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Personal Breathing Zone Exposures among Hot-Mix Asphalt Paving Workers; Preliminary Analysis for Trends and Analysis of Work Practices That Resulted in the Highest Exposure Concentrations

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Abstract

An exposure assessment of hot-mix asphalt (HMA) paving workers was conducted to determine which of four exposure scenarios impacted worker exposure and dose. Goals of this report are to present the personal-breathing zone (PBZ) data, discuss the impact of substituting the releasing/cleaning agent, and discuss work practices that resulted in the highest exposure concentration for each analyte.

One-hundred-seven PBZ samples were collected from HMA paving workers on days when diesel oil was used as a releasing/cleaning agent. An additional 36 PBZ samples were collected on days when B-100 (100% biodiesel, containing no petroleum-derived products) was used as a substitute releasing/cleaning agent. Twenty-four PBZ samples were collected from a reference group of concrete workers, who also worked in outdoor construction but had no exposure to asphalt emissions. Background and field blank samples were also collected daily. Total particulates and the benzene soluble fraction were determined gravimetrically. Total organic matter was determined using gas chromatography (GC) with flame ionization detection and provided qualitative information about other exposure sources contributing to worker exposure besides

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asphalt emissions. Thirty-three individual polycyclic aromatic compounds (PACs) were determined using GC with time-offlight mass spectrometry; results were presented as either the concentration of an individual PAC or a summation of the individual PACs containing either 2- to 3-rings or 4- to 6-rings. Samples were also screened for PACs containing 4- to 6-rings using fluorescence spectroscopy.

Arithmetic means, medians, and box plots of the PBZ data were used to evaluate trends in the data. Box plots illustrating the diesel oil results were more variable than the B-100. Also, the highest diesel oil results were much higher in concentration than the highest B-100 results. An analysis of the highest exposure results and field notes revealed a probable association between these exposures and the use of diesel oil, use of a diesel-powered screed, elevated HMA paving application temperatures, lubricating and working on broken-down equipment, and operation of a broom machine.

Keywords

asphalt paving emissions; personal-breathing zone; total organic matter; polycyclic aromatic compounds; diesel; biodiesel

INTRODUCTION

Hot-mix asphalt (HMA) paving workers can be exposed to polycyclic aromatic compounds (PACs) through inhalation and dermal exposure routes.^(1,2) The source of PAC exposures may include asphalt emissions as well as other workplace factors, such as the use of diesel oil and the exhaust from diesel-powered equipment. The concentration of PAC exposures may also be influenced by specific work practices.

As reported in a previous pilot study,⁽³⁾ a standard work practice in the HMA paving industry includes the use of diesel oil (a petroleum distillate ~C-10 through C-28) as a releasing/cleaning agent for tools and equipment. Companion publications using multivariate linear mixed effects models have identified both the use of diesel oil and HMA paving application temperature as determinants of airborne exposure,⁽⁴⁾ dermal exposure,⁽⁵⁾ and levels of urinary PAC metabolites.⁽⁶⁾

Use of diesel oil as a releasing/cleaning agent for the beds of dump trucks carrying HMA to the work site was largely discontinued years ago, because the diesel oil can easily solubilize asphalt causing flushed spots in the pavement that can negatively affect the quality of the finished mat. However, HMA paving crews have continued to use diesel oil as a releasing/cleaning agent to rinse down their paving equipment and tools such as shovels, lutes (or rakes), and putty knives. This occurs in various ways, either by squeezing out diesel oil onto the equipment from a plastic jug, spraying the equipment using a hose, or dipping the equipment in a container filled with diesel oil.

While use of diesel oil is particularly high at the end of the work shift when the paver is rinsed for the night, diesel oil is used to a lesser extent at the beginning of and throughout the work shift. The diesel oil is sprayed onto the hopper area of the paver or shuttle buggy

units, releasing substantial diesel oil fumes and vapors because the sprayed surfaces are still hot. (A shuttle buggy is a transfer device designed to keep the paver moving continuously.) Even when the surfaces are not hot, diesel oil fumes and vapors can be released when sprayed. The consequence of allowing the cold asphalt to accumulate without being cleaned off causes premature wear on the hydraulic motors that move the conveyors and augers on the asphalt equipment. Diesel oil is not only a good solvent for asphalt, but has the additional advantage of being readily available because the paver is powered by diesel fuel.

Diesel oil contains PACs⁽⁷⁾ and its contribution to HMA paving personal-breathing zone exposures has previously been noted. One study of road pavers in Hungary (Tompa et al.⁽⁸⁾) examined chromosomal aberrations (CAs) in blood samples and found that increases in CAs could be attributed to the presence of genotoxic agents other than those in asphalt emissions, mainly compounds in diesel exhaust and in the petroleum-based solvent used for cleaning the equipment. When use of this petroleum-based solvent for cleaning was restricted, levels of CAs fell to background levels, but CAs rose again when the workers returned to using the same petroleum-based solvent.⁽⁸⁾ Similarly, Weker et al.,⁽⁹⁾ in a dermal exposure study among asphalt pavers, showed that diesel oil may be a significant source of PAC exposure and a confounding agent in exposure studies during HMA paving applications. Another study by Boogaard⁽¹⁰⁾ concluded that co-exposures such as asphalt emissions and diesel oil contribute to elevated levels of urinary PAC metabolites. Burstyn et al.⁽¹¹⁾ have reviewed many determinants of exposures in the road construction industry including the influence of the use of hydrocarbon solvents as cleaners, and concluded that these solvents can be significant sources of PAC exposures.

