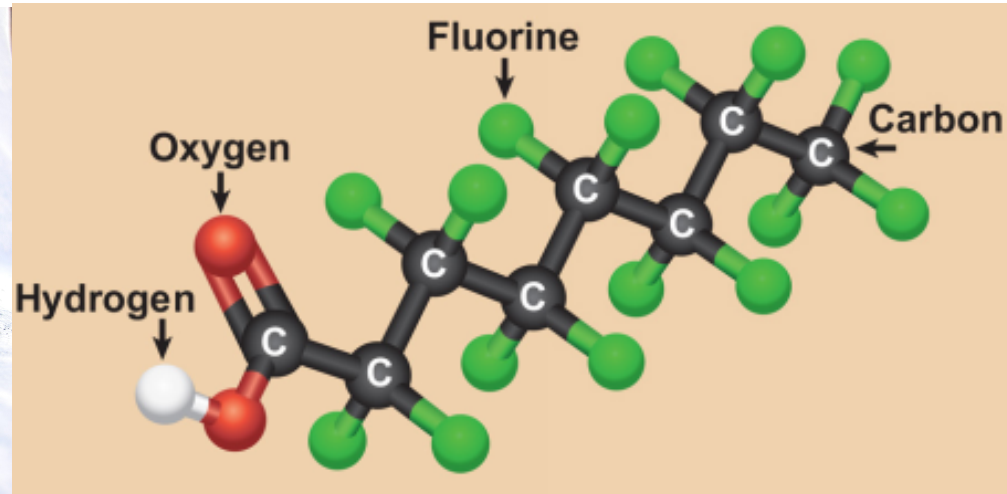
Hazen




# PFAS in Biosolids: State of Knowledge and Treatment Opportunities

**NEWEA Conference: Sustainable Biosolids Management – A Sure Bet!**

**October 18, 2019**

**Jay Surti, PE, Residuals Practice Lead – Northeast**

# Agenda

What are PFAS chemicals and why is it an issue for the biosolids industry?

Why is PFAS difficult to treat?

Can we treat biosolids for PFAS and produce high quality biosolids or value-added products?

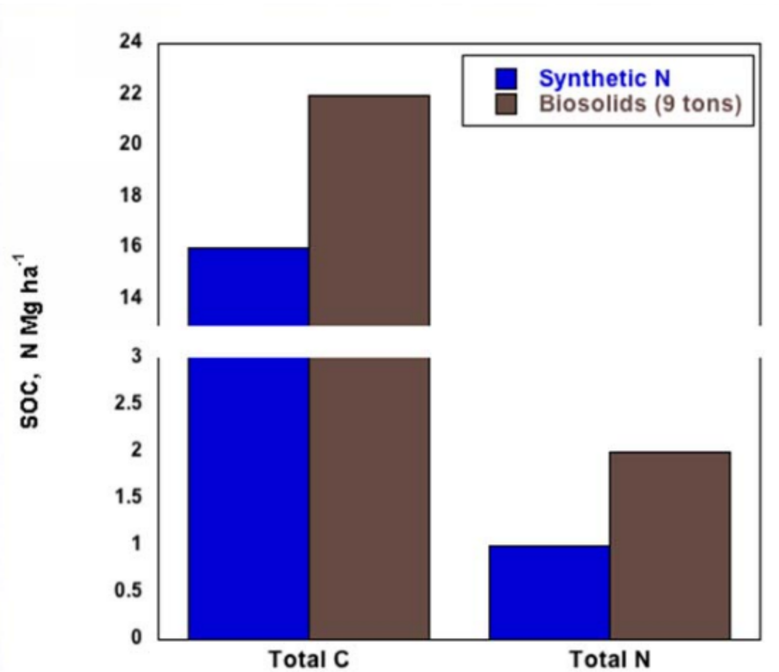
Take-Aways!

# The Biosolids Promise

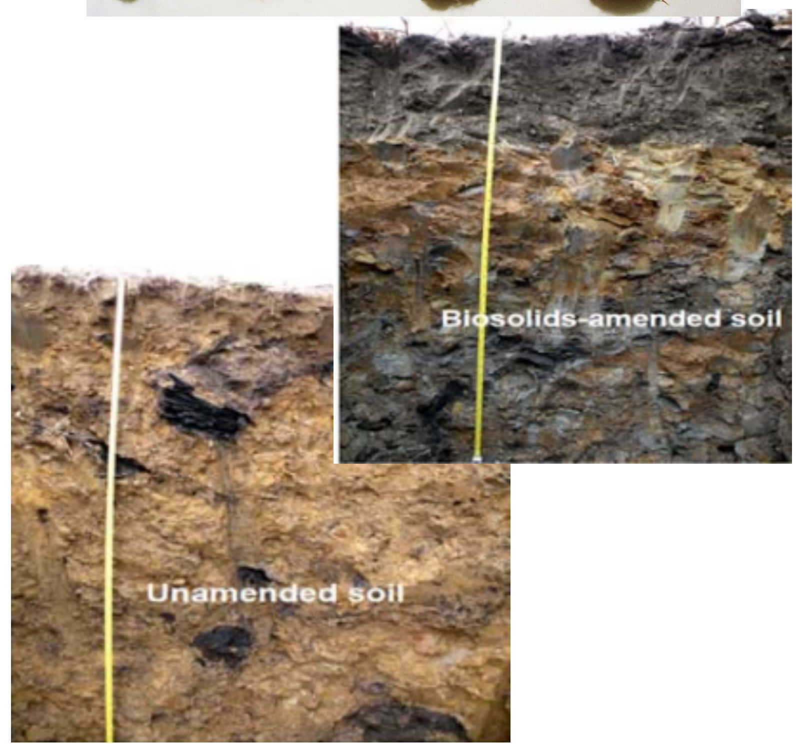
***Organics*** and ***nutrients*** in biosolids improve soil quality

