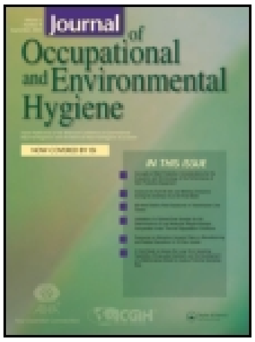

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Physical and Chemical Characterization of Asphalt (Bitumen) Paving Exposures

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The purpose of this research was to characterize the physical and chemical properties of asphalt (bitumen) fume and vapor in hot mix asphalt roadway paving operations. Area and personal air samples were taken using real-time equipment and extractive sampling and analytical methods to determine worker asphalt exposure, as well as to characterize the properties of the particulate and vapor phase components. Analysis of personal inhalation and dermal samples by gas chromatography/mass spectroscopy showed that the polycyclic aromatic hydrocarbon profile is dominated by compounds with molecular weights below 228, and that substituted and heterocyclic polycyclic aromatic hydrocarbons comprised approximately 71% of the detectable mass concentration (vapor and particulate combined). Principal components analysis shows that the polycyclic aromatic hydrocarbons with molecular weights greater than 190 are the driving force behind the polycyclic aromatic compound exposures measured for the dermal and particulate phases; there was no clear trend for the vapor phase Most of the aerosol particles are fine (mass median aerodynamic diameter 1.02 μm; count median diameter 0.24 μm).

Keywords asphalt, bitumen, polycyclic aromatic compounds, polycyclic aromatic hydrocarbons, aerosol size

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INTRODUCTION

Asphalt (bitumen) is a residual product from the distillation of crude petroleum such that its composition reflects the complexity of the source material. Crude petroleum is comprised mainly of aliphatic compounds; cyclic alkanes; aromatic hydrocarbons; heterocyclic compounds containing nitrogen, oxygen, and sulfur atoms; and metals, e.g., iron, nickel, and vanadium.(1) Elemental analyses indicate that most asphalts contain 79 to 88 weight percent (wt%) carbon, 7 to 13 wt% hydrogen, traces to 8 wt% sulfur, 2 to 8 wt% oxygen, and traces to 3 wt% nitrogen.(2)

In the United States, the predominant method of roadway paving is the application of hot-mix asphalt (HMA). These asphalt products are reported to comprise approximately 85% of the production of asphalt paving products.(1) In HMA, asphalt cements make up 4–10% of the mixture (by mass).(2,3) Other types of asphalt including cutback asphalts (produced by dissolving asphalt cement in a solvent) and asphalt emulsions (asphalt mixed with a surfactant in water) are primarily used for sealing, maintenance and repair of existing roadways.

In HMA, the asphalt binder and mineral aggregate are mixed at temperatures ranging from about 149 to 177°C (300 to 350°F). The HMA is transported to the paving site, usually by truck, and applied to the roadway at temperatures between 112 and 162°C (235 and 325°F).(1) During and after application, vapors released from the HMA cool and condense to form asphalt fume; however, as noted by NIOSH in 2001, the physical nature of fumes and vapors has not been well characterized.(1) HMA paving workers are exposed to atmospheres containing vapor and fume mixtures as this phase transition occurs. Because the members of the paving crew work at different locations around the paving equipment, there may be substantial variability in the physical properties and chemical composition of the exposure between workers.

The purpose of this research was to characterize the physical and chemical properties of asphalt (bitumen) fume and vapor in HMA roadway paving operations. The results of these studies can be compared with other data on the characteristics of field- and laboratory-generated asphalt fumes. This information on the nature of the emissions that result in worker exposure by inhalation and dermal uptake can provide insights into the source(s) of these exposures, and can also be used for risk assessment, risk management, and risk communication.

BACKGROUND

Historically, the assessment of occupational exposure to PAHs has relied primarily on air monitoring.(4) When monitoring PAH exposure, personal air samples have typically been analyzed using NIOSH Method 5506, or a similar HPLC method which specifically targets 16 standard unsubstituted parent PAHs. Asphalt, however contains a complex mixture of unsubstituted PAHs, substituted PAHs, and PAH heterocyclic derivatives and may not be adequately characterized using NIOSH Method 5506.(5)

In response to this issue, NIOSH Method 5800 was developed to measure total polycyclic aromatic compounds (PACs) in exposure samples collected from asphalt workers.(6) The analysis of total PACs can be optimized to target large PAHs (four, five, or six aromatic rings), representing the fraction that is typically thought to be carcinogenic. This is accomplished by a flow injection HPLC method after the column was removed with the UV fluorescence detector at 254 nm excitation and 400 nm emission. Smaller PAHs (two, three, or four rings) are preferentially detected using 254 nm excitation and 370 nm emission.