In the current study we sampled 12 HMA paving workers over three consecutive days during four workweeks. During three of the workweeks, the HMA paving workers used diesel oil for a releasing/cleaning agent; however, during the fourth workweek, the HMA paving workers used biodiesel for a releasing/cleaning agent. For this article, the goals and objectives were to present the personal-breathing zone (PBZ) exposure data, discuss the impact of substituting the releasing/cleaning agent, and discuss work practices that resulted in the highest exposure concentration for each analyte.

METHODS

Study Design

We recruited four members of three HMA paving crews (12 total HMA paving workers) and four members of a concrete crew (reference group—workers who had no exposure to asphalt emissions and did not use diesel oil or B-100 as a releasing/cleaning agent) to participate in this study. The study was carried out during the 2008 paving season (June to October) and involved three asphalt paving crews and one Portland cement concrete crew. Each crew was comprised of four workers. Three of the four jobs in the asphalt crews were the same, i.e., the paver operator who ran the paving machine, the screedman, whose job it was to ensure the quality of the asphalt mat being laid down, and the raker, who followed behind the paver and made appropriate adjustments to the mat as necessary. The job title and function of the fourth worker varied for the three crews and included a foreman (who primarily worked as a screedman), a laborer (who helped with raking and many miscellaneous tasks), and a shuttle

buggy operator (who operated the remixing and storage device used to transfer HMA between the truck and the paver). Historically, within HMA paving crews, these were the members most highly exposed to HMA paving emissions. Each of the four concrete workers performed the same work (referred to as Workers 1, 2, 3, or 4).

Three construction companies were engaged in this study; one based in Wisconsin and two based in Indiana. Each HMA paving worker was sampled over three consecutive days during four workweeks (12 sampling days, total of 144 worker days). Each member of the reference group was sampled over three consecutive days during four workweeks (6 sampling days, total of 24 worker days). For each HMA paving crew, three of the 12 sampling days in one randomly chosen week involved using the biodiesel for a releasing/cleaning agent substitute (36 worker days) compared to nine of the 12 sampling days where diesel oil (108 worker days—note: one sample was lost) was used. Class A (large, highway-size) pavers with engineering controls were used on all but one of the 36 sampling days. A shuttle buggy was used by only one HMA paving crew and on 11 of the 12 sampling days. On the 12th sampling day, the study participant identified as the “shuttle buggy operator” instead operated a Bobcat compact tractor behind the paver most of the day. Sampling days were selected based on job/crew availability.

Asphalt binder types also varied within this study and included Superpave performance grades (PG) 64-22 (11.8 sampling days), PG 58-28 (22.4 sampling days), and PG 76-22 (1.8 sampling days). The standard nomenclature is PG XXYY; XX represents the seven-day maximum pavement design temperature (average), in °C, and -YY signifies the minimum likely pavement design temperature, in °C, that can be used without failure.⁽¹²⁾ This grading system assures that the asphalt binder has the fundamental engineering properties for a given climate, using various measures of the asphalt binder's flow properties to establish its grade.

During one workweek, diesel oil (normally used as a releasing agent and to clean tools and equipment) was substituted with biodiesel containing no petroleum-derived products and designated by convention as B-100—biodiesel 100%.⁽¹³⁾ Biodiesel consisted of long-chained alkyl esters derived from vegetable oil and animal fat. This B-100 consists of methyl soyate and rapeseed methyl ester (CAS numbers: 67784-80-9 and 73891-99-3) that was used as a substitute for diesel oil because it contained no PACs.

While sampling in the field, HMA paving application temperatures were monitored at the mat just behind the screed area periodically throughout the workday. A minimum of six different application temperature readings were collected per day using a HMA Lab Supply 8” Stainless Steel Dial Stem thermometer, with a 0–204°C range (HMA Lab Supply Inc., Richmond, Virginia; Catalog # TM-4500). Wind speed, air temperature, humidity, and other weather-related conditions were monitored twice during the first half of the sampling period and twice during the second half of the sampling period (four times per day) using a Kestrel 4000 Pocket Weather Tracker (Kestrel, Champlain, NY). Observations were recorded throughout the study, allowing association of work practices and environmental conditions with results. Ethical principles and guidelines for research involving human subjects were followed and the research protocol was approved by the National Institute for Occupational Safety and Health (NIOSH) Human Subjects Review Board.

Research for the entire study is fully described elsewhere.⁽¹⁴⁾ Cavallari et.al,⁽⁴⁾ have provided multivariate linear mixed effects models to identify predictors of inhalation exposure from this research.

Collection of Air Samples

Each worker wore a personal sampling train that included a 2- μ m PTFE 37-mm filter housed in a closed-faced cassette with a 4-mm inlet and a XAD-2 polymeric resin/charcoal tube connected in series.⁽¹⁴⁾ Using a personal sampling pump operating at 2 L/min, the time of sample collection continued over the entire work shift for each worker. To account for PACs in ambient air independent of asphalt paving or concrete work, one background sample was collected each day, positioned upwind of the paving operation or concrete work. Descriptive data were collected on potential confounders from the site, e.g., vehicle exhaust, construction dust, releasing/cleaning agents, and any other background interferences. Field blanks were also collected (one per day) to account for contaminant loadings, on the sampling media, that may have resulted from accumulative field and laboratory activities.

Of the 108 planned PBZ samples from HMA paving workers on days when diesel oil was used as a releasing/cleaning agent, only 107 were collected and analyzed because one air sampler could not be retrieved from the newly paved roadway when the sampler fell from the HMA paving worker. An additional 36 PBZ samples were collected from HMA paving workers on days when B-100 was used as a substitute releasing/cleaning agent. Twenty-four PBZ samples were collected from a reference group of concrete workers who also worked in outdoor construction but had no exposure to asphalt emissions.

