



**PAVEMENT COATINGS TECHNOLOGY COUNCIL
WHITE PAPER 1301**

**CRITICAL REVIEW OF USGS CONCLUSIONS
REGARDING SOURCES OF PAHS IN LAKE
SEDIMENTS**

Executive Summary

Experts in environmental forensics have concluded in several peer reviewed articles that refined tar-based sealers (RTS) are not an identifiable source of polycyclic aromatic hydrocarbons (PAHs) in urban sediment. Although RTS have been banned in Austin, Texas and the state of Washington, no quantifiable environmental benefit has been shown to exist with respect to PAHs measured in sediment affected by the bans. Nevertheless, a small group of scientists, predominantly from governmental agencies, has advocated that RTS should be banned throughout the country. The Pavement Coatings Technology Council (PCTC) offers this White Paper as a detail analysis of the data and methods used by this small group of scientists to arrive at their conclusions.

The White Paper is premised upon scientific literature published by (a) government researchers, (b) PCTC - funded researchers, and (c) other researchers who have explored these issues “independently.” Multiple environmental forensic methods are described within this literature and overall confirm that RTS are not a significant source of PAHs in the studied urban sediments. Indeed, comparison of results using different “fingerprinting” methods indicates that the dominant source of PAHs in urban sediments is likely atmospheric deposition, with little to no identifiable contribution from RTS.

All efforts have been made to include the most current studies and evidence available, including data and documents produced by the USGS in response to Freedom of Information Act (FOIA) request USGS-2011-00093, cited in this White Paper as Kurfirst (2011). Despite the pendency of this FOIA request for more than two years, the USGS response is not yet complete. Thus, it may be necessary to supplement this White Paper at a later date.

Introduction

In a 2011 “Fact Sheet,” the United States Geological Survey (USGS) published the following assertions regarding sources of polycyclic aromatic hydrocarbon compounds (PAHs) found in various lakes across the country (Mahler and Van Metre, 2011):

- Coal-tar-based sealcoat¹ is the largest source of PAH contamination in 40 urban lakes studied, accounting for one-half of all PAH inputs.
- Coal-tar-based sealcoat use is the primary cause of upward trends in PAHs, since the 1960s, in urban lake sediment.

These assertions are based on a body of work that has been generated, in large part, by two USGS scientists: Peter Van Metre and Barbara Mahler. The specific conclusion naming RTS as “the largest source of PAH contamination” is based on a paper by Van Metre and Mahler (2010) titled *Contribution of PAHs from Coal-Tar Pavement Sealcoat and Other Sources to 40 U.S. Lakes* (hereinafter the “40 Lakes Paper”). According to Van Metre and Mahler, the findings set forth in the 40 Lakes Paper are consistent with conclusions that they and other government researchers reached in previously published studies involving RTS.

This White Paper is organized into two main sections. The first section evaluates an initial set of PAH “fingerprinting” studies published between 2005 and 2009, including articles published by Van Metre and Mahler. These studies focus on a variety of strategies for source identification and apportionment of PAHs found in sediment. The second section analyzes in detail the 40 Lakes Paper in which Van Metre and Mahler contend that the chemical mass balance model (CMB) is the most reliable method for PAH source identification and apportionment and why their conclusions are flawed.

USGS Studies of PAHs in Sediments: 2005-2009

PAHs are ubiquitous – they occur naturally in fossil fuels and also are made when organic matter is burned (*e.g.* ATSDR, 1995). . Because PAHs are everywhere, an enormous amount of scientific research has been published worldwide covering just about every aspect of PAHs, including studies that attempt to identify and apportion sources of PAHs occurring in soils (*e.g.*, Kay *et al.* 2003; Mauro *et al.*, 2006) and sediments (*e.g.*, Stout *et al.* 2004 and the papers summarized in the Attachment to this White Paper).

PAH source identification – sometimes called “PAH forensics” – typically involves using graphical and statistical methods in an effort to identify source-

¹ RTS are characterized as “coal-tar-based sealcoat” or “CTS” by the USGS.

specific chemical characteristics – “fingerprints” – to distinguish sources. For example, Figure 1 contains a principle component analysis (PCA) plot of PAH data. The data (but not the statistical analysis) were published by the USGS team for sediments in Washington State (Lake Ballinger; Van Metre & Mahler, 2010) with samples from parking lots said to be treated with refined tar-based pavement. It is easy to see that there is no overlap of PAHs in Lake Ballinger sediments with PAH parking lot dust and parking lot scrapings data the USGS collected from lots that were said to be sealed.

Overlapping data can be an indication of a source-sink relationship between PAHs in samples. Likewise, the absence of an overlap, along with different trends in sample PCA plots can be an indication of the absence of a source-receptor relationship. It’s not always straightforward – sometimes chemical data may overlap, but this doesn’t necessarily mean that there is a source relationship. In cases of overlap, most scientists working in the field of environmental forensics suggest additional forensic analysis should be pursued. A requirement in source identification is consistency internally and among all the different forensic methods used (O’Reilly *et al.*, 2012). In cases such as the Lake Ballinger data in Figure 1, in which the data neither overlap nor display similar trends, the absence of a relationship is strongly suggested.

