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Correspondence/Rebuttal

Response to Comment on "Parking Lot Sealcoat: An Unrecognized Source of Urban Polycyclic Aromatic Hydrocarbons"

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Response to Comment on "Parking Lot Sealcoat: An Unrecognized Source of Urban Polycyclic Aromatic Hydrocarbons"

We welcome the opportunity to address the issues raised by DeMott and Gauthier concerning our publication (*1*). We address their points in the order in which they present them. Here (as in the original publication), when we refer to total PAH, we are referring to 12 parent PAHs plus 2-methylnaphthalene, the PAH summation used for the consensus-based sediment quality guidelines (*2*) and denoted here as ΣPAH_{SQG}.

First, DeMott and Gauthier question our use of the benzo[*a*]pyrene:benzo[*e*]pyrene ratio (BaP:BeP) to compare PAH assemblages, citing the instability of BaP in the environment. Some degree of weathering is evident when the BaP:BeP ratio of 1.7 in the National Institute of Standards and Technology (NIST) standard reference material (SRM) 1597 ("complex mixture of PAHs from coal tar") is compared to the mean BaP:BeP ratios for scrapings from two surfaces recently (1 week) sealed with coal-tar based sealcoat (1.42 ± 0.12 SD), for scrapings from six surfaces with aged coal-tar sealcoat (2 months to 3 years) (1.21 ± 0.12), for particles in runoff from coal-tar sealed parking lots (0.92 ± 0.091), and for particles in stream suspended sediment (1.14 ± 0.20) (Figure S1, Supporting Information). (Data for computation of assemblage ratios, ΣPAH_{SQG} concentrations, and event ΣPAH_{SQG} stream suspended sediment loads are available in refs *3* and *4* and are included in the Supporting Information.) The ratios for the particles in the runoff and stream suspended sediment, however, greatly exceed the BaP:BeP ratio of 0.18 for diesel particulate matter (NIST SRM 1650a), which DeMott and Gauthier invoke as an alternative PAH source. If diesel particulate matter were the predominant source of the PAHs in the stream suspended sediment, then the stream sediment would have a BaP:BeP ratio similar to or less than that of the diesel SRM, not six times greater.

DeMott and Gauthier request substantiation of the comparability of the PAH data reported in ref *1* for the stream suspended sediments and the particulates in parking lot runoff. These data are for the same medium (suspended sediment), collected by the same agency (USGS), processed in the same way (filtration through PTFE filters), and analyzed by the same laboratory (the USGS National Water Quality Laboratory in Denver, CO). The extraction techniques differed in that the stream suspended sediment samples were extracted with dichloromethane in a Soxhlet extractor [any use of trace, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government] as described in refs *3* and *5*, and the parking lot particles were extracted using accelerated solvent extraction (ASE) with a mixture of water and isopropyl alcohol (*6*). The two methods provide comparable results (*6*) for the higher molecular weight PAHs, which dominate the parking lot runoff and stream suspended sediment samples. The Soxhlet extraction method tends to underreport concentrations of anthracene, naphthalene, and phenanthrene compared to ASE, but these PAHs account for only about 10% of the ΣPAH_{SQG} concentration of the samples reported in ref *1*. All extracts were analyzed by gas chromatography/mass spectrometry. Sample collection methods for the inflows to Lakes Echo, Como, and Fosdic are given in ref *3*, as cited in ref *1*. The Williamson Creek samples were collected using the same methods described for other Austin, TX, creeks in ref *5* and cited in ref *1*.

