PFAS - More Than You Ever Wanted to Know and Then Some

Linda S. Lee et al.

March 13, 2019
2019 BIOSOLIDS CONFERENCE
“Challenges and Opportunities”
Overview

• A few PFAS basics
• Biodegradation: Precursor PFAS to other PFAS
• PFAS in waste-derived fertilizers (Purdue Research)
• Brief highlights on 4 field studies
• Comment on treatment strategies
• Comment on analytical & sampling Challenges
• A few take-home message/recommendations
Per- and Poly- Fluoroalkyl Substances (PFAS)

Examples

Perfluorooctane sulfonate (PFOS)

\[
\begin{array}{c}
\text{F}_3\text{C-CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_3^- \\
\text{Tail} \\
\text{Head}
\end{array}
\]

Perfluorooctane carboxylate (PFOA)

\[
\begin{array}{c}
\text{F}_3\text{C-CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CO}_2^- \\
\text{Tail} \\
\text{Head}
\end{array}
\]

Polyfluorinated Substances

\[
\begin{array}{c}
\text{F}_3\text{C-CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{SO}_3^- \\
\text{Head} \\
\text{Tail}
\end{array}
\]

\[
\begin{array}{c}
8:2 \text{ FTOH} (8:2 \text{ fluorotelomer alcohol}) \\
\text{Head} \\
\text{Tail}
\end{array}
\]

\[
\begin{array}{c}
\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{SO}_3^- \\
\text{6:2 Fluorotelomer sulfonate (6:2 FtS)}
\end{array}
\]

‘Head’ also referred to as terminal functional group or polar functional group

IRTC PFAS Fact Sheet (Fig. 2.2); Buck et al., 2011
• > 3000 PFAS produced
• Numerous subclasses
• 100+ homologues
  \[ \text{CF}_3\text{-(CF}_2\text{)}_n \text{—‘head, terminal group’} \]
  \[ n = 1 \text{ to } 18 \]
• Shorter chains more mobile, but less bioaccumulative
• Head group also affects mobility

PFOS, PFOA...

Wang et al., 2017, ES&T, 51:2508–2518
Electro-Chemical Fluorination (ECF)

- \( C_nH_{2n+1} + SO_2Cl_2 + (2n+2)HF \)
- \( C_nF_{2n+1}SO_2F + HCl + byproducts \)
- \( C_8F_{17}SO_2F \)
- \( C_8F_{17}SO_2H \) or \( C_8F_{17}SO_2M \)

- 3M process (used until 2000)
- Linear and branched chains
- ‘\( M \)’ can be many things, e.g.,


- CF₃CF₂(CF₂CF₂)ₙI + C₂H₂
- \( CF_3(CF_2CF_2)_nC_2H_2I \)
- (FT alcohols, FTOHs)
- \( R_1CH_2CH_2OH \)
- Acrylates, stearates, phosphates, urethanes

- CH₂CH₂ linkage between fluoroalkyl tail and ‘head’
- DuPont, Asahi Glass, others
- Linear even numbered chains
Example of the Electrochemical Process Leading to Multiple Isomers

Even PFOS is not a single compound!

Chromatographic separation options:

- Single peak: all isomers
- 2 peaks: linear, branched
- 3 & 4:
- 5:
- 6:
PFAAs more than the infamous C8 PFOA and PFOS

There ~C4-C18 homologues

Persistent like PCBs BUT much more mobile (low pK\textsubscript{a} values so ~anionic)

Level of concern are at the ppt (ng/L) level.

Our challenge for the next few decades.

PFAS Precursor

In soils, during composting, during remediation targeting other chemicals….

