Biosolids and Soil
Remarkable Media for Managing Trace Organic Chemicals of Potential Concern

Informal Webinar w/ NEWEA Microconstituents Committee

Ned Beecher • North East Biosolids & Residuals Association

Thursday, March 24, 2016 - Noon – 1:10 pm, EDT
Trace Organic Chemicals (TOrCs) in biosolids

- Biosolids use
- Historic context
- Research spreads to biosolids:
  - Presence
  - Fate
  - Impacts
- Varieties of analytes
- Bioassays
- What does it mean?
- Biosolids & soils: Remarkable media for managing TOrCs!
Gordon Price, Dalhousie Univ., NS – this region’s sole current biosolids TOrCs researcher

TOrCs research spreads to biosolids… presence, fate, impacts
Historic context

- Trace chemicals in biosolids are not new
- 45+ years of research (e.g. PCBs, priority pollutants)
- EPA dioxin risk assessment – early 2000s
- 2006-08: WEF “Microconstituents” CoP TPU's
- March 2008: AP news
- 2008 / 2011: NEBRA Info:
  http://www.nebiosolids.org/resources/#/microconstituents/
Xia et al., 2005 (state-of-science of land application conference, U. Florida): “Although PPCPs, such as fragrances, flame retardants, surfactants, and their metabolites, have been detected in biosolids, there is limited information on the occurrence of many other PPCPs in biosolids. This lack of information is largely due to analytical limitations because of the complexity of the biosolids matrix.”

Harrison et al., 2006: literature review reporting 516 trace organic chemicals measured in biosolids

Heidler et al. / Halden 2006: TCC up to 50 mg/kg in biosolids


Heidler and Halden 2007: TCS partitions to solids (MN has banned sale of TCS-containing products effective January 1, 2017)

2009: EPA Targeted Sewage Sludge Survey included TOrCs
Xia et al., 2005: The most common drugs

Table 2. The most commonly used prescription and over-the-counter pharmaceuticals in the United States.

<table>
<thead>
<tr>
<th>Active compound</th>
<th>CAS number</th>
<th>log K_{ow}</th>
<th>Brand name</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocodone</td>
<td>125-29-1</td>
<td>0.98</td>
<td>Hydrocodone w/AAP</td>
<td>analgesic, antitussive, antipyretic</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>103-90-2</td>
<td>1.18</td>
<td>Liptab</td>
<td>lipid-lowering agent</td>
</tr>
<tr>
<td>Acetaminetin</td>
<td>13241-60-5</td>
<td>0.12</td>
<td>Acetaminetin</td>
<td>beta-3-adrenergic blocking agent</td>
</tr>
<tr>
<td>Arcanol</td>
<td>29122-68-7</td>
<td>0.23</td>
<td>Arcanol</td>
<td>steroid hormones</td>
</tr>
<tr>
<td>Lophathexin</td>
<td>61-48-0</td>
<td>0.16</td>
<td>Synethard</td>
<td>estrogen (female hormones)</td>
</tr>
<tr>
<td>Etoxine</td>
<td>53-16-9</td>
<td>3.22</td>
<td>Premarin</td>
<td></td>
</tr>
<tr>
<td>Equilin</td>
<td>474-86-2</td>
<td>3.03</td>
<td>Equilin</td>
<td></td>
</tr>
<tr>
<td>17α-Dihydrocodein</td>
<td>5966-19-5</td>
<td>4.20</td>
<td>17α-Dihydrocodein</td>
<td></td>
</tr>
<tr>
<td>17α-Estradiol</td>
<td>87-90-0</td>
<td>2.39</td>
<td>17α-Estradiol</td>
<td></td>
</tr>
<tr>
<td>Equilinol</td>
<td>517-89-9</td>
<td>3.07</td>
<td>Equilinol</td>
<td></td>
</tr>
<tr>
<td>17α-Dihydrocodeinol</td>
<td>68-39-99-2</td>
<td>3.12</td>
<td>17α-Dihydrocodeinol</td>
<td></td>
</tr>
<tr>
<td>Acrithicin</td>
<td>83805-01-8</td>
<td>1.84</td>
<td>Acrithicin</td>
<td></td>
</tr>
<tr>
<td>Paroxetine</td>
<td>56-35-9</td>
<td>1.96</td>
<td>Paroxetine</td>
<td></td>
</tr>
<tr>
<td>Amoxicillin</td>
<td>32787-78-0</td>
<td>water soluble</td>
<td>Amoxicillin</td>
<td>antibiotic</td>
</tr>
<tr>
<td>Amiobiotic</td>
<td>88154-42-9</td>
<td>water soluble</td>
<td>Amiobiotic</td>
<td>antibiotic</td>
</tr>
<tr>
<td>Bexylate</td>
<td>96-15-3</td>
<td>1.23</td>
<td>Bexylate</td>
<td>diuretic (treating hypertension, congestive heart failure, and edema)</td>
</tr>
<tr>
<td>Hydrochloethiazide</td>
<td>56-93-5</td>
<td>1.23-1.34</td>
<td>Hydrochloethiazide</td>
<td>diuretic and antihypertension</td>
</tr>
</tbody>
</table>

Prescription drugs (top 10 prescribed in the United States in 2002) (RxList, 2004)

Common over-the-counter drugs (Arthritis Foundation, 2004; RxList, 2004)