Although these detector emission wavelengths are more sensitive to particular PAC ring sizes (e.g., molecular weight), it is not exclusive; compounds outside of these ring sizes may contribute, in part, to the signal response. The method is particularly useful because total PACs includes alkylated or otherwise substituted PAHs that may also be mutagenic or carcinogenic, but would be missed if analyses were restricted to the 16 unsubstituted parent PAHs. However, specific chemical identification of individual PACs with this flow injection technique is not possible because a single discrete signal is produced in lieu of a poorly separated chromatogram when analyzed with the HPLC column in place.

Additionally, there is currently no standardized method for measuring dermal exposure to PAHs and few studies have evaluated dermal contact among asphalt workers. Using polypropylene exposure pads as adsorbing materials, Jongeneelen et al. evaluated dermal exposure among paving workers exposed to coal tar.(7) The exposure pads were attached to five different locations on the skin of each worker using an adhesive backing material. Similarly, Wolff et al. evaluated dermal exposure among roofers by collecting pre-shift and post-shift skin wipes from a measured area of each worker's forehead.(8) Both studies found substantial levels of dermal PAH contamination, suggesting that an assessment of PAH exposure that fails to address dermal absorption may considerably underestimate cumulative exposure.

In a series of studies of asphalt paving workers, we identified significant determinants of inhalation and dermal exposure, and evaluated the relative contribution of the inhalation and dermal pathways with regard to total absorbed dose.(9,10) The initial investigation included the collection of inhalation and dermal patch samples from 20 paving workers during three consecutive work shifts. The 20 workers were divided among three crews and each worker conducted one of four tasks: paver operator, roller operator, screed man, or raker. All samples were analyzed for PACs, pyrene (PYR), and benzoapyrene (BAP) via HPLC and the exposure data were analyzed using linear mixed-effects models to identify significant determinants of exposure.

The inhalation and dermal PAC exposures were found to vary significantly by task, crew, and the extent to which the mix contained recycled asphalt product (RAP). The inhalation results were consistent with a task's proximity to the primary sources of asphalt fume (hopper and screed auger of paving machine), such that the highest inhalation exposures were measured for paver operators and screed men while the lowest exposures were measured for rakers and roller operators. The dermal results were consistent with the extent to which each task involves contact with asphalt-contaminated tools, such that the highest dermal exposures were measured for rakers and screed men while the lowest exposures were measured for roller operators and paver operators.(9)

The second phase of our previous investigation included the collection of pre-shift, post-shift, and bedtime urine samples from 20 paving workers during three consecutive days. The urinary 1-OHP levels were found to be significantly different by paving task such that levels were highest for screed men and rakers and lowest for paver operators and roller operators. These results suggest that dermal contact is the primary route of exposure among asphalt paving workers when using urinary 1-OHP as an indicator of exposure.(10)

METHODS

Area and personal air samples were taken using real-time equipment and extractive sampling and analytical methods to determine worker asphalt exposure, as well as to characterize the properties of the particulate and vapor phase components. Two surveys were conducted on employees of the same U.S. paving company in 1999 and 2000.

In the 1999 survey, 20 highway pavers applying HMA were sampled each for 3 consecutive days. The survey included 3 paving crews, each consisting of 6–8 workers conducting 4 different tasks. A paver operator (1 worker) sat between the hopper and the screed while operating the paving machine; screedmen (2) stood on a platform attached to the back of the paving machine, each operating controls to apply the proper width and depth of HMA on the road surface; rakers (2–3), also known as lutemen raked and shoveled HMA using hand tools to fill holes and gaps behind paver, smooth edges, and prepare seams; and a roller operator (1 or 2) drove the equipment to compact newly paved surface. The study population included workers from each of the four task categories (paver operators, screed men, rakers, and roller operators) in three different crews.

The overall sampling strategy and methods have been described in detail.(9) Briefly, each day of sampling included the collection of personal air samples (particulate and vapor), dermal patch samples and urine samples. Personal air samples were collected in accordance with NIOSH Method 5506, utilizing a Teflon filter followed with an XAD-2 sorbent tube.(5)

The filter (particulate) and tube (vapor) samples were analyzed separately for PAC, pyrene (PYR), and benzo(a)pyrene (BAP) by HPLC (NIOSH methods 5800 and 5506) with emission and excitation wavelengths of 254 nm and 415 nm, respectively.(5,6) (Instrument response was optimized for these samples by using 415 nm, rather than 400 nm as the emission wavelength.)