Perfluorocarboxylic acids (PFCAs)

Perfluorooctanoic acid (PFOA C8)

Perfluorooctane sulfonic acid (PFOS C8)

Perfluorosulfonic acids (PFSAs)

Perfluoroalkyl acids (PFAAs)

PFAS vs Perfluoroalkyl acids (PFAAs)
Red Circles are terminal and mobile metabolites.
• ECF-based PFAS can yield PFSAs
• Yield is typically low
• Unlike PFCAs

PFAS in Aqueous Film Forming Foams (AFFFs)

**Electrochemical fluorination (ECF)-based PFAS**

**Telomer-based PFAS**

Perfluorosulfonic acids
PFSAs (PFOS \( pK_a < 0 \))

Perfluorocarboxylic acids
PFCAs (PFOA \( pK_a < 4 \))

\[ \Sigma = \text{PFAAs} = \text{per/polyfluoro alkyl acids} \]
.....to the Wastewater Treatment Plant

PFAAs: Effluent >> Influent

_Biotransformation of precursors during aerobic wastewater treatment_

Schultz et al., Environ. Sci. & Technol., 2006, 40(5)
History & Regulations of Perfluoroalkyl Acids (PFAAs)

40-50s
Commercial PFAA-based products

60-80s
Employee concerns

90-00s
Globally detected in wildlife; EPA raises concerns

2010-15
Reduce PFOA emissions by 95%

~ 2016
EPA announced Provisional health advisory values of 70 ng/L (ppt) combined PFOA & PFOS

6:2 FTSA & PFHxS are added the list of UCMR3 by EPA

2017 - current
More occurrences States moving ahead of EPA to declare their own health advisories

EPA Proposes a plan to regulate some PFAS
The # of tox. Studies is increasing, but results are not consistent so effects are still not clear

# of papers regarding PFOA/PFOS

Number of publications

Year
0 100 200 300 400 500 600 700
PFAS – Health Concerns?!?

- May 2016 - EPA Lifetime Health Advisory of 70 ppt
- May 2018 - EPA PFAS Summit
  - MCL process to be investigated
  - PFOA and PFOS to be made CERCLA hazardous substances
  - Draft of toxicity assessment for GenX (PFAS substitute and PFBS) – Nov 2018
- Epidemiological studies and laboratory animal studies have not shown consistent and conclusive findings
- ATSDR draft Toxicological Profile for Perfluoroalkyls contains Minimum Risk Levels (MRLs) for PFOA, PFOS, PFHxS, and PFNA
- Australian Expert Health Panel (May 2018)
  - “… there is mostly limited, or in some cases no evidence, that human exposure to PFAS is linked with human disease” and “there is no current evidence that suggests an increase in overall cancer risk”
  - “… even though the evidence for PFAS exposure and links to health effects is very weak and inconsistent, important health effects for individuals exposed to PFAS cannot be ruled out based on the current evidence”
- Jan 2019 - EPA announces plans to regulate cancer-causing chemicals found in America's drinking water
PFAS health concerns are impacting wastewater and biosolids management......
PFAS health concerns are impacting wastewater and biosolids management…….

Wisconsin case shows how sewage plants spread unregulated toxins across landscape

January 27, 2019

“As Wisconsin discovers more PFAS contamination it will decide whether to follow the lead of Michigan and investigate the role of wastewater treatment plants in spreading the indestructible, toxic compounds across the landscape.”

The hard truth: Under current practices, the PFAS coming into a WWTP are going to come out in either the effluent or in the sludge.
State reactions for effluent and biosolids are led by drinking water and clean-up divisions...

- **Michigan, 2014** Surface water human fish consumption PFOS limit: 12 ppt
- **Alaska, 2016**
  - Proposed migration-to-groundwater soil cleanup levels:
    - PFOA: 1.7 ug/kg (ppb)
    - PFOS: 3 ug/kg
- **New York, 2017**
  - DEC interim preliminary screening level for one specific permit:
    - PFOA + PFOS: 72 ug/kg
  - Typical biosolids *can* meet this.
- **Maine, 2018**
  - DEP Chapter 418 non-agronomic residuals screening level
    (developed using EPA RSL calculator):
    - PFOA: 2.5 ug/kg
    - PFOS: 5.2 ug/kg
  - Typical biosolids *can’t* meet those.
  - What does this mean for effluent & biosolids?
- **VT, 2017**
  - DEC added PFOA & PFOS to Haz. Waste list for liquids: PFOA + PFOS >20 ppt

*Reality check:* The science has not caught up. It’s too early to set a defensible screening number for biosolids.
Challenge: Protecting the Agricultural Value of Biosolids & Composted Wastes and Human Health

versus

And where does the leachate go.....in many cases, back to a WWTP plant...???
Waste-based Fertilizers and PFAAs

- **Benefits of waste-derived fertilizers:** Recycling wastes for plant nutrients and improving soil health
- **Current challenge:** Potential leaching of PFAAs to water sources and plant uptake and trophic transfer
- **Question being addressed:** What PFAAs are present in waste-derived fertilizers and what may be leachable?