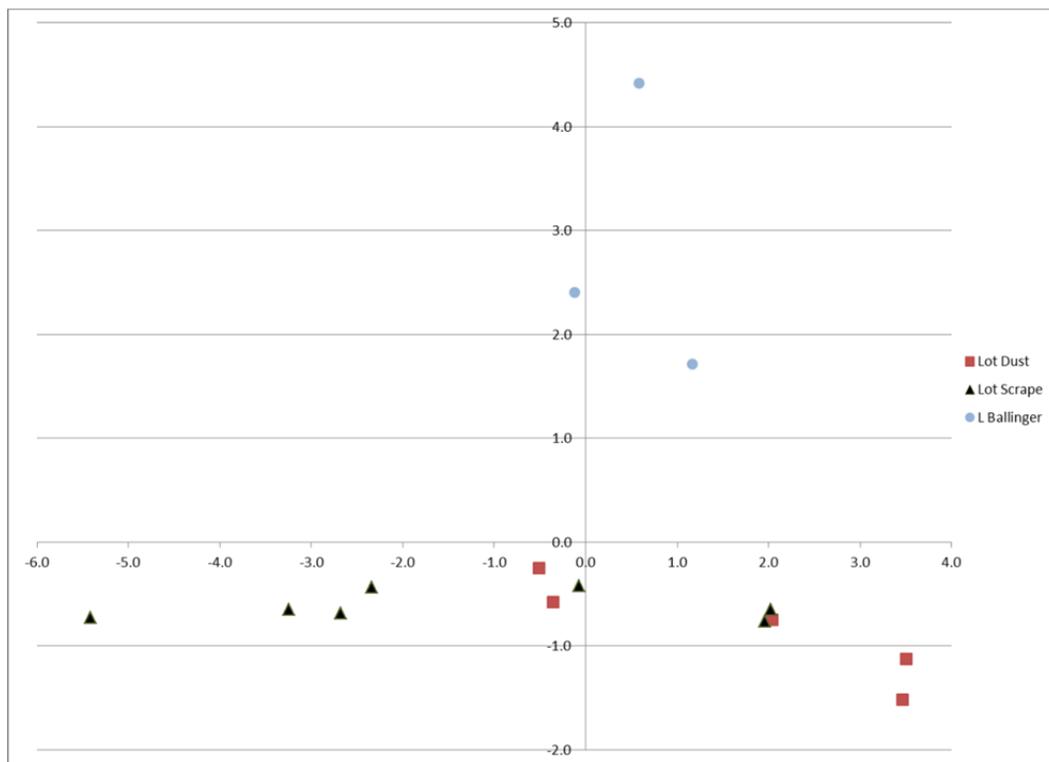
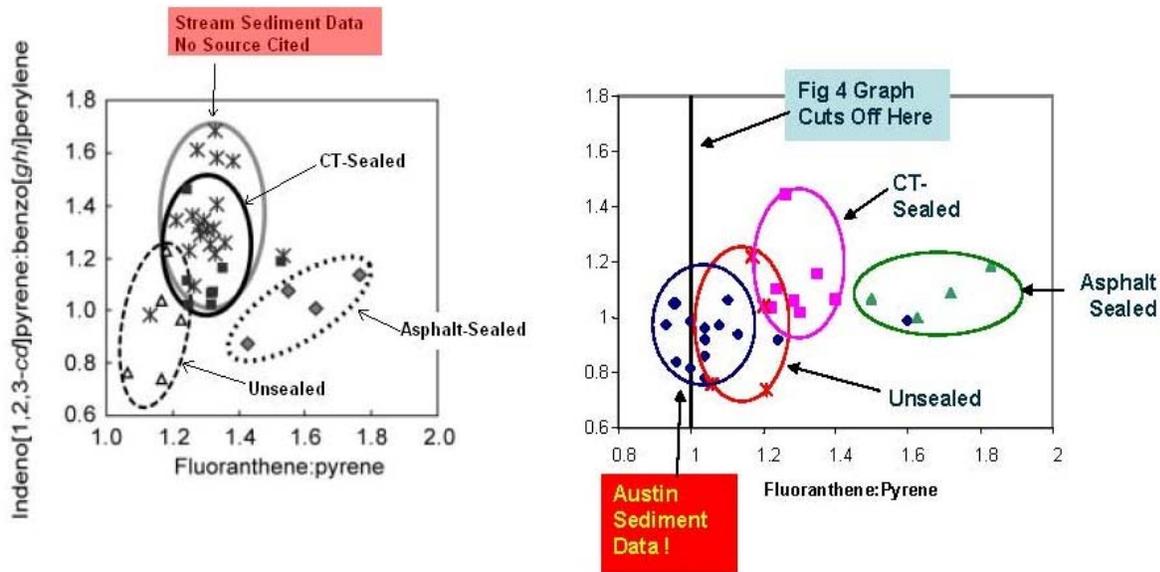


Figure 1. Principle Component Analysis (PCA) does not support the claim that RTS is a significant source of PAHs in the sediment of Lake Ballinger, located near Seattle, WA. The results are consistent with the WA Department of Ecology’s conclusion that residential wood burning is the largest source of PAHs in sediments of Western Washington.

In their earliest publication about pavement sealers in Austin, TX, the USGS team used double ratio plots as the method of source identification (Mahler *et al.*, 2005). Inconsistencies, however, have been identified in the published data (DeMott & Gauthier, 2006; see Figure 2, below), and the source of the sediment data shown in the Mahler *et al.* (2005) figure remains unidentified to this day.



ES&T Article

Re-Plot with Austin Sediments

Figure 2. Comparison of double ratio plot from Mahler *et al.* (2005, on left) with graph of the same sealed parking lot data (DeMott & Gauthier, 2006, on right). The USGS states that the sediment data used in the graph on the left is not the data provided by the City of Austin and used in the graph on the right. The source of the USGS sediment data as well as the data themselves remain unidentified.

As is always the case when a science journal such as Environmental Science & Technology (ES&T) publishes a critical comment on a specific article, a response by the article’s authors is also published. The DeMott & Gauthier (2006) comment, which critiqued Mahler *et.al.* (2005), focused on two main points:

- (1) With regard to the PAH ratio analysis, we could not identify the source of the values presented for stream sediment samples, and the values that we could identify from the City of Austin appear to contradict the interpretation developed by the authors [*i.e.*, Mahler *et al.* (2005)].

(2) With regard to the mass balance analysis, we could not identify the source for values from one watershed, the values presented for the other watersheds do not appear to match those from the cited sources, and the previously published values suggest the relative contribution of PAHs from parking lot sources is substantially less than the “majority” source suggested by the authors [*i.e.*, Mahler *et al.* (2005)].

Neither of these points was addressed by Mahler *et al.* (2006) in their response. Rather, the response addressed topics that are, at best, secondary issues raised in the DeMott & Gauthier comment. Topics raised in the response are as follows:

- (1) A discussion of the use of specific PAH double-ratio plots, with highly debatable representations about the impact that concentrations may have had on ratios (debatable because ratios are not concentration dependent).
- (2) Commentary that data used in the DeMott and Gauthier plot may not be comparable to the Mahler *et al.* (2005) data, but with no indication of what the source of the data in Mahler *et al.* was.
- (3) A discussion of possible overestimation versus underestimation in mass balance calculations.
- (4) A discussion of comparability of load calculations made for the Fort Worth and Austin, TX calculations.
- (5) A correction of load calculations errors made in Mahler *et al.* (2005).
- (6) An assertion that certain yield calculations support the conclusions of Mahler *et al.* (2005).
- (7) An unreferenced statement that the sealing of parking lots is a fairly common practice, so sealants must be a “major contributor of PAHs to the urban watersheds studied.”

Follow-up studies in Austin waterways confirm that RTS are not an identifiable source of PAHs in Austin when using either the double ratio plot of Mahler *et al.* (2005) (shown in Figure 2 above) or principle component analysis (shown in Figure 3, below; DeMott *et al.*, 2010; O’Reilly *et al.*, *in preparation*).

