Evaluation of USGS's Assessment of PAH Sources in Sediments of the San Antonio River Watershed

Key Finding

The City of San Antonio is concerned that refined tar sealers (RTS) may be an important source of polycyclic aromatic hydrocarbons (PAHs) found in sediments of the San Antonio River and its tributaries. This concern is based on the results of a study using an environmental forensic technique called chemical mass balance (CMB) modeling presented in the U.S. Geological Survey (USGS) report, "Assessment of selected contaminants in streambed- and suspended-sediment samples collected in Bexar County, Texas, 2007–09" (Wilson 2011). We evaluated the modeling effort described in the report, and found that the technical findings are subject to significant error due to a failure to include a complete and appropriate list of potential source inputs to CMB. The contribution of PAHs that the USGS report attributed to RTS was associated with a source sample of dust collected from RTS-sealed lots. When we use USGS data from <u>non-sealed parking-lot dust</u> (a source sample that the author did not use), we obtain essentially the same estimated contribution. This finding indicates that prior use of RTS on the parking lots was not a definitive contributing factor to determining PAH sources in sediments. When we replaced parking-lot dust with a source input derived from samples collected from an RTS test plot (therefore, unquestionably related to RTS), CMB-estimated PAHs in San Antonio River sediments contain, at most, a minor contribution from RTS. The conclusion of our evaluation is that USGS's claim concerning the role of RTS is not supported by the proper application of CMB modeling. No other data set or data analysis in the USGS report indicates that RTS is having a negative effect in the San Antonio River watershed.

Background

A website sponsored by the City of San Antonio (2014) states that the USGS report "*suggested that the largest source of PAH infiltration in local waterways came from coal-tar sealcoat dust emitted across paved parking lots*." The USGS report (Wilson 2011) describes an evaluation of the contaminant chemistry of sediment samples collected from the San Antonio River and tributary creeks in and around San Antonio, Texas. The classes of chemicals evaluated included metals, halogenated organics, and PAHs. The purpose of the study was to determine the occurrence and distribution of the compounds of interest, compare them to sediment-quality guidelines, and consider potential sources.

Wilson and her USGS colleagues, Van Metre and Mahler, have been investigating the role of RTS as a source of PAHs for over a decade (Mahler et al 2005; Van Metre et al 2009; Van Metre and Mahler 2010). While they have interpreted their data to suggest that RTS is an important contributor, the USGS's methods and conclusions have been called into question (DeMott et al 2010; DeMott and Gauthier 2006, 2010; O'Reilly et al 2012, 2014, 2015) and are the subject of an ongoing Information Quality Act evaluation (USGS 2016). Exponent has been following the USGS's research on the role of RTS as a potential source of PAHs in urban sediments since 2009 and was asked to evaluate claims made in the USGS report concerning the potential role of RTS as a source of PAHs in sediment of the San Antonio River watershed.

USGS Report

The report presented PAH results from two data sets, one from the USGS and the other from the US Air Force. The USGS data set includes the results of 35 streambed sediment samples collected from 20 locations, and 13 suspended sediment samples collected from 6 locations. It reports results of chemical analysis for 12 individual PAHs. The total PAH concentrations of these samples ranged from 56 µg/kg to 4000 µg/kg, with a median of 300 µg/kg. The Air Force data set included 145 samples measured for 12 PAHs. The total PAH concentrations of these samples ranged from not detected to 26,570 µg/kg, with a median of 246 µg/kg. A median concentration of 240–300 µg/kg indicates that San Antonio River watershed sediments are consistent with those expected for background concentrations in urban systems (Stout et al. 2004).

The USGS's claim concerning the relative contribution of RTS is based on application of EPA's chemical mass balance model. CMB was developed to evaluate sources of chemicals and particles in the atmosphere (Coulter 2004), but it has been used by the USGS (Van Metre and Mahler 2010) and others (Li et al. 2004) to estimate sources of PAHs in sediments. The inputs to CMB are the chemical profiles of proposed sources and the measured chemical concentrations of individual sediment samples. The model mathematically mixes the proposed sources to find the best fit between a mixture and each sediment sample. As described in the CMB manual (Coulter 2004), model output is sensitive to the specific source profiles selected by the user, and proper source selection is subject to a number of important assumptions.

