Status of PPCP Research in Biosolids and Michigan Waters

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Overview

- Emphasis on Michigan or nearby states
- Chemical Classes
- Sources
- WWTP effects on water
- Biosolids effects on soils and water
Emerging Chemical Contaminants

- Pharmaceuticals (human and veterinary)
  - Intended to be bioactive
  - Do not generally bioaccumulate
  - Not toxic to humans (or intended animals)
  - May have unintended consequences for non-target organisms
    - Fluoxetine/fish
    - Diclofenac/vultures
  - Degradation products may be toxic
    - Acetaminophen forms toxics during chlorination
    - Carbamazepine (antiepileptic) photodegrades to acridine (mutagen)

- Personal Care Products (chemicals in lotions and potions)
  - Not toxic to humans
  - Not intended to be ingested
  - May have unintended consequences for non-target organisms
Emerging Chemical Contaminants

- Antibiotics (human and veterinary)
  - Some veterinary antibiotics are toxic to humans
  - Concern over antibiotic resistance in bacteria
- Hormones and steroids (natural and prescribed)
  - Clearly influence reproduction and endocrine function
- Detergents, disinfectants, fragrances, fumigants, etc. and their by-products
  - Not intended to be consumed
  - Several compounds have reported endocrine disruption effects (detergent by-products such as nonylphenols, musk fragrances, bisphenol A, triclosan)
- Fire-retardants
  - PBDEs found to bioaccumulate
- Newer chlorinated and fluorinated compounds also bioaccumulation concern-PFOS
Endocrine Disruptive Compounds

- Occur in many chemical classes
  - Hormones
  - Pesticides (atrazine, diazinon)
  - Industrial (bisphenol A, other plasticizers)
  - Fragrances (AHTN, HHCB)
  - Detergent by-products (nonyl- and octyl-phenols)

- Of particular concern because these are active at very low concentrations and influence reproduction and growth
Chemical Structure Affects Fate and Function

- Bioaccumulate or not
- Endocrine disrupter or not
- For WWTP: biodegradation, release to effluent, or sorption to solids
- Susceptibility to chemical or advanced treatment
- Few generalities!
Some Compounds “Prefer” Water — Others “Prefer” Sediments (Or Solids)
The factors that influence fate and transport in the environment also influence behavior in the WWTP.

In general, each chemical behaves differently.

Barber and others, 1995
Human Sources

- WWTPs
- CSOs
- Land application of municipal biosolids or septage
- Illicit connections to storm or agricultural drains
Animal Sources

Manure contains veterinary pharmaceuticals and cleaning agents
Septic System

<table>
<thead>
<tr>
<th></th>
<th>Liquid (μg/L)</th>
<th>Solid (μg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHTN (tonalide)</td>
<td>ND</td>
<td>18000</td>
</tr>
<tr>
<td>Triclosan</td>
<td>2.0</td>
<td>19000</td>
</tr>
<tr>
<td>p-nonylphenol</td>
<td>18</td>
<td>55000</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Caffeine</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Cotinine</td>
<td>1.7</td>
<td></td>
</tr>
</tbody>
</table>

Antibiotics found in all swine waste lagoons sampled (N=78):

<table>
<thead>
<tr>
<th>Compound</th>
<th>%</th>
<th>Med</th>
<th>Max  μg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTET</td>
<td>90</td>
<td>19</td>
<td>1000</td>
</tr>
<tr>
<td>SMTH</td>
<td>85</td>
<td>6.2</td>
<td>6000</td>
</tr>
<tr>
<td>LINC</td>
<td>75</td>
<td>25</td>
<td>1200</td>
</tr>
<tr>
<td>TET</td>
<td>60</td>
<td>1.4</td>
<td>150</td>
</tr>
<tr>
<td>OTET</td>
<td>50</td>
<td>10</td>
<td>410</td>
</tr>
<tr>
<td>SDIMX</td>
<td>25</td>
<td>2.5</td>
<td>150</td>
</tr>
<tr>
<td>TYLO</td>
<td>25</td>
<td>0.2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

WWTPs As Sources

- Widely considered a primary source because
  - Numerous studies show a wide variety of PPCPs in WWTP effluent
  - Effluent input to environment is constant
- Less is known about biosolids
  - Analyses are difficult
  - Biosolids are intermittently applied to fields
Chemicals and Concentrations in WWTP Effluent Depend on Influent to the Plant

- Phillips et al. 2010, ES&T 44: 4910-4916
- Two WWTP in NY state that receive more than 20% of influent from pharmaceutical manufacturing plants (PMP)
- Maximum concentrations of pharmaceuticals such as opioids, barbiturates, and muscle relaxants were 10-1000 times higher than for 23 WWTP around the US that do not have PMP influents
# Chemical Release in Effluent Depends on Treatment Processes