Analytical Methods

For the filter portion of the sampling train, traditional gravimetric procedures using NIOSH Method 5042 were employed to quantify HMA paving worker exposure for airborne total particulates (TP) and the benzene soluble fraction (BSF) as described elsewhere.^(14,15) TP refers to the nonspecific gravimetric amount of organic and inorganic particles, and represents the total particulate that is collected on the filter and that passes through the 4-mm inlet of the sample cassette. BSF is the gravimetric amount of the TP that is soluble in benzene, is also nonspecific, and does not differentiate between sources of exposure. It is theoretically 100% of the organic fraction of the total particulate and includes aliphatic and aromatic compounds.

Separately, the XAD-2+charcoal portion of the sampling train was eluted with 10 mL of dichloromethane. With the charcoal at the top, the sorbent tube was vertically aligned just above a 10-mL volumetric flask and held in place with a rubber band. The top plug of glass wool was removed and dichloromethane carefully added to elute the organics retained on the sorbents until the 10 mL mark was reached. To obtain the total organic matter, five mL of this extract was combined with the BSF residue for all additional analyses. (Note: the BSF residue uses 1/2 of its extract.)

It is important to characterize the total organic matter since this corresponds to the fume condensates used in animal studies. Total organic matter (TOM) refers to the amount of

organics collected on the sampler (BSF and materials collected on the XAD-2+charcoal), ranging from C-6 through C-42 as determined by gas chromatography equipped with a flame ionization detector (GC/FID), described elsewhere,^(14,16) using a modification of EPA Method SW846–8015B.⁽¹⁷⁾ This method provided the amount and the chromatographic profile of these exposures. We quantified the TOM by comparison to the standard(s) most similar to the pattern detected from the airborne exposure; in this case, gasoline, kerosene, diesel oil, and lube oil.

A total of 33 individual PAC results were obtained using gas chromatography/time of flight mass spectrometry (GC/TOFMS) following the guidelines of EPA SW-846 8270C⁽¹⁸⁾ and a published procedure.^(14,19) A subset of these compounds are known or suspected carcinogens and their presence or absence in worker exposure helps to provide an indication of the hazard of emissions within the personal-breathing zone (PBZ).

PACs containing 4- to 6-rings (FL-PACs) were determined using a previously published fluorescence method.⁽²⁰⁾ The instrument, a Perkin Elmer LS 50 B fluorescence spectrometer, was set to 385 nm excitation and 415 nm emission making the results more selective for the PACs, in the sample, containing 4- to 6-rings than the PACs containing 2- to 3-rings and was calibrated using diphenylanthracene (DPA). Results were reported as DPA equivalents providing exposure concentrations for the workers. The fluorescence results were also normalized using the TOM data and reported as emission units per gram (EU/g), which was calculated as EU/TOM (g/mL) /10,000. This fluorescence method was specifically developed for asphalt fume emissions. The presence of asphalt binder and other confounders cannot be differentiated using this method. Although the fluorescence response for asphalt binder is different from the asphalt fume response, this screening method provides relative differences. Results below the detection limit ($\sim 0.04 \mu\text{g}/\text{m}^3$ air as DPA) indicate minimal exposure to PACs containing 4- to 6-rings. Detectable results require further investigation to determine the source of the 4- to 6-ring PACs because mixed exposures may be present. Typical paving emissions yield low fluorescence results because they contain little if any PACs containing 4- to 6-rings.⁽²¹⁾ An important distinction between the fluorescence method and the speciation of individual PACs by GC/TOFMS is that the fluorescence response also includes alkylated PACs that tend to be more prominent than their parent structures in these emissions.⁽²¹⁾

PBZ exposure data were summarized in box plots and individual data provided in supplemental tables. Results were summarized separately for the HMA paving group using either diesel oil or B-100 as a releasing/cleaning agent, for the reference group, and for the background samples and field blanks.

QA/QC was performed in accordance with each individually cited method. In cases where the arithmetic mean field blank was statistically significantly different from zero, blank correction was performed. Full details of blank correction and LOD determination are provided in Cavallari et al.⁽⁴⁾ and Kriech et al.⁽¹⁴⁾ Background samples were collected to understand the potential for environmental contributions; they were not used to correct sample data.

Data and Statistical Analysis

Because of limited sample size, expected variability based on previous experience conducting asphalt emissions research, and a literature review, we expected that we would need to statistically model the data. However, before putting data into a statistical model, we examined the data to assess “does this make sense?” and to see if patterns would start to unfold. We compiled tables of the data with various objectives in mind (some of those tables are included as supplemental tables). We calculated the arithmetic mean, median and standard deviations for various blocks of the data to quantitatively describe the results and determine whether there were any findings that could be uncovered without doing statistical modeling. The data also were graphed in a variety of ways to help assess trends. For this article, box plots (minimum, first quartile, median, third quartile, maximum, arithmetic mean, and error bars defining the 10th and 90th percentiles) have been included. Detailed field notes were collected for later review to determine if a particular work practice resulted in elevated exposure concentrations.

