumulation**
  Long chain PFAS bioaccumulate in humans (protein rich compartments)
- **Toxicity**
  Coupled with bioaccumulation, contributes to low regulations for some PFAS

# Poly- and Perfluoroalkyl Substances (PFAS)

4,730 known compounds

**More Commonly Regulated**

## Polyfluorinated “PFAA Precursors”

1000’s of individual parent compounds, and hundreds of common intermediates, e.g. 6:2 FTS, 5:3 acid

## Perfluorinated Compounds(PFCs) or Perfluoroalkyl Acids (PFAAs)

~25 common individual compounds, terminal daughters
e.g. PFOS, PFOA, PFHxS, PFBA, PFHxA



Environmental / Higher Organism Biotransformation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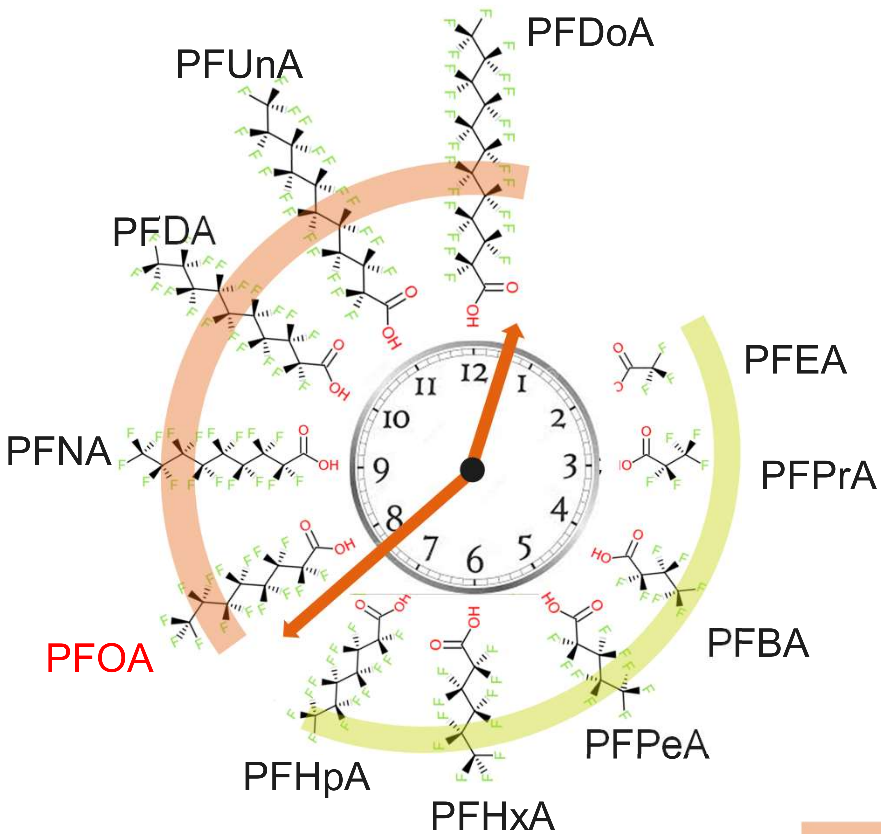
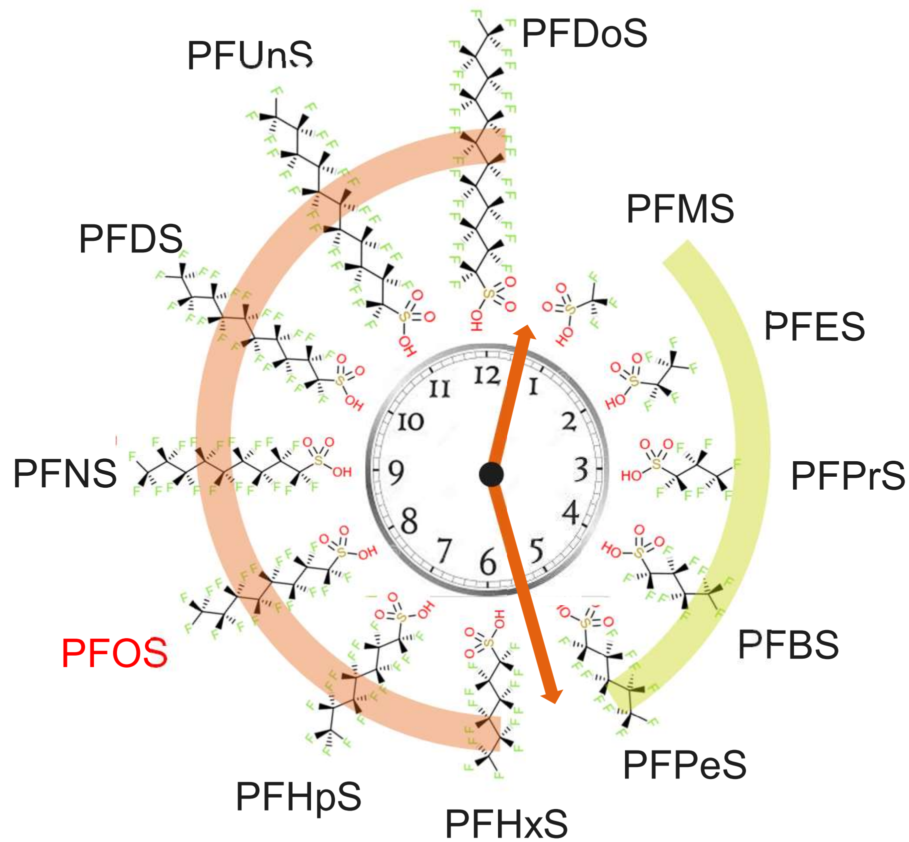
# Long Chain vs. Short Chain




**PFCAs**




**PFSAs**

Long Chain
Short Chain

# NEWS HEADLINES


**Horsham Water and Sewer Authority Takes 2 Wells Out of Service Due to Detection of Perfluorooctane Sulfonate (PFOS) Above Provisional Health Advisory Level**

Two of the Authority supply wells, Well No. 26 and Well No. 40 were recently found to have PFOS above the PHA level (detected at 0.7 ppb and 1.0 ppb respectively). PFOS was also detected in other Authority wells but not above the PHA level. **After consulting with DEP, the Authority decided to take Well Nos. 26 and 40 off-line.**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## Hoosick Falls Water Contamination

Recently, members of the Hoosick Falls community have contacted the U.S. Environmental Protection Agency (EPA) with concerns and questions about whether they should drink, bathe in, or cook with their water, which has been found to contain perfluorooctanoic acid (PFOA).

