United States Environmental Protection Agency

Session 6: PFAS Treatment in Biosolids – *State of the Science*

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US EPA Office of Research and Development

PFAS Science Webinars for EPA Region 1 and State & Tribal Partners

September 23, 2020

Wastewater Treatment and Land Application of Biosolids/Wastes

Problem: Lack of knowledge regarding end-of-life management of PFAS-containing consumer and industrial products in wastewater

Action:

- Characterize wastewater and relate discharge streams (e.g., municipal and industrial wastewater, land applied waste streams)
- Evaluate efficacy of existing management technologies to manage end-of-life disposal (e.g., land application of biosolids, sewage sludge incineration)
- Evaluate performance and cost to manage these waste streams and environmental PFAS releases

Results: Provide technologies, data and science-based tools to manage wastewater

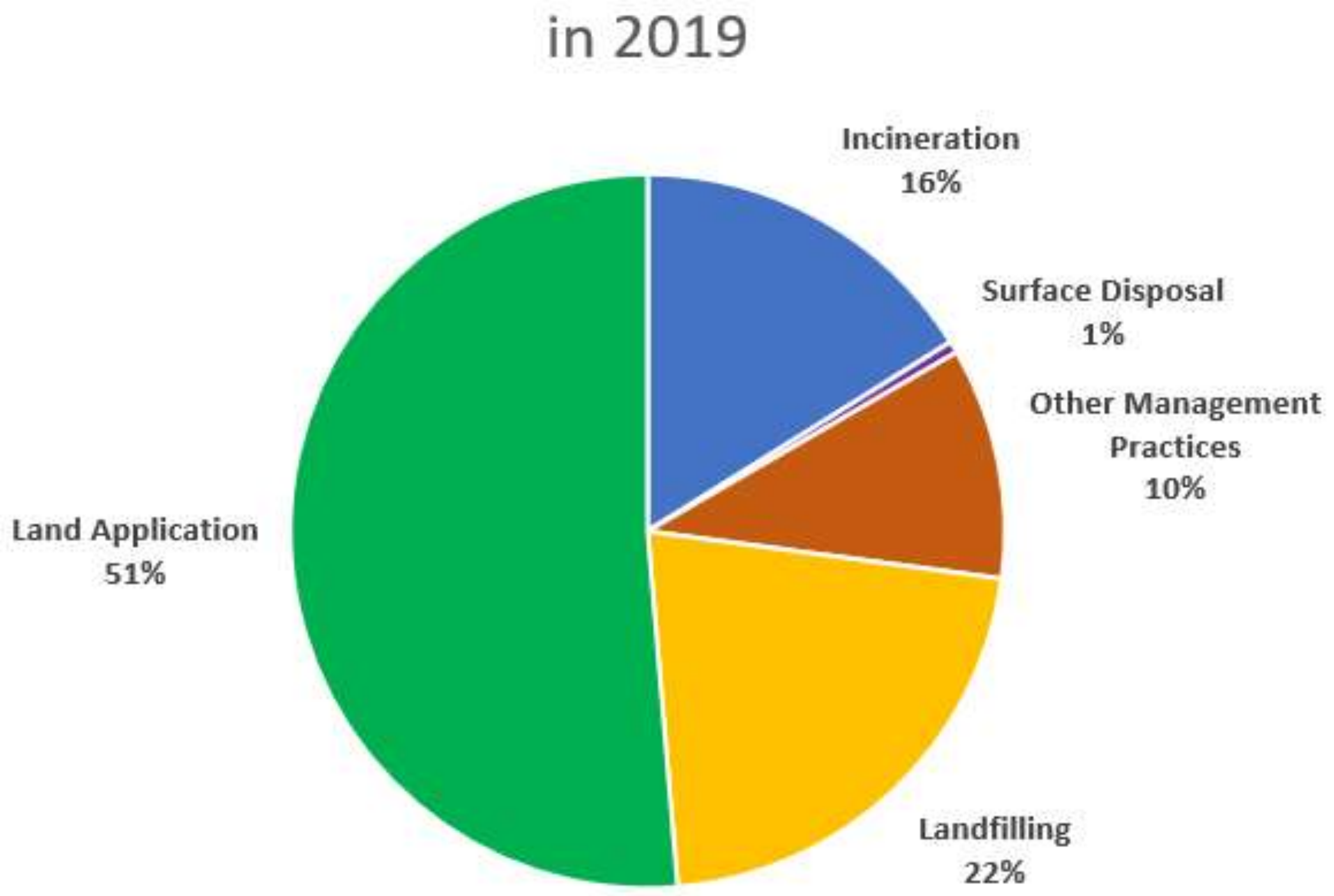
Impact: *Responsible officials, utilities and municipalities will be able to manage PFAS-containing waste streams*

Daily Production of Biosolids/residuals

- >15,000 Publicly Owned Treatment Works (POTW) in the US
- Majority of land application occurs in eastern US where depth to groundwater is relatively shallow

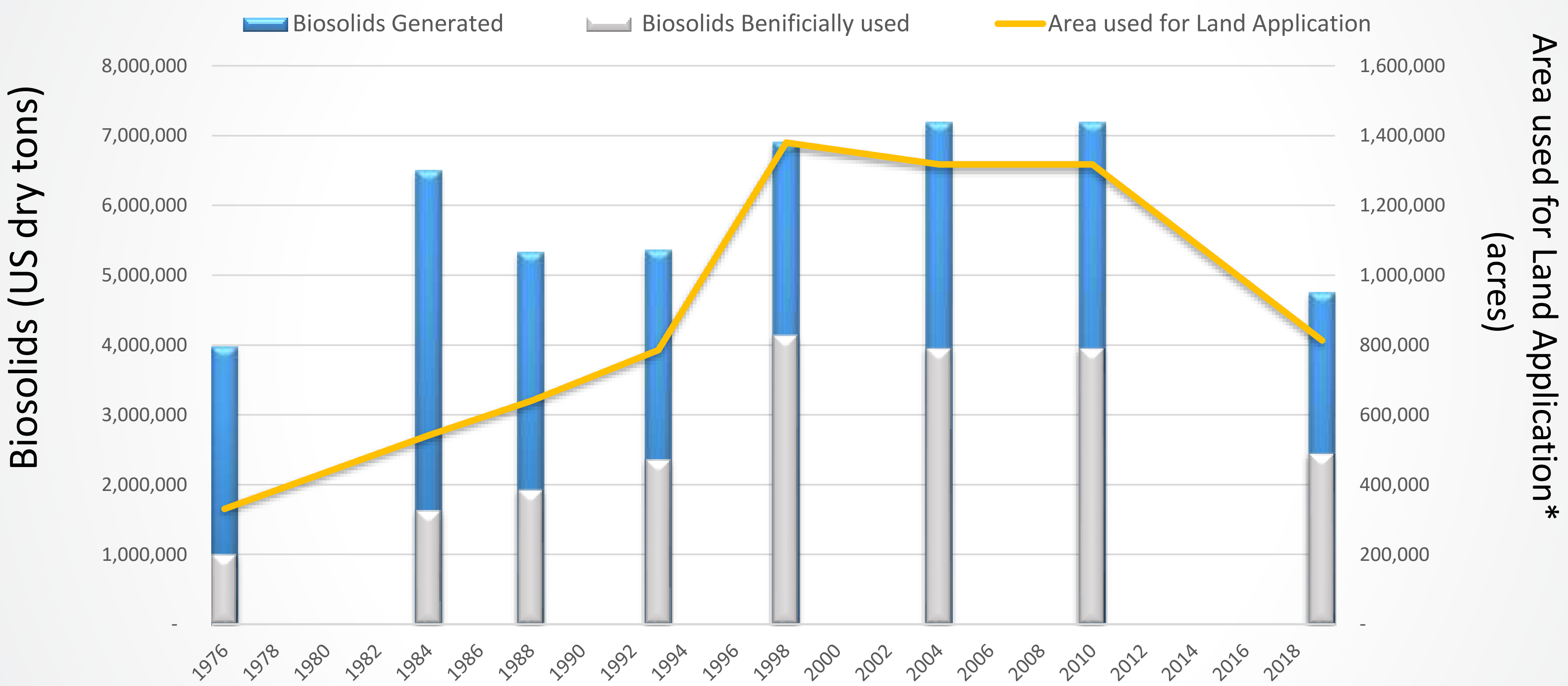
T. Seiple, et al., J.Environ.Manage. 197 (2017) 673-680

Biosolids Use & Disposal



2019 EPA electronic reporting data available [Enforcement and Compliance History Online (ECHO)]

Biosolids Generated compared to Land Applied Beneficial Reuse



- Sewage sludges applied pre-regulations (1980s)
- Many fields have 20+ years of biosolids land application
- **Other wastes are also land applied** – pulp/paper sludge, concentrated animal feeding operation (CAFO) wastes, refinery/industrial wastes, drinking water residuals, etc.