<table>
<thead>
<tr>
<th>Active compound</th>
<th>CAS number</th>
<th>log K_{ow}</th>
<th>Brand name</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaminophen</td>
<td>103-90-2</td>
<td>1.18</td>
<td>Anacina, Excedrin, Panadol, Tylenol</td>
<td>analgesic, anti-inflammatory</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>50037-27-1</td>
<td>0.82</td>
<td>Advil, Mobic 3, Nuparin</td>
<td>anti-inflammatory, analgesic, antipyretic</td>
</tr>
<tr>
<td>Aspirin</td>
<td>50-78-2</td>
<td>1.39</td>
<td>Anacina, Aspirin, Bayer, Bufferin, Ecotrin, Excedrin tablets</td>
<td>anti-inflammatory, analgesic, antipyretic</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>125-71-5</td>
<td>0.63</td>
<td>eucalyptus cough syrup</td>
<td>relieving pain</td>
</tr>
<tr>
<td>Diphenhydramine</td>
<td>50-73-3</td>
<td>0.27</td>
<td>Benadryl</td>
<td>antihistamine, cold and cough medicine</td>
</tr>
<tr>
<td>Loratadine</td>
<td>79894-75-8</td>
<td>4.56</td>
<td>Claritin</td>
<td>antihistamine</td>
</tr>
<tr>
<td>Omeprazole</td>
<td>73599-58-6</td>
<td>1.39</td>
<td>Prilosec</td>
<td>treating heartburn</td>
</tr>
<tr>
<td>Additive compound</td>
<td>CAS number</td>
<td>log $K_{ow}$</td>
<td>Characteristics</td>
<td></td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>------------</td>
<td>--------------</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Musk kretene</td>
<td>81-14-1</td>
<td>3.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Musk xylene</td>
<td>81-15-2</td>
<td>3.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galaxolide (HHCB)</td>
<td>1222-05-5</td>
<td>4.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tumalide (ABIT)</td>
<td>2138-57-7</td>
<td>4.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phentanolide (AHME)</td>
<td>55321-06-0</td>
<td>4.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tramolide (ATIB)</td>
<td>60857-95-4</td>
<td>4.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Celosolide (ADSH)</td>
<td>13776-06-1</td>
<td>4.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cashmeron (DPM)</td>
<td>33734-61-9</td>
<td>4.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrabromodiphenyl A</td>
<td>79-94-7</td>
<td>6.38-5.34</td>
<td>Used as an additive in flexible polyurethane foam, in textile coatings for furniture, and in plastics for electrical and electronic equipment.</td>
<td></td>
</tr>
<tr>
<td>Polybrominated diphenylether</td>
<td></td>
<td></td>
<td>(commercial available PBBs primarily consist of penta-, octa-, deca-PBDE)</td>
<td></td>
</tr>
<tr>
<td>Penta- and octabromodiphenyl ether</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexabromocyclododecane</td>
<td>23774-50-1</td>
<td>4.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentabromobenzene</td>
<td>87-84-3</td>
<td>4.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexabromobenzene</td>
<td>23774-50-1</td>
<td>4.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tris(2,3-dibromopropyl) phosphate</td>
<td>316-72-7</td>
<td>&gt;4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloro (2,4,6-trichloro-2-hydroxy diphenyl ether)</td>
<td>3380-34-5</td>
<td>2.39-4.54</td>
<td>Bactericide added in detergents, dishwashing detergents, laundry soaps, deodorants, cosmetics, lotions, creams, toothpastes and mouthwashes, footwear, and plastic ware.</td>
<td></td>
</tr>
<tr>
<td>Biphenylol</td>
<td>99-43-7</td>
<td>2.67-2.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorophene</td>
<td>126-32-1</td>
<td>3.37-3.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DECT ($\text{N}$,N-dieutylthiomaleamide)</td>
<td>134-62-3</td>
<td>2.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butylparaben (alkyl-$\text{p}$-hydroxybenzoate)</td>
<td>94-26-8</td>
<td>1.89-3.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkylphenol polyethoxylates (usually branched monol or acetyl; ethoxylate units = 1-20)</td>
<td></td>
<td>&gt;4.5</td>
<td>Non-ionic surfactants added in detergents (National Library of Medicine Specialized Information Services, 2004).</td>
<td></td>
</tr>
<tr>
<td>Sodium dodecylbenzenesulfonate</td>
<td>25335-36-0</td>
<td>water soluble</td>
<td>Ionic surfactants added in detergents (National Library of Medicine Specialized Information Services, 2004).</td>
<td></td>
</tr>
<tr>
<td>Benzalkonium chloride</td>
<td>8801-54-5</td>
<td>water soluble</td>
<td>Ionic surfactants added in detergents, preservative and disinfectant in contact lens solutions (National Library of Medicine Specialized Information Services, 2004).</td>
<td></td>
</tr>
</tbody>
</table>
**Table 3: Concentration of organic chemicals reported in biosolids**

(Modified from Harrison et al. 2006). ND = non detect.