Public Meeting: PFOA in Drinking Water

January 14, 2016 •6:00 pm

Hoosick Falls Central School,

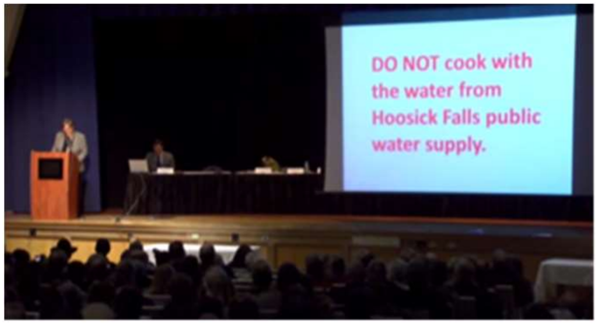
Toxic chemical foam plume found at National Guard base in Alpena


Shutterstock

**The FDA Just Banned These Chemicals in Food. Are They the Tip of the Iceberg?**

*FDA banned three toxic food packaging chemicals and is considering banning seven cancer-causing food flavoring chemicals, but food safety advocates say the process highlights flaws in the system.*

By Elizabeth Grossman on January 6, 2016



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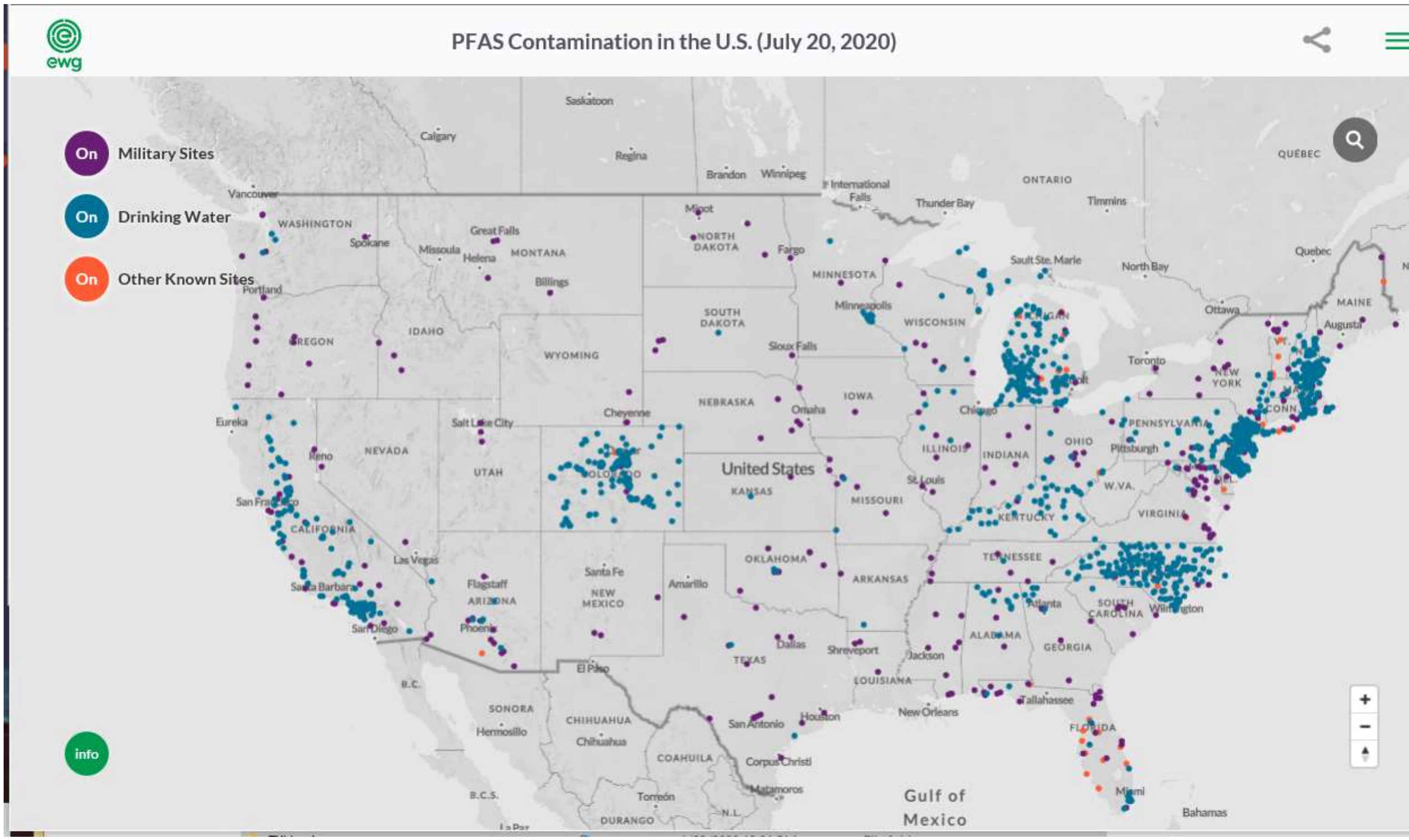
# PFAS Impacts are widespread

States with highest density of PFAS sites reflects programmatic testing




https://www.ewg.org/interactive-maps/pfas_contamination/map/

# Michigan as Model for Emerging Regulation

- State-wide testing of drinking water (2018)
  - MCLs for PFOS, PFOA and 5 other PFAS
- Wastewater treatment plants (2018)
  - Industrial pre-treatment testing for PFAS users
    - Landfills, Chrome plating, Airports, industry with AFFF fire suppression
  - Limits on sewer discharge based on Great Lakes surface water standards
    - Total maximum daily limit of PFAS discharge at each WWTP for permits
  - Surface water sampling at industrial sites (2019)
    - Surface water standards among the strictest in country (2018)
    - PFOS 11/12 ng/L, PFOA 420/1200 ng/L for drinking water/non-drinking water sources
  - Industrial air emissions standards under development (2020)

# Other Trends Affecting Business

Landfill acceptance of PFAS-containing waste limited in anticipation of hazardous substance regulation

- Subtitle D landfills with specialized leachate treatment
- Zero discharge landfills in arid regions
- Subtitle C landfills

USEPA Significant new use rule (SNUR) and Toxic release Inventory rule (TRIR)

- Increasing restrictions on use and administrative reporting requirements

USEPA cancelled incineration testing for PFAS wastes over concerns about incomplete treatment

# Changing U.S. Regulatory Climate

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## Drinking Water (µg/L - ppb)

**Washington**
- **PFOA = 0.010**
- **PFOS = 0.015**
- **PFNA = 0.014**
- PFHxS = 0.070
- PFBS = 1.3

**Nevada**
- **PFOA = 0.667**
- **PFOS = 0.667**
- PFBS = 66.7

**Alaska**
- **PFOA = (0.070)**
- **PFOS = (0.070)**

**California**
- **PFOA = 0.0051**
- **PFOS = 0.0065**

**Michigan**
- **PFOA = 0.008**
- **PFOS = 0.016**
- **PFNA = 0.006**
- PFHxA = 400
- PFHxS = 0.051
- PFBS = 0.420
- GenX = 0.370

**Minnesota**
- **PFOA = (0.035)**
- **PFOS = (0.027)**
- PFHxS = (0.047)
- PFBS = (2)
- PFBA = (7)

**New York**
- **PFOA = 0.010**
- **PFOS = 0.010**

**New Hampshire**
- **PFOA = 0.012**
- **PFOS = 0.015**
- **PFNA = 0.011**
- PFHxS = 0.018

**Vermont**
- **PFOA = (0.020)**
- **PFOS = (0.020)**
- **PFNA = (0.020)**
- PFHxS = (0.020)
- PFHpA = (0.020)

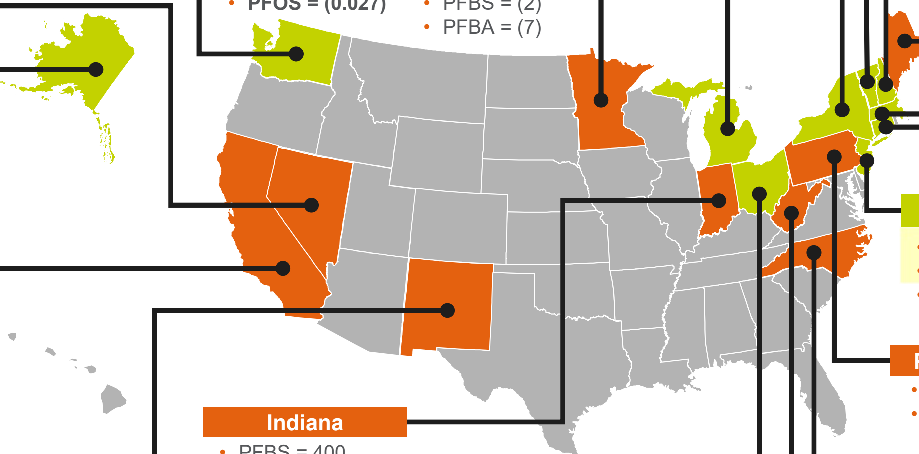
**Maine**
- **PFOA = (0.070)**
- **PFOS = (0.070)**