Sustain cropland productivity

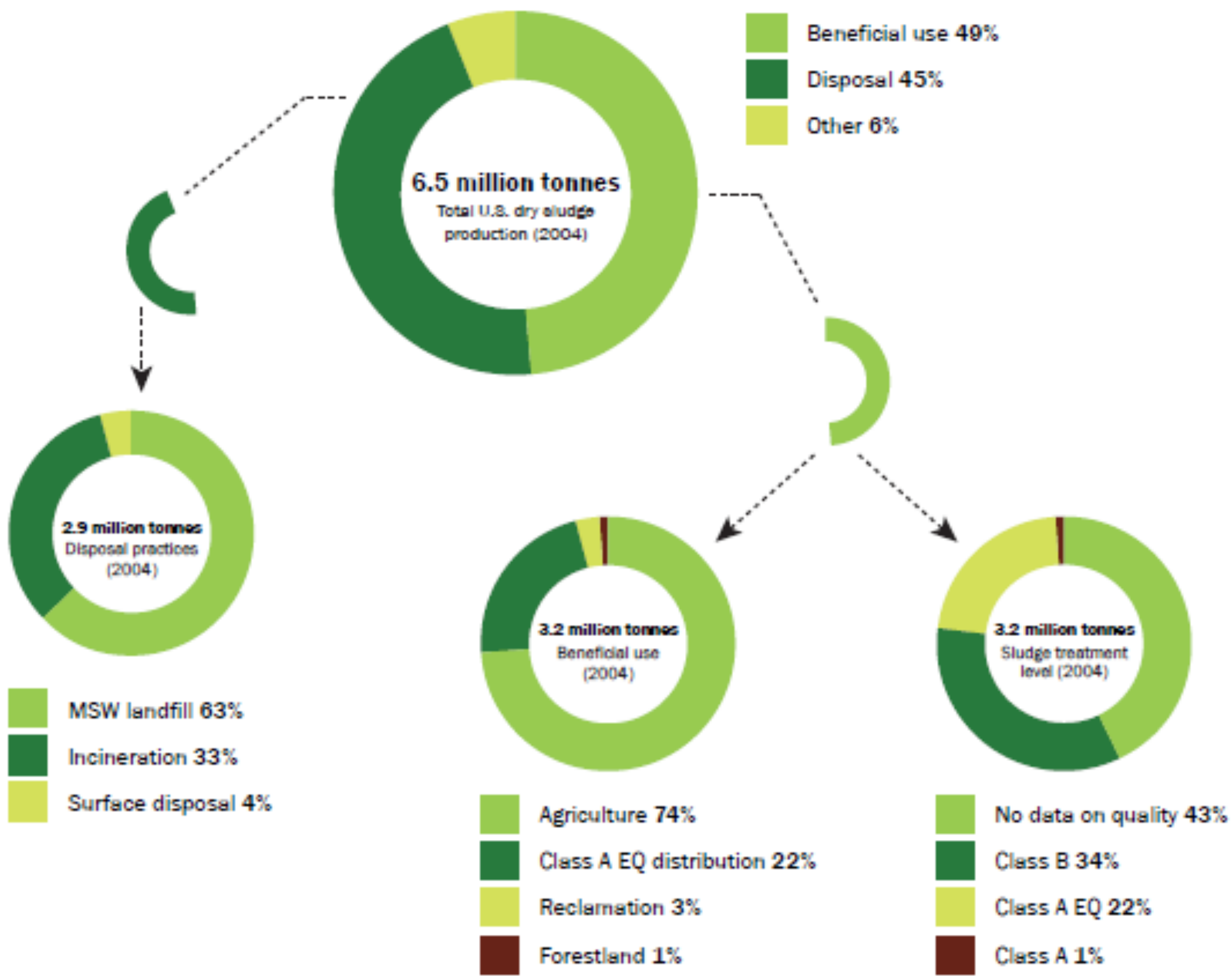
Reduce soil erosion




Source: Dryland wheat, WA (Pan et al. 2017)

# Magnitude of PFAS Impacts!




Source: Sludge Management, Opportunities in Growing Volumes, Disposal Restrictions & Energy Recovery , GWI, 2012

# Biosolids Land Application has had its Challenges!

Odors

Persistent public opposition

Land application errors

*…and now PFAS*


# What are PFAS?

Family of manmade fluorinated chains (>3,000 chemicals)

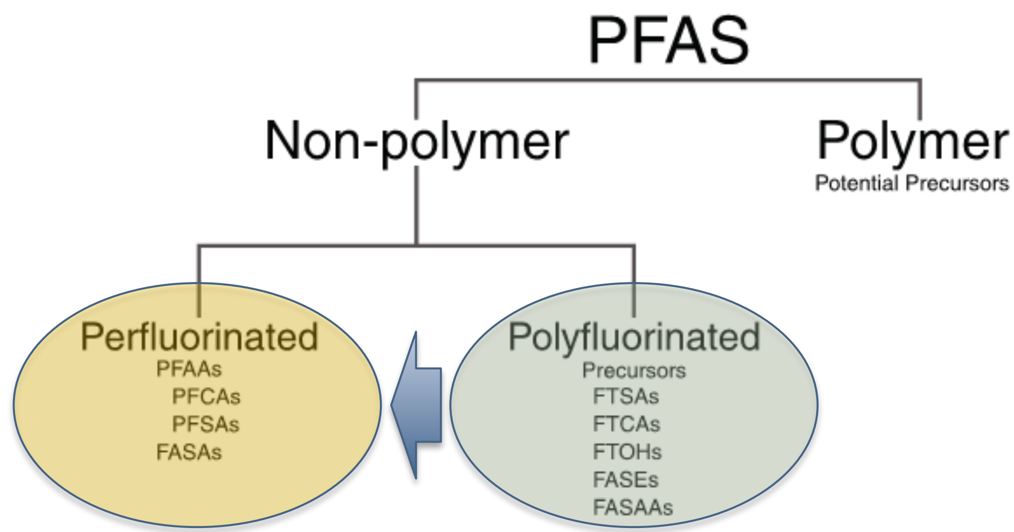
Perfluoroalkyl substances

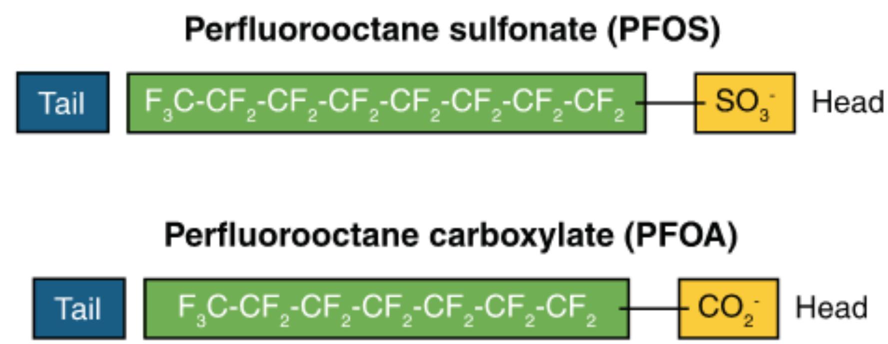
- All H atoms attached to carbon atoms are replaced by F atoms
- Short chain and long chain PFAS

Polyfluoroalkyl substances

- H replaced by F on at least one C atoms
- Some can degrade to PFAA

*Terminal degradation products (biotic and abiotic) of precursor chemicals*




Source: ITRC Factsheet, Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS)

# PFAS Discovery and Manufacturing History

| PFAS[1] | Development Time Period | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1930s | 1940s | 1950s | 1960s | 1970s | 1980s | 1990s | 2000s |
| PTFE | Invented | Non-Stick Coatings | | | Waterproof Fabrics | | | |
| PFOS | | Initial Production | Stain & Water Resistant Products | Firefighting foam | | | | U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2]) |
| PFOA | | Initial Production | Protective Coatings | | | | | |
| PFNA | | | | | Initial Production | Architectural Resins | | |
| Fluoro-telomers | | | | | Initial Production | Firefighting Foams | | Predominant form of firefighting foam |
| Dominant Process[3] | | Electrochemical Fluorination (ECF) | | | | | | Fluoro-telomerization (shorter chain ECF) |
| Pre-Invention of Chemistry / | | | Initial Chemical Synthesis / Production | | | Commercial Products Introduced and Used | | |

**Notes:**
1. This table includes fluoropolymers, PFAAs, and fluorotelomers. PTFE (polytetrafluoroethylene) is a fluoropolymer. PFOS, PFOA, and PFNA (perfluorononanoic acid) are PFAAs.
2. Refer to Section 3.4.
3. The dominant manufacturing process is shown in the table; note, however, that ECF and fluorotelomerization have both been, and continue to be, used for the production of select PFAS.

**Sources:** Prevedouros et al. 2006; Concawe 2016; Chemours 2017; Gore-Tex 2017; US Naval Research Academy 2017

**Commercial and Consumer Products Containing PFAS:**

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

Source: ITRC Factsheet, History and Use of Per- and Polyfluoroalkyl Substances (PFAS)

