Triclocarban, Triclosan, Polybrominated Diphenyl Ethers, and 4-nonylphenol in Biosolids and in Soil Receiving 33-year Biosolids Application

Kang Xia
Associate Professor
Virginia Tech

kxia@vt.edu
540-231-9323
Outline

- What are Trace Organic Chemicals (TrOCs)?
- Occurrence of TrOCs in biosolids
- Fate of TrOCs in biosolids-applied land
- Future research needs
What are TrOCs?

Triclocarban (TCC)
Triclosan (TCS)
Polybrominated Diphenyl Ethers (PBDEs)
4-nonylphenol (4-NP)

*Are Trace Organic Chemicals (TrOCs)*
**Human uses**

- Prescription drugs
- over-the-counter drugs
- Therapeutic drugs
- Veterinary drugs
- Fragrances
- Cosmetics
- Sun-screen products
- Diagnostic agents
- Nutraceuticals (e.g., vitamins)
- Illegal drugs
- Flame retardants
- Additives in consumer products

**Animal production uses**

- Therapeutic (disease control)
- Sub-therapeutic (growth promotion)
Antibiotic for respiratory tract infections

Antilipidemic, lipid lowering drug

Insect repellent

Hypertension medication

TrOCs in wastewater influent of two WWTPs in Beijing, China (Environ. Sci. Technol. 2011, 45:3341–3348)
**Predicted half lives of many TrOCs?**

http://www.pbtprofiler.net

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**Results**

*Orange or red highlights indicate that the EPA criteria have been exceeded.*

**Black-and-white version**

<table>
<thead>
<tr>
<th>Persistence</th>
<th>Bioaccumulation</th>
<th>Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>3380-34-5 Phenol, 5-chloro-2-(2,4-dichlorophenoxy)-</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**PBT Profiler Estimate = PBT**

<table>
<thead>
<tr>
<th>Media</th>
<th>Half-Life (days)</th>
<th>Percent in Each Medium</th>
<th>BCF</th>
<th>Fish ChV (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td><strong>60</strong></td>
<td>7%</td>
<td>640</td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td><strong>120</strong></td>
<td>80%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sediment</td>
<td><strong>540</strong></td>
<td>13%</td>
<td></td>
<td>0.071</td>
</tr>
<tr>
<td>Air</td>
<td>1</td>
<td>0%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Additional information*
Characteristics of wastewater treatment plants

- large volume of influent and effluent
- short detention time (hours to few days)
- treatment guidelines are pathogen and heavy metal driven

<table>
<thead>
<tr>
<th>Compound</th>
<th>Predicted half life (day)</th>
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<tr>
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<tr>
<td>PBDE-47</td>
<td>180</td>
</tr>
<tr>
<td>4-NP</td>
<td>15</td>
</tr>
</tbody>
</table>
If there is not enough time to degrade TrOCs in WWTPs, where do they go?

**A case study: Fate of 4-NP in secondary WWTPs**

### Compound of interest

4-nonylphenol (4-NP) is a metabolite of nonylphenol polyethoxylates (NPnEOs)

- NPnEOs are nonionic surfactants

\[
\text{R} - \left( \begin{array}{c}
\text{O} - \text{C} - \text{C} - \text{OH} \\
\text{H} - \text{H} - \text{H}
\end{array} \right)_{n} \quad (3-20)
\]

- Annual production
  - worldwide: \( \sim 500,000 \ T \)
  - U.S.: \( \sim 200,000 \ T \)

### Study sites

- 13 secondary WWTPs (GA, SC, KS)
- Population served by the WWTPs: 5,000 to 0.5 million
- Wastewater treated by the WWTPs: 0.75 MGD - 0.5 BGD
- Biosolids produced in the WWTPs: 0.6 to 100,000 dry ton/day
Case study results

4-NP and its precursors in WWTP influent of #13
4-NP and its precursors in effluent of WWTP #13

![Graph showing the distribution of NPnEOs (ethoxylate number)](image)

- **NPnEOs (ethoxylate number)**
- **Effluent**

**[NPnEOs] (μg L⁻¹)**
- ND (Not Detected)
4-NP and its precursors in biosolids of WWTP #13

Concentration (mg kg⁻¹)

0.11 – 1.56 mg kg⁻¹

biosolids

R – \( \text{O-C-C-OH} \)

\( n = (3-20) \)
Daily mass balance for 4-NP in WWTP #13

4-NP input

61% from influent
39% produced in WWTP

4-NP output

94% in biosolids
6% degraded? effluent?
4-NP levels in biosolids and compost from the WWTPs investigated
Levels of 4-NP in biosolids from WWTPs in California.
Can WWTPs remove 4-NP from influent?
- Yes!

However
- WWTPs are ineffective for 4-NP degradation – there just not enough time!
- 4-NP is sequestered by biosolids

Can biosolids sequester other TrOCs?
Biosolids from 16 WWTPs of 5 states
4 PPCPs: triclocarban, triclosan, PBDEs, 4-NP
300 – 704,000 μg kg⁻¹ dry weight
Biosolids from 7 states

25 PPCPs: antiepileptic, antihistamine, antidepressant, fragrance, disinfectant, detergent metabolites, preservative, fire retardants, plasticizer, fragrance, steroids

15 – 1,520,000 μg kg⁻¹ organic C

Kinney et al., ES&T, 2006, 40:7207-7215
Fig. 1 – Rank order of mean concentrations for 38 PPCPs detected in composites of a total of 110 U.S. biosolids samples from 94 treatment plants in 32 states and the District of Columbia. Newly detected compounds are shown in darker hue. Error bars depict ± one standard deviation (n = 5). Some concentrations represent estimates only (†) and some analytes were detected inconsistently (‡).
4-NP levels in biosolids and compost from the WWTPs investigated
Concentration reduction of target compounds in biosolids compared with composted biosolids from the same WWTP.