Data source - References 1 and 2

PFAS Fate and Transport for WWTPs & Biosolids

Wastewater Treatment Plants (WWTPs) may introduce PFAS into the environment through:

- Effluent discharge to surface water
- Land application of biosolids and disposal of residuals
- Air emissions

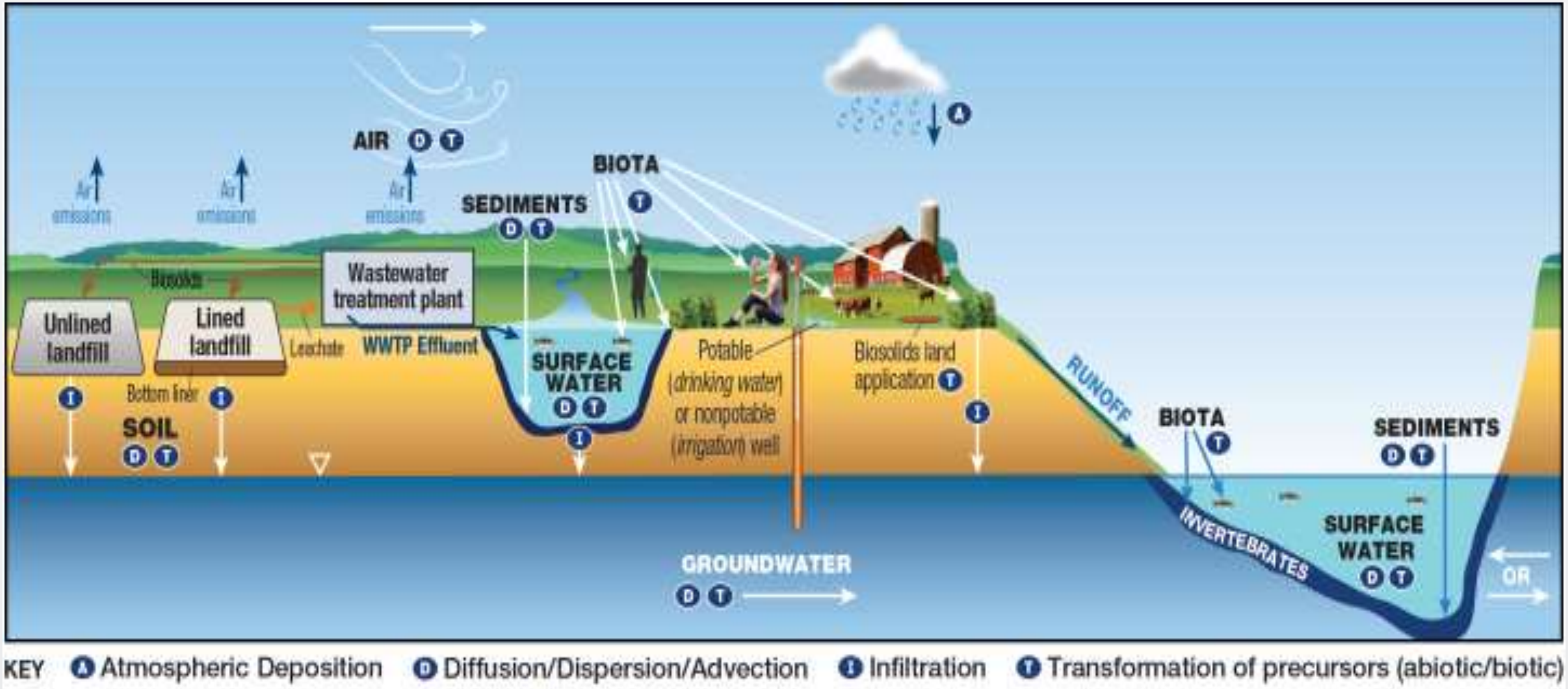
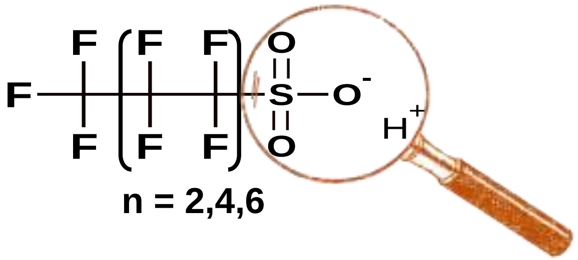


Figure 3. Conceptual site model for landfills and WWTPs.

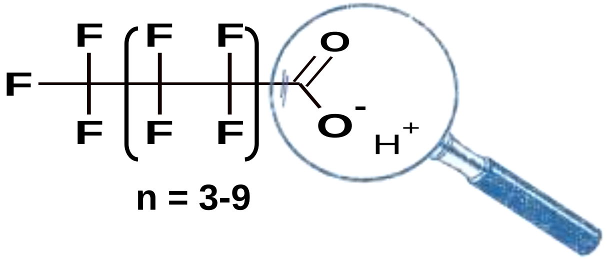
Common PFAS Chemical Structures

- Perfluorinated



Perfluoro<u>sulfonic Acids</u> (PFSAs)

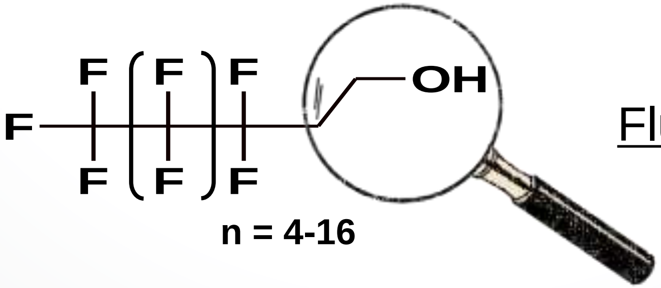
PFBS, PFHS, PFOS



Perfluoro<u>carboxylic Acids</u> (PFCAs)

C_6 acid – C_{12} acid
PFOA C8 acid

- Polyfluorinated



<u>Fluorotelomer Alcohols</u>

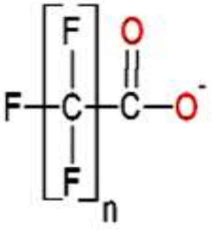
6:2, 8:2 and 10:2

Many PFAS

Perfluoroalkyl Sulfonates

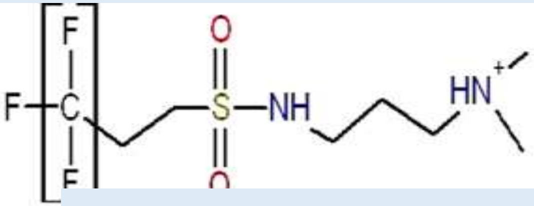
PFBS	n = 4
PFPeS *	n = 5
PFHxS	n = 6
PFHpS	n = 7
PFOS	n = 8
PFNS *	n = 9
PFDS	n = 10

Perfluoroalkyl Carboxylates



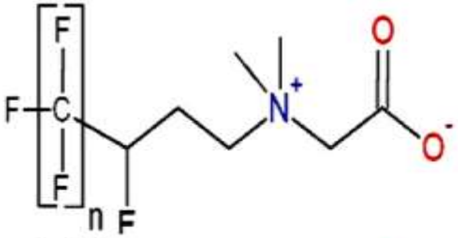
PFBA	n = 4
PFPeA	n = 5
PFHxA	n = 6
PFHpA	n = 7
PFOA	n = 8
PFNA	n = 9
PFDA	n = 10
PFUdA	n = 11
PFDoA	n = 12
PFTrA	n = 13
PFTeA	n = 14