**Massachusetts**
- **PFOA = (0.020)**
- **PFOS = (0.020)**
- **PFNA = (0.020)**
- PFHxS = (0.020)
- PFHpA = (0.020)
- PFDA = (0.020)

**New Jersey**
- **PFOA = 0.014**
- **PFOS = 0.013**
- **PFNA = 0.013**

**Pennsylvania**
- **PFOA = (0.070)**
- **PFOS = (0.070)**

**Connecticut**
- **PFOA = (0.070)**
- **PFOS = (0.070)**
- **PFNA = (0.070)**
- PFHxS = (0.070)
- PFHpA = (0.070)



**Indiana**
- PFBS = 400

**New Mexico**
- **PFOA = (0.070)**
- **PFOS = (0.070)**
- PFHxS = (0.070)

**Ohio**
- **PFOA = (0.070)**
- **PFOS = (0.070)**
- **PFNA = 0.021**
- PFHxS = 0.140
- PFBS = 140
- HFPO-DA = 0.700

**North Carolina**
- **PFOA = 2**
- **GenX = 0.140**

**West Virginia**
- **PFOA = 150**

**Drinking Water Advisory Guideline**

**Drinking Water Enforceable Standard**

Parenthetical values represent combined standards (sum of PFAS)

Highlighted PFAS represent new standards and guidelines adopted or proposed since October 2019



**U.S. EPA Lifetime Health Advisory for Drinking Water**
- PFOA = (0.07)
- PFOS = (0.07)

EPA is in the process of determining whether MCLs will be set (as of 2020)

Updated August 07, 2020

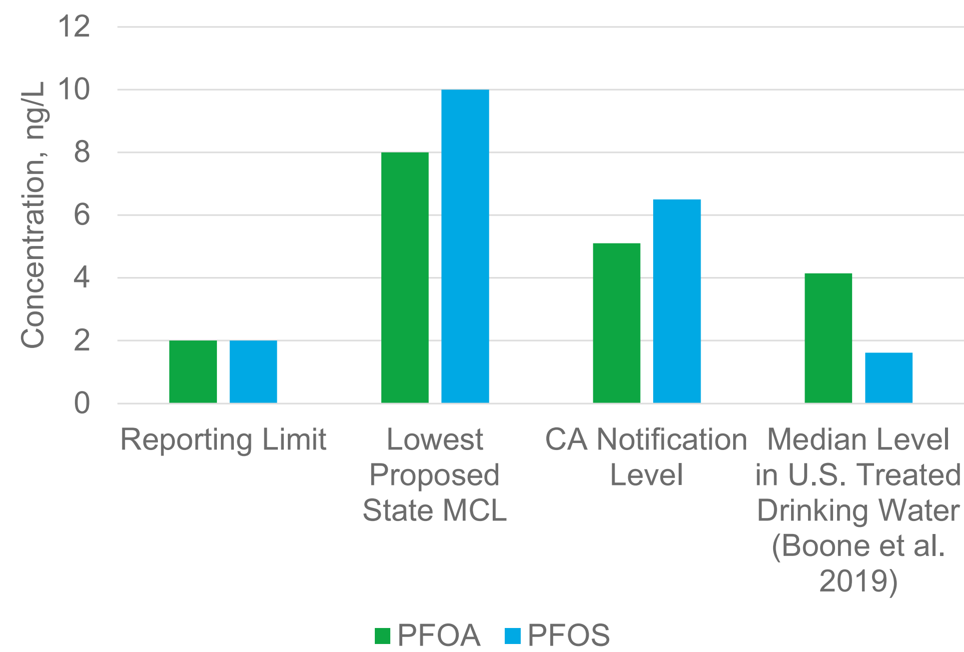
# Reporting Limits and/or regulations are converging on background

Typical reporting limits for PFOS and PFOA in drinking water are 2 ng/L; lower limits are achievable

State-proposed drinking water criteria and enforceable MCLs range between 5 and 20 ng/L

- Recently issued draft CA Environmental Screening Levels are below 1 ng/L

Median levels of PFOS/PFOA are within a factor of ~2x RLs



# PFAS Liquid Treatment Quick Take-Aways

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- PFAS defy conventional remediation engineering
  - does not bio**degrade**
  - nearly impractical to chemically **oxidize**
  - has minimal removal through **phase changes**
  - **energy-intensive** to destroy
- Current state of the practice is a **combination** of treatment technologies
- Goal is to **concentrate** PFAS for energy-intensive destruction

**ADSORPTION** | **SEPARATION/ CONCENTRATION** | **DESTRUCTION**

# PFAS Solid Treatment Quick Take-Aways

CleanTech Alliance

- Solid treatment technologies available, but **minimal drivers** to necessitate full-scale remediation
- The treatment technologies theoretically/conceptually viable are currently being vetted at the laboratory or pilot scale for effectiveness on short chain PFAS and precursors
- Large mobilization costs complicate small-scale field-scale pilot testing

