Occurrence and Concentrations of PBDEs in Minnesota Environment

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• Scientists and regulatory agencies have raised concerns about the presence of PBDEs in the environment as an emerging contaminants.

• During the past decade, nearly every monitoring program indicated sharp increases of the levels of PBDEs in the biotic and abiotic matrices of the environment.

• In contrast to other persistent organic pollutants (PCBs, dioxins, DDT), PBDEs levels have increased since late 1970s.
Environmental studies in Europe, Japan, and North America indicate that PBDEs are ubiquitous in the environment.

The threat to the environment and ecosystem health is due to the long term transport, environmental persistent, bioaccumulative potential, and possible reproductive and toxicity effects.
Environmental Concerns

- Chemically Similar to PCBs and Dioxins
  - Accumulate in aquatic and terrestrial ecosystems
  - Cross boundaries between environmental media
  - Toxicity

- Unlike PCBs, PBDEs are manufactured and used in increasing quantities

- Potential to form Br- dioxins & Br- furans under incineration

- No laws, no regulations, no environmental criteria /standards in US
Objectives

- Conduct a low-cost, focused survey to determine whether PBDEs are present in biotic and abiotic matrices in the Minnesota Environment.
  - Landfill Leachates and sludge of leachates
  - Waste Water Treatment Plant Sludge
  - Fish and sediment collected from rivers below WWTP effluent discharges
Polybrominated Diphenyl Ethers

2,2',4,4'-tetrabromodiphenyl ether (BDE-47)
Properties of PBDEs

- Persistence, with $t_{1/2}$ in
  - atmosphere $>2$ days;
  - water $>2$ mos;
  - soil & sediment $>6$ mos

- Bioaccumulation
  - BCF $>5000$, High $\log K_{ow} > 5$
  - Lower congeners are more bioaccumulative

- Low solubility ($<1\mu g/kg$)
  - strong adsorption to soil, sediment, sludge
<table>
<thead>
<tr>
<th>Type</th>
<th>Congeners</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Congener: 209 possible configurations of the number and position of bromines on the two phenyl rings</td>
</tr>
<tr>
<td></td>
<td>Homologue: Nine sets of congeners having the same number of bromines (1 to 10 Br)</td>
</tr>
<tr>
<td>Mono-</td>
<td>BDE-15</td>
</tr>
<tr>
<td>Di-</td>
<td>BDE-15</td>
</tr>
<tr>
<td>Tri-</td>
<td>BDE-28 + 33</td>
</tr>
<tr>
<td>Tetra-</td>
<td>BDE-49, BDE-75</td>
</tr>
<tr>
<td>Penta-</td>
<td>BDE-85, BDE-99, BDE-100, BDE-126</td>
</tr>
<tr>
<td>Hexa-</td>
<td>BDE-153, BDE-154</td>
</tr>
<tr>
<td>Hepta-</td>
<td>BDE-190</td>
</tr>
<tr>
<td>Nona-</td>
<td>BDE-206, BDE-207, BDE-208</td>
</tr>
<tr>
<td>Deca-</td>
<td>BDE-190</td>
</tr>
</tbody>
</table>
## Predominant PBDE Congeners

<table>
<thead>
<tr>
<th>PBDE Number</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>2, 2’, 4, 4’-tetraBDE</td>
</tr>
<tr>
<td>77</td>
<td>3, 3’, 4, 4’-tetraBDE</td>
</tr>
<tr>
<td>99</td>
<td>2, 2’, 4, 4’, 5-pentaBDE</td>
</tr>
<tr>
<td>100</td>
<td>2, 2’, 4, 4’, 6-pentaBDE</td>
</tr>
<tr>
<td>126</td>
<td>3, 3’, 4, 4’, 5-pentaBDE</td>
</tr>
<tr>
<td>153</td>
<td>2, 2’, 4, 4’, 5, 5’-hexaBDE</td>
</tr>
<tr>
<td>154</td>
<td>2, 2’, 4, 4’, 5, 6’-hexaBDE</td>
</tr>
<tr>
<td>183</td>
<td>2, 2’, 3, 4, 4’, 5’, 6-hepaBDE</td>
</tr>
<tr>
<td>209</td>
<td>2, 2’, 3, 3’, 4, 4’, 5, 5’, 6, 6’-DecaBDE</td>
</tr>
</tbody>
</table>
Commercial PBDEs Products

Graph showing the percentage of different congeners in commercial PBDE products:
- DeBDE
- OcBDE
- PeBDE

Legend:
- Green: Tetra
- Red: Penta
- Blue: Hexa
- Yellow: Hepta
- Magenta: Octa
- White: Nona
- Orange: Deca
Toxicity of Commercial PBDEs

- PeBDE >> OBDE > DBDE
- DBDE & OBDE
  - May be low risk to biological receptors
  - Concerns
    - Presence of lower brominated congeners in OBDE
    - Photolytic and/or anaerobic debromination
    - Formation of PBDDs/PBDFs
A unique PBDE database for five important matrices including potential sources & receptors.

