The Influence of Source Selection on Chemical Mass Balance Modeling Results: Implications for Source Control Policy

Sungwoo Ahn and Kirk O'Reilly
Exponent, Bellevue, WA, USA

ABSTRACT

U.S. EPA's Chemical Mass Balance (CMB) model is used to evaluate sources of polycyclic aromatic hydrocarbons (PAHs) in sediments. The model works by finding a solution that best fits the chemical concentrations measured in receptor (sediment) samples as a mixture of the potential sources. Successful application requires knowledge of the important PAH sources and an understanding of whether they meet the model's underlying assumptions. Three critical assumptions are 1) all important sources have been identified, 2) their source profiles are known and stable, and 3) there are sufficient differences between sources so that they are linearly independent of one another. Ultimately, the validity of a model's output depends on the quality of the source inputs.

Because the results of CMB are used to promote source control policies, it is important to understand the sensitivity of the model to source input parameters. This study describes an evaluation of whether refined tar pavement sealers (RTS) are an important source of PAHs to urban sediments. The U.S. Geological Survey (USGS) used dust collected from RTS sealed lots as the RTS source profile in CMB evaluation of sediments from 40 lakes across the United States (Van Metre and Mahler 2010). In our study, we evaluated the effect of replacing the sealed lot dust profile with dust collected from unsealed lots or samples collected from an RTS test plot. Negative control runs without any RTS or dust source inputs were also evaluated. The remaining proposed sources were those suggested by the USGS.

There was an excellent fit (R^2>0.99) between measured and modeled PAH concentrations with each of the RTS source profiles and with the negative control. In all cases, the modeled contribution of unsealed parking lost dust was similar to or exceeded that of RTS sealed lot dust. The modeled contribution based on the PAH profile of the RTS test plot, the only certain RTS source, was at or near zero.

These results do not support the USGS hypothesis that RTS are an important source of PAHs in urban sediments, and indicate the importance of providing a full range of CMB outputs.

INTRODUCTION

Chemical Mass Balance (CMB) Model

- A receptor model by U.S. EPA.
  - The model works by finding a solution that best fits the chemical concentrations measured in receptor (sediment) samples as a mixture of the potential sources.
- Used to evaluate sources of polycyclic aromatic hydrocarbons (PAHs) in sediments.
- Successful application of CMB requires:
  - Knowledge of the important PAH sources
  - Meeting the model's underlying assumptions
  - Identifying all important sources
  - Known and stable source profiles.
  - Sufficient differences between sources so that they are linearly independent.
- Ultimately, the validity of the model's output depends on the quality of the source inputs.

A Case Study – PAH Sources to Urban Lake Sediment

- USGS used the "dust" collected from RTS sealed lots as the RTS source along with other PAH sources in CMB evaluation of sediments from 40 lakes across the U.S. (Van Metre and Mahler 2010).
  - Other PAH sources include coal combustion source, vehicle related source (traffic tunnel air), fuel-oil combustion source, and wood burning soot particles.
  - RTS has been claimed as the largest PAH source.
- The re-evaluation of (RTS) as an important source of PAHs to urban sediments.
  - Replace the sealed lot dust with different sources (RTS related and non-RTS related).
  - Negative control run.
  - Review of the selected RTS PAH sources.

METHODS

Inputs and Sources Used in CMB

- Receptors
  - 120 sediment samples collected from 40 urban lakes in the U.S.
- Sources (in USGS study)
  - RTS sealed lot dust collected from six U.S. cities
  - Coal combustion source (coal average)
  - Vehicle related source (traffic tunnel air)
  - Fuel oil combustion particles
  - Wood burning source (pine-wood soot particles)
- Alternative sources tested in the case study in place of RTS sealed lot dust
  - Dust collected from unsealed lot (in use)
  - RTS Test plot (RTS sealed, but not exposed to vehicle use)
  - Negative control
- PAHs – 11 or 12 PAHs out of 16 EPA Priority Pollutants PAHs

RESULTS

CMB Modeling with Different RTS or Dust source

- The modeled contribution of unsealed parking lot dust exceeds that of RTS sealed lot dust (Table 1).
- Little or no contribution from the RTS samples collected from the test plots.
- The CMB modeling results from the alternative RTS sources indicate that RTS is unlikely to be an important source of PAHs.
- The USGS has only shared the results of the RTS sealed lot dust runs in their publications, website and presentations to policy makers.
- CMB does an excellent job of fitting the source profiles to the 120 sediment samples in all four model runs (Figure 1).
- Minor differences between runs are within the model's range of uncertainty.
- When CMB results are being used in setting source control policy, it is critical that decision makers get the complete story.

