TRICLOSAN, TRICLOCARBARAN (AND OTHER TRACE ORGANICS) IN BIOSOLIDS

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Research Motivation

- **Background**
  - Large Production of Antimicrobial compounds (e.g., 2004 US TCC production $2.3 \times 10^5$ kg)
  - Relatively long half lives and limited transformation in soils, esp. for TCC

- **Key Questions**
  - How do the chemicals affect soil microbial communities and their key “ecosystem services”? 
  - Are the chemicals subject to runoff at concentrations of concern?
Antimicrobial Compound Structures

**Triclocarban (TCC)**
- $\text{Log } K_{\text{OW}} = 4.2$
- $S_w \ (\text{mg/L}) = 0.65 - 1.55$
- $pK_a = 12.7$

**Triclosan (TCS)**
- $\text{Log } K_{\text{OW}} = 4.8$
- $S_w \ (\text{mg/L}) = 1.97 - 4.6$
- $pK_a = 7.9$

Loftsson, T et. al., 2004 & Halden et. al., 2005
Marketing drives consumption

- American Medical Association indicates no benefit from addition of TCC/TCS to consumer products
- Soaps containing TCC/TCS are “Not less effective than controls”
## Results from EPA National Biosolid Survey

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>% Detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-47</td>
<td>73</td>
<td>5,000</td>
<td>709</td>
<td>100</td>
</tr>
<tr>
<td>BDE-99</td>
<td>64</td>
<td>4,000</td>
<td>716</td>
<td>100</td>
</tr>
<tr>
<td>BDE-209</td>
<td>150</td>
<td>17,000</td>
<td>2,181</td>
<td>98.5</td>
</tr>
<tr>
<td>Ciprofloxacin</td>
<td>75</td>
<td>40,800</td>
<td>10500</td>
<td>100</td>
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<tr>
<td>TCC</td>
<td>187</td>
<td>441,000</td>
<td>39,433</td>
<td>100</td>
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<tr>
<td>TCS</td>
<td>334</td>
<td>133,000</td>
<td>16,097</td>
<td>92.4</td>
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<tr>
<td>Cholestanol</td>
<td>3,860</td>
<td>4,590,000</td>
<td>680,046</td>
<td>100</td>
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<tr>
<td>Cholesterol</td>
<td>2,340</td>
<td>5390000</td>
<td>1,129,268</td>
<td>96.9</td>
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<tr>
<td>Coprostanol</td>
<td>7,720</td>
<td>43,700,000</td>
<td>4,366,714</td>
<td>100</td>
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<tr>
<td>Epicoprostanol</td>
<td>868</td>
<td>6,030,000</td>
<td>1,702,708</td>
<td>98.5</td>
</tr>
</tbody>
</table>

Representative analytes selected, all concentrations in ug/kg dry weight.

<table>
<thead>
<tr>
<th>WWTP</th>
<th>Sludge (n = 6)</th>
<th>Biosolids (n = 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TCC (mg/kg)</td>
<td>TCS (mg/kg)</td>
</tr>
<tr>
<td></td>
<td>TCC (mg/kg)</td>
<td>TCS (mg/kg)</td>
</tr>
<tr>
<td>1</td>
<td>5.3 ± 0.10</td>
<td>1.9 ± 0.4</td>
</tr>
<tr>
<td>1</td>
<td>8.5 ± 0.78</td>
<td>12 ± 2.3</td>
</tr>
<tr>
<td>1</td>
<td>16 ± 3.7</td>
<td>16 ± 3.0</td>
</tr>
<tr>
<td>6</td>
<td>28 ± 0.9</td>
<td>47 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>12 ± 1.8</td>
<td>28 ± 6.8</td>
</tr>
<tr>
<td></td>
<td>9.4 ± 0.91</td>
<td>16 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>17 ± 0.42</td>
<td>29 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>8.2 ± 0.35</td>
<td>11 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>11 ± 1.2</td>
<td>16 ± 1.9</td>
</tr>
</tbody>
</table>
# TCC and TCS removal

<table>
<thead>
<tr>
<th></th>
<th>Mesophilic Anaerobic (n=6)</th>
<th>Thermophilic Anaerobic (n=1)</th>
<th>Aerobic (n=1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCC</td>
<td>72.6 - 45.0%</td>
<td>41.8%</td>
<td>30.9%</td>
</tr>
<tr>
<td>TCS</td>
<td>75.6 - 6.25%</td>
<td>40.0%</td>
<td>48.6%</td>
</tr>
</tbody>
</table>
Potential Accumulation of TCC in Soil