# Environmental and Human Impacts

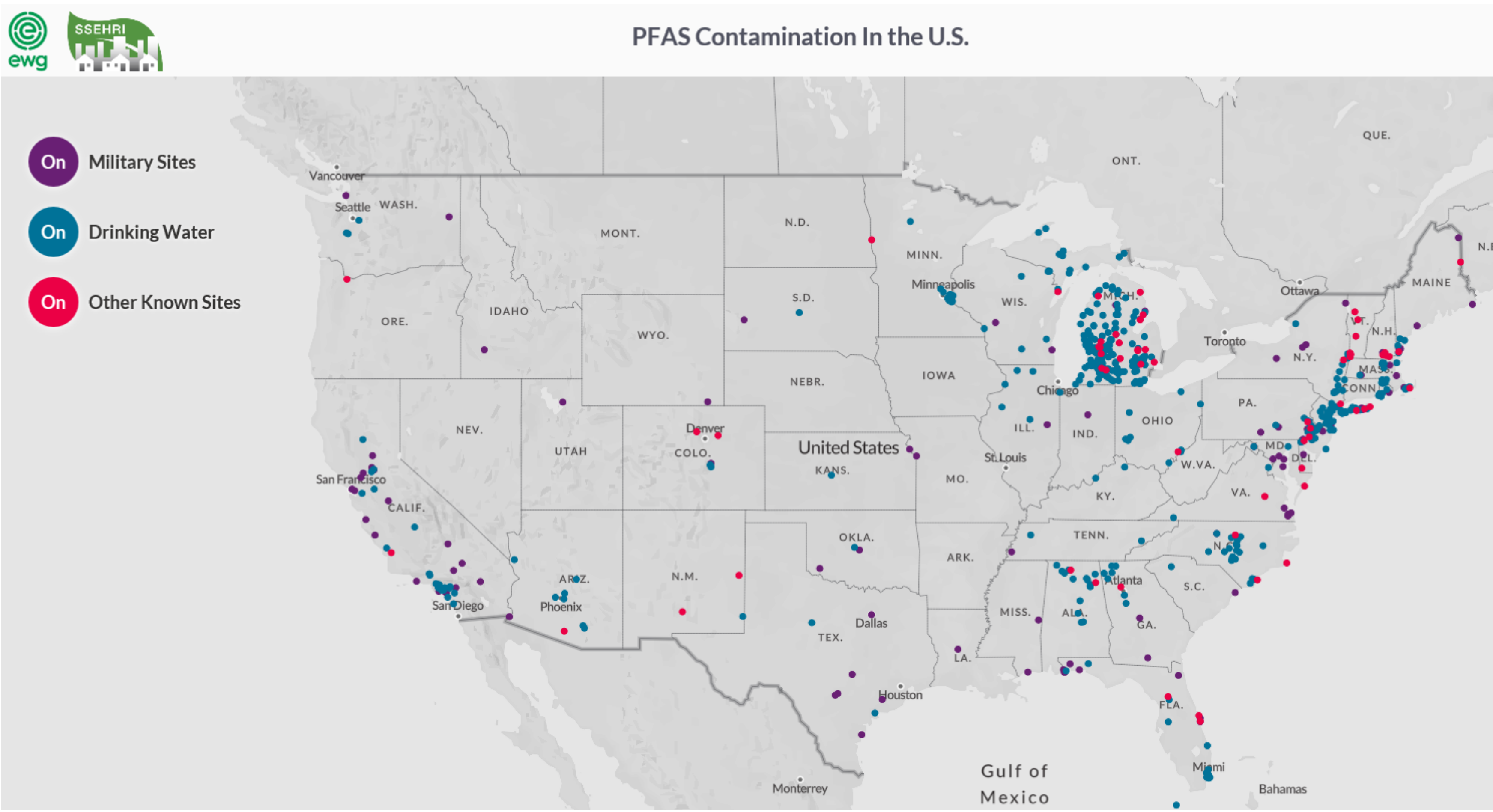
- PFAS are persistent in the environment
- Humans are often exposed to PFAS through food, dust, consumer products, clothing, and water
  - Half life in humans is several years (slow elimination)
  - Exposure is cumulative
- Longer-chain molecules bioaccumulate more than shorter chain molecules
  - Phase-out of PFOS and PFOA
  - Manufacturers simply switch to shorter chain PFAS
  - Short-chain PFAS are MORE CHALLENGING to treat

# Health Effects

Reproductive and developmental, liver and kidney, and immunological effects in laboratory animals. Both chemicals have caused tumors in animal studies. The most consistent findings from human epidemiology studies are increased cholesterol levels among exposed populations, with more limited findings related to:

- Infant birth weights,
- Effects on the immune system,
- Cancer (for PFOA), and
- Thyroid hormone disruption (for PFOS).

# PFAS is a National Issue

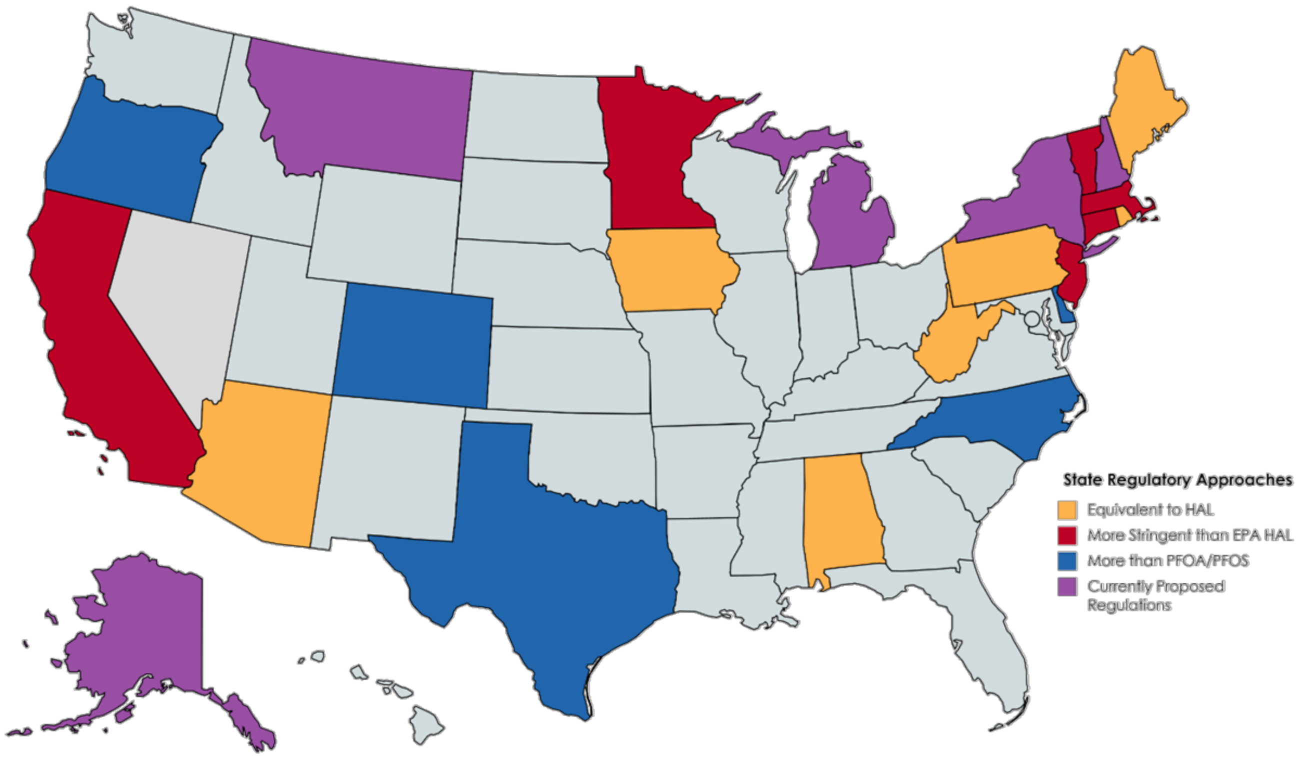



https://www.ewg.org/interactive-maps/2019_pfas_contamination/map/

# State PFAS Drinking Water Regulations Impact Biosolids Land Application

| State | Standards/Guidelines |
|---|---|
| Alabama | Combined 70 ppt PFOA + PFOS HA (long term exposure) |
| Arizona | Combined 70 ppt PFOA + PFOS |
| California | 14ppt PFOA, 13ppt PFOS Notification Limit |
| Colorado | Combined 70 ppt PFOA + PFOS (HA and GWQ standard) |
| **Connecticut** | **70 ppt total Alert Level (PFOS, PFOA, PFNA, PFHxS, PFHpA)** |
| Delaware | Combined 70 ppt PFOA + PFOS HA (PFBS GW standard) |
| Iowa | Combined 70 ppt PFOA + PFOS (GW standard) |
| **Maine** | **Combined 70 ppt PFOA and PFOS** |
| **Massachusetts** | **70 ppt total Guidance Values (PFOS, PFOA, PFHxS, PFNA and PFHpA)** |
| Michigan | Combined 70 ppt PFOA and PFOS, 11ppt PFOS in Surface Water |
| Minnesota | 35 ppt PFOA, 27 ppt PFOS Health Based Levels (+ PFBA, PFBS, PFHxS*) |
| Montana | Health Advisory for PFOA (41 ppt), PFOS (41 ppt), PFOA + PFOS < 70ppt |
| **New Hampshire** | **Proposed MCL for PFOA (38), PFOS (70), PFOA + PFOS <70, PFNA (23) and PFHxS (85)** |
| New Jersey | 14 ppt PFOA (MCL), 13 ppt PFOS (MCL), 13 ppt PFNA (MCL) |
| **New York** | **MCL expected soon (10 ppt PFAS, 10 ppt PFOA)** |
| North Carolina | Health Goal:140 ppt GenX |
| Pennsylvania | Combined 70 ppt PFOA + PFOS HA (MCL under review*) |
| **Rhode Island** | **Combined 70 ppt PFOA + PFOS HA** |
| **Vermont** | **Proposed Preventative Action Limit - 20 ppt total for 5 PFAS (PFOA, PFOS, PFHxS, PFHpA, and PFNA)** |
| West Virginia | Combined 70 ppt PFOA + PFOS HA |