<table>
<thead>
<tr>
<th>Legacy Contaminants</th>
<th>Category</th>
<th>Range mg/kg dry wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>dieldrin</td>
<td>pesticide</td>
<td>ND-64.7</td>
</tr>
<tr>
<td>toxaphene</td>
<td>pesticide</td>
<td>51</td>
</tr>
<tr>
<td>bisphenol-A</td>
<td>phenols</td>
<td>0.00010-32 100</td>
</tr>
<tr>
<td>phthalates</td>
<td>phthalate acid ester/plasticizers</td>
<td>ND-58 300</td>
</tr>
<tr>
<td>dioxins and furans</td>
<td>polychlorinated biphenyls, naphthalenes, dioxins and furans</td>
<td>ND-1.7</td>
</tr>
<tr>
<td>(polychlorinated dibenzof)</td>
<td></td>
<td>ND-765</td>
</tr>
<tr>
<td>PCB congeners</td>
<td>polychlorinated biphenyls, naphthalenes, dioxins and furans</td>
<td>ND-44</td>
</tr>
<tr>
<td>anthracene</td>
<td>polynuclear aromatic hydrocarbons acenaphthene</td>
<td>ND-24.7</td>
</tr>
<tr>
<td>benzopyrene congeners</td>
<td>polynuclear aromatic hydrocarbons acenaphthene</td>
<td>ND-6610</td>
</tr>
<tr>
<td>naphthalene</td>
<td>polynuclear aromatic hydrocarbons biphenyl</td>
<td>ND-199</td>
</tr>
<tr>
<td>total PAH</td>
<td>polynuclear aromatic hydrocarbons biphenyl</td>
<td>216.9</td>
</tr>
<tr>
<td>coprostanol</td>
<td>sterols, stanols and estrogens</td>
<td>&lt;1-30,200</td>
</tr>
<tr>
<td>alkylbenzene sulfonates</td>
<td>surfactants</td>
<td></td>
</tr>
</tbody>
</table>
Kinney et al., 2006: 
...yes, TOrCs are in biosolids...

<table>
<thead>
<tr>
<th>Organic Wastewater Contaminants</th>
<th>Use</th>
<th>Log $K_{ow}$</th>
<th>Median of all Biosolids (μg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbamazepine</td>
<td>antiepileptic</td>
<td>2.45</td>
<td>68</td>
</tr>
<tr>
<td>diphenhydramine</td>
<td>antihistamine</td>
<td>3.27</td>
<td>340</td>
</tr>
<tr>
<td>fluoxetine</td>
<td>antidepressant</td>
<td>4.05</td>
<td>370</td>
</tr>
<tr>
<td>d-limonene</td>
<td>fragrance</td>
<td>4.57</td>
<td>630</td>
</tr>
<tr>
<td>tolanide (AHTN)</td>
<td>fragrance</td>
<td>5.70</td>
<td>11,600</td>
</tr>
<tr>
<td>galaxolide (HHCB)</td>
<td>fragrance</td>
<td>5.90</td>
<td>3,900</td>
</tr>
<tr>
<td>indole</td>
<td>fragrance</td>
<td>2.14</td>
<td>19,600</td>
</tr>
<tr>
<td>4-test-octylphenol</td>
<td>detergent metabolite</td>
<td>5.28</td>
<td>4,030</td>
</tr>
<tr>
<td>para-nonylphenol-total</td>
<td>detergent metabolite</td>
<td>5.92</td>
<td>261,000</td>
</tr>
<tr>
<td>nonylphenol, dioxy-total</td>
<td>detergent metabolite</td>
<td>4.21</td>
<td>7,010</td>
</tr>
<tr>
<td>bisphenol A</td>
<td>fire retardant</td>
<td>3.32</td>
<td>4,690</td>
</tr>
<tr>
<td>3-beta-coprostanol</td>
<td>steroid</td>
<td>8.82</td>
<td>126,000</td>
</tr>
<tr>
<td>cholesterol</td>
<td>steroid</td>
<td>8.74</td>
<td>209,000</td>
</tr>
<tr>
<td>beta-aminosterol</td>
<td>steroid</td>
<td>9.65</td>
<td>131,000</td>
</tr>
<tr>
<td>stigmastanol</td>
<td>steroid</td>
<td></td>
<td>174,000</td>
</tr>
<tr>
<td>phenol</td>
<td>disinfectant</td>
<td>1.50</td>
<td>2,180</td>
</tr>
<tr>
<td>triclosan</td>
<td>disinfectant</td>
<td>4.53</td>
<td>10,200</td>
</tr>
<tr>
<td>diethylhexyl phthalate</td>
<td>plasticizer</td>
<td>7.88</td>
<td>10,500</td>
</tr>
<tr>
<td>para-cresol</td>
<td>preservative</td>
<td>1.97</td>
<td>4,400</td>
</tr>
<tr>
<td>xcatol</td>
<td>fecal indicator</td>
<td>2.60</td>
<td>2,510</td>
</tr>
</tbody>
</table>
Research spreads to biosolids: Fate

- Buyuksonmez and Sekeroglu, 2005: composting certainly degrades many TOrCs.

- Lappen et al., 2008: worst-case field application scenario with spiking of PPCPs led to measured PPCPs in tile drainage

- Kinney et al. 2008: USGS study on fate: trace organics from biosolids & swine manure is found in worms (http://toxics.usgs.gov/highlights/earthworms.html)

- Gottschall et al., 2012, 2013: no significant impact on tile drainage water quality from biosolids land application

- Gottschall et al. 2012, Hale et al. 2012, Sauborin et al. 2012. These studies generally demonstrated low risk to human health from biosolids borne PPCPs, PBDEs, hormones and parabens, citing low rates of plant uptake and minimal impact on ground water quality
Topp et al., 2009: “PPCPs are detected in tile drainage and in surface runoff, sometimes months after application. Maximum concentrations of PPCPs detected in effluent are generally lower following application of DMB* than application of LMB**. Incorporation of LMB eliminates the potential for loss via runoff. Application of LMB using an Aerway device reduces contamination via tile drainage, compared to surface applied and incorporated. The mass transport (fraction of chemical applied that is exported) varied widely. Maximum concentrations of PPCPs detected in effluents were generally far below toxic thresholds for a variety of endpoints drawn from the literature.”

