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Mass Balance Modeling of Polycyclic Aromatic Hydrocarbons Sources to Urban Sediments

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Receptor Models

Receptor models are tools for characterizing potential sources and quantifying their contribution to the chemicals found in environmental samples.
Uses of Receptor Models in Sediment PAH Source Evaluations

- Characterizing the sources that result in urban background
  - Considering source control policies

- Characterizing the contribution of site specific sources
  - Allocating remedial liability
Chemical Mass Balance Mixing Models

- Modeler pre-identifies sources and inputs their chemical profiles
- Model calculates best fit to the receptor (sediment) data to estimate relative contributions of the sources

The validity of the results depends on the validity of the source inputs.
Principal Component Analysis

• PCA simplifies multidimensional variability into fewer dimensions

• Samples that are more chemically similar, plot closer together
Question: Is there a method of evaluating the sufficiency of the source inputs used in CMB modeling?

• Hypothesis:
  – On a Principal Component Analysis (PCA) plot, mixtures should be within the area bounded by the proposed sources.

• Application:
  1) Testing proposed source profiles
  2) Selecting appropriate source profiles
Identified five proposed PAH source profiles from VanMetre and Mahler (2010)

Used Excel to generated 100 random but known mixtures of 2, 3, 4, or 5 of the sources

Ran PCA on the sources and mixtures and plotted the results
PCA Plots of 2, 3, 4, and 5 Source Mixtures are Consistent with the Hypothesis
Case Study: Use of CMB to Evaluate of the Role of Refined Tar Pavement Sealers (RTS) in Urban Lake Sediments

- Van Metre and Mahler (2010) used CMB to evaluate whether RTS is an important contributor to PAH urban background
- Source inputs, calculated from various types of published data, have not been validated to be appropriate
- Authors highlight results of just 4 out of over 200 model runs
- Others are applying the same approach to similar sediment data sets
Most of Van Metre’s sediment samples do not plot within the area bounded by the proposed sources indicating the source profiles are not appropriate.

Source: O’Reilly et al. 2014. IEAM, 10:279–285
Proper selection is critical because minor changes in inputs can result in significantly different outputs.

Average CMB modeled source contributions for 4 runs with different source profiles:

<table>
<thead>
<tr>
<th>RTS or Urban Dust Source Profile</th>
<th>Model vs Measured Correlation [r]</th>
<th>RTS or Dust Source</th>
<th>Vehicle Tunnel</th>
<th>Wood Smoke</th>
<th>Coal</th>
<th>Fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTS Lot Dust</td>
<td>0.99</td>
<td>46</td>
<td>36</td>
<td>5.0</td>
<td>9.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Unsealed Lot Dust</td>
<td>0.97</td>
<td>60</td>
<td>25</td>
<td>11</td>
<td>3.5</td>
<td>0.4</td>
</tr>
<tr>
<td>RTS Test Plot</td>
<td>0.98</td>
<td>0.0</td>
<td>42</td>
<td>57</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>No RTS</td>
<td>0.98</td>
<td>--</td>
<td>48</td>
<td>51</td>
<td>1.2</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Use of PCA to Identify Appropriate CMB Source Profiles

• Run PCA on sediment samples and potential sources

• Evaluate PAH fingerprints of samples that plot differently

• Using site knowledge, PCA results, and sample chemistry to select samples that best represent sources
Conclusions

- Proper source selection is critical when using chemical mass balance models
- Principal component analysis can be used to evaluate potential CMB source inputs
- The ability of CMB to accurately characterize sources of urban background is unproven
- RTS’s role as a contributor to urban background is unproven
Acknowledgment

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