PFAS 101
Applied to the Solid Waste Industry

WDNR Solid Waste
Interested Parties
May 15, 2019

Ken Quinn
Technical Director
TRC Environmental Corp.
PFAS in the News

Traces of two PFAS compounds found in four additional Madison wells

STEVEN VERBURG sverburg@madison.com  Apr 10, 2019
PFAS 101 for Solid Waste

- Summary – What’s the Big Deal?
- PFAS – What are they – a little chemistry
- PFAS in Manufacturing
- Fate and Transport, and Toxicology,
- Regulatory Status
  - Emerging regs for long chain PFAS
  - Short chain PFAS regs, are they coming?
- PFAS in Landfills
- Treatment and Remediation
And Should We Be Concerned?

- **Regulations** – Developing rapidly – (e.g., 8 states added rules in 2018, 19 Total)

- **PFAS are Ubiquitous** – Used in industry and in numerous commercial products since 1960s.

- **Public:** Public concern is growing (e.g., opposition groups using PFAS presence to argue against facilities)

- **Standards in PPT:** Varies by state. Water standards are typically 70 ppt, or less.

- **Highly Mobile:** Migration occurs easily and rapidly in groundwater, surface water and air.

- **Degradation:** No degradation of basic perfluorinated compounds

- **Difficulties with PFAS:**
  - Complicated: Sampling and analytical methods
  - Difficult to treat ($$$$$) – especially in leachate
What and Where are PFAS?

**PFAS – Per- and Polyfluoroalkyl Substances.** A large group of fluorinated compounds used for their stable, unreactive properties.

- **Fire Fighting Foams:**
  - Type B fire fighting foams – Airports, refineries, etc.
- **Textiles and Leather**
  - Carpets, clothing, etc.
- **Paper Products**
  - Food contact materials
- **Metal Plating Facilities**
- **Industrial Surfactants, Resins, Molds, Plastics**
- **Photolithography, Semiconductor Industry**
- **Biosolids**
  - Paper mill sludge
  - Certain POTW sludge

- **Landfills**
  - Industrial wastes
  - Leaching from consumer products
  - Landfill fires, depending on whether foam was used.

Photos: Charles Hutchins, Yossi Zamir, Windell Oskay, Jean-Pierre, White/S. Shawn Carroll, Jack W. Feil
A Little PFAS Chemistry
Quick Chemistry Lesson #1

- PFAS are **Per** and **Poly**fluoroalkyl substances
- **Per-fluoroalkyl substances**: can’t be degraded, the fully fluorinated tail is very stable.
- **Examples of Per-fluorinated compounds**

**PFOA**
Perfluorooctanic Acid

COOH = Carboxylic Head

Alkyl tail, fully fluorinated

**PFOS**
Perfluorooctanic Sulfonic Acid

SO₃H = Head
Examples of Poly-fluorinated compounds

Poly-fluoroalkyl substances: non-fluorine atom (typically hydrogen or oxygen) attached to at least one carbon atom

8:2 Fluorotelomer Alcohol (8:2 FTOH)

Polyfluoroalkyl substances may also be degraded to perfluoroalkyl substances (e.g. PFOS or PFOA, etc.)
The Evolution of PFAS
As Shown in Fire Fighting Foams (AFFF)

1st Generation
Long Chain
PFOS AFFF
1960-2002

- PFOS based (80%)
- Developed in 1960s
- Production ended in 2002

2nd Generation
Long Chain
Fluorotelomer AFFF
1970s-2016

- Sold from 1970s - 2016
- Long-chain fluorotelomers (8:2 FTS) can breakdown to PFOA

Modern
Short Chain
Fluorotelomer AFFF

- Most foam mfrs transitioned to this
- No PFOS and no breakdown to PFOS
- Short-chain fluorotelomers (6:2 and 4:2 FTS)
- May contain trace amts of PFOA and PFOA precursors
- Considered lower in toxicity and reduced BAP

