Environmental Science & Technology Letters

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pubs.acs.org/journal/estlcu

Correspondence on Identification and Toxicological Evaluation of Unsubstituted PAHs and Novel PAH Derivatives in Pavement Sealcoat Products

The report by Titaley et al. in 2016 suffers from several methodological limitations that reduce its scope of inference. The refined coal tar-based (CT) sealer and scraping samples under study were prepared by the U.S. Geological Survey (USGS) in 2009.[1] Titaley et al. provide no details about how the samples were stored for 7 years or how and when they were transferred between laboratories. This adds uncertainty to the interpretation of time-course and toxicity findings because the integrity of the samples cannot be gauged. Van Meter et al.[1] reported collecting scrapings 1.6 h and 1, 5, 16, 45, 149, 232, 328, and 376 days after application. Titaley et al. present data for only four of the nine time points and provide no explanation for why all time point samples were not analyzed.

The concentrations of PAHs in Table S1 are at odds with the findings of Van Meter et al.,[1] which showed summed concentrations of U.S. Environmental Protection Agency's (EPA's) priority pollutant PAHs decreasing between the 1.6 and 24 h time points. In contrast, the sum concentration of these PAHs shown in Table S1 increases from the 1.6 to 24 h sample and then decreases. The sum PAH concentration reported by the authors for the 1 h time point is also 900% higher than the value reported by Van Meter et al.

Titaley et al. speculate that nitro-PAHs (NPAHs) and oxygenated PAHs (OPAHs) formed through phototransformation of PAHs in the sealcoat. Figure S2 shows concentration trends that do not support direct transformation to OPAHs. Because scrapings were collected from a sealcoated parking lot that was in use for up to 149 days and were not collected in replicate, it is impossible to determine if the apparent trend reflects photodegradation, is an artifact of the study design, or is due to the imprecision inherent in collection of scraping samples. An equally plausible explanation is that NPAHs and OPAHs from alternative sources were aerially deposited onto the sealcoated pavement. Reports by the Oregon State University laboratory and others support this hypothesis.[2−6] The reasons that concentrations of certain NPAHs and OPAHs increased over time might be identified in a more robust time-course study that includes collection of field duplicates as well as sampling of the underlying asphalt that was unaffected by sealcoating and either asphalt-based sealcoated pavement or untreated pavement.

Titaley et al. conclude that including additional MW-302 PAHs in the benzo[*a*]pyrene toxic equivalent (B[*a*]P-TE) calculation results in "greater potential risk to human health" compared to not including them. U.S. EPA's EPISuite software (version 4.1) estimates that MW-302 isomers are 65−95% less soluble than BaP and adsorb to organic carbon greater >10 times more strongly than BaP. The combined effect of these factors is expected to reduce bioavailable B[*a*]P-TE concentrations compared to the author's estimates.

It is suggested that MW-302 PAHs can serve as "unique molecular markers" for refined coal tar-based product use. Reports show that MW-302 PAHs are present in a variety of environmentally relevant matrices beyond refined coal tar-based sealants, including atmospheric particulate matter,[7−11] marine sediment,[9] diesel exhaust,[12] automobile tires,[13] urban dust,[14,15] and urban soil.[14] These reports call into question the specificity of MW-302 PAHs as markers for refined coal tar-based sealants.

Titaley et al. claim that the bioavailability of NPAHs and OPAHs is increased compared to that of PAHs. No data or citations are provided to substantiate the claim. Employing U.S. EPA's EpiSuite software (version 4.1) to estimate fish bioconcentration and skin permeability factors shows no evidence of increased bioavailability for NPAHs or OPAHs compared to that of their parent PAHs.

The study reports that laboratory extracts containing PAHs, MPAHs, and MW-302 PAHs are mutagenic. This is not surprising. However, it is surprising that the authors reached conclusions about the mutagenic hazard of whole refined coal tar-based products based on testing 11 discrete fractions that were prepared by removing "high levels of impurities" via solid phase extraction. The bioassay results are specific to solvent-dissolved fractions of the sealants that do not simulate realistic ecological or human exposure scenarios. It is outside the scope of inference of the experimental design to make statements about the mutagenicity of whole technical products. The whole products may have shown an antagonistic mutagenic response because of the "impurities" in the sealant products.[16−20]

The abstract of Titaley et al. states, "The Ames assay indicated that the asphalt-based product was not mutagenic, but the coal tar-based sealcoat products were. The zebrafish developmental toxicity tests suggested that fractions where NPAHs and OPAHs eluted have the most significant adverse effects." This statement strongly implies that refined coal tar-based sealants cause the strongest developmental effects in the zebrafish assay. However, a close inspection of the results in Figure S5 clearly shows that the asphalt-based sealant was the most toxic in the zebrafish assay of all products when either fraction C (heteroPAHs) or fraction D (NPAHs and OPAHs) was tested. The four scraping samples from the CT-1 product were 10 times less toxic than the asphalt product when fraction C was tested and 100 times less toxic than the asphalt product when fraction D was tested.

They concluded "that there is the potential for impact to aquatic organisms living downstream from pavement." The zebrafish assay involved dechorionating embryos prior to chemical exposure. The chorion shields developing embryos from the external chemical and physical environment.

Received: September 16, 2016
Revised: September 21, 2016
Accepted: September 22, 2016

DOI: 10.1021/acs.estlett.6b00360
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Removing the chorion maximizes the likelihood of seeing positive responses.[21] In contrast, guideline tests for evaluating fish embryo acute toxicity[22,23] do not include removal of the chorion prior to exposure. Thus, the data do not suggest potential impacts to aquatic organisms but rather show potential hazards that reflect a non-environmentally relevant study design. A more detailed discussion of all of these points is available elsewhere.[24]

Brian H. Magee*
Norman D. Forsberg
ARCADIS, One Executive Drive, Suite 303, Chelmsford, Massachusetts 01824, United States

AUTHOR INFORMATION

Corresponding Author

*E-mail: brian.magee@arcadis.com. Phone: (978) 322-4519. Fax: (978) 937-7555.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors declare that funding to prepare this correspondence was provided by the Pavement Coatings Technology Council (PCTC). The comments do not necessarily represent the official view of the PCTC.

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DOI: 10.1021/acs.estlett.6b00360
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