A statewide survey of trace metals and organic chemicals in municipal wastewater

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Outline

- Introduction
- Collaboration
- Study Design
- Analytical Methods
- Results
- Conclusions / Summary
How did this begin?

• 2007 Legislative Bill
• Required DEQ & municipalities to address “Persistent Pollutants”:
  – Toxic and either persists in the environment or accumulates in the tissues of humans, fish, wildlife, or plants
• Municipalities to implement reduction plans for toxics that are found to be present in effluent
Collaboration & Stakeholder Involvement

• To complete the tasks required by the legislation, DEQ convened:
  – Persistent Pollutant Science Workgroup
  – Methods Workgroup
  – Trigger Level Peer Review Group
  – Monitoring Workgroup
  – QAPP / SAP Workgroup

• Workgroups were tasked with providing specific & focused advice to DEQ
Workgroups

• Included experts in:
  – Fate & transport
  – Hydrology
  – Toxicology (human health & aquatic life)
  – Analytical methods

• Represented:
  – Academia
  – Local, state, & federal governments
  – Industry groups
  – Environmental groups
Major Groups of Chemicals Analyzed

- Plant/animal sterols
- Metals (including MeHg)
- Pharmaceuticals
- Consumer products
- Flame retardants (PBDEs)
- Industrial chemicals
- Pesticides
- Combustion by-products (PAHs)
- PCBs
- Perfluorinated surfactants
- Polychlorinated naphthalenes
- Dioxins / Furans
Examples
Monitoring

• 52 major facilities (> 1 MGD dry weather flow)

• Final effluent samples
  – Whole water not filtered
  – Compliance point for facility

• 2 sampling events
  – Seasonal use patterns / hydrologic effects
    • Summer / Low flow – mid-July – August
    • Winter / High flow – November – mid-December
Facilities Types / Population Sizes

• Treatment types and levels varied & included:
  – Activated sludge, trickling filter, stabilization lagoons
  – Levels ranged from standard primary to advanced tertiary

• Design capacities / population sizes
  – Design range from 1 MGD – 50 MGD
  – Population range from 3,385 – 721,420 served

• Pretreatment programs at 32 of 52 facilities
## Methods (15 total)

<table>
<thead>
<tr>
<th>Method Reference / Name</th>
<th>Major Groups of Analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA 200.8</td>
<td>Metals</td>
</tr>
<tr>
<td>EPA 1630</td>
<td>Methyl mercury</td>
</tr>
<tr>
<td>EPA 8270 – Semi-volatiles</td>
<td>PAHs, pesticides, industrial chemicals</td>
</tr>
<tr>
<td>EPA 8270 – Micro-shakeout</td>
<td>Musks, siloxanes</td>
</tr>
<tr>
<td>PCNs</td>
<td>Polychlorinated naphthalenes</td>
</tr>
<tr>
<td>EPA 1694</td>
<td>Pharmaceuticals /Personal Care</td>
</tr>
<tr>
<td>EPA 8321 (LC/MS/MS)</td>
<td>Pesticides</td>
</tr>
</tbody>
</table>
## Methods (con’t)

<table>
<thead>
<tr>
<th>Method Reference / Name</th>
<th>Major Groups of Analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA 8321 – direct injection – UPLC/MS/MS</td>
<td>TBTO, pesticides, TBBPA, galaxolide, anti-bacterial</td>
</tr>
<tr>
<td>Brominated cmpds – UPLC/MS/MS</td>
<td>Hexabromocyclododecane</td>
</tr>
<tr>
<td>EPA 1698</td>
<td>Steroids / Hormones</td>
</tr>
<tr>
<td>EPA 1613</td>
<td>Dioxins / Furans (as TEQ)</td>
</tr>
<tr>
<td>PFAA / PFSA</td>
<td>Perfluorinated surfactants</td>
</tr>
<tr>
<td>EPA 1614</td>
<td>PBDEs (flame retardants)</td>
</tr>
<tr>
<td>SM 6640</td>
<td>Phenoxy herbicides</td>
</tr>
<tr>
<td>EPA 1668</td>
<td>PCBs</td>
</tr>
</tbody>
</table>
Summary of Results

- 114 chemicals detected above LOQ (406 analyzed)
- 3 most frequently detected groups:
  - Plant / animal sterols
  - Metals
  - Pharmaceuticals
- PCNs / dioxins & furans – not detected
- Seasonal variation in some classes of compounds
- Very few detections exceeded established criteria
Average frequency of detection based on class of compound
Percent Detection of Current Use Pesticides with Maximum Concentration Detected

