PFAS

Current State of Sources, Exposure and Regulations

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Meet Our Panelist

John Baker

Mr. Baker has completed several feasibility studies to evaluate the most cost effective technologies to treat PFAS (and other parameters that may interfere with PFAS treatment) in complex wastewaters including landfill leachate, wastewater and contaminated surface water to local limits. He has recently worked with the Michigan Waste and Recycling Association (MWRA) to peer review the largest study on PFAS in landfill leachates in North America that was prepared for the Michigan environmental agencies. This also involved evaluating publicly available data for PFAS in at POTWs and biosolids.

PFAS Experience 50Y

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Introduction to Per-and Polyfluoroalkyl Substances (**PFAS**)

- Description of PFAS Compounds
- Environmental Agency Concerns
- Environmental Impacts
- Regulatory Responses
- PFAS Sources
- Sampling and Analyses Challenges
- Remediation and Treatment Options

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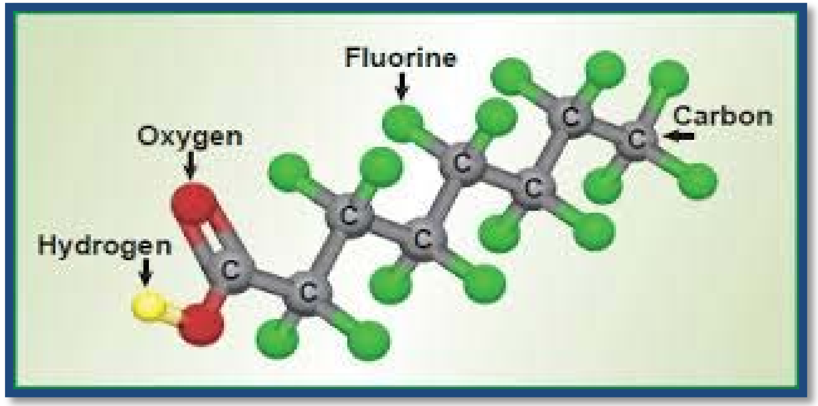
What are **PFAS** Compounds?

- Per-and polyfluoroalkyl substances are collectively referred to as **PFAS** and are terms used to describe a large group of organic fluorinated chemicals
- PFAS are anthropogenic chemicals and do not occur naturally in the environment
- PFAS are a group of chemicals that are comprised of a carbon backbone containing many carbon-fluorine (C-F) bonds
- The C-F bond is the shortest and strongest in nature
- Due to their unique chemical structure, PFAS are very stable in the environment and are relatively resistant to biodegradation
- The 2 most studied PFAS are
    - Perfluorooctanoic Acid (PFOA)
    - Perfluorooctane Sulfonate (PFOS)
- PFAS family = thousands of diverse compounds
- 24 PFAS Compounds identified by MDEQ



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Chemical and Physical Properties

- Properties of PFAS range and are not well understood
- PFASs are commercially useful because they repel both oil and water
- The fluorinated carbon tail is both lipophobic/oleophobic (repelled by fats and oils) and hydrophobic (repelled by water)
- The functional group head can vary but is often hydrophilic (attracted to water)
- Because of these properties, they are often used as surfactants and stain preventers

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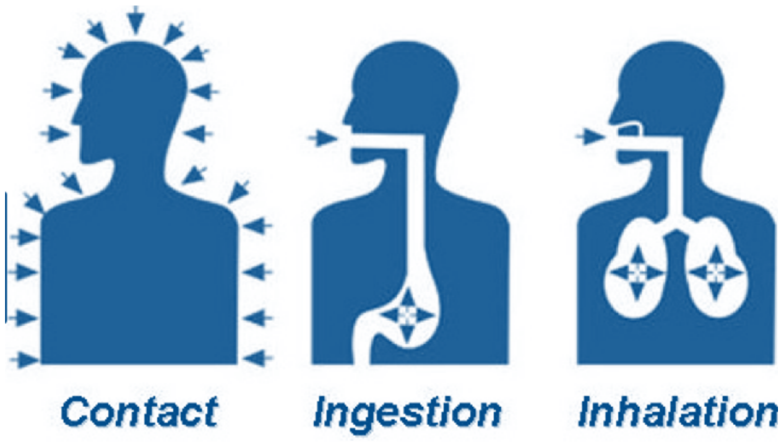
Federal and State Environmental Agency Concerns

- Known or suspected toxicity, especially for PFOS and PFOA
- PFOA cancer risk – Kidney & testicular (humans) & liver (animals)
- PFOS cancer risk—Liver tumors in animals
- PFOA and PFOS exposures in humans over certain levels may result in adverse health effects, including changes in cholesterol, low birth weight, liver effects and thyroid effects
- Bioaccumulation
- Some have very long half lives (several years), especially in human

Human Exposure

- PFAS can be inhaled, ingested and/or absorbed via skin
- PFAS are found virtually everywhere in the world
- Blood serum of >99% of Americans
- Toxicological studies have linked PFAS in serum to adverse health affects



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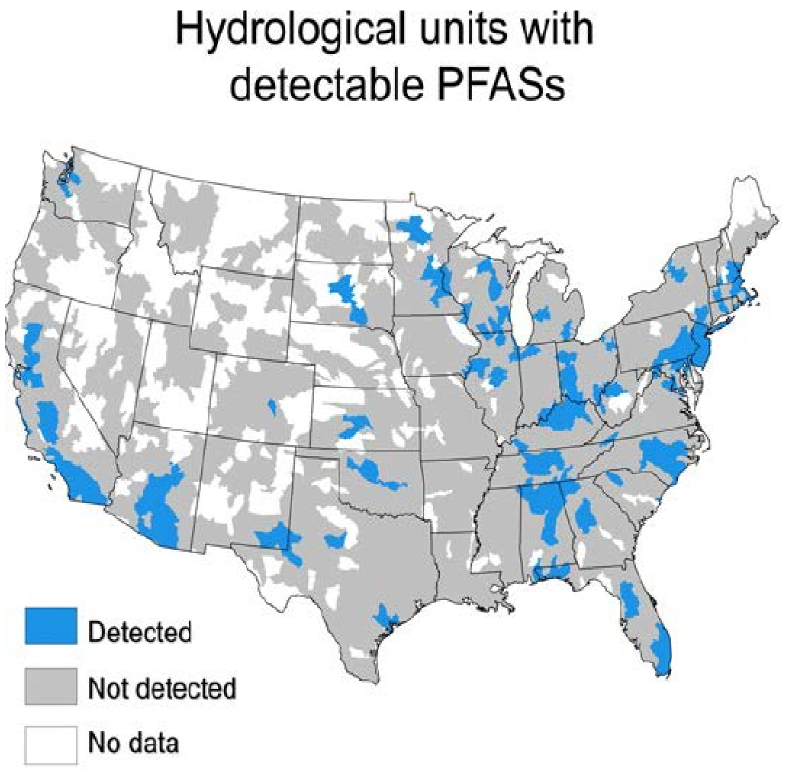
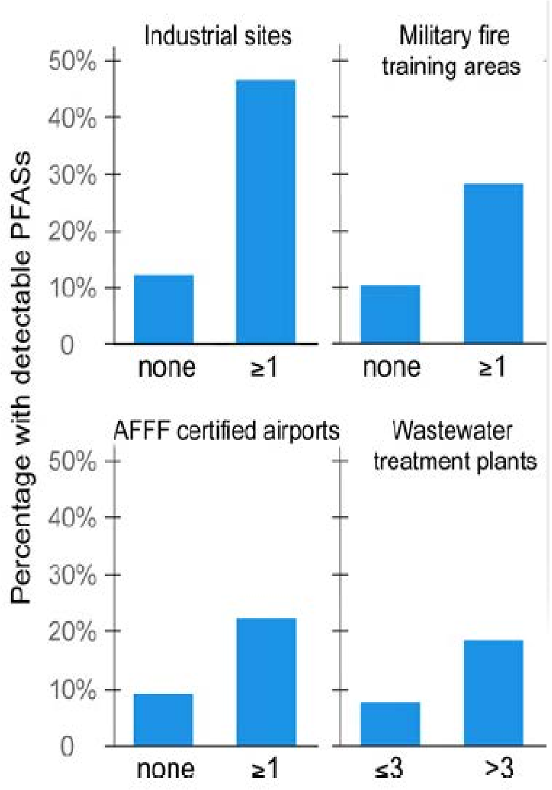
PFAS Persistence

