The Integrated Atmospheric Deposition Network

Great Lakes Binational Toxics Strategy (GLBTS)
B(a)P / HCB Workgroup Meeting
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Great Lakes National Program Office
U.S. Environmental Protection Agency
Acknowledgements

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- Binational IADN Steering Committee
- Tom Dann of Environment Canada for NAPS data
- And of course Melissa Hulting
Integrated Atmospheric Deposition Network (IADN)

- Joint EPA-Environment Canada project
  - Grantee is Ron Hites at Indiana University
- In operation since 1990 (GLWQA and CAAA of 1990)
- Measure PBTs in air and precipitation at 15 sites around the Great Lakes (U.S. runs five)
- Goals:
  - Determine atmospheric loadings
  - Look at trends in concentrations
  - Use data to measure progress
The NAPS program is a cooperative federal-provincial-territorial network of over 800 ambient air quality monitoring instruments across Canada, mostly in urban centres.

Substances measured:
- PAH
- PCDD/PCDF
- Hexachlorobenzene (HCB)
- Pentachlorophenol (PCP)
- Octachlorostyrene (OCS)
- Nitro-PAH - C13 to C22, 24 species including dinitropyrenes
- Dioxin like PCBs
- Metals - Hg, Cd, Pb
- VOC - 1,4-dichlorobenzene

http://www.etc-cte.ec.gc.ca/NAPS/
Why air?

- Primary pathway for input to the Lakes
- Air concentrations respond rapidly to changes in emissions
Annual Variation in Hexachlorobenzene Concentrations (ng/ m³) at Ontario Sites (1997-2006)
Hexachlorobenzene

Vapor-phase conc. (pg/m³)

Particle-phase conc. (pg/m³)

Precip. conc. (pg/L)

Half-lives (years)

Max to min ratios

Maximum dates

Particle-phase conc.: not measured
Half-Lives for gas-phase HCB are decreasing......

Most likely, increases in HCB in the late 1990s/early 2000s lengthened half-lives calculated previously.

<table>
<thead>
<tr>
<th></th>
<th>2001</th>
<th>2002</th>
<th>2003</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eagle Harbor (Superior)</td>
<td>29</td>
<td>23.7</td>
<td>18</td>
</tr>
<tr>
<td>S.B. Dunes (Michigan)</td>
<td>15</td>
<td>15.7</td>
<td>12</td>
</tr>
<tr>
<td>Sturgeon Pt. (Erie)</td>
<td>18</td>
<td>17.1</td>
<td>15</td>
</tr>
<tr>
<td>IIT (Chicago)</td>
<td>19.4</td>
<td>8.3</td>
<td></td>
</tr>
</tbody>
</table>

Data through 2003

Buehler et al. 2004
Sun et al. 2006
Benzo(a)pyrene
Urban PAH levels are 10-100x higher in Chicago than in rural areas.
Rural BaP concentrations are about 10x lower than urban.

Benzo(a)pyrene Concentrations (ng/m³) 2005-2006
(Mean, 10th and 90th percentiles)
PAHs and PCBs are now largely an urban problem.

The graph shows a linear relationship between the population within a 25 km radius and the concentration of PAHs or PCBs in the air. The correlation coefficients are $r^2 = 0.907$ for PAHs and $r^2 = 0.877$ for PCBs.

Key locations marked on the graph include:
- BI
- EH
- BR
- SBD & PP
- SP
- Chi
PAHs in precipitation are generally decreasing at Chicago.

<table>
<thead>
<tr>
<th>Location</th>
<th>Phenanthrene</th>
<th>Pyrene</th>
<th>Retene</th>
<th>Benz[a]pyrene</th>
<th>Total PAH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brule River</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eagle Harbor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chicago</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Sleeping Bear</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Dunes</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Sturgeon Point</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Burnt Island</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point Petre</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

- Phenanthrene: 10^1 to 10^4 ng/L
- Pyrene: 10^1 to 10^4 ng/L
- Retene: 10^1 to 10^4 ng/L
- Benz[a]pyrene: 10^1 to 10^4 ng/L
- Total PAH: 10^1 to 10^4 ng/L

Chart shows monthly PAH concentrations from 1998 to 2004 with a trend line indicating decreasing concentrations.
Some evidence of decreasing BaP concentrations on particles..... but are levels increasing at Sleeping Bear Dunes?

<table>
<thead>
<tr>
<th>Site</th>
<th>Precipitation</th>
<th>Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eagle Harbor (Superior)</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>S.B. Dunes (Michigan)</td>
<td>ns</td>
<td>-11 (ms)</td>
</tr>
<tr>
<td>Burnt Island (Huron)</td>
<td>ns</td>
<td>11 (ms)</td>
</tr>
<tr>
<td>Sturgeon Pt. (Erie)</td>
<td>ns</td>
<td>4.8</td>
</tr>
<tr>
<td>Pt. Petre (Ontario)</td>
<td>ns</td>
<td>11 (ms)</td>
</tr>
<tr>
<td>IIT-Chicago</td>
<td>2.4</td>
<td>9.6 (ms)</td>
</tr>
</tbody>
</table>

But decreases in low MW PAHs at Cdn sites

BaP half-lives for data through 2003
Seasonal Variation of B(a)P (ng/m³) at Ontario Sites (1996-2006)
Trend in Benzo(a)pyrene Concentrations (ng/m³) (1990-2006)

NAPS sites - Small or no decrease

- Montreal - Ontario St.
- Montreal - Riviere
- Toronto - Junction
- Toronto - Evans/Judson
- Hamilton
- Windsor
- Winnipeg
- Edmonton

Trend in Benzo(a)pyrene Concentrations (ng/m³) (1990-2006)
Possible decrease in mean in major source areas?

Benzo(a)pyrene Concentrations (ng/m³) at Jonquière
Urban Impact for benzo(a)pyrene and other PAHs Significant: Chicago load increases Lake Michigan load by about 50%

Dry Deposition of BaP to the Great Lakes

- L Superior
- L Michigan
- Chicago
- L Huron
- L Erie
- Cleveland
- L Ontario
Conclusions: HCB

- Levels are decreasing slowly again after increases in the late 90s
- Little spatial variation in concentrations
Conclusions: BaP/PAHs

- **Rural sites:**
  - In general, no trend over time for BaP and other PAHs in precipitation, except:
  - Decreases in low MW PAHs in precip seen only at Canadian IADN sites
  - Some evidence of decreases in the particle phase, except possible increase at Sleeping Bear Dunes (L Michigan)

- **Chicago**
  - PAHs in precipitation at Chicago are decreasing with a half-life of 2-5 years (2.4 years for BaP)
  - Half-life for BaP on particles is 9.6 years (marginally significant)

- **Source reductions may be having an impact in urban/source areas**

- **Retene increasing at Brule River, Eagle Harbor and Sleeping Bear Dunes (due to wood burning?)**
IADN Resources

- Main website: Station and other info, data request
- U.S. IADN Information Page: Links to reports, Resource Page with SOPs, etc.
  - http://www.epa.gov/glnpo/monitoring/air_new_design/idadn_info.html
- U.S. IADN Government Reporting Indicator Page
  - http://www.epa.gov/glnpo/glindicators/air/airb.html
- Todd Nettesheim (EPA), Liisa Jantunen (EC)
Thank You!

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