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Predictors of Airborne Exposures to Polycyclic Aromatic Compounds and Total Organic Matter among Hot-Mix Asphalt Paving Workers and Influence of Work Conditions and Practices

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Objectives: We evaluated personal airborne exposures to polycyclic aromatic compounds (PACs) and total organic matter (TOM) among hot-mix asphalt (HMA) paving workers. The primary objectives of this study were to identify predictors of airborne PAC exposures, identify PAC exposure sources, and characterize how work practices may affect personal airborne exposure to PACs.

Methods: Four workers were recruited from each of three asphalt paving crews (12 workers) and were monitored for three consecutive days over 4 weeks for a total of 12 sampling days per worker (144 worker-days). Three sampling weeks were conducted while maintaining standard working conditions with regard to airborne exposures. The fourth week included the substitution of biodiesel for diesel oil used to clean tools and equipment. Linear mixed-effects models were used to evaluate predictors of airborne exposures including weather parameters (air temperature, wind speed, and relative humidity), worksite conditions (HMA application temperature, work rate, asphalt grade, and biodiesel use), and personal factors (minutes sampled, minutes of downtime, and smoking status).

Results: Concentrations of the 33 individual PACs measured in personal air samples were generally below detection limits under all conditions with the exception of fluorene [geometric mean (GM) = 65 ng m^{-3}], naphthalene (GM = 833 ng m^{-3}), phenanthrene (GM = 385 ng m^{-3}), and pyrene (GM = 57 ng m^{-3}). The summary measures of TOM (GM = 864 μg m^{-3}) and four- to six-ring PAC (GM = 0.13 μg m^{-3}) were detected in the majority of air samples. Although task was not a predictor of airborne exposures, job site characteristics such as HMA application temperature were found to significantly ($P \leq 0.001$) affect summary and individual PAC exposures. Based on the results of multivariate linear mixed-effects models, substituting biodiesel for diesel oil as a cleaning agent was associated with significant ($P \leq 0.01$) reductions in TOM, four- to six-ring PACs, and naphthalene and pyrene concentrations that ranged from 31 to 56%. Using multivariate linear mixed-effects models under standard conditions, reducing the application temperature of HMA from 149°C (300°F) to 127°C (260°F) could be expected to reduce airborne exposures by 42–82%, varying by analyte.

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Conclusions: Promising strategies for reducing airborne exposures to PACs among HMA paving workers include substituting biodiesel for diesel oil as a cleaning agent and decreasing the HMA application temperature.

Keywords: airborne exposure; asphalt; diesel; polycyclic aromatic compounds; total organic matter

INTRODUCTION

Asphalt (or bitumen) consists of a complex mixture of organic compounds including polycyclic aromatic compounds (PACs) which varies based on crude oil source, refinery process, additives, and application practices (Gamble *et al.*, 1999; NIOSH, 2001). Hot-mix asphalt (HMA) paving materials are a mixture of ∼5% asphalt and ∼95% mineral aggregate which has been heated, mixed, and delivered to the paving site and placed through the paver by a crew. Asphalt paving workers have been shown to have exposure to PACs in asphalt vapors and fume via inhalation and dermal absorption (NIOSH, 2001; McClean *et al.*, 2004).

While the carcinogenicity of exposure to asphalt emissions remains under investigation (NIOSH, 2001; Schulte, 2007), exposure to asphalt emission is a recognized irritant (NIOSH, 2001) and may cause declines in lung function (Ulvestad *et al.*, 2007), and it is prudent to reduce exposures where possible. It has been over a decade since reductions in exposure have been achieved with the introduction of engineering controls on highway-class pavers (NIOSH, 1997). There remains a need to further optimize exposure reduction strategies. To do so, it is necessary to characterize PAC exposures and identify the sources and work practices that affect exposure. Yet, few studies have examined predictors of airborne exposures among HMA paving workers (Burstyn *et al.*, 2000; Burstyn *et al.*, 2002; McClean *et al.*, 2004).

Accordingly, we assembled a collaborative partnership composed of representatives from government, industry, labor, and academia to address remaining questions about the source and work practices that affect exposure to PACs among asphalt paving workers. Here, we present the results of our effort to identify predictors of airborne exposures. In addition to evaluating predictors under standard HMA paving work conditions, we also sought to evaluate airborne exposure to total organic matter (TOM) and PACs during the substitution of biodiesel for the diesel oil that is typically used as a cleaning agent, which the partnership deemed as a practical and feasible modification to typical work practices. Details of the collaborative partnership, overall study design, and sampling and analytical methods are reported elsewhere (Kriech *et al.*, 2011).