| FIXATION | SEPARATION | DESTRUCTION |
| --- | --- | --- |

# PFAS Treatment Technologies for Liquid

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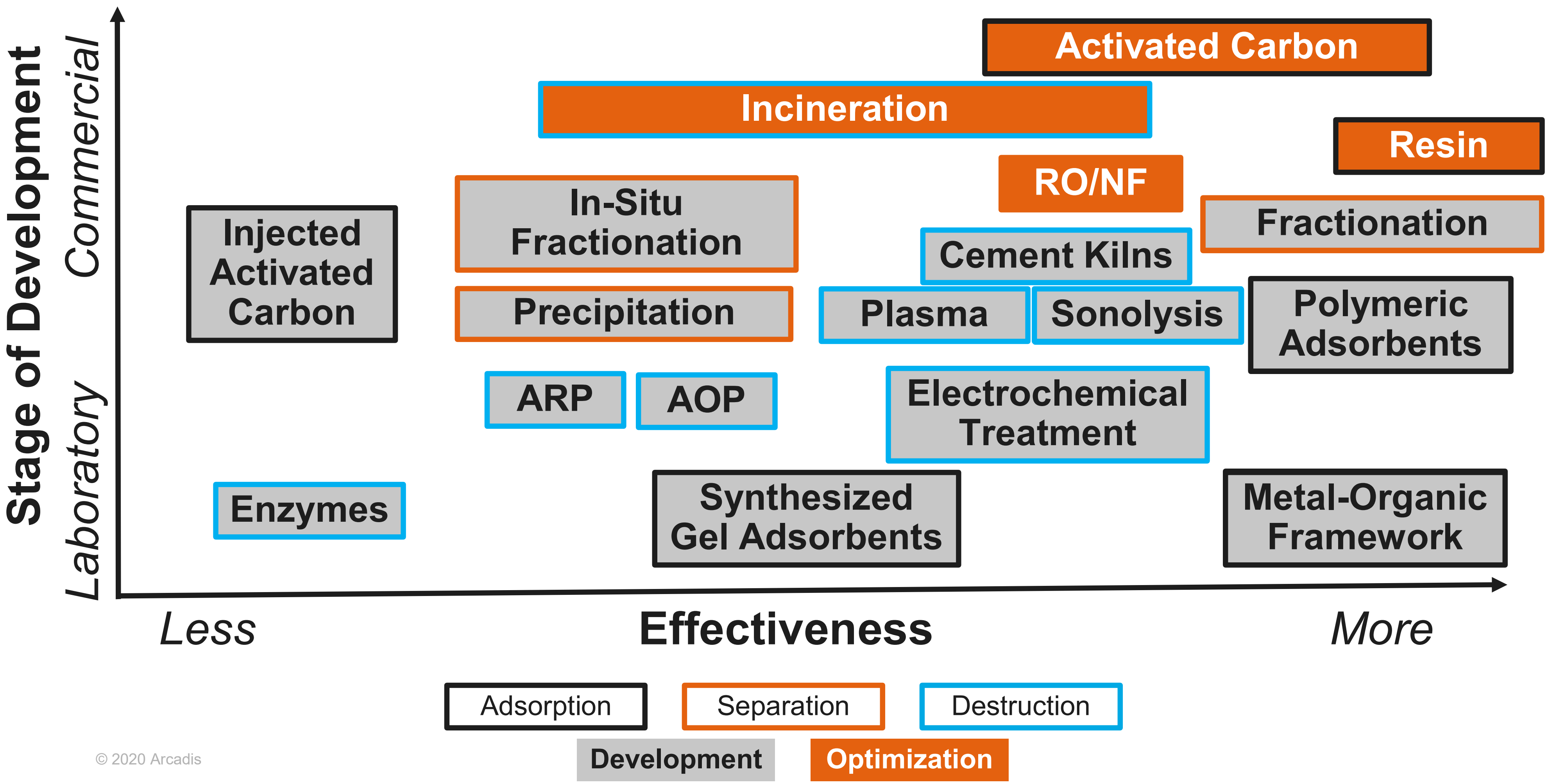

# PFAS Treatment State of the Practice

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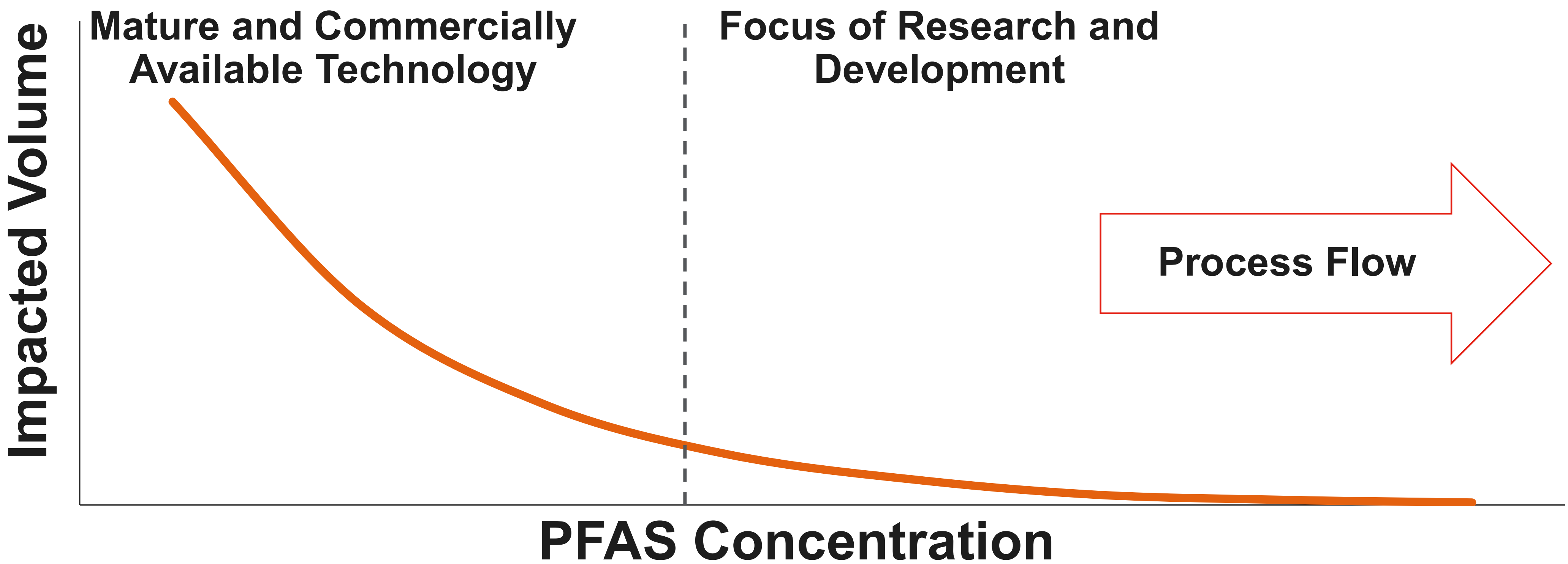