DeMott and Gauthier plot bed sediment data collected by the City of Austin together with data from ref *1* but have not substantiated that the data are comparable. The bed sediment sample medium, collection methods, collecting agency, and laboratory are different from those used for the parking lot runoff and stream suspended sediment samples. Further, DeMott and Gauthier have incorrectly plotted our data for the three types of parking lots (*4*); we direct readers to Figure 4 in ref *1* for the correct plot. More importantly, however, diesel exhaust particles cannot be the dominant source of the PAHs in at least three of the bed sediment samples in DeMott and Gauthier's figure, as the ΣPAH_{SQG} concentration in those samples exceeds that in the diesel particulate matter SRM by a factor of 1.3−8.8. The inability of diesel particulate matter to account for the PAHs in the environmental samples is even more striking if some of the individual higher molecular weight PAHs are considered. For example, of the bed sediments (DeMott and Gauthier's Figure 1) and the stream suspended sediment samples (*1*) in which BaP was detected (43 samples total), the BaP concentration in 36 of them exceeds that in diesel particulate matter (Figure 1). Coal tar has much higher concentrations of PAHs and BaP than diesel particulate matter. The coal tar used to create NIST SRM 1597 is about 44% ΣPQH_{SQG} by weight (436 000 mg/kg) and has a BaP concentration of about 13 800 mg/kg, easily accounting for even the highest concentrations measured in the environmental samples (Figure 1).

DeMott and Gauthier note that we might have overestimated parking lot related loading when we assumed that all particles mobilized from a surface enter the stream. However, we likely underestimated parking lot related loading by our accompanying assumption (stated in the same sentence) that our simulation of 2 mm of light rain was sufficient to mobilize all particles. Because of these assumptions as well as other uncertainties (e.g., analytical, extrapolation to unsampled lots), we showed a wide range of potential loading from parking lots (Figure 5 in ref *1*) and did not put a precise estimate on the contribution to storm loading from parking lots. We stand by our assertion, however, that particles from sealed parking lots could be dominating PAH loading in watersheds with commercial and residential land use in which sealants are in use.

DeMott and Gauthier incorrectly observe that storm loads of total PAH reported for the three Fort Worth sites in ref *3* are much greater than loads reported in ref *1* for the same sites and storms. They are trying to compare two different total PAH summations. In ref *3*, total PAH was expressed as the summation of 18 parent PAHs plus the homologous series of 2- to 5-ringed PAH (T-PAH) (ref *3*; p 12) whereas Mahler et al. (ref *1*; p 5562) used ΣPAH_{SQG}.

During review and compilation of data for this response, we found that some of the storm flows, which enter into the computation of storm loads used to construct Figure 5 in ref *1*, had been revised. We welcome this opportunity to publish the figure (Figure S2, Supporting Information) using the updated flows. The revisions do not change our conclusions regarding the comparison of estimated loading from sealed parking lots to storm loads in the streams. At three of the four sites the mean load estimated from sealed parking lots exceeds the geometric mean storm load. At the fourth site (inflow to Echo Lake) the estimated sealed parking lot load is less than the mean storm load,

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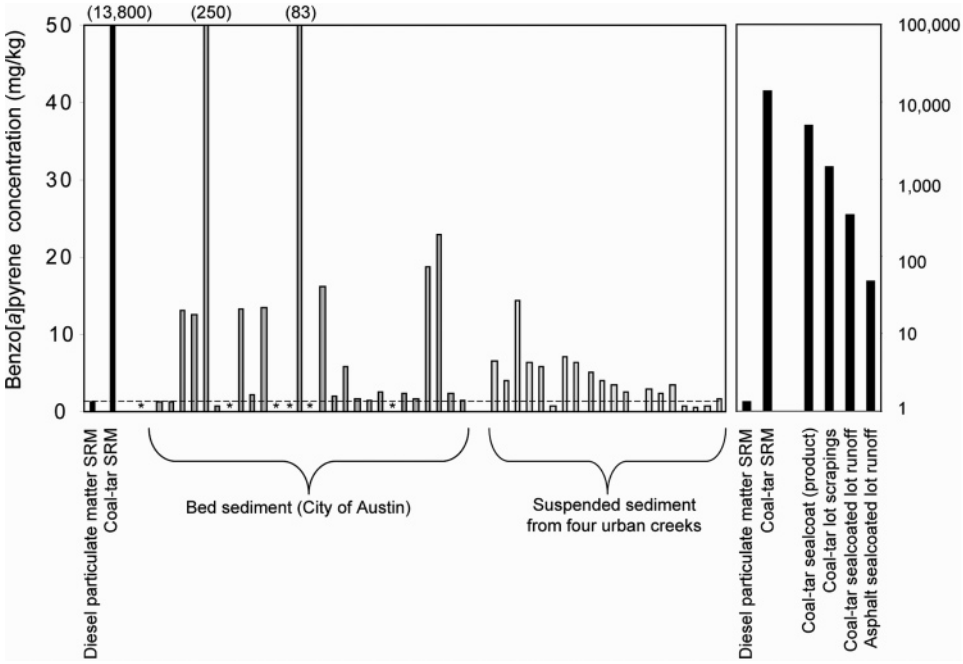

