Research Overview
National Water Quality Laboratory
USGS
Lakewood, CO

NRP/LEAG Meeting
April 22, 2009

Jeff McCoy
Chief, Methods Research & Development Program
Agenda

- Quick overview of the NWQL
- Ongoing research at the NWQL
- Snapshots of a few current projects
- Future directions…
The NWQL: What we do…

- Develop modern methods for environmental analysis
- Analyze water, wastewater, soil and tissue in support of international, national and state programs
- Collaborative research with other government agencies
NWQL Areas of Expertise

- Methods Research and Development
- Inorganic, Organic and Radiochemistry
- ID & Quantitation of Benthic Invertibrates
- Varied Matrices:
  Water, Wastewater, Sediment, Tissue
- Admin, Support Services, QAS, IT, BDT
Key Inorganic Chemistry Capabilities

- **Nutrients**: Ortho-P, ammonia, nitrate, nitrite
- **Metals**: whole & filtered water: ICP & ICP/MS

- Bromide: filtered by IC
- Iodide, silica: filtered by colorimetric flow
- Fluoride: filtered by ISE
- Major anions: filtered by IC
- Radchem, Hg, As speciation
- Etc., etc. – see online catalog at nwql.usgs.gov
Key Organic Chemistry Capabilities

- Pesticides
- Volatiles
- Emerging Contaminants
  - Wastewater Indicators
  - Pharmaceuticals
  - Hormones
  - Endocrine Disruptors
- High Production Volume chemicals
Biological Services

- Macroinvertebrate Sample Production
  - Subsampling & Sorting
  - Taxonomic Identification
  - ~ 800 samples/yr.
  - Key to USGS ecosystems focus
Method Development at the NWQL
Methods Research at the NWQL:

Analytical Focus

- Improved integrative sampling technology
  - Suspended Sediment Integrative Samplers
  - Polar Organic Chemical Integrative Sampling (POCIS)

- Improved Sensitivity and Selectivity:
  - Direct Aqueous Injection LC/MS/MS
  - High mass resolution TOF/MS
  - Isotope dilution MS/MS

- Green Chemistry, Automation & Efficiency:
  - ASE Sediment/Tissue Prep Methods
  - Replacement of Cadmium w/ nitrate reductase
  - Kone Discrete analyzer
Ongoing Research Projects (incomplete list)

- Integrated suspended sediment samplers
- Pharmaceuticals in water, tissue and sediment
- Wastewater indicators from biosolids
- Persistence of emerging contaminants through the waste treatment processes
- Hormones in water, sediment and tissue
- High Production Volume chemicals in water
- Elimination of Cadmium with NO₃⁻ Reductase
- Silica: move from SFF to Discrete method
Glyphosate in suspended sediment in streams from two agricultural areas of the United States

Mark Sandstrom, Max Stroppel, Michael Meyer, Claire Rose, Richard Coupe, and Steven Kalkhoff
U.S. Geological Survey
(SETAC, 2008)
Glyphosate-based herbicides are used for control of weeds on corn, soybeans, and cotton. (High volume, broad geographical usage)

Glyphosate is strongly adsorbed by soils and stream sediment.

Dissolved glyphosate has been found frequently in tile drains and streams in agricultural areas (Battaglin and others, 2005).
Study Objectives

- Evaluate importance of suspended sediment in transport and fate of glyphosate from agricultural fields into streams

- Evaluate time-integrating sediment samplers ability to collect fine-grained suspended sediment
Time-integrated suspended sediment sampler for small watersheds

- Operates unattended, no power requirements
- Composite sample collected continuously over period of days to weeks
  - Samples entire storm runoff event
- Collects sufficient mass for variety of geochemical analyses

Time-integrated suspended sediment sampler for small watersheds
Suspended sediment sampler operation

- Sampler submerged in stream with inlet orientated directly into the flow
- Within main cylinder flow velocity is reduced by ~600 times ambient flow
- Reduction in flow velocity induces sedimentation
## Fraction of total glyphosate in suspended sediment

<table>
<thead>
<tr>
<th>Stream Site</th>
<th>Sample Event</th>
<th>Glyphosate in sediment samplers, in ng/g</th>
<th>Median concentration of suspended sediment in mg/L</th>
<th>Calculated glyphosate in suspended sediment in ng/L</th>
<th>Median concentration of glyphosate in filtered stream samples, in ng/L</th>
<th>Glyphosate in suspended sediment, in percent of total glyphosate in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blairsburg, IA</td>
<td>1</td>
<td>111</td>
<td>44</td>
<td>4.9</td>
<td>80</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>172</td>
<td>34</td>
<td>5.8</td>
<td>675</td>
<td>0.9</td>
</tr>
<tr>
<td>New Providence, IA</td>
<td>1</td>
<td>37</td>
<td>19.5</td>
<td>0.7</td>
<td>60</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>79</td>
<td>204</td>
<td>16.1</td>
<td>320</td>
<td>5.0</td>
</tr>
<tr>
<td>Tommie Bayou, MS</td>
<td>1</td>
<td>1043</td>
<td>110</td>
<td>114.7</td>
<td>890</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>437</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bogie Phalia, MS</td>
<td>1</td>
<td>1755</td>
<td>86</td>
<td>150.9</td>
<td>1,690</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1528</td>
<td>81</td>
<td>123.8</td>
<td>1,015</td>
<td>12.2</td>
</tr>
</tbody>
</table>
Conclusions