**Reduce impacted volume while concentrating PFAS for energy-intensive destruction**

# Conventional Technologies for PFAS



## Activated carbon (AC)

*Photo Source: Evoqua 2017*

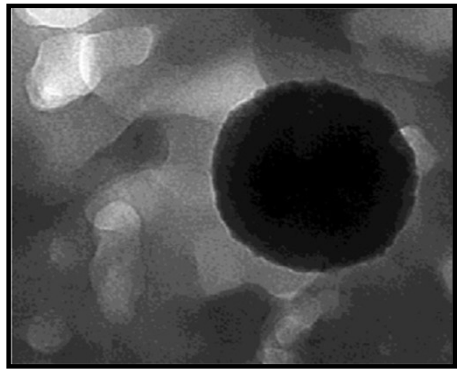


*Photo Source: Zaggia et al. 2016*

## Anion/Ion Exchange Resins

*Photo Source: Evoqua 2017*

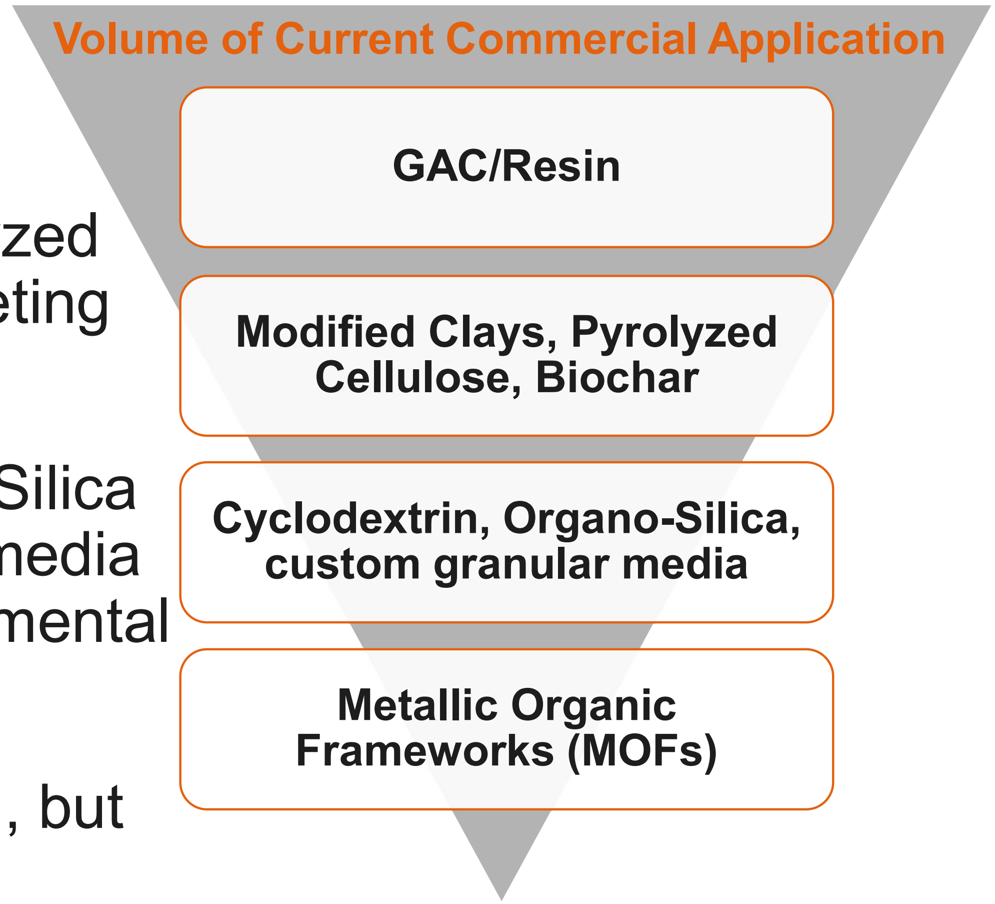
## Reverse Osmosis/Nanofiltration

*Photo Source: Peter Storch 2018*

# PFAS-Relevant Adsorbents

CleanTech Alliance

- GAC/Resins: Current “de facto” IRM adsorbents
- Modified clays (FluoroSorb®), pyrolyzed cellulose, biochar – available, competing with GAC/resin for PFAS relevance
- Cyclodextrin (CycloPure®), Organo-Silica (PQ-Osorb®), customized granular media (Puraffinity®) – promising but experimental
- MOFs, hydrogels, and two-phase composites – somewhat esoteric still, but huge potential adsorption capacities



# Fractionation + Ozone = Ozofractionation

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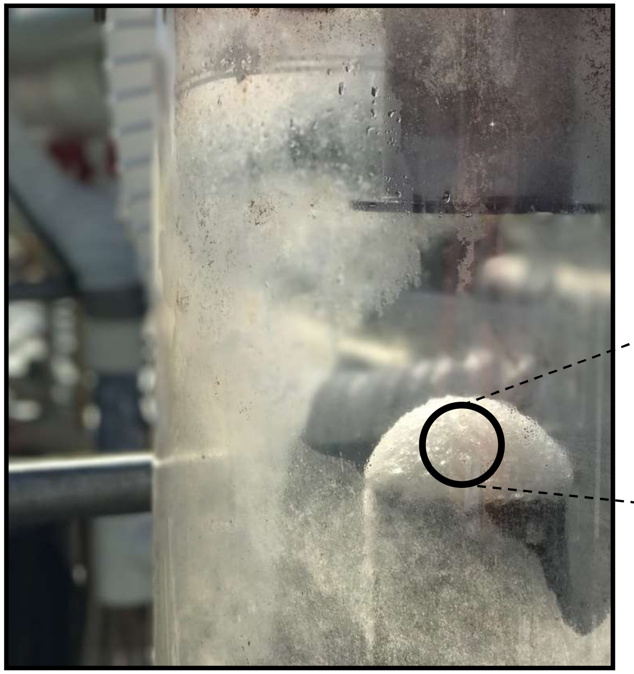


*Photo Source: Evocra 2017*

# Incinerating PFAS in Liquids

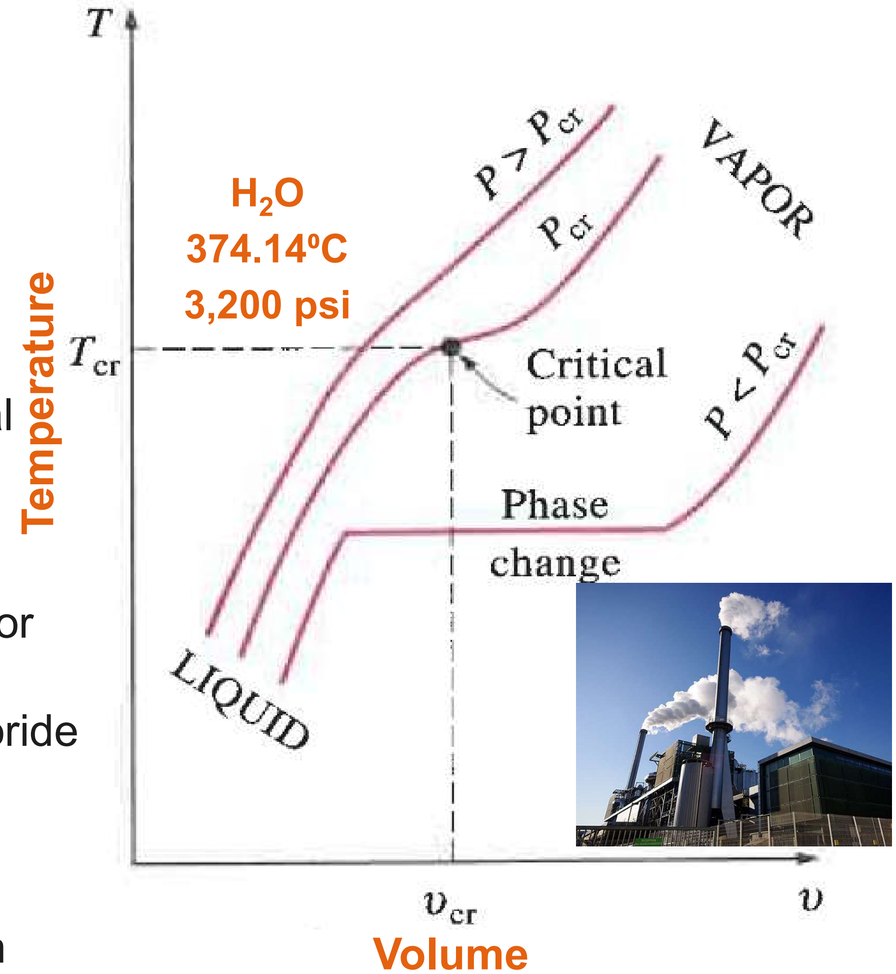
CleanTech Alliance

**Applicability:**

- Destruction of PFAS via high temperatures*
- PFOA defluorination at 300ºC to 350ºC*
- PFOS defluorination at 600ºC*.
- Applicable to solids and concentrated waste streams.
- Currently a termination of treatment trains for municipal and small-scale systems.

