Potential for Perfluoroalkyl Acid Bioaccumulation in Food Crops

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September 8, 2014
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Perfluoroalkyl acids (PFAAs)

- Fully fluorinated chemicals that repel both oil and water
- PFAA-based precursors used in coatings for textiles and paper packaging products, fire-fighting foams, etc.
- Persistent, Bioaccumulative, and Toxic (PBT)
- Widely detected in wildlife and humans
- Relatively mobile and yet bioaccumulative
So, again, what are PFAAs?

Perfluorooctane sulfonate (PFOS)
$\text{C}_8\text{F}_{17}\text{SO}_3$

Good news: C-F bond is one of the strongest chemical bonds known

Bad news: C-F bond is one of the strongest chemical bonds known

PFAAs are extremely persistent in the environment!
Why do we care?


Why should YOU care?

Decatur, Alabama

- Fluorochemical-manufacturing plant discharged to local WWTP, leading to contaminated biosolids
  - Biosolids were applied to farms, contaminating soil and groundwater
  - In 2009, led to development of EPA’s provisional health advisories for PFOS and PFOA:

<table>
<thead>
<tr>
<th></th>
<th>PFOA</th>
<th>PFOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sub-Chronic Reference Dose</td>
<td>0.2 µg/kg-day</td>
<td>0.08 µg/kg-day</td>
</tr>
<tr>
<td>Provisional Health Advisory (PHA) - Drinking Water</td>
<td>0.4 µg/L</td>
<td>0.2 µg/L</td>
</tr>
<tr>
<td>Residential Soil Screening Levels</td>
<td>16,000 µg/kg</td>
<td>6,000 µg/kg</td>
</tr>
</tbody>
</table>

- ~22% of groundwater samples exceeded PHA for PFOA*
- No federal regulations exist, but some states developing state regulations

Are there other Decatures?

“The Loopers Bend sewage sludge, known as biosolids, has been composted and sold to businesses and individuals in the Dalton area since 2003. Dalton Utilities has estimated that 80 million pounds of the compost have been sold and distributed. Dalton Utilities ceased its distribution of the compost in July 2009 after receiving data indicating elevated levels of PFCs in the compost.”

“PFOS CHROMIUM ELECTROPLATER STUDY
U.S. ENVIRONMENTAL PROTECTION AGENCY-REGION 5

“The data clearly indicated that decorative chromium electroplaters discharge PFOS and other PFCs to WWTPs in concentrations higher than background levels. Data also indicated that mist suppressants have very specific PFC mixtures, which may be found in the resulting electroplater effluent. The concentrations vary widely....”

“Care should be taken when comparing results from one facility to another, as the study included facilities of different operational sizes and production schedules. Facilities also varied widely in the brand of mist suppressant used, and amount added to the plating baths.”
PFAAs in typical biosolids-amended soils

• Clear relationships between cumulative biosolids loading rate and PFAA content
  - Biosolids are the source!

• Regressions can be used to predict PFAA soil concentrations based on cumulative loading rate

PFAA Precursors

- **N-EtFOSE polymer**
- **N-EtFOSE**
- **N-EtFOSAA**
- **FOSA**
- **PFOS**

- **8:2 FTOH polymer**
- **8:2 FTOH**
- **8:2 FTCA**
- **Black Arrow**

**PFOA**

**PFNA**
Sources of PFAAs to Foodcrops

- Houses
- Cities
- Factories
- Agricultural Fields or Home Gardens

WWTP

Influent

Biosolids

Effluent
Why be concerned?

