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Response

Response to authors' reply on "Coal-tar-based sealcoated pavement: A major PAH source to urban stream sediments"

I appreciate the editor's invitation to respond to Dr. Witter's reply to my letter to the editor, which concerned the article by Witter et al. (2014).

My point is that results of Witter's analysis do not support the claim made in the title, for the following reasons:

- Similarity in PAH profiles does not demonstrate causation.
- The PAH profiles of pavement sealers are not unique, but are similar to and overlap with those of other pyrogenic sources.
- Source contributions calculated by receptor models, such as EPA's Chemical Mass Balance Model (CMB), are valid only if the actual sources are known and their behavior meets model assumptions.
- Witter et al. (2014) did not demonstrate whether the literature-derived source profiles were appropriate or sufficient. Potentially important local sources were not included.
- Consideration of a negative control is important when evaluating a hypothesis about the role of a specific source.
- Witter's reply over-relied on the approach of Van Metre and Mahler (2010) while ignoring the vast body of literature on PAH source analysis.

Most of my letter focused on the application of EPA's CMB model. Witter's reply indicated that I did not provide sufficient information to respond to these comments. Like her, I stated that I applied the CMB using non-sealer source profiles described by Van Metre and Mahler (2010) and Witter's sediment data. From my reading of Witter et al. (2014), a difference in our approaches is that I used one of the Van Metre and Mahler sealer profiles, while it appears that she used an average of their profiles. Witter also excluded wood smoke as a source input, even though Van Metre and Mahler (2010) showed high correlation between smoke and sediment PAH profiles, and residential wood burning has been indicated as a major PAH source in some studies (Valle et al., 2007; WADOE, 2011). A key issue raised in the letter is that neither Witter nor Van Metre and Mahler presented the negative control of the CMB application. Because CMB calculates an excellent fit between mixtures of source profiles and the sediment data with or without inclusion of a sealant source, the results do little to support a hypothesis concerning the role of sealers as a PAH source. While beyond the scope of the letter, significant concerns exist as to whether the assumptions underlying CMB are met sufficiently to distinguish among similar PAH source profiles. I point the reader to Galarneau (2008) and O'Reilly et al. (2014) for more detailed discussions.

Witter claimed that she did not cite papers that presented opinions different from her hypothesis, because those papers did not present the "actual data used to draw the conclusion," even though O'Reilly et al. (2012) referred to the same sources of data used in her paper (compare Table 1 of O'Reilly et al., 2012 to Table 4 of Witter et al., 2014). O'Reilly et al. (2012) raises questions about the validity of using unweathered emission profiles but weathered sealer sources when evaluating their contribution to the weathered PAH profiles found in sediment. While consistent with most environmental science publications, DeMott et al. (2010) did not present the results for every sample analyzed, although it presented a significant amount of data. Witter claimed that she cited only the work of Van Metre and Mahler and their collaborators, because the USGS presents its data on-line. I found that the USGS required a formal Freedom of Information Act request and payment of thousands of dollars to obtain unpublished details of their CMB results. The comment about referenced sources in my letter discussed only papers dealing specifically with the sealer issue, but Witter et al. (2014) also failed to reference any of the key publications in the field of sediment PAH source characterization, such as Yunker et al. (2002), Stout et al. (2004), or Lima et al. (2005).

As Witter's reply states, I do support the use of multiple lines of evidence to evaluate chemical source contributions. But neither the GIS evaluation nor principal component analysis (PCA) provide any sealer-specific evidence, pointing only to the influence of land use on PAH sediment chemistry. As described by Witter, the inverse-distance weighting results—indicating that PAH sediment concentrations were not significantly correlated with either the total area of parking lots or their proximity to the sample locations—seem inconsistent with the sealer source hypothesis. An integrated multiple-lines-of-evidence approach would be to use PCA to identify potential source profiles that could be applied to CMB, or to include the source profiles used in CMB as inputs to the PCA. Using the sediment data presented in Witter et al. (2014), I was able to recreate the PCA results shown in their Fig. 4. I then reran the PCA but included the PAH source profiles used in Van Metre and Mahler (2010). While these may not be exactly the same as Witter's, they are derived from the same published sources. I also included an average source profile of three unweathered sealer samples. As shown in Fig. 1, the urban sediment samples are surrounded by the source profiles, suggesting that mixtures of these sources could account for the sediment chemistry. Specifically, the sediment samples are surrounded by pyrogenic sources derived from petroleum on one side, and pyrogenic sources derived from coal and wood on the other. Consistent with the CMB results summarized in Fig. 1 of my letter, these findings indicate that the sediment profiles can be explained without sealers being a PAH source.

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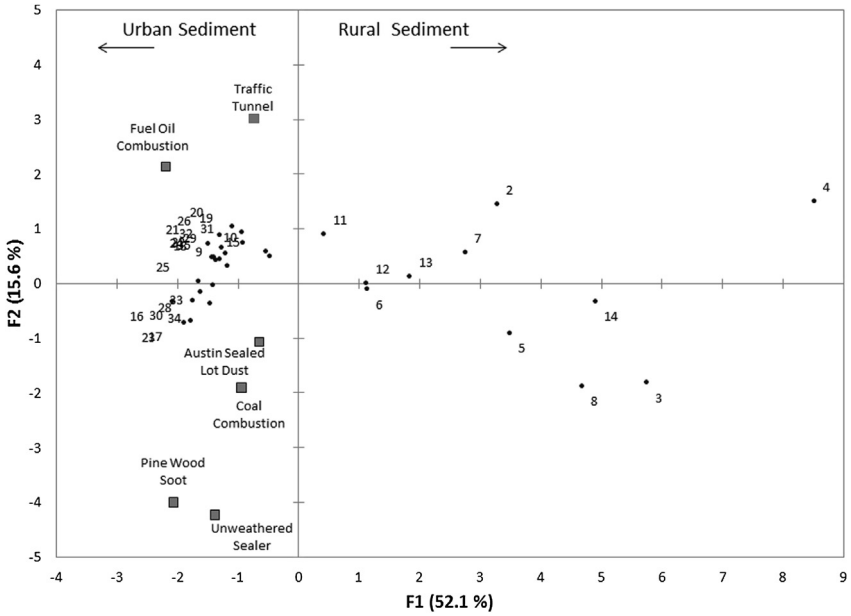

Fig. 1. Principal component analysis of the sediment data (numbered data points) of Witter et al. (2014) and CMB source inputs used by Van Metre and Mahler (2010). The results suggest that urban sediment PAH profiles are consistent with a mixture of pyrogenic sources derived from petroleum and pyrogenic sources derived from coal and wood.

Another problem with Witter's reliance on Van Metre and Mahler's approach for assessing the potential role of sealers is that it ignores the role of other coal tar sources. Industrial processes that produce coal tars include manufactured gas plants and coking operations, both of which have had long histories in Pennsylvania. An EPA-sponsored survey (U.S. EPA, 1985) indicated that three of the towns in the Conodoguinet Creek watershed, Carlisle, Mechanicsburg, and Shippensburg, had a manufactured gas plant in the past. The study also found that Pennsylvania had more of these sites than any state but New York or New Jersey. From the early days of the automobile, the wastes from such facilities were sometimes incorporated into road base, thus spreading the material throughout a region (Hubbard and Draper, 1911; Reinke and Glidden, 2007). The potential role of these sources was not considered by Witter even though they have been suggested as a potential source of PAHs in sediments (Ahrens and Depree, 2010).

In conclusion, while Witter et al. (2014) is an interesting study of the relationship between watershed land use and sediment PAH chemistry, the results do not support the claim made in the title concerning the role of pavement sealers.

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