Safer Soaps: The FDA's Proposed Action on Triclosan

Outline

- Contributors to this Presentation
- Rationale & Methodology
  - Archived Samples – ASU Human Health Observatory
  - Sewage Metrology
  - Mass Balances & Chemical Inventories
- Results
  - TCS & TCC
  - Other Contaminants of Emerging Concern (CECs)
- Questionnaire
- Summary & Conclusions
- Acknowledgements & References
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Sewage Metrology

Bird’s Eye View of an Urban Chemical Observatory

Sewage Metrology – Population Health Status

Toxic chemicals, drug & medication use, stress levels, chemical consumption, behavior

ASU Human Health Observatory (H2O)
U.S. National Sewage Metrology Sample Repository

- >160 U.S. cities
- >10% of U.S. population
- Time points thus far: 2001, 2006/7, present
- >200 U.S. WWTPs total
- Representative of 16,000+ U.S. WWT plants

H2O Repository at ASU:
U.S. Geographic Coverage with WWTPs

Methodology

<table>
<thead>
<tr>
<th>AP &amp; APEOs (4)</th>
<th>PCPs (13)</th>
<th>BFRs (77) and Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas chromatography mass spectrometry (GC-MS)</td>
<td>Liquid chromatography tandem mass spectrometry (LC-MS/MS)</td>
<td>GC-MS (EPA Method 1614) and LC-MS/MS</td>
</tr>
</tbody>
</table>

Statistically selected to represent 16,000+ WWTPs in U.S.

Archived soil mesocosm samples

5 MEGA composites

110 MSS samples

2001 NSSS

Solids from 21-24 WWTPs
Methodology – Studying the Persistence and Fate of CECs in Sludge-amended Outdoor Soil Mesocosms

- 2005 – 2008
- Baltimore, Maryland
- MSS/soil mixtures (1:2)
- Kept outdoors & sampled over 3 years


Sewage Treatment Plants

as Chemical Observatories by Example of Triclocarban & Triclosan

Removal ≠ Degradation

Triclocarban (TCC)
**Fate of Triclocarban During Activated Sludge Treatment**

- Mass in effluent: 21 ± 30% (765 g/d)
- Mass in sludge: 795 ± 1% (127 g/d)
- Mass transformed/lost: 2815 ± 30% (76 g/d)

**Fate of Triclosan in Activated Sludge WWTP**

- Mass in effluent: 2 ± 1% (55 g/d)
- Mass in sludge: 48 ± 1% (1480 g/d)
- Mass transformed/lost: 50 ± 19% (1640 g/d)

**PPCPs in NSSS Samples Collected in 2001**

- 38 out of 72 detected
- TCC & TCS most abundant: 36 ± 8 & 12.5 ± 3.8 mg/kg dw
- ∑PPCPs load in biosolids:
  - 210 – 250 metric t
  - 2001 vs 2006/7
  - Limited fluctuation over years
Triclosan and Triclocarban

Fate of PPCPs in Outdoor Mesocosms

- 15 of 72 PPCPs detected in biosolids-amended soil
- TCC & TCS most abundant
  - 2.8 & 1.3 mg/kg dw, respectively
- No loss observed for triclocarban
- Triclosan displayed half-life of 0.5 years in soil

Timeline
Contact Time is Key

~6 Seconds (ineffective)

Lifetime toxic exposure of aquatic organisms (toxic)

Source: US EPA

Toxic Threshold Values: What Organisms Are Most Sensitive?

- Triclocarban
- Triclosan

TCS/TCC are more "anti-algae, crustacean and fish" than "antimicrobial"

Concentrations Extant in U.S. Environment Exceed Thresholds of Various Organisms

Exposure Concentrations

Mussels
Algae
Crustacean
Fish

Threshold Values

Concentrations Extant in U.S. Environment Exceed Thresholds of Various Organisms

- Sediment
- Soil pore water
- Soil
- Groundwater
- Surface water
- Activated sludge
- MBR influent
- MBR effluent
- Diuron

Threshold Values

Exposure Concentrations

Mussels
Algae
Crustacean
Fish
Where Does the Sludge Go?

Used by consumers
Sequestered in sludge
Applied onto soils

Approximately 57,000 ± 233,000 kg/yr of Triclosan and 140,000 ± 211,000 kg/yr of Triclocarban are applied inadvertently on U.S. agricultural land as a result of sewage sludge disposal.