METHODS

The study population included three HMA paving crews from three construction companies based out of Wisconsin and Indiana, USA. Four volunteers were recruited from each crew for a study population of 12 workers. Each crew included a paver operator, screedman, and raker, while the fourth worker varied by crew (foreman, laborer, and shuttle buggy operator). The paver operator primarily sat on top of the paver to control the speed and direction, while the screedman typically stood at the back of the paver to control the depth and width of the asphalt mat. Rakers were responsible for spreading asphalt mixtures using rakes and lutes around joints and contours that are not easily handled by the paver. This included breaking up lumps, fixing defects, and smoothing and tamping asphalt surfaces inaccessible to a roller. The laborer worked with the raker and drove the tack truck (which sprayed an asphalt emulsion on the pavement prior to paving), as well as other miscellaneous duties such as marking the road with spray paint. His position was more mobile causing him to be somewhat removed from the primary source of HMA over half of the time. The shuttle buggy operator, when needed, controlled a machine used to remix and store the HMA during transfer between the truck and the paver. The foreman functioned in the screedman capacity for half the time and also performed some raking and general foreman duties but was often working in the vicinity of the screed while supervising the crew.

Study protocols were reviewed and approved by National Institute for Occupational Safety and Health (NIOSH) Human Subjects Review Board and written informed consent was received by each volunteer prior to participation.

Study design

A repeated measures study design was used to monitor airborne exposure to PACs and TOM from August through October in 2008 with simultaneous monitoring of the three crews of four workers each. Each of 12 workers was sampled over three consecutive days during four work weeks, resulting in 12 sampling days per worker and a total of 144 worker-days. As part of a larger study, each of the four work weeks was designed to evaluate a different scenario: (i) standard operating conditions (baseline scenario), (ii) providing gloves, hat and neck cloth, and clean pants and long sleeved shirts to reduce dermal exposure (dermal protection scenario), (iii) using powered air-purifying respirators (PAPR) to reduce inhalation exposure (PAPR scenario), and (iv) substituting biodiesel for diesel oil used as a cleaning agent (no diesel scenario). For this analysis of airborne exposures, the baseline, PAPR, and dermal protection scenarios were combined because the introduction of PAPRs or dermal protection was not intended or expected to affect personal airborne exposures as the personal air sampling media was located outside the PAPRs. Therefore, each of these three exposure scenarios represents standard working conditions with regard to airborne exposures. In the 'no diesel' scenario, diesel oil normally used to clean tools and equipment was removed from the site and replaced with B-100 a biodiesel product composed of 100% mono-alkyl esters of long-chain fatty acids, that is often produced from vegetable oil or animal fats and contains no PACs (Bajpai and Tyagi, 2006). Each crew member maintained the same exposure scenario. The order of the week-long exposure scenarios was randomized among the three crews and the cross-over design allowed each worker to serve as his own control.

Site conditions and worker observations

Workers were monitored while performing normal paving work that included large primary roads and a parking lot. Highway-class pavers with engineering controls (NIOSH, 1997) were used on all but one occasion when a paver equipped with a widener was used to accommodate logistical road issues. Asphalt binder types also varied by crew and project and included the following Superpave performance grades (PG): PG 64-22, PG 58-28, and PG 76-22.

HMA temperatures were monitored at various times throughout the workday. A minimum of six temperature readings were collected daily from the asphalt mat at the back of the screed using an HMA Lab Supply 8'' Stainless Steel Dial Stem thermometer, with a 0–400°F range (Catalog # TM-4500). Measurements of wind speed, air temperature, and humidity using a Kestrel® 4000 Pocket Weather Tracker as well as weather related comments were collected four times each sampling day. Job specifications including asphalt grade and tonnage use were recorded daily.

Participant characteristics including sex, age, height, weight, and smoking status were obtained at the start of the study. Daily observations of down time (when workers were away from asphalt while eating lunch, waiting for delivery of asphalt, working on equipment, or other activities with no asphalt emission exposure) were estimated in minutes by onsite personnel based on field records.