- **At Purdue:** We have been quantifying PFAA concentrations in different types of waste-derived and commercially available fertilizers and PFAA ‘availability’ potential by PFAAs in associated pore-water.
**PFAA Levels in Composts and Biosolids Products**

- **17 PFAAs**
  - 13 PFCAs (C4 to C18): $\text{CF}_3(\text{CF}_2)_n\text{COOH}$
  - 4 PFSAs (C4, C6, C8 and C10): $\text{CF}_3(\text{CF}_2)_n\text{SO}_3^-$

- **18 Commercially Available Fertilizers**
  - 11 biosolids-based (<2 mm fraction evaluated except for granular biosolids)
  - 7 non-biosolids-based (< 2 mm fraction evaluated)
  - Freeze-dried

- **10 Municipal Solid Waste (MSW) Composts**
  - Obtained in 2017 via Zero-Waste Washington
### Commercially Available Fertilizers (2014)

<table>
<thead>
<tr>
<th>Fertilizer</th>
<th>Description</th>
<th>Post-treatment</th>
<th>Biosolids/non-biosolids based</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Food and yard compost</td>
<td>Composting</td>
<td>Non-biosolids</td>
</tr>
<tr>
<td>B</td>
<td>Compost with untreated wood products</td>
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</tr>
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<td>Manure compost</td>
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</tr>
<tr>
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<td>Manure and peat compost</td>
<td>Composting</td>
<td>Non-biosolids</td>
</tr>
<tr>
<td>E</td>
<td>Mushroom compost</td>
<td>Composting</td>
<td>Non-biosolids</td>
</tr>
<tr>
<td>F</td>
<td>Mushroom compost</td>
<td>Composting</td>
<td>Non-biosolids</td>
</tr>
<tr>
<td>G</td>
<td>Peat/compost based growing mix</td>
<td>Composting</td>
<td>Non-biosolids</td>
</tr>
<tr>
<td>H</td>
<td>Heat-dried granular biosolids</td>
<td>Heat-treated</td>
<td>Biosolids</td>
</tr>
<tr>
<td>I</td>
<td>Heat-dried granular biosolids</td>
<td>Heat-treated</td>
<td>Biosolids</td>
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<tr>
<td>J</td>
<td>Heat-dried granular biosolids</td>
<td>Heat-treated</td>
<td>Biosolids</td>
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<td>K</td>
<td>Heat-dried granular biosolids</td>
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</tr>
<tr>
<td>L</td>
<td>Heat-dried granular biosolids</td>
<td>Heat-treated</td>
<td>Biosolids</td>
</tr>
<tr>
<td>M</td>
<td>Biosolids blended with maple sawdust and aged bark</td>
<td>Blending</td>
<td>Biosolids</td>
</tr>
<tr>
<td>N</td>
<td>Composted biosolids with woodchips</td>
<td>Composting</td>
<td>Biosolids</td>
</tr>
<tr>
<td>O</td>
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<td>Composting</td>
<td>Biosolids</td>
</tr>
<tr>
<td>P</td>
<td>Composted biosolids with municipal solid waste</td>
<td>Composting</td>
<td>Biosolids</td>
</tr>
<tr>
<td>Q</td>
<td>Composted biosolids with residential yard trimmings</td>
<td>Composting</td>
<td>Biosolids</td>
</tr>
<tr>
<td>R</td>
<td>Composted biosolids with plant materials</td>
<td>Composting</td>
<td>Biosolids</td>
</tr>
</tbody>
</table>
Example of Historical Use Trends of a Commercially Available Biosolid-based Fertilizer (Fertilizer M) Annual Gross Revenue (the year of 2018 included the revenues from January to September).
## Composted MSW Fertilizer*
*(Obtained with help from Zero Waste Washington)*