RESULTS

Field Observations

The median HMA paving application temperature during the 27 sampling days when workers used diesel oil was 139°C (range = 100–163) and was 143°C (range = 107 – 161) during the nine sampling days when B-100 was substituted for diesel oil. Median ambient air temperature was 18.6°C (range = –0.7 – 29.2) during sampling days when diesel oil was used versus 19.9°C (range = 11.9–27.5) when B-100 was used. Median wind speed was 7.4 kph (range = 0–21.6) during the sampling days when diesel oil was used and 5.8 kph (range = 0–18.9) when B-100 was used. Median relative humidity during the diesel oil sampling days was slightly lower: 56.0% (range = 24.0–100) when diesel oil was used and 64.6% (range = 40.6–96.0) when B-100 was used. All median and range values reported were determined using all of the daily observations collected during the work period only.

For the weeks when diesel oil was used, its use and estimated quantity and the use of other PAC containing products was documented. These records indicate a range of diesel oil usage from minimal usage (~0–1 gallons or 0–3.8 L) for some workers to ~10–15 gallons (38–57 L) in one day for one worker. All paving workers used diesel oil at least part of the time. The heaviest users of diesel oil were generally the paver operators and the worker who rinsed down the shuttle buggy hopper throughout the day. The person who sprayed down the screed area at the end of the day also used large quantities of diesel oil. Specific amounts of diesel oil used were not measured; the amounts reported in this study were estimated based on field observations or were based on usage information provided by the workers.

B-100 usage was similarly noted and was consistent in terms of who and why; however, the workers used less volume of B-100 as compared to diesel oil. This is likely because B-100 does not evaporate from the equipment surfaces as quickly as diesel oil. B-100 has no volatile components and its vapor pressure remains very low until it reaches the initial boiling point of ~300°C.⁽²²⁾ Diesel fuel, on the other hand, contains some volatile components and has a vapor pressure of 0.40 mg Hg.⁽²³⁾

Air Sampling

We analyzed all samples for TP, BSF, FL-PACs, TOM, $\Sigma 2$ -to 3-ring PACs, $\Sigma 4$ - to 6-ring PACs, and 33 individual PACs. Except for 9 of the 33 individual PACs for which too little data were available arithmetic means for all of these analytes are presented in Table I. Table I includes both the asphalt paving study group (with and without the use of diesel oil) and the reference group with background and field blank data summaries. Arithmetic means, geometric means, and range (minimum and maximum results obtained) for select analytes for HMA paving workers using either B-100 or diesel oil for a releasing/cleaning agent and the reference group are included in Supplemental Table 1. Except for the individual 33 PACs, individual analyte results for the HMA paving workers when diesel oil or B/100 was used as a releasing/cleaning agent are presented in Supplemental Table 2 and Supplemental Table 3, respectively. Except for the individual 33 PACs, individual analyte results for the reference group are included in Supplemental Table 4. The individual results for the 33 PACs tested in each sample are not included in Supplemental Tables 2–4 because of the large size of the dataset and the fact that many samples contained non-detectable concentrations for some if not most of the PACs. Similar summary statistics for background and field blank data are included in Supplemental Table 5.

Box plots shown in Figure 1 display the minimum, first quartile, median, third quartile, and maximum data for six analytes: TP, BSF, FL-PACs, TOM, $\Sigma 2$ - to 3-ring PACs, and $\Sigma 4$ - to 6-ring PACs (PAC summations are based on detectable results). Figure 1 includes representation of three groups; the HMA group that used diesel oil as a releasing/cleaning agent, the HMA group that used B-100 in place of diesel oil as a releasing/cleaning agent, and the reference group of concrete workers. Each box plot includes the actual median values and the arithmetic means for each analyte.

TP data were highest for the reference group, primarily from when the workers sawed concrete. BSF for the reference group was near the limit of detection (0.04 mg/m^3), and the median value was zero.

For asphalt paving workers, summary statistical data show no substantial difference in exposure to TP when either diesel oil or B-100 was used. For BSF exposures, the median data shown in Figure 1 are similar whether diesel oil or B-100 was used. However, the plotted data show a spread that includes much higher concentrations when diesel oil was used. The arithmetic mean data show a BSF reduction of 22% when B-100 was substituted for diesel oil. Likewise, the FL-PACs show a similar pattern on the box plots; however a 33% reduction is seen based on the arithmetic mean data, but only a 21% reduction when the median was used.

TOM, representing volatile and semivolatile organic compounds, shows median values to be about twice the concentration when diesel oil was used as compared to B-100 and a 44% reduction based on arithmetic mean data. Similarly, the $\Sigma 2$ - to 3-PACs, which are prominent in asphalt emissions exposures, showed median values to be about twice the concentration for diesel oil versus B-100 (arithmetic means show a 40% reduction). Median values for the $\Sigma 4$ - to 6-ring PACs show similar values regardless of the releasing/cleaning agent used, yet the arithmetic means show a 41% reduction when B-100 is used in place of diesel oil. In all

cases, diesel oil use showed consistently higher maximum exposure concentrations when compared to B-100 use and much higher variance. Differences in percent reductions are probably because arithmetic means are more influenced by variability in the data (see Figure 1) than median values.

Table II outlines the highest exposures detected for the HMA paving crews and the corresponding daily observations that may explain why they occurred. For the diesel oil use subset of HMA paving workers, a screedman had the highest TP exposure; a diesel-powered screed was used on this day (10-06-08). On this same day, when the diesel-powered screed was used, the shuttle buggy operator had the highest BSF exposure. The highest FL-PAC exposure was for the paving operator on 10-09-08 when a diesel-powered screed was being used in the morning for the base. Highest exposures for TOM, Σ 2- to 3-ring PACs, Σ 4- to 6-ring PACs occurred when the HMA paving workers were using large quantities of diesel oil as a releasing/cleaning agent.