# No Consistent Regulatory Approach




Reference: ITRC Fact Sheets

**22 States have or are considering specific guidance or regulations related to PFAS in Drinking Water and/or Groundwater (Beyond EPA HAs)**

# Recent Developments That may Result in Additional Challenges for Biosolids Land Application

The **EPA OIG Report**

– Are Biosolids Safe? Are the Current Part 503 Regulations Protective of Human Health and the Environment?

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF INSPECTOR GENERAL

*Cleaning up and revitalizing land*

**EPA Unable to Assess the Impact of Hundreds of Unregulated Pollutants in Land-Applied Biosolids on Human Health and the Environment**

Report No. 19-P-0002 November 15, 2018

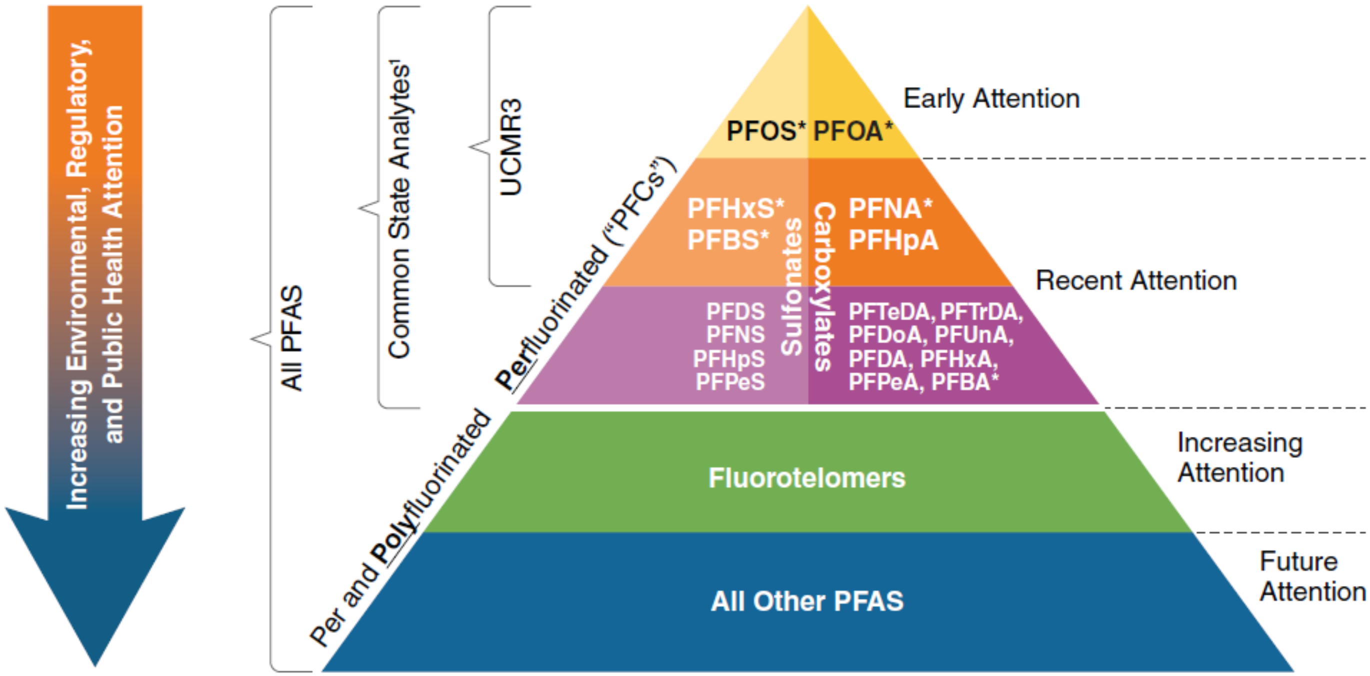
# Un-regulated Pollutants in Biosolids

The EPA identified 352 pollutants in biosolids but cannot yet consider these pollutants for further regulation due to either a lack of data or risk assessment tools. Pollutants found in biosolids can include pharmaceuticals, steroids and flame retardants.

EPA OIG Report dated Nov 15, 2018

- Un-regulated pollutants include:
  - Pharmaceuticals (e.g., ciprofloxacin, diphenhydramine and triclocarban);
  - Steroids and hormones (e.g., campesterol, cholestanol and coprostanol);
  - **Flame retardants. Perfluoroalkyl substances (PFAS)**
- Of the *352 biosolids pollutants*:
  - 32 are hazardous wastes under RCRA (four of which are acutely hazardous)
  - 35 are EPA priority pollutants.
  - 16 are NIOSH hazardous drugs.

# Evolving Regulatory Environment!




*Common regulatory criteria or health advisories
¹Sum of informal poll (NJ, NH, MN)

Thematic and not proportional.
Bottom of triangle indicates additional number of compounds; not a greater quantity by mass, concentration, or frequency of detection.

**Figure 3-1. Emerging awareness and emphasis on PFAS occurrence in the environment**
*(Source: J. Hale, Kleinfelder, used with permission)*

Source: ITRC Factsheet, History and Use of Per- and Polyfluoroalkyl Substances (PFAS)

# State of Maine Imposes a Moratorium on Biosolids Land Application – March 22, 2019

Testing of PFAS (PFOA, PFOS and PFBS) required for all biosolids to be land applied