<table>
<thead>
<tr>
<th>Compound Type</th>
<th>Primary Settling</th>
<th>Filtration</th>
<th>Activated Sludge</th>
<th>Trickling Filter</th>
<th>Anaerobic Digestion</th>
<th>Chemical Addition</th>
<th>Disinfection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steriods</td>
<td>-5 to 15</td>
<td>50-70</td>
<td>50-&gt;90</td>
<td></td>
<td>65-&gt;95</td>
<td></td>
<td>&gt;90</td>
</tr>
<tr>
<td>Organo-halides</td>
<td></td>
<td>&lt;50</td>
<td>&lt;20</td>
<td>70-&gt;90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkyl Phenols</td>
<td>40-45</td>
<td>5-90</td>
<td></td>
<td>6-98</td>
<td></td>
<td></td>
<td>20-90</td>
</tr>
<tr>
<td>PAHs</td>
<td></td>
<td>75-&gt;90</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plasticizers</td>
<td></td>
<td>&gt;90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50-80</td>
</tr>
</tbody>
</table>

WERF, 2005, Technical Brief: Endocrine Disrupting Compounds and Implications for Wastewater treatment
# USGS/ Metcalf and Eddy — Wastewater Treatment Plant Study

<table>
<thead>
<tr>
<th>Plant</th>
<th>Secondary Biological Treatment</th>
<th>Tertiary Treatment</th>
<th>Disinfection</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Extended Aeration Activated Sludge</td>
<td>Sand/Anthracite Microfiltration</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>B</td>
<td>Extended Aeration Activated Sludge</td>
<td>Sand Filtration</td>
<td>Chlorination/ Dechlorination</td>
</tr>
<tr>
<td>C</td>
<td>Two Stage Activated Sludge</td>
<td>Sand Filtration</td>
<td>Chlorination/ Dechlorination</td>
</tr>
<tr>
<td>D</td>
<td>Trickling Filter</td>
<td>Sand Filtration</td>
<td>Chlorination/ Dechlorination</td>
</tr>
</tbody>
</table>
Plants Varied In Ability To Reduce PPCPs in Effluents
River Raisin

- All urban contaminants are in greater concentration downstream of Adrian
- Not exclusively WWTP input
  - Septic
  - Urban runoff
Musk fragrances (AHTN/HHCB) only downstream of WWTPs
Generally fewer detections on upstream reaches
Antibiotic compounds shift from animal to human moving downstream on the Pinnebog River.

Largest concentrations of compounds downstream of WWTPs.
Concerns Over PPCPs in Water

- Drinking water – PPCPs have been found in drinking water in Michigan and elsewhere.
- Effects on aquatic animals – endocrine disruption, change in behavior, toxicity.
- What is the effect of multiple chemicals?
  - Water with PPCPs may also have pesticides, herbicides, industrial pollutants, heavy metals, mercury, etc.
Biosolids Retain Many Compounds

- Three major studies document a wide range of compounds in biosolids
  - During wastewater treatment, various compounds preferentially associate with the solid phase
  - Association with the solid phase has been reported to account for much of the reduction between influent and effluent
  - Depending on the chemical, solid conditions in the WWTP, and retention time, many compounds may remain unchanged
  - These processes are difficult to study!
USEPA Targeted National Sewage Sludge Surveys

- 2006/2007: 74 POTWs in 35 states, 72 PPCPs
  - ciprofloxacin, diphenhydramine, and triclocarban and flame retardants in all samples
  - hormones in few samples
- 5 composites of 2001 samples archived from 94 POTWs
  - Triclocarban (36 mg/kg) and triclosan (12.6 mg/kg) most abundant
  - Multiple antibiotics, ibuprofen, carbamazepine, other pharmaceuticals detected
USEPA Results for Archived Biosolids

Similar Results in Another Biosolid Study

- Kinney et al., 2006, ES&T 40: 7207-7215
Triclosan Detected in Michigan Agricultural Soils Following Biosolids Application

- Cha et al., 2009, Water Research 43:2522-2530
- Tested both triclocarban and triclosan in biosolids and 10 soils amended with biosolids
- Both were detected in all soils but could not be related to soil characteristics or date of last biosolids application.
PPCPs Transformed to Tile Water Following Biosolids Application

- Edwards et al., 2009, Science of the Total Environment, 407:4220-4230
- Studies in Ontario, Canada
- Both liquid and dewatered municipal biosolids; both injection and surface application
- Some ECs detected up to 9 months after application
- Triclosan concentrations may reach toxicological endpoints
PPCPs May be Taken Up By Soil Organisms

- Earthworms collected from field sites where municipal biosolids, manure, or no organic amendments were made
- Earthworms from the biosolids application site contained the largest number of emerging contaminants (25 compounds including pharmaceuticals, musk fragrances, detergent metabolites)
- Earthworms had greater concentrations of some ECs than the applied material (e.g., 27 times the amount of triclosan from the biosolids-amended site)

Kinney et al. 2008, ES&T 42:1863-1870
PPCPs May be Taken up By Crops

- Wu et al., 2010, ES&T 44:6157-6161 (University of Toledo) Soybean plants - Carbamazepine, triclosan, and triclocarban were found to be concentrated in root tissues and translocated into above-ground parts including beans, whereas accumulation and translocation for diphenhydramine and fluoxetine was limited.
Summary

- As in other states, water in Michigan may contain PPCPs and other emerging chemical contaminants.
- Many sources, both human and other, contribute these contaminants to Michigan water.
  - Biosolids are a potential source to water via runoff and tile drains.
- Biosolids contain numerous PPCPs and may influence soil organisms.
- Concentrations are usually low in water or biosolids, but
- Usually complex mixtures of chemicals.
  - Cannot assume only the tested chemicals are present.