Establish benchmarks to guide future monitoring efforts & to track environmental trends.
The Sampling was focused on areas most likely to be impacted by PBDEs.

To ensure geographical representation, fish and sediment samples were collected from six major river basins in MN below WWTP:

- Mississippi River
- St. Croix River
- St. Louis River
- Red River
- Minnesota River
- Rainy River
# Sampling Waste Stream

<table>
<thead>
<tr>
<th>Waste Stream</th>
<th>Matrix</th>
<th>(n)</th>
<th>%Organic Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sanitary Landfills</td>
<td>Leachate</td>
<td>(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sludge</td>
<td>(1)</td>
<td>TOC = &lt; 1%</td>
</tr>
<tr>
<td>Industrial Landfill</td>
<td>Leachate</td>
<td>(1)</td>
<td>TOC = &lt; 1%</td>
</tr>
<tr>
<td></td>
<td>Sludge</td>
<td>(1)</td>
<td>TOC = &lt; 1%</td>
</tr>
<tr>
<td>Demolition Landfill</td>
<td>Leachate</td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>Municipal WWTPs</td>
<td>Sludge</td>
<td>(4)</td>
<td>TOC = 32 - 40%</td>
</tr>
</tbody>
</table>
### Sampling Ambient Environment

<table>
<thead>
<tr>
<th>Major River Basins</th>
<th>Matrix</th>
<th>Lipid &amp; TOC (%)</th>
<th>Fish Length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mississippi, Twin Cities</td>
<td>Carp*</td>
<td>6</td>
<td>593</td>
</tr>
<tr>
<td></td>
<td>Sediment**</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>St. Croix, Stillwater, MN</td>
<td>Carp</td>
<td>10</td>
<td>568</td>
</tr>
<tr>
<td></td>
<td>Sediment</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Minnesota, Mankato, MN</td>
<td>Carp</td>
<td>12</td>
<td>554</td>
</tr>
<tr>
<td></td>
<td>Sediment</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>St. Louis, Duluth, MN</td>
<td>Carp</td>
<td>7</td>
<td>685</td>
</tr>
<tr>
<td></td>
<td>Sediment</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Red, Moorhead, MN</td>
<td>Carp</td>
<td>13</td>
<td>566</td>
</tr>
<tr>
<td></td>
<td>Sediment</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Rainy, International Falls, MN</td>
<td>Red horse</td>
<td>10</td>
<td>558</td>
</tr>
<tr>
<td></td>
<td>Sediment</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

* All fish samples are whole-tissue composites of 3 fish.
** All sediment samples are composite of the upper 5 cm of sediment.
Sampling Strategy

- Waste Stream
  - 5 Landfills
    - Leachates
  - 2 WWTP
    - Primary SLudge
    - Final Sludge
- Ambient Environment
  - Six Major River Basins
    - Fish
    - Sediment
Metropolitan WWTP (MCES)

- Located on ↑ St. Paul, Minnesota
- Type ↑ Advanced secondary with chlorination
- Capacity ↑ 250 million gallons per day
- Discharges to ↑ Mississippi River
- From ↑ 63 communities and 800 industries
- Population served ↑ 1.8 million
- Interceptors to plant ↑ 332 miles
Located on Lake Superior Basin, in Duluth, Minnesota

Type: Advanced secondary with chlorination

Capacity: 43 million gallons per day

Discharges to St. Louis Bay

From 11 communities and 14 industries

Interceptors to plant 50 miles
Municipal Sewage Sludge (Biosolids) Management in Minnesota

MN Production: 180,000 ton/year dry weight

- Incinerated: 57%
- Recycled: 26%
- Landfilled: 17%
Samples of sediment, sludge, and leachates were placed in a solvent rinsed dark glass container, and then stored in -20°C.

Fish samples were wrapped in a solvent rinsed aluminum foil and stored in -4°C.

All samples were sent for PBDEs analysis to AXYS Analytical Services.
Extraction and clean up for filters was the same as EPA method 1668A for PCB congeners.

Filtered samples were spiked with nine $^{13}$C$_{12}$ labeled internal standards.

Solvent extracted and cleaned with liquid chromatography, and further analyzed by high resolution GC/HRMS.