* dewatered municipal biosolids
** liquid municipal biosolids
Hundal et al. 2009, Chicago: “The data suggest limited mobility of biosolids borne TCC, TCS, total PBDEs, and 4-NP in biosolids-amended soils. Although the concentrations of, TCC, TCS, 4-NP, and total PBDEs in soil were greater in the biosolids-amended plots than in the Control plots, the contaminants had no detrimental effects on the soil biota. Indeed, microbial community studies showed that the microbial populations were more diverse and much more biologically active in the biosolids-amended plots than in the control plots.”
Wu et al., 2010

- Considerable media attention
- Soybean plant uptake
- Greenhouse study
- Spiked samples
- Past research on trace metals and chemicals shows similar over-estimation of effect when spiked samples of the pollutant are used
Triclosan (TCS)
- In toothpaste: 3,000 mg/kg
- Wu et al. maximum measured concentration in plant (conservative scenario): 0.1 mg/kg
- Typical land application calculated estimated soil concentration: 0.05 mg/kg
- TCS (& TCC) decompose in soil at a moderate rate.
- Young, (Univ. of CA, Davis): “increased nitrogen added with biosolids stimulates nitrogen cycling sufficiently to offset any detrimental impacts on the nitrogen cycling caused by Triclosan at realistic application concentrations.”
“Biosolids at application, and crop samples following harvest, were analyzed for 118 pharmaceuticals and transformation products, 17 hormones or hormone transformation products, and 6 parabens. Analyte concentrations in the biosolids were consistent with those detected in other surveys. Eight of the 141 analytes were detected in one or two crop replicates at concentrations ranging from 0.33 to 6.25 ng/g dry weight, but no analytes were consistently detected above the detection limit in all triplicate treated plots. Overall, this study suggests that the potential for micropollutant uptake into crops under normal farming conditions is low.”
Concentrations of TOrCs in biosolids

Clark and Smith, 2010
Large review on fate & impacts

Assessing the Fate and Significance of Microconstituents and Pathogens in Sewage Biosolids
Update of the 2001 WEAO Report on Fate and Significance

Hydromantis, 2010
## Process Rankings for TOrC Removal


<table>
<thead>
<tr>
<th>Location</th>
<th>Treatment Process Assessed</th>
<th>Score total</th>
<th>Number of TOrCs (counts)</th>
<th>Reduction efficiency (avg score)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gatineau Val.</td>
<td>Biological – compost</td>
<td>49</td>
<td>27</td>
<td>1.81</td>
</tr>
<tr>
<td>Moncton</td>
<td>Biological – compost</td>
<td>57</td>
<td>31</td>
<td>1.84</td>
</tr>
<tr>
<td>Prince Albert</td>
<td>Biological – compost</td>
<td>72</td>
<td>29</td>
<td>2.48</td>
</tr>
<tr>
<td>Halifax N-Viro</td>
<td>Phys.-chem. (alkaline stabilis’n)</td>
<td>116</td>
<td>35</td>
<td>3.31</td>
</tr>
<tr>
<td>Red Deer</td>
<td>Biological – meso. an. dig.</td>
<td>115</td>
<td>34</td>
<td>3.38</td>
</tr>
<tr>
<td>Eganville (Septage)</td>
<td>Physical – geotextile bag dewatering</td>
<td>97</td>
<td>28</td>
<td>3.46</td>
</tr>
<tr>
<td>Salmon Arm</td>
<td>Biological – ATAD</td>
<td>111</td>
<td>32</td>
<td>3.47</td>
</tr>
<tr>
<td>Saskatoon</td>
<td>Biological – meso. an. dig</td>
<td>118</td>
<td>34</td>
<td>3.47</td>
</tr>
<tr>
<td>Smiths Falls</td>
<td>Physical – thermal drying</td>
<td>100</td>
<td>27</td>
<td>3.70</td>
</tr>
<tr>
<td>Gander</td>
<td>Physical – filter press dew.</td>
<td>102</td>
<td>27</td>
<td>3.78</td>
</tr>
<tr>
<td>Saguenay</td>
<td>Physical – filter press dew.</td>
<td>108</td>
<td>27</td>
<td>4.00</td>
</tr>
</tbody>
</table>
WERF: State of the Science

Executive Summary


- Available from WERF website
- Foundation for future WERF research on the topic
Noteworthy concerns being researched...