Also seen in Table II, for the B-100 use subset of HMA paving workers, the highest TP exposure was due to the operation of a broom machine to prepare the road surface. The highest exposures for BSF, FL-PACs, TOM, and Σ 2- to 3-ring PACs were all measured on the same day, for the same crew, when the highest HMA paving application temperature was being used during the study (153°C, which was ~15°C higher than the arithmetic mean of all of the other paving days for that HMA paving crew). Finally, the highest exposure for Σ 4- to 6-ring PACs occurred when the foreman had to work underneath the HMA paver to make repairs and used lubricating oil. For all analytes measured, the highest exposures for the “diesel oil use” data were much higher than the “B-100 use” data.

For possible comparison to future worker exposure data, statistical summary data for the normalized fluorescence results reported as EU/g are included in Table I and Supplemental Table 1. Comparing the median, arithmetic means, or geometric means, the B-100 data show higher values than the diesel oil data. Since the TOM values were higher for the diesel oil data, this is expected. Similar to all other data, the spread of the EU/g results was larger for the diesel oil than the B-100.

DISCUSSION

In general, BSF personal-breathing zone exposures (Personal-breathing zone exposures from this point forward will be referred to as exposures) for HMA paving workers were below the American Conference of Governmental Industrial Hygienists (ACGIH[®]) threshold limit value-time weighted average (TLV[®]-TWA) of 0.5 mg/m³ as inhalable benzene-soluble aerosol⁽²⁴⁾ which has been shown to be equivalent to BSF of total particulate asphalt fume exposures.^(25,26) However, three HMA paving workers had exposures that exceeded this TLV[®] during a sampling day when the HMA paving crew used an older paver configured with a diesel-powered screed. These data, shown in Figure 1, are the highest three BSF points for diesel oil use (concentrations shown in Supplemental Table 2). All other HMA pavers used in this study were equipped with an electric screed (34 out of 36 sampling days). For over 15 years, large HMA paver makers have used electric screeds, eliminating the need for diesel-powered screeds and the resulting diesel exhaust fumes. In addition to BSF, use of

the diesel-powered screed also increased the concentrations of other analytical results. These results appear to support claims made by manufacturers of pavers that electric screeds reduce worker exposures. Some non-highway class, small HMA pavers still use diesel-powered screeds.

Since the TP for the reference group was high and the BSF for the reference group was near the limit of detection (0.04 mg/m^3), the implication for the paving industry is that TP and BSF do not necessarily correlate. When inorganic dust is present, you would not expect these two parameters to necessarily correlate. In cases where TP is strictly from asphalt emissions, BSF would correlate with TP.

In this study, a review of the study notes and exposures greater than the 90 percentile suggest that five modifiable work practices during hot-mix asphalt paving application may be associated with the highest breathing zone exposure concentrations. These five modifiable work practices are: use of diesel oil, use of a diesel-powered screed, elevated HMA paving application temperatures, lubricating and working on broken-down equipment, and operation of a broom machine.

Study results show that when HMA paving workers do not use diesel oil as a releasing/cleaning agent, their breathing zone exposures to TOM and PACs are reduced when B-100 is used instead. Use of diesel oil as a releasing/cleaning agent is currently widespread in the HMA paving industry. Based on an ongoing relationship with one of the HMA paving crews, it is known that the crew continued using B-100 after the completion of the study. It was observed in this study that the HMA paving workers used less B-100 than diesel oil, perhaps because B-100 does not evaporate as readily as diesel oil due to vapor pressure differences, as previously described. These properties, however, may have ramifications for facilitating transport of carcinogenic PACs through the skin, because B-100 stays on the skin longer than diesel oil. This possibility will be addressed in future publications.

The arithmetic mean HMA paving application temperatures and geometric mean results for TOM data from this study are compared to two similarly conducted studies. Kriech et al.⁽²¹⁾ data show TOM = 1.23 mg/m^3 and Kriech et al.⁽²⁶⁾ data show TOM = 1.41 mg/m^3 ; for both studies, the arithmetic mean HMA paving application temperature was 150°C . In the current study, the arithmetic mean data show TOM = 1.03 mg/m^3 at an arithmetic mean HMA paving application temperature of 139°C for diesel oil use. With B-100 use, the arithmetic mean data show TOM = 0.51 mg/m^3 at a HMA paving application temperature of 141°C . In each of these studies, the same sampling and analytical methods were used to collect and determine TOM. Except during the sampling days when B-100 was used in the current study, diesel oil was used as the releasing/cleaning agent for each of these studies. In addition, except for one sampling day in the current study, engineering controls were in use on the paving machines for all studies. Over the time period that these studies were conducted (i.e., 1998–2008), the arithmetic mean HMA paving application temperatures have decreased, supporting claims by industry that application temperatures are being lowered, when possible, as recommended by NIOSH.⁽²⁾ Averaging the TOM exposure data from the two earlier studies^(21,26) (1.32 mg/m^3) and comparing the result to our TOM

exposure data for when diesel oil was used shows an estimated TOM reduction of 22% and corresponds to an HMA paving application temperature decrease of $\sim 11^{\circ}\text{C}$.

Because the substitution of B-100 for diesel oil reduced TOM exposures by $\sim 50\%$ in the current study, it appears that the combination of the reduced HMA paving application temperatures ($\sim 9^{\circ}\text{C}$) and substitution of B-100 for diesel oil for these studies is responsible for the TOM exposure reduction. Use of B-100 in place of diesel oil appears to have a greater impact on reducing TOM exposures than HMA paving application temperature reductions alone.

