Characterization of a Wide Array of Fluorinated Organic Compounds in Contaminated Soils

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Outlines

Study Backgrounds
- What are the Fluorinated Organic Compounds (FOCs)?
- Biosolid & Current Issues at Decatur, AL
- 2009 Field Survey Plan & Results

Instrumental Analyses
- Extraction Methods for FOCs in Soil
- LC/MS/MS for 20 PFCs Determination
- GC/MS for 10 FTOHs Determination

Analytical Results & Conclusions
- Identification of Target Peaks in Soil Extract
- Distribution of FOCs in Biosolid-applied Soils
- Modeling Disappearance Rates from Soils
- Conclusions
What are Fluorinated Organic Compounds?

- **Man-made chemicals** with unique properties (C-F bond)
- Used as oil, stain, and grease-repellent coatings for **paper**, textile, leather, **clothing**, thread-sealant tape, **non-stick cookware**, etc.
- U.S. market value for fluoropolymers and fluorotelomers combined is approximately **$1.7 billion** annually
- Perfluorinated compounds (**PFCs**) and volatile Fluorotelomer alcohols (**FTOHs**) are of **present interests**
What are the FOCs? (con’d)
- Structures of PFCs in present Study

PFASs
(Perfluoroalkyl sulfonates)

\[
F(CF_2)_n - \text{SO}_3\text{OH}
\]

PFOS (C=8); \(n = 4, 6 \text{ and } 8\)

PFCAs
(Perfluoroalkyl carboxylates)

\[
F(CF_2)_n - \text{CO}_2\text{OH}
\]

PFOA (C=8); \(n = 3 - 13\) acid

- Structures of FTOHs in present Study

FTOHs
(Fluorotelomer alcohols)

\[
F(CF_2)_n - \text{(CH}_2\text{)}_2\text{OH}
\]

n = 6, 8, 10, 12 and 14

\[
F(CF_2)_n - \text{CH} - \text{OH}
\]

CH$_3$

n = 7, 9, 11 and 13
Biosolids Application & FOC
Contamination Issues at Decatur, AL

Elevated PFCs Levels in Soils (2007)
- Biosolids from local wastewater treatment
- Agricultural soils treated with local biosolids

Occurrence of PFCs in Waters (2009)
- Surface water (25%> health advisory limit for PFOA)
- Well water (all samples < PFOA and PFOS limit)

Historically
- Biosolids are known as good soil conditioner
- Biosolids from local WWTP applied for 10 years
EPA finds record PFOS, PFOA levels in Alabama grazing fields

Because of very high levels of perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and other perfluorochemicals found in agricultural soils near Decatur, Ala., scientists with the U.S. EPA, the U.S. Department of Agriculture (USDA), and the U.S. Food and Drug Administration (FDA) are investigating whether perfluorinated chemicals have entered the human food chain and contaminated meat.

The source of PFOA and PFOS, both of which occur at low part-per-million levels, is treated municipal sewage sludge, or biosolids, that were applied to some 5000 acres of agricultural land, according to Gail Mitchell, EPA Region 4's deputy director of water management. EPA is still investigating how the chemicals got into the sludge, adds Cathy Fehrenbacher, chief of EPA's exposure assessment branch. Sampling private drinking-water wells located much closer to the fields found no contamination. These wells serve fewer than 100 people, Mitchell estimates.

EPA officials notified both USDA and FDA about the high levels of perfluorinated chemicals because the land was used for grazing cattle. Mitchell says USDA is responsible for inspecting raw meat such as beef or chicken for potential contamination, and FDA oversees processed foods. But neither USDA nor FDA has analyzed any samples.

The high concentrations of perfluorochemicals in the Decatur sludge could be a rare situation, or a common one—published data on the concentrations of perfluorinated chemicals in sludge are minimal, and almost nothing is known about concentrations in soils, says Christopher Higgins of the Colorado School of Mines.
News 2 : Mar 23, 2009

**The Decatur Daily**

**USDA to test area cattle for toxin from DU sludge**

Lawrence farmer concerned about contaminated cows

**Action :**
Interagency investigation (EPA, FDA, and USDA)
Aims for 2009 Decatur-AL Monitoring

- To Develop Analytical Methods for a Wide Array of FOCs in Soil Matrix
- To Examine the Extent of PFCs and FTOHs in Biosolid-applied Soils near Decatur, AL
- To Study the Impacts of Historical Biosolid Application on the Fate of PFCs and FTOHs
- To Investigate the Potential Transfer of FOCs to Vegetations from Soils on site
2007 & 2009 Field Sampling
# 2009 Surface Soil Sampling
## - US EPA Region 4 Personnel

<table>
<thead>
<tr>
<th>Field</th>
<th># Sites</th>
<th>Description</th>
<th>Composite from 5 aliquot soils for each site sample!</th>
</tr>
</thead>
<tbody>
<tr>
<td>S17-1a</td>
<td>5</td>
<td>Biosolid-applied</td>
<td></td>
</tr>
<tr>
<td>S1-4</td>
<td>5</td>
<td>Biosolid-applied</td>
<td></td>
</tr>
<tr>
<td>S18-9</td>
<td>5</td>
<td>Biosolid-applied</td>
<td></td>
</tr>
<tr>
<td>S15-3</td>
<td>5</td>
<td>Biosolid-applied</td>
<td></td>
</tr>
<tr>
<td>S14-1</td>
<td>3</td>
<td>Biosolid-applied</td>
<td></td>
</tr>
<tr>
<td>SALMG4A</td>
<td>1</td>
<td>Dairy Field</td>
<td></td>
</tr>
<tr>
<td>S101</td>
<td>2</td>
<td>No biosolid application</td>
<td></td>
</tr>
</tbody>
</table>
## 2009 Field Sampling Results
- US EPA Athens & RTP Labs