Potential pathway for contamination of water and food with antimicrobials and drug-resistant microbes

Triclosan & Triclocarban: Key Sludge Pollutants

TCS and TCC are only two of 72 drugs monitored by EPA Method 1694.
Yet, these two antimicrobials account for >60% of the mass of all drugs detectable in sewage sludge.
### Chemistry of Biosolids Collected in 2001 vs. 2006/7

<table>
<thead>
<tr>
<th>Compound</th>
<th>2007 Mean Concentration (ppm)</th>
<th>2001 EPA TNMSS Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclocarban</td>
<td>36</td>
<td>39</td>
</tr>
<tr>
<td>Triclosan</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>Ciprofloxacin</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Ofloxacin</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Cimetidine, 4-Epitetracycline, Miconazole, Tetracycline</td>
<td>0.3 – 2.5</td>
<td>1 – 2</td>
</tr>
</tbody>
</table>


### First U.S. Nationwide Inventory for Alkylphenols & AP Ethoxylates in Sewage Sludge

- 656 ± 272 mg/kg dw
- 2,408 – 7,149 t in sludge
- 1,204 – 4,289 t to U.S. soils
- $t_{1/2} = 301$ – 495 d
- U.S. levels exceed EU regulatory limits 10-fold
- U.S.: no regulatory limits


### First U.S. Nationwide Inventory of Polyfluorinated Compounds in Sewage Sludge

- 13 PFCs, 10 PFCs 100% detection
- PFOS: 403 ± 127 μg/kg dw; PFDA: 34 ± 22 μg/kg dw
- ∑PFCs estimated at 2,749 – 3,450 kg/year
- No difference: pre-phase out (2001) and post phase-out (2006/7)

Nitrosamines in TNSSS Samples - Methods

- LC-MS/MS method developed for 8 nitrosamines
- Analysis of 80 MSS samples (2006-7 survey)

Spike isotope-labeled standard (250 ng)
Extract with dichloromethane (ww X2 mL)
Rotary shaker (2 h) + sonication (1 h)
Blow down with N₂ gas
Reconstitute with 2 mL acetonitrile
Analyze by LC-MS/MS


First U.S. Nationwide Study of N-Nitrosamines in Sewage Sludge

- 7 of 8 NAs detected
  - NDMA, NIPA, NPEA, NIPA, MPA, NMP, NDPhA
- Most abundant: NDMA at 504 (87 – 920) ng/g (d.w.)
- Groundwater cleanup goal: 0.7 ng/L.
- 1 kg dry sludge: enough mass to contaminate up to 1.3M liters of groundwater with NDMA
- Most frequent: NDPhA at 10 (0.7 – 147) ng/g (d.w. (79%)
- Detection frequency (DF) positively correlates with Log Kow


Geographic Variation in Occurrence and Concentration of N-Nitrosamines in Sewage Sludge

Big Picture: TCS/TCC & Other CECs in U.S. Sewage Sludge

- 123 of 231 chemicals detected
- 0.04 – 0.15% of dry sludge mass is chemicals (only from this study)
- 5.1 - 6.4 M metric dry t of sludge annually (US EPA)
- 2,614 – 7,905 t of chemicals to US soils annually

Chemical Load

<table>
<thead>
<tr>
<th>Metric Tons/Year</th>
<th>(Biosolids Production)</th>
<th>APA/APEOs</th>
<th>PPCPs</th>
<th>BFRs</th>
<th>PFCs</th>
<th>Bromanes</th>
<th>BrCl/DIF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(12^2)</td>
<td>1</td>
<td>10^6</td>
<td>(4)</td>
<td>(19)</td>
<td>(28)</td>
<td>(28)</td>
</tr>
</tbody>
</table>


WWTPs as Chemical Observatories

- Chemicals detected at >1 ppm

Chemical Load

<table>
<thead>
<tr>
<th>% chemical’s production volume sequestered in sewage sludge</th>
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<tbody>
<tr>
<td>Neonicotinoid</td>
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Using Sewage Sludge Analysis as a Diagnostic Tool Informing Chemical Regulation

- 55 potentially bioaccumulative chemicals
- 93% are halogenated
- 8 priority chemicals
  - 3 BFRs
  - 3 Surfactants
  - 2 Antimicrobials

Similar Toxic Burden in Sludge & U.S. Population

- CDC National report on human exposure to environmental chemicals
- 139 Chemicals in human samples

Environmental chemicals
- Detected in biosolids only: 30%
- Detected in humans and biosolids: 70%
- Similar Toxic Burden in Sludge & U.S. Population


Municipal Wastewater Treatment Plants as Chemical Observatories for Public Health Protection

Identify chemicals that are...
- in societal use today (chemical inventories)
- persist even under optimized biodegradation conditions (long half-lives)
- diminish value of biosolids as a soil amendment (soil & GW pollutants)
- cause toxic human exposures (exposure science)
- produce harmful transformation products (e.g., nonylphenol from APEs)
- bioaccumulate in people


National WWTP Survey

- What is missing?
  - Last nationwide survey conducted in 2006/7 by U.S. EPA
  - 2000 new chemicals/year
  - ~14,000 new chemicals (in 2014) in commerce without fate information
  - Environmental and human health risks?