Based on the box plots in Figure 1, relative to the reference group, except for TP, all the median values and most of the arithmetic means for each analyte were higher for the HMA paving workers than for the reference group. The median TP value for the reference group was elevated because they were sawing concrete and considerable dust was generated. As illustrated in Figure 1, use of diesel oil causes greater variance as compared to B-100. We also examined relationships using regression analyses of all analyte versus analyte combinations shown in Table III. Diesel oil would theoretically impact all the analytes studied and could contribute to the quantitation of reported results. Hence, there is an increase in the variation in both the x and y values which may explain the R^2 value decrease for each of those analytes in the diesel oil scenario. Eight out of the 12 comparisons have an R^2 of 0.22 or less.

On the other hand, except for possibly the TP and BSF results, B-100 would not have as much impact on any of the reported results. Because B-100 has less of an impact on the data for either the x or y values, one would expect a smaller impact on the R^2 values. Looking at Table III, 8 out of 12 comparisons have an R^2 of 0.52 or better. Specifically, comparisons between the FL-PACs, TOM, $\Sigma 2$ - to 3-ring PACs and $\Sigma 4$ - to 6-ring PACs when B-100 was used show R^2 values of 0.62–0.88, whereas when diesel oil was used these R^2 values were 0.01–0.48. All of these analytical methods can be used to assess exposure; Table III provides insight as to how these analyses may relate to each other when diesel oil or B-100 was used a releasing/clearing agent.

Exposure trends were examined here using descriptive statistics and were helpful. However, because of the variability of the results and that arithmetic means are more influenced by variability in the data than median values, analysis of median values and arithmetic mean values resulted in different conclusions regarding exposure reductions, emphasizing the importance of the statistically modeled data as reported by Cavallari et al.⁽⁴⁾ In addition to looking at the highest points, we looked at all data above the 90th percentile. Using a diesel-powered screed, using diesel oil, higher HMA paving application temperatures, maintenance work, and sweeping appeared to explain these results. Interestingly, the percentage of data above the 90th percentile followed this order: operator (35.9%), screedman (24.4%), shuttle buggy (19.2%), raker (12.8%), laborer (5.1%), and foreman (2.6%). This order is consistent with field observation data.

Results from this investigation emphasize the importance of documenting observations during sample collection including the HMA paving application temperatures and the use of

other products that may confound exposures. This study also shows that sampling and analytical methods that only collect particulates would have underestimated the HMA paving workers' exposures. The additional sampling and analytical methods used in this study allow collection of most organic exposures that occur, thus making it possible to identify many of the confounding exposures. These results will be discussed in future publications. Thus, the ability to reduce worker exposures is enhanced when all exposure sources are known.

These results support the idea that work practices do influence exposures. To minimize the possibility of high exposures during application of HMA paving, the industry should consider modifying five work practices:

1. Limit the use of diesel oil as a releasing/cleaning agent
2. Reduce HMA paving application temperatures
3. Limit the use of diesel-powered screeds
4. Consider the use of non-PAC containing lubricants during maintenance of equipment
5. Limit exposure to dust when operating a broom machine to prepare the road surface or consider adding engineering controls to minimize dust

These modifications should lower the high variation of exposures and help prevent approaching or exceeding the TLV[®], thereby minimizing workplace hazards.

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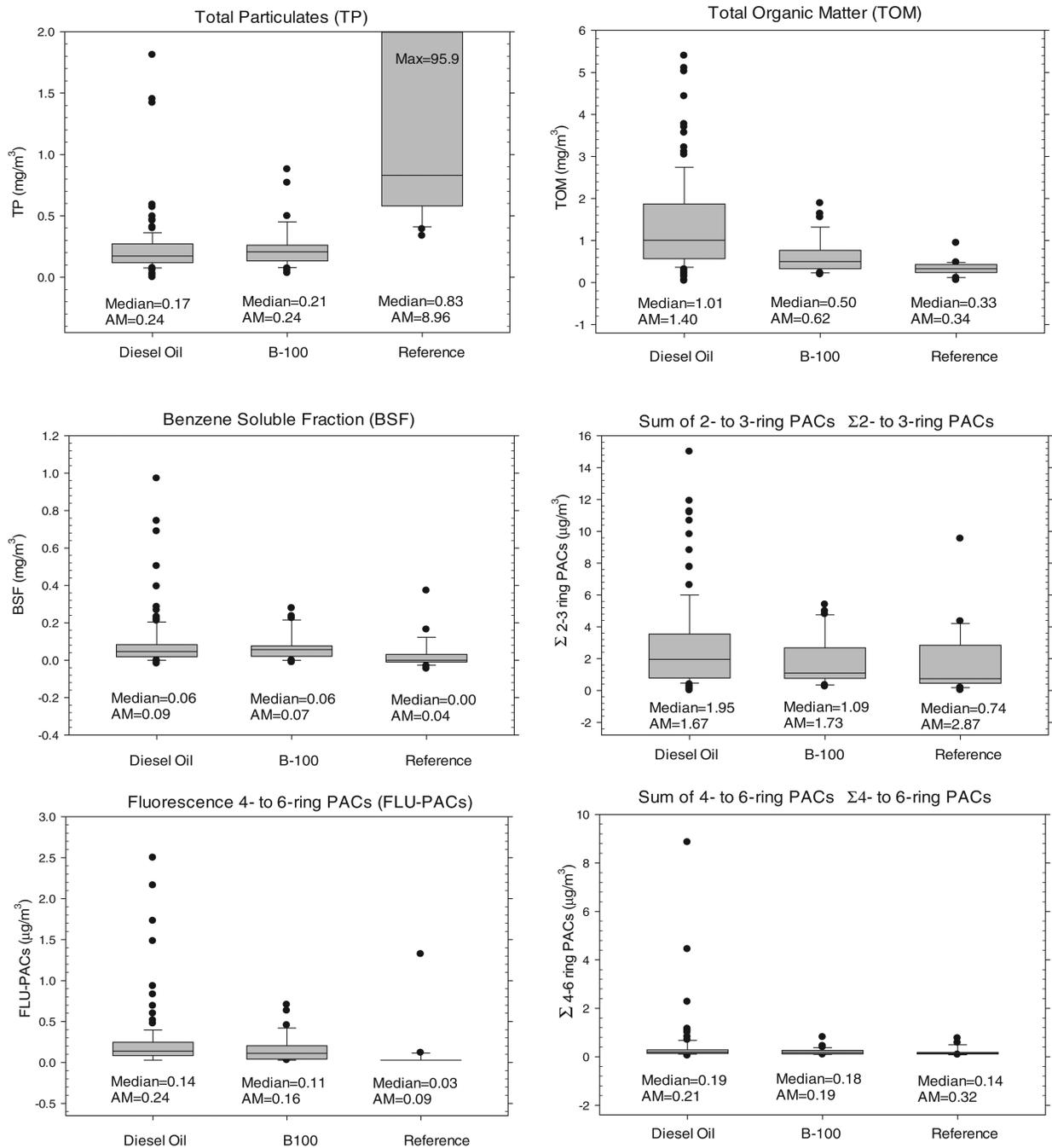