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<tr>
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<td>Leaves and grass waste from municipalities</td>
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<td>Residential backyard waste compost bin.</td>
</tr>
<tr>
<td>10</td>
<td>Leaves</td>
</tr>
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* Some may also be commercially available
**Experimental Approach**

**Extraction Method**

1. Freeze-dried fertilizer (< 2 mm)
2. Add MeOH+NH₄OH mixture
3. Vortex
4. Heated sonication bath
5. Rotator 2 h
6. Centrifuge
7. Evaporate combined extract to dryness under nitrogen
8. Reconstitute with 99:1 (v/v) MeOH and glacial acetic acid
9. **Clean up and analysis**
   - Add MeOH+NH₄OH mixture
   - Vortex
   - Centrifuge
   - ENVI-Carb clean up
   - Vortex
   - Centrifuge
   - Transfer to HPLC vial
   - UPLC-Q-ToF

**Pore-water Measurement**

1. Incubate at a fixed residence time (48h)
2. Freeze-dried fertilizer in CaCl₂+NaN₃ solution
3. Collect leachate
4. Centrifuge
5. Add isotopically labeled surrogate

*Modified method from Sepulvado et al., 2011*
Result: PFAAs in 2014 Commercial Fertilizers

Commercially available
Non-biosolids based fertilizers

Commercially available
Biosolids based fertilizers

Long chains (C ≥ 6) dominant

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*PFAA concentration in < 2mm fraction (36-80%) normalized to total mass (assumes PFAA is negligible in the fraction > 2 mm)

Kim Lazcano et al., Manuscript in preparation
Possible Temporal variation
(Milorganite - heat-treated biosolid-based fertilizer)

• ~80% PFOS (C8) reduction from 2014 to 2018
• ~30% PFHxA (C6) reduction from 2014 to 2018

Keep in mind:
Only 17 PFAAs were analyzed.
PFOA and PFOS in Blood: Decreasing Blood Trends too (National Health & Nutrition Examination Survey - NHANES)

- Decreasing trends with for PFOS and PFOA – direct response to phase-out
- Note - blood levels reported in ppb (µg/L)
- Bioconcentration over time ~100-fold
- Effected by PFAS type and chain length

Compiled by Stephen Zemba, Sanborn Head & Associates
**Result: What about PFAAs in Municipal Waste Composts (2017)**

Choi et al., Manuscript in preparation; Zero Waste Washington was provided the samples.

- Higher PFAA concentrations in municipal waste composts with food waste + food serviceware or packaging

*PFAA concentration in < 2mm fraction (30-69%) normalized to total mass (assumes PFAA concentrations is negligible in the fraction > 2 mm)

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<td>Residential back yard compost bin</td>
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<td>Leaves</td>
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</table>

**Diagram:**

- **Leaves, grass**
  - Backyard compost
  - Includes food waste & compostable food serviceware

- Concentration (µg PFAAs/kg Fertilizer)
  - Short chains (C ≤ 6) dominant

- PFHxDA, PFTeDA, PFTrDA, PFDoA, PFUdA, PFDA, PFOS, PFNA, PFOA, PFHxS, PFHpA, PFHxA, PFBS, PFPeA, PFBA

Leaves and grass waste from municipalities

Residential back yard compost bin

Leaves
PFAS in Food Packaging (Schaider et al 2017)

- FDA approves more than 90 monomer and polymer PFAS for use in food contact materials.
- “PFOA-free” food packaging ≠ PFAS free
- Direct land application of compost with PFAS-containing food packaging may result in elevated soil concentration and enhanced phytoaccumulation.