The results of the USGS study have been used to advocated for RTS product bans. More complete site specific evaluations fails to support the claim that RTS is an important source of PAHs. In each case, the modeled percent contribution is similar or greater when unsealed parking lot dust is used as a source input than that for RTS sealed lot dust (Figure 2).

While this poster focuses on comparing the results of changing just one of the CMB source profiles used in Van Metre and Mahler (2010), it is critical to evaluate the appropriateness of all model inputs. As discussed in O'Reilly et al. (2014) the failure of the proposed sources to bound the sediment samples in a principal component analysis plot indicates that additional refinement of source inputs is required (Figure 3).

Table 1. CMB modeled contributions with different RTS or dust sources

	CMB Modeled Contribution (%)				
	RTS or Dust Source	Vehicles	Wood combustion particle	Coal combustion	Fuel oil combustion
RTS sealed lot dust (USGS)	46	36	5	9	3
Unsealed lot dust	60	25	11	3.5	0.4
RTS test plot	0.0	42	57	1.0	0.0
No RTS	–	48	51	1.2	0.0

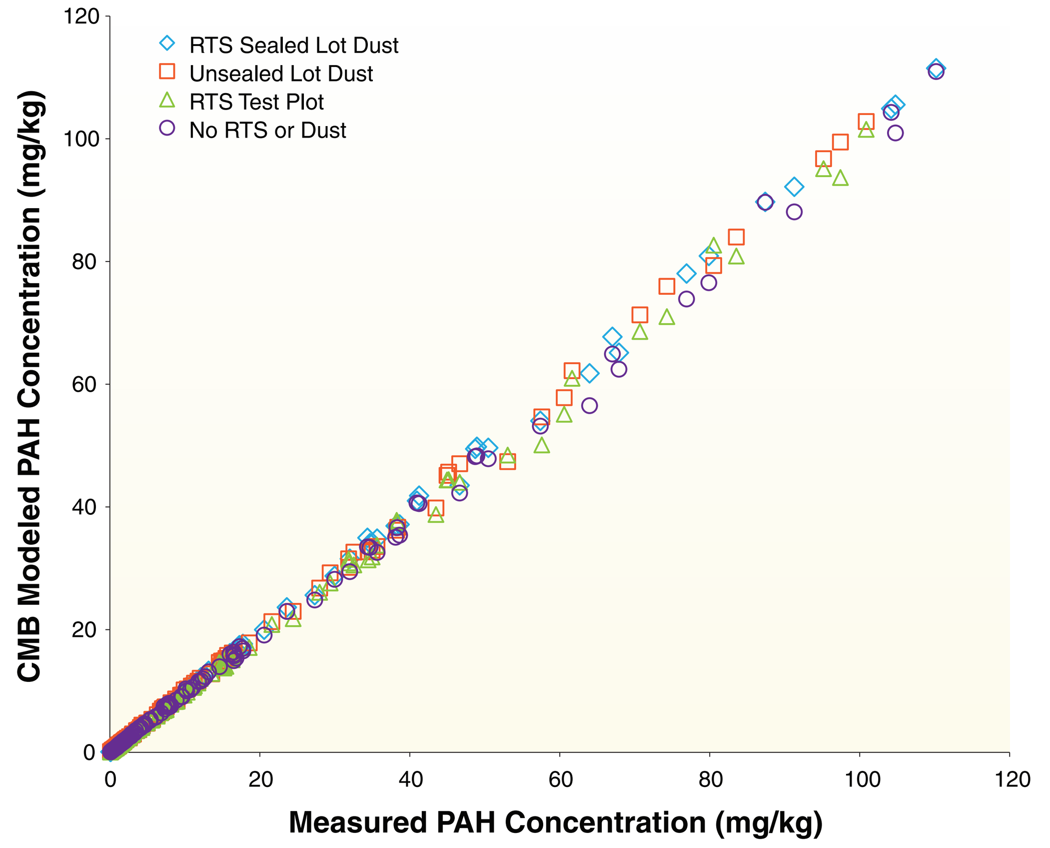

Figure 1. Comparison between measured PAH concentrations and calculated PAH concentrations from four different CMB model runs

Selection of RTS Source Material

- Pearson correlation of various RTS materials collected indicate that there is wide variation among RTS materials (Data from Van Metre and Mahler 2010).
- Only CMB results using last two RTS-related materials as RTS sources were presented in the USGS study.
- Low similarity between the sealant products and the dusts collected from the sealed lots may indicate the dusts may contain materials other than RTS-related material (Table 2 and Figure 4).