Transpiration Stream Concentration Factor (TSCF):

\[
TSCF = \frac{[\text{Contaminant Concentration in Xylem}]}{[\text{Contaminant Concentration in Solution Adjacent to Roots}]}
\]

- Plant uptake models suggest maximal TSCF at \(\log K_{ow} \sim 2\)
- New model suggests sigmoidal relationship with \(\log K_{ow}\)
- Many CECs of interest are small, polar, and/or charged and have low \(\log K_{ow}\) values (if measurable)

Overall Approach

Biosolids Studies
- Greenhouse-based studies of lettuce, radishes, tomatoes, celery, and snap peas
- Pilot-scale field trials of lettuce, tomatoes
- Field-based corn study

Reclaimed Water Studies
- Greenhouse-based studies of lettuce and strawberries
Robust Analytical Methods Needed

• Need to measure PFAAs in a wide variety of matrices (soil, water, different plant tissues)
  – Non matrix-matched approach needed

• All PFAAs measured using liquid chromatography tandem mass spectrometry (LC-MS/MS)
  – Stable isotope surrogates employed whenever possible
Biosolids: Greenhouse Experiments

Crops
- Edible root: radish (*Raphanus sativus*)
- Edible stem/leaf: celery (*Apium graveolens* var. *dulce*)
- Edible leaf: lettuce (*Lactuca sativa* ‘Multy’)
- Edible fruit: tomato (*Lycopersicon lycopersicum* ‘Stupice’)
- Edible fruit/seed: sugar snap pea (*Pisum sativum*)

Soils
- “Control” - Field-collected unamended soil
- “Industrially-Impacted” - Control + composted biosolids (10% mass)
- “Municipal Soil” - Field-collected biosolids-amended soil
Biosolids: PFAAs in Lettuce in Tomato

Mean and standard error are shown (n = 5)
Values marked with an asterisk are significantly different (α = 0.05) than the control treatment
Values less than the LOQ are denoted by <.

Biosolids: BAFs for PFAA in Lettuce and Tomato

Field Trial Plots

Crops
• Edible Leaf (lettuce)
• Edible Fruit (tomato)

Biosolids-Amended Plots – 3 replicate plots each
• Control (unamended)
• 0.5X agronomic rate for N (single application)
• 1X agronomic rate for N (single application)
• 2X agronomic rate for N (single application)
• 4X agronomic rate for N (single application)
# BAFs for PFAAs: Greenhouse vs. Field

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Greenhouse Lettuce (Municipal Soil)</th>
<th>Greenhouse Lettuce (Industrially-Impacted Soil)</th>
<th>Field Trial Lettuce (4X Soil)</th>
<th>Greenhouse Tomato (Industrially-Impacted Soil)</th>
<th>Field Trial Tomato (4X Soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBA</td>
<td>28.38 ± 5.21</td>
<td>56.84 ± 3.45</td>
<td>39.89 ± 2.41</td>
<td>12.16 ± 1.71</td>
<td>18.22 ± 5.34</td>
</tr>
<tr>
<td>PFPeA</td>
<td>10.21 ± 1.52</td>
<td>20.43 ± 2.70</td>
<td>16.29 ± 2.35</td>
<td>17.06 ± 3.74</td>
<td>14.85 ± 1.96</td>
</tr>
<tr>
<td>PFHxA</td>
<td>11.66 ± 2.11</td>
<td>9.90 ± 1.37</td>
<td>2.90 ± 0.87</td>
<td>6.84 ± 0.81</td>
<td></td>
</tr>
<tr>
<td>PFBS</td>
<td>14.47 ± 3.84</td>
<td>4.22 ± 0.37</td>
<td>2.02 ± 0.32</td>
<td>0.42 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>PFHxS</td>
<td>1.08 ± 0.11</td>
<td>7.56 ± 0.86</td>
<td>1.51 ± 0.11</td>
<td>0.50 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>PFOS</td>
<td>0.32 ± 0.02</td>
<td>1.67 ± 0.32</td>
<td>0.10 ± 0.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Full-Scale Field Sampling

Crop
- Stover – stem and leaves from corn plant
- Corn – kernels

Soils
- Urban site (control)
- Urban site (1X agronomic rate for N)
- Urban site (2X agronomic rate for N)
- Rural site (control)
- Rural site (0.5X agronomic rate for N)
# Full-Scale BAF Comparisons