Initial sampling and testing completed by May 7, 2019

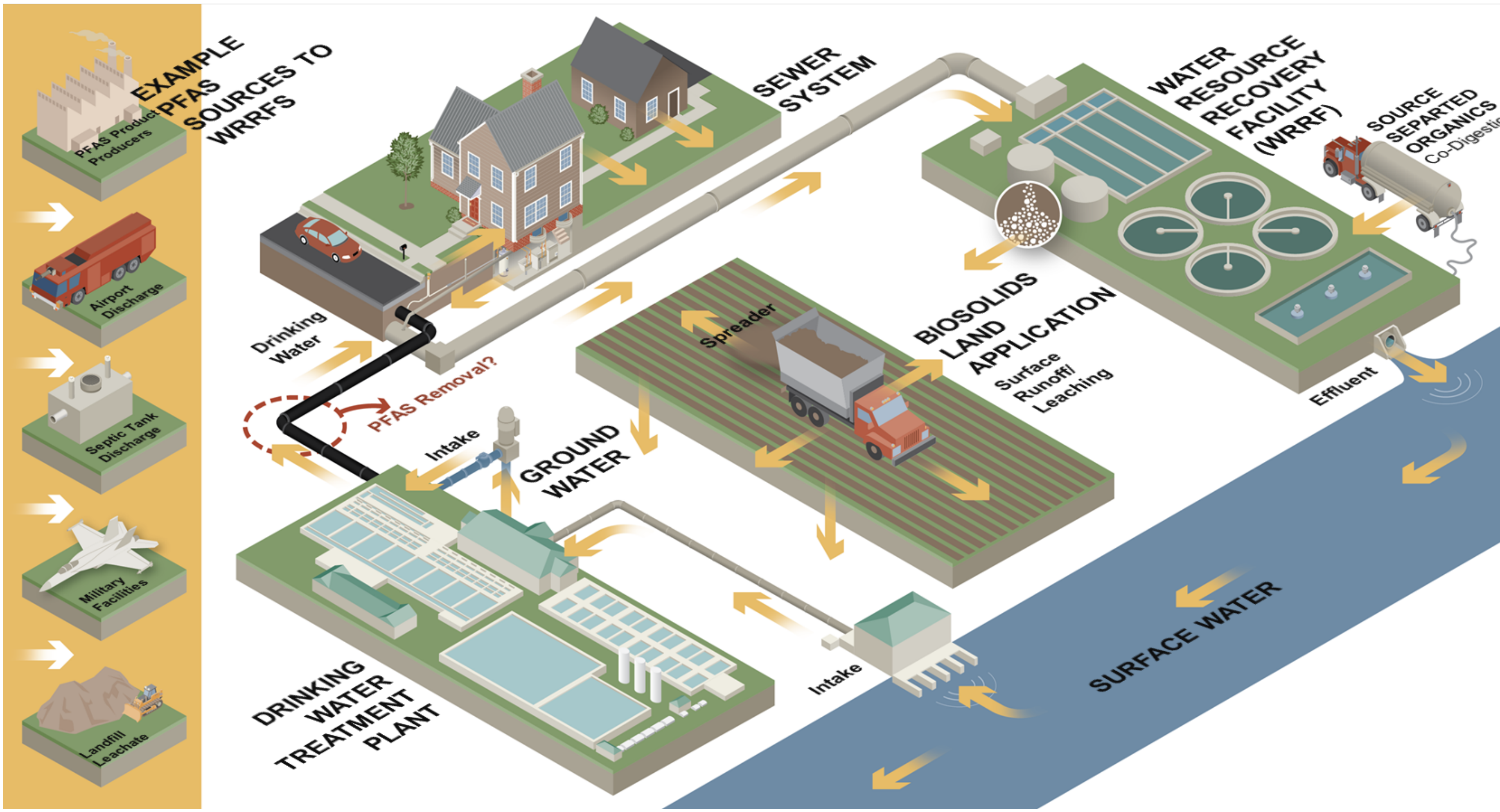
| Screening Concentrations for PFAS in Biosolids (Maine) | |
|---|---|
| PFOA | 0.0025 mg/kg |
| PFOS | 0.0052 mg/kg |
| PFBS | 1.9 mg/kg |

*Other New England and northeast states may consider restrictions on biosolids land application*

# Biosolids Disposal in Landfills

- State level pressures
  - Organic waste diversion
  - Land application limitations
  - Landfill capacity limitations
- Pressure from landfill operators
  - Odors
  - Workability
  - High costs
  - Quantities that can be accepted
  - Nutrients and PFAS

# PFAS is Ubiquitous - Where should it be Removed?



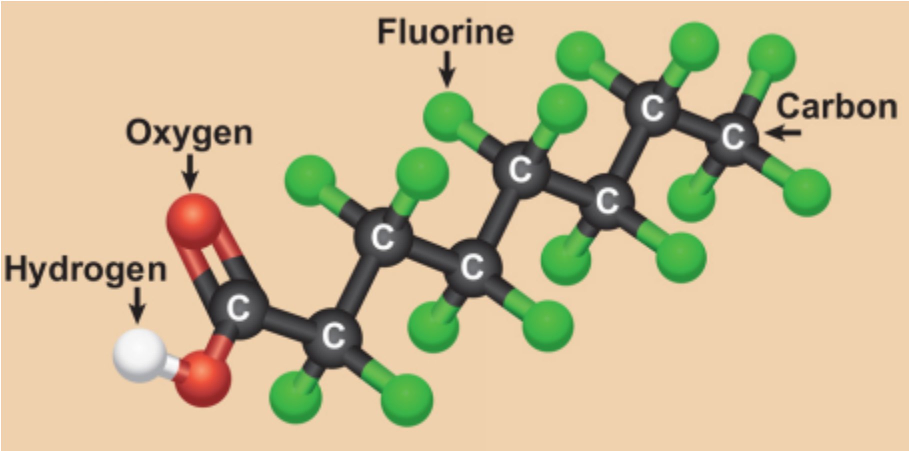
# Treating PFAS Chemical – Difficult to Treat!

Terminal PFAAs are extremely ***stable*** compounds

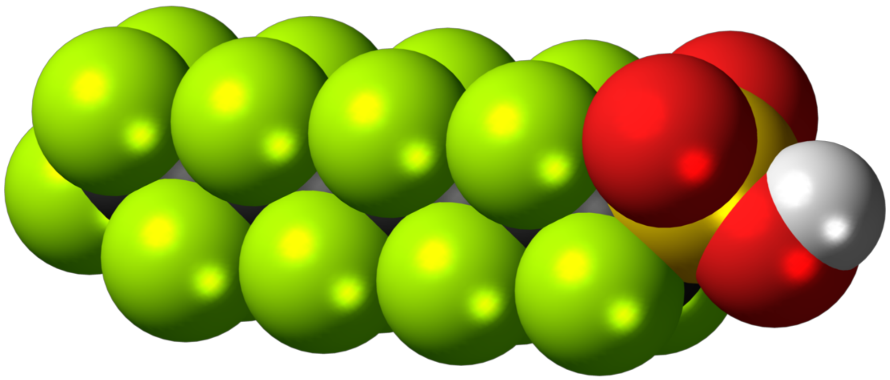
Strong ***C-F bond,*** and ***carbon shielding***