- Persistent due to C-F Bonds
- Half-life of PFOA in water is 92 years
- Half-life of PFOS in water is 41 years
- First manufactured in 1940s
- Phase out in USA
  - PFOA (2015) from 8 manufacturers
  - PFOS (2002) from its only manufacturer





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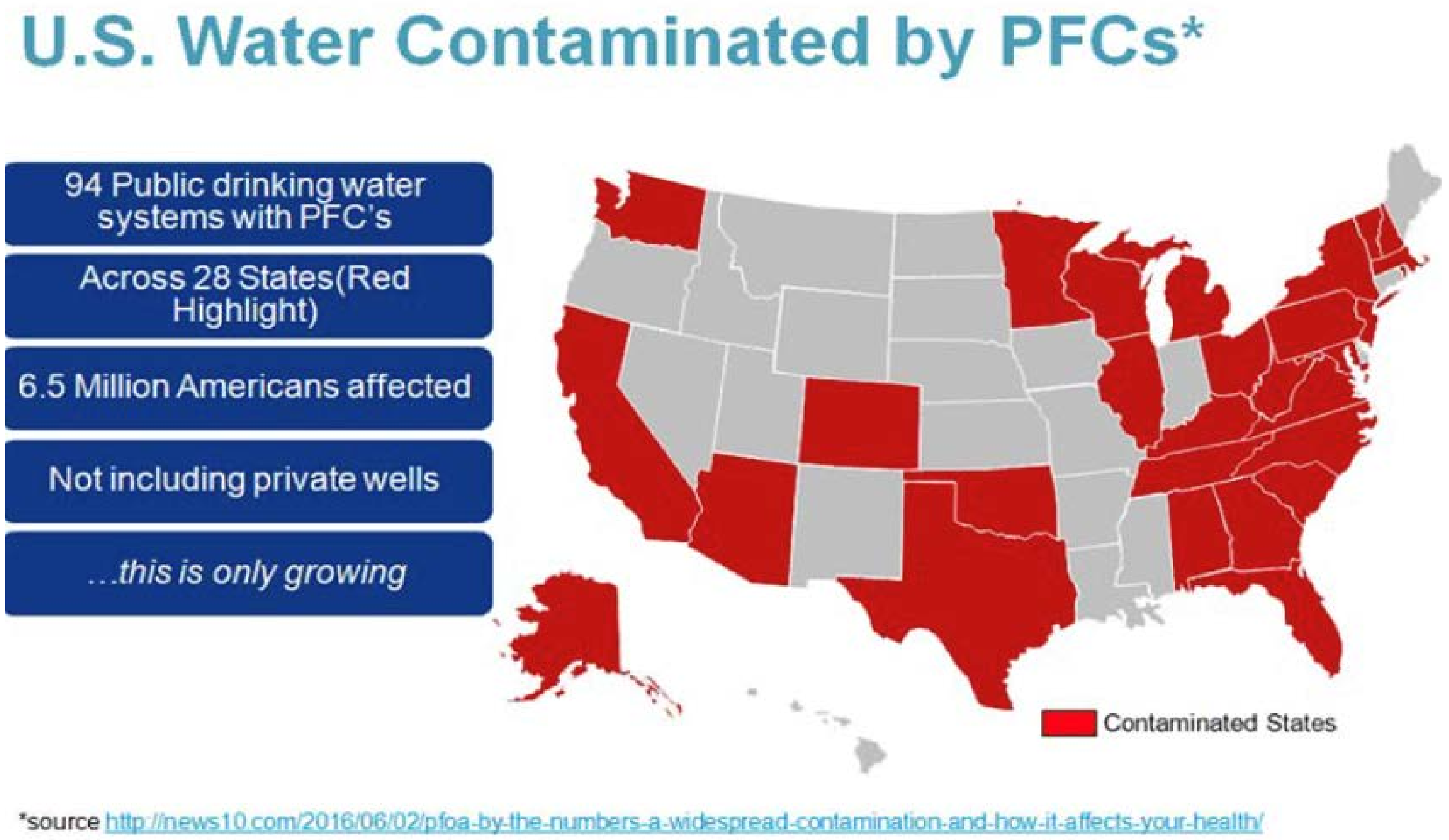
States with PFAS detected in 94 Public Utilities



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USEPA & State Standards/Advisory Limits

Regulatory responses vary…

Jurisdiction		**PFOA** (ppt)	**PFOS** (ppt)	**Notes**
Advisory or Regulatory Standard				
U. S. EPA, 2016	**Advisory**	**70**		for combined
New Hampshire, 2016, AGWQ	**Standard**	**70**		for combined
Vermont, 2016	**Standard**	**20**	**20**	
Australia, January 2017 interim drinking water guidance	**Advisory**	**5,000**	**500** (includng PFHxS)	
Australia, April 2017 final drinking water guidance	**Advisory**	**70**	**560** (including PFHxS)	
Canada, proposed June 2016	**Standard**	**200**	**600**	
Michigan, non-cancer values, 2014		**420**	**11**	
Minnesota drinking water (as of 2016) (as of 2017)	**Standard** **Advisory**	**300** **35**	**300** **27**	PFBA & PFBS = 7000 Adopted 5/2017
New Jersey preliminary health-based guidance	**Advisory**	**40**		
West Virginia (as of 2016)	**Standard**	**400** or **500**		
Maine CDC, 2014, health-based MEG		**100**		
Maine residential groundwater RAG	**Advisory**	**560**	**130**	
California Water Resources Board				Considering Prop. 65 listing

…but the difference is that we're talking *ng/L* drinking water advisories & limits

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PFAS Sources

Production and Manufacturing Facilities

- Textiles and Leather
  - Factory and consumer applied coating to repel water, oil, and stains
- Paper products
  - Surface coatings to repel grease and moisture
- Metal Plating and Etching
  - Corrosion prevention, wear reduction, surfactant, fume suppressant
- Wire Manufacturing
  - Coating and insulation
- Pesticides
  - Cleaning products, polishes, photo processing

