Quantifying PAHs and Phthalates in Air Collected in the Tacoma Tideflats
Polycyclic Aromatic Hydrocarbons (PAHs):
- nonpolar
- carcinogenic, mutagenic, teratogenic
- organic pollutants
- markers of (incomplete) combustion processes

Phthalates—plasticizers in products such as PVC (poly vinyl chloride) piping\(^1\)
- change hormone levels and cause birth defects in high concentrations
PAHs sources

Combustion

$C_{\text{source}} + 2 \, O_2 \rightarrow CO_2 + 2 \, H_2O + \text{energy}$
Part of the Puget Sound Partnerships’s Action Agenda is to ‘Reduce the Source of Toxic Chemical Entering Puget Sound’

- PAH levels in fish explicitly stated as part of this goal
- Atmospheric deposition and surface runoff have been estimated to be a significant source of PAHs in Puget Sound
Study design

- Quantify PAHs and phthalates in local air over 1 year period (every 6 days)
- Analysis of PAHs in gas and particulate phase to calculate total PAH concentration
- Use seasonal variation in PAH concentrations in combination with the observed variation in meteorology to estimate source strength
From the Air to the Analysis

1. Collect Air
2. Extract PAHs
3. Separate PAHs
4. Quantify PAHs
Air Sampling

- TISCH Corp Hi-Vol Air Sampler located on roof of Center for Urban Waters
  - Approximate height of sampler = 16.8 m above sea level

- Two Phases of Samples Collected:
  - Total suspended particulate (TSP) w/ quartz filters for particulate-phase species
  - Gas-phase w/ polyurethane foam (PUF) media for gas-phase species
Extraction

Extraction solvent: 90:10 hexane/diethyl ether

1 → 2 → 3 → 4
1mL final extract
Gas Chromatography–Mass Spectrometry (GC–MS)
Analyze solutions of known concentration to calibrate the instrument response
Use calibration curve to determine mass of PAHs in sample extracts
In order to evaluate laboratory contamination and instrument performance, blanks and standard spikes are analyzed as part of each batch
Method Limit of Detection (LOD) is calculated using PAH concentrations in lab blanks.

PAH mass per sample is converted to concentration in sampled air.
<table>
<thead>
<tr>
<th>Gas phase % Above Limit of</th>
<th>Particulate Phase Limit of</th>
<th>Target Compound</th>
<th>% Above Limit of</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limit of Detection (ng/m³)</td>
<td>Limit of Detection (LOD) (ng/m³)</td>
<td></td>
<td>Detection (ng/m³)</td>
</tr>
<tr>
<td>0.234</td>
<td>100</td>
<td>1-Methyl Naphthalene</td>
<td>0.147</td>
</tr>
<tr>
<td>0.109</td>
<td>100</td>
<td>2-Methyl Naphthalene</td>
<td>0.062</td>
</tr>
<tr>
<td>0.019</td>
<td>97</td>
<td>Acenaphthylene</td>
<td>0.004</td>
</tr>
<tr>
<td>0.041</td>
<td>88</td>
<td>Acenaphthene</td>
<td>0.016</td>
</tr>
<tr>
<td>0.131</td>
<td>100</td>
<td>Phenanthrene</td>
<td>0.110</td>
</tr>
<tr>
<td>0.040</td>
<td>100</td>
<td>Anthracene</td>
<td>0.044</td>
</tr>
<tr>
<td>0.069</td>
<td>100</td>
<td>Fluoranthene</td>
<td>0.060</td>
</tr>
<tr>
<td>0.048</td>
<td>100</td>
<td>Pyrene</td>
<td>0.041</td>
</tr>
<tr>
<td>0.009</td>
<td>61</td>
<td>Benzo (a) Anthracene</td>
<td>0.004</td>
</tr>
<tr>
<td>0.092</td>
<td>21</td>
<td>Chrysene</td>
<td>0.004</td>
</tr>
<tr>
<td>0.029</td>
<td>6</td>
<td>Benzo (a) Pyrene</td>
<td>0.004</td>
</tr>
<tr>
<td>0.118</td>
<td>0</td>
<td>Indeno (1,2,3-c,d) Pyrene</td>
<td>0.013</td>
</tr>
<tr>
<td>0.333</td>
<td>0</td>
<td>Dibenz (a,h) Anthracene</td>
<td>0.011</td>
</tr>
<tr>
<td>0.116</td>
<td>0</td>
<td>Benzo (g,h,i) Perylene</td>
<td>0.017</td>
</tr>
</tbody>
</table>
PAH Level, Largely in Gas Phase