The method was calibrated with a set of 19 PBDE congeners (mono- to deca-BDEs) based on Cambridge Isotope Labs (CIL) analytical standards.

PBDEs were quantified by isotope dilution internal standard against $^{13}$C$_{12}$ labeled compounds and individual response factors were determined for each reported congener.
**Similar to predominant PBDE Congeners**

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<tr>
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<tr>
<td>209</td>
<td>2, 2’, 3, 3’, 4, 4’, 5, 5’, 6, 6’-DecaBDE</td>
</tr>
</tbody>
</table>
Calibration standard of 19 PBDE congeners (mono to hepta), allows for identification & quantification of 41 congeners. Standards prepared by Cambridge Isotope Labs (CIL)

<table>
<thead>
<tr>
<th>PBDEs IUPAC #</th>
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</tr>
</thead>
<tbody>
<tr>
<td>1. MonoBDE</td>
<td>10. PentaBDE</td>
</tr>
<tr>
<td># 2</td>
<td># 85</td>
</tr>
<tr>
<td>2. DiBDE</td>
<td>11. PentaBDE</td>
</tr>
<tr>
<td># 8</td>
<td># 99</td>
</tr>
<tr>
<td>3. DiBDE</td>
<td>12. PentaBDE</td>
</tr>
<tr>
<td># 11</td>
<td># 100</td>
</tr>
<tr>
<td>4. TriBDE</td>
<td>13. HexaBDE</td>
</tr>
<tr>
<td># 17</td>
<td># 138</td>
</tr>
<tr>
<td>5. TriBDE</td>
<td>14. HexaBDE</td>
</tr>
<tr>
<td># 28</td>
<td># 153</td>
</tr>
<tr>
<td>6. TriBDE</td>
<td>15. HexaBDE</td>
</tr>
<tr>
<td># 33</td>
<td># 154</td>
</tr>
<tr>
<td>7. TetraBDE</td>
<td>16. HexaBDE</td>
</tr>
<tr>
<td># 47</td>
<td># 166</td>
</tr>
<tr>
<td>8. TetraBDE</td>
<td>17. HeptaBDE</td>
</tr>
<tr>
<td># 66</td>
<td># 183</td>
</tr>
<tr>
<td># 75</td>
<td># 190</td>
</tr>
<tr>
<td>19. DecaDBE</td>
<td></td>
</tr>
<tr>
<td># 209</td>
<td></td>
</tr>
</tbody>
</table>
Dominant PBDE Congeners in Fish from major Rivers in Minnesota

- Red
- Mississippi
- St. Criox
- St. Louis
- Minnesota
- Rainy

Graph shows ng/g Lipid levels for different rivers with different congeners indicated by colors (28+33, 47, 49, 100, 154).
Total PBDEs in Sediment from Major Rivers in Minnesota

- **St. Louis**: 900 ng/g TOC, 100 ng/g dw
- **Mississippi**: 600 ng/g TOC, 100 ng/g dw
- **St. Croix**: 300 ng/g TOC, 100 ng/g dw
- **Minnesota**: 200 ng/g TOC, 100 ng/g dw
- **Rainy**: 150 ng/g TOC, 100 ng/g dw
- **Red**: 100 ng/g TOC, 100 ng/g dw
Dominant PBDE Homologues in Sediment Samples
Total PBDEs in Wast water Treatment Plants

- WLSSD
- MCES

ng/g dry weight

- Raw Sludge
- Final Sludge
Total PBDEs in WWTP

- **Total PBDEs (ng/g dry weight)**
- **Total PBDEs (ng/g TOC)**

Y-axis: ng/g

- WLSSD Raw
- WLSSD Final
- MCES Raw
- MCES Final
PBDE Congeners in the Sludges of the Two Wastewater Treatment Plants

PBDE Congeners

WLSSD-Raw
WLSSD-Final
MCES-Raw
MCES-Final
Total PBDEs in the Five Landfill Leachates in Minnesota

Picograms per Liter

- Pine Bend
- Spruce Ridge
- SKB-Demolition
- Burnsville
- SKB-Industrial
Dominant PBDE Homologues in the Five Landfill Leachates

- SKB Industrial
- Burnsville
- SKB Demolition
- Spruce Ridge
- Pine Bend

Picograms per Liter

Di  Tetra  Penta  Hexa  Nona
Dominant PBDE Congeners in Landfill Leachates

- Pine Bend
- Spruce Ridge
- SKB Demolition
- Burnsville
- SKB Industrial

Picograms per Liter

Dominant PBDE Congeners
Congener 209 in Leachates of the Landfills

ng/L

- Pine Bend
- Spruce Ridge
- SKB Demolition
- Burnsville
- SKB Industrial

PBDE - 209
Dominant PBDE Congeners in the Two Landfill Sludges

Picograms per Gram (dry weight basis)