Industrial Uses of PFAS


Aerospace


Apparel


Building and Construction


Chemicals and Pharmaceuticals


Electronics


Oil & Gas


Energy

Healthcare and Hospitals


Aqueous Film Forming Foam


Semiconductors

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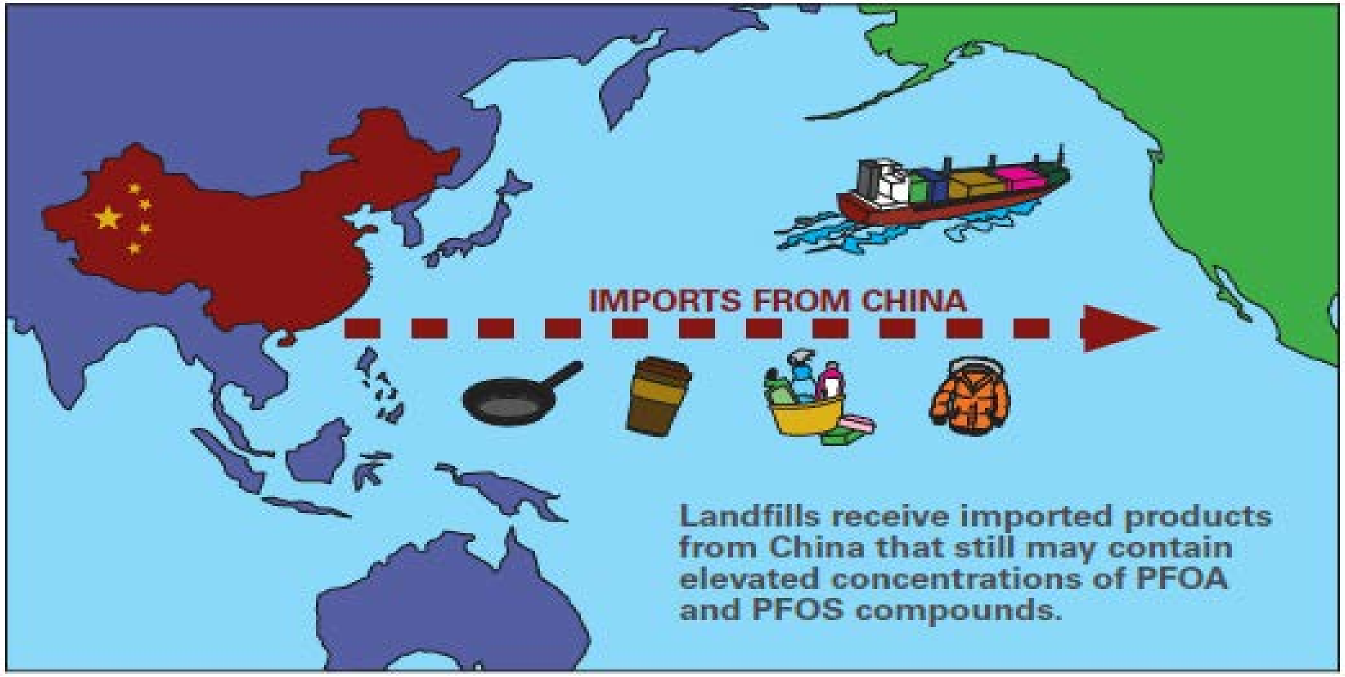
PFAS Production in USA

If PFAS Production in USA has been discontinued, where are the new sources coming from?



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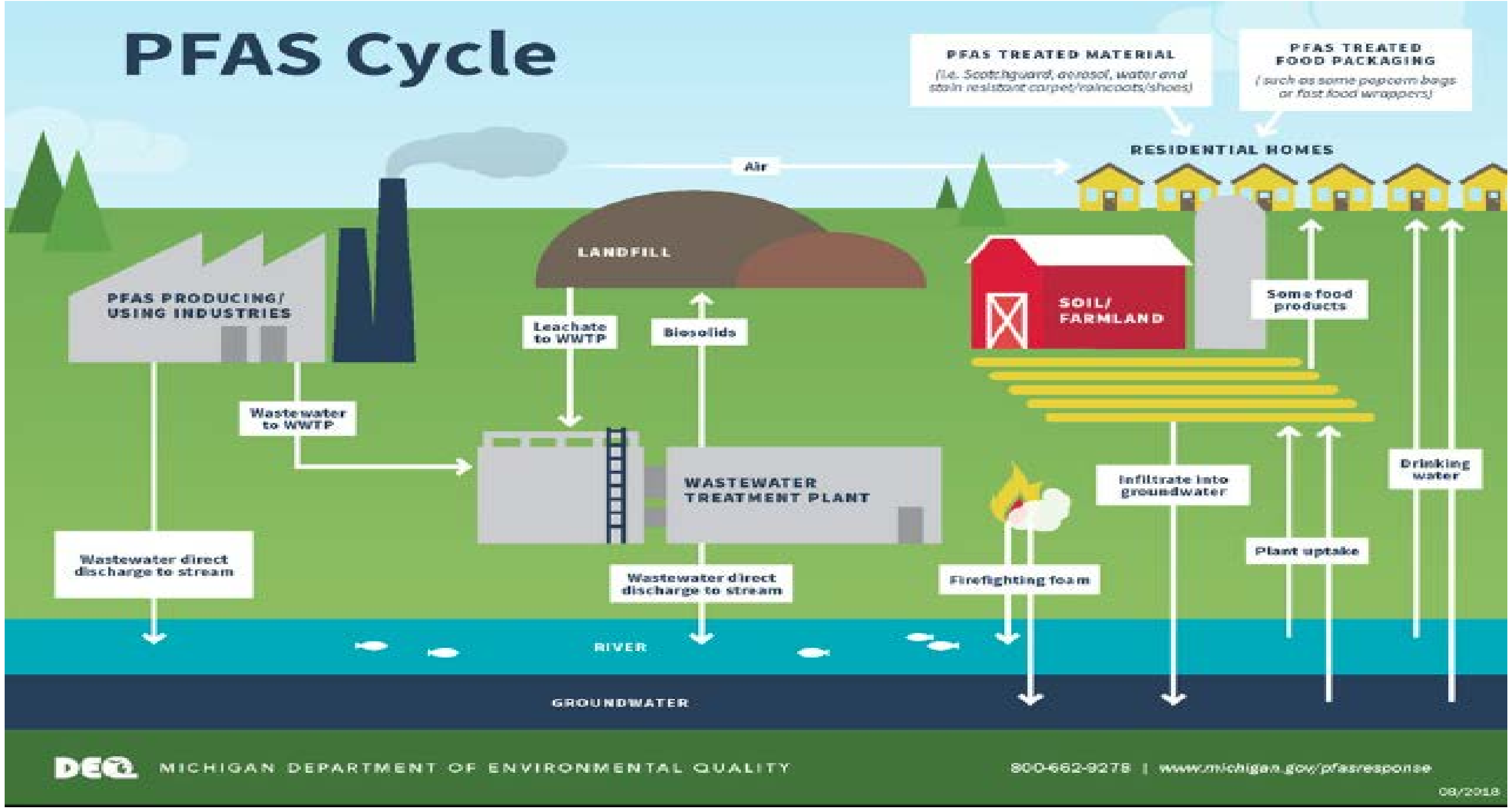
PFAS Cycle



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Potential PFAS Exposure Pathways

