Analytical chemical measurements to improve nonpoint pollution assessments in Indiana’s Lake Michigan Watershed: designing a strategic plan to improve water quality

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July sunset from Chesterton, Indiana
Point Sources and Nonpoint Sources of Pollutants Have Negative Impacts on Northwest Indiana

Social, Health, Ecological and Economic Impacts
Nonpoint Pollution

“Nonpoint Source Pollution: pollution that occurs when rainfall, snowmelt, or irrigation runs over land or through the ground, picks up pollutants, and deposits them into rivers, lakes, and coastal waters or introduces them into ground water.”
http://www.epa.gov/waterscience/biocriteria/glossary.html

Typical Nonpoint Pollution Sources:
✓ Urbanization (altered drainage, soil erosion, stormwater, fertilizers etc.)
✓ Agriculture
✓ Atmospheric deposition
✓ Leaking septic systems

“It’s pollution that can come from our construction sites, our parking lots, our farms, our roads, and even our own backyards.”
http://www.in.gov/idem/nps/
Urban nonpoint pollution

• Nationally, the first comprehensive effort to characterize the quality of urban runoff did not take place until the conception of the Nationwide Urban Runoff Program (NURP), US EPA, 1983

• Simultaneously, municipalities incorporated Best Management Practices (BMPs) to improve water quality.

• To control sources of urban pollutants:
  – Reduce air pollution
  – Institute manageable size watershed planning
  – Improve BMP
  – Improve infrastructure and planning
  – Stress RESEARCH to better characterize pollution sources and to reduce pollutant loads

*Nonpoint Sources of Pollution to the Great Lakes Basin; Based on the Findings of a Workshop to Assess the Status of Nonpoint Source Pollution Control in the Great Lakes Basin, Toledo, Ohio, September 16-18, 1998; February 2000; ISBN 1-894280-14-8*
Salt Creek Watershed Management Plan

In 2006, Save the Dunes Conservation Fund (SDCF) received funds from the Indiana Department of Environmental Management (IDEM) to “coordinate the development of a watershed management plan for the Salt Creek watershed.”


- Goal 1: Reduce nitrate by 65%, phosphorus by 66%, and sediment loading 33% by 2028.
- Goal 2: Reduce pathogen (*E. coli*) concentrations by 86% by 2028.
- Goal 3: Improve stakeholder and public involvement.
- Goal 4: Improve biotic communities so that the density and diversity of EPT taxa improves by one scoring metric level.”

http://www.savedunes.org/water_program/water_program/Salt%20Creek/Salt%20Creek%20_files/SCWMP_6_17_08_2.pdf
Salt Creek → Little Calumet River → Burns Ditch → Lake Michigan

Southern Lake Michigan beaches

Burns Ditch

Little Calumet East and West Sampling sites – both merge to Burns Ditch (confluence)
How can analytical science assist in the challenges of nonpoint pollution?
**INTEGRATED APPROACH**

**Local Watershed Management Groups**

**Goal:** to work with communities to:
- **Document** current water quality and biological integrity to address nonpoint sources of pollution
- Make **recommendations** for the improvement of water quality
- Conduct **public outreach** and education

**Monitoring:** conductivity, DO, DO% saturation, *E. coli*, nitrate-nitrogen, pH, temperature, turbidity, and flow at a minimum of six sites during six events in 2010 and six events in 2011.

Better Identify & Mitigate Specific Causes & Behaviors Leading to Impairment

**Research Including an Analytical Chemistry Approach**

**Goal:**
- Use a strategic sampling design to identify chemical markers that can be attributed to specific activities occurring at points within the watershed all year.

**Monitoring:**
- Fluorescent Whitening Agents (FWAs) associated with household wastewater.
- Specific ions (e.g. Cl⁻ from road salt).
- Pesticides
- Total Suspended Solids
Salt Creek Watershed

Land Use Map

Major interstate highways

Little Calumet River

South end of Salt Creek


Bacteria sources: wildlife, pets, livestock, malfunctioning or poorly located septic systems, sewer overflows (10 permitted wastewater plants in the watershed), sewage by-passes

http://www.savedunes.org/water_program/water_program/Salt%20Creek/Salt%20Creek%20_files/SCWMP_6_17_08_2.pdf
Salt Creek Watershed Management Plan
sampling sites

Five selected sites for water Collections/analytical measurements:
1, 4, 5, 12, 13
SITE 1
- Outfall/effluent from affluent community
- Mostly residential
- Lake within the larger community

Analytical markers: FWAs, pesticides, nutrient ratio
SITE 5

- Large number of septic systems
- High wetland density
- Highway department storage of road salts
- Misc water outfall pipes

Analytical markers: FWAs, Cl⁻,
SITE 12
• History of high conductivity (road salts, farms?)
• Many outfall pipes
• Few feet from road

Analytical markers: Cl⁻, other ions
SITE 13
- Major construction underway for a new hospital
- Mix of factors (residential, agricultural; currently, massive changes in landscape)

Analytical markers: FWAs, pesticides, ions, suspended solids
Analytical targets and tests

- Cl⁻ and other ions
- FWAs, pesticides, ions, suspended solids
- FWAs, pesticides
- Pesticides, nitrates, phosphates, suspended solids
- FWAs, Cl⁻
FWAs and SOLID PHASE EXTRACTION

- Solid phase extraction allows for the concentration of the FWAs
- A C18 bonded phase SPE disk is equilibrated by passing a small amount of MeOH and a small amount of water through
- One (or two) liter volumes of the filtered water samples are concentrated and collected in the disk and extracted using 10 mL of methanol
- Analysis with HPLC/ Fluorescence detection

- None detected in sampling sites, but presence is high in effluent water of sewage treatment plants
- Method works very well.
- Extraction discs recover 90-100% in standardized samples.