The measures of total PACs determined by NIOSH Method 5800 are made using a flow injection HPLC method with the column removed. The UV fluorescence detector is set at 254 nm excitation, while the excitation wavelength can be optimized to respond to smaller PAHs (two, three, or four rings) at 370 nm emission, these results are reported as PAC 370.(6) The analysis of total PACs can be optimized to target large PAHs (four, five, or six aromatic rings), representing the fraction that is typically thought to be carcinogenic by using 400 or 415 nm emission, these results are reported as PAC 400 or PAC 415.

Personal dermal patch samples were collected from the wrists of each worker. The dermal samples were obtained from each worker on three consecutive days following a modification of the method described by Jongeneelen et al. and Van Rooij et al.(7,11) Two samples per worker per day were collected by attaching the patches to the underside of each wrist. Samples were analyzed for PAC, PYR, and BAP by HPLC (NIOSH methods 5800 and 5506). These analyses were conducted in the Harvard Organics Laboratory.

The limits of detection for the analytes were 0.2 ug/m^3 for PAC, and 0.01 ug/m^3 for PYR and BAP. In the statistical analysis, all values less than detection limits were used in all analyses. This approach was selected because many "non-detected" values were detected above the instrument detection limit, but after blank-correcting were below the method detection limit which was conservatively estimated as three times the standard deviation of the field blanks. The use of actual concentrations, whether or not below the limit of detection, is considered a valid approach for the statistical analysis of this data.

Using the archived sample extracts (168 samples in dimethyl sulfoxide {DMSO}), the principal components of aerosol, vapor and dermal exposures were determined by Gas Chromatography/Mass Spectrometry (GC/MS) in 2005 to develop a PAH profile for each sample. The analytical method was derived from EPA Compendium Method TO-13A, Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS), EPA/625/R 96/010b to determine 18 unsubstituted PAHs (Acenaphthene, Dibenz(a,h)anthracene, Acenaphthylene, Fluoranthene, Fluorene, Anthracene, Benzo(b)fluoranthene, Benz(a)anthracene, Indeno(1,2,3-cd)pyrene, Benzo(a)pyrene, Naphthalene, Benzo(e)pyrene, Benzo(g,h,i)perylene, Phenanthrene, Benzo(k)fluoranthene, Pyrene, Chrysene, and Perylene), as well as alkylated PAHs, and S-PACs with and without alkyl groups, which have been reported in field and laboratory-generated asphalt fume.(12) These analyses were conducted by the Harvard Organics Laboratory. The limits of detection for the PAHs ranged from 0.7–4.9 ng/m^3 for the PAHs by GCMS.

The results of the PAH profiles by GC/MS were incorporated in a principal components analysis (PCA) to identify the groups of individual PAHs that are most explanatory of the PAC 415 measurements for the particulate, vapor and dermal exposure measurements. The approach described by Burstyn was followed, using the PROC PRINCOMP in SAS.(13)

In a separate survey conducted in 2000, gravimetric sampling was performed on two HMA paving days to determine exposures to total particulate matter (TPM) and the benzene soluble fraction of particulate matter (BSF) by NIOSH Method 5042. Personal and area sampling was also conducted with a 5-stage personal impactor to determine PAC concentration for different size ranges (PTFE substrates, cut points: filter, 0.5, 1.0, 3.5, and 10 μm). Vapor phase PAC was collected with Orbo 42 sorbent tubes in series behind the impactors. Both of these sample types were analyzed for PAC 370 and 400 using hexane/DMSO extraction with HPLC analysis (NIOSH Method 5800). Particle size distributions were also obtained using a Grimm Optical Particle Counter, Model 1.106, which counts and classifies individual particles based upon the amount of light scattered (Cut points: 0.35, 0.5, 0.75, 1, 2, 3.5, 5, 6.5 μm). These measurements were made at points determined to be representative of work locations for the paving crew. These included the rear center of the paver deck and operator seats, the center of screed platform, and the distance at which the rakers trailed the paving machine, approximately 3 to 10 m. The temperature of the HMA mix was approximately 149°C (300°F) during the sampling period.(14) These analyses were conducted by Datachem Laboratories, which was the primary contract laboratory for NIOSH. LOD for the PAC determinations was 0.06 ug/m^3