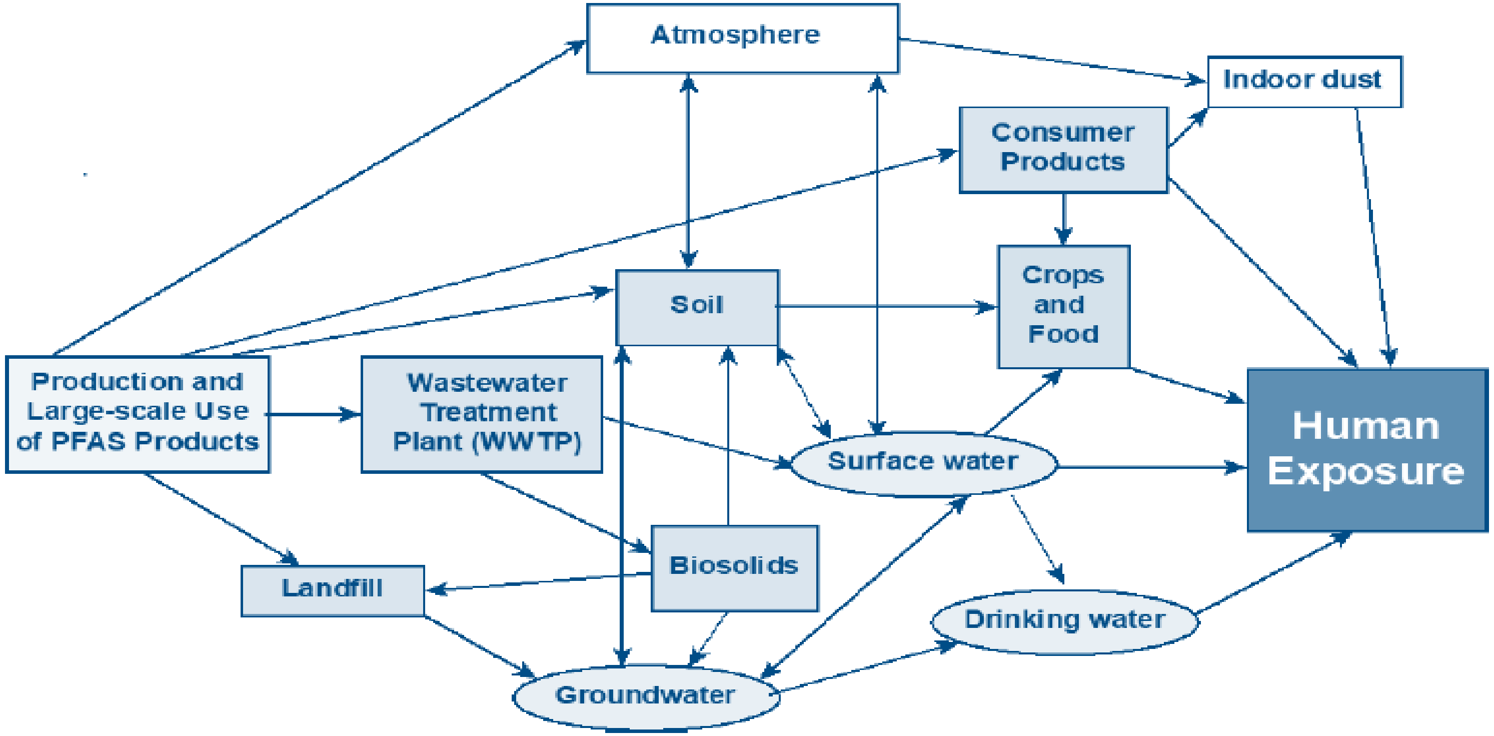
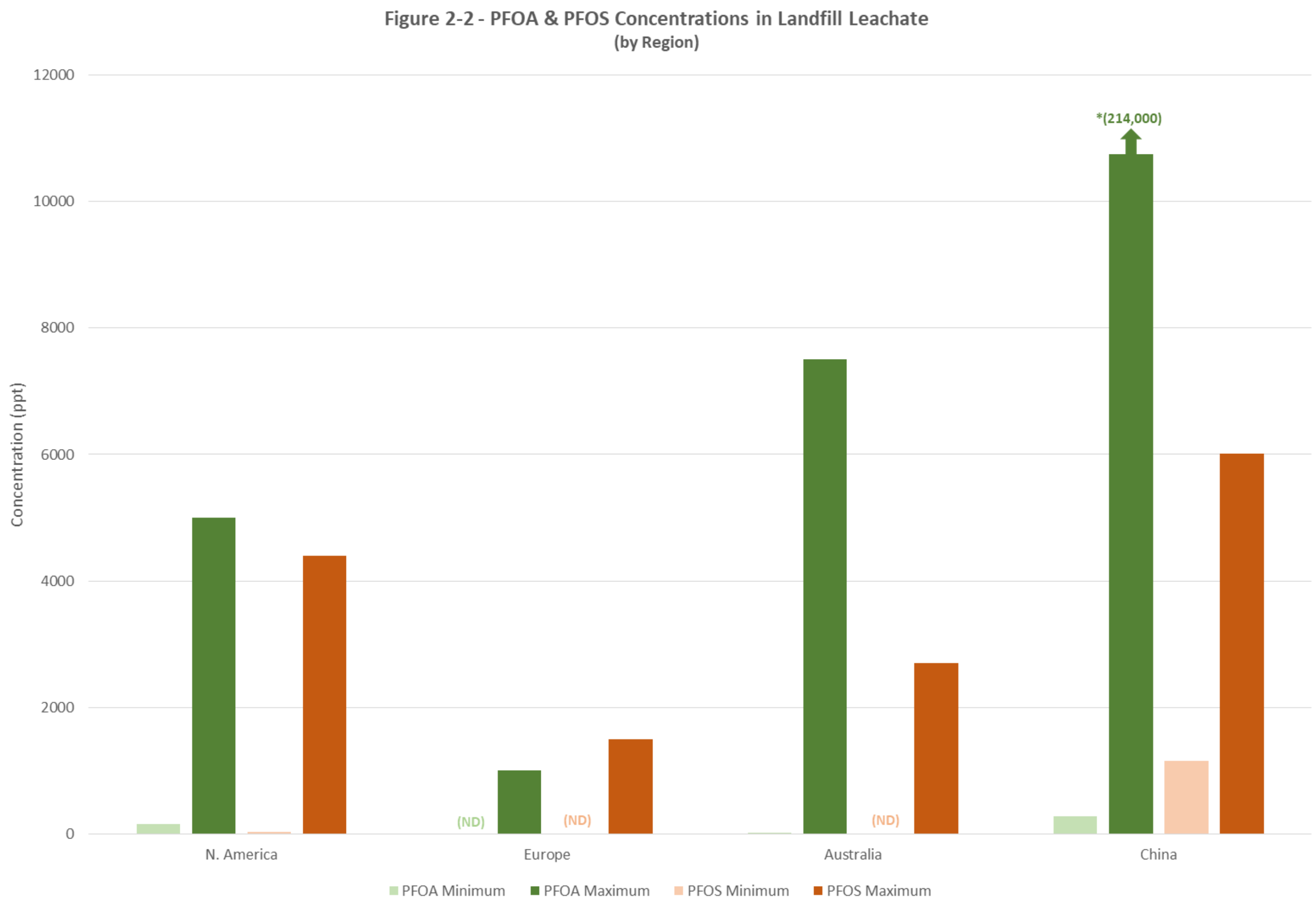


Figure 3. Environmental transport of PFAS in the context of pathways to human exposure. Figure adapted from (Ahrens and Bundschuh 2014).