Fluorotelomer Sulfonamide Amines

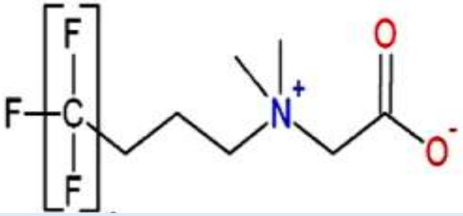


6:2 FtSaAm	n = 6
8:2 FtSaAm	n = 8

Fluorotelomer Betaines

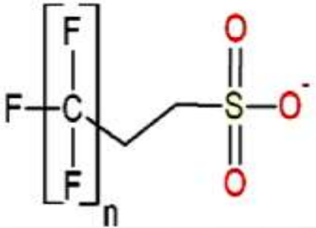


5:1:2 FtB	n = 5
7:1:2 FtB	n = 7
9:1:2 FtB	n = 9



5:3 FtB	n = 5
7:3 FtB	n = 7
9:3 FtB	n = 9

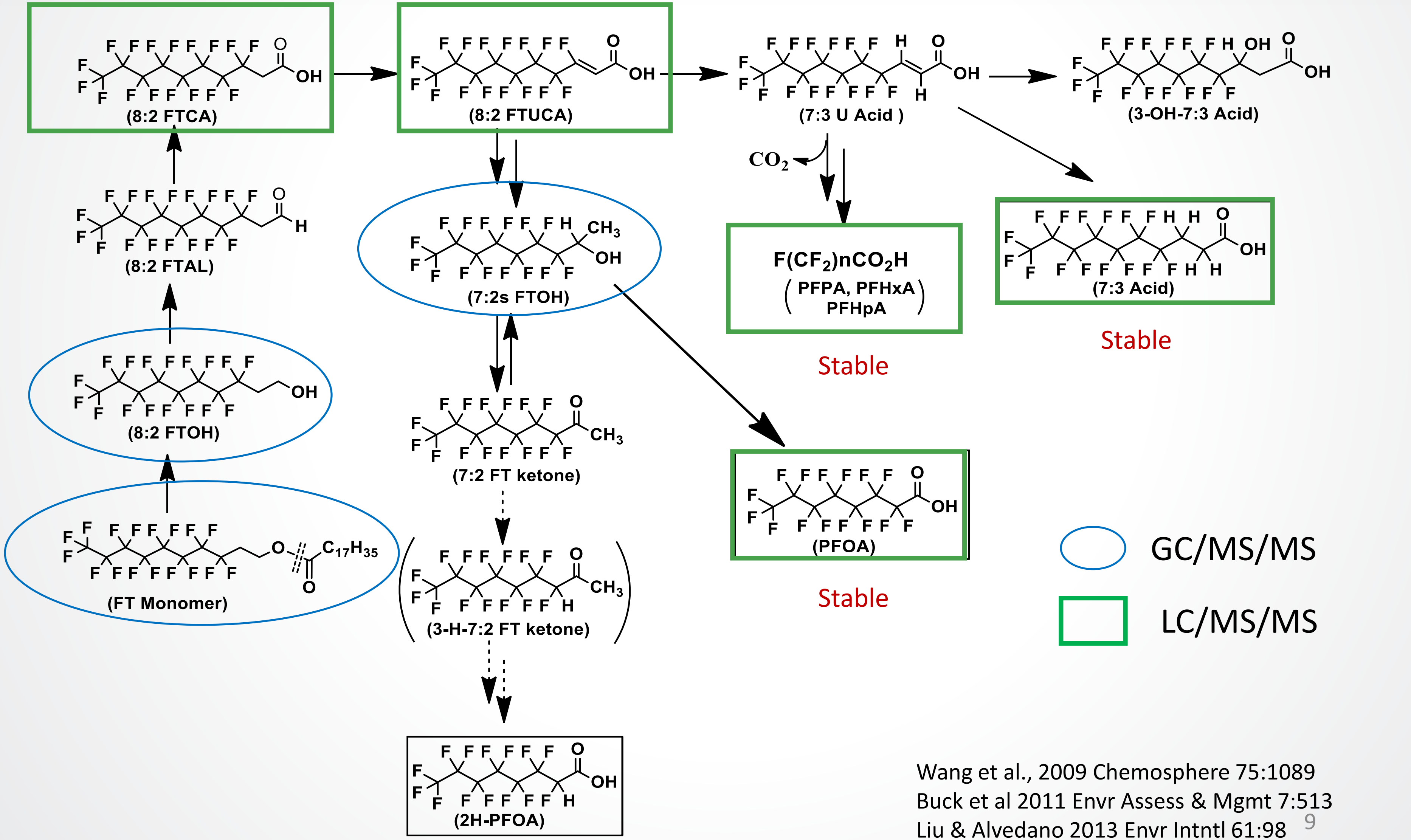
Fluorotelomer Sulfonates



4:2 FtS	n = 4
6:2 FtS	n = 6
8:2 FtS	n = 8

Backe et al. 2013 ES&T 47:5226

Transformation of PFCAs



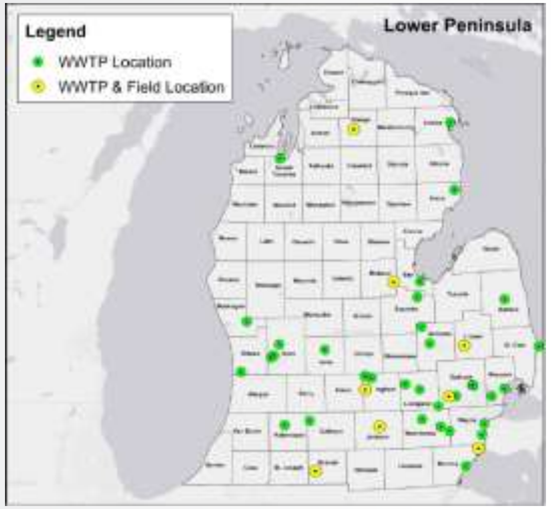
Wang et al., 2009 Chemosphere 75:1089
Buck et al 2011 Envr Assess & Mgmt 7:513
Liu & Alvedano 2013 Envr Intntl 61:98

Reported Concentrations in Biosolids

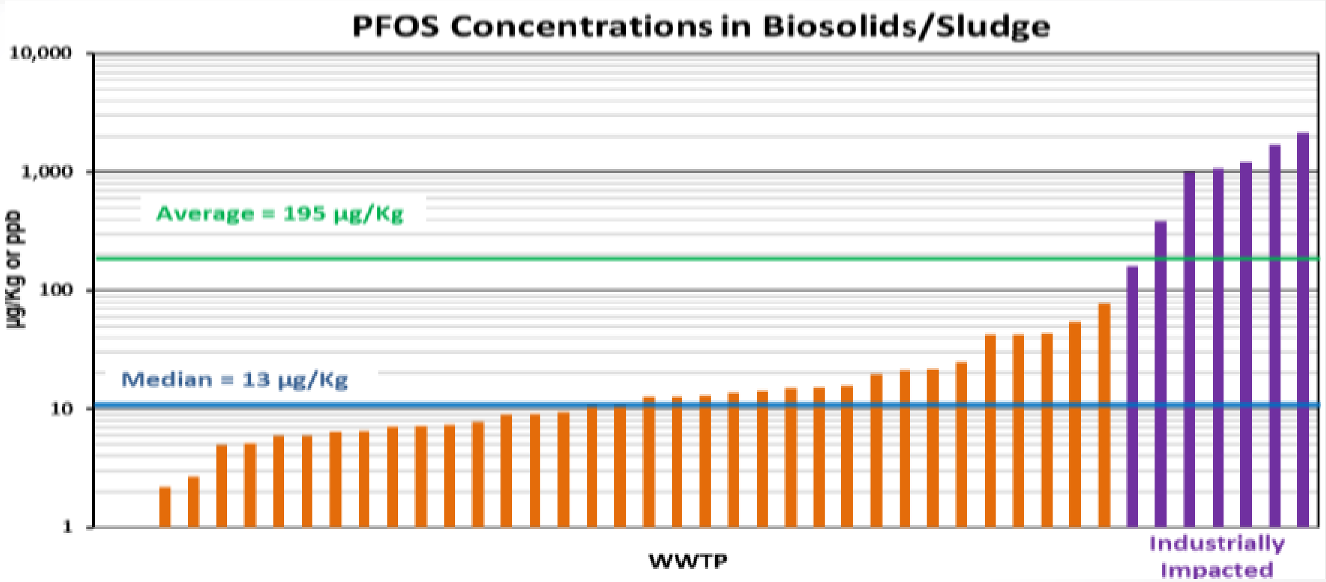
Year Sampled	PFOA (ng/g dry wt)	PFOS (ng/g dry wt)	Reference
2001	12 - 70	308 - 618	Venkatesan, 2013
2004-2007	8 - 68	80 - 219	Sepulvado, 2011
2005	16 - 219	8.2 - 110	Loganathan 2007
2005	18 - 241	<10 - 65	Sinclair, 2006
2006		81 - 160	Schultz, 2006
2006-2007	18 - 69	31 - 702	Yu, 2009
2007	20 -128	32 - 418	Yoo, 2009
2011	1 - 14	4 - 84	Navarro, 2016
2014	10 - 60	30 - 102	Mills, Dasu (in prep)
2018	1-11	2 – 1,100	EGLE, 2020