FIGURE 1. Comparison of benzo[*a*]pyrene (BaP) concentrations in coal tar and diesel particulate matter to concentrations in bed sediment collected by the City of Austin (as cited in DeMott and Gauthier) and in suspended sediment from Williamson Creek, Austin, TX, and three creeks in Fort Worth, TX (data in Supporting Information). The concentration in coal tar was computed from NIST SRM 1597 ("complex mixture of PAHs from coal tar"; note that this SRM is not pure coal tar but rather a coal-tar extract that has been diluted into toluene) and the concentration in diesel particulate matter is NIST SRM 1650a. Concentrations higher than 50 mg/kg are indicated in parentheses above the corresponding bar. The dashed line represents the BaP concentrations in the diesel particulate matter. The NIST SRMs also are compared to mean BaP concentrations in coal-tar based sealcoat products, scrapings from parking lots sealed with coal-tar based sealcoat, particles in washoff from parking lots sealed with coal-tar based sealcoat, and particles in washoff from parking lots sealed with asphalt-based sealcoat (*1*). *, not detected.

probably because there is much more extensive industrial land use there (*1*). Industrial areas could have additional PAH sources not found in commercial and residential areas.

The urban surfaces that contribute to nonpoint-source loading of PAH are parking lots, rooftops, roads, and driveways (*7*). Comparison of PAH yields from sealed lots to those from other sources supports the conclusion that sealed lots are a major source of PAHs to these watersheds. The mean yield of ΣPAH_{SQG} from sealed lots is 740 $\mu g/m^2$ and from unsealed lots is 14 $\mu g/m^2$ (*1*). All of the vehicle-related and atmospheric deposition sources noted by DeMott and Gauthier and identified by other researchers previously are present on both sealed and unsealed lots; the only factor that can account for the 50-fold difference in yield is the sealcoat. Van Metre and Mahler (*8*) quantified PAH washoff from rooftops in Austin using a methodology similar to that used in ref *1* and reported concentrations and yields of T-PAH. When recomputed for ΣPAH_{SQG}, the mean yield was 3.7 $\mu g/m^2$ (Van Metre, USGS, unpublished data), 200 times less than the yield from sealed parking lots. Similarly, Steuer et al. (*7*) found that for a watershed in Marquette, Mich., roads, rooftops, and driveways covered 12%, 13%, and 4.2% of the watershed area and contributed 18%, 4%, and 3% of the PAH load, respectively. In contrast, commercial parking lots covered only 4.6% of the watershed but contributed 64% of the PAH load; at least one of the parking lots studied was sealcoated (W. Selbig, USGS, personal communication, 2006).

The importance of the contribution of particles from sealcoated parking lots to stream PAH loads is not as surprising as it may seem: in the state of Texas alone, an estimated 20 000 tons (18 000 Mg) of coal-tar based sealants are applied to asphalt pavement every year (*9*); coal-tar based sealants contain in the range of 3.5−20% ΣPAH_{SQG} by weight (*1*); and sealcoat manufacturers recommend reapplication about every 3 years. The PAH assemblages, mass balance calculations, and yield comparisons all support our conclusion that sealed parking lots are a major contributor of PAHs to the urban watersheds studied.

Acknowledgments

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Supporting Information Available

Additional figures, tables, and references. This material is available free of charge via the Internet at http://pubs.acs.org.

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