RESULTS

The results of the GCMS reanalysis of the archived samples are presented in Table I for each of the three sample types (vapor, particulate, and dermal). Overall the PAH profile is dominated by compounds with molecular weights below 228. Not included in the table are the results for benzo(a)anthracene, C4-phenanthrenes/anthracenes, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, C1-chrysenes, dibenz(ah)anthracene, indeno(123-cd)pyrene, C2-chrysenes, C3-chrysenes, benzo(ghi)perylene, and C4-chrysenes. These compounds were detectable in less than 5% of the sample extracts, so they were not reported or included in any further examination of the data.

The prominence of the substituted and heterocyclic PAHs is also noteworthy. These compounds comprised approximately 71% of the detectable PAH mass concentration (vapor and particulate combined). In the air samples, the vapor phase PAH concentrations substantially exceed the particulate phase, particularly for the lower MW PAHs. Higher MW PAHs (MW >192 C1-phenanthrenes/anthracenes) tend to predominate in the dermal samples.

TABLE I. Summary Statistics of PAH Analysis by GCMS

		Particulate (DL = 1.7 ng/m^3)		**Vapor (DL = 1.7 ng/m^3)**		**Dermal (DL = 0.2 ng/cm^2)**	
Analyte	**Molecular Weight**	**%Detect**	**Mean (SD) (ng/m^3)**	**%detect**	**Mean (SD) (ng/m^3)**	**%detect**	**Mean (SD) (ng/cm^2)**
Napthalene	128	56.4	91.9 (267)	96.4	190.4 (135)	23.2	9.4 (39)
2-methylnapthalene	142	36.4	7.4 (12)	96.4	597.9 (570)	19.6	0.9 (3)
1-methylnapthalene	142	36.4	4.5 (8)	96.4	297.0 (269)	19.6	0.5 (1)
Acenapthylene	152	10.9	11.4 (50)	60.0	50.3 (86)	7.1	6.5 (34)
Acenapthene	154	3.6	8.6 (45)	50.9	55.6 (88)	5.4	6.6 (34)
C2-napthalenes	156	1.8	0.9 (7)	96.4	687.1 (575)	17.9	1.1 (3)
Fluorene	166	1.8	0.5 (3)	89.1	168.1 (154)	10.7	3.5 (19)
C3-napthalenes	170	0.0	0.0 (0)	92.7	397.9 (328)	7.1	0.6 (2)
Phenanthrene	178	30.9	12.4 (24)	98.2	623.3 (618)	42.9	6.0 (9)
Anthracene	178	3.6	3.4 (18)	69.1	70.9 (75)	5.4	0.1 (1)
C1-fluorenes	180	0.0	0.0 (0)	81.8	149.4 (136)	8.9	0.7 (2)
C4-napthalenes	184	1.8	1.5 (11)	74.5	154.8 (143)	1.8	0.1 (1)
Dibenzothiophene	184	5.5	2.3 (13)	90.9	106.4 (101)	33.9	2.1 (9)
C1-phenanthrenes/ Anthracenes	192	14.5	29.6 (84)	89.1	434.1 (374)	35.7	13.5 (26)
C2-fluorenes	194	1.8	0.4 (3)	72.7	105.1 (105)	12.5	2.0 (6)
C1-dibenzothiophenes	198	14.5	9.0 (24)	89.1	190.8 (168)	42.9	4.4 (7)
Fluoranthene	202	50.9	28.8 (45)	87.3	114.2 (111)	37.5	1.9 (3)
Pyrene	202	54.5	26.2 (37)	89.1	63.0 (55)	30.4	1.5 (3)
C2-phenanthrenes/ Anthracenes	206	9.1	33.8 (120)	63.6	162.1 (174)	19.6	8.1 (21)
C3-flourenes	208	0.0	0.0 (0)	0.0	0.0 (0)	0.0	0.0 (0)
C2-dibenzothiophenes	212	23.6	32.2 (73)	85.5	204.4 (178)	28.6	4.6 (11)
C3-phenanthrenes/ Anthracenes	220	16.4	47.7 (134)	12.7	17.4 (59)	10.7	3.9 (13)
C3-dibenzothiophenes	226	18.2	26.0 (65)	52.7	55.0 (66)	3.6	0.4 (2)
benzo(a)anthracene	228	29.1	6.6 (13)	0.0	0.0 (0)	0.0	0.0 (0)
Chrysene	228	30.9	8.2 (16)	0.0	0.0 (0)	0.0	0.0 (0)