Release to porewater: Subset of PFAA Pore-water Concentrations

- Overall trend of increasing PFAA ‘release’ concentrations with increasing PFAA load in the fertilizers regardless of source.
- Some PFAA pore-water concentrations >> regulatory or provisional guidance levels
- However, PFAAs will be diluted and attenuated depending on the application site characteristics, management and chain length.
An additional analysis to explore remaining precursor PFAS

Total Oxidizable Precursor (TOP) assay (Houtz and Sedlak 2012)

Dried-Fertilizer Extract

Add 60 mM potassium sulfate + 150 mM sodium hydroxide mixture

Vortex

Heated water bath (85 °C for 6 h)

Ice water bath

Add HCl

Clean up & Analysis

- High pH (> 11.5) heat-activated persulfate oxidation for a few hours
- Can be useful with potentially > 3000 PFAS available
- Limited number of analytical standards and methods available
- Allow “semi-quantification” of PFAA precursor concentrations
- Note: The TOP assay can transform a single precursor PFAS to more than 1 PFAA
TOP assay: Exploring for additional *precursor* PFAS (1 of 2)

Kim Lazcano et al., Manuscript in preparation
Of the total 28 fertilizers evaluated, only 6 appeared to have a significant mass of additional precursor PFAS.
Summary from Purdue Research on Waste-based Fertilizers

- Higher PFAA concentrations in municipal waste composts with known food waste and food serviceware or packaging.
- Higher PFAA concentrations in commercial biosolids-based fertilizers than non-biosolids based fertilizers but may an artifact of a temporal trend.
- The decline in long chain PFAAs from 2014 to 2018 for Milorganite suggests that the differences in relative chain lengths between municipal waste composts vs. biosolids-fertilizers is likely temporal and unrelated to the absence vs. presence of biosolids.
- “Pore water” concentration >> regulatory or provisional guidance levels. However, PFAAs will be diluted and attenuated depending on the application site characteristics, management and PFAA chain length.
- For some PFAAs, a strong correlation between pore water PFAA concentrations and total PFAA concentrations was observed (e.g., higher level of PFAAs → higher pore water concentration → higher leaching potential).
Field studies are limited, but once land-applied.....

Sepulvado et al, 2011 (IL, USA) PFOA & PFHxA with depth in long term (LT) plots at various cumulative loading rates of 2004-2007 Chicago MWWTP biosolids (8-68 ng/g PFOA & 80-219 ng/g PFOS).

- Control = 0 Mg/ha
- LR 1 = 553 Mg/ha
- LR 2 = 1109 Mg/ha
- LR 3 = 2218 Mg/ha

- Transport does occur
- Dilution does occur
- However, given unprecedented low ppt level advisory levels, concerns/challenges are not diluted
• PBDEs, other BFRs and PFAAs were detected in tile drainage and 2 m groundwater throughout the post-application study period.

• No PBDEs, other BFRs, or PFAAs were detected in wheat grain.
Other scenarios → Scant literature shows some leaching to groundwater possible at levels approaching the EPA PHA concentration → Regulators concerned.

BUT drinking water did no support concern at this New Hampshire site.

Monofill used in 1980s. Since ~1996, all biosolids from WWTP (11.5 MGD) have been land applied, some on farm field shown. Kind of a worst-case scenario? But no drinking water impacts found.

Modified from Ned Beecher, NEBRA
Another case for New York site – Regulatory response in March 2017 drove recycle paper mill residuals to landfill. Composting business laid off workers. Due to non-drinking, surface water levels up to combined 240 ng/L (ppt).

Not drinking water. Do all surface water meet drinking water screening levels?)

Perception?

Facility continues to operate, but is challenged.

Modified from Ned Beecher, NEBRA
# A moving target: State Groundwater Standards/Guidelines