- Antibiotics – manures & biosolids are sources to soils; resistance is concern, but appears to be short-lived
- Nanoparticles
- PBDEs – POPs, being phased out, are substitutes any better?
- Polychlorinated alkanes – significant concentrations (~1800 ppm)
- Perflourinated – persistent, low concentrations in biosolids
- Synthetic musks – persistent, Europe limits in biosolids
- See Clark & Smith 2010.
“The most highly exposed people, theoretically, are those people who apply sewage sludge as a fertilizer to their crops and animal feed and then consume their own crops and meat products over their entire lifetimes. EPA's analysis shows that even for this theoretical population, only 0.003 new cases of cancer could be expected each year or only 0.22 new cases of cancer over a span of 70 years. The risk to people in the general population of new cancer cases resulting from sewage sludge containing dioxin is even smaller…”

EPA Risk Assessment
## Context for dioxin

<table>
<thead>
<tr>
<th>Source</th>
<th>Concentration (ppt TEQ dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maine Biosolids Average (31 samples 1995-1997)</td>
<td>6.3</td>
</tr>
<tr>
<td>Maine Biosolids Regulatory Limit</td>
<td>27</td>
</tr>
<tr>
<td>U.S. soils average (rural) EPA data</td>
<td>4</td>
</tr>
<tr>
<td>U.S. soils average (urban) EPA data</td>
<td>19</td>
</tr>
<tr>
<td>Leaf and yard waste composites (range of 29 samples)</td>
<td>5 - 91</td>
</tr>
<tr>
<td>Cow Manure (6 samples from 2003 European study)</td>
<td>3.6</td>
</tr>
<tr>
<td>Fish (EPA data)</td>
<td>0.59</td>
</tr>
<tr>
<td>Ben &amp; Jerry's Vanilla Ice Cream (1 sample)</td>
<td>0.79</td>
</tr>
<tr>
<td>Times Beach, Missouri</td>
<td>Up to 340,000</td>
</tr>
</tbody>
</table>

Slide courtesy of Andrew Carpenter, Northern Tilth
How to proceed?

- Research and risk assessment… chemical by chemical – long and costly process!

- Must prioritize (as has been done mostly so far):
  - high production chemicals
  - most toxic
  - most persistent

- Better = bioassays:
  - Screens for total impacts
  - Addresses concern of impacts of mixtures
  - Addresses concern of persistent exposure (of even short-lived compounds)
Bioassays...
...a logical & efficient approach to assessing potential impacts
Bioassay work...

- 1980s & ‘90s: Sopper (Penn State Univ.): testing of plant and rabbit health on sites reclaimed with biosolids (with focus on heavy metals)
- 2000s: Brown (Univ. of WA), USDA, and others: testing of plant and rabbit health on sites reclaimed with biosolids
- 2010: University of Guelph – fate of endocrine disruption during biosolids treatment processes
- 2010: College of William and Mary: bioavailability of PDBEs using earthworms and crickets in laboratory
- 2013: Park, et al. (Tom Young team, UC Davis): Triclosan has “little relative impact on overall community composition…” and “TCS slightly increased biomarkers of microbial stress, but stress biomarkers were lower in all biosolid treated soils, presumably due to increased availability of nutrients mitigating potential TCS toxicity.”
- 2013: Puddephat thesis (Lynda McCarthy team, Ryerson Univ.): lab bioassays in Ontario using earthworms, springtails, *brassica rapa*, beans, corn, and various aquatic organisms
Figure 1. Possible contamination pathways and specific bioassays for the assessment of biosolids application impact.
Puddephat / McCarthy research (Puddephat, 2013)
Puddephat / McCarthy research (Puddephat, 2013)

Brassica rapa

Zea mays

Figure 17: Avoidance chamber setup for Folsomia candida

Figure 30: Feeding of Earthworms in Ryerson Long-Term Bioassay Chambers. Image shows the mating chambers atop the Evan’s Boxes
Conclusions of Puddephat / McCarthy research:

Puddephat, 2013:

“The findings showed that biosolids had little negative impact on the terrestrial biota examined and as a general rule, there was no impact observed. Where effects were observed, the majority of instances were positive. In the few instances where there was negative impact observed, for example in the initial growth stages of the plant bioassays, with further development of the organism, there was no longer a significant difference between the reference and treatment plants.”
The different microconstituents...
...antibiotics to pharmaceuticals to dibenzo-p-dioxins

Information on the following 14 slides mostly from Clark and Smith, 2010
Antibiotics / antimicrobials

- Main concern: spread of antibiotic resistance
- Found in solids: norfloxacin, ofloxacin, ciprofloxacin, trimethoprim, sulfamethoozole and doxycycline. (Bold indicates most commonly found in low mg/kg range.)
- More persistent in soils than in aquatic environment.
- Natural antibiotics are synthesized in soils, and natural resistance develops.
- Maintenance of resistance is not a benefit when stressor disappears / degrades.
- Ciprofloxacin more resistant and of potential concern.
- Antibiotic use in animals is much greater than human use.
Antibiotics / antimicrobials: solids treatment & time reduce resistance

Analysis of viable pathogenic bacteria or antibiotic-resistant coliform bacteria on plate counts did not reveal significant treatment effects of fertilization with Class B biosolids or untreated sewage sludge on the vegetables. Numerous targeted genes associated with antibiotic resistance and mobile genetic elements were detected by PCR in soil and on vegetables at harvest from plots that received no organic amendment. However, in the season of application, vegetables harvested from plots treated with either material carried gene targets not detected in the absence of amendment. Several gene targets evaluated using qPCR were considerably more abundant on vegetables harvested from sewage sludge-treated plots compared to controls in the season of application, whereas vegetables harvested the following year revealed no treatment effect. Overall, results of the present study suggest that producing vegetable crops in ground fertilized with human waste without appropriate delay or pre-treatment will result in an additional burden of antibiotic resistance genes on the harvested crops.