FIGURE 1.

Distributions for hot-mix asphalt paving worker personal-breathing zone exposures for diesel ($n = 107$), B-100 ($n = 36$), and the reference group ($n = 24$). The ends of the boxes define the 25th and 75th percentiles, with a line at the median and error bars defining the 10th and 90th percentiles. The median and arithmetic mean (AM) values were included. Except for the reference data for TP, hot-mix asphalt paving worker personal-breathing zone

results for each analyte clearly show increased variability and exposures when workers use diesel oil as compared to B-100.

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TABLE I

Arithmetic Means (AM) of Analytes for the Hot-mix Asphalt (HMA) Paving Crews and the Reference Group (a Concrete Crew) and their Corresponding Background and Field Blanks

Analyte PAC [*] , ng/m ³	HMA Paving Crews, AM				Reference Group, AM		
	Diesel Oil	B-100	Background	Field Blanks	Reference Group	Background	Field Blanks
Acenaphthene	218	165	17.4	3.28	5.30	3.06	3.10
Fluoranthene	78.5	31.3	5.12	3.76	5.47	7.97	5.42
Fluorene	208	160	6.15	2.80	4.69	3.98	4.04
Phenanthrene	652	461	38.6	6.03	85.5	56.32	18.2
Pyrene	118	81.3	5.75	5.99	10.4	18.86	5.43
Anthracene	25.3	7.54	3.82	5.89	4.97	4.85	4.92
Benzo[b]naphtho[2,3-d]thiophene	19.4	10.8	6.54	7.33	7.12	52.02	7.05
Acenaphthylene	76.0	10.1	2.99	3.92	26.5	3.79	3.85
Naphthalene	1593	884	69.5	14.2	1529	13.89	2.42
3-Methylcholanthrene	11.1	13.5	5.91	5.28	7.68	7.50	7.60
Triphenylene	14.5	4.41	5.50	4.92	7.15	70.55	7.08
Benz[a]anthracene	29.2	11.7	8.95	7.56	8.26	8.07	8.18
Benzo[a]pyrene	12.6	7.68	6.51	7.74	29.6	17.55	62.7
5-Methylchrysene	14.5	4.51	5.63	5.03	7.32	7.15	7.25
Chrysene	15.9	6.02	5.00	5.57	6.49	6.34	6.43
Benzo[b]fluoranthene	57.2	30.6	37.9	33.8	72.0	49.07	128
Benzo[ghi]perylene	8.56	4.16	5.19	4.64	6.75	6.59	6.68
Dibenz[a,h]anthracene	8.76	4.58	5.72	5.11	7.42	7.26	7.35
Indeno[1,2,3-cd]pyrene	7.30	3.92	4.89	4.37	6.35	6.21	6.30
Benzo[e]pyrene	12.8	6.04	5.32	5.36	17.9	6.26	42.4
1-Nitropyrene	15.9	9.69	12.1	10.8	15.7	15.35	15.6
7,12-Dimethylbenz[a]anthracene	29.0	19.5	24.4	21.8	31.7	30.93	31.3
Dibenz[a,h]acridine	16.2	10.5	13.1	11.7	17.0	16.67	16.9
Dibenz[a,j]acridine	21.3	16.2	20.2	18.1	26.2	25.65	26.0
Total Particulates, mg/m ³	0.24	0.24	0.05		8.96	0.10	
Benzene Soluble Fraction, mg/m ³	0.09	0.07	0.01		0.04	0.02	
FL-PACs, µg/m ³	0.24	0.16	0.03	0.03	0.09	0.03	0.03
FL-PACs, EU/g	28.5	38.1	20.3	20.2	24.5	20.0	20.4
Total Organic Matter, mg/m ³	1.40	0.62	0.10	0.06	0.34	0.10	0.13
Σ2- to 3-ring PACs, µg/m ³	2.87	1.73	0.13	0.05	1.67	0.15	0.12
Σ4- to 6-ring PACs, µg/m ³	0.32	0.19	0.12	0.11	0.21	0.23	0.31

PAC = polycyclic aromatic compound; B-100 = 100% biodiesel with no petroleum-derived products; FL-PACs = polycyclic aromatic compounds containing 4- to 6-rings determined by fluorescence spectroscopy; EU/g = emission units per gram calculated as EU/TOM (g/mL) /10,000, fluorescence results normalized using Total Organic Matter; Σ2- to 3-ring PACs and Σ4- to 6-ring PACs = summation of the concentrations of the individual PACs containing either 2- to 3-rings or 4- to 6-rings as determined by gas chromatography/time-of-flight mass spectroscopy (GC/TOFMS). If an individual PAC was a negative value, 0.001 was used for statistical calculations. Geometric means and ranges (minimum and maximum values) were included in Supplemental Table 1.