Collection of air samples

Personal breathing zone air samples were collected daily from each worker in accordance with NIOSH Method 5042 (NIOSH, 1998; Kriech *et al.*, 2011). At the beginning of each work shift, workers were fitted with a sampling train including a Teflon filter housed in a cassette and a XAD-2 polymeric resin/charcoal tube connected in series and attached to a personal air sampling pump operating at 2 l min^{-1}. The sampling train was placed on the workers lapel near the breathing zone. The sampler was located in the same position during all exposure scenarios, such that during the PAPR scenario, the inlet was positioned to sample unfiltered air (attached below and to the side of the face shield with the inlet pointing down). Flow rates were checked before, during, and after sample collection using a calibrated rotameter. At the end of the work shift, samples were collected and stored at −20°C for transport and until further analysis.

Laboratory analysis of air samples

For all laboratory analysis methods described below, details of the methods, sample preparation, and instrumental and experimental conditions used for this study can be found elsewhere (Kriech *et al.*, 2011). A brief summary of the analytes and methodology is given below.

Traditional gravimetric procedures were used to quantify exposure to airborne total particulate matter and benzene-soluble fraction (BSF) in accordance with NIOSH Method 5042 (NIOSH, 1998). TOM refers to the amount of organics collected on the sampler (BSF and materials collected on the XAD-2/Charcoal) ranging from C6 to C42 as determined by gas chromatography equipped with a flame ionization detector (GC/FID) performed using a modification of EPA Method SW846-8015B (EPA, 1996; Kriech *et al.*, 2011).

A total of 33 individual PACs concentrations were obtained using gas chromatography/time of flight mass spectrometry (GC/TOFMS) following the guidelines of EPA SW-846 8270C using a published procedure (Kriech *et al.*, 2002).

Additionally, the total four- to six-ring PAC content was measured using the asphalt fume fluorescence (AFF) test protocol (Osborn *et al.*, 2001) using an excitation wavelength of 385 nm and an emission wavelength of 415 nm. The instrument, a Perkin Elmer LS 50 B, was calibrated using diphenylanthracene (DPA) and results were reported as DPA equivalents. The fluorescence method differs from the speciation of individual PACs by GC/TOFMS in that the fluorescence response also includes alkylated PACs, which tend to be more prominent than their parent structures in these emissions. Industrial hygiene sample collection and laboratory analysis were performed by Heritage Research Group, Indianapolis, IN, USA, with on-site assistance and oversight during sample collection from NIOSH.

A field blank was collected daily for each crew for a total of 36 field blanks representing 25% of the total number of primary samples. Blank correction by crew was only performed for naphthalene where the mean field blank was statistically significantly different from zero, and analysis of variance identified a statistically significant difference in blanks between crews. Laboratory values were used as reported. When no value was reported, the LOD divided by the square root of two was substituted. The limit of detection (LOD) was defined as the instrument detection limit (IDL) with the exception of naphthalene where a method detection limit (MDL = three times the standard deviation of the field blanks) could be calculated. Additional information on blank correction and LOD determination is presented elsewhere (Kriech *et al.*, 2011).

Data analysis

Distributions of the personal air monitoring data were examined using histograms and normal probability plots. Shapiro–Wilks' tests and graphical displays indicated that the air monitoring data were not normally distributed, and therefore, the air monitoring data were log transformed to achieve an approximately normal distribution. Accordingly, geometric means (GMs) and standard deviations are reported and statistical modeling was performed on the log-transformed data. For summary statistics, only analytes detected in at least 30% of samples were included in tables and multivariate analysis was performed on analytes detected in at least 75% of samples. To examine the relationship between the summary and individual PAC exposures, correlation coefficients were calculated using linear mixed-effects models as described by Hamlett *et al.* (2003).

Importantly, for this analysis of personal airborne exposures, the baseline, PAPR, and dermal protection scenarios were combined because the introduction of PAPRs or dermal protection was not intended or expected to affect measured airborne exposures as compared to baseline (confirmed via analyses not shown). Accordingly, our analysis of airborne exposures in this paper compares 3 weeks of baseline conditions to 1 week of biodiesel substitution.

Since multiple personal airborne exposures samples were collected from each worker, linear mixed-effects models were used to evaluate the determinants of each four- to six-ring PACs, TOM, or individual PACs using a compound symmetry covariance matrix structure. The repeated measures design and the use of linear mixed-effects models allows each worker to serve as his own control while evaluating changes between exposure scenarios. Potential predictors of airborne exposures included weather parameters (air temperature, wind speed, and relative humidity), worksite conditions (HMA application temperature, work rate, asphalt grade, and biodiesel use), and personal factors (minutes sampled, minutes of down time, and smoking status).