– Rahube et al., 2014

Same results found in study of manure applications (Marti et al., 2013)
Bisphenol A

- Widely used, high production (diminishing in consumer products)
- Degrades in wastewater treatment
- In solids in low ug / kg to mid mg / kg
- Half-life in soil ~ 3 days
- Greatest human exposure is in domestic environment
Nanoparticles

- Increasing use in consumer products – especially silver
- Colman, 2010 (Duke Univ.) found negative impacts on soil microbial activity and plants when biosolids and spikes of silver nanoparticles were added to soil in a microcosm study. Significant publicity ensued, including in Scientific American. This research methodology is not representative of field conditions with nanoparticles aged in solids.
- Continued research suggested.
Organotins

- Highly toxic in aquatic environment
- Use being phased out in UK and elsewhere
- Rarely > 1 mg/kg in wastewater solids.
- 20% - 50% remained in soil after 2 months in laboratory study (Marcic et al, 2006)
Phthalate acid esters

- 20% - 40% of many plastics
- High $K_{ow}$ - sorbs to solids
- Large variability in concentrations in different solids and same solids over time: 1 – 3500+ mg/kg
- Most common is DEHP di(2-ethylhexyl) phthalate
- Wastewater treatment and composting degrade them (AD less so, variably)
- Sorption to solids precludes significant plant uptake
- Greater phthalate on crops from plastics used in agriculture
Most common are BDE47 and BDE99 (penta) and BDE209 (deca)

Persistent (UNEP POP since 2008)

Manufacture of penta ended in 2004 in No. America and it and octa are now restricted in EU.

Are replacements better environmentally?
  - e.g. Tetrabromophthalate: .12 - 3.749 mg/kg in biosolids (Davis et al. 2012)

  No significant plant uptake.

  Greatest human exposure is in domestic environment (house dust)
Polychlorinated alkanes

- More than 10,000 possible congeners
- Found in solids from 1 – thousands mg/kg, but data are limited
- Greater controls on use are underway in EU
- Risk assessment using UK mean concentration of 1800 mg/kg showed direct ingestion by pica child could lead to exceeding tolerable daily intake of 100 ug / kg
- Further research recommended (Clark & Smith, 2010)
Polydimethylsiloxanes

- Industrial applications and in consumer products
- U. S. range of biosolids concentrations: 290 – 5155 mg/kg, but more research would be helpful
- Low toxicity
- Degrade in soils via abiotic processes; drier soil estimated half life of 4 – 28 days. Measured half life in moist soil: 876 – 1443 days.
Perfluorinated compounds

- Persistent and widely found in environment
- Bioaccumulative
- Normal concentrations in solids (without manufacturer input): low ug / kg
- PFOA and PFOS are being restricted by EU and phased out in No. America too, but their long use and persistence means they will be around a long time.
- Application of biosolids at Decatur, AL led to EPA remedial action; treatment plant received manufacturer discharges
Norwegian study that evaluated ~1400 pharmaceuticals in use there. These 14 were identified as needing further research regarding their potential impacts via the biosolids pathway (Ericksen et al., 2009)
Quaternary ammonium compounds

- Cationic surfactants
- Sorb strongly to solids & sediments
- One study found 22 – 103 mg/kg in solids
- Degrade quickly in wastewater treatment and anaerobic digestion
- Short half-life in soil: 17 – 40 days
Steroids / hormones

- Negative impacts known in aquatic environments
- Also enters environment via livestock
- High rate of degradation in WRRFs
- Fast degradation in soils.
Synthetic musks

- persistent
- Concentrations in solids: 0.1 – 81 mg/kg
- Germany and other EU countries proposing limits in biosolids
- More research recommended
“This study investigated the effect of carbamazepine and verapamili (0.005 – 10 mg/kg) on a range of plant responses in zucchini (*Cucurbita pepo*). Uptake increased in a dose-dependent manner, with maximum leaf concentrations of 821.9 and 2.2 mg/kg for carbamazepine and verapamili, respectively... At soil concentrations >4 mg/kg the mature leaves suffered from burnt edges and white spots as well as a reduction in photosynthetic pigments but no such effects were seen for verapamili. For both APIs, further investigations revealed significant differences in the concentrations of selected plant hormones (auxins, cytokinins, abscisic acid and jasmonates).” --Carter et al., 2015, *Env. Sci. & Tech.*, 49:12509-12518
But…

- No biosolids used in this study.
- Fresh chemicals were spiked
- Soils had little organic matter or clay (worst case for sorption).
- 4-week lab study growing plants in pots (NO zucchinis!)
- Nothing to do with a biosolids application scenario.
- Even with this worst-case scenario, no significant impact of verapamil and minimal impact of carbamazepine at biosolids application relevant concentrations. Sabourin et al. 2012 found these same 2 chemicals in biosolids, but no measurable plant uptake when they were applied to soils at a typical rate.
“De minimis risk to human health”

Note: Review used data from spiked sample studies and unrealistic (high) application rates

“This study reviewed the literature for studies that reported residues of PPCPs in the edible tissue of plants grown in biosolids- or manure- amended soils or irrigated with wastewater. These residues were used to determine the estimated daily intake of PPCPs for an adult and toddler. Estimated daily intake values were compared to acceptable daily intakes to determine whether PPCPs in plant tissue pose a hazard to human health.... Our assessment indicates that the majority of individual PPCPs in the edible tissue of plants due to biosolids or manure amendment or wastewater irrigation represent a de minimis risk to human health. Assuming additivity, the mixture of PPCPs could potentially present a hazard.” – Environ. International 2015 75:223-233
Extensive, multi-year research on real-world field sites using biosolids applied at typical rates.