**Limitations:**

- Incomplete mineralization leads to discharge of PFAS or other by-products with long atmospheric half lives*.
- Complete PFAS mineralization results in hydrogen fluoride (toxic and corrosive)*.
- Applicability to liquid waste streams may be limited to aqueous critical point*.
- Insufficient analytical and sampling methods to confirm mineralization




*Citations available upon request*

# Advanced Reducing Processes - ARP

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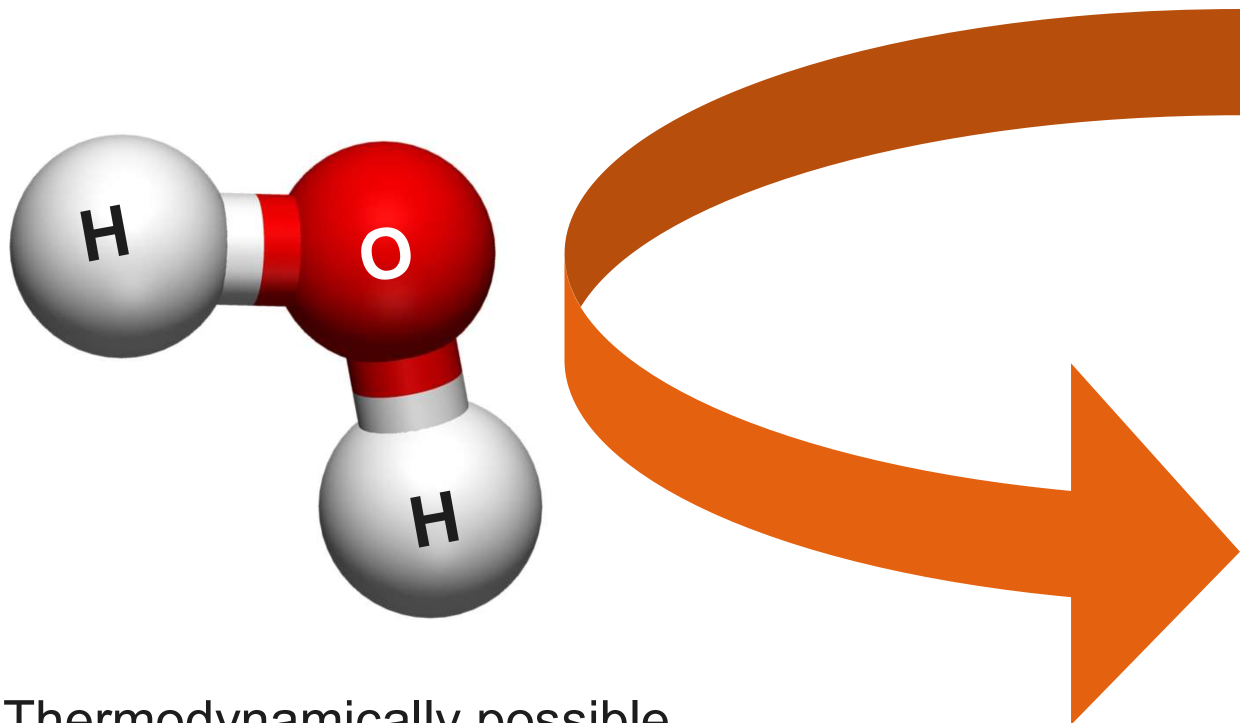



**Sound waves**

**Electricity**

**Radiation**

H•

Disproportionation into oxidizing and reducing radicals

OH•

e•

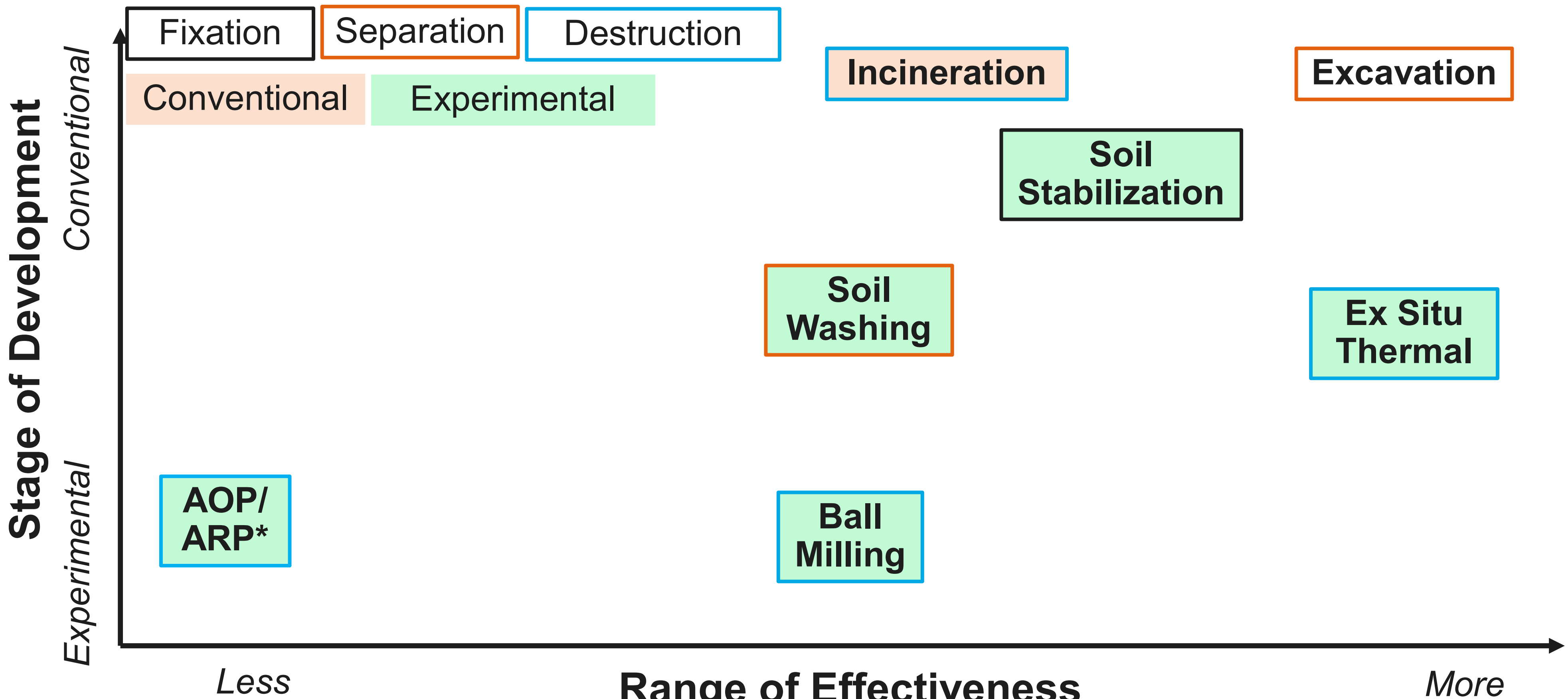
- Thermodynamically possible...
- Kinetically meaningful (scavengers)?