Biosolids production, usage, and disposal in U.S.

Benefits:
- primary nutrients
- secondary nutrients
- root growth promoters
- enhance soil structure
- C sequestration


Source: U.S. EPA, 1999
TrOCs

Influent  →  WWTP  →  Effluent

Biosolids

deposition

volatilization

degradation

leaching

uptake

runoff

Surface Water
Fate of TrOCs in biosolids-applied land

A field study:

TCC, TCS, PBDEs, and 4-NP in soil after 33 consecutive years of biosolids application
Experimental design

- Study site: established in 1973 Fulton County, IL
- Treatments: Four
  1. Control: 336N-224P kg/ha-yr
  2. Biosolids: 16.8 Mg/ha-yr
  3. Biosolids: 33.6 Mg/ha-yr
  4. Biosolids: 67.2 Mg/ha-yr
  *All treatments received K @ 112 kg/ha-yr
- Crop: Corn (Zea mays L.)
- Target TrOCs: TCC, TCS, PBDEs, 4-NP

33-y cumulative rates: 554.5, 1109, 2218 Mg/ha
### Characteristics of the compounds investigated in this study

<table>
<thead>
<tr>
<th>Compound</th>
<th>Log Kow</th>
<th>Use</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-nonylphenol (4-NP) CAS # 104-40-5</td>
<td>4.75*</td>
<td>metabolite of nonylphenol polyethoxylates (non-ionic surfactants)</td>
<td><img src="image1" alt="Chemical structure of 4-nonylphenol" /></td>
</tr>
<tr>
<td>polybrominated diphenyl ethers (PBDEs)</td>
<td>log $K_{ow} = 0.621(#Br) + 4.12$</td>
<td>flame retardant</td>
<td><img src="image2" alt="Chemical structure of polybrominated diphenyl ethers" /></td>
</tr>
<tr>
<td>Triclosan (TCS) CAS # 3380-34-5</td>
<td>4.19*</td>
<td>bactericides</td>
<td><img src="image3" alt="Chemical structure of Triclosan" /></td>
</tr>
<tr>
<td>Triclocarban (TCC) CAS # 101-20-2</td>
<td>4.48*</td>
<td></td>
<td><img src="image4" alt="Chemical structure of Triclocarban" /></td>
</tr>
</tbody>
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• **biosolids: anaerobic digestion**
  
  (Metropolitan Water Reclamation District of Greater Chicago)

<table>
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<th>concentration (mg kg^{-1}, dry weight)</th>
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<tbody>
<tr>
<td>TCC</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>24</td>
</tr>
</tbody>
</table>

• soil was sampled at:
  
  0 – 15 , 15 – 30, 30 – 60, 60 – 120 cm

• plant tissue sampled at harvest: leaf, stalk, kernel
Concentrations of TCC, TCS, ΣPBDEs, and 4-NP in 0 – 15 cm depths of soil amended with biosolids at four rates
Concentrations of TCC, TCS, $\Sigma$PBDEs, and 4-NP at different depths in biosolids-amended soil
Estimated % recoveries of \( \sum \text{PBDEs}, \) 4-NP, TCC, and TCS, in top 120 cm soil after 33-year of annual application of biosolids.

Mass Balance =
\[
\frac{\text{amount detected in soil}}{\text{33-year cumulative input}} \times 100\% = \frac{D_{\text{soil}} \times A_{\text{soil}} \times B D_{\text{soil}} \times (C_{\text{soil}} - C_{\text{soil}}^o)}{Y_{\text{biosolids}} \times R_{\text{biosolids}} \times C_{\text{biosolids}}} \times 100\% \]

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Concentration ratio of 4-NP, TCC, ΣPBDEs, and TCS in biosolids and surface soil (0-15 cm) amended with biosolids at accumulative 33-year loading of 2218 Mg ha⁻¹.
### Field case study result summary:

<table>
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<th>Target compounds</th>
<th>Results</th>
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<tr>
<td>Levels in soil</td>
<td>increase with biosolids loading</td>
</tr>
<tr>
<td>Levels in soil</td>
<td>sharp decrease with soil depth</td>
</tr>
<tr>
<td>PBDEs</td>
<td>persistent</td>
</tr>
<tr>
<td>TCC, TCS, 4-NP</td>
<td>less persistent</td>
</tr>
<tr>
<td>Concentrations in soil</td>
<td>4-NP &gt; TCC &gt; PBDEs &gt; TCS (180:26:14:1)</td>
</tr>
<tr>
<td>PBDEs, 4-NP</td>
<td>immobile</td>
</tr>
<tr>
<td>TCC, TCS</td>
<td>limited mobility</td>
</tr>
<tr>
<td>Plant (corn) uptake</td>
<td>No</td>
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Influent WWTP Effluent Biosolids Surface Water

- TrOCs
- Influent
- WWTP
- Effluent
- Deposition (limited)
- Volatilization (limited)
- Degradation (varies)
- Uptake (no)
- Leaching (limited)
- Runoff ?

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Future research needs

- Fast, inexpensive, accurate, multi-compound analytical methods for detecting TrOCs in environmental samples
- Evaluation of new wastewater and biosolids treatment technologies
- Long term monitoring of wider range of TrOCs in biosolids-amended soils and surrounding environment
- TrOCs transformation in storm water runoff
- Plant and animal uptake of TrOCs in biosolids-amended soils
Acknowledgement:

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