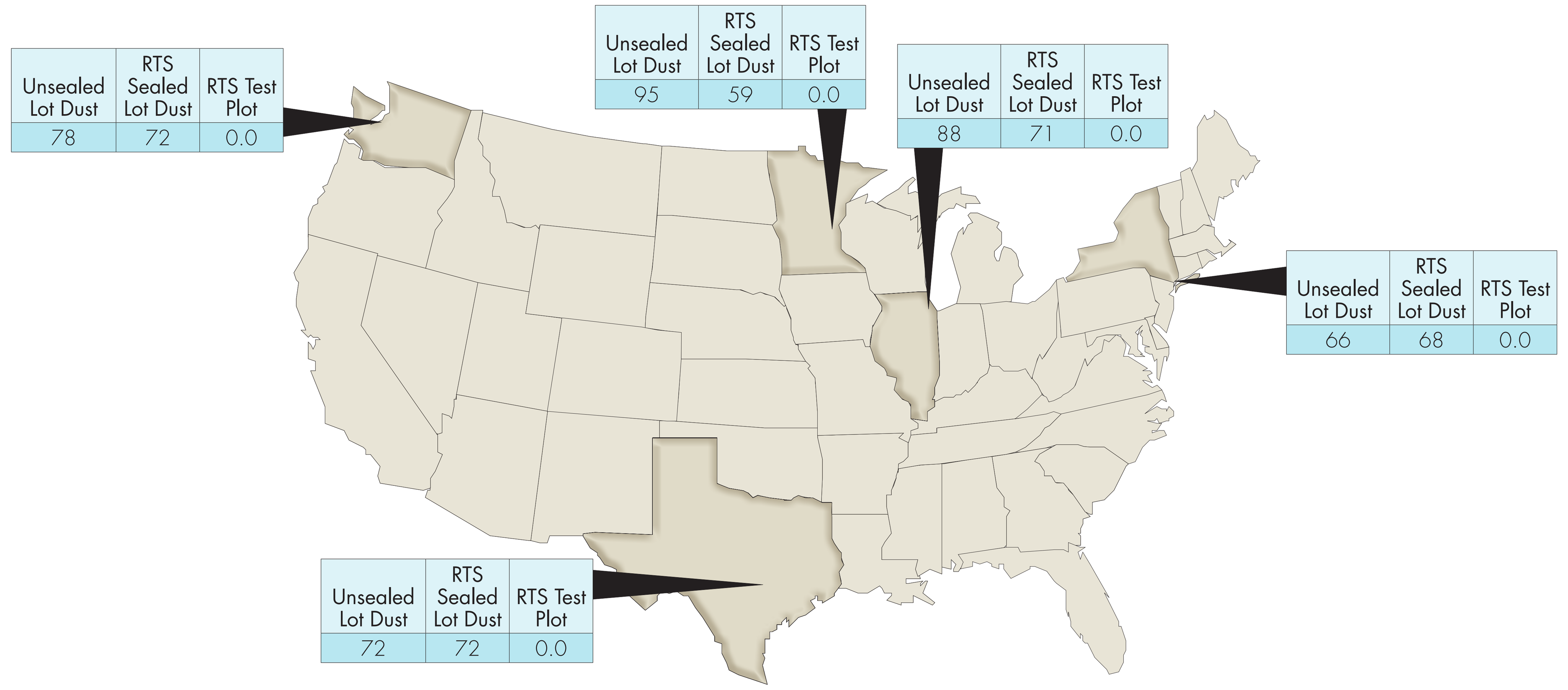

Figure 2. Locations of proposed or enacted RTS bans. The inserted tables show the site specific results of the contributions of the different RTS or dust sources calculated from CMB

Table 2. Pearson correlation coefficients between different RTS-related materials

	NIST coal tar	RTS products	1-week old RTS scraping	RTS scraping Milwaukee, WI	RTS scraping Austin, TX	RTS pavement dust from six cities	RTS pavement dust from Austin, TX