- Time-integrating sediment samplers were effective in the collection of suspended sediment during major storm-runoff at each location.
- Glyphosate in suspended sediment represented a small fraction (1 - 12 percent) of the total glyphosate concentration in the stream.
Fate of Antidepressants Downstream of the Boulder Creek, CO Wastewater Treatment Facility

- Ed Furlong, Melissa Schultz - NWQL
- Note: data is preliminary, research ongoing
- Matrices: water, fish brain, sediment
- Bottom line: Are differences seen due to metabolism in fish? Due to chemical property differences in water vs. sediment?
## Boulder Creek Antidepressants: Comparison Between Media Downstream of WW Outfall

<table>
<thead>
<tr>
<th></th>
<th>Water (ng/L)</th>
<th>Brain (ng/g)</th>
<th>Sediment (ng/g)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoxetine</td>
<td>9</td>
<td>0.6</td>
<td>12</td>
</tr>
<tr>
<td>Norfluoxetine</td>
<td>4</td>
<td>0.9</td>
<td>2.3</td>
</tr>
<tr>
<td>Sertraline</td>
<td>3</td>
<td>1.5</td>
<td>11</td>
</tr>
<tr>
<td>Norsertraline</td>
<td>4</td>
<td>2.5</td>
<td>8.7</td>
</tr>
<tr>
<td>Paroxetine</td>
<td>4</td>
<td>ND</td>
<td>2.4</td>
</tr>
<tr>
<td>Citalopram</td>
<td>60</td>
<td>0.07</td>
<td>10</td>
</tr>
<tr>
<td>Bupropion</td>
<td>50</td>
<td>0.05</td>
<td>1.7</td>
</tr>
<tr>
<td>Venlafaxine</td>
<td>220</td>
<td>ND</td>
<td>21</td>
</tr>
</tbody>
</table>

*Provisional Results*
Mobilization of Microconstituents from Land-Applied Biosolids via Simulated Rainfall

- Ed Furlong, (NWQL), Thomas Borch, Jessica Davis (CSU), Tracy Yager (USGS Colorado WSC)
- Coordinated with Metro Wastewater Reclamation District
- First-time application of biosolids (Roggen, CO)
- Artificial rainfall applied; runoff collected.
- Samples analyzed for:
  - Wastewater indicators
  - Pharmaceuticals, hormones
  - Nutrients, Organic carbon
Mobilization of Wastewater-Indicator Compounds From Biosolids Treated Sites - Simulated Rainfall

<table>
<thead>
<tr>
<th>Elapsed time following application</th>
<th>1 day</th>
<th>8 days</th>
<th>35 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Triclosan Concentration ug/l</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainfall Simulation - Beginning</td>
<td>0.25</td>
<td>0.20</td>
<td>0.38</td>
</tr>
<tr>
<td>Rainfall Simulation - Middle</td>
<td>0.33</td>
<td>0.34</td>
<td>0.39</td>
</tr>
</tbody>
</table>
| Rainfall Simulation - End          | 0.31  | 0.32   | 0.50    | (preliminary results)
## Mobilization of Wastewater-Indicator Compounds From Biosolids Treated Sites - Simulated Rainfall

<table>
<thead>
<tr>
<th>Elapsed time following application</th>
<th>1 day</th>
<th>8 days</th>
<th>35 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average DEET Concentration ug/l</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainfall Simulation - Beginning</td>
<td>0.14</td>
<td>0.48</td>
<td>ND</td>
</tr>
<tr>
<td>Rainfall Simulation - Middle</td>
<td>0.10</td>
<td>0.59</td>
<td>ND</td>
</tr>
<tr>
<td>Rainfall Simulation - End</td>
<td>0.09</td>
<td>0.33</td>
<td>ND</td>
</tr>
</tbody>
</table>

(preliminary results)
Future Directions in Method Development

- Collaborate with ecosystem-focused studies
- Ecological biomagnification / metabolism studies
- Data Mining / Automation
- Direct Aqueous Injection

**LC/MS/MS**
- Pharmaceuticals
- HPV Compounds
- Pesticides
- Polar Indicators

**LC/ToF MS for TICs**