A priori, we included a four-level categorical variable for task (paver operator, screedman, raker, and other) within each model based on prior studies suggesting the importance of task as predictor of exposure (McClean *et al.*, 2004). We also included a dichotomous variable to indicate whether biodiesel was substituted for diesel oil as a cleaning agent. Other potential predictors were evaluated first in a univariate model and included air temperature, wind speed, relative humidity, crew (categorical), HMA application temperature, hourly work rate (tons of asphalt applied per hour), daily work rate (tons of asphalt applied per day), asphalt grade (categorical variable), minutes sampled, minutes of down time, and smoking status. Next, multivariate models were constructed including all variables that were marginally statistically significant ($P < 0.10$) in 50% of univariate models. Models were further refined stepwise including only variables that were marginally significant ($P < 0.10$) in ≥50% of the multivariate models. Multivariate models were confirmed using *a priori* predictors and predictors identified via univariate analyses using a forward selection procedure. The non-linearity of HMA application temperature was evaluated by categorical and squared variables using likelihood ratio tests. All statistical analyses were conducted in SAS statistical software (v. 9.2; Cary, NC); statistical significance is reported at the 0.05 level, unless otherwise noted.

RESULTS

The 12 workers who participated in this study were all male, with a mean age of 36 years (range of 24–59 years). Six of the workers smoked cigarettes, five were non-smokers, and one worker quit smoking during the study period. One non-smoker chewed tobacco. The workers were monitored over a wide range of weather conditions as indicated by the observed range of air temperature, wind speed, and humidity (Table 1). Similarly, HMA application temperatures ranged from 121 to 154°C (250–310°F). HMA application temperatures varied by crew, with one crew using a wide range of temperatures from 127 to 154°C (260–310°F), the second a smaller range on the higher end from 146 to 152°C (295–305°F), and the third using lower temperatures ranging from 121 to 145°C (250–293°F). There was a wide range of asphalt use, work rates, and down time experienced over the 36 sampling days. In general, sampling occurred over the entire work shift with a median time sampled of 652 min or ~11 h and a range from 6.5 to 13.6 h. The crews primarily used asphalt grade PG 58-28 (61%) as compared to PG 64-22 (33%) and PG 76-22 (6%), and the majority of the work was applying surface course (91%) as compared to base (3%) or leveling (6%).

Personal airborne exposures are summarized in Table 2. Summary measures of personal airborne exposures indicate low concentrations of four- to six-ring PACs measured using the AFF test protocol with a GM of 0.13 μg as DPA m^{-3} as compared to TOM with a GM of 864 μg m^{-3}. In the air samples, the majority of the 33 individual PACs had ≥50% samples below the LOD with the exception of acenaphthene,

Table 1. Summary of worksite conditions over 36 sampling days.

	Median	Range
Air temperature, °C (°F)	21 (69)	8 (46)–31 (87)
Wind speed, km h^{-1} (m h^{-1})	6.9 (4.3)	1.0 (0.6)–17.0 (10.6)
Humidity, %	58.5	32.0–90.5
Hot-mix temperature, °C (°F)	144 (291)	121 (250)–154 (310)
Daily work rate, tons day^{-1}	1449	418–3300
Hourly work rate, tons h^{-1}	149	46–289
Time sampled, min	652	387–818
Down time, min day^{-1}	120	75–700

Table 2. Summary of personal airborne exposure levels from 144 HMA paving worker-days for analytes with ≥30% detection.

Analyte	LOD	% Detect	GM (GSD)	Minimum–maximum
Summary measures (μg m^{-3})				
4–6 Ring PACs[a]	0.04	83	0.13 (2.7)	0.04–2.50
Benzene soluble fraction (BSF)	39	62	35.3 (4.8)	22–972
Total organic matter (TOM)	80	99	864 (2)	142–5395
Total particulate matter (TPM)	17	99	181 (2)	18–1811
Individual PACs[b] (ng m^{-3})				
Acenaphthene	3.00	71	47.3 (9.2)	9.66–2162
Fluoranthene	5.24	61	19.9 (5.0)	7.17–841
Fluorene	3.91	78	64.6 (6.5)	14.2–1631
Naphthalene	3.76	87	833 (5)	301–13767
Phenanthrene	4.86	99	385 (3)	49.4–4421
Pyrene	5.25	92	56.6 (3.5)	8.53–926

