Emerging Concerns in Pesticides and Their Effects – Metabolites, Degradates and Impurities (PFAS)

Vicki S. Blazer, PhD
U.S. Geological Survey
Eastern Ecological Science Center – Leetown Research Laboratory
Long-Term Monitoring and Assessment Study
USGS, state agencies in PA, WV and MD

• 2013 – 2019 – integrated monitoring of surface water chemical concentrations, comprehensive fish health assessments of adult smallmouth bass in spring (pre-spawn) and fall (recrudescence) and health monitoring of young-of-year in early summer

• Surface water samples were collected monthly (twice a month in spring) and some storm flow samples

• Focused on agricultural land-use
  – Pesticides, hormones, phytoestrogens/sterols were routinely analyzed
  – Pharmaceuticals and waste-water associated chemicals more sporadically analyzed
  – Four sites – two in the Potomac and two in the Susquehanna River drainages
Biological Endpoints

• Adult Bass
  – Morphometric, age, condition factor
  – Documented visible abnormalities
  – Blood sample – vitellogenin, archived plasma samples
  – Tissue samples of all organs for pathology
  – Samples of liver and anterior kidney for gene expression
  – Anterior kidney for immune function
  – Tissue archived for chemical analyses

• Young of Year
  – Documented visible abnormalities
  – Fixed for pathology
Sites

- Evaluating data at both the immediate and upstream catchment scale
- Immediate hydrologic unit containing the sampling site while upstream is the immediate plus all upstream catchments
- Some chemicals may persist longer and so upstream might be important
- Some significant differences in landcover at the two scales
## Land-use Comparison – Upstream Catchment

<table>
<thead>
<tr>
<th>Site</th>
<th>Drainage area (km²)</th>
<th>Percent Agriculture</th>
<th>Percent Pasture</th>
<th>Percent Crop</th>
<th>Percent Forest</th>
<th>Percent Developed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antietam Creek</td>
<td>730</td>
<td>49</td>
<td>21</td>
<td>28</td>
<td>32</td>
<td>17</td>
</tr>
<tr>
<td>South Branch Potomac River</td>
<td>3,150</td>
<td>14</td>
<td>13</td>
<td>1</td>
<td>81</td>
<td>3</td>
</tr>
<tr>
<td>West Branch Mahantango Creek</td>
<td>218</td>
<td>32</td>
<td>12</td>
<td>20</td>
<td>60</td>
<td>7</td>
</tr>
<tr>
<td>Pine Creek</td>
<td>2,437</td>
<td>9</td>
<td>8</td>
<td>1</td>
<td>84</td>
<td>4</td>
</tr>
</tbody>
</table>
### Key Exposure Periods

<table>
<thead>
<tr>
<th>Period</th>
<th>Events</th>
<th>Images</th>
</tr>
</thead>
<tbody>
<tr>
<td>April – May</td>
<td>Nest/eggs – sediment/water, Final maturation, sperm quality</td>
<td>![Nest/eggs Image]  ![Final maturation Image]</td>
</tr>
<tr>
<td>Late May - June</td>
<td>Water, maternal, sediment, YOY – sexual differentiation and organ development</td>
<td>![Water, maternal, sediment Image]  ![YOY Image]</td>
</tr>
<tr>
<td>August – Dec</td>
<td>Water food, sediment, Adults - recrudescence</td>
<td>![Water food Image]  ![Adults Image]</td>
</tr>
</tbody>
</table>
# Pesticides Commonly Detected

<table>
<thead>
<tr>
<th>Site</th>
<th>Water Samples</th>
<th>Atrazine</th>
<th>Simazine</th>
<th>Metolachlor</th>
<th>Fipronil</th>
<th>Metalaxyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine</td>
<td>(43)</td>
<td>19(^b)</td>
<td>1 (0)</td>
<td>12 (1)</td>
<td>0 (0)</td>
<td>1 (0)</td>
</tr>
<tr>
<td>WB Mahantango</td>
<td>(47)</td>
<td>41 (17)</td>
<td>12 (1)</td>
<td>34 (9)</td>
<td>2 (0)</td>
<td>2 (0)</td>
</tr>
<tr>
<td>Antietam</td>
<td>(42)</td>
<td>41 (17)</td>
<td>36 (3)</td>
<td>39 (5)</td>
<td>11 (0)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>SB Potomac</td>
<td>(41)</td>
<td>18 (0)</td>
<td>3 (0)</td>
<td>10 (1)</td>
<td>0 (0)</td>
<td>1 (0)</td>
</tr>
</tbody>
</table>

\(^a\)Total number of water samples from 11/2014 through 7/2017  
\(^b\)Total detects  
\(^c\)Dectects above the 100 ng/L assessment threshold
2015 Atrazine (ng/L) Site Comparison