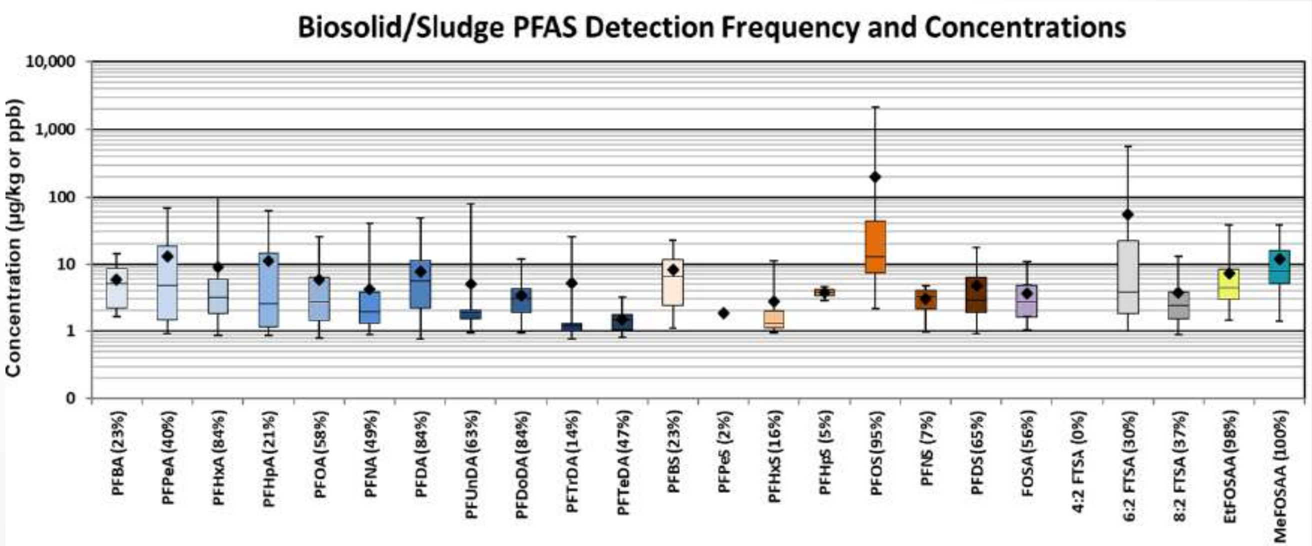
- Does not include other PFAS and precursors that may have been present

Results from Survey of Michigan WWTPs



SUMMARY REPORT:
Initiatives to Evaluate the Presence of PFAS in Municipal Wastewater and Associated Residuals (Sludge/Biosolids) in Michigan. June 2020





Results give a good feel for the PFAS ranges for wastewater plants treating both industrial and non-industrial sources

Research with PFAS and Biosolids

Analytical Methods for PFAS in Wastewater Treatment (WWT) Matrices

- **Analytical Chemistry Methods Development**
  - ORD collaborating with EPA Regions and program offices (OW, OLEM) and other federal agencies (e.g., USGS, USDA, FDA)
  - Target analytes from multiple methods (with more being considered): PFCAs C4-C14; PFSAs C4-C10; 12 precursors and intermediates
  - Non-targeted methods and Total PFAS methods also in development
  - Matrices
    - Environmental waters such as surface water, wastewater (WW) influent and effluent
    - Soils, sludges, biosolids and sediments

- **Past Outputs**
  - EPA Region 5 methods accepted as ASTM methods (ASTM D7979 and ASTM 7968)
  - SW 846 8327 Direct Injection for non-potable waters
    - Multi-laboratory validated method
    - Released as draft method in 2019
    - Final method scheduled to be available by Fall 2020

- **Upcoming Outputs**
  - Evaluating Method 533 for non-potable matrices
  - Conducting methods validation studies for 1600 Series/SW-846 methods for non-potable waters, wastewater, leachate, soils, biosolids, sediments, and tissue samples
    - Single-laboratory validation study underway
    - Multi-laboratory validation study planned

Analytical Methods for PFAS in WWT Matrices

	ASTM 7979-17/ Region 5 method	US EPA SW 846 8327/3215 (draft Multilab Validated)	ASTM 7968/ Region 5 method	US EPA 1600 Series method (in development)
Matrix	Non-potable water	Non-potable water	Solids, soils, sediments, sludges	non-potable waters, solids, & tissue samples
Analytes				
PFCAs	C4-C14	C4-C14	C4-C14	C4-C14
PFSAs	C4-C10	C4-C10	C4-C10	C4-C10
PFSA precursors and intermediates	FOSA; N-EtFOSAA; N-MeFOSAA	FOSA; N-EtFOSAA; N-MeFOSAA	FOSA; N-EtFOSAA; N-MeFOSAA	N-EtFOSAA; N-MeFOSAA; N-MeFOSE; N-EtFOSE; N-EtFOSA; N-MeFOSA
PFCA precursors and intermediates	4:2, 6:2, & 8:2 FTS; 6:2, 8:2, 10:2, & 7:3 FTCA; 6:2 & 8:2 FTUCA	4:2, 6:2, & 8:2 FTS	4:2, 6:2, & 8:2 FTS; 6:2, 8:2, 10:2, & 7:3 FTCA; 6:2, 8:2, & 10:2 FTUCA	4:2, 6:2, & 8:2 FTS
Other PFAS				HFPO-DA; ADONA; 9Cl-PF3ONS; 11Cl-PF3OUdS
Analysis				
Prep	Direct inject	Direct inject	Direct inject	Solid Phase Extraction
Surrogate stds	14	14	14	-
Internal stds	no	no	no	yes
Quantitation	2 SRM and ion ratios	2 SRM and ion ratios	2 SRM and ion ratios	2 SRM and ion ratios
Reporting limit	most 10 ng/L	most 10 ng/L	20 ng/kg	Target 10 ppt or less

Other analytical methods under development

- **Air Measurements**
  - Considering both sampling and analysis methods
  - Monitoring for fugitive emissions, deposition, receptor exposure
  - Ambient/Near-Source – Field deployable Time of Flight/Chemical Ionization Mass Spectrometer for real time detection/measurement
  - Semivolatile and Volatile PFAS, targeted and non-targeted analysis
- **GC-MS/MS analysis of PFAS**
  - Research methods to measure specific PFAS precursors and volatile species
  - Matrices – water, wastewater, and solids
- **Total Oxidizable Precursors (TOP) assay***
  - Available at some contract labs, but lacks a multi-lab validated standard method
  - Estimate of PFAS precursors and intermediates

*Houtz et al 2012 ES&T 46:9342

- **Total Organic Fluorine**
  - Removing the background inorganic F- from the sample is important to make sure that the reported F- is organic
  - High priority for EPA. ORD working with OW-OST to develop a draft method in 2020

Land Application of Biosolids: PFAS uptake into edible parts of plants

EPA Regional Applied Research Effort (RARE) project

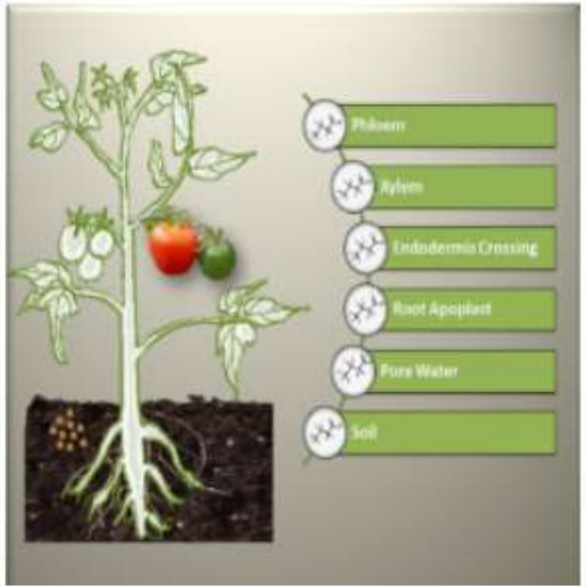
EPA Region 5/Kim Harris, in collaboration with Chris Higgins at Colorado School of Mines

A variety of food crops were grown in soil amended with biosolids

- The biosolids contained PFAAs
- PFAA concentrations in edible portion of the plants were measured.