Assumptions
- 51 mg/kg TCC in biosolids
- 5.5 tons/ac/yr Ag scenario
- 136 tons/ac/yr DLD scenario
- Linear equilibrium partitioning
- Davis, CA average precipitation
- Soil half life 120 d
Challenge to define an appropriate “control” since ~all US biosolids contain TCC and TCS, but we know biosolid addition will affect the soil microbial community.
Biosolids increase total bacterial biomass, TCS impacts are negligible

TCS: 0, 10, or 50 ppm

Bacteria 16S rRNA gene copy numbers/g dry weight soil

- 0 day
- 7 day
- 1 month

no biosolids + biosolids
TCS has little relative impact on overall community composition, time and +/- biosolids have much bigger influence.
TCS reduces ammonia oxidizing bacteria

AOB copy numbers/g dry weight soil

no biosolids

AOB copy numbers/g dry weight soil

+ biosolids

0 day 1 week 1 month
TCS also reduces ammonia oxidation activity

TCS conc: 0, 10, 50 ppm

μg NO$_2$ g soil$^{-1}$ hr$^{-1}$

Days: 0, 7, 30

no biosolids

+ biosolids

Soil-AOP

SB-AOP
TCS addition increases biomarkers of stress

[Graph showing the effect of TCS addition on biomarkers of stress over different days and conditions.]
Summary of microbial bioassay findings

- TCS addition decreased ammonia oxidation (activity and populations) and increased microbial stress.
- Biosolid addition had a larger effect on monitored parameters than TCS did.
- Presence of biosolids mediated effects relative to soils spiked with similar levels of TCS, presumably by reducing bioavailability of TCS.
Testing Runoff Potential

- **Biosolids**
  - Obtained from local WWTP, dried at 190°C for 12 h

- **Soil**
  - Agricultural sandy loam, pH = 8.0, Org C = 0.37%
  - 1 x 2 x 0.38 m plots

- **Rainfall Simulators**
Runoff Simulation Methods
Rainfall Simulation Summary

Timeline:

- Control Storm
- Biosolids Applied
- Storm 1
- Storm 2
- Storm 3

Day:

- 0
- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9
- 10
- 11
- 12
- 13
- 14
- 15
- 16
- 17
- 18
- 19
- 20
- 21
- 22
- 23
- 24

Temperature:

- Minimum: 1 °C Sun, Apr 5, 7:00 am
- Average: 15 °C
- Maximum: 34 °C Mon, Apr 20, 5:00 pm, ...

Wind Speed:

- Minimum: 0 mph Wed, Apr 22, 12:00 am, ...
- Average: 8 mph
- Maximum: 30 mph Sun, Mar 29, 12:00 pm, ...
TCC Runoff from Soil

Total Mass Lost = 151 to 415 ng

Event Mean Concentration = 6.3 to 17.3 ng/L
TCS Runoff from Soil

Total Mass Lost = 6800 to 7440 ng

Event Mean Concentration = 282 to 310 ng/L
Octylphenol Runoff from Soil

- Total Mass Lost = 1000 to 4900 ng
- Event Mean Concentration = 42 to 203 ng/L
Controls on TCC and TCS Runoff

- Why the difference in mobility of TCC and TCS?
  - TCS pKa = 7.9, soil/runoff pH = 7.8 to 8.0
  - Approximately 50% of TCS ionized

- Topp et al 2008 (runoff, soil pH = 7.5)
  - TCS: Total mass lost = 4260 ng, EMC = 258 ng/L

- Edwards et al 2009 (tile drain, soil pH = 7.0 – 7.5)
  - TCC average conc. = 0.73 ng/L
  - TCS average conc. = 43 ng/L, peak conc. = 230 ng/L
TCC Effects on Aquatic Organisms

- Test species: *Potamopyrgus antipodarum*
  - Invasive freshwater mudsnail
  - All female; asexual reproduction and live-bearing
  - Lifespan up to 1 year
  - Embryo production used previously as bioassay for endocrine disrupting compounds (EDCs)
Bioassay Methods

- NZMS collected on Putah Creek, Winters CA
- 60 specimens in each individual 1 L jar
- Synthetic freshwater spiked with solution of TCC in ethanol
- Complete water replacement and respiking every 3 days
- Aerated, 14°C, 16:8 hr lt/dk rhythm
Bioassay Analysis

- At 0, 14, and 28 days 15 specimens from each jar removed
- Photographed and length measured
- Dissected and embryos counted
Dose Response for Unshelled Embryos

Aqueous TCC Concentration (µg/L)

Embryos (% relative to control)

NOEC: 50 ng/L
LOEC: 200 ng/L
EC10: 500 ng/L
EC50: 2500 ng/L
Sustainable Biosolids Management?
Acknowledgments

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