- Antietam
- SB Potomac
- WB Mahantango
- Pine

Jan  Feb  March  April  May  June  July  Aug  Sept  Oct  Nov  Dec

Values:
- Antietam: 670, 2930, 694, 890
- SB Potomac: 450
- WB Mahantango: 300
- Pine: 150, 50
Antietam Annual Variation in Herbicide Concentrations

2015-2017

- Atrazine: 670, 1820
- Simazine: 426, 1500
- Metolachlor: 346, 851

Legend:
- Atrazine
- Simazine
- Metolachlor

ND: Not Detected
Complexities in Determining Potential Effects of Pesticide Exposure to Aquatic Organisms

- Complex mixtures of the parent compounds – vary seasonally and annually
- Metabolites/degradates or transformation products of the parent compounds
- Perfluorinated compounds (PFAS)
  - Constituents
  - Contaminants from packaging etc.
Herbicide Metabolites/Transformation Products

- 2018-2019 a different analytical schedule was used which measured a number of metabolites

- Atrazine
  - Didealkyl atrazine
  - Deisopropyl atrazine
  - Deethylatrazine
  - Hydroxy atrazine
  - 2-Hydroxy atrazine

- Metolachlor
  - Dechlorometolachlor
  - Hydroxy metolachlor
  - Metolachlor oxanilic acid
  - Metolachlor ethanesulfonic acid
Antietam Atrazine/Didealkyl Atrazine Temporal Analysis 2018-2019

No data
<table>
<thead>
<tr>
<th>Date</th>
<th>Antietam Atrazine</th>
<th>Antietam Didealkyl atrazine</th>
<th>WB Mahantango Atrazine</th>
<th>WB Mahantango Didealkyl atrazine</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/13/2018</td>
<td>14.2</td>
<td>541</td>
<td>5.88</td>
<td>16.3</td>
</tr>
<tr>
<td>4/2/2018</td>
<td>10.6</td>
<td>509</td>
<td>5.98</td>
<td>BD</td>
</tr>
<tr>
<td>4/16/2018</td>
<td>12.8</td>
<td>333</td>
<td>12.4</td>
<td>311</td>
</tr>
<tr>
<td>5/8/2018</td>
<td>174</td>
<td>431</td>
<td>176</td>
<td>BD</td>
</tr>
<tr>
<td>5/21/2018</td>
<td>172</td>
<td>354</td>
<td>183</td>
<td>BD</td>
</tr>
<tr>
<td>6/4/2018</td>
<td>250</td>
<td>547</td>
<td>52.5</td>
<td>53.4</td>
</tr>
<tr>
<td>7/9/2018</td>
<td>62.7</td>
<td>850</td>
<td>86.5</td>
<td>BD</td>
</tr>
<tr>
<td>8/14/2018</td>
<td>29.9</td>
<td>585</td>
<td>44.2</td>
<td>62.6</td>
</tr>
<tr>
<td>9/5/2018</td>
<td>26.9</td>
<td>647</td>
<td>33.5</td>
<td>36.6</td>
</tr>
<tr>
<td>10/9/2018</td>
<td>17.5</td>
<td>507</td>
<td>12.3</td>
<td>26.1</td>
</tr>
</tbody>
</table>

These data are preliminary and provisional and have not received final approval of the U.S. Geological Survey (USGS). Neither USGS or the US Federal Government shall be held liable for any damage resulting from authorized or unauthorized use of the data.
Antietam Metolachlor/Metolachlor ESA Temporal Analysis 2018-2019

- Metolachlor
- Metolachlor ESA

No Data
<table>
<thead>
<tr>
<th>Date</th>
<th>Antietam Metolachlor</th>
<th>Antietam Metolachlor ESA</th>
<th>WB Mahantango Metolachlor</th>
<th>WB Mahantango Metolachlor ESA</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/20/2018</td>
<td>10.4</td>
<td>159</td>
<td>8.3</td>
<td>754</td>
</tr>
<tr>
<td>3/13/2018</td>
<td>12.9</td>
<td>220</td>
<td>3.9</td>
<td>472</td>
</tr>
<tr>
<td>4/2/2018</td>
<td>9.6</td>
<td>139</td>
<td>3.2</td>
<td>423</td>
</tr>
<tr>
<td>4/16/2018</td>
<td>18.3</td>
<td>197</td>
<td>18</td>
<td>232</td>
</tr>
<tr>
<td>5/8/2018</td>
<td>92.3</td>
<td>228</td>
<td>13.5</td>
<td>330</td>
</tr>
<tr>
<td>5/21/2018</td>
<td>84.6</td>
<td>207</td>
<td>180</td>
<td>592</td>
</tr>
<tr>
<td>6/4/2018</td>
<td>132</td>
<td>275</td>
<td>27</td>
<td>459</td>
</tr>
<tr>
<td>7/9/2018</td>
<td>39.1</td>
<td>317</td>
<td>22.1</td>
<td>421</td>
</tr>
<tr>
<td>8/14/2018</td>
<td>28.4</td>
<td>304</td>
<td>19.4</td>
<td>1080</td>
</tr>
<tr>
<td>9/5/2018</td>
<td>21.5</td>
<td>382</td>
<td>7.5</td>
<td>529</td>
</tr>
<tr>
<td>10/9/2018</td>
<td>22.2</td>
<td>452</td>
<td>5.3</td>
<td>796</td>
</tr>
<tr>
<td>11/14/2018</td>
<td>17.4</td>
<td>296</td>
<td>10.4</td>
<td>611</td>
</tr>
</tbody>
</table>