Conclusions:

- The edible portions had measurable levels of PFOA, among other PFAS
- Data suggest that edible crops grown in soil conventionally amended with municipal biosolids may contain PFAS, and further studies are needed to characterize mechanisms of uptake from various soils and crops

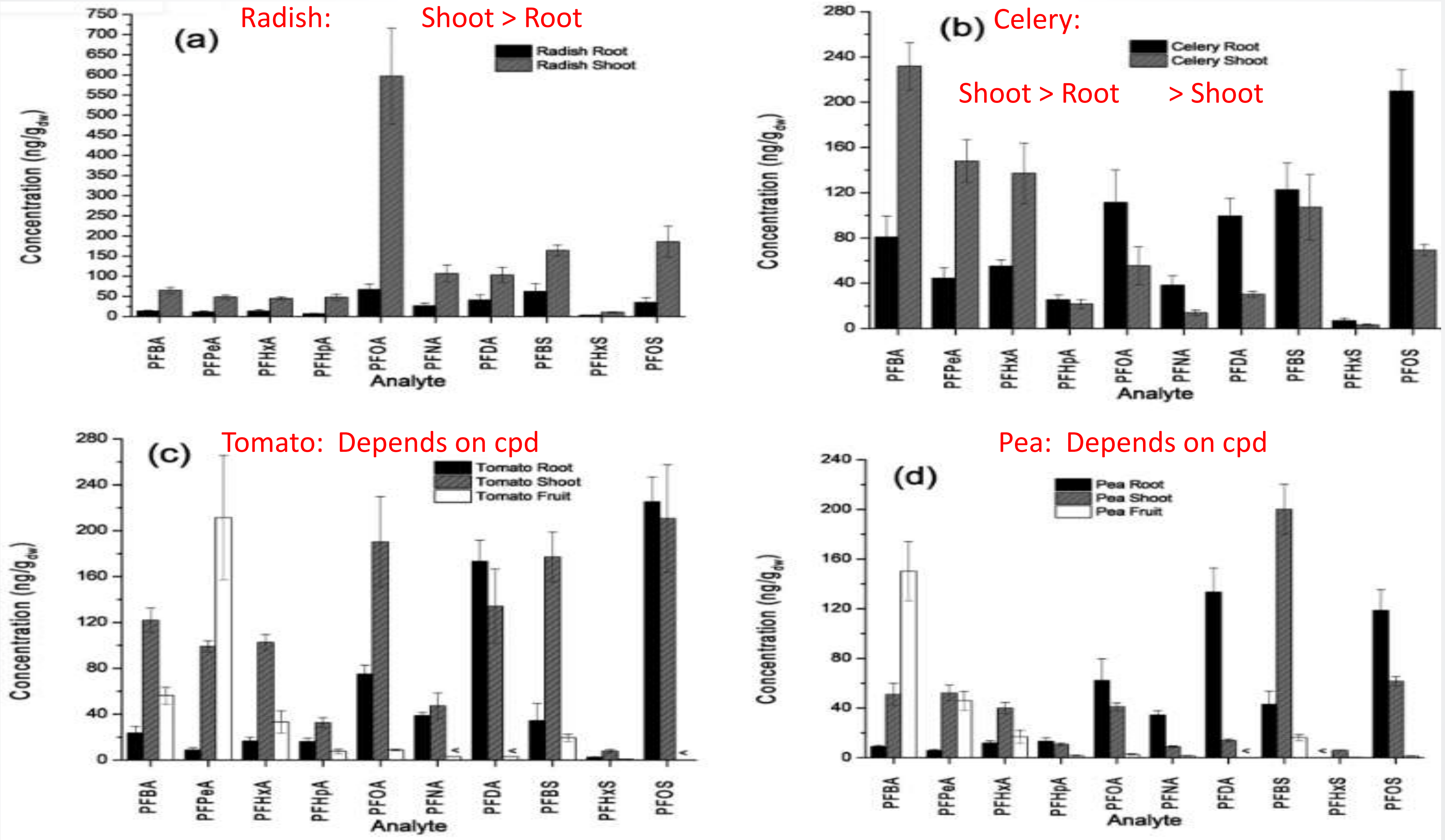


Blaine, et al (2013). ES&T 47(24): 14062-14069
Blaine, et al (2014). ES&T 48(14): 7858-7865.

In 4 plants: **Accumulation in produce from soil amended with biosolids**

Preferential uptake ≤C7 for these plants and analytes

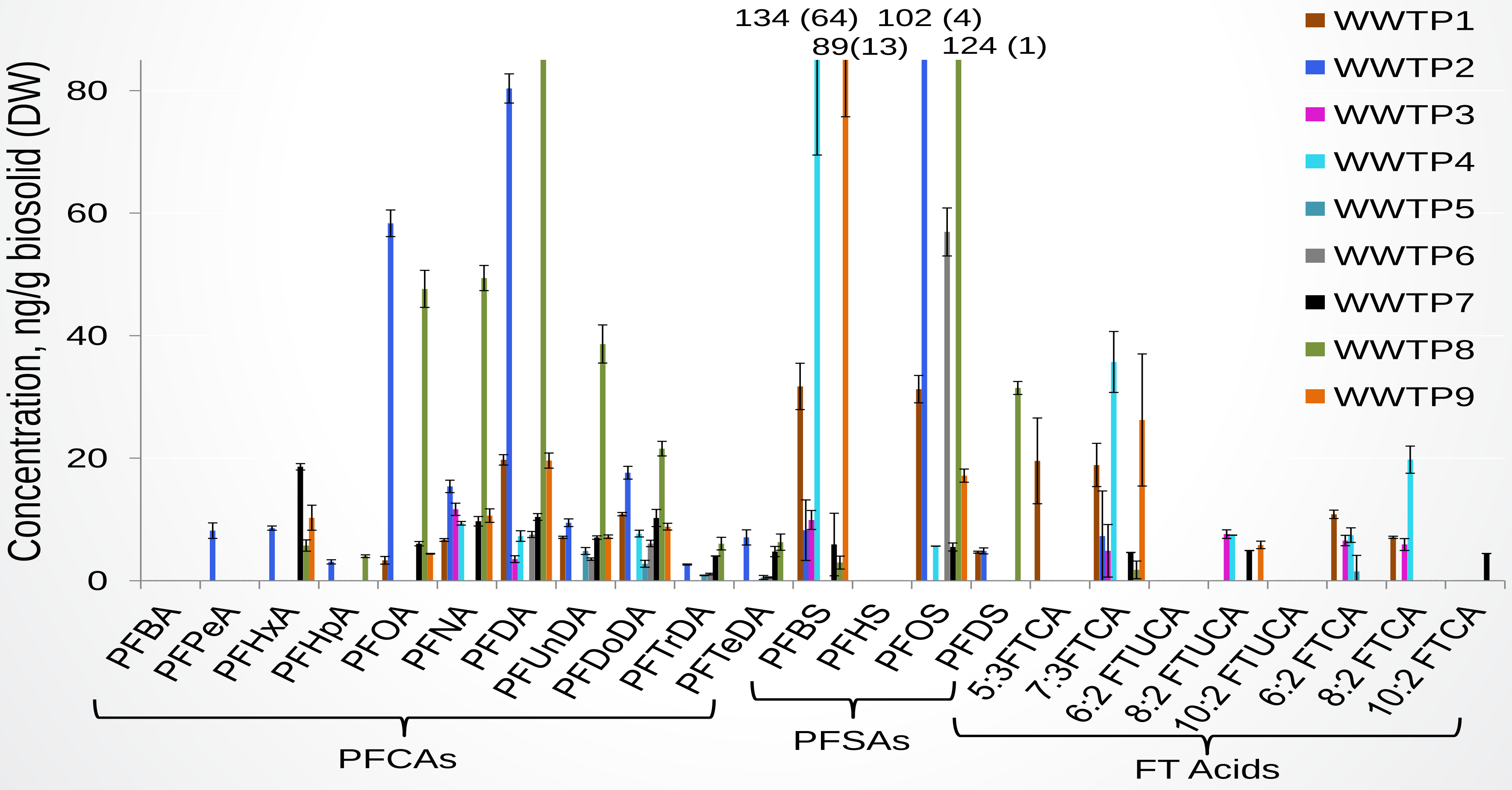
Differential uptake to various compartments within the plant



Summary – In RARE project with Region 6, 9 WWTPs were sampled seasonally

- The solids treatment included anaerobic digestion and aerobic digestion
- Solid residuals and effluent were analyzed for PFAAs, precursors and transformation products