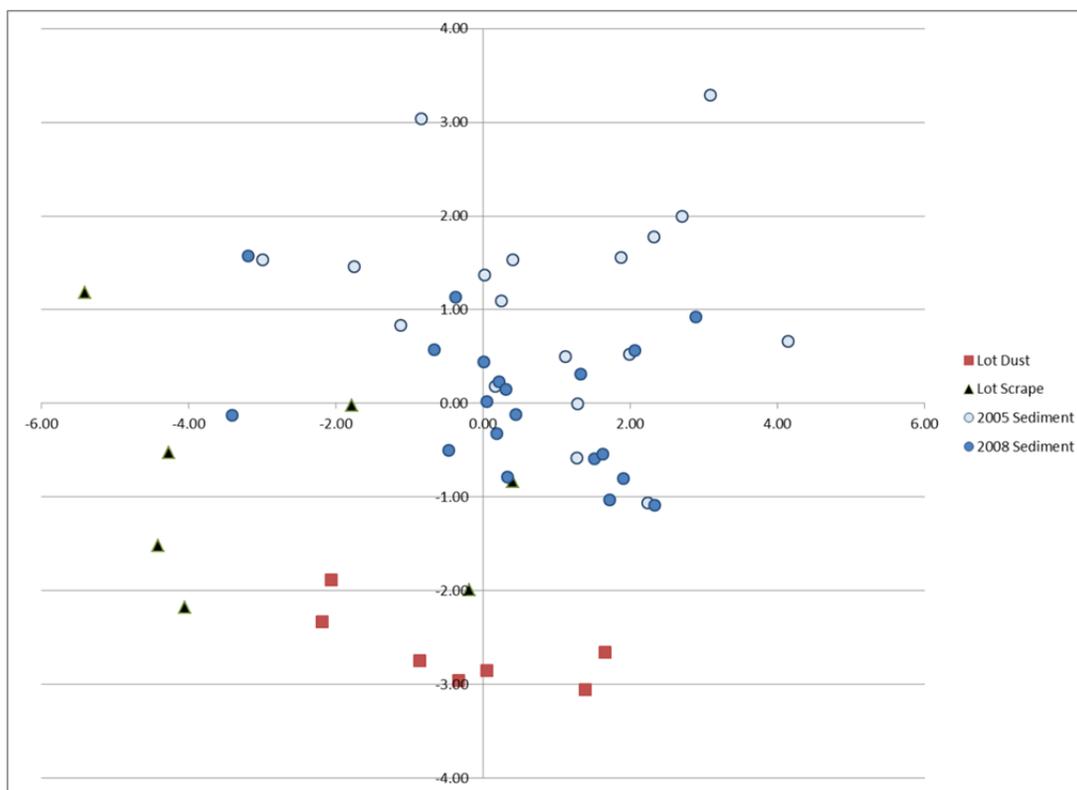


Figure 3. PCA evaluation comparing creek sediments in Austin, TX waterways to Austin parking lot dust and scrapings. PCA results combined with results of additional forensic methods do not support a claim that the lots are a significant source of PAHs. PAH data are from Mahler *et al.* (2005) and DeMott *et al.* (2010). Figure is from O’Reilly *et al.* (in preparation).

In a subsequent paper, Van Metre *et al.* (2009) again used a double ratio plot to display sediment data from 9 lakes and dust/scrapings data collected from parking lots and driveways in the vicinity of some of these lakes. This time, however, the plots and data were used to demonstrate a purported difference in ratios between samples collected in the Western U.S. versus samples collected in Central and Eastern U.S. As discussed in O’Reilly *et al.* (2012), the range of PAH ratios in samples collected from 10 ponds in the Minneapolis area is similar to the range of ratios in samples from nationwide locations presented in Van Metre *et al.* (2009), indicating that the apparent geographic differences in ratios is likely an artifact.

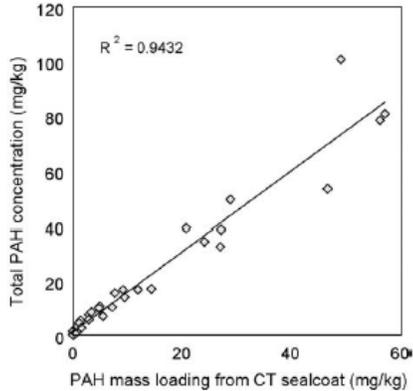
Instead of using one of the well-studied PAH fingerprinting methods to identify samples alleged to be influenced by RTS in the 9 lakes paper, the authors assert (not for the last time) that an elevated PAH concentration in a sample *must* indicate the “use of coal-tar-based sealcoat on this lot” (Mahler *et al.*, 2009, p. 21). This type of assumption and circular reasoning does not reflect sound scientific methodology. Indeed, the authors fail to mention that in a previous study of these lakes (Van Metre *et al.* 2000), they concluded that changes in PAH concentrations and chemical profiles were linked to increased automobile use within the respective watersheds.

USGS Studies of PAHs in Sediments: The 40 Lakes Study

In a 2010 study of 40 lakes across the country (Van Metre & Mahler, 2010; a/k/a the “40 Lakes Paper”), the USGS research team expanded its effort to determine the extent to which RTS contribute PAHs to urban sediments. O’Reilly *et al.* (2011) was a comment on the methods of PAH source identification and apportionment used by the USGS research team not only in the previously mentioned 9 Lakes study, but also in the 40 Lakes Paper. Van Metre and Mahler were given an opportunity to respond in the same journal at the same time (Van Metre and Mahler, 2011). The table below summarizes the comments and responses:

	COMMENT (O’Reilly <i>et al.</i> , 2011)	RESPONSE (Van Metre & Mahler, 2011)
1.	Results for individual samples are not consistent between papers on this topic by the same authors.	Stated that overall conclusions are consistent between the papers, apparently agreeing that individual results are inconsistent.
2.	To validate results of any single source apportionment method, run and compare multiple methods in one study to determine if results are consistent.	Without factual support, stated that different methods used with different data in separate studies to reach the same conclusion.
3.	Cited Stout & Graan (2010) as an example of a multi-forensic method investigation, and the types of expected results.	Did not address the point that Stout & Graan is an example of internal consistency within a multi-method forensic analysis, but did claim that Stout & Graan might have recognized the role of sealers if they had been considered.
4.	There is a poor correlation between the results of double ratio plot analysis and the CMB model used in the 40 lakes study. For example, only about 50% of the samples they modeled to be >75% sealer-derived PAHs have PAH ratios claimed to be diagnostic for sealer impacts.	Restated the data a different way and claim the restatement shows the original statement to be right.
5.	Cited Ahrens & Depree (2010) as an example of the expected relationship between PAH ratios and percent contribution	Dismissed Ahrens & Depree result as hypothetical and not expected for environmental samples. As Ahrens & Depree was a discussion of environmental

	COMMENT (O'Reilly <i>et al.</i> , 2011)	RESPONSE (Van Metre & Mahler, 2011)
		samples, the response seems to miss the point. The response did not address why there is no relationship between PAH ratios and percent concentration even for samples claimed to be almost all sealer.
6.	Explained concerns with application of the CMB model because of issues with source sufficiency and stability. Cited Galarneau (2008) as a paper that highlights the potential pitfalls of applying receptor modeling to PAHs.	Stated that the comment on “sufficiency and stability” was too vague to respond. Claimed it does not matter as Galarneau was focused on atmospheric modeling not sediment. Among other things, this response ignores that emissions were used as an alternative sources, and emissions are subject to atmospheric processes. Also ignores that the CMB was developed as an atmospheric source allocation model, and not as a sediment evaluation model.
7.	Combustion emissions were used as the CMB sources, but reactions that change PAH profiles were not taken into account.	Ignored the differences between fresh emission sources and post atmospheric reaction depositional particles
8.	Suggested application of multivariate methods such as PCA that do not require pre-identification of sources.	Stated that multivariate methods do require that sources be identified. Ignoring the difference between methods where sources are identified upfront and those that use the results of analysis to identify sources. Claimed that Watts et al (2010) use of PCA supported their conclusions. But, Watts only looked at samples taken from within a limited test area and considered sealers as the only source.
9	The null hypothesis was not tested, so atmospheric deposition as a primary source was not eliminated.	Restated claims from previous papers, in which the same authors concluded sealers were an important source of PAHs. Provided a circular argument referring to the figure below from Van Metre & Mahler (2010) in which sample concentration is a used to calculate both the X and Y axis:

COMMENT (O'Reilly <i>et al.</i> , 2011)	RESPONSE (Van Metre & Mahler, 2011)
	

Ultimately, the conclusion offered by O'Reilly *et al.* (2011) in their Comment to the 9 Lakes Study and 40 Lakes Paper is worth repeating:

In papers published in ES&T, PAH ratios were used to link PAHs associated with CT-sealed parking lots to urban sediments. Without this evidence, there is little basis for claims regarding the relative role of CT-sealants, and less for the use of such superlatives as the “dominant” source or “substantial” contribution. While the points raised in this commentary do not eliminate CT-sealants as a potential PAH contributor in some urban systems, we suggest that the authors apply and compare the results of multiple source characterization techniques including sample chemistry (PAH ratios and concentration histograms), receptor models, and multivariate methods.