Similar evolution in other industrial uses
PFAS in Landfills, Leachate, and Gas
PFAS in Landfill Leachate

- **US Landfill Study (Lang et al., 2017)** – 95 samples from 18 landfills
  - 70 PFAS measured, 19 PFAS detected in >50% of samples
  - PFOS: 3 to 200 ppt
  - PFOA: 100 to 1,000 ppt
  - Total PFAS: 2,000 to 29,000 ppt
  - 5:3 FTCA (precursor) dominant in most leachates: 400 to 15,000 ppt

- **Canadian Landfill Study (Li, 2012)** samples for 28 landfills
  - PFAS detections in all 28 samples
  - PFOA detected in all samples, mean concentration of 439 ppt

- **German Landfill Study (Busch, 2009)** – 22 German landfills
  - 38 PFAS detected
  - Total PFAS: 30.5 ppt to 13,000 ppt
Michigan PFAS in Leachate & Effects on POTWs

https://docs.wixstatic.com/ugd/6f7f77_9b845fefde8b4fd3b42e6a7bd321e21f.pdf

- 30 Mich. LFs, leachate analysis of PFOA & PFOS
  - PFOA – range 3 to 800 ppt vs. MDEQ SW criterion 420 ppt
  - PFOS – range 100 to 710 ppt vs. MDEQ SW criterion 11 ppt

- Landfills as PFOA/PFOS sources to WWTP are relatively minor

- Non-leachate sources contribute greater mass to WWTP influent than leachate.

- Study limitation: Analyzed for PFOA & PFOS only
  - No precursor analyses.
  - Precursors can be present in anaerobic conditions (i.e., in leachate), with degradation to PFOA and PFOS in aerobic treatment system.
Landfill Gas

- PFAS detected in:
  - Landfill Gas
  - Landfill gas condensate
  - Ambient air around landfill (and waste water treatment plants)

- Volatile Precursors
  - Some PFAS (e.g. fluorotelomer alcohols like 8:2-FTOH) have moderate volatility
  - These compounds can break down to form regulated PFAS in the environment
  - Significant PFAS (mostly FTOH) emissions (>1000 g/year) have been calculated from WWTPs and landfills (Ahrens et al, 2011)
Fate and Transport and Toxicology
Source: March 2018 ITRC Factsheet: Environmental Fate & Transport for PFAS, used with permission
PFAS Mobility

BTEX Plumes
Chlorinated Ethene Plumes
Other CVOC Plumes
PFAS Plumes
Exposure in Humans

- Majority of US population exposed to PFAS
- Half-life = 2 - 10 years (humans)
- Prevalent in blood and urine samples – baseline exists
- Can cross placental barrier – exposure to developing fetus
- C8 Health project, 70,000 residents with drinking water exposure linked to serum-PFOA concentrations and variety of health outcomes

- High cholesterol
- Ulcerative colitis
- Thyroid disease
- Pregnancy-induced hypertension
- Cancer (testicular, kidney)
Average blood Serum Concentrations US

Reported Average Blood Serum PFOS Concentrations

Serum (ug/l)

Most toxicology studies have focused on PFOA and PFOS
- Conflicting study results in literature
- Has a low affinity to lipids and preferentially binds to proteins
  - Liver, kidney, muscle and blood

Biological Fate in Humans

- Dec 2018 USEPA IRIS announced 5 PFAS (PFNA, PFBA, PFHxA, PFHxS, PFDA) will be reviewed for toxicity assessment
  - Some of these are the short chain PFAS compounds that form the bases for Modern AFFF
Regulatory Status
What is Occurring? – What to Expect?
U.S. EPA’s Recent Actions

EPA PFAS Action Plan: An Overview

- PFOA & PFOS proposed to be listed as hazardous substances under CERCLA
- Development of MCLs for PFOA & PFOS
- Expand monitoring of PFAS in UCMR5
- Consider PFAS for Toxics Release Inventory
- Develop risk communication toolbox
- Develop toxicity standards for select PFAS
- Develop new analytical methods for PFAS
- Evaluate treatment options for PFAS
- PFOA & PFOS groundwater cleanup recommendations

- April 25, 2019 Draft Groundwater Remediation Standards for public comment
  - 40 ng/L for a screening level
  - 70 ng/L for the preliminary remediation goal (PRG)
Comprehensive Environmental Response, Compensation, and Liability Act

Provides broad authority to federal government (including natural resource trustees) to respond directly to releases or threatened releases of hazardous substances that may endanger public health or the environment.