Results – PFAAs and PFAS precursors with varying distributions



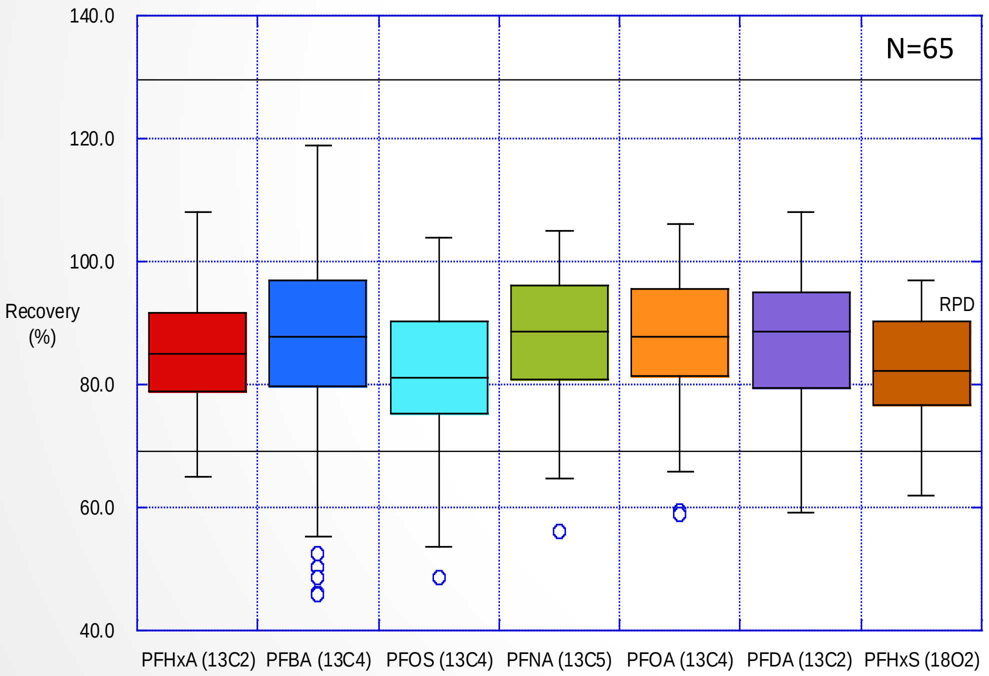
PFAAs concentrations in biosolids collected during fall sampling

Land Applied Materials: Field Site 2

- Evaluate different application methods (liquid and solid biosolids)
- Evaluate natural attenuation for various analytes including PFAS
- Design
  - Controlled site consisting of 20 inches sandy loam soil
  - Planted with fescue/rye grass mix
  - Measure: PFAS, nonylphenol, metals and microbes over year long study
  - Controls: soil only and biosolids only

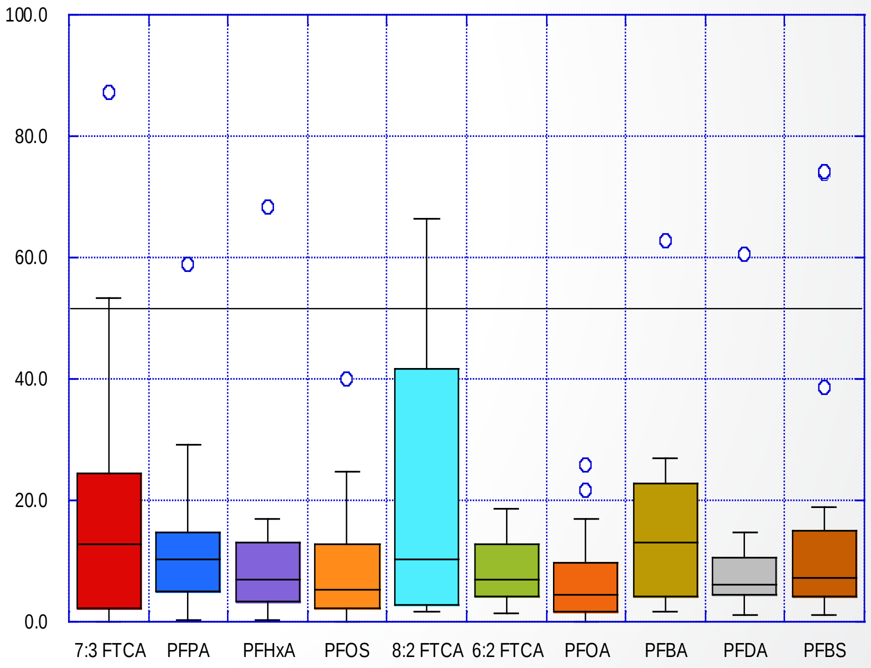
Analytical Methods Performance for Field Site 2 ASTM/EPA Region 5 method

Accuracy - Isotopic Surrogates – met goals



PFAS for each surrogate	7:3 FTCA PFHxA 6:2 FTCA	PFPeA PFBA	PFOS	8:2 FTCA	PFOA	PFDA	PFBS

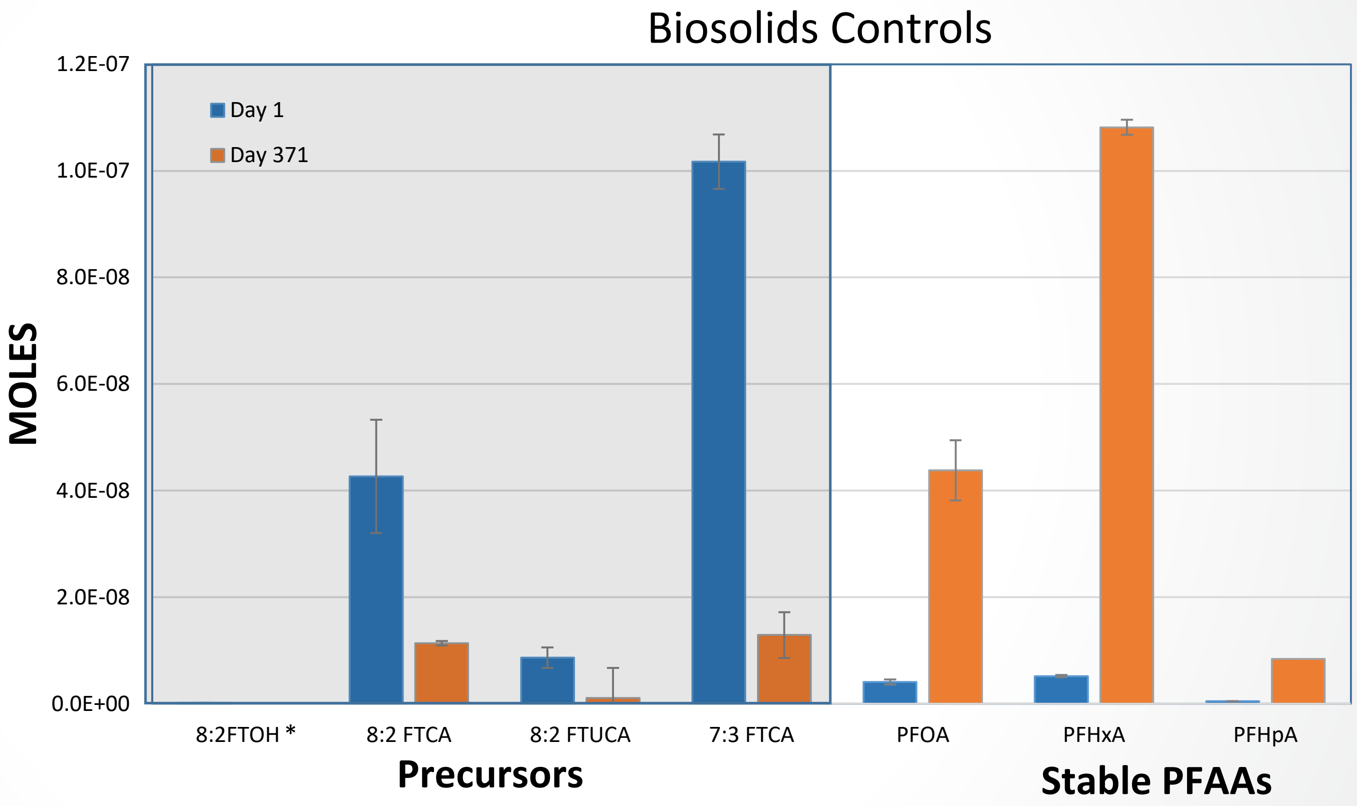
Precision – Duplicates - met goals

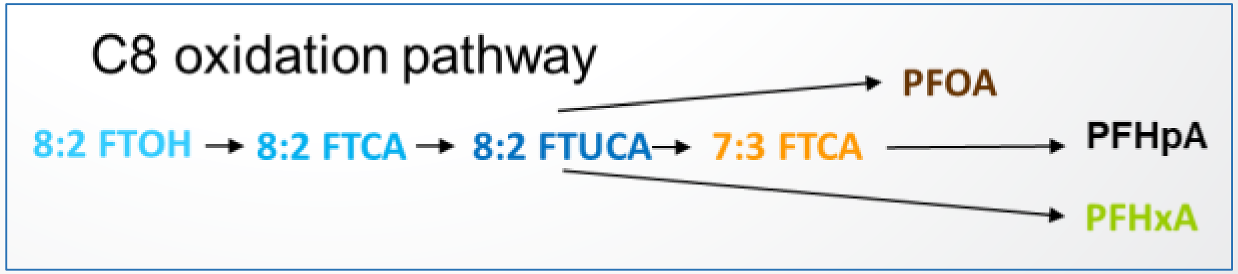


- Outliers not shown: 7:3 FTCA 136 %, and PFBA 200%
- N = 16 to 18 except 8:2 FTCA n= 4, 6:2 FTCA n=3, and PFBA n=14

