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Parsing Pyrogenic PAHs—Urban Background or Refined Tar Products?

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The Great Pyrogenic Challenge: A Number of Potential Sources Have Similar Profiles

Therefore, a number of potential sources are similar to sediments

USGS Hypothesis: Refined Tar-Based Pavement Sealants Are Major PAH Sources to Urban Lake Sediments
Questions

- Are refined tar sealers (RTS) a significant source of PAHs in urban sediments?
- Can the sources of pyrogenic PAHs be differentiated?
- Do multiple lines of evidence support the findings?
Use of Chemical Mass Balance (CMB) Model to Evaluate of the Role of Refined Tar Pavement Sealers in Urban Lake Sediments

- USGS researchers used CMB to test the hypothesis that RTS is a significant PAH source (Van Metre and Mahler 2010)

- Lack of negative controls limited value for hypothesis testing

- Multiple lines of evidence need to support findings

http://water.usgs.gov/nawqa/home_maps/sealcoat.html
Most of the 40 Lakes in the Study are Within Expected Urban Background Concentrations

Max. Average Total PAH16 (Stout et al. 2004)
EPAs CMB Model

- **Forward-Calculating Least-Squares Mixing Model**
  - Modeler pre-identifies sources and inputs source profiles
  - Model calculates best fit to the receptor (sediment) data to estimate relative contributions of sources
Key Assumptions of CMB

1. All sources with a potential for contributing to the receptor have been identified

2. Source profiles are constant

3. Source profiles are linearly independent of each other

4. Chemical species are stable and do not react with each other

5. Measurement uncertainties are random, uncorrelated, and normally distributed

Source: Galarneau 2008
Hypothesis Testing Requires a Negative Control

- **Comparison of three CMB Model runs**
  
  - **Published Results**: Model A from Van Metre et al. 2010. RTS source profile is the mean of dust from six sealed lots.

  - **Negative Control**: Did not include RTS as a source profile. Remaining sources from Van Metre et al. 2010.

Examples of USGS’s CMB Source Profiles

- Profiles obtained by averaging literature values
- RTS source profile average of samples collected from Austin, Texas
Including a Negative Control is Critical when using CMB for Hypothesis Testing

- Excellent match between measured and modeled concentrations with or without RTS as a proposed source

\[ R^2 > 0.996 \text{ for each method} \]
CMB Results Do Not Support the Hypothesis that RTS are Significant Contributors of PAHs to Sediments

Lake Ballinger - Mountlake Terrace, WA

- Wood
- Oil
- Coal
- Vehicle
- RTS

Town Lake- Austin, TX

Upper Mystic Lake- Winchester, MA
Evaluation of Multiple Lines of Evidence is Essential

- **Site-specific information and histories**

- **Application of a range of tools**
  - Similar results with different methods provides support for and increases confidence in conclusions
  - Different results indicate presence of uncertainties that need to be addressed
Multiple Lines of Evidence: Are All Sources Considered?

Patrick Herron, Mystic Monitoring Network director at the Mystic River Watershed Association (MyRWA), said the water quality in the watershed was already “very poor” due to contamination from sewage seepage, fertilizer runoff, and drainage from at least one Superfund site in Woburn, and this new study “adds insult to injury.”
Multiple Lines of Evidence: Principal Component Analysis (PCA) Does Not Support the USGS Hypothesis

![Graph showing data points on a scatter plot, with factors 1 and 2 labeled. The factors are explained as follows: Factor 1 (46%) and Factor 2 (24%). The data points are categorized into MA Lakes, Test Plot Dust, Lot Dust, and Lot Scrape.](image)
MA Lake Sediments Are Not Similar to the Austin, TX, RTS Samples
Multiple Lines of Evidence: Independent Watershed Studies Indicate that Sealers Are a Minor PAH Source

Multiple Lines of Evidence: Comparison of RTS Free Model Output with Regional Emission Source Study

WA DOE (2011) Assessment of Selected Toxic Chemicals in the Puget Sound Basin
RTS Evaluation Summary

- The results do not support the hypothesis that RTS is a significant source of PAHs in sediments
  - The correlations between modeled and measured total PAH concentrations were similar with or without RTS
  - The PAH profile of sediments from all 40 lakes can be characterized without any contribution of RTS
  - PCA indicates that sediments are not similar to RTS sealant samples
Key Messages

- Parsing the sources of pyrogenic PAH in urban sediments is a technical challenge
- Present multiple lines of evidences to minimize uncertainty
- Receptor models are powerful tools, but have important limitations
- All sources should be considered
- Use negative controls where appropriate

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Thank You!
References