*Filter samples only analyzed through 1/10/2012
*No data collected 2/17/2012 - 3/3/2012

Beijing: 11.3 ng/m$^3$

PAH Level, Largely in Gas Phase

- Filter samples only analyzed through 1/10/2012
- No data collected 2/17/2012 - 3/3/2012
PAH Level, Largely in Gas Phase

*Filter samples only analyzed through 1/10/2012
*No data collected 2/17/2012 –3/3/2012

Baltimore winter: 8.3–18ng/m$^3$

Phenanthrene

200 Beijing: 47.7ng/m$^3$

2009

PAH Level, Largely in Gas Phase

Total PAH Concentration in Air (ng/m$^3$)
PAH Level, Largely in Gas Phase

*Filter samples only analyzed through 1/10/2012
*No data collected 2/17/2012 – 3/3/2012

**Anthracene**

Baltimore winter: 0.330–1.14

Baltimore summer: 0.213–0.4

Beijing: 7.8ng/m$^3$

2001

2009
PAH Contributions From Gas and Particulate Phases

*Filter samples only analyzed through 1/10/2012
*No data collected 2/17/2012 – 3/3/2012

Baltimore winter: 2.5–5.74
Baltimore summer: 7.28–13.5
2011

Beijing: 27.5ng/m³
2009
PAH Contributions From Gas and Particulate Phases

*Filter samples only analyzed through 1/10/2012
*No data collected 2/17/2012 - 3/3/2012

Baltimore Winter: 2.24–6.00
Baltimore Summer: 3.94–6.75

Beijing: 20.4 ng/m$^3$ 2009
PAH Level, Largely in Particulate Phase

*Filter samples only analyzed through 1/10/2012
*No data collected 2/17/2012 – 3/3/2012

Beijing: 7.1ng/m³ 2009

Indeno (1,2,3-c,d) Pyrene

Gas
Particulate
Temperature (deg C)

Total PAH Concentration in Air (ng/m³)

Temperature (deg C)
PAH Level, Largely in Particulate Phase

*Filter samples only analyzed through 1/10/2012
*No data collected 2/17/2012 – 3/3/2012

Beijing: 7.7 ng/m$^3$

Benzo (g,h,i) Perylene

- Gas
- Particulate
- Temperature (deg C)

Total PAH Concentration in Air (ng/m$^3$)

Temperature (deg C)

*Filter samples only analyzed through 1/10/2012
*No data collected 2/17/2012 – 3/3/2012

Beijing: 7.7 ng/m$^3$ 2009

Benzo (g,h,i) Perylene

- Gas
- Particulate
- Temperature (deg C)
Conclusions

- Consistently observe all PAHs of interest in at least one phase
- Gas phase PAHs dominate total mass in the air
- LOD was consistently below 0.25ng/m$^3$
- General range of “light” PAH concentrations: 0.5–5ng/m$^3$
  - Tend to be found in gas phase
- General range of “medium” PAH concentrations: 0.5–3ng/m$^3$
- General range of “heavy” PAH concentrations: 0.5–2ng/m$^3$
  - Tend to be found in particulate phase
Next Steps

- Sampling (4 days, 7%)
- Final soxhlet extractions (11 batches)
- Run final sequences through GC/MS (~4 sequences)
- Data analysis (~60%)—quantify PAH’s and phthalates
- Infer roots of contamination at different times of year and compare data to previous works
Acknowledgements

- Justin Miller-Schulze, Ph.D.
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- City of Tacoma
- Shristi Prakash
Questions?
References


5. Puget Sound Clean Air Agency and The University of Washington, “Tacoma and Seattle Area Air Toxics Evaluation” 2010