Land Application of Biosolids Field Study 2: PFAS Precursors

- Precursor concentrations similar to PFAA concentrations
- Intermediate concentrations decrease with time
- Stable PFAAs increased
- 85% mole balance





* Preliminary measurements

Land Application of Biosolids
Field Study 3: Dry Land Agriculture

Study Design

- Field site operated for more than 20 years
- Measure concentrations of PFAS and other chemicals as a function of depth and biosolids application loadings (control to 30 dry tons/acre)
- Measure PFAS in plants from the application sites
- Develop conceptual model of biosolids application sites and compare to real world data with the goal of predicting PFAS concentrations

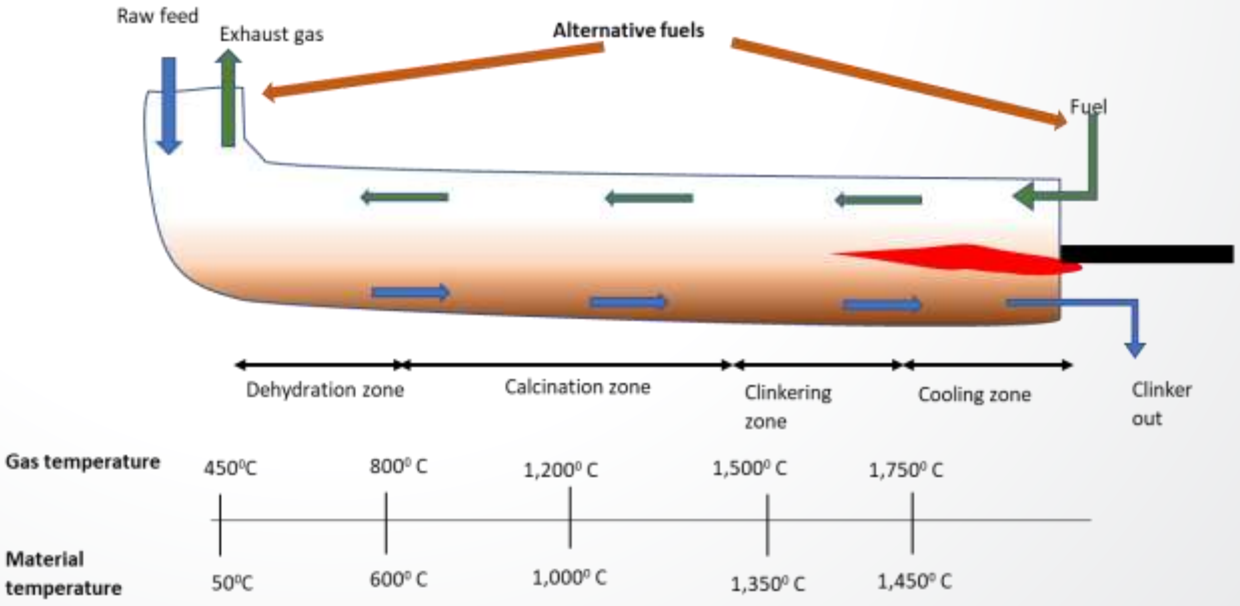
Schedule

- Sample collection this fall

Sewage Sludge Incineration (SSI)

SSI is one of several thermal treatment processes that are currently being considered for bench to full-scale studies

- ORD has a bench-scale project started to understand basic impacts of operation conditions such as time, temperature, media, etc.
- ORD is considering field scale studies for FY21



EPA

State Responses

Example: The State of Maine has taken action on biosolids applications

Per- and Polyfluoroalkyl Substances (PFAS)

Updates

Managing PFAS in Maine, Final Report from the Maine PFAS Task Force, January 2020

Maine PFAS data (2007-2020) as of June 2, 2020. For questions regarding this data, please email pfas.dep@maine.gov

February 2020 Maine PFAS Mapper (Under Development), please direct any feedback to pfas.dep@maine.gov

September 6, 2019 - Maine sludge and bioash spreading information (Excel), please note the file contains links that will not work. Please direct any feedback to pfas.dep@maine.gov

August 14, 2019 Emergency Sludge Dewatering State Wastewater Infrastructure Planning and Construction Grants Available

June 10, 2019 letters from the Northeast Committee on the Environment to US Committee on Environment and Public Works and Congressional PFAS Task Force.

On March 22, 2019, the Department notified sludge/biosolids program licensees and related composting facilities of a new requirement to test for PFOA, PFOS, and PFBS. Upcoming deadlines include submission of an updated Sampling and Analytical Work Plan by April 12, 2019, and initial sampling to be conducted by May 7, 2019.

- March 22, 2019 memo re: Requirement to analyze for PFAS compounds. Includes sampling protocol and list of approved laboratories for PFAS analysis. (pdf)
- Per- and Polyfluoroalkyl Substances (PFAS) Laboratory Recommendations follow-up memo (pdf)

DEP Announces Testing of All Sludge Materials Before Land Application

Governor Mills Signs Executive Order Establishing Task Force Charged with Studying Effects of PFAS Prevalence in Maine

https://www1.maine.gov/dep/spills/topics/pfas/index.html

Follow the Leader? Maine's Strict Stance on PFAS and Biosolids Land Application Sets the Stage for Further State Regulation

Wednesday, December 11, 2019

As the United States Environmental Protection Agency ("EPA"), Congress, and state regulatory agencies continue to push forward with per-and polyfluoroalkyl substances ("PFAS") regulations, the Maine Department of Environmental Protection has taken a bold stance regarding PFAS and the land application of biosolids. In a March 22, 2019 memorandum, the Acting Director of Maine's Bureau of Remediation and Waste Management, announced the State's decision to screen biosolids for perfluorooctanesulfonic acid ("PFOS") and perfluorooctanoic acid ("PFOA") – two of the more widely known PFAS substances – to 2.5 parts per billion ("ppb") and 5.2 ppb, respectively. This decision, which required initial sampling to be completed by May 7, 2019, effectively establishes a moratorium on biosolids land application within the state unless compliance with the established thresholds can be satisfied. With the standard set, will other states follow suit?

https://www.natlawreview.com/article/follow-leader-maine-s-strict-stance-pfas-and-biosolids-land-application-sets-stage