Wilson's (2011) method for running CMB was consistent with that described in Van Metre and Mahler (2010) (i.e., the CMB paper). These USGS researchers identified more than 20 different source profiles, seven of which they claimed to represent RTS. Of these, five were either fresh or applied RTS material, and the other two were dust from parking lots the authors believed had been treated with RTS. Eleven of the remaining source inputs were products of the combustion of wood, coal, or petroleum, while the other sources were materials such as used motor oil or tire particles. All the source profiles consist of 12 PAH molecules with three to six rings. Van Metre and Mahler (2010) said they ran the model more than 200 times to test different sets of source inputs, but they focused their discussion on only four runs. In these four runs, the profile representing parking-lot dust was modeled to be a major contributor of PAHs. Since the model outputs generated using dust from RTS-sealed lots were not compared to those generated using dust from unsealed lots; therefore, the results presented in the CMB paper are insufficient to support the claim that RTS is an important source of PAHs.

Wilson ran CMB fifteen times using different combinations of seven of the twenty source profiles described in the CMB paper. Parking-lot dust from a subset of parking lots was again used as the "RTS source." The other sources were associated with coal combustion, vehicle emissions, motor oil, or tire particles. Actual RTS was not used as a model input. Wilson ran the CMB model on the nine USGS sediment samples in which all twelve PAHs were detected.

Using these test conditions, CMB estimated that the profile associated with parking-lot dust contributed over 70% of the PAHs.

Evaluation

CMB output is valid only if the proper source inputs are used. We have previously identified a number of problems with the approach that USGS used to characterize non-RTS source profiles by averaging widely variable values found in the literature (O'Reilly et al 2012, 2014, 2015). There is a method for assessing whether CMB source inputs may be appropriate for a given set of sediment samples. Principal component analysis (PCA) is a multivariate statistical approach for evaluating similarities and differences among samples in a data set. The output of PCA includes graphs in which samples that are similar plot closer together, and samples that differ significantly plot farther apart. Because of similarities in the underlying mathematical concepts of PCA and CMB, true mixtures of sources should plot within the PCA area bounded by the sources (Johnson et al 2004; Pasadakis et al 2008). In practice, this means that if one runs PCA with both the sediment samples and the proposed CMB source inputs, the sediment samples should plot within the area bounded by the sources (O'Reilly et al 2015; Saba and Su 2013).

In our evaluation we ran PCA and CMB on sediment data obtained from the USGS report. While that report only included nine sediment samples in its CMB model runs, we increased the number to 30 by including samples with four or fewer non-detects for the 12 PAHs used in USGS's modeling. Figure 1 shows the results of PCA that includes the 30 sediment samples and USGS's seven CMB source profiles. Almost none of the sediment samples plotted within the area bounded by the proposed sources. This means that it is unlikely that combinations of these source profiles could account for the actual PAH mixtures found in the sediment samples. It is interesting to note that the parking-lot dust sample is the source input that plots closest to most of the sediment samples. While this does not indicate it is a true source, it does explain why CMB calculates a good fit between it and many of the sediment samples.

The USGS used dust from parking lots thought to be treated with RTS to represent a RTS source input to CMB, but failed to run a control using dust from unsealed parking lots, even though the data to do so are available in an earlier USGS document (Van Metre et al. 2007). Using the 2008 USGS data, we generated a non-sealed-lot dust profile using the same approach they had used to generate their sealed-lot dust profile. To generate a source profile from a known RTS source, we used data that USGS collected from an experimental RTS test plot (Mahler et al. 2005).