* PACs investigated, but below the limit of detection included: benzo[k]fluoranthene, benzo[j]fluoranthene, 7H-dibenzo[c,g]carbazole, dibenzo[a,e]pyrene, benzo[rs]t]pentaphene, dibenzo[a,h]pyrene, dibenzo[a,l]pyrene, cyclopenta[cd]pyrene, dibenzo[a,e]fluoranthene

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TABLE II

Highest Exposure Results with Corresponding Field Note Comments.

Analyte	Concentration	Job Title/Function	Date	Comments
		Diesel Oil		
TP, mg/m ³	1.81	Screedman	10/6/08	Diesel-powered screed
BSF, mg/m ³	0.97	Shuttle Buggy	10/6/08	Diesel-powered screed
FL-PACs, µg/m ³	2.50	Paving Operator	10/9/08	Used diesel-powered screed in the morning for the base
TOM, mg/m ³	5.40	Paving Operator	9/10/08	Used diesel sprayer to spray down paver at beginning and end of day
Σ2- to 3-ring PACs, µg/m ³	15.0	Shuttle Buggy	9/10/08	Sprayed 10–15 gallons of diesel oil over the day
Σ4- to 6-ring PACs, µg/m ³	8.86	Screedman	8/26/08	Used diesel sprayer for rinsing tools, etc.
		B-100		
TP, mg/m ³	0.77	Laborer	9/23/08	Operated broom machine creating quite a dust storm
BSF, mg/m ³	0.28	Shuttle Buggy	9/17/08	Highest HMA Application Temperature (153°C ^A)
FL-PACs, µg/m ³	0.70	Shuttle Buggy	9/17/08	Highest HMA Application Temperature (153°C ^A)
TOM, mg/m ³	1.89	Paving Operator	9/17/08	Highest HMA Application Temperature (153°C ^A)
Σ2- to 3-ring PACs, µg/m ³	5.40	Paving Operator	9/17/08	Highest HMA Application Temperature (153°C ^A)
Σ4- to 6-ring PACs, µg/m ³	0.81	Foreman	9/02/08	Paver got stuck. Foreman was underneath paver working on equipment using lubricating oils.

TP = total particulates; BSF = benzene soluble fraction; FL-PACs = polycyclic aromatic compounds containing 4- to 6-rings determined by fluorescence spectroscopy; TOM = total organic matter; Σ2- to 3-ring PACs and Σ4- to 6-ring PACs = summation of the concentrations of the individual PACs containing either 2- to 3-rings or 4- to 6-rings as determined by gas chromatography/time-of-flight mass spectroscopy (GC/TOFMS); HMA = hot-mix asphalt; A = this was the highest daily arithmetic mean HMA paving application temperature, the overall arithmetic mean HMA paving application temperature for that crew was 140°C.

TABLE III

Analyte to Analyte Comparisons: Results of Regression Analysis.

Analyses		Diesel Oil		B-100	
x-axis	y-axis	R ²	Equation of the Line	R ²	Equation of the Line
TOM	Σ2- to 3-ring PACs	0.48	1762X + 328	0.88	3273X – 269
BSF	FL-PACs	0.65	2.11X + 0.06	0.79	1.99X + 0.03
TOM	FL-PACs	0.13	1.08X + 1.12	0.74	2.26X + 0.25
TOM	BSF	0.14	2.88X + 1.13	0.70	4.88X + 0.28
FL-PACs	Σ4- to 6-ring PACs	< 0.01	262X + 334	0.67	476X + 115
TOM	Σ4- to 6-ring PACs	< 0.01	77.5X + 291	0.62	175X + 84
BSF	Σ2- to 3-ring PACs	0.03	15.0X + 3574	0.60	15848X + 657
FL-PACs	Σ2- to 3-ring PACs	0.22	3474X + 1915	0.52	6600X + 669
BSF	Σ4- to 6-ring PACs	0.01	736X + 333	0.28	1024X + 138
Σ2- to 3-ring PACs	Σ4- to 6-ring PACs	0.01	0.04X + 289	0.21	0.0436X + 132
BSF	TP	0.73	0.49X – 0.03	<.01	0.0006X + 0.068
FL-PACs	TP	0.53	0.48X + 0.12	0.02	0.13X + 0.13

TP = total particulates; BSF = benzene soluble fraction; FL-PACs = polycyclic aromatic compounds (PACs) containing 4- to 6-rings determined by fluorescence spectroscopy; TOM = total organic matter; Σ2- to 3-ring PACs and Σ4- to 6-ring ring PACs = summation of the concentrations of the individual PACs containing either 2- to 3-rings or 4- to 6-rings as determined by gas chromatography/time-of-flight mass spectroscopy (GC/TOFMS). TP vs. TOM, Σ2- to 3-ring PACs, and Σ4- to 6-ring PACs were all <0.17 R².