- **Truro, Nova Scotia**
- Various trace chemicals evaluated in biosolids, soils, groundwater, and plants.
- Included metabolomics evaluation of earthworms.
- Initial results being written up now.
What does it mean for biosolids management?
Chemicals of greatest concern in biosolids have…

- High log $K_{ow}$ - octanol-water partition coefficient
- High toxicity (to some species)
- Long half-lives (persistent)
- Bioaccumulative
- Dioxins/furans are excellent example: thoroughly studied and not found to require regulation (EPA, 2003)

Far greater concerns and impacts are in the WRRF effluent and receiving aquatic environment.
Greatest concern for plant uptake:

Absorption & membrane permeability are more likely when…

- \( \text{Log} \, \text{K}_{\text{ow}} < 3 \)
- Molecular Weight < 300
- H-bond donors < 3
- H-bond acceptors < 6

Useful for screening compounds for further risk assessment. Vast majority of TOrCs in biosolids do not meet these criteria.
What does it mean?

**Perspective:**

4 times as much antimicrobials used in agriculture than humans

U. S. manure: ~ 1.1 billion wet tons / year

U. S. biosolids: ~ 36 million wet tons / year

TOrCs in wastewater are removed/broken down during treatment or remain in effluent or solids. A few increase in concentrations due to biochemical processes.

TOrCs in biosolids are generally strongly adsorbed to organic matter and in mineral form (hydrophilic compounds are in effluent). Their generally high log $K_{ow}$ values mean that solid phase retention is great and that release is small, that leaching through soils and subsequent groundwater contamination is likely small, that water solubility is likely low, and that availability to organisms dependent on water solubility (plant uptake) is likely small.

Decades of research on organic compounds in soils provide understanding for TOrCs/PPCPs: most degrade (half-lives vary, but most are less than six months).

Pot studies spiked with fresh chemicals (PPCPs, etc.) are not representative of field conditions.
What does it mean?

Healthy, microbially-active soils are the best medium for treatment of traces of organic chemicals.

Significant impacts to biota have been measured in aquatic environments, but not in biosolids-amended soils.

Risk to human health through biosolids-application-to-soil pathways appear to be negligible. Far greater human exposure to most are through daily use of products.

Source reduction should focus on persistent compounds with known or potential toxicity.

Remember:

1 ppm = 1 second in 11.6 days

1 ppb = 1 second in 31.7 years

1 ppt = 1 second in 31,700 years
BPA – Bisphenol A

Save your credit card receipts?
BPA in credit card receipts = 8-17 g/kg

BPA in biosolids = 0.1-4.6 mg/kg

➢ How much more concentrated is BPA in these receipts than in biosolids?
a) Equal  b) 400x  c) 4000x

Modified from Sally Brown, PhD, Univ. of WA
Biosolids:
Understanding the risk

Putting it into perspective - how does using biosolids or compost made with biosolids compare to chemical exposures in everyday life?

Number of years of contact = 1 dose

<table>
<thead>
<tr>
<th>PRODUCTS</th>
<th>Number of CONTACT (YEARS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 tablet of ibuprofen</td>
<td>Over the counter pain reliever</td>
</tr>
<tr>
<td>93</td>
<td>1 tablet of azithromycin</td>
</tr>
<tr>
<td></td>
<td>Prescription antibiotic</td>
</tr>
<tr>
<td>1 hand wash with triclosan</td>
<td>Antimicrobial agent in antibacterial soaps, toothpaste and deodorant</td>
</tr>
</tbody>
</table>

Legend:
- Gardener
- Child
- Hiker

What is a Risk Analysis?
A risk analysis estimates the risk to human health by examining how harmful a chemical is (toxicity) and the amount of contact with that chemical (exposure). Risk = Toxicity x Exposure

From NW Biosolids fact sheet
Pharmaceutical – 17α-Ethynilestradiol

Not ready to start a family?

How much biosolids do you have to eat to get 1 low dose of birth control pill?

- EE2 in a low dose birth control pill = 50 µg
- EE2 in biosolids = 4.6 µg/kg
  - 10 kg biosolids = EE2 in one pill

Modified from Sally Brown, PhD, Univ. of WA
Biosolids & soils: Remarkable media for managing TOrCs!
Q: Where do we want to put TOrCs? (We can’t remove every bit from wastewater.)

A: Get them into the solids…and into soils…

…because healthy soils (e.g. enriched with biosolids and/or other organic amendments) are the best media for degrading most TOrCs.

“These terrestrial systems have orders of magnitude greater microbial capability and residence time to achieve decomposition and assimilation compared with aquatic systems.”

– Overcash, Sims, Sims, and Neiman, 2005
Best management to address TOrcs

Focus on biosolids quality.
Source reduction works. Enforce industrial pretreatment. Support phase-outs of persistent TOrcs.