PFOA & PFOS Landfill Leachate by Global Region



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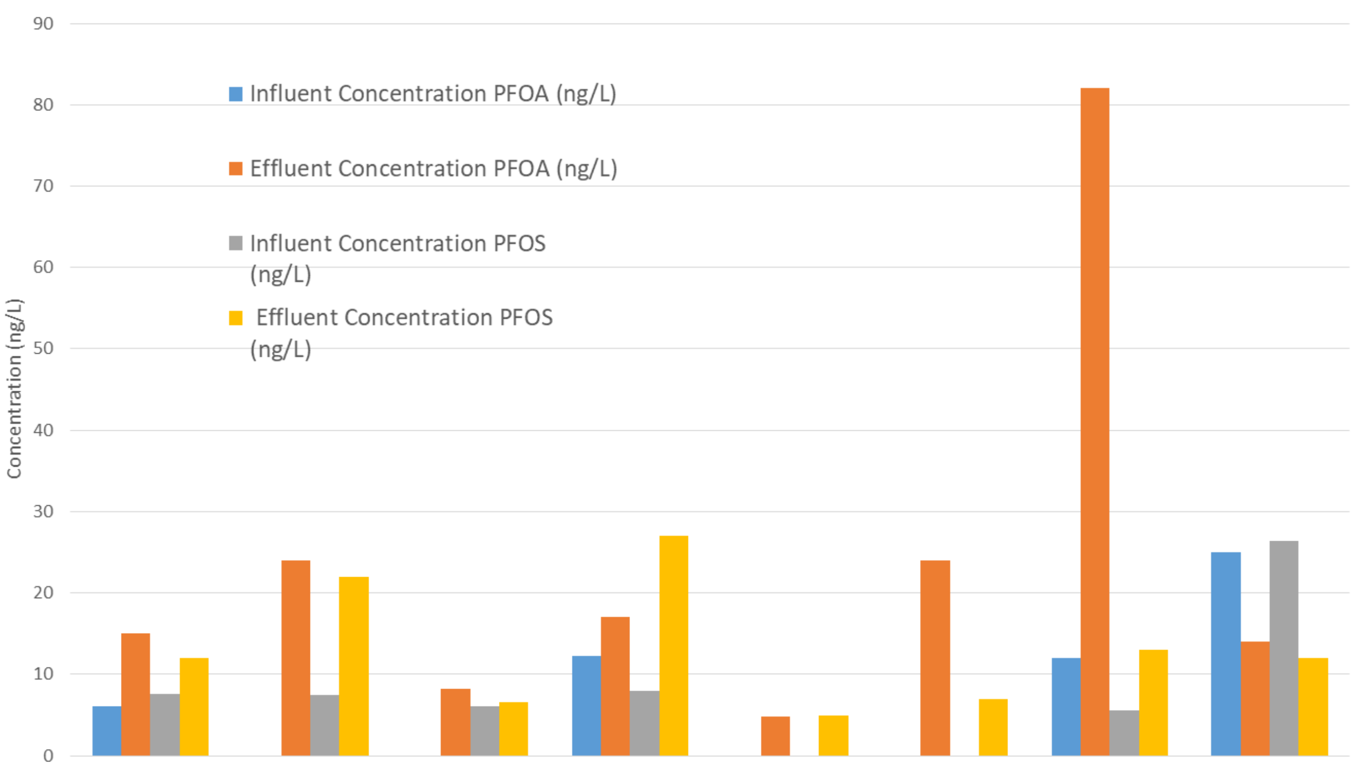
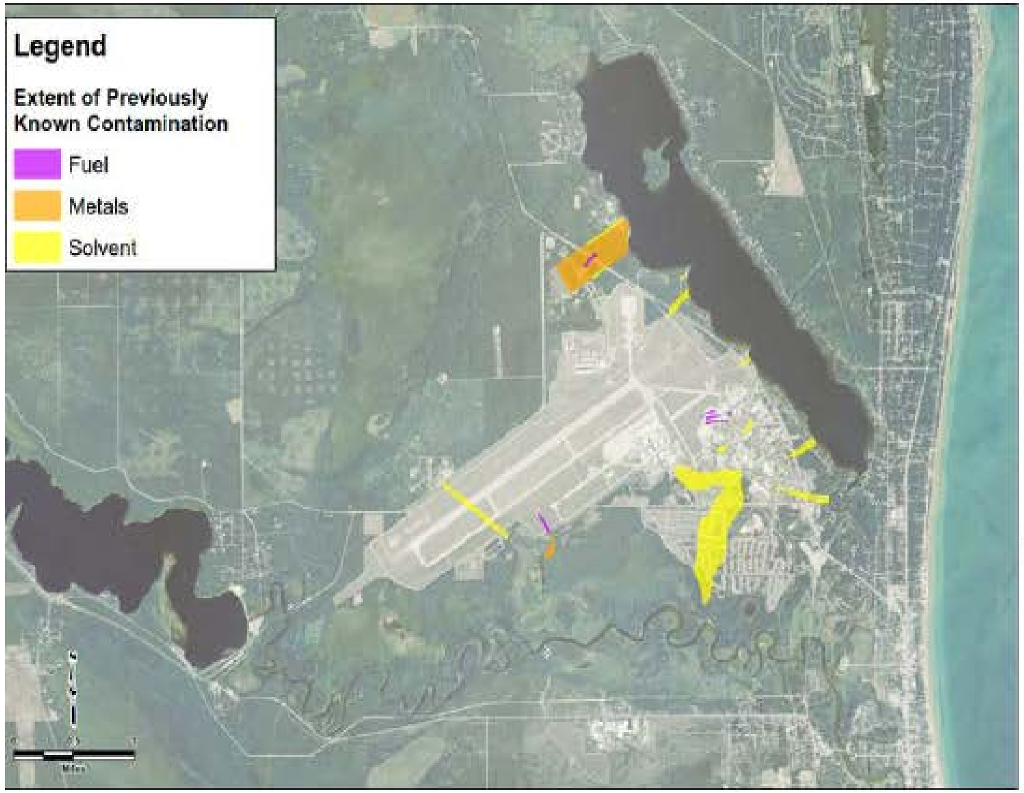
Effluent PFAS in Higher Concentrations than Influence in Most POTWs in MI