<table>
<thead>
<tr>
<th>State</th>
<th>PFOA</th>
<th>PFOS</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>AI, CA, CO, DE, FL, ME, NH, NY, RI</td>
<td>70 ng/L (ppt)</td>
<td></td>
<td>Adopted EPA HAL</td>
</tr>
<tr>
<td>Alaska and Illinois</td>
<td>400 ng/L</td>
<td>200 ng/L</td>
<td></td>
</tr>
<tr>
<td>Maine</td>
<td>130 ng/l</td>
<td>560 ng/l</td>
<td></td>
</tr>
<tr>
<td>Massachusetts &amp; Connecticut</td>
<td>70 ng/l</td>
<td></td>
<td>Includes sum of 5 PFAS</td>
</tr>
<tr>
<td>Michigan</td>
<td>420 ng/L</td>
<td>11 ng/L</td>
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<tr>
<td>Minnesota</td>
<td>35 ng/L</td>
<td>27 ng/L</td>
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<td>14 ng/L</td>
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<tr>
<td>North Carolina</td>
<td>1,000 ng/L</td>
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<td>Texas</td>
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<td>Vermont</td>
<td>20 ng/L</td>
<td></td>
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</tr>
<tr>
<td>West Virginia</td>
<td>500 ng/L</td>
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Compiled by Stephen Zemba, Sanborn Head & Associates
Treatment Study: Water Research Foundation (WRF) Report (#4322)

- State of Knowledge as of ~2015/2016 – research is increasing rapidly but still no silver bullet
- Focused on evaluation of full-scale treatments common in U.S. and included some bench scale experiments
- Full-scale conventional treatments, such as coagulation followed by physical separation processes; and chemical oxidation, aeration and disinfection were not effective in removing PFASs.
- Full-scale anion exchange and GAC column treatments were more effective at removing long-chain PFASs and PFSAs than PFCAs. Competition by natural organic matter (NOM) for GA sorption reduced ability to adsorb PFCAs and PFSAs.
- Full-scale RO demonstrated significant removal for all the PFASs, including the smallest PFAS currently of concern (perfluorobutanoic acid -PFBA).
Analytical Challenges

• Requires advanced analytical instrumentation
• Cost is high
• PFAS during sampling and handling can cause contamination (equipment, apparel, lab procedures), which is a big deal when we are talking low ppt
• Therefore, quality assurance and quality control (QAQC) documents are a must
• Approved contract labs are still limited
• The list of PFAS that may be regulated is likely to grow including PFAS substitutes that are replacing the phase-out PFAS (GenX, ADONA, etc.)
Some More PFAAs Take-Home Messages

- Loss through microbial degradation will not lead to reduction in PFAA concentrations; PFAAs are terminal metabolites of PFAS precursor degradation

- **Pore water concentrations ≠ groundwater concentration**: Actual concentrations measured in groundwater will be dependent upon numerous factors including subsurface soil properties, groundwater flow from other sources, well screen intervals, etc. and other PFAA sources

- Field studies with biosolids are limited and results vary, but higher than targeted PFAA concentrations can end up in groundwater, tile drainage, and groundwater

- **Simulations (not shown today) indicate that repeated applications of PFAA-containing biosolids to the same site will result in detectable concentrations in groundwater** (e.g., estimated at > 50 ppt for PFOA for a ‘typical’ scenario)

- Repeated higher application rates of PFAA-containing biosolids (e.g., > 100 tonnes/ha/yr) or high PFAA concentrations (e.g., > 100 µg PFOA/kg) will result in higher groundwater concentrations (e.g., potentially > 1,000 ppt PFOA)

- Guidance should be developed for industrial and municipal WWTPs concerning the disposal practices of PFAA-containing biosolids

- **Negligible impacts on groundwater quality can occur if appropriate consideration is given to both biosolids application rate and potential PFAA concentrations in the biosolids** (e.g., control source to WWTP!)
Some Recommendations/Application

- PFAAs analysis on municipal waste composts was used to help pass two bills by the Washington State Legislative.
  1. HB 2658 - 2017-18: Concerning the use of PFAS in food packaging
  2. SB 6413 - 2017-18: Reducing the use of certain toxic chemicals in firefighting activities
- Decreasing the use of PFAA-containing products such as a food serviceware could help to reduce PFAA loads in waste-derived fertilizers.
- Separating the sources of composts and making careful decisions on what we compost could decrease PFAAs.
- Risk assessment should include subsequent attenuation (sorption and dilution) of PFAA concentrations leaching from waste-derived fertilizers.
- Improve understanding, design and affordability of WWTP processes
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