Indeed, one of the primary flaws readily apparent in Van Metre and Mahler (2010), and in other USGS publications about RTS, is the temptation to confuse chemical similarity with causation. For many years, there has been a broad consensus that the PAH profile of urban soils and sediments is dominated by pyrogenic PAHs (*e.g.*, Boehm, 2006; Kay *et al.*, 2003; Mauro *et al.*, 2006; Stout *et al.*, 2004; Stout & Graan, 2010). Parsing the relative contributions of pyrogenic sources has numerous challenges which are routinely minimized in publications to date by the USGS-led research team. Quite simply, demonstrating that sealers are more similar to certain urban sediment PAH profiles than other sources of PAHs does not demonstrate that sealers are a “dominant” source.

In the 40 Lakes Paper, the USGS research team overstates the applicability of the chemical mass balance (CMB) model. The USGS research team adapted the CMB model (now version CMB 8.2) developed by the U.S. Environmental Protection Agency (EPA) to identify and apportion potential sources of atmospheric pollutants. The CMB model is designed to fit various summations of sources to the receptor profiles (Coulter, 2004). If one potential source has a similar profile to the receptor, whereas other sources have dissimilar profiles, the

model will indicate a higher contribution of the similar source. Like many source apportionment methods, CMB is ultimately a similarity indicator. Such similarity is not proof that a proposed source is an actual source. One reason for applying multiple forensic techniques to a source apportionment exercise is that demonstrating consistency among methods strengthens the weight-of-evidence that a proposed source is a probable source.

The CMB model was developed by EPA as an aid to identification of potential sources of air pollution in atmospheric studies, not for source apportionment of chemical components in sediments. The CMB model has been used in a number of published sediment evaluations, but conclusions reached based on CMB output are usually confirmed using other apportionment tools to validate that the input parameters used result in solutions consistent with the system under investigation.

Application of the CMB model requires use of appropriate source profiles as input. Published examples of using CMB to evaluate sediment are focused on individual watersheds (see Attachment for summary of examples). The USGS approach of using a single set of general source profiles for a nationwide sample set is not consistent with model assumptions. For example, in companion papers evaluating PAH sources in Chicago's Lake Calumet, Li *et al.* (2003) and Bzdusek *et al.* (2004) calculated different model outputs. Specifically, they calculated different fractional contribution scenarios from different potential PAH sources arrived at by using 9 different CMB and 2 different factor analysis model runs (Figure 4). Using different source profile inputs for different runs demonstrates how sensitive model outputs are to model inputs. For example, PAHs from "traffic" sources (identified on Figure 4 as traffic, tunnel air or diesel) results in modeled fractional contributions ranging from about 15% to over 60%, depending solely on the source input profile used.

In the 40 lakes paper, it is stated that "The CMB model was run more than 200 times using various combinations of source profiles, fitting parameters (PAHs), estimates of uncertainty, and combinations of lake-sediment samples." (p. 337) Out of the 200 runs, Van Metre and Mahler chose 4 that most closely matched the parameters chosen to represent a "good fit" for the 5 PAH sources chosen as source inputs, and then reported fractional contributions using an average of results of the 4 chosen source input models. It may be possible to evaluate the sensitivity of source profile inputs and graphically show results of the sensitivity analysis if data for all 200 model runs (or for that matter, even for the 4 chosen model runs) considered as source input models for the 40 Lakes Paper are made available in response to the FOIA request (Kurfirst, 2011). In the

meantime, the data on the sensitivity of calculated fractional contribution results on different source inputs in a local watershed, as developed by Li *et al.* (2003) and Bzdusek *et al.* (2004), and as illustrated in Figure 4, must serve as a sensitivity barometer for the 40 Lakes Paper.

As illustrated in Figure 4, use of the CMB model to estimate fractional contribution of different sources requires use of appropriate source profiles as input. Other researchers have published examples of using CMB to evaluate potential sources of PAHs in sediment – much as the Lake Calumet study discussed above – but these studies are focused on individual watersheds. The approach in the 40 Lakes Paper is to use a single set of general source profiles and apply them to a data set consisting of a small (but variable) number of samples collected at many locations nation-wide. Some of the studied lakes are dammed reservoirs which, like Town Lake (now called Lady Bird Lake) in Austin, Texas, has for at least a substantial part of its existence served as a cooling pond for an electric power plant.

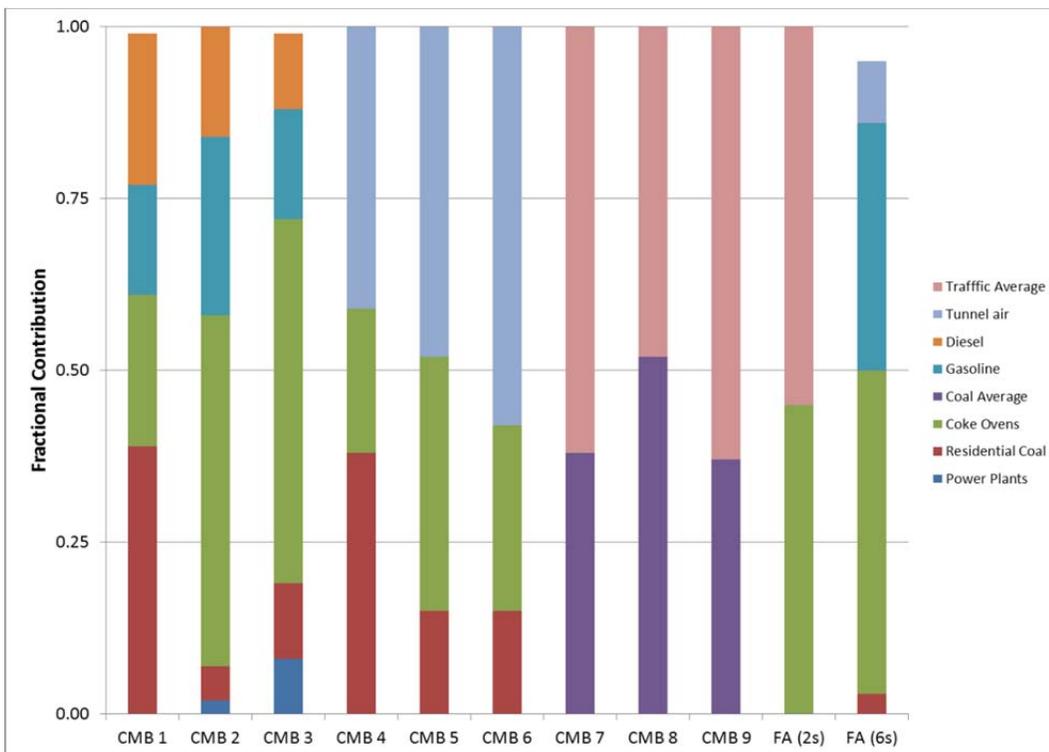


Figure 4. Fractional contribution of various PAH source types to sediment of Lake Calumet (Chicago, IL) based on nine CMB and two Factor Analysis model runs. Data from Li *et al.* (2003) and Bzdusek *et al.* (2004). Figure from O’Reilly *et al.* (in preparation).