The principal components analysis of the PAH profiles confirms these apparent patterns. Principal components analysis shows that the higher molecular weight compounds are the driving force behind the PAC measurements for the dermal and particulate phases, but not the vapor phase. When these factors are entered into a linear mixed effects model (Table II), the high MW compounds are found to be significant for both particulate ($p = 0.002$) and dermal phases ($p = 0.06$). For particles, Factor 1 is comprised of primarily the higher MW PAHs, significant in mixed models. Factor 3 comprised of the lower MW compounds, is not significant. For dermal samples, Factor 1 (higher MW PAHs) is significant in mixed models, while Factor 2, comprised of lower MW compounds, is not significant. For vapor, there was no clear pattern, as both Factors 1 and 2 were significant.

The surveys conducted in 2000 were intended to characterize the physical and chemical properties of the airborne emissions and the resulting exposures from the HMA process.(14) The results of personal sampling for TPM, BSF, and PAC (370 and 400) are presented in Table III. By all exposure metrics, the three primary work tasks can be ordered as paver operators > screed operators > rakers (lutemen). PAC 370 substantially exceeds PAC 400 for all work tasks, indicating that the lower MW compounds (2, 3, and 4 ring) predominate since this excitation wavelength is more sensitive to these compounds.

The rakers who are farthest from the paving machine appear to be exposed to atmospheres that contain a slightly greater fraction of the total PAC 370 and 400 in the vapor state than the paver operators and screed operators. The vapor-phase PAC accounts for a small portion (10–25%) of the total PAC over all personal samples, as well as area samples collected on the paver deck and above the screed auger (Figure 1). As only 2 to 4 samples were collected at each location for comparison of vapor and particulate phase PAC, only means and ranges are reported for these measurements. For the Paver Operator samples, the mean percent volatile PAC 370 was 13.5, range 10.0–15.2 (4 samples); Screed Operator mean 15.6, range

TABLE II. Results of Principal Components Analysis for PAH

	Particulate Factors					Vapor Factors					Dermal Factors				
Analytes	**1**	**2**	**3**	**4**	**5**	**1**	**2**	**3**	**4**	**5**	**1**	**2**	**3**	**4**	**5**
napth	−0.1	0.0	0.9	−0.1	0.2	0.6	0.4	0.8	0.5	0.2	−0.1	0.9	0.1	0.0	0.0
2-methylnapthalene	0.1	−0.1	0.9	−0.1	−0.4	0.8	0.4	0.2	0.8	0.1	0.1	1.0	0.2	0.1	0.0
1-methylnapthalene	0.1	−0.1	0.9	−0.1	−0.4	0.9	0.5	0.3	0.8	0.1	0.2	1.0	0.2	0.1	0.0
acenapthylene	−0.2	−0.1	0.9	−0.1	0.2	0.4	0.4	0.9	−0.1	−0.1					
acenapthene						0.3	0.5	0.9	0.1	0.0					
C2-napthalenes						0.9	0.5	0.3	0.7	0.1	0.3	0.9	0.1	0.1	0.0
fluorene						0.8	0.8	0.7	0.3	0.0	0.0	0.9	0.3	0.1	0.0
C3-napthalenes						1.0	0.6	0.4	0.5	0.1					
phenanthrene	0.9	0.5	0.0	−0.2	0.1	0.8	0.9	0.5	0.3	−0.1	0.2	0.3	0.9	0.4	0.0
anthracene	−0.2	−0.1	−0.1	1.0	0.0	0.5	0.9	0.4	0.2	−0.1					
C1-fluorenes						0.9	0.7	0.4	0.3	0.1	0.9	0.2	0.1	0.1	0.0
C4-napthalenes						0.9	0.6	0.5	0.4	0.1					
dibenzothiophene						0.8	0.8	0.6	0.2	−0.1	0.0	0.0	0.0	0.0	1.0
C1-phenanthr/anthr	0.5	1.0	−0.1	−0.1	0.2	1.0	0.8	0.4	0.5	0.0	0.9	0.1	0.6	0.3	0.0
C2-fluorenes						1.0	0.5	0.3	0.5	0.0	1.0	0.1	0.2	0.1	0.0
C1-dibenzothiophenes	0.7	0.5	0.0	−0.1	0.4	0.9	0.8	0.4	0.4	−0.1	0.2	0.0	0.5	0.9	0.0
fluoranthene	0.9	0.4	0.0	−0.2	0.0	0.7	1.0	0.5	0.4	−0.1	0.3	0.1	0.9	0.5	0.0
pyrene	0.9	0.6	−0.1	−0.2	0.2	0.7	1.0	0.5	0.4	−0.1	0.8	0.1	0.8	0.3	0.0
C2-phenanthr/anthr	0.3	1.0	−0.1	−0.1	0.2	0.9	0.6	0.3	0.6	0.1	0.9	0.0	0.3	0.1	0.0
C2-dibenzothiophenes	0.7	0.9	−0.1	−0.1	0.3	0.9	0.8	0.4	0.4	0.0	0.1	0.1	0.4	0.9	0.0
C3-phenanthr/anthr	0.6	0.9	−0.1	−0.1	0.2	0.5	0.6	0.1	0.8	−0.1	1.0	0.0	0.3	0.1	0.0
C3-dibenzothiophenes	0.5	0.9	0.0	−0.1	0.1	0.7	0.9	0.3	0.4	0.0					
benzo(a)anthracene	0.9	0.4	0.1	−0.1	−0.2	0.1	−0.1	0.0	0.0	1.0					
chrvsene	0.9	0.5	0.0	−0.1	−0.1										
PAC (p-values)[A]	0.0002	0.004	0.34	0.19	0.19	0.03	0.02	0.90	0.04	0.14	0.06	0.62	0.02	0.12	0.69