Figure 5-4
Influent vs Effluent PFOA and PFOS Concentrations at POTWs

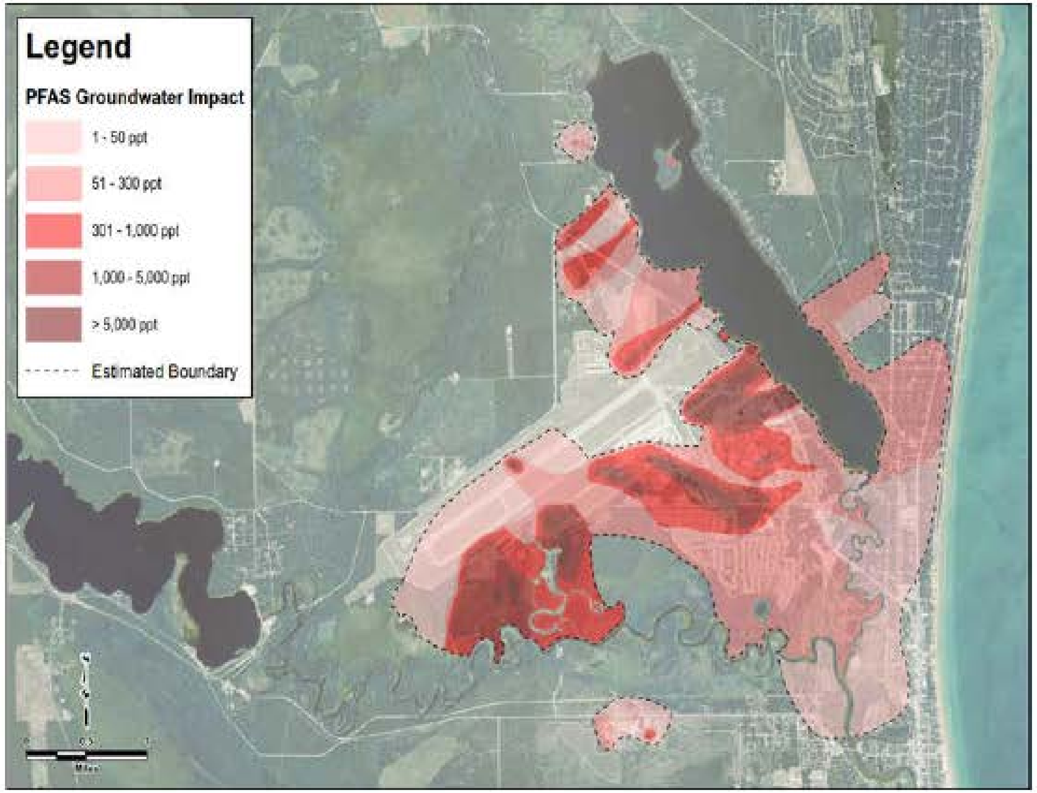


Potential PFAS Re-Opener

Extent of Non-PFAS Impact



Extent of PFAS Impact



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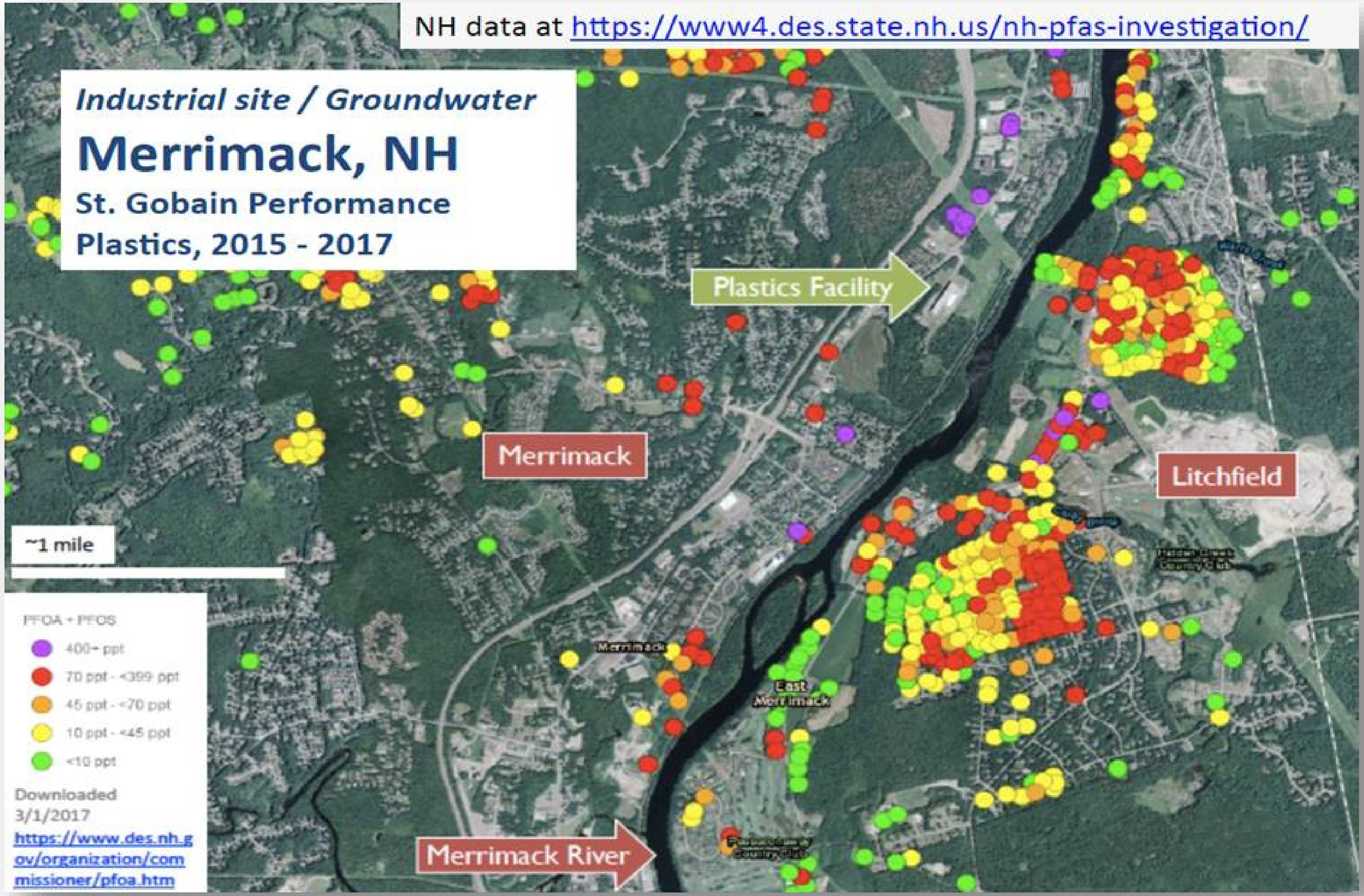
PFAS Site