The RTS research team’s application of the CMB model does not account for the expected variability in both source profiles and location-specific variables,

which further casts doubt on the consistency of model application with model assumptions. Furthermore, the 40 Lakes Paper has no negative controls. The USGS research team has not demonstrated that sediments with and without RTS effects can be accurately distinguished.

By using results of analysis of emissions in the USGS adaptation of the CMB model, the methods used to generate source profiles ignore the large changes in PAH chemistry that have been demonstrated to occur as a result of atmospheric processes. In the 40 Lakes Paper, a point is made of explaining why using weathered samples to represent sealer source profiles is important, yet the authors did not apply the same reasoning to other source profiles.

The CMB model has five key assumptions that are applicable to identification of chemicals in sediments (Coulter, 2004). As detailed in the table below, all five assumptions are violated in the adaptation and application of the CMB model described in the 40 Lakes Paper.

	CMB Model Assumption	USGS Adaptation
1	The composition of each source emission is consistent over the period modeled and, as applied to a nation-wide data set in the 40 lakes paper, over the geographic area modeled.	<ul style="list-style-type: none"> - No site specific emission data were used, so no measure of consistency over time or space is available. - The source profiles used were averages of published data with no indication of how representative they are of actual sources that may impact each of the 40 lakes. - The types of emission sources used are known not to be consistent, changing with fuel and process conditions.
2	Chemical species do not react with each other or the environment	<ul style="list-style-type: none"> - PAHs have been shown to react quickly in the atmosphere so emission chemistry should not be expected to represent depositional chemistry. The USGS CMB application ignored this factor. - PAHs in RTS weather, and may weather differently in different climates, which would result in changes in the PAH profile. Some possible effects of weathering were accounted for in the 40 Lakes Paper. - The combination of ignoring atmospheric

	CMB Model Assumption	USGS Adaptation
		changes while considering weathering effects increases the likelihood of identifying RTS as sources.
3	All sources that contribute significantly to the receptors have been identified and their profile is known.	<ul style="list-style-type: none"> - The USGS application considered a limited set of sources assumed to be applicable nation-wide. - It is highly uncertain whether the source profiles used as inputs in the USGS application represent actual sources in each/any/all of the sample locations.
4	The composition of each source is linearly independent of other sources	<ul style="list-style-type: none"> - The adaption and application of the CMB model described in the 40 Lakes Paper indicate a positive relationship between the mass of PAHs sourced by RTS and the mass sourced by other sources ($R^2=0.63$). Samples with more sealer also had more other sources. - This positive relationship is the opposite of the result expected if sealers were actually a source.
5	Measurement uncertainties are random, uncorrelated, and normally distributed	<ul style="list-style-type: none"> - As noted in the 40 Lakes Paper, this assumption could not be met with most input source data so a generic uncertainty factor (UF) of 40% was applied. - This UF value was based on analytical uncertainty, ignoring the inherent variability in the chemical profiles of potential sources, as well as geospatial variability. - Profiles based on a limited set of published data are not expected to be random, uncorrelated, or normally distributed.

Based on explanations in the methods section of the 9 Lakes Study and 40 Lakes Paper, it appears that, with the sole exception of pavement, most source profile inputs are not the chemistry of individual samples or sources but averages of published data. It is not clear whether these mathematically generated source

profiles represent actual sources in the watersheds for which conclusions about the percentage contribution by sealers were reached by the USGS research team. In a study of PAHs in sediments in nine urban waterways across the US, Stout *et al.* (2004) found differences in PAH distributions between and even within different urban settings, thus concluding that “there is no single ‘representative’ urban background...PAH signature.”

Averaging can make sense for duplicate samples of the same source, but averaging potential sources across wide geographic areas is not appropriate to represent what can be a very wide range of possible profiles for sources that may be similar in process but not in the many other parameters that influence PAH profiles. As demonstrated by the example shown in Figure 5, the profile for Source 1 is similar to the receptor but if it is averaged with Source 2, the resulting profile eliminates this relationship and results in a profile that doesn’t look like either source. The proper approach is to run the model with each source profile as inputs (O’Reilly *et al.*, in preparation).