[A] Mixed models used to evaluate the effect of five factors.

13.0–21.2 (4 samples); Lutemen mean 21.0, range 19.2–22.6 (2samples); Paver Operator (area) mean 10.2, range 8.0–14.5 (4 samples); Screed Operator (area) mean 13.2, range 12.0–14.5 (4 samples); Roller (bkgd) mean 24.9, range 13.0–26.0 (4 samples).

The results of personal and area sampling utilizing the 5-stage personal impactor are presented in Table IV. For the paver operator and screed operators, the particle size fractions 1–3.5 μm and 0.5–1.0 μm predominate, with approximately 86% of the total particulate PAC 370 mass in these ranges. The pattern is somewhat different for the rakers, however, as only 61% of the PAC 370 mass is in the 0.5–3.5 μm size range, while 34% is in the <0.5 μm size fraction. A similar pattern of results was seen for the PAC 400 measurements.

TABLE III. Worker TWA Exposure Summary (Ranges)

Job	Paver Operator	Screed Operator	Raker/ Lutemen
Total Particulate (mg/m^3)	1.3−1.4	0.4−1.1	0.58−0.62
Benzene Soluble Fraction (%)	85−95	72−84	45−58
Total PAC 370 (ug/m^3)	197−198	52−206	51−55
PAC 370 (% volatile)	26−27	26−35	32−41
Total PAC 400 (ug/m^3)	35−39	9−40	8.4−11
PAC 400 (% volatile)	25	25−32	32−35

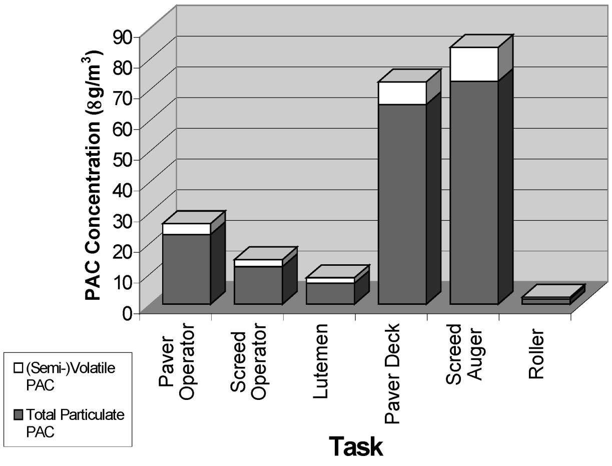

FIGURE 1. Mean Particulate and (Semi-)Volatile PAC Concentration by Task (8-Hour TWA)

TABLE IV. Breathing Zone Mean PAC 370/400 Concentrations (μg/m^3) by Particle Size (μm)

Job	>10	3.5–10	1–3.5	0.5–1	<0.5	Vapor
Paver Op.	2.1/0.2^A	2.0/0.2	74.0/14.2	52.3/10.2	14.9/3.2	51.9/9.2
Screed Op	1.8/0.4	1.4/0.4	24.6/4.7	70.0/13.7	11.6/4.0	42.1/7.9
Screed Op/ Foreman	0.8/1.2	0.5/0.6	7.4/1.0	22.0/4.0	7.9/1.6	17.9/3.3
Raker/Lutemen	0.8/(0.3)^B	0.6/ND	4.6/(0.6)^B	16.0/3.2	11.6/2.2	19.3/3.2

[A] Comparison of the PAC concentrations at 370 nm and 400 nm as emission wavelengths.
[B] Below limit of quantitation.