*Adapted from Horst et al 2020*

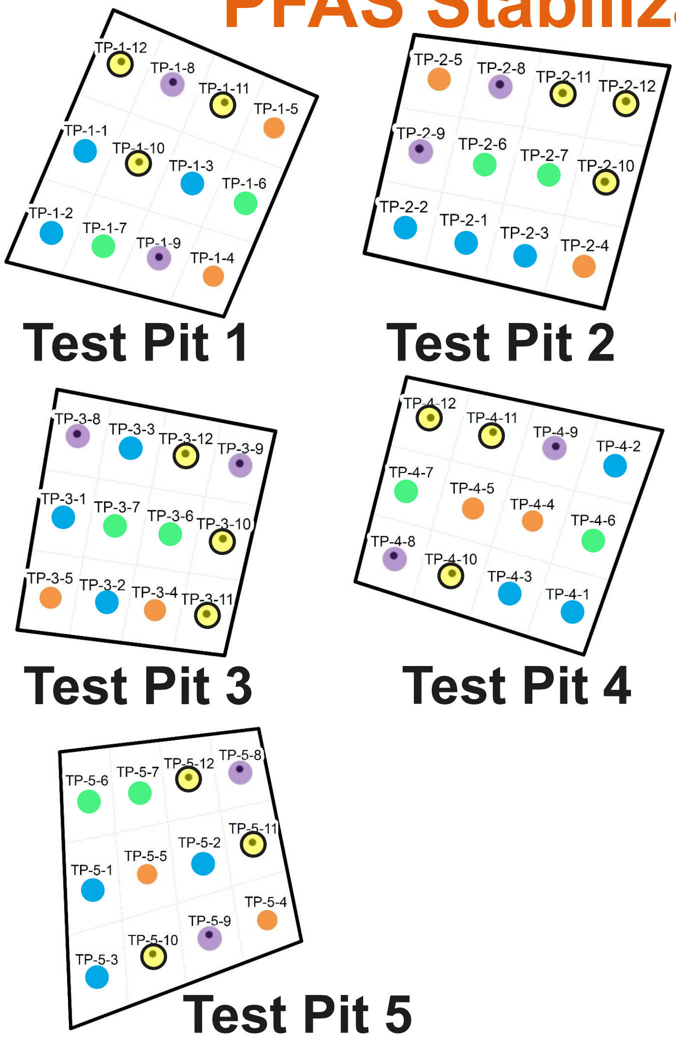
# PFAS Treatment Technologies for Solids

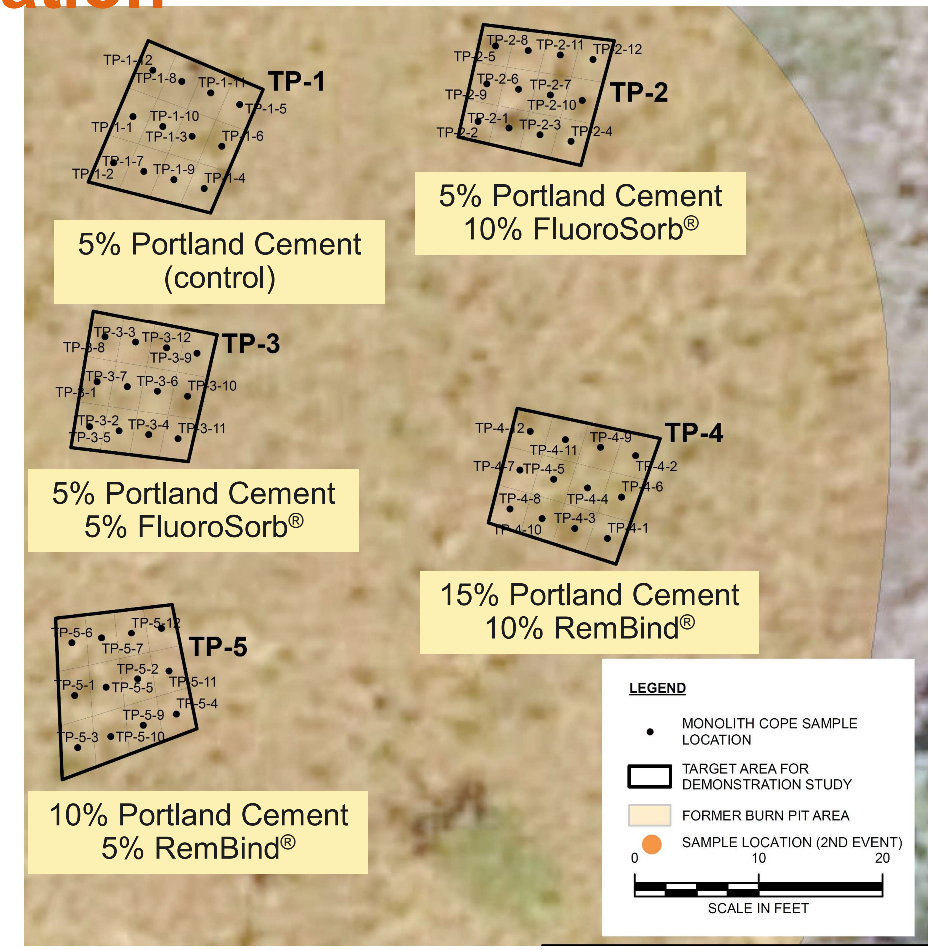


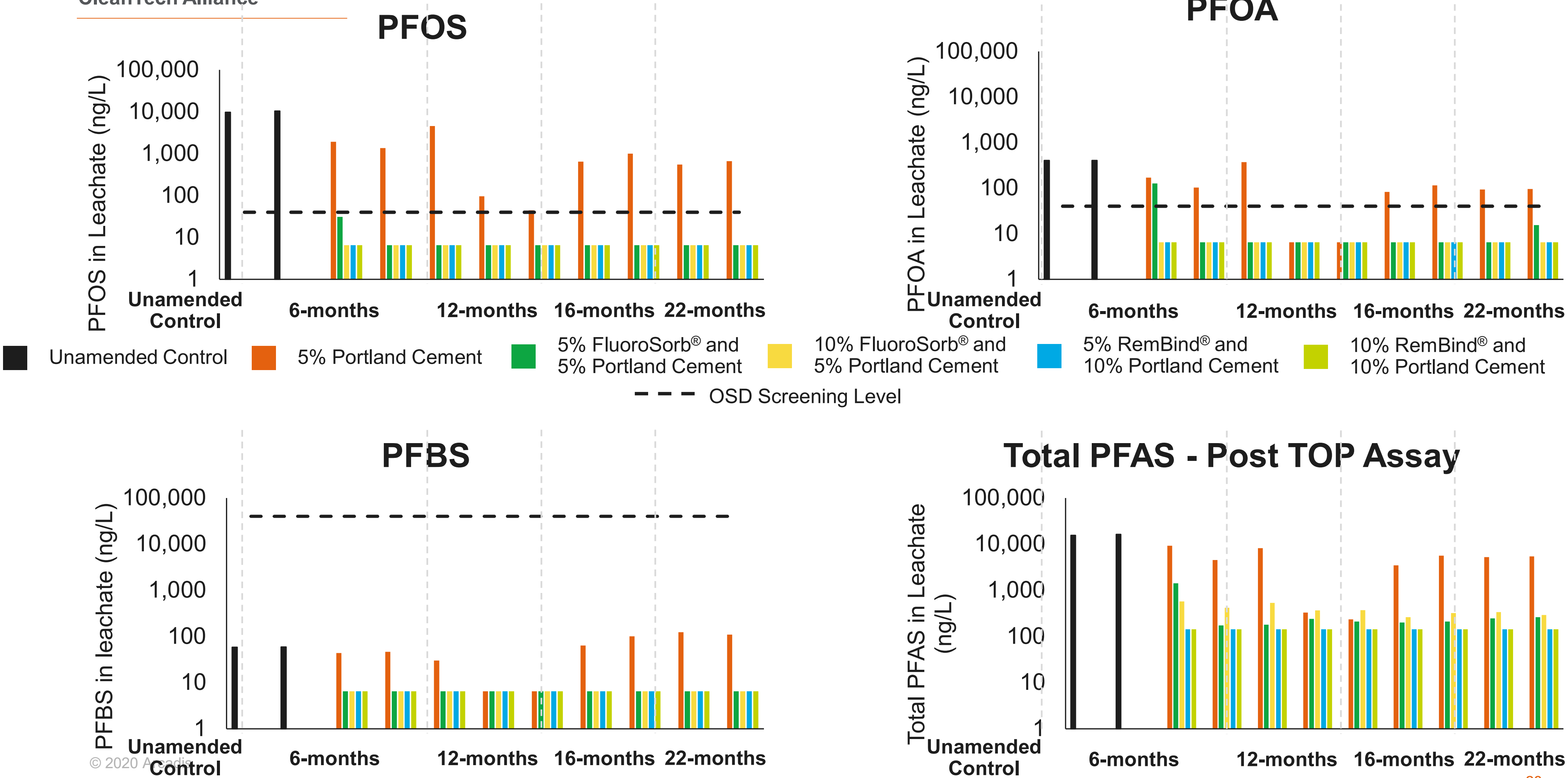
# Field-Scale Demonstration of PFAS Stabilization

- Dec 2018
- Jul 2019
- Oct 2019
- Apr 2020
- *Oct 2020

*tentative dates based on access, no dig, etc.