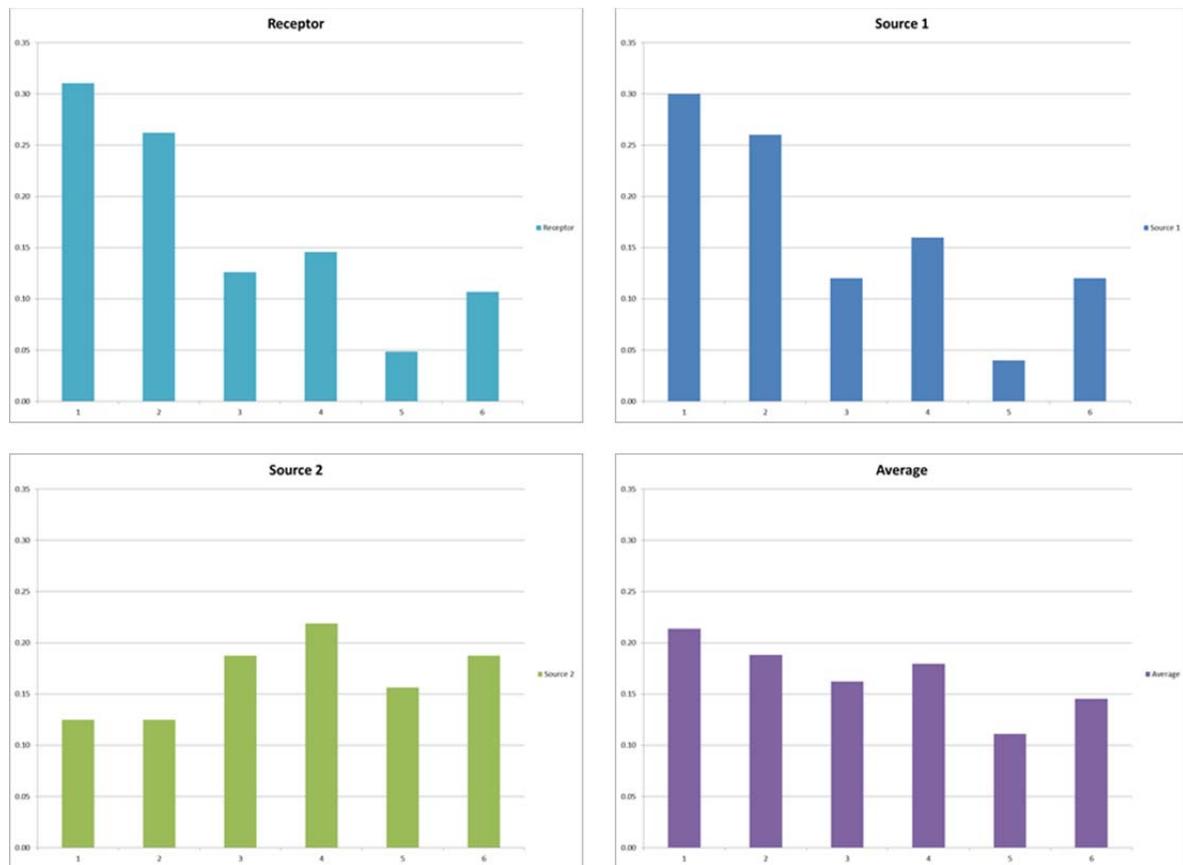


Figure 5. A hypothetical example of the effects of averaging PAH data. The profile for Source 1 is similar to the receptor but if it is averaged with Source 2, the resulting profile eliminates this relationship and results in a profile that doesn’t look like either source. The proper approach is to run the model with each source profile as inputs. (O’Reilly *et al.*, in preparation).

Comparison of Results of USGS Adaptation of CMB Model with Other PAH Source Apportionment Methods

O'Reilly *et al.* (2012) applied multiple well studied and commonly used source apportionment methods to evaluate the same data that was generated by the USGS. This must be contrasted to Van Metre and Mahler using just one method – the previously discussed adaptation of the CMB model – to try to identify sources of PAHs. Methods used by O'Reilly *et al.* included:

- Diagnostic double ratio plots, in which the ratio of two PAHs is plotted on the x-axis and the ratio of a second pair of PAHs is plotted on the y-axis and potential differences are identified by comparing the coordinates of samples to each other, to known sources, and to published values;
- Pearson correlations to evaluate similarities between PAHs in sediments and potential PAH sources;
- Principal component analysis (PCA) to compare sediment samples and suspected source materials; and
- Another EPA receptor model, UNMIX 6.0, to evaluate specifically the same data evaluated by Van Metre and Mahler (2010) using EPA's receptor model CMB.

O'Reilly *et al.* (2012) also emphasized the significance of the null hypothesis, ignored by the USGS authors in their body of work:

A hypothesis is a proposed explanation for observed phenomenon that is typically tested by attempting to demonstrate the null hypothesis. A hypothesis is supported if the phenomenon could occur only if the proposed explanation is correct, while the null hypothesis is appropriate if other explanations cannot be eliminated. The goal of this study was to evaluate the hypothesis that RT-sealers are a dominant (Mahler *et al.*, 2005) or substantial (Van Metre *et al.*, 2009) source of PAHs to urban sediments. The hypothesis would be supported if the PAH profile in the lakes studied could not be explained without inclusion of the sealants as a source. The results of this study indicate that while RT-sealer cannot be eliminated as a PAH source, sediment chemistry can be explained in the absence of any contribution from sealers. While VanMetre and Mahler's work has identified similarities between the PAH profiles of RT-sealer and urban sediments, such profiles are not unique, so the similarity does not prove that one is the source of the other.

In addition to results presented in O'Reilly *et al.* (2012), detailed forensic source apportionment investigation results have been presented at annual meetings of the Society of Environmental Toxicology and Chemistry (SETAC) and are the topic of papers in preparation. One set of results includes evaluations of PAHs in the lake sediments that are the topic of a web page in need of

correction. To use four of these lakes as examples, the table below summarizes the different conclusions reached by the USGS authors using only the USGS adaptation of CMB and by evaluation of the same data using multiple PAH source apportionment forensic methods.

Water Body	Percentage sealer, Multiple Forensic Methods	Percentage sealer, USGS Model
Lake Ballinger, WA	Little to None	~70%
Lake in the Hills, IL ²	Little to None	~70%
Newbridge Pond, NY	Little to None	~65%
Town Lake, TX ³	Little to None	~80%

The data in the above table is illustrated in Figures 5 and 6 below. Figure 5 contains results of PCA for the four lakes listed in the above table. The ranges of PAH values in none of the four lakes overlaps the range of PAH values in samples known to be directly derived from refined tar-based pavement sealer.

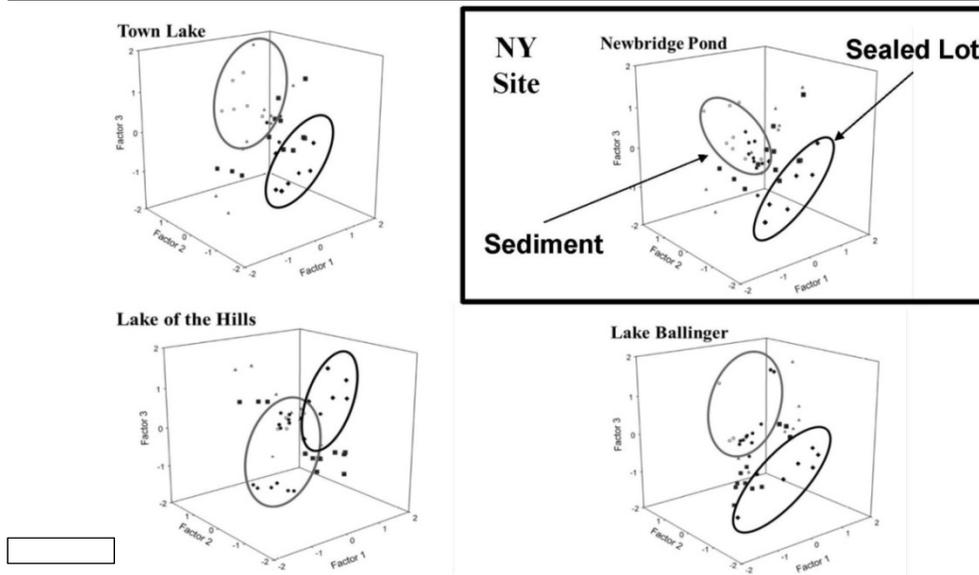


Figure 5. Three dimensional PCA plots of data from four lakes illustrating that none of the sediment data collected from the four lakes overlap data from RTS sealed lots. Data used are as reported in USGS publications. Rotating the Lake of the Hills plot reveals the absence of overlap. PCA analysis and plots courtesy of K. O'Reilly.

² Rotating the Lake in the Hills plot in 3 dimensions illustrates the absence of overlap between the fields.

³ Town Lake, now known as Lady Bird Lake, is located in downtown Austin, TX, and is a reservoir that formerly served as a cooling pond for the Holly Street Power Plant, located on the lake shore.