RTS products	0.99						
1-week old RTS scraping	0.94	0.96					
RTS scraping Milwaukee, WI	0.91	0.94	0.96				
RTS scraping Austin, TX	0.50	0.59	0.75	0.76			
RTS pavement dust from six cities	0.53	0.61	0.75	0.81	0.97		
RTS pavement dust from Austin, TX	0.13	0.23	0.43	0.49	0.90	0.89	

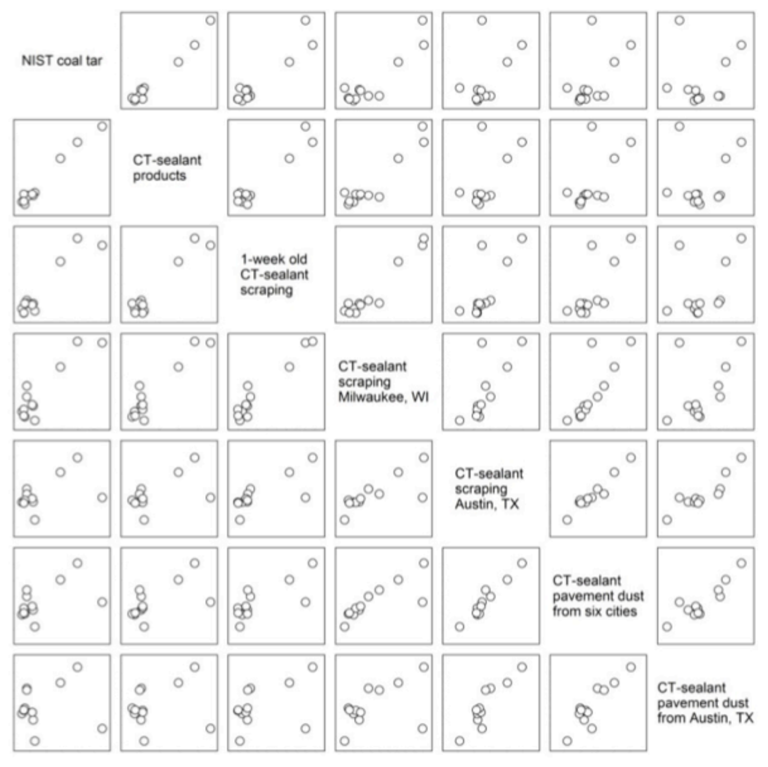

Figure 4. Scatter matrix of Pearson correlation of different RTS-related materials