GM, geometric mean; GSD, geometric standard deviation.
[a]PACs obtained using a fluorescence method.
[b]A total of 33 individual PACs results were obtained using gas chromatography/time of flight mass spectrometry. PACs investigated, but detected in <30% of the samples include acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, 5-methylchrysene, 1-nitropyrene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene, benzo[j]fluoranthene, 7,12-dimethylbenz[a]anthracene, benzo[e]pyrene, 3-methylcholanthrene, dibenz[a,h]acridine, dibenz[a,j]acridine, 7H-dibenzo[c,g]carbazole, dibenzo[a,e]fluoranthene, dibenzo[a,e]pyrene, benzo[r,s,t]pentaphene, dibenzo[a,h]pyrene, dibenzo[a,l]pyrene, benzo[b]naptho[2,3- d]thiophene, cyclopenta[c,d]pyrene, triphenylene.

fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene. Of the individual PACs with sufficient (≥30%) samples above the detection limit, the PACs were in the two to three ring range with the exception of pyrene with four rings. Across all the samples, naphthalene was present in the highest concentrations with a GM of 833 ng m^{-3}, followed by phenanthrene (GM of 385 ng m^{-3}). With an order of magnitude lower concentrations, the GMs of fluorene, pyrene, acenaphthene, and fluoranthene ranged from 65 to 20 ng m^{-3}. The fluorene, naphthalene, phenanthrene, and pyrene concentrations were strongly correlated with each other and had correlation coefficients ranging from 0.38 to 0.86. TOM was correlated with fluorene, naphthalene, phenanthrene, and pyrene ($0.60 \leq r \leq 0.73$). As expected, four- to six-ring PAC content was most highly correlated with pyrene, a four-ring PAC ($r = 0.69$), and correlated with the other individual PACs ($0.45 \leq r \leq 0.62$). Based on the frequency of detection, TOM, four- to six-ring PACs, fluorene, naphthalene, phenanthrene, and pyrene were included in additional statistical analyses.

Potential predictors of airborne exposures were identified through univariate models assessing each analyte individually. We observed a statistically significant ($P < 0.05$) positive linear relationship between air temperature and fluorene, phenanthrene, and pyrene but not naphthalene, TOM, or 4–6 ring PACs. A statistically significant ($P < 0.05$) inverse relationship was observed between wind speed and fluorene, naphthalene, phenanthrene, and pyrene; an inverse relationship was also observed for TOM and four- to six-ring PAC, but only four- to six-ring PAC was marginally significant ($P < 0.10$). No significant relationships were observed between humidity and any of the six analytes. This was also the case for smoking status and the worksite variable asphalt grade. The worksite variable crew was a moderately statistically significant ($P < 0.10$) predictor of each analyte. Likewise, HMA application temperature was a statistically significant ($P < 0.05$) predictor of each analyte. Minutes sampled was only statistically significant ($P < 0.05$) for naphthalene and four- to six-ring PAC. Yet, minutes of down time was inversely associated with fluorene, phenanthrene, pyrene, and four- to six-ring PAC content, all of which were statistically significant ($P < 0.05$). The relationship between hourly work rate and each analyte was inconsistent with marginally significant ($P < 0.10$) positive linear relationships observed for fluorene and phenanthrene and a marginally significant ($P < 0.10$) inverse relationship observed for TOM and no association for the remaining analytes. A similar association was observed for daily work rate, although only fluorene and TOM were marginally significant ($P < 0.10$). In addition to our *a priori* covariates of interest (task and biodiesel use), predictors considered for multivariate models meeting the criteria of moderately significant ($P < 0.10$) in ≥50% analyte models included air temperature, wind speed, crew, hot-mix temperature, minutes of downtime, and hourly work rate. However, due to the relationship between crew and HMA application temperature (with limited variation in HMA application temperature by crew), crew was excluded from the multivariate models.

Table 3 shows the parameter estimates, standard errors, and P values for the final models identifying predictors of personal airborne exposures. The final models do not include wind speed as it was not statistically significant in any model, possibly due to its correlation with HMA application temperature (Spearman correlation coefficient = −0.49) and air temperature (Spearman correlation coefficient = −0.23). Minutes of downtime was also not a statistically significant predictor of air exposures, with exception of pyrene, and was removed from the final models. The predictors retained in the final multivariate models included our *a priori* variables of interest (task and diesel oil use), air temperature, HMA application temperature, and hourly work rate.