The FWA chosen for this study was distyrylbiphenyl (DSBP), commercially known as Tinopal CBS-X.
The Fish Tank Experiment

- 7.0L of stream water were collected and added to a 10 gallon fish tank.
- 2” of sand/mud from the stream bed was added to the fish tank and it was completely covered in tin foil and kept out of light.
- After a sample was extracted for a background, the fish tank was spiked with FWA to a concentration of 7ppm.

Results from Fish Tank:
- After only one hour, the concentration had decreased to 0.46ppm.
- After one day, the detectable limit of FWAs had disappeared.
- Next move: If the FWAs are adsorbing to the suspended solids or mud, can we extract them?
Fish Tank Results

Fish Tank

<table>
<thead>
<tr>
<th>Time</th>
<th>Concentration (PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>7</td>
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<tr>
<td>1 hr.</td>
<td>0.5</td>
</tr>
<tr>
<td>1 day</td>
<td>0.1</td>
</tr>
<tr>
<td>2 day</td>
<td>0.1</td>
</tr>
<tr>
<td>5 day</td>
<td>0.0</td>
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</tbody>
</table>
Water filtrations and Ion Chromatography/ TOC

<table>
<thead>
<tr>
<th>Site</th>
<th>week</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>62.02</td>
<td>29.76</td>
<td>62.67</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>60.94</td>
<td>12.87</td>
<td>69.32</td>
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<tr>
<td>1</td>
<td>3</td>
<td>49.15</td>
<td>18.08</td>
<td>70.85</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>58.42</td>
<td>24.14</td>
<td>67.77</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>57.03</td>
<td>32.39</td>
<td>69.49</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>58.51</td>
<td>25.15</td>
<td>71.51</td>
</tr>
<tr>
<td>1</td>
<td>7</td>
<td>51.11</td>
<td>18.39</td>
<td>71.28</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>55.57</td>
<td>25.14</td>
<td>71.64</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>85.17</td>
<td>25.39</td>
<td>72.17</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>62.70</td>
<td>21.59</td>
<td>77.45</td>
</tr>
<tr>
<td>1</td>
<td>11</td>
<td>119.08</td>
<td>32.28</td>
<td>69.69</td>
</tr>
<tr>
<td>1</td>
<td>12</td>
<td>82.80</td>
<td>15.84</td>
<td>71.89</td>
</tr>
<tr>
<td>1</td>
<td>13</td>
<td>47.10</td>
<td>10.02</td>
<td>61.73</td>
</tr>
<tr>
<td>1</td>
<td>14</td>
<td>55.53</td>
<td>16.55</td>
<td>77.31</td>
</tr>
</tbody>
</table>

All values are in ppm (mg/L)

TOC = Total organic carbon
Chloride Ion concentrations and LOAD (kg/day)

## TSS and Weather

<table>
<thead>
<tr>
<th>Week</th>
<th>Date</th>
<th>Weather</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9/10/10</td>
<td>Bright and Sunny, Very little rain past week</td>
</tr>
<tr>
<td>2</td>
<td>9/17/10</td>
<td>Sunny with little Rain, low 70's</td>
</tr>
<tr>
<td>3</td>
<td>9/24/10</td>
<td>Rain in the Morning, cloudy and windy</td>
</tr>
<tr>
<td>4</td>
<td>10/8/10</td>
<td>Breezy, party cloudy</td>
</tr>
<tr>
<td>5</td>
<td>10/15/10</td>
<td>Overcast to Sunny, high 50's</td>
</tr>
<tr>
<td>6</td>
<td>10/22/10</td>
<td>Sunny, no precipitation last week, high 50s</td>
</tr>
<tr>
<td>7</td>
<td>11/5/10</td>
<td>Precipitation day before, flurries/sleet, upper 30s</td>
</tr>
<tr>
<td>8</td>
<td>11/19/10</td>
<td>Cold and Windy, no precipitation</td>
</tr>
<tr>
<td>9</td>
<td>12/10/10</td>
<td>1-2&quot; snow, ice over most sites, Cold and Sunny</td>
</tr>
<tr>
<td>10</td>
<td>2/11/11</td>
<td>Over 1' snow in areas, freezing</td>
</tr>
<tr>
<td>11</td>
<td>2/15/11</td>
<td>TONS OF SNOW MELTING! Warm</td>
</tr>
<tr>
<td>12</td>
<td>2/18/11</td>
<td>Most snow melted, cold</td>
</tr>
<tr>
<td>13</td>
<td>3/4/11</td>
<td>about 0.5&quot; rain, high 50s</td>
</tr>
<tr>
<td>14</td>
<td>4/1/11</td>
<td>0.10&quot; rain/sleet in early morning, 40s</td>
</tr>
</tbody>
</table>

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Conclusions

• Watershed Management Plans are valuable in a variety of ways.
• More in-depth scientific investigations offer additional information and knowledge for identifying and tackling nonpoint source pollution.
• Nonpoint source pollutants are problematic all year around, and often to a greater degree in winter months.
• Integration of watershed management with research science is a valuable approach to addressing nonpoint source pollution problems.
Special thanks to:

- IU Northwest Undergraduate Research Students: JJ Cox and Nicole Graber
- NSF’s LSAMP student research funding and the IUN undergraduate research fund
- Save the Dunes and Jennifer Birchfield