When the particle size distribution characteristics from the impactor samples are calculated for PAC 400 (Table V), the paver and screed operators are seen to be exposed to aerosols with a mass median aerodynamic diameters (MMAD) of 1.1 and 0.9 μm respectively, while rakers' aerosol exposure has a MMAD of 0.4 μm with a very large geometric standard deviation (5.2). A similar pattern is presented in the size distribution statistics for PAC 370 (Table V).

Measurements made with the optical particle counter (OPC) show that asphalt fume is fine, with approximately 90% of the mass being detected in particles less than 3.5 μm in diameter. Mass median diameter for the particulate material exposure over all the tasks conducted by the paving crew was 1.02 μm (GSD = 2.1), with a count median diameter of 0.2 μm. The characteristics of the particle size distribution measured by OPC are presented in Table VI.

DISCUSSION

The complexity of the mixture that asphalt workers encounter has long been a challenge to exposure assessment. In fact, when NIOSH prepared the 1977 Criteria Document on Asphalt Fume, it reported that no measurements of personal exposure were found.(15) The difficulty in making such exposure measurements was probably a major factor in the lack of sampling data.

Since then, a number of approaches have been used to characterize exposures, including total particulate matter, the benzene-soluble fraction of the total particulate, the identification and quantitation of individual PAHs, and the non-specific approach to measure the class of polycyclic aromatic compounds (PAC) without attempting separation, NIOSH method 5800. In its 2000 Hazard Review, NIOSH concluded that the results from methods based on liquid chromatography and UV detection should not be considered to be reliable measures of individual PAHs from asphalt fume in air.(1) Methods utilizing GCMS, therefore, are the approaches of choice in identifying, and quantifying the constituents of asphalt exposures.

Our previously reported results of the 1999 surveys showed that inhalation and dermal exposures to PAC, PYR and BAP among paving workers varied significantly among different tasks and among different crews.(9,10) In particular, the amount of recycled asphalt mix (RAP) was a significant predictor of air and dermal exposure. Inhalation and dermal exposures were significantly higher when paving workers used "high RAP" (>26%) asphalt mix as compared to "low RAP" asphalt mix. The effect of RAP did not vary by task. Among paving workers, the highest PAC inhalation exposures were estimated for paver operators (Low RAP: 5.6 μg/m^3, High RAP: 26 μg/m^3) and screedmen (3.5 μg/m^3, 16 μg/m^3) while the lowest exposures were estimated for rakers (1.7 μg/m^3, 7.9 μg/m^3), and roller operators (0.7 μg/m^3, 3.0 μg/m^3). The highest PAC dermal exposures were estimated for rakers (194 ng/cm^2, 412 ng/cm^2) and screedmen (164 ng/cm^2, 347 ng/cm^2) while the lowest exposures were estimated for roller operators (56 ng/cm^2, 118 ng/cm^2) and paver operators (34 ng/cm^2, 73 ng/cm^2).

TABLE V. Particle Size Distribution by Job PAC 370/400

Job	Paver	Screed Oper.	Raker/ Lutemen	All Jobs
Mass Median Diameter (um)	1.2/1.1^A	0.9/0.9	(0.5)^B/(0.4)^C	1.0/0.9
GStandard Deviation	2.7/2.2	2.7/3.6	3.9/5.2	2.6/2.9
Mass Fraction <l um (%)	46/48	75/73	82/86	63/64
Percent Respirable	86/88	91/88	92/92	89/88

[A] Comparison of the PAC concentrations at 370 nm and 400 nm as emission wavelengths.
[B] MMD ranged from 0.30–0.7; lower MMD approximated and may be biased due to low sample loading.
[C] MMD ranged from 0.15–0.6; lower MMD approximated and may be biased due to very low sample loading.