- What we provide?
  - State-of-the-art evaluation of human health by studying WWTPs
  - Nationwide occurrence, distribution, fate and risks of chemicals
  - Archiving in Human Health Observatory & National Sewage Sludge Repository at ASU
  - Help assess WWTP performance for harmful substances

- How can you help?
  - Participate in national network of WWTPs
  - Provide 24h-composited samples of wastewater influent, effluent and treated sewage sludge
  - Provide info on WWTP & sewershed (flow volume, treatment units, population, etc.)

Contaminants Studied Thus Far

- Emerging contaminants
  - Pharmaceuticals and personal care products
  - Brominated flame retardants
  - Perfluorinated compounds
  - Hormones
  - Alkylphenol surfactants
  - Brominated dioxins and furans
  - Nitrosamines

- Future
  - More traditional and emerging contaminants
  - Human health indicators (biomarkers)
  - Illicit drugs
  - Biological agents

Questionnaire

- Do you want to know the performance of your WWTP?

- Would you like to participate in a nationwide WWTP survey?

- Please check any criteria that would prevent your participation in this survey:

Questionnaire (continued)

- Will you provide samples (influent/effluent/biosolids), under the condition that the identity of your facility is NOT revealed?

- Which sampling frequency would you participate in?
Summary & Conclusions

- TCS and TCE are examples of poorly designed, non-green chemicals featuring PBT characteristics (PBT: persistent, bioaccumulative, toxic)
- Sewage metolology can serve to inexpensively determine inventories of PBT chemicals and releases to soils/nematode
- Halogenated compounds pose particular concern
  - All Fluorocarbon compounds are organohalogens
  - 75 percent of DOD's regulated organocompounds are at least one or more halogens
- Biosolids can harbor water-soluble pollutants that may leach into soil & groundwater
  - e.g., PCE, carcinogenic contaminants including NDMA
- Monitoring chemicals in biosolids can identify problematic compounds and inform biomonitoring & regulatory actions
- ASU offers opportunity for you to learn more about your facility by participating in a nationwide WWTP survey

Acknowledgments

US EPA
NIHES
CDC
NIH

References

Poll

- Did you wash your hands with antibacterial soap today?

- Do you brush your teeth with Colgate Total?
Widespread Exposure

- at least 1 million lbs produced annually in US
- 75% Americans surveyed with triclosan in urine
- Dramatic rise in blood levels after brushing with triclosan toothpaste for 14 days

Human Health Concerns

- Hormone disruption
- Weakened muscles
- Allergies and Asthma

Bacterial Impacts

- Antibiotic Resistance
  - Potential to promote drug-resistant bacteria
- Beneficial Communities
  - Microbiome
  - Wastewater treatment plants
Unnecessary Exposure

No more effective than plain soap and water.

“At this time, FDA does not have evidence that triclosan added to antibacterial soaps and body washes provides extra health benefits over soap and water.”

April 2010

Initiatives

Bans
- Minnesota (2014)
- UT Austin (2012)
- Chicago (pending)

Procurement
- Minnesota (2013)
- Jamtland, Sweden (2010)
- San Jose, CA (2008)
- East Bay Municipal Utility District (2007)
- Palo Alto, CA (2006)
Regulatory Authority

- Federal Insecticide, Fungicide, and Rodenticide Act (EPA)
- Food, Drug, Cosmetics Act (FDA)
- New Drug Application
- OTC Monograph
- Colgate Total
- Antibacterial Soap

Key Events:

- 1974: Proposal To Establish a Monograph for OTC Topical Antimicrobial Products
- 1978: Tentative Final Order
- 1994: Amended Tentative Final Monograph
- 2010: NRDC sues FDA to finalize Final Monograph
- 2013: NRDC and FDA settle lawsuit
Natural Resources Defense Council
www.nrdc.org
NRDC Factsheet
www.nrdc.org/health/files/antimicrobials.pdf

Thank You