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Greenhouse Lettuce (Industrially-Impacted Soil)</th>
<th>Field Corn Stover (2X Soil)</th>
<th>Previous Study: Grass*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBA</td>
<td>56.84 ± 3.45</td>
<td>64.76 ± 15.35</td>
<td>- 0.2 log units</td>
</tr>
<tr>
<td>PFPeA</td>
<td>20.43 ± 2.70</td>
<td>41.08 ± 9.00</td>
<td>3.40 ± 2.60</td>
</tr>
<tr>
<td>PFHxA</td>
<td>9.90 ± 1.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFHpA</td>
<td>2.66 ± 0.47</td>
<td></td>
<td>0.90 ± 0.66</td>
</tr>
<tr>
<td>PFOA</td>
<td>2.52 ± 0.48</td>
<td></td>
<td>0.25 ± 0.23</td>
</tr>
<tr>
<td>PFNA</td>
<td>2.85 ± 0.47</td>
<td></td>
<td>0.12 ± 0.08</td>
</tr>
<tr>
<td>PFDA</td>
<td>0.52 ± 0.08</td>
<td></td>
<td>0.10 ± 0.08</td>
</tr>
<tr>
<td>PFOS</td>
<td></td>
<td></td>
<td>0.07 ± 0.04</td>
</tr>
</tbody>
</table>

Plant distribution: PFAAs in Celery and Peas

- Two compartment crop grown in biosolids-amended soil
- Three compartment crop grown in biosolids-amended soil

Biosolids: PFAA Fruit-Soil Concentration Factors

Tomato Fruit: \( y = -0.54 \pm 0.06 \) \( x \) + \( 2.84 \pm 0.35 \)

Pea Fruit: \( y = -0.58 \pm 0.08 \) \( x \) + \( 3.05 \pm 0.37 \)

Implications

- PFAAs can bioaccumulate into plants from PFAA contaminated biosolids-amended soils and reclaimed water
- Plant uptake factors for PFAAs dependent on chain length and head group
  - short-chain > long-chain
  - carboxylates > sulfonates
- PFAA distribution within plants
  - short-chain in fruit crops
  - long-chain in shoot or root crops
- Concentration-dependent uptake suggests passive uptake
- Data suggest new plant accumulation models and further toxicological studies on short-chain PFAA’s may be needed
Putting into Context – initial efforts for PFAAs

• Interim human subchronic oral reference doses for PFOS and PFOA (EPA 2009) of 80 and 200 ng/kg/day, respectively
  – Assuming 70 kg person, suggests interim subchronic doses of 5600 and 14,000 ng per day for PFOS and PFOA

• Consuming 1 entire head of lettuce per day (~500 g$_{gw}$ or ~25 g$_{dw}$):
  – If grown in industrially-impacted biosolids-amended soil (10% amendment rate), 1875 ng PFOS, 5000 ng PFOA
  – If grown in municipal biosolids-amended soil (33 years of biosolids application), 2500 ng PFOS, 500 ng PFOA

Better characterization of sources of high levels of PFAAs to WWTPs is needed!
Disclaimer & Acknowledgements

“The opinions expressed are those of the speaker. Findings, opinions, and conclusions in this presentation do not represent and should not be construed to represent any U.S. EPA determination or policy.”

Funding provided by:
• U.S. EPA Regional Applied Research Effort (RARE) Grant: Measuring for Perfluorochemicals in Field Soils and Crops
• U.S. Department of Agriculture AFRI Grant #2011-67019-21118
• An Associated Project of ReNUWIt: Re-Inventing the Nation’s Urban Water Infrastructure (National Science Foundation)
FLUOROS 2015
An International Symposium on Fluorinated Organics in the Environment

July 12-14, 2015
Golden, Colorado