As noted, there were some differences between the non-RTS source inputs used in the model runs highlighted in Wilson (2011) and those of Van Metre and Mahler (2010). Because of our previous experience with the combination of sources described as the inputs to Model A in the CMB paper, we used these for this evaluation, to allow comparison across more data sets. We ran four variations of this model using sediment samples from the USGS report. Four source inputs were kept constant, one each representing vehicle exhaust, and coal, fuel oil, and wood combustion. The fifth source input was varied using input values developed for three parking-lot-related sources: (1) dust from RTS-sealed parking lots, (2) dust from unsealed parking lots (Mahler et al 2007), or (3) samples from the USGS RTS test plot (Mahler et al 2005), representing source parameters that are unquestionably related to RTS. As a negative control, we ran a model variation using only the four constant sources without a parking-lot-dust or any other RTS-associated source. Figure 2 summarizes the results of our four CMB model runs for both Wilson's nine sediment and the 30 sediment samples. The first critical observation is that <u>RTS treatment history makes little difference in the relative parking-lot dust contribution from these CMB configurations</u>. In the two cases involving parking -lot dust (sealed and unsealed lots), the estimated contributions of PAHs from RTS were around 70%, which is consistent with Wilson's results. Second, CMB did not identify the PAH profile associated with USGS's RTS test plot as contributing more than a few percent of the PAHs found in San Antonio River sediments. The negative control demonstrates that CMB can fit the other sources to the sediment, whether or not a parking-lot dust or specific RTS source is included. Together, these results indicate that the CMB, as applied in the USGS report, does not support a claim that RTS is an important source of PAHs.

In addition to estimating the relative contribution of the various sources to each sediment sample, CMB calculates the PAH profile of such mixtures. While the model attempts to bring the measured and modeled profiles as close together as possible, given the constraints of the inputs used, there are typically some variations. Comparing these differences across the data set can help determine which model conditions may be better than others. We used Pearson correlation coefficients to compare the similarity between the measured and modeled PAH profiles for the CMB runs with parking-lot dust from either RTS-sealed or unsealed parking lots. For about half the samples evaluated (14 of 30), Pearson results suggested a better fit when the dust from RTS-sealed lots was used as the source profile (Figure 3). Using the unsealed-lot profile as the source resulted in greater similarity between measured and modeled profiles for the other half of the samples (16 of 30). These results indicate that the ability of CMB to fit the sediment samples is similar, whether or not the parking-lot dust profile came from RTS-sealed or unsealed parking lots.

Conclusions

The City of San Antonio is concerned that RTS may be an important source of PAHs found in San Antonio River and its tributaries. This concern is based on results of chemical mass balance modeling presented in Wilson (2011). Wilson's application of CMB to evaluate PAH sources is based on the approach of Van Metre and Mahler (2010). The goal of the earlier study was not to test a hypothesis concerning the role of RTS as a PAH source, but to identify a set of model conditions that would appear to implicate RTS.

In our evaluation of the USGS report, we found that:

- The set of source profiles used as CMB input are inappropriate for the San Antonio River sediment data set. PCA indicates that mixtures of the proposed sources could not account for the PAH profiles measured in many of the sediments.

- CMB estimates essentially the same source contribution from parking-lot dust, whether or not RTS had been used at the lots. The RTS use history of the parking lots does not affect the similarities between measured and modeled sediment PAH chemistry. While these findings suggest that the PAH chemistry of parking-lot dust, and potentially other urban dust, is similar to urban sediments, it does not support a claim about the relative role of RTS.

- CMB found, at most, a very small contribution for a source input based on RTS test plot data (Mahler et al. 2005). This further indicates that CMB results do not support the claim that RTS is an important source of PAHs in the San Antonio River watershed.