Substituting biodiesel for diesel oil during cleaning was associated with a significant decrease in TOM ($P < 0.0001$), four- to six-ring PACs ($P < 0.0001$), naphthalene ($P = 0.01$), and pyrene ($P = 0.001$) concentrations as compared to the baseline scenario after controlling for other factors. HMA application temperature was a significant predictor ($P < 0.01$) across all analytes, with increases in temperature showing increased exposures. Likelihood ratio tests indicated that a linear term (as compared to categorical or squared variables) best fit the relationship between HMA application temperature and individual analyte concentrations within our data set. Air temperature was a significant predictor of fluorene ($P = 0.002$) and pyrene ($P = 0.001$), with increases in temperature showing increased exposure. Hourly work rate was a statistically significant predictor for individual PACs with increased work rate showing increases in exposures. Surprisingly, task was not a significant predictor of any analyte while adjusting for other factors. Our final model included predictors that explained both between- and within-worker variability. As compared to a null model, predictors in our multivariate model accounted for 24–46% of the total variation of

Table 3. Determinants of personal airborne exposure among hot-mix asphalt (HMA) paving workers, based on multivariable linear mixed-effects models.

Parameters	TOM		4–6 Ring PACs[a]		Fluorene		Naphthalene		Phenanthrene		Pyrene	
	β (SE)	*P* value	β (SE)	*P* value	β (SE)	*P* value	β (SE)	*P* value	β (SE)	*P* value	β (SE)	*P* value
Fixed effects												
Intercept	−3.87 (1.10)	0.01	−8.08 (1.62)	0.001	−9.56 (2.02)	0.002	−1.75 (2.21)	0.45	−2.58 (1.24)	0.07	−7.95 (1.37)	0.0004
Biodiesel substitution	−0.77 (0.15)	<0.0001	−0.47 (0.21)	0.02	−0.14 (0.35)	0.68	−0.82 (0.33)	0.01	−0.37 (0.20)	0.07	−0.73 (0.21)	0.001
Asphalt application temperature (per 100°C)	2.44 (0.41)	0.001	3.95 (1.08)	0.0004	7.61 (1.51)	<0.0001	5.45 (1.55)	0.001	5.08 (0.90)	<0.0001	−7.25 (0.98)	<0.0001
Task		0.67		0.84		0.23		0.53		0.17		0.25
Rakers	Reference		Reference		Reference		Reference		Reference		Reference	
Screedman	0.17 (0.38)	0.66	0.59 (0.65)	0.39	0.71 (0.32)	0.06	0.63 (0.52)	0.26	0.59 (0.24)	0.04	0.60 (0.28)	0.06
Paver operator	0.47 (0.38)	0.25	0.26 (0.65)	0.70	0.19 (0.33)	0.57	0.70 (0.53)	0.22	0.39 (0.24)	0.14	0.29 (0.28)	0.33
Other	0.25 (0.38)	0.52	0.28 (0.65)	0.68	0.43 (0.32)	0.22	0.64 (0.52)	0.26	0.34 (0.24)	0.19	0.18 (0.28)	0.52
Air temperature (per 1°C)	0.019 (0.013)	0.16	0.024 (0.019)	0.21	0.090 (0.028)	0.002	−0.006 (0.029)	0.84	0.031 (0.017)	0.07	0.063 (0.018)	0.001
Hourly work rate (tons h^{-1})	−0.0005 (0.001)	0.64	−0.0008 (0.001)	0.58	0.0076 (0.002)	<0.0001	0.004 (0.002)	0.04	0.004 (0.001)	0.0	0.0035 (0.001)	0.01
	Variance Components		Variance Components		Variance Components		Variance Components		Variance Components		Variance Components	
Random effects												
σ^2_{BW} (Full model)[b]	0.2		0.0		0.0		0.2		0.0		0.0	
σ^2_{WW} (Full model)[b]	0.4		2.2		2.2		1.9		0.7		0.8	
σ^2_{BW} (Intercept-only)[c]	0.2		0.5		0.5		0.4		0.2		0.6	
σ^2_{WW} (Intercept only)[c]	0.5		3.0		3.0		2.0		0.8		1.1	
Between-worker variability explained (%)	21		100		100		32		92		93	
Within-worker variability explained (%)	26		25		25		3		12		21	

[a]PACs—polycyclic aromatic compounds, obtained using a fluorescence method.
[b]Between-worker (σ^2_{BW}) and within-worker (σ^2_{WW}) variance estimates from full model.
[c]Between-worker (σ^2_{BW}) and within-worker (σ^2_{WW}) variance estimates from intercept-only model.

exposures, varying by analyte with the exception of naphthalene where the model explained only 7% of the variability in exposure.