These data are preliminary and provisional and have not received final approval of the U.S. Geological Survey (USGS). Neither USGS or the US Federal Government shall be held liable for any damage resulting from authorized or unauthorized use of the data.
Take-Aways to Date

• We need a better understanding of effects of exposure to mixtures of various pesticides at key developmental periods

• Need to understand the environmental factors that regulate the breakdown/transformation of the parent compounds

• Need more information on the effects of pesticide metabolites or transformation products
Preliminary Analyses of Perfluoroalkyl Chemicals in Plasma

- Used the 2018 archived plasma samples
- 13 PFAS including 9 perfluorocarboxylic acids and 4 perfluorosulfonates
- Analyzed by SGS-AXYS, Sidney, British Columbia by LC-MS/MS
- Concentrations in ng/ml plasma
Compounds Detected in Smallmouth Bass Plasma

• Four compounds were detected in every plasma sample
  - PFOS (perfluorooctane sulfonate) – 8 carbon sulfonate
    - Ranged from 20 – 574 ng/ml
  - PFUnA (perfluoroundecanoate) – 11 carbon carboxylic acid
    - Ranged from 3 – 55 ng/ml
  - PFDA (perfluorodecanoate) – 10 carbon carboxylic acid
    - Ranged from 2 – 37 ng/ml
  - PFDoA (perfluorododecanoate) – 12 carbon carboxylic acid
    - Ranged from 1 – 34 ng/ml

• Two additional compounds were detected in some samples
  - PFOSA (perfluorooctane sulfamide) – 8 carbon sulfonate
    - Ranged from BD – 1.7 ng/ml
  - PFNA (perfluorononanoic acid) – 9 carbon carboxylic acid
    - Ranged from BD – 1.3 ng/ml
Significant Site Differences

PFOS concentrations were significantly higher than other compounds and all four sites were significantly different.

Other three compounds showed the same pattern but South Branch, Potomac and Pine Creek were not significantly different.
Temporal Comparisons

Antietam Annual

<table>
<thead>
<tr>
<th>Year</th>
<th>PFOS</th>
<th>Total PFAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>2017</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2018</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2019</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Comparison with Other Studies

• Difficult to compare to many other studies as most analyze PFAS in muscle (fillets) or liver
  – Most species studied find plasma/blood > liver > muscle
  – For studies worldwide that have analyzed blood/plasma our results at Antietam are some of the highest.
  – Striped bass from Cape Fear downstream of a PFAS production plant were higher
    – Highest concentration in Antietam smallmouth was 585 ng/ml PFOS
    – Highest concentration in Cape Fear striped bass was 977 ng/ml PFOS
Conclusions

Pesticides, PFAS and Fish Health

• PFAS concentrations likely to have adverse effects are detected at some sites within the Chesapeake Bay watershed

• While pesticide application may be a source, there are many other sources
  - Wastewater treatment effluent – domestic and industrial
  - Runoff/groundwater contamination from military facilities, airports etc.
  - Landfill leachate
  - Biosolid applications

• Need much more research on sources to determine if pesticides are a major contributor
  - Current analytical schedule measures >40 PFAS compounds rather than 13

• We have seen correlations with various biological responses in smallmouth bass, including endocrine and immune endpoints. Need to use the concentrations measured to evaluate effects of environmentally-relevant exposures in the lab – for both various PFAS and pesticide transformation products
Acknowledgements

Funded by USGS Ecosystem Mission Area’s Environmental Health, Species Management (Fisheries) and Land Management (Chesapeake Bay) Programs.

We thank the many state biologists in PA Fish & Boat Commission, PA Department of Environmental Protection, Maryland Department of Natural Resources and West Virginia Division of Natural Resources and numerous students who assisted with fish necropsies.