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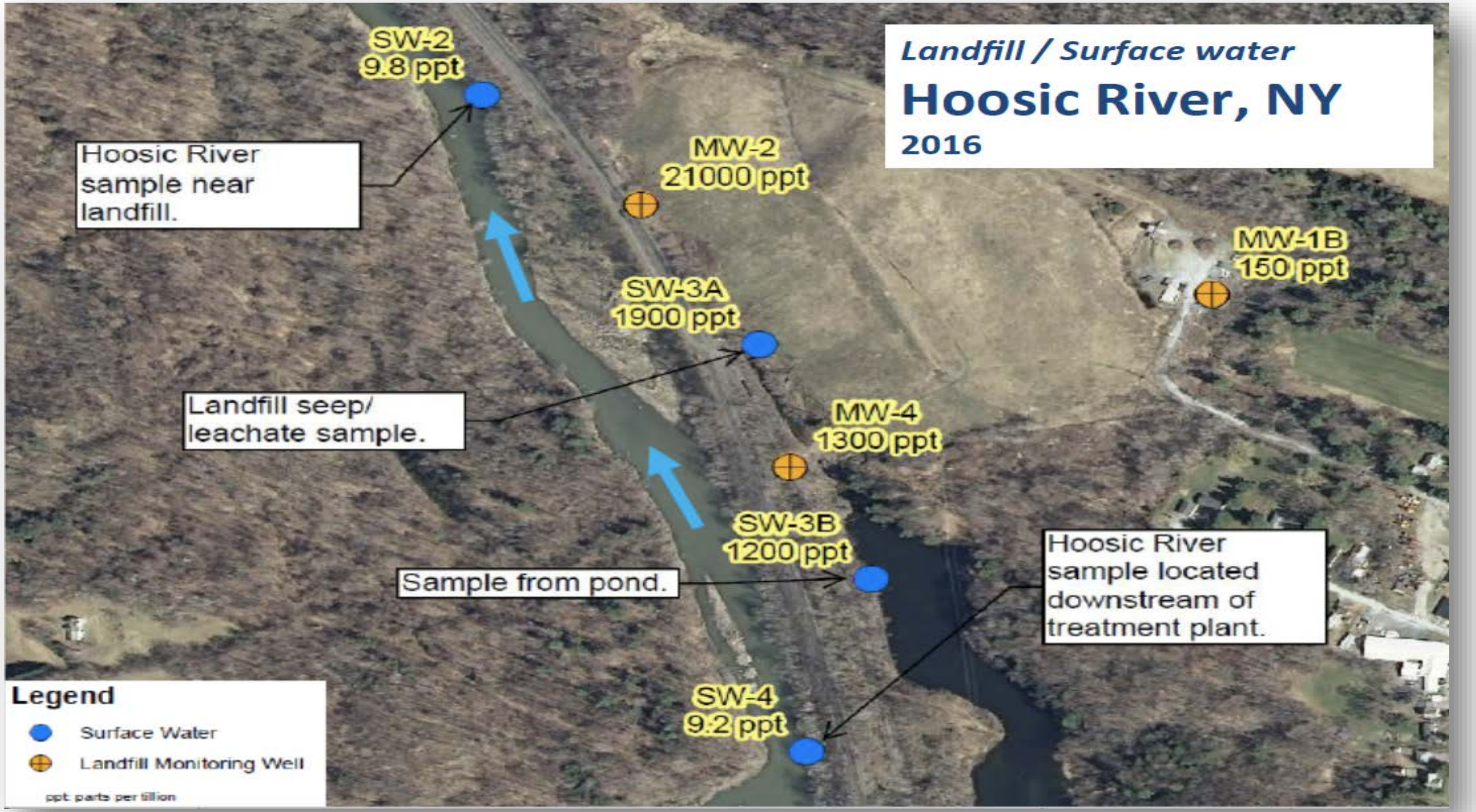
Closed Landfill PFAS in Groundwater/Surface Water



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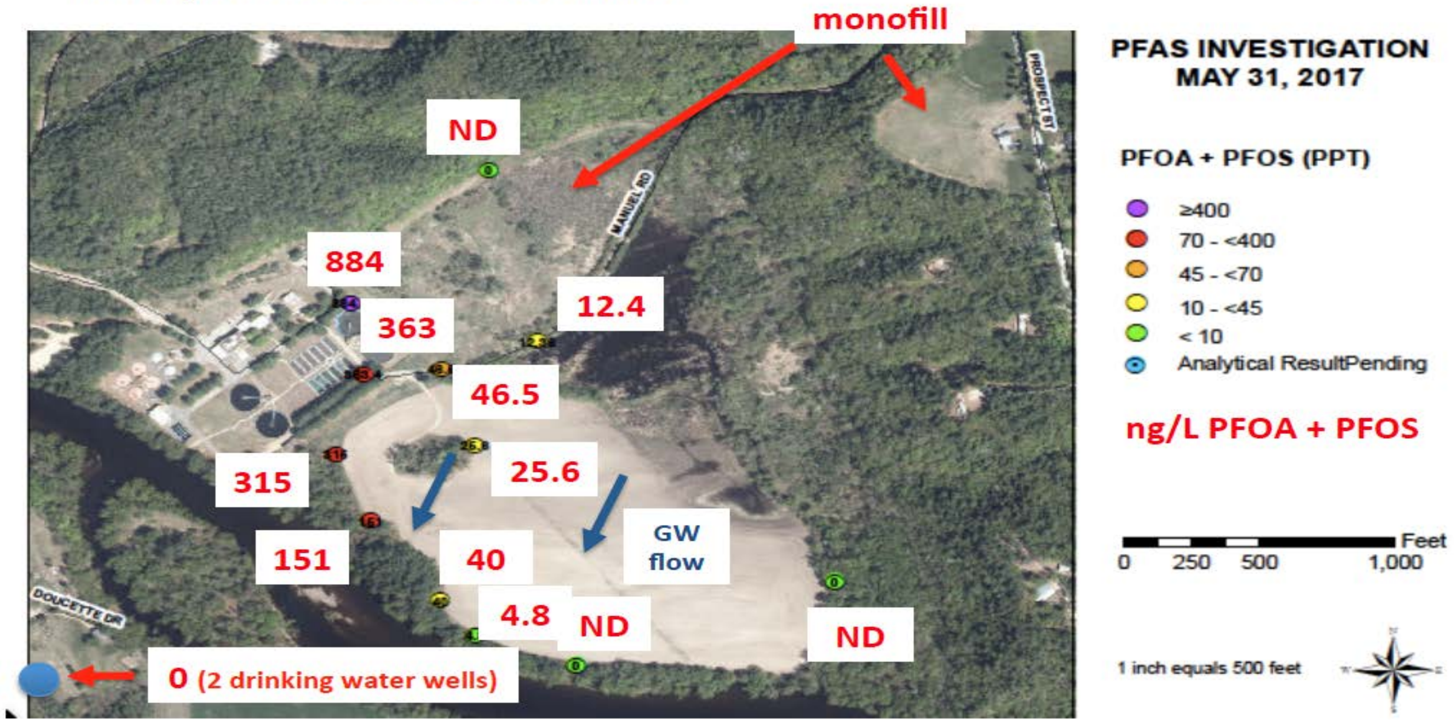
Paper Sludge Compost Facility

Groundwater Impacts Boisolids Monofill & Land Application

Monitoring well testing at biosolids 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?