To ease interpretation of our findings in Table 3, Table 4 presents the adjusted GM airborne exposure levels by analyte to show the combined effects of the biodiesel substitution (unrestricted diesel oil use versus biodiesel substitute) and HMA application temperature (149 or 127°C). Since the data analysis was conducted using logged data, the GM exposure concentrations were estimated by exponentiating the estimates from the adjusted models. The adjusted GM concentration of TOM with unrestricted use of diesel oil and the higher HMA application temperature of 149°C (1400 μg m^{-3}) is ~3.7 times the adjusted GM concentration of TOM associated with the biodiesel substitute and the lower HMA application temperature of 127°C (380 μg m^{-3}). A similar comparison of the adjusted GM concentrations estimated a 4.8-fold decrease of fluorene, a 7.6-fold decrease of naphthalene, a 4.5-fold decrease in phenanthrene, and a 10.6-fold decrease in pyrene with biodiesel substitution and a lower HMA application temperature of 127°C.

DISCUSSION

Few studies have identified the determinants of personal airborne exposures during HMA paving (Burstyn *et al.*, 2000; Burstyn *et al.*, 2002; McClean *et al.*, 2004) despite the need to identify modifiable factors that influence airborne exposures. The primary goal of this analysis was to characterize personal airborne exposures using current industry practices during asphalt paving in order to identify predictors of personal airborne exposures and evaluate the impact of substituting biodiesel for diesel oil. Using adjusted models, our findings quantify significant reductions in the airborne concentration of PACs after substituting biodiesel for diesel oil as a cleaning agent. Additionally, our findings suggest that airborne PAC exposures are positively associated with HMA application temperature, suggesting that decreasing the application temperature would likely decrease inhalation exposures.

Using standardized methods, we monitored personal airborne exposures to PACs in a group of 12 workers. The individual PACs present in substantial levels (>60%) above the LOD were two- to three-ring PACs (acenaphthene, fluoranthene, fluorene, naphthalene, and phenanthrene) with the exception of four-ring pyrene. Studies of European asphalt workers show a higher prevalence of low-boiling PACs, specifically naphthalene, in personal air samples (Hicks, 1995; Järvholm *et al.*, 1999; Burstyn *et al.*, 2002; Heikkilä *et al.*, 2002; Väänänen *et al.*, 2003; Cirla *et al.*, 2007). In addition to similarities in composition, the levels of individual PACs including acenaphthene, fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene that we observed were within the same order of magnitude as concentrations reported in recent exposure studies (Väänänen *et al.*, 2005; Cavallo *et al.*, 2006; Väänänen *et al.*, 2006; Cirla *et al.*, 2007).

Since a standard work practice in the asphalt paving industry is to use diesel oil to rinse down paving equipment, shovels, lutes (or rakes), putty knives, and other tools, we hypothesized the diesel oil may be a potential PAC source and therefore evaluated its contribution by replacing diesel oil with biodiesel. While the contribution of diesel oil to inhalation exposures during HMA paving has yet to be fully explored, diesel oil has been shown to be a source of dermal PAC exposures during paving operations (Weker *et al.*, 2004). Furthermore, diesel oil may contribute to total PAC dose as well as health effects as a study of Hungarian asphalt pavers found that diesel oil use contributed to chromosome aberrations (Major *et al.*, 2001). Using mean adjusted models at 149°C (300°F), HMA application temperature, substituting biodiesel for diesel oil use resulted in a 54 and 38% reduction in airborne TOM and

Table 4. Adjusted[a] GM airborne exposure levels over different worksite conditions.