TABLE VI. Particle Size Distribution Measured by Grimm Optical Particle Counter

Parameter	Paver	Screed	Raker
MMD	1.19 μm	0.98 μm	0.72 μm
GStd Dev	1.98	2.12	2.17
MF < 1 μm	40.2%	54.5%	73.1%

MMD-Mass median aerodynamic diameter.
MF-Mass fraction.

The partitioning of analytes between the particulate phase (filter) and the vapor phase (XAD tube) was evaluated. The PAC and BAP partitioning found the majority of PAC was detected on the filters (65%–84%) and BAP was detected on filters exclusively (100%). Pyrene was detected primarily in the vapor phase among the paving workers overall (76%).

Our reanalysis of archived sample extracts by GCMS confirmed some aspects of the information gained by analyzing the samples for PAC 370 and 400, and significantly enhanced the characterization of PAH composition. One finding of note is the apparent difference in the particle to vapor partitioning between the PAC measures and the measures of individual PAHs. In both rounds of surveys (1999 and 2000), PAC exposure measures were dominated by the particulate phase, with vapor typically comprising 10–35% of the total PAC collected in the sampling train. The opposite pattern is seen for the individual PAHs (Table I), as the mass found in the vapor phase exceeded the particulate phase for all of the analytes except C3-phenanthrenes/anthracenes, benzo(a)anthracene, and chrysene, which were the highest MW compounds detected. When the PAH profiles were examined by PCA, both for particulate and dermal samples, Factor 1 was comprised of primarily the higher MW PAHs, and it was found to be a significant predictor of PAC (both particulate and dermal) in mixed models. Considering these facts together, this suggests that most of the PAC measured was not due to unsubstituted PAHs.

In addition to the complexity of the chemical composition, the semivolatile nature of many polycyclic compounds must be considered. The difference in temperatures between the air in the outdoor environment, and the temperature of the HMA at the point of application suggests that there can be rapid phase transformations as vapors cool, condense onto ambient particulate material, and agglomerate to form larger clusters or chains.

There are few data available on the size distributions of particles in the HMA paving environment. Hicks reported in 1995 that approximately 76% of the particles collected above the screed auger were between 1 and 5 μm in diameter.(16) The measurements we made by two different methods (extractive sampling with inertial classification by cascade impactors, and optical particle counting) were remarkably comparable given the differences between the measurement principles. Our data indicate that MMAD of the particles in the paving environment is about 1 μm, and the great majority of the mass is contained in particles less than 3.5 μm in aerodynamic diameter.

CONCLUSIONS

Most of the inhalation PAC exposure among HMA pavers is comprised of small particles (1 μm aerodynamic diameter and smaller). This vapor to particle partitioning is apparently reversed for the PAHs with MW less than 220, as the vapor phase concentrations measured substantially exceed the particulate phase mass. This may be an artifact caused by the semivolatile nature of the PAH compounds, resulting in air stripping of the particulate material collected on the filter. This suggests that air sampling methods that do not incorporate a sorbent tube in line with the filter (such as the TP and BSF methods) will not accurately measure PAHs. For both particulate and dermal phases of HMA exposures, compounds with MW between 190 and 228 tend to drive the PAC measure, while for vapor, there was no clear trend. The similarity in PAH profiles between airborne particulate and dermal samples suggests that they are from a common source.

RECOMMENDATIONS

Given the importance of particle aerodynamic diameter in the pattern of pulmonary deposition, animal exposure studies should be conducted utilizing aerosols that will be deposited in the animals' respiratory tract in a manner that is representative of the human exposure to workplace atmospheres. As Bottin noted in the study of genotoxic effects of exposure to bitumen fume in rats, particles in the size range they generated (MMAD 4.6 μm) are unlikely to reach the terminal bronchioles in rats.(17) In mice, deposition of particles larger than 2 μm in the combined tracheobronchial and pulmonary regions has been estimated to be less than 6.5%.(18)

Given our findings that the mean aerodynamic diameter of particles that constitute exposure in HMA is approximately 1 um, which are captured at approximately 97% efficiency in the gas-exchange region of the human lung,(19) animal studies should be designed to expose animals to particles that will be retained with similar efficiency.

DISCLAIMER

The findings and conclusions are those of the author(s) and do not necessarily represent the views of the National Institute for Occupational Safety and Health (NIOSH). It has not been formally disseminated by NIOSH, and it does not represent and should not be construed to represent any agency determination or policy. Mention of any company name or product does not constitute endorsement by NIOSH.

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