PFOS
PFOS in Leachate (ng/L)
100,000
10,000
1,000
100
10
1
Unamended Control
6-months
12-months
16-months
22-months
PFOA
PFOA in Leachate (ng/L)
Unamended Control
6-months
12-months
16-months
22-months
Unamended Control
5% Portland Cement
5% FluoroSorb® and 5% Portland Cement
10% FluoroSorb® and 5% Portland Cement
5% RemBind® and 10% Portland Cement
10% RemBind® and 10% Portland Cement
OSD Screening Level
PFBS
PFBS in leachate (ng/L)
Unamended Control
6-months
12-months
16-months
22-months
Total PFAS - Post TOP Assay
Total PFAS in Leachate (ng/L)
Unamended Control
6-months
12-months
16-months
22-months

# Emerging Contaminants Summary

- Emerging contaminants are considering emerging as the toxicological and regulatory status is evaluated and evolves
- Emerging contaminants such as 1,4-dioxane and PFAS present a new set of challenges to practitioners
- In situ and ex situ management strategies are being developed, remedial technologies in research and development
- Practical laboratory quantification is a topic of focus as emerging contaminants have low targets

# Q&A

# Thank you!

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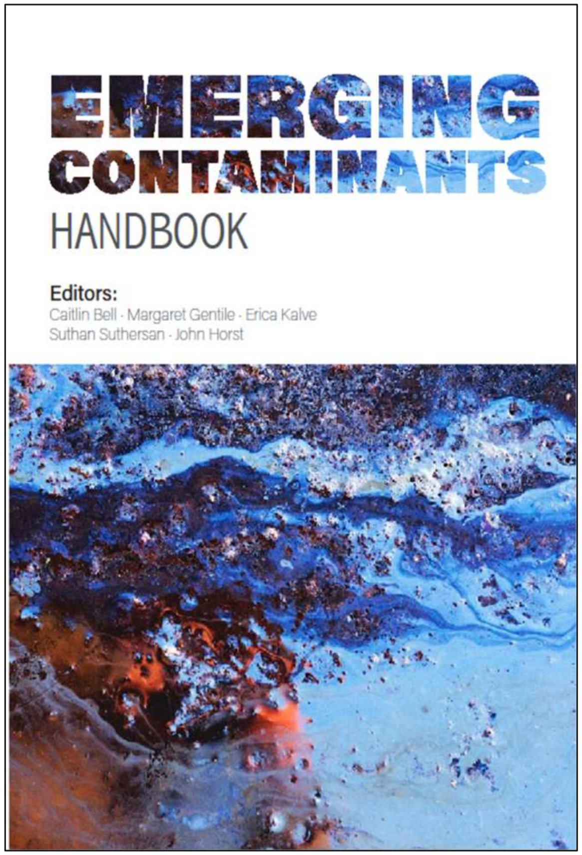
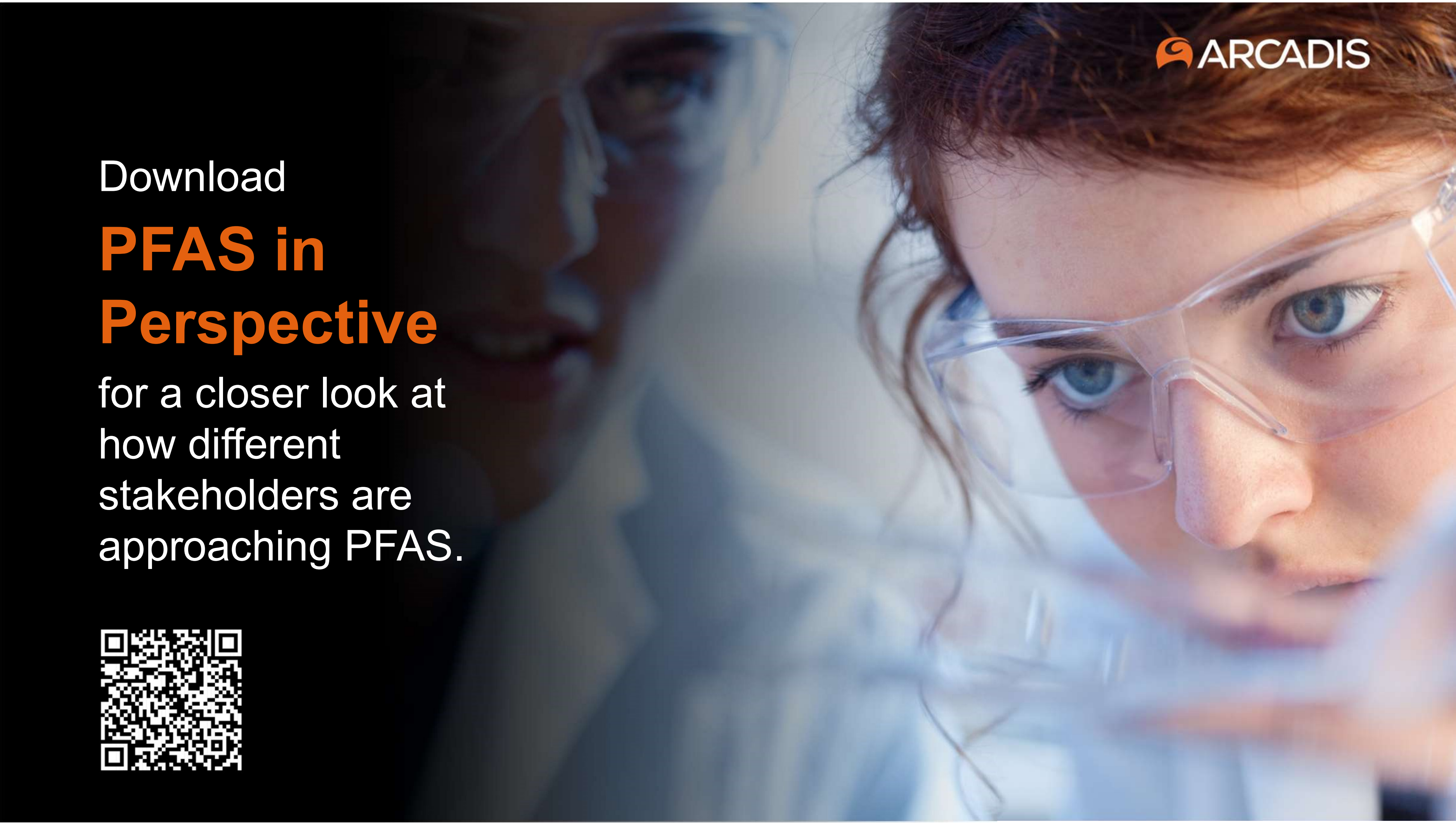



CRC Press 2019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PFAS in Perspective
for a closer look at how different stakeholders are approaching PFAS.

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