Asphalt application temperature	Diesel oil use	TOM, μg m^{-3}	4-6 Ring PACs[b], μg m^{-3}	Fluorene, ng m^{-3}	Naphthalene, ng m^{-3}	Phenanthrene, ng m^{-3}	Pyrene, ng m^{-3}
149°C (300°F)	No restriction	1398	0.21	157	1868	701	127
149°C (300°F)	Biodiesel substitute	647	0.13	181	826	487	62
127°C (260°F)	No restriction	814	0.09	29	557	227	25
127°C (260°F)	Biodiesel substitute	376	0.06	33	247	157	12

[a]Models adjusted for task, air temperature, and hourly work rate as well as asphalt application temperature and biodiesel use. Predicted geometric mean results are for screedman, at the median air temperature of 21°C (69°F) and median hourly work rate of 149 tons h^{-1}.
[b]PACs obtained using a fluorescence method.

four- to six-ring PAC concentrations, with individual PAC reductions of 31–56% for naphthalene, phenanthrene, and pyrene; yet, no statistically significant change in fluorene concentration was observed.

HMA application temperature was a statistically significant predictor of air TOM and four- to six-ring PAC summary measures as well air fluorene, naphthalene, phenanthrene, and pyrene exposures. Mean adjusted models indicate that under baseline conditions with no restriction on diesel oil use, a reduction in HMA application temperature from 149°C (300°F) to 127°C (260°F) may result in a 42–57% reduction in airborne TOM and four- to six-ring PAC levels with individual reductions in PACs ranging from 68 to 82%, analyte dependent. In a study of asphalt workers in Norway with application temperatures ranging from 20 to 160°C (68–320°F), a lowering of exposure to total organic vapors was observed with lower asphalt application temperatures (Burstyn *et al.*, 2002). Likewise, an evaluation of historical exposures among European asphalt pavers found an association between airborne asphalt vapor exposure and asphalt temperature (Burstyn *et al.*, 2000). Because of the correlation between crew and HMA application temperature, we could not simultaneously evaluate crew and HMA application temperature effects; however, the positive statistically significant linear association that we observed lends further evidence to a relationship between HMA application temperature and airborne exposures.

Mean adjusted models predict that with both biodiesel substitution and lowering the HMA application temperature to 127°C (260°F), 73–71% reductions in TOM and four- to six-ring PAC may be achieved with individual PAC analyte reductions of 78–91%. However, the combined effect of substituting biodiesel and changing the HMA application temperature were not explicitly investigated in this study and additional studies are needed to estimate the effect of the combined exposure scenarios.

Task has been identified as a determinant of air PAC concentration (Heikkilä *et al.*, 2002; McClean *et al.*, 2004) as it serves as an indicator for the proximity of each worker to the HMA. Yet, we found no association between task and airborne exposure levels, but given only three workers for each task, the study may have been underpowered to observe differences in airborne exposure by task, which was not an original study aim. Crew has also been identified as a potential predictor of airborne exposures among HMA paving workers (McClean *et al.*, 2004), yet due to little variation in HMA application temperature by crew, we could not evaluate the association between crew and airborne exposures despite the fact that mean exposure estimates of TOM varied nearly 3-fold by crew (0.46, 1.08, 1.29 μg m^{-3}).

The current study was limited to 12 workers over three study crews. While the small sample may limit the generalizability of the study results, it does not affect the internal validity of the study. Despite the unbalanced design comparing 3 weeks with standard airborne exposures to only 1 week with biodiesel substitution, we still observed a statistically significant decrease in personal airborne exposures of many analytes with biodiesel substitution. One crew used a biodiesel/diesel oil blend (20/80) during the three standard air exposure scenarios; yet, reductions in airborne exposures were still observed when the crew switched to 100% biodiesel. There are no estimates on how widespread cleaning with diesel oil use is in the asphalt paving industry; yet, among our population, it was standard practice. Furthermore, some of the crews continued using biodiesel after the study period as workers were able to use less biodiesel as compared to diesel oil, perhaps due to its lower volatility. However, while biodiesel exhaust emissions have been characterized under field and lab conditions and studies comparing health effects of biodiesel and diesel fuel exhaust are on-going (Swanson *et al.*, 2007), exposure characterizations and potential health effects of using biodiesel oil as a cleaner have not been performed. While we attempted to evaluate a number of potential predictors of airborne exposure, there may be additional predictors that influence airborne exposures that we did not account for.

CONCLUSION

Reductions in personal airborne exposure to PACs among asphalt paving workers may be achieved by substituting biodiesel for diesel oil as a cleaning agent and decreasing the HMA application temperature.

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