<table>
<thead>
<tr>
<th>Media</th>
<th># Samples</th>
<th>Organization</th>
<th>Analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Soil</td>
<td>26</td>
<td>EPA/Athens</td>
<td>PFCs, FTOHs</td>
</tr>
<tr>
<td>Subsurface Soil</td>
<td>6</td>
<td>EPA/Athens</td>
<td>PFCs, FTOHs</td>
</tr>
<tr>
<td>Biosolid</td>
<td>1</td>
<td>EPA/Athens</td>
<td>PFCs, FTOHs</td>
</tr>
<tr>
<td>Surface Water</td>
<td>45</td>
<td>EPA/RTP</td>
<td>PFCs</td>
</tr>
<tr>
<td>Drinking Water</td>
<td>5</td>
<td>EPA/RTP</td>
<td>PFCs</td>
</tr>
<tr>
<td>Plant</td>
<td>7</td>
<td>EPA/Athens</td>
<td>PFCs, FTOHs</td>
</tr>
<tr>
<td>Cow</td>
<td>10*</td>
<td>USDA/FDA</td>
<td>PFCs</td>
</tr>
</tbody>
</table>

* Number of animals
Quality Control for Field and Lab.

Field Blanks/Reference Soil
- Ottawa Sand/Cowart topsoil

Field Duplicates
- A metric of the repeatability from heterogeneity of the distribution of analytes at the sampling scale in the field

Background Field Samples (S101)

Laboratory Fortified Soil Extracts
- ±30% of the theoretical values

GC/MS Identification of FTOHs in Soil Extracts
- [M+1] ion & Derivatization with trimethylysilylimidazole (TMSI)

Laboratory Recovery Internal Standards
- $^{13}$C$_4$-PFOA & $^2$H$_2$$^{13}$C$_2$-8:2FTOH
# Extraction Methods for FOCs in Soils

## Perfluorinated Acids
- Sieved soils
  - 1~2g (wet wt)
- Extractant
  - 4mL Acetonitrile
  - × 3 Overnight
- Extract cleanup
  - Ion Pairing
- Quantitation
  - Isotopic Dilution
- Extraction Recovery
  - 90~110%

## Fluorotelomer Alcohols
- Sieved soils
  - 1~2g (wet wt)
- Extractant
  - 4mL MTBE
  - 5mL Water
  - × 3 Overnight
- Quantitation
  - Isotopic Dilution
- Extraction Recovery
  - 90~110%
**Instrumental Analyses**

Perfluorinated acids using LC-MS/MS (e.g., PFOS & PFOA)
Semi-volatile compounds using GC-MS (e.g., FTOHs)

**Target matrices:**
sludge, soil, plants, & others

**UPLC Waters Acquity MS/MS Quattro Premier XE**
Waters BEH C₁₈ column

**Agilent 6890 GC - 5975 MSD**
PCI/NCl mode
Restek Rtx-1701 column
Distributions of PFCs by Field

Geomean PFCs in Soil (ng/g, dw)

Detailed data by site is available at http://www.epa.gov/region4/water/PFCindex.html
Identification of target FTOHs in Soils

A. Quantification Ion for 14:2 FTOH ([M+1]⁺)

\[ m/z \ 765 \]

B. Qualification Ion for 14:2 FTOH (-[HF+H₂O])

\[ m/z \ 727 \]
Distributions of FTOHs by Field

Geomean FTOHs in Soil (ng/g dw)

Detailed data by site is available at http://www.epa.gov/region4/water/PFCindex.html
Modeling Disappearance Rate - PFCs
(= wash-off + biodegradation + etc.)

\[
y = 150x - 440
\]
\[
r^2 = 0.804
\]

Disappearance half-life (d)

Fluorinated Carbon Number
Modeling Disappearance Rate - FTOHs
(= wash-off + biodegradation + volatilization + etc.)

<table>
<thead>
<tr>
<th></th>
<th>r²</th>
<th>k (1/yr)</th>
<th>t_{1/2} (day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:2 FTOH</td>
<td>0.791</td>
<td>0.675</td>
<td>375</td>
</tr>
<tr>
<td>10:2 FTOH</td>
<td>0.812</td>
<td>0.791</td>
<td>320</td>
</tr>
<tr>
<td>12:2 FTOH</td>
<td>0.779</td>
<td>0.660</td>
<td>383</td>
</tr>
<tr>
<td>14:2 FTOH</td>
<td>0.707</td>
<td>0.399</td>
<td>634</td>
</tr>
</tbody>
</table>
Exposure Pathways Scenario

1) to cattle on land amended with biosolid
2) to general public (?)
Conclusions

- Analytical methods for detecting and quantifying over 30 FOCs in soils were developed using LC/MS/MS and GC/MS
- Elevated concentrations of PFCs and FTOHs in biosolid-applied soils - PFOA, PFOS, PFDA, and 8:2 FTOH, 10:2 FTOH
- Secondary FTOHs (e.g., 7:2 sFTOH) observed
- Fast disappearance rates for short PFCs
- Decrease of PFCs and FTOHs concentrations upon the cessation of biosolid application
- 55% (~ 4 million metric tons) of biosolids is land applied nationwide annually – More fate studies for FOCs in biosolid-applied fields required
Very appreciated !!!

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