- 2,4-D
- 2,4-DB
- Dicamba
- Dichloprrop
- Diuron
- Fluridone
- Imazapyr
- Prometon
- Simazine
- Tertbutylazine
- Triclopyr
- Azobenzene
- Baygon
- Carbaryl
- Imidacloprid
- Propiconazole
- Pentachlorophenol

[Graph showing pesticide concentrations and detection rates]
Pharmaceuticals & Personal Care Products
% of Facilities with Detection by Compound

- DEET
- Venlafaxine
- Sulfamethoxazole
- Ibuprofen
- Diphenhydramine
- Cotinine
- Codeine
- Carbamazepine
- Caffeine
- Acetaminophen

0%  20%  40%  60%  80%  100%
## Pharmaceuticals / Personal Care

<table>
<thead>
<tr>
<th>Analyte</th>
<th># of detects (N=102)</th>
<th>med (ng/L)</th>
<th>max (ng/L)</th>
<th>% Detection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfamethoxazole</td>
<td>94</td>
<td>1040</td>
<td>5280</td>
<td>92%</td>
</tr>
<tr>
<td>Venlafaxine</td>
<td>87</td>
<td>412</td>
<td>749</td>
<td>85%</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>84</td>
<td>206</td>
<td>577</td>
<td>82%</td>
</tr>
<tr>
<td>DEET (N,N-diethyl-m-toluamide)</td>
<td>80</td>
<td>232</td>
<td>13600</td>
<td>78%</td>
</tr>
<tr>
<td>Diphenhydramine</td>
<td>78</td>
<td>673</td>
<td>2610</td>
<td>76%</td>
</tr>
<tr>
<td>Codeine</td>
<td>23</td>
<td>331</td>
<td>570</td>
<td>23%</td>
</tr>
<tr>
<td>Cotinine</td>
<td>17</td>
<td>239</td>
<td>1660</td>
<td>17%</td>
</tr>
<tr>
<td>Caffeine</td>
<td>15</td>
<td>7110</td>
<td>81500</td>
<td>15%</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>5</td>
<td>3350</td>
<td>17000</td>
<td>5%</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>2</td>
<td>2955</td>
<td>3300</td>
<td>2%</td>
</tr>
</tbody>
</table>
Flame retardants

- Polybrominated diphenyl ethers (PBDEs)
  \[
  \begin{array}{c}
  \text{Br}_m \quad \text{O} \quad \text{Br}_n
  
  \end{array}
  \]
- Similar to PCBs in bioaccumulation & persistence in environment
- 21 congeners detected
  - Similar to other wastewater studies
  - 9 of the 21 detected also found in Osprey eggs in Oregon (Henny et al., 2009)
Methyl mercury

- Contaminant of concern in Oregon
- State water quality criteria
  - 0.04 mg/kg wet weight, fish tissue
- Detected in 65% of samples
- Range 0.18 ng/L – 1.36 ng/L
- Highest concentration present in lagoon treatment systems
Seasonal variation in detection frequency

- Chemicals such as Stigmasterol, 2-Methylphenol, Dichlorophenol, Estrone, Carbamazepine, DEET, Codeine, Diuron, 1,4-Dichlorobenzene, and PBDE-07T show significant seasonal variation in detection frequency.

- Detection frequency is higher in the Fall for some chemicals compared to the Summer.

- The graph visually represents the percentage of detection frequency for each chemical across seasons.
Certain chemicals exhibited seasonal detection patterns
Variety of detection / composition of effluent likely related to population size & to a lesser extent geography within state
No clear relationship between detection of industrial compounds and pretreatment plans
Similar compounds detected in other studies
  - PAHs, PCBs, PBDEs, pharmaceuticals
Presence of consumer & commercial pesticides not previously reported in wastewater
Pesticides detected are similar to those detected in other DEQ monitoring efforts
Summary

• Wastewater effluent is one pathway for chemicals to reach surface waters
• Other pathways include:
  – stormwater
  – Agricultural run-off
  – Airborne
  – Biosolid disposal
• Toxic effect of these chemicals is unknown
  – Synergistic / additive toxicity
• Oregon DEQ Laboratory, Toxics Monitoring
  – http://www.deq.state.or.us/lab/wqm/toxics.htm
• Oregon DEQ Senate Bill 737 Implementation
  – http://www.deq.state.or.us/wq/SB737/index.htm


• Hope, BK, Pillsbury, L, Boling, B. A state-wide survey in Oregon (USA) of trace metals and organic chemicals in municipal effluent. Sci Total Env 2012 (417-418):263-272
Contact Information

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