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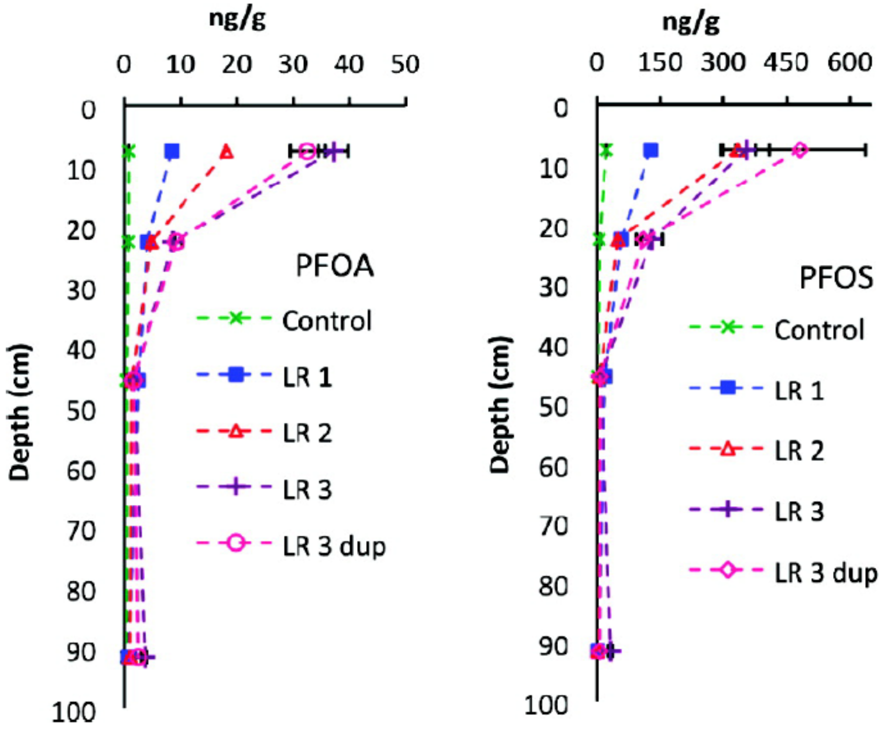
PFAS Vertical Profile from Surface Application Biosolids

Some PFAS leach in soil

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



Land Application of Biosolids PFAS Studies

Conclusions of Gottschall et al. 2017

- Perfluorinated chemicals detected in both groundwater and tile discharge after a single large biosolids application.
- Chemicals detected for months after the application.
- The contributions of leaching through soil matrix, and preferential flow through macropores are unknown.

Known Treatment Technologies for PFAS Compounds

Ineffective	Partially effective	Effective
• Coagulation • Sedimentation • Aeration • Microfiltration • Ultrafiltration • Ozone • Chlorine • Ultraviolet Photolysis • Advanced Oxidation Process • Municipal Treatment	• Anion Exchange • Granular Activated Carbon (GAC)	• Reverse Osmosis

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Emerging Treatment Technologies

- Electro Coagulation
- Electro-chemical coagulation
- New membrane technologies
- Others in development

Just when you think you understand PFAS

Lab Analysis Limitations

- EPA Method 537: for Drinking Water Only!
  - 14 Analytes, all in OSRTI List
    - PFOS, PFOA, N-EtFOSAA, N-MeFOSAA, PFBS, PFDA, PFDoA, PFHpA, PFHxS, PFHxA, PFNA, PFTreA, PFTriA, PFUnA.
  - 3 Surrogates
    - MPFHxA, MPFDA, MN-EtFOSAA
  - 3 Internal Standards
    - ^{13}C-PFOA, ^{13}C-PFOS, d_3-N-MeFOSAA
- Modified 537 Methods: varied, uncertain QC
- ASTM D7979 and D7968 (2017 versions)
  - Heavily single lab validated on multiple matrices
  - 31 Target Analytes and 14 Surrogates
    - Ten Additional Target Analytes added to Appendix with all MRM transitions, Tune parameters, recoveries in matrices ...
    - Five Additional Surrogates (Isotopes) added to Appendix with all MRM transitions, Tune parameters, recoveries in matrices...
    - NEBRA encouraging states to encourage U. S. EPA to approve ASTM methods

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See recprded NEBRA webinar: Analyzing PFAS in Wastewater, Solids & Soils, at https://www.nebiosolids.org

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PFAS Analytical Challenges

Pace Analytical®

PFAS – Analytical Challenges

	EPA 537	EPA 537 v 1.1	EPA 537M	ISO 25101	ASTM D7979-16	DoD QSM 5.1	DoD QSM 5.1
Matrix	Drinking water	Drinking water	All Matrices	Drinking, ground, surface water	Water & wastewater	Matrices other than drinking water	Soil & sediment
Analytes	6	14	24+	2 (PFOA, PFOS)	21	24	24
Sample size	250 mL	250 mL	250 mL	~ 500 mL	5 mL	As received	2 g
Holding time	14/28	14/28	14/28	14	28	14/28	14/28
Surrogate	3	3	3	-	9	19	19
Extraction	SPE	SPE	SPE	SPE	Liquid/liquid filtration	SPE, ENVI-Carb cleanup	Sonicate and shake/SPE
RLs (ng/L)	3 - 14	2 -14	2 -14	2 - 10	10-300	-	-
Quantification	Internal Std.	Internal Std.	Internal Std.	Internal Std.	External Std.	Isotope dilution or internal std.	Isotope dilution or internal s td.
Branch isomer	Yes	Yes	Yes	No	No	Yes	Yes

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Sampling Guidelines

Best Practices	What To Avoid
Sample Container Items	
HDPE or Polypropylene (PP)	No glass or LDPE containers
Lined or unlined HDPE or	No Teflon™ lined caps
Field Equipment	
High density polyethylene(HDPE) or polypropylene	No Teflon ™ containing materials
Silicon tubing	No Teflon™ tubing
Loose paper (non-water resistant)	No waterproof field books
Aluminum field clipboards or Masonite	No plastic clipboards, binders, or spiral notebooks
Sharpies, pens	No Post-it Notes
Regular Ice	No chemical (blue) ice packs

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Sampling Guidelines (continued)

Best Practices	**What To Avoid**
Field Clothing and Personal Protection Equipment	
Well-launched clothing, defined as clothing that has been washed six or more times after purchase, made of synthetic or natural fibers (preferable cotton)	No new clothing or water resistant, waterproof, or stain-treated clothing containing Gore-Tek™
No fabric softener	No clothing laundered using fabric softeners
Cotton clothing	No Tyvek®
Boots made with polyurethane and polyvinyl chloride (PVC)	No boots containing Gore-Tek™
Sunscreens – all organic natural sunscreen, that are "free" or "natural". Check the label, insect repellants –various natural one, DEET, check the label	No cosmetics, moisturizers, hand creams, or other related products as part of personal cleaning/showering routine on the morning of sampling
Field Equipment Decontamination Items	
Alconox® and/or Liquinox®	No Decon 90
Food Items	
Bottled water and hydration drinks (i.e., Gatorade® and Powerade®) to be brought and consumed only in the staging area	No food and drink, with exceptions hydrating items listed on the left

Sample Containers

PFAS – Sample Containers

Matrix	Container	Preservative	Method	Notes
Drinking Water	2 x 250 ml HPDE or PP	Trizma	EPA Method 537 or EPA Method 537M	Trizma is a buffer and removes free chlorine.
Groundwater, surface water, waters	2 x 250 ml HPDE or PP	none	EPA Method 537M	
Effluent	2 x 250 ml HPDE or PP	Trizma	EPA Method 537M	Finished samples may require Trizma.
Soil, sediment, bio-solids	1 x 250 ml (or 4 ounce) HPDE or PP	none	EPA Method 537M	

Sample extraction = 14 days *Sample analysis = 28 days*

Learn More

References

Michigan Waste & Recycling Association Landfill Leachate Summary and Technical Reports

North East Biosolids & Residuals Association

Interstate Technology & Research Council PFAS Fact Sheets

Test America and Pace Laboratories

American Water Works

AECOM

Great Lakes Water Authority

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Questions?

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