***Thermal destruction*** (mineralization) require temperatures greater than 1,000˚C (1,832˚F).

***Chemical hydrolysis, oxidation and reduction*** is challenging due to the ***fluorine effect!***

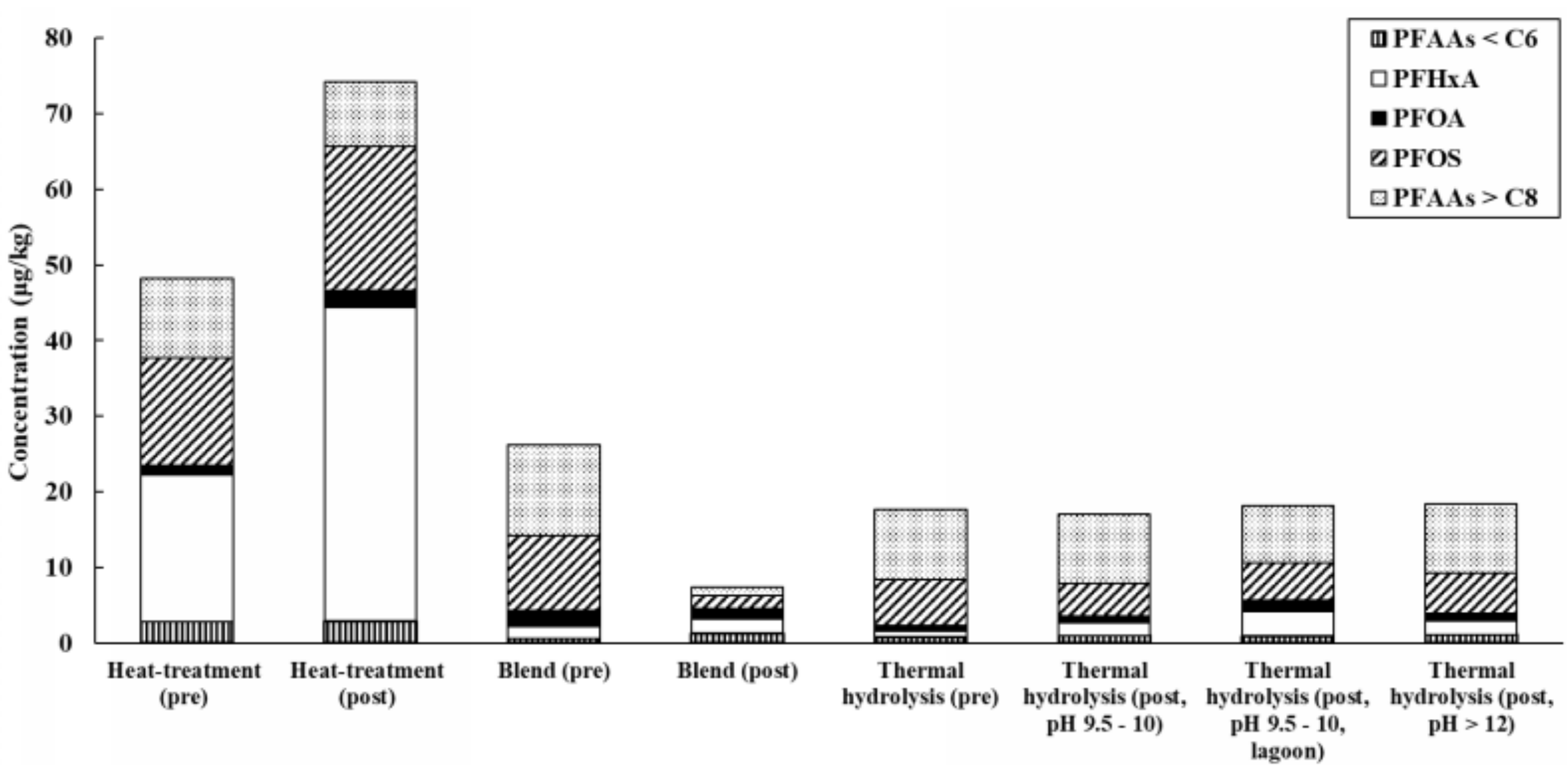



Perfluorooctanoic Acid (PFOA)



# Fate of PFAS through Biosolids Treatment Processes

*Total PFAA Concentrations (μg/kg, dry wt.) for the < 2 mm Fraction of Fertilizers Pre- and Post-Treatment*




Source: Per- and Polyfluoroalkyl Substances in Commercially Available Biosolids-Based Fertilizers: The Effect of Post-Treatment Processes; by Rooney Kim Lazcano, Chloe de Perre, Michael L. Mashtare and Linda S. Lee. Presented at the WEF/IWA Residuals and Biosolids Conference 2019.

# Thermal Processes

## Potential to Treat/Destruct/Remove PFAS from Biosolids

### Combustion:

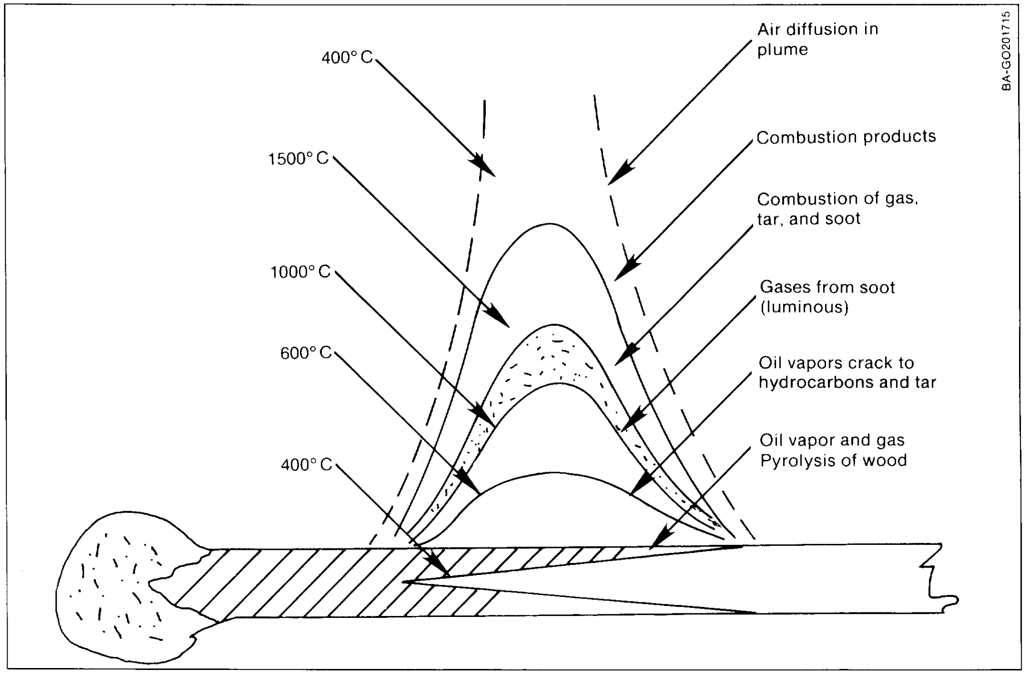
Biomass +Stoichiometric Oxygen → Hot combustion products

### Pyrolysis:

Biomass + Heat → Biochar, oil, gas

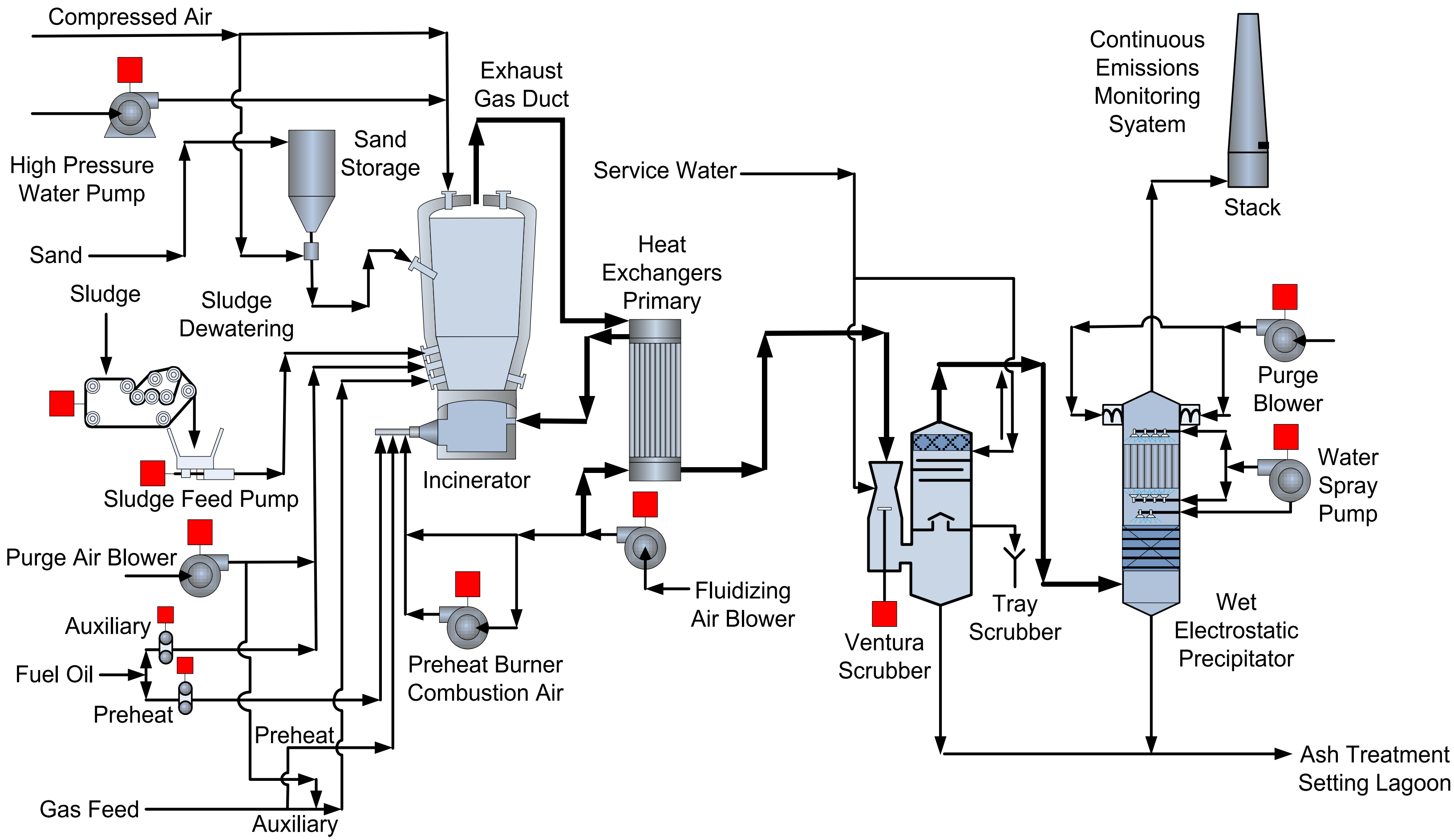
### Gasification:

Biomass + Limited Oxygen → Syngas, Biochar



# Sewage Sludge Incineration

Municipal wastewater sludge incinerators typically operate at ***1,450°F to 1,550°F.***

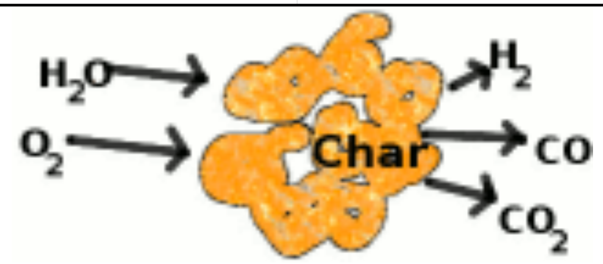


# Gasification and Pyrolysis

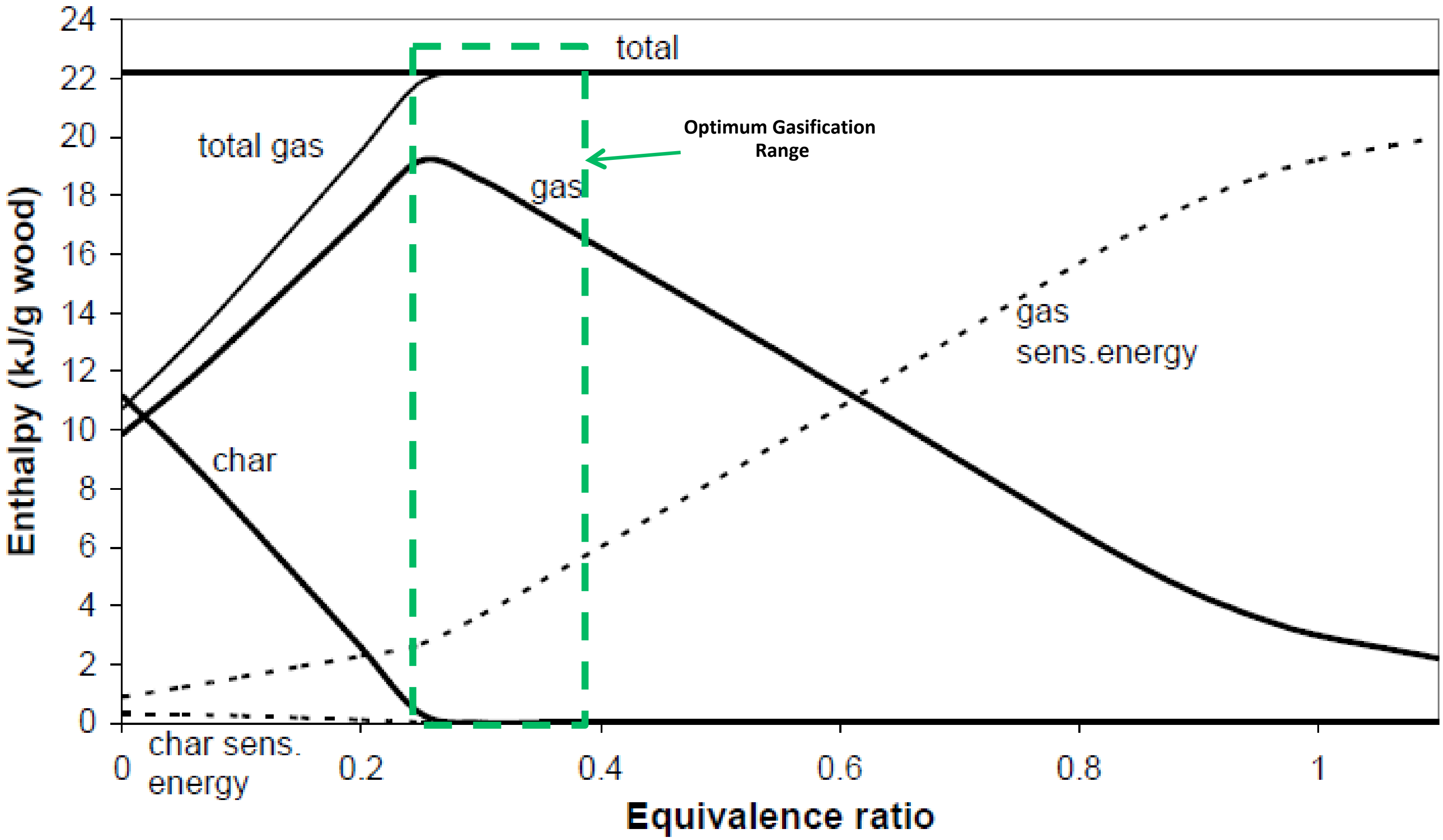
## Emerging Thermal Processes

Technologies that use advanced thermal and chemical processes to convert the carbon-based fraction of a waste stream into a renewable fuel (syngas) which can then be used to produce heat, electricity, chemicals and/or liquid fuels

| Technologies | |
|---|---|
| **Gasification** | **Pyrolysis** |
| 1,400 – 2,500°F | 750 – 1,650°F |
| Limited supply of oxygen | In absence of free oxygen |
| Ash with some char | Char |
| | |