Figure 6 (Figure 4 of the 40 Lakes Paper) shows the source percentages calculated for each lake considered in Van Metre and Mahler (2010), highlighting the four lakes listed in the table above. It is interesting to note how PAH mass loading in Lake Ballinger (West region) was reportedly greater than what was found to exist in Lake in the Hills and Town Lake (Central region), even though the USGS asserts that RTS generally have not been used west of the Rockies.

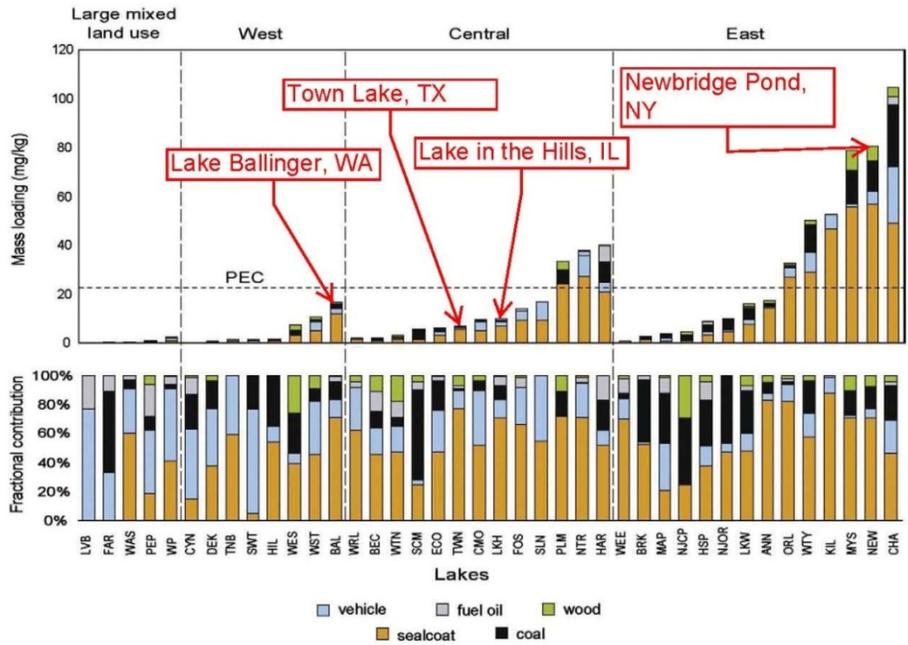


Fig. 4. PAH mass loading and fractional contribution from five source categories to Σ PAH (mean of four best CMB model runs). Lakes are grouped by region in order of increasing EPAH concentration. Horizontal dashed line indicates the probable effect concentration (PEC), the concentration of total PAH above which adverse effects to benthic biota are expected to occur (MacDonald et al., 2000).

Figure 6. Van Metre & Mahler (2010), with the four lakes discussed in the text and Figure 5 highlighted.

Conclusions

The data interpretation presented in the 40 Lakes Paper inherently lacks objectivity as no other possible solutions are considered, nor are conclusions presented in the context of the voluminous body of PAH source identification and apportionment literature that exists. All results in the 40 Lakes Paper are presented as though they demonstrate only the USGS hypothesis concerning RTS and no other conclusions are possible. Neither the null hypothesis nor any alternate hypotheses are considered. VanMetre and Mahler (2010) also ignore the uncertainty inherent in CMB results. Uncertainties should be quantified and discussed, and the sensitivity of outputs (fractional contributions) to different source profile inputs should be evaluated.

Other adaptations of the CMB model and similar approaches have been used in targeted evaluation of various individual watersheds. Attached to this White Paper is a summary of literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source. In all reviewed cases, sediment chemistry can be explained without including RTS as a source. Just as this does not prove that some sediments may be influenced by sealers, results of the USGS adaptation of CMB do not prove that sealers are a contributor to PAHs in sediments.

The USGS research team has used two methods to reach the conclusion that RTS is a “dominant” or “significant” source of PAHs in sediments in the United States: (1) the alleged similarity of between PAHs in double ratio plots of sample results of sealed pavement and unidentified sediment samples in Austin, TX (Mahler *et al.*, 2005) and (2) results of an adaptation of the CMB model. O’Reilly *et al.* (2011) pointed out that the two methods give inconsistent results, raising questions about whether reaching the same conclusion is warranted. O’Reilly *et al.* (2012 and in preparation) demonstrate that conclusions based on the CMB model as presented in the 40 Lakes Paper do not comport with conclusions reached evaluating the same data using other source identification and apportionment technique, including EPA’s UNMIX receptor model. The USGS has not and, based on their data, cannot demonstrate a link between PAHs in RTS and PAHs in most urban sediments. Communications to the contrary posted on the USGS web sites constitute a dissemination of information that does not meet the USGS standards for data quality.

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**PAVEMENT COATINGS TECHNOLOGY COUNCIL
WHITE PAPER 1301**

**CRITICAL REVIEW OF USGS CONCLUSIONS
REGARDING SOURCES OF PAHs IN LAKE SEDIMENTS**

ATTACHMENT



Literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source is summarized in the following table. These results are in conflict with the USGS's hypothesis that sealers are a widespread source of PAHs.

Citations for literature summarized in the table are as follows (numbers shown in first column of table).

1. Su, Ming-Chein, Erik R. Christensen, Jay F. Karls, Sailaja Kosuru, Ipek Imamoglu. 2000. Apportionment of Polycyclic Aromatic Hydrocarbon Sources in Lower Fox River, USA, Sediments by a Chemical Mass Balance Model. *Environ. Tox. & Chem.* Vol. 19, No 6, pp. 1481-1490.
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Summary of literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source. These results are in conflict with the USGS's hypothesis that sealers are a widespread source of PAHs.

Ref	Water Body	Source Characterization	Forensic Methods
1	Fox River (Green Bay, WI)	<p>Coke oven emissions are in the range of 40 to 90% of total PAHs, and this fraction decreases from 1930 to 1990, except in core Fox River-A (FR-A). The overall highway dust (HWY) contribution is between 10 and 75%, and this fraction increases from 1930 to present, except in core FR-A. The wood burning (WB) contribution (i.e., wood burning or coal gasification) is less than 7% in cores FR-B, FR-C, and FR-D. In core FR-A, a maximum (ø23%) is found around 1960. The contribution of wood burning has changed from less than 6% in 1950 to between 3 and 10% in 1995.</p>	<p>CMB with inclusion of biodegradation.</p>
2	Lake Michigan (Chicago, IL & Gary IN)	<p>The relative abundances of individual PAH compounds from Lake Michigan sediments, PM-10 aerosol of Chicago, and a coke oven signature are statistically similar establishing a linkage between combustion sources in the south, atmospheric deposition, and sediment accumulation. Further support for this linkage is the historical PAH accumulation in lake sediments and historical coal use in Illinois over the same time period. The major source of PAHs to Lake Michigan sediments is coke and steel production found in the urban/industrial complex around Chicago, IL, and Gary, IN. These PAHs are deposited primarily in the southern basin after which they are redistributed throughout the lake as a result of in-lake integration processes (water and sediment transport).</p>	<p>The relative distributions of 27 PAHs were calculated to assess the source(s) of PAHs to Lake Michigan. Sources contributing to PAH accumulations in sediments are assessed using the relative concentrations of individual compounds and comparing them to the relative amounts from specific sources either in the form of compound ratios or on the distribution of an entire suite of PAHs.</p>

Summary of literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source. These results are in conflict with the USGS's hypothesis that sealers are a widespread source of PAHs.