Figures

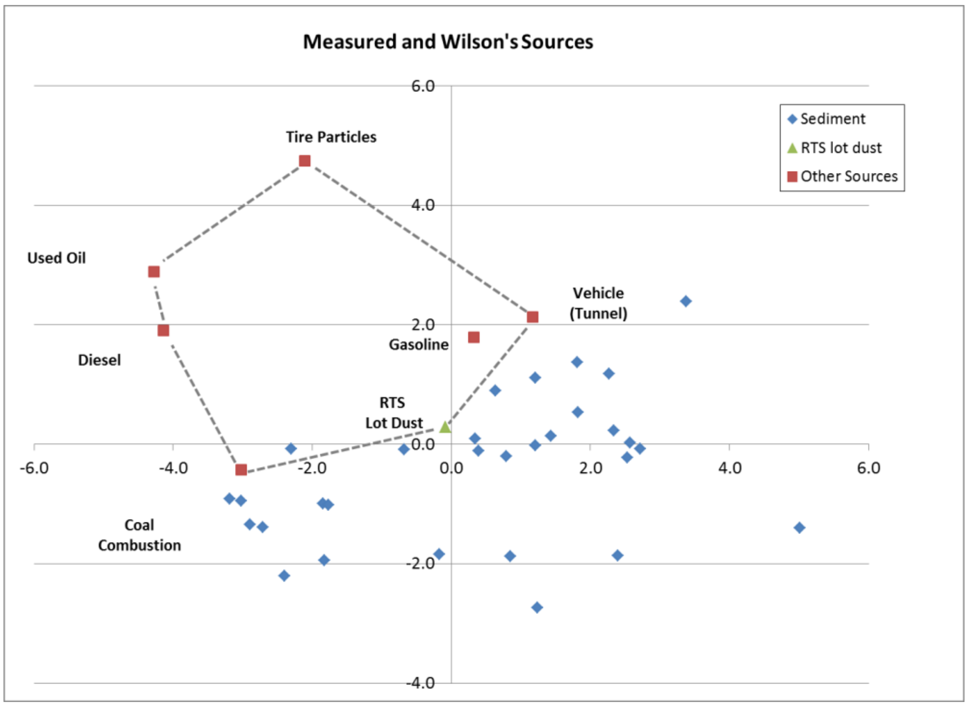

Figure 1. PCA plot of sediment samples and Wilson's (2011) CMB source. Few of the sediment samples plotted within the area bounded by the proposed sources.