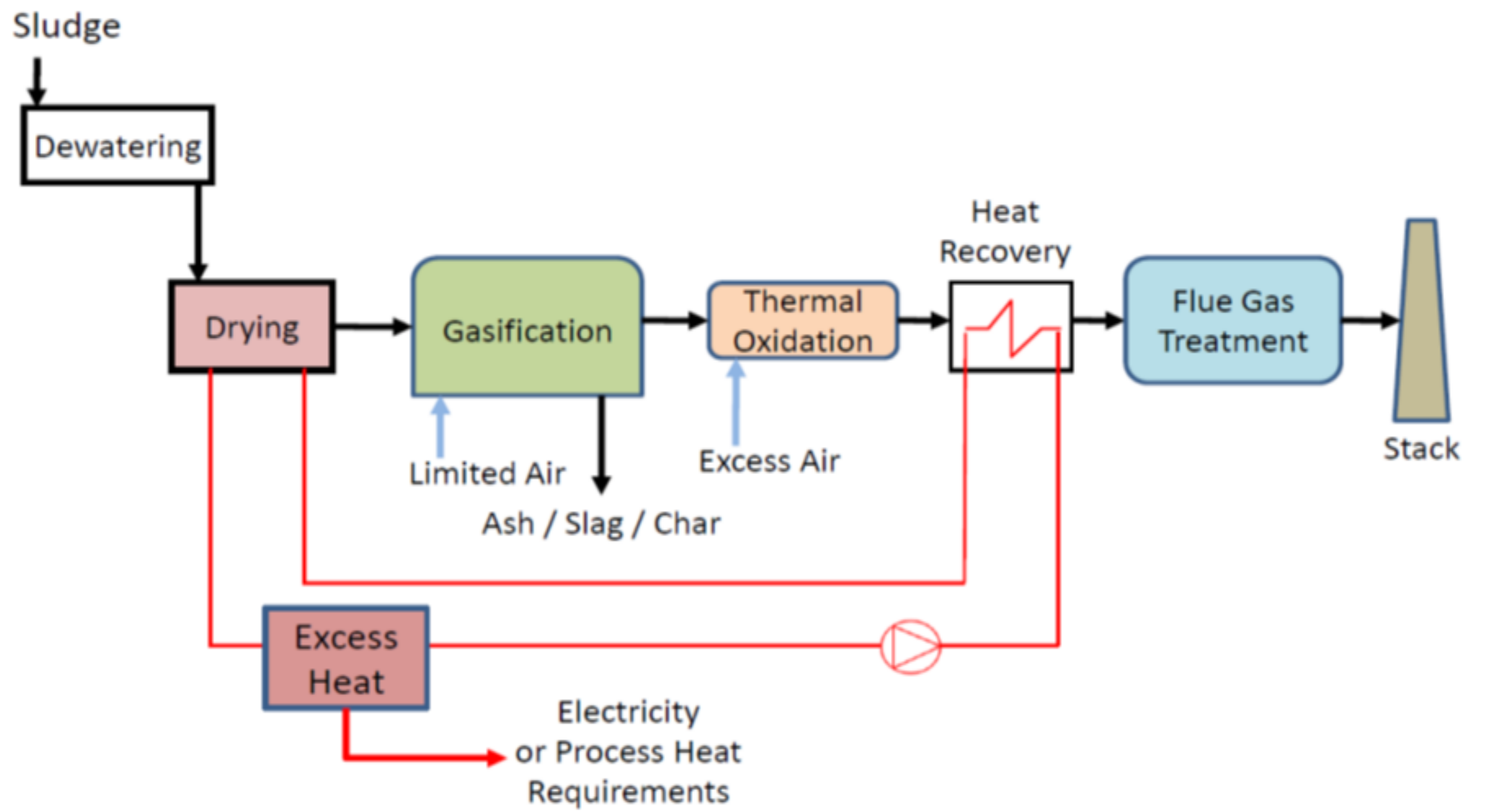


# Energy Balance – Gasification using Air



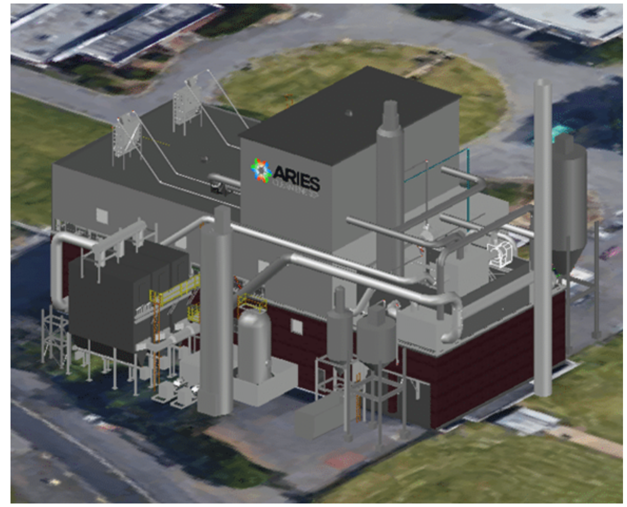

Source: Prins, M.J., Thermodynamic analysis of biomass gasification and torrefaction, 2005

# Closed Couple Gasification System Reaching Commerical Scale



# Biosolids Gasification and Pyrolysis Facilities Across US

Silicon Valley Clean Water, CA – Biologicial Drying + Pyrolysis
Courtesy: **BioForceTech Corporation**




Linden Roselle Sewerage Authority, NJ – Gasification
Courtesy: **Aries Clean Energy**

Morrisville, PA – Drying + Gasification
Courtesy: **Ecoremedy, LLC**

# Biochar Provides Diversification

| Use | Biochar | Biosolids Cake |
|---|---|---|
| |  |  |
| **Landfill** | **X** | **X** |
| **Soil Amendment** | **X** | **X** |
| **Potting Soil** | **X** | |
| **Fuel Source** | **X** | |
| **Mine Reclamation** | **X** | **X** |
| **Retail Sale** | **X** | |
| **Nutrient Recovery** | **X** | **X** |
| **Insulation** | **X** | |
| **Air and Water Purification** | **X** | |

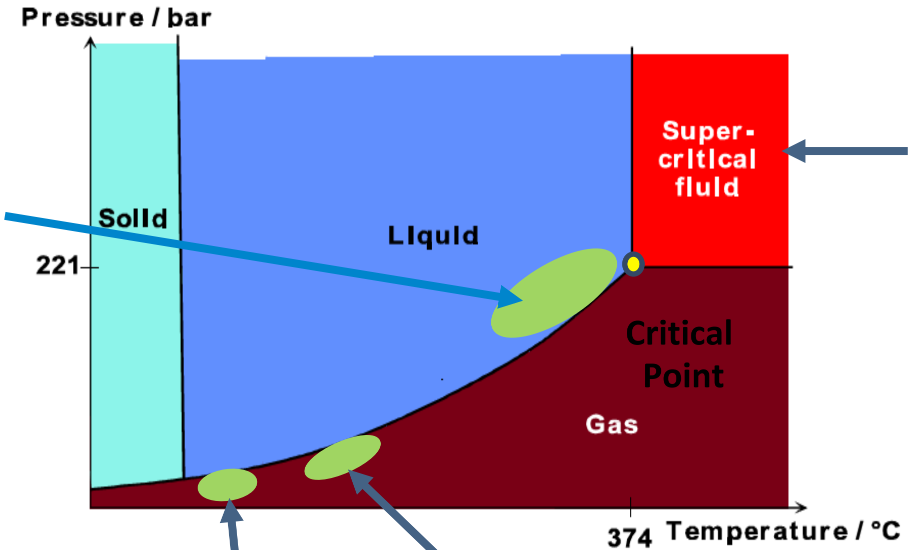
# Can Emerging Technologies Help Treat PFAS in the Future?

*Produce better quality, stable and marketable biosolids, and diversification to produce valuable products!*

| Wet Solids Based Technologies |
|---|
| • Hydrothermal liquefaction |
| • Hydrothermal carbonization |
| • Thermal hydrolysis (intermediate and post anaerobic digestion) |
| • Thermal and chemical hydrolysis |
| • Supercritical water oxidation |

# Can Wet Solids Based Technologies Treat PFAS?

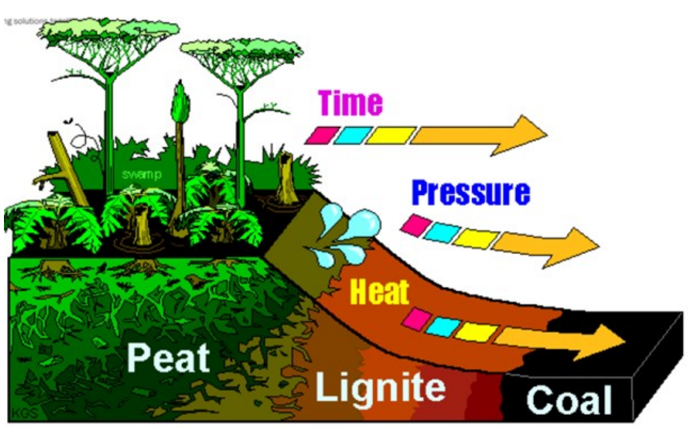
Uses subcritical water stage to treat wet organics in wastewater sludge. Produce value added products (biocrude oil and natural gas) – ***Hydrothermal liquefaction***




Supercritical water behaves as both a gas and a liquid and thus provides the condition for rapid diffusion and increased solubility of organics. – ***Supercritical water oxidation***

Thermal and chemical hydrolysis

Superheated steam used to promote hydrolysis and carbonization to form char and coke (carbon is conserved) – ***Hydrothermal carbonization***




10.000 years ⟶ 100.000 years+

# Take Aways

- **Near to short term (up to 2021/2022)**
  - Plan for increase in biosolids management costs. ***Flexibility*** is key as biosolids end use outlets will reduce or will be farther away.
  - Investigate sources of PFAS to your WRRF
  - Is source control an option?
  - Regulatory environment for biosolids is uncertain
  - Public outreach program to address potential citizen concerns
  - If biosolids are land applied than consider demonstrating that land application is not impacting ambient soil and ground water quality
- **Long Term**
  - Effective **source control**
  - **Thermal technologies** (incineration, gasification, pyrolysis) and other **emerging technologies** likely to gain attention to treat PFAS
  - Interest in **high quality biosolids** or **value-added products** (biochar, bio-oil, etc.)

# Acknowledgements

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Northeast Biosolids and Residuals Association

# Thank You


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