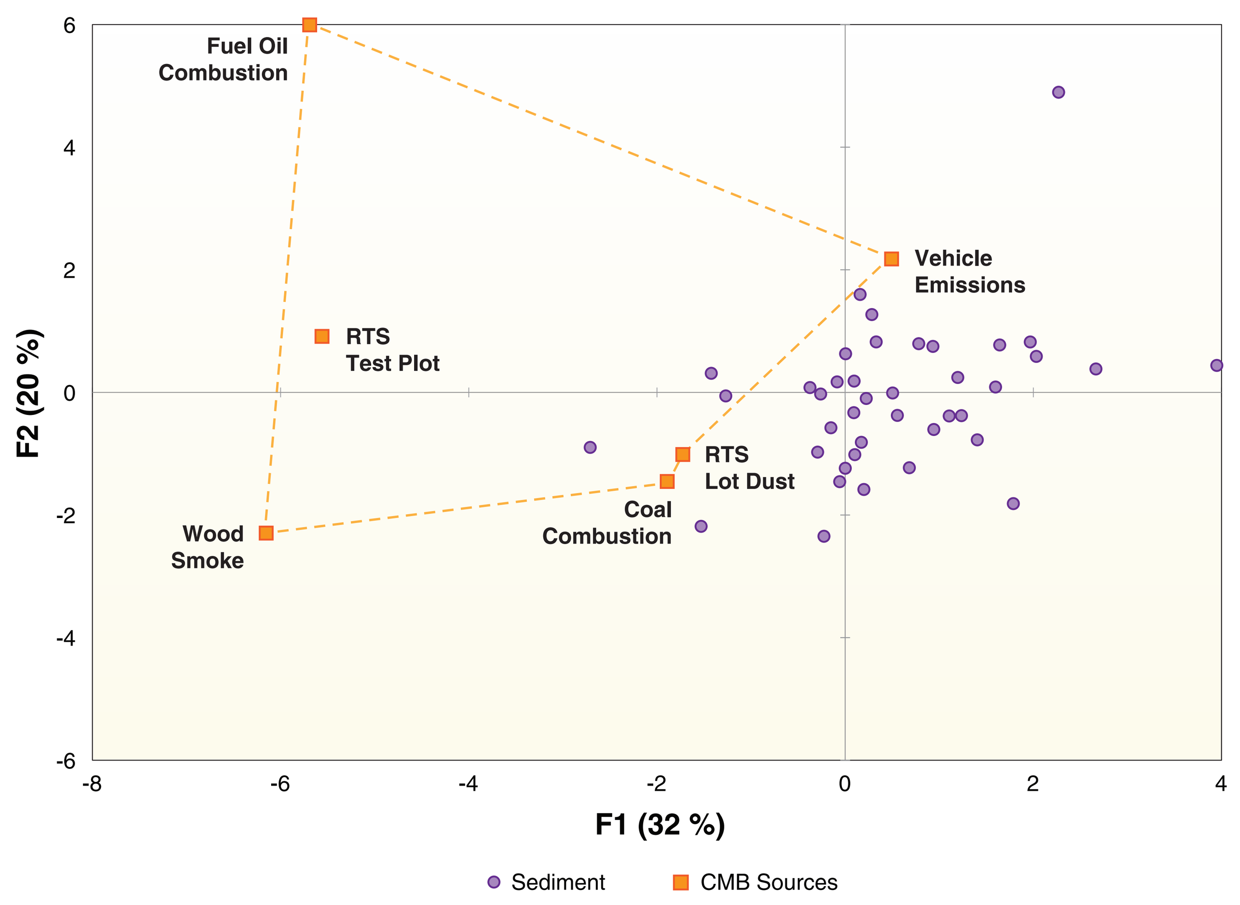

Figure 3. Principal Component Analysis plot showing the proposed PAH sources and the other PAH sources tested in this case study with the urban lake sediment samples (O'Reilly et al., 2014)

DISCUSSION

- There was an excellent fit (R^2>0.99) between measured and modeled PAH concentrations with each of the RTS source profiles and with the negative control tested in this study.
- The modeled contribution of unsealed parking lost dust was similar to or exceeded that of RTS sealed lot dust. The modeled contribution based on the PAH profile of the RTS test plot, the only certain RTS source, was at or near zero.
- These results do not support the USGS hypothesis that RTS are an important source of PAHs in urban sediments, and indicate the importance of providing a full range of CMB outputs.
- The USGS website presents an incomplete and biased description of the use of CMB to evaluate whether RTS is an important of source of PAHs in urban sediments.

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Acknowledgement

This work was supported by the Pavement Coatings Technology Council

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