- 99
- 47
- 49
- 100
- 153
- 154
- 183

Spruce Ridge
SKB Industrial/TOC
Dominant PBDE Congeners in Landfill Leachates

- Pine Bend
- Spruce Ridge
- SKB Demolition
- Burnsville
- SKB Industrial

Picograms per Liter

Dominant PBDE Congeners

15 47 49 99 100 153 154 207 208
Preliminary Results

- Fish Samples
  - Total PBDEs are ~ 400 to 2500 ng/mL
  - Dominant homologues are tetra > penta > tri > hexa
  - Dominant Congeners are 47> 100> 28+33> 49> 154
  - Highest level in fish from Red> Mississippi> St. Crioix> St. Louis> MN> Rainy
Preliminary Results

- Sediment Samples
  - Total PBDEs are ~ 6 to 936 ng/g TOC
  - Dominant homologues are deca > Penta > tetra > hexa
  - Dominant Congeners are 99 > 47 > 100 > 209 > 153
  - Highest level in sediments from St, Louis > Mississippi > St. Criox > MN > Rainy > Red
Preliminary Results

- **Wastewater Treatment Plants**
  - Total PBDEs are ~ 2000 to 14000 ng/g TOC
  - Dominant homologues are deca > Penta > tetra > hexa
  - Dominant Congeners are 99 > 47 > 100 > 207 > 153
  - Highest level in WWTP sludge from MCES Raw > MCES Final > WLLSD Final > WLSSD Raw
Preliminary Results

- Landfill Leachates and their sludge
  - Total PBDEs are ~ 29 to 249 ng/L
  - Dominant homologues are deca > penta > tetra > nona
  - Dominant Congeners are 209 > 99 > 47 > 49 > 100~207
  - Highest level in leachates from
    SKB-Dem > Pine Bend > SKB-ind > Spruce Ridge > Burnsville
Acknowledgements

- Funding was provided by the Minnesota Pollution Control (MPCA).
- Special thanks to Marvin Hora and Daniel Helwig for their support and developing the Emerging Issue Program at the MPCA. Many thanks also to Doug Hall, Todd Beiwen for their support and supervision. Without Harold Weigner’s sampling skills this work was not possible.
- Without AXYS Analytical Services support and expertise this research could not be completed.
Chromatographic Cleanup Procedures

- The extract was applied to a Florisil column.
- The column was eluted with hexane (F1), dichloromethane/hexane (F2).
- The elutes were combined (F1 + F2), a fraction of was concentrated and transferred to an auto-sampler vial.
- An aliquot of recovery standard (\(^{13}\text{C}_{12}\)-labeled PCB-153) was added.
- The capped auto-sampler was ready for PBDEs analysis.
Extraction Procedures

- **Aqueous Samples**: An accurately measured sample, to which an aliquot of surrogate standard solution had been added, was extracted by shaking three times with dichloromethane.

- **Sediment and Tissue Samples**: Weighted wet samples were dried with anhydrous sodium sulfate. The mixtures were transferred to a soxhlet thimble, an aliquot of surrogate standard solution was added. The mixtures were soxhlet extracted. The cooled extracts were concentrated prior to chromatographic cleanup.

- **Tissue Samples** were through a gel permeation column to remove lipids and interferences. The second fraction was concentrated prior to chromatographic cleanup.
HRGC/HRMS analysis of PBDEs in the F1+F2 fraction was carried out using VG high resolution mass spectrometer (MS) equipped with a Hewlett Packard 5890 Gas chromatograph, a CTC autosampler and a data system running VG software.

- The MS was operated at a 10,000 static mass resolution in the electron ionization (EI) mode.

- Data were acquired in the voltage Selected Ion Mode (SIM) to enhance sensitivity, acquiring two ions for each target analyte and surrogate standard.

- Chromatographic separation was achieved with DB-5HT capillary chromatography column.
Using the isotope dilution (internal standard) method of quantification, concentration of target analytes were calculated.

Compounds were quantified by comparing the area of the quantification to that of corresponding $^{13}$C$_{12}$- labeled standard and correcting for response factors.

Response factor were determined daily, using authentic PBDEs.

Concentrations of analytes were corrected based on the % recovery of surrogate standards.

Concentrations were reported on dry weight basis for sediments, wet weight basis for tissues, and on volume basis for leachates.