- At present, CERCLA lists ~800 hazardous substances
- EPA has initiated the regulatory development process for listing PFOA & PFOS as CERCLA hazardous substances. This would allow:
  - EPA to require responsible parties to carry out and/or pay for response actions
  - Private parties to seek cost recovery for their response actions

Potential for CERCLA reopeners at 5-year review

Potential impacts to existing state cleanup programs for PFAS
Enforceable limits
Non-enforceable advisories, notification levels, etc.
No standards
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### PFAS: The Rapidly Changing Regulatory Landscape

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Sampling and Evaluation
# PFAS Sampling Dos and Don’ts

A few examples from TRC’s SOP

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<thead>
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<th>WHAT SHOULD I AVOID?</th>
<th>USE INSTEAD</th>
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<tr>
<td>Equipment with <strong>Teflon®</strong> (e.g., bailers, tubing, parts in pump) during sample handling or mobilization/demobilization</td>
<td>✓ High density polyethylene (HDPE) or silicone tubing/materials in lieu of Teflon®</td>
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<td>Low-density polyethylene (LDPE) or glass sample containers or containers with Teflon-lined lids</td>
<td>✓ HDPE or polypropylene containers for sample storage</td>
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<tr>
<td>Tyvek® suits and waterproof boots</td>
<td>✓ HDPE or polypropylene caps</td>
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<tr>
<td></td>
<td>✓ Clothing made of cotton preferred</td>
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<tr>
<td></td>
<td>✓ Boots made with polyurethane and polyvinyl chloride (PVC)</td>
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<tr>
<td>Waterproof labels for sample bottles</td>
<td>✓ Paper labels with clear tape</td>
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<tr>
<td><strong>Sunscreens, insect repellants</strong></td>
<td>✓ Products that are 100% natural, DEET</td>
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<tr>
<td>Sharpies</td>
<td>✓ Ballpoint pens</td>
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<tr>
<td>Aluminum foil</td>
<td>✓ Thin HDPE sheeting</td>
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A few examples only. A complete list available in the TRC SOP for PFAS Sampling.
Separating Impacts

Example: Fingerprinting Multiple Sources of Fire Fighting Foam

- Blue – PFOS
- Green - PFHxS
- Orange PFOA
- Grey PFHxA

Area 1
Area 2
Area 3
Area 4
Reservoir
Treatment and Remediation
PFAS Waste Water Treatment

PFAS Remediation Challenges

- Low Volatility (rules out stripping)
- Moderate solubility
- Strength of C-F Bond
- Treatment efficiency must be very high because of low (ppt) remediation objectives

Water Treatment Technologies

- Sorption/Ion Exchange
  - Carbon (can be effective for some PFAS, but can be inefficient)
  - Ion Exchange Resins (costly)
  - Need to remove all other organics before PFAS treatment
PFAS Remediation Alternatives

Ex-Situ Technologies

- Sorption/Ion Exchange
  - Carbon (can be effective for some PFAS, but can be inefficient)
  - Ion Exchange Resins (costly)

- Emerging technologies:
  - Reverse Osmosis
  - Membrane filtration
  - Thermal Treatment
  - SAFF – Surface Activation Foam Fractionation

In Situ Technologies

- Emerging(?) technologies:
  - Carbon injection
    - PRB or Source Area
  - Electro-Chemical Oxidation
  - ART In-Well Circulation System
Questions?

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