<table>
<thead>
<tr>
<th>Year</th>
<th>Cadmium</th>
<th>Chromium</th>
<th>Copper</th>
<th>Lead</th>
<th>Nickel</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1973</td>
<td>33</td>
<td>712</td>
<td>700</td>
<td>1,261</td>
<td>148</td>
<td>2,031</td>
</tr>
<tr>
<td>1983</td>
<td>12.5</td>
<td>360</td>
<td>361</td>
<td>421</td>
<td>79</td>
<td>1,701</td>
</tr>
<tr>
<td>1993</td>
<td>7.3</td>
<td>209</td>
<td>764</td>
<td>225</td>
<td>51</td>
<td>1,444</td>
</tr>
<tr>
<td>2000</td>
<td>4.2</td>
<td>115</td>
<td>566</td>
<td>178</td>
<td>53</td>
<td>1,619</td>
</tr>
</tbody>
</table>

Philadelphia Water District biosolids quality over time, courtesy of Bill Toffey.
What biosolids managers can do…

Focus on biosolids quality.

• When possible, use treatment processes that degrade TOrCs: biological processes are most effective.

• Use multiple processes, e.g. anaerobic digestion followed by composting & application.
What biosolids managers can do…

Use Best Management Practices.

• Apply at agronomic rate*, which limits total mass of TOrCs while providing optimum level of benefits.

• Maintain setbacks from surface & groundwater*, which keeps TOrCs out of the more sensitive aquatic environment.

• Apply to aerated soils and incorporate when possible, which aids decomposition of TOrCs and avoids direct ingestion.

• Use the same BMPs for manures/other residuals.

• Follow research & update BMPs.
Lewiston-Auburn WPCA biosolids composting facility

Biosolids Use
MAXIMIZE BENEFICIAL USES OF RESOURCES

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Benefits</th>
<th>Concerns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>valuable in agriculture in dry times</td>
<td>cost of transport</td>
</tr>
<tr>
<td>Organic matter</td>
<td>vital to soils</td>
<td>putrescible, odor</td>
</tr>
<tr>
<td>Nutrients</td>
<td>plant &amp; animal food</td>
<td>impacts to water</td>
</tr>
<tr>
<td>Energy</td>
<td>renewable, displaces oil/gas</td>
<td>air emissions, no use of nutrients &amp; organic matter if incinerated</td>
</tr>
</tbody>
</table>

MANAGE TO MINIMIZE POTENTIAL RISKS

Reduce/control/mitigate trace elements (e.g. metals), pathogens, synthetic and natural organic chemical compounds, odors, nuisances
Biosolids management in U. S.:
7,180,000 dry U. S. tons/year (~35.9 million wet tons)

55% is used on soils

Biosolids Use and Disposal Practices
2004 U.S. Totals

- Beneficial Use: 49%
- Disposal: 45%
- Other: 6%

These data need updating...
Biosolids improve soils and address environmental challenges.
Biosolids use: Agriculture

- Bulk material markets: animal feed crops (corn, hay), grains (wheat, hops), soy, other commodity crops

- Prices:
  - Class B - $0 - $30 / wet ton
  - Class A – up to $60 / ton

- Trend: increasing demand; waiting lists in some areas

Moorhead, MN: Feed corn grown with liquid injected, Class B, anaerobically-digested biosolids, July 2012
Biosolids use: Forestry

Photos courtesy of King County, WA
http://dnr.metrokc.gov/WTD/biosolids/

- Only in some areas
- Speeds up harvest cycle in actively managed stands
- Price:
  - Class B $0 - minimal

Photo courtesy of Philadelphia Water Dept.
Biosolids use:
Horticulture / Landscaping / Turf

- Class A bulk material markets: potting mixes (e.g. Tagro), golf courses (e.g. Milorganite), parks, lawns, growing turfgrass (e.g. in RI), sports fields (hi-spec turf)
- Prices:
  - Class A bulk – up to $60 / ton
  - Class A bagged/retail – up to $450 / ton
- Trend: increasing demand for quality, consistent products

Biosolids compost use on my home garden – raspberries, May 2014
Biosolids Use: Topsoil Blending

- Bulk biosolids given or sold to topsoil blenders
- Prices: vary, often $0
- A way to use less processed material
- Topsoils used for reclamation, landfill cover, highway embankments, construction sites
- Trend: steady use

Topsoil blending with paper mill residuals and biosolids, central MA, 2006
Reclamation of Disturbed Sites

Spectacle Island in Boston Harbor was reclaimed with biosolids compost and other recycled organics, 2004.

- Bulk material market
- Used to restore healthy soil ecosystem and either native vegetation or cropland
- Prices: vary, often $0
  - Uses a lot of biosolids
- Trend: increasing use, because of huge benefits – biosolids use is best practice for this kind of reclamation
Reclamation of Disturbed Sites

Pennsylvania mine before

Same Pennsylvania mine after

Photos courtesy Bill Toffey, MABA
Biosolids Use:
Landfill Leachate Treatment

Slide courtesy of Sylvis, Vancouver, BC
Biosolids Use: Energy
Anaerobic digestion (followed by use or disposal)

- A biosolids treatment process that results in biosolids to be used or discarded.

- Trend: Huge interest & activity now, across the continent.
General biosolids resources

http://www.endless-films.com/site/?portfolio=biosolids

http://www.loopforyoursoil.com

http://www.nebiosolids.org/about-biosolids/
Thanks for... your invitation, your attention, & your questions and comments.

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603-323-7654