Ref	Water Body	Source Characterization	Forensic Methods
3	Chesapeake Bay	Most of the benz[a]anthracene, benzo- [a]pyrene, benzo[b]fluoranthene and their isomers in air, rain, and surface waters of Chesapeake Bay appear to be derived from automotive sources. Lesser, but still significant amounts (53%) of these PAHs in the sea surface microlayer near urban areas are motor vehicle-derived, with 47% being coal-derived. In contrast, PAHs in surface sediments of Chesapeake Bay are predominantly coal-derived (86%) and at most 14% motor vehicle derived. Thus, carcinogenic PAHs input to the bay from motor vehicles are either degraded prior to deposition to the sediments or are diluted by previously deposited coal derived PAHs in the seabed.	PCA, Ratio analysis. Photooxydation in atmosphere considered.
4	Lake Calumet (Chicago, IL)	Overall, the average contribution from coke oven emissions calculated by different operations ranges from 21% to 53% of all sources, and that from traffic ranges from 27% to 63%. The pattern of source contributions shows spatial and temporal variations.	Chemical Mass Balance (CMB) Model 8.2
5	Lake Ontario (Hamilton Harbor, ONT)	Both methods predicted similar contributions from coal tar/coal combustion sources to the harbor (19 and 26%, respectively). One PCA factor was identified as contributions from vehicular emissions (61%); PMF was able to differentiate vehicular emissions into two factors, one attributed to gasoline emissions sources (28%) and the other to diesel emissions sources (24%). Overall, PMF afforded better source identification than PCA with MLR.	Principal component analyses (PCA) with multiple linear regression analysis (MLR) and positive matrix factorization (PMF).

Summary of literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source. These results are in conflict with the USGS's hypothesis that sealers are a widespread source of PAHs.

Ref	Water Body	Source Characterization	Forensic Methods
6	St. Lawrence River (from outflow of Lake Ontario to Massena, NY)	The sediment inventory of PAH is characterized by the dominance of 4 to 6 ring parent compounds, with the PAH ranging from 0.8 to 6700 mg/g. The high abundance of high molecular weight parent compounds, high parent/alkylated PAH ratios and ¹³ C-enriched values recorded for individual PAH are consistent with a dominant combustion PAH source for the sediments upstream of the Massena area, but areas receiving higher petroleum contribution were also identified (e.g., Prescott-Ogdensburg, Cornwall). PAH contribution from aluminum smelting operations in the Massena area is pronounced in the southern bank of the St. Lawrence River, where sediment samples display the highest PAH and higher ¹³ C values for three ring PAH than for sediments immediately upstream. Thus, sediments at the international segment of the St. Lawrence River show localized enrichments in petroleum-related and aluminum smelter contributions against the regional backdrop of combustion-dominated PAH sources in sediments.	Alkyl-PAH compound specific stable isotope analysis (C13).
7	Elizabeth River (near Chesapeake, VA)		Principal component analysis (PCA), with identification of source-specific isomer ratios and compound-specific carbon isotope ratio analysis (CSIA).

Summary of literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source. These results are in conflict with the USGS's hypothesis that sealers are a widespread source of PAHs.

Ref	Water Body	Source Characterization	Forensic Methods
8	Black River (North-central OH) and Ashtabula River (NE OH)	FA results for a three-source solution indicate traffic (58%), coke oven (26%), and wood burning/coal tar (16%) are the primary PAH sources to Black River sediments. The primary PAH sources to the Ashtabula River sediments are traffic (51%), coke oven (44%), and wood burning (5%).	Factor analysis (FA) model with nonnegative constraints.
9	Lake Michigan (Milwaukee Basin)	PAH apportionment results indicate the dominance of coke oven emissions from 1925–1976, and of highway inputs from 1983–1992 for most of the seven cores. This is consistent with results of carbon particle analysis from the same basin. Milwaukee and Port Washington appear to be primary contributors of point source inputs of PAHs from coke ovens and highway dust. Wood burning is a minor source (<13%).	Chemical Mass Balance (CMB) Model
10	Little Menomonee River (Milwaukee, WI)	"In total, creosote and urban background contributed 27 and 73% (14%) of eight carcinogenic PAHs (CPAHs), respectively, in this part of the River. The concentrations of CPAHs derived from urban background were highest in surface sediments (0-6 in.; 20 (17 mg/kg), particularly near major roadway crossings, increased in the downstream direction, and (onaverage) exceeded the 15mg/kg regulatory cleanup threshold. Weathered creosote derived CPAHs were widespread at low concentrations (4.8 (8.1 mg/kg) although some discrete sediments, mostly at depths below 6 in., contained elevated CPAHs derived from creosote."	Principal component analysis (PCA), chemical fingerprinting, and positive matrix factorization (PMF).
11	Lake Michigan	Wood burning was identified as a third major source of PAHs in the area (20% of the total PAH flux). The other two sources petroleum (traffic), 45%, and coal (coke oven emissions), 35%, became more apparent, where the contributions are based on the sum of concentrations of 16 PAH compounds. A reduced mixing depth (1.0–1.5 cm) was found to be more appropriate than the originally estimated mixing depth (1.5–2.0 cm).	Factor analysis model with nonnegative constraints.

Summary of literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source. These results are in conflict with the USGS's hypothesis that sealers are a widespread source of PAHs.

Ref	Water Body	Source Characterization	Forensic Methods
12	Lake Calumet (SE Chicago, IL)	FA results for a two-source solution indicate coke oven (45%) and traffic (55%) are the primary PAH sources to Lake Calumet sediments. A six-source FA solution indicates that coke oven (47%) and traffic (45%) related sources are major PAH sources and wood burning-coal residential (2.3%) is a minor PAH source. From the six-source solution, two coke oven profiles are observed, a standard coke oven profile (33%), and a degraded or second coke oven profile (14%) low in phenanthrene and pyrene. Observed traffic related sources include gasoline engine (36%) exhaust and traffic tunnel air (9.3%).	Factor analysis model with nonnegative constraints.
13	Lake Anne, Lake Ballinger, Lake Fairfax, Lake Harriet, Newbridge Pond, Orange Reservoir, Lake Packanack, Palmer Lake, Town Lake, White Rock Lake (VA, WA, VA, MN, NJ, NJ, NJ, MN, TX, TX)	The assemblage of PAH compounds in the cores indicates a general shift in PAH source over the last 40 years from uncombusted to combusted fossil fuels, coincident with increased concentrations and urbanization. Uncombusted sources (e.g., oil seeps, petroleum spills) contain predominantly two- and three-ringed compounds, whereas combustion (e.g., vehicle exhaust, domestic heating with coal, forest fires) results in predominantly four- and five-ringed species. The results of this study is that urban growth or sprawl outside the watershed may adversely affect water quality within the watershed.	PAH concentrations linked to time of sediment deposition, profiles, evaluation of local land use.