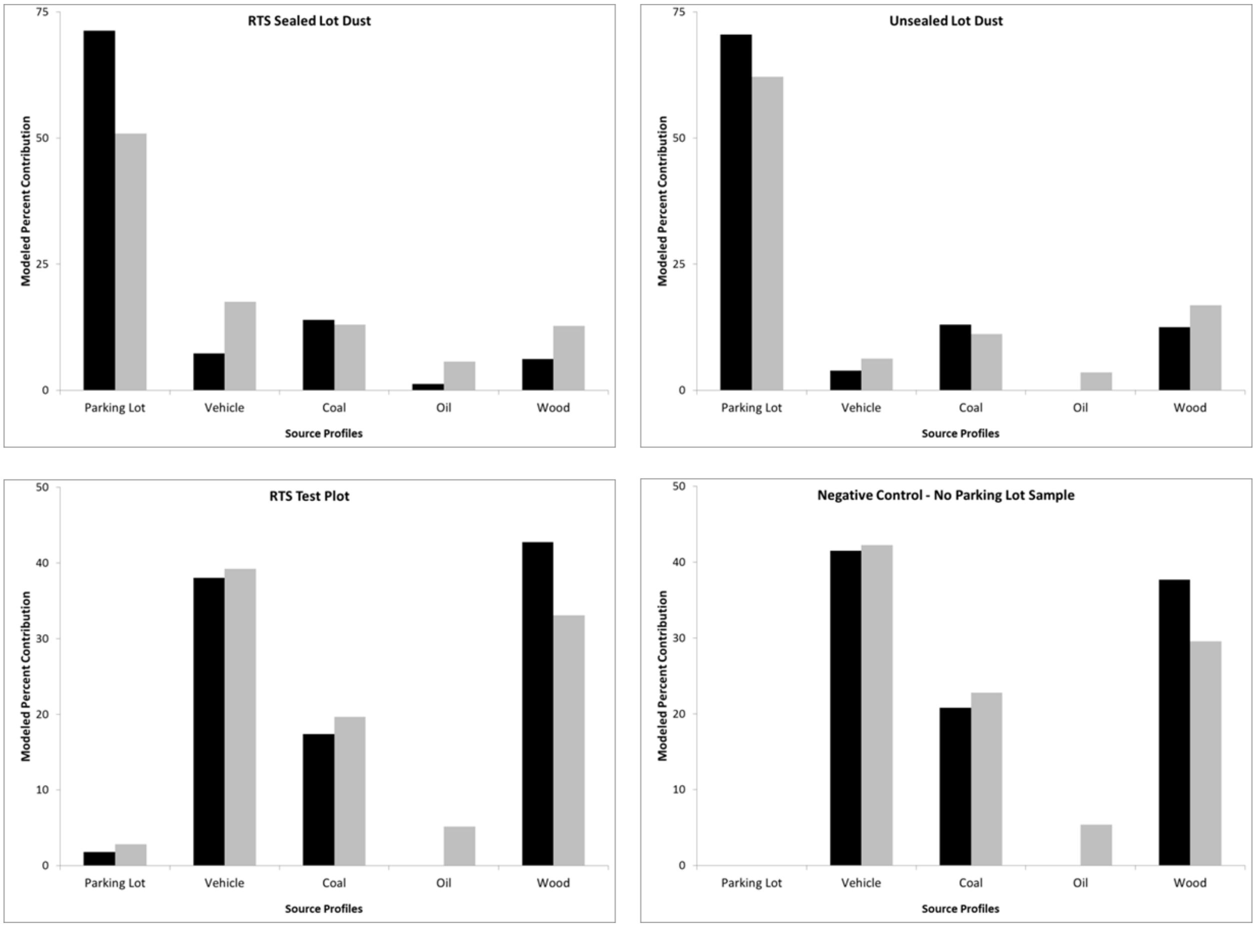

Figure 2. Average of CMB-estimated source contributions. The results for RTS-sealed and unsealed parking lots are very similar. The black bars are for nine sediment samples highlighted by Wilson. The gray bars are for the 30 sediment samples with four or fewer non-detects for the 12 PAHs.

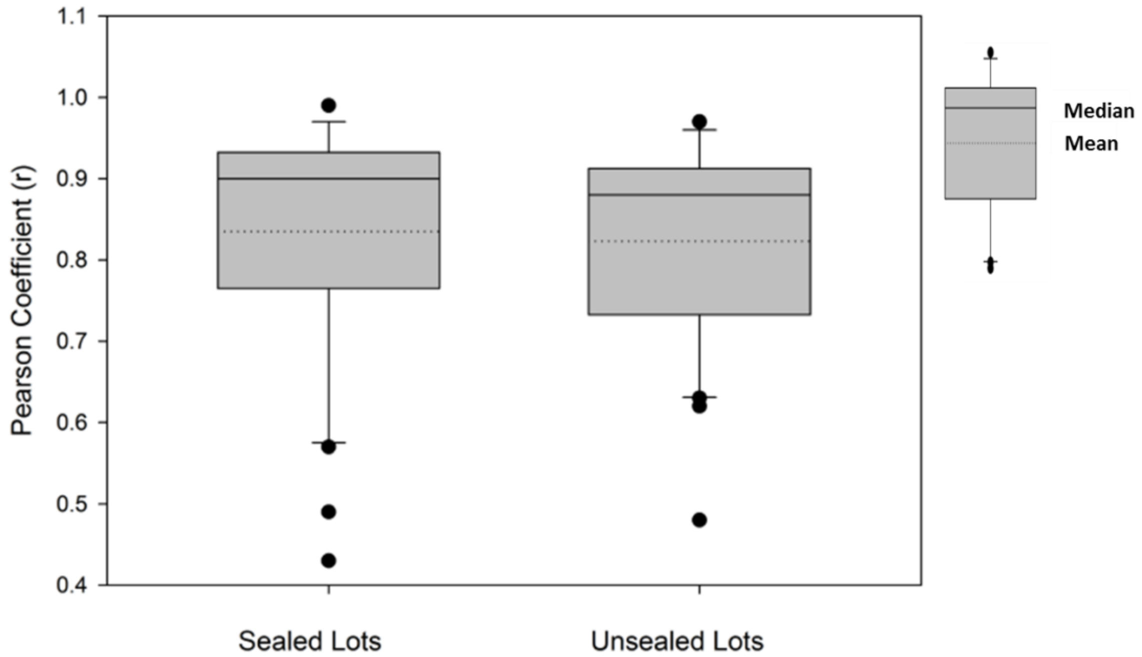

Figure 3. Comparison of the distribution of Pearson coefficients of sample-by-sample comparison (n=30) of measured versus CMB-estimated PAH concentration profiles using either RTS-sealed or unsealed parking-lot dust at a source input.

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