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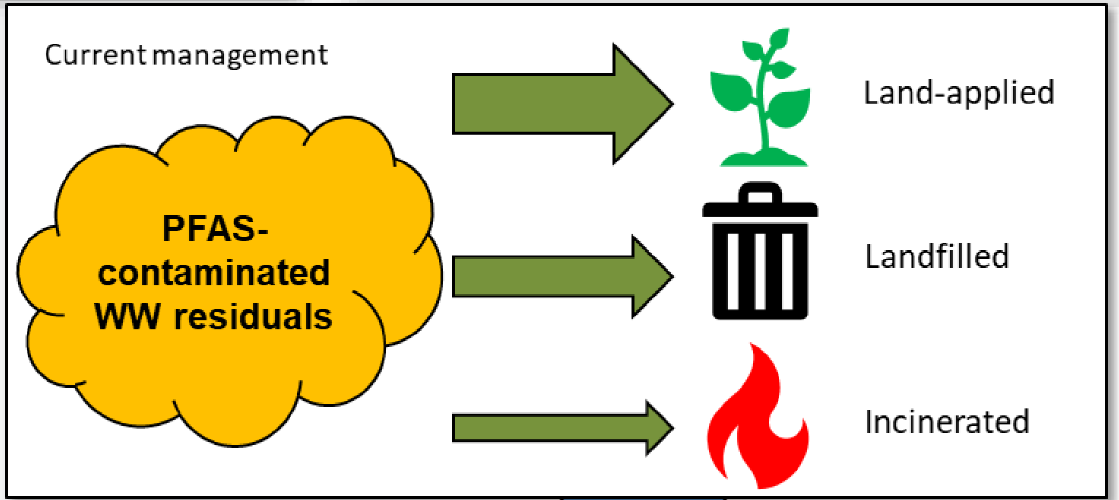
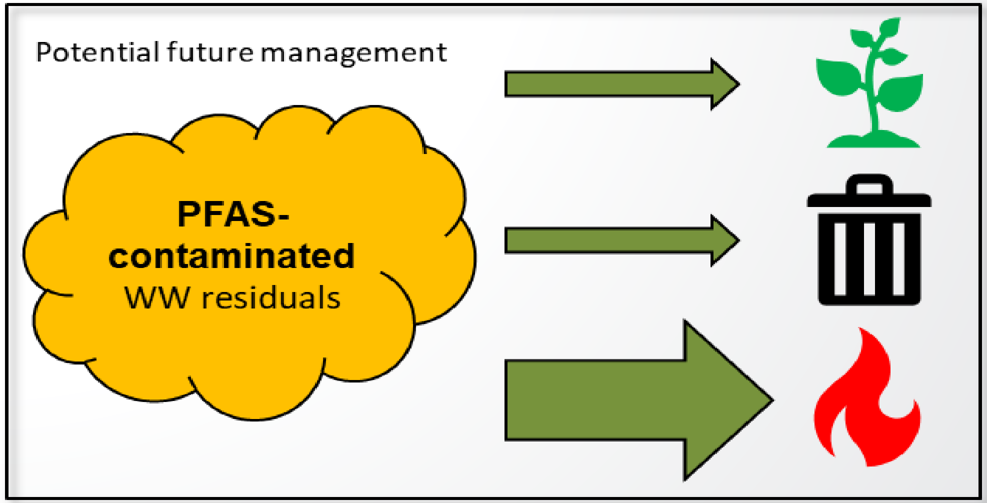
Changing Fate of Wastewater Residuals



USEPA is looking for partners for sampling full-scale sewage sludge incinerators

- Wastewater residual incineration may increase as policies shift to address PFAS in wastewater
- Lack data on the fate of PFAS in full-scale incinerators



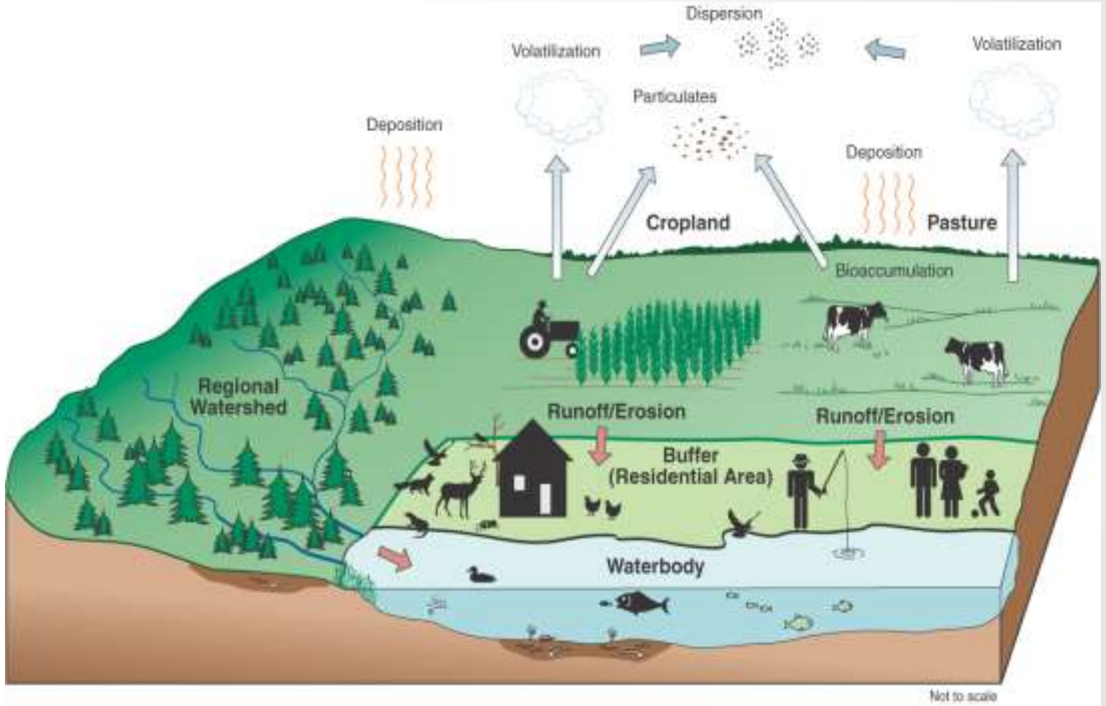
Chemical Risk Assessments for Biosolids

Project:

Exposure, Hazard and Toxicokinetic Data for Chemicals in Biosolids

Description:

- Leverage the computational toxicology approaches developed for the TSCA inventory to evaluate chemicals which may be present in biosolids for risk assessment prioritization
- Goal is to synthesize information from traditional and new approach methods (NAMs) to understand:
  - The overall degree of potential concern related to human health and the environment
  - The relative coverage of potentially relevant human health and ecological toxicity and exposure information that could inform level of effort and resources that may be needed to evaluate that specific substance



EPA Research Grants

STAR Grants: Practical Methods to Analyze and Treat Emerging Contaminants (PFAS) in Solid Waste, Landfills, Wastewater/Leachates, Soils and Groundwater to Protect Human Health and the Environment

- Project: Decreasing PFAS in municipal wastewater effluent and minimizing release from land-applied biosolids (Linda Lee, Purdue)
- Project: A systems-based approach to understand the role of waste type, management strategies and treatment methods on the occurrence, source and fate of PFAS in landfills (Timothy Townsend, Univ of Florida)
- Project: Electron Beam Technology for Destruction of Short-Chain and Perfluoroalkyl Substances in groundwater, wastewater, sewage sludges and soils (Suresh Pillai, Texas A&M)

National Priorities: Research on PFAS Impacts in Rural Communities and Agricultural Operations

- To better understand the impacts of PFAS on water quality and availability in rural communities and agricultural operations across the US
- New information on PFAS occurrence, fate and transport in water sources used by rural communities and agricultural operations
- New or improved PFAS treatment methods in small drinking water systems and typical small wastewater treatment system trains, including influents, effluents and biosolids/residuals
- Closed February 11, 2020

Technical and Program Office Support

To request technical support, contact EPA Region or Program Office partners

EPA Office of Water

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5	Kim Harris, Carole Braverman, Linda Holst	Carole Braverman
6	Michael Morton, Greg Lyssy	Michael Morton
7	Daniel O'Connor, Amy Shields, Catherine Wooster-Brown	Christopher Taylor
8	Sarah Bahrman, Lisa Kahn, Lisa McClain-Vanderpool	Alfred Basile
9	Matthew Small	Matthew Small
10	Linda Anderson-Carnahan	Rob Elleman

For More Information

- The research discussed in this presentation is part of EPA's overall efforts to rapidly expand the scientific foundation for understanding and managing risk from PFAS

- For more information on EPA's efforts to address PFAS, please visit the following websites
  - EPA PFAS Action Plan – https://www.epa.gov/pfas/epas-pfas-action-plan
  - EPA PFAS Research – https://www.epa.gov/chemical-research/research-and-polyfluoroalkyl-substances-pfas

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Learn more about EPA Research on PFAS

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References

Slide 5 :

1. EPA reports: EPA-430/9-76-013, EPA-625/10-84-003, EPA-821/R/3006, EPA/625/R-95/001, EPA-530-R-99-009
2. NEBRA 2007

Slide 10:

1. Venkatesan and Halden, 2013, Journal of Hazardous Materials 252-253:413-418
2. Sepulvado et al., 2011, Environmental Science and Technology 45:8106-8112
3. Loganathan et al., 2007, Water Research 41:4611-4620
4. Sinclair and Kannan, 2006, Environmental Science and Technology 40:1408-1414
5. Schultz et al., 2006 , Environmental Science and Technology 40:7350-7357
6. Yu et al., 2009, Water Research 43:2399-2408
7. Yoo et al., 2009, Journal of Chromatography A 1216:7831-7839
8. Navarro et al., 2016, Environmental Research 149:32-39
9. Michigan Department of Environment, Great Lakes, and Energy (EGLE), 2020. Summary Report: Initiatives to Evaluate the Presence of PFAS in Municipal Wastewater and Associated Residuals.