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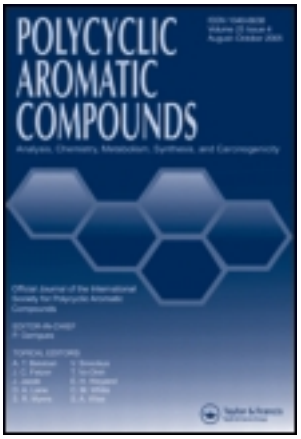

Polycyclic Aromatic Compounds
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Pilot Study for the Investigation of Personal Breathing Zone and Dermal Exposure Using Levels of Polycyclic Aromatic Compounds (PAC) and PAC Metabolites in the Urine of Hot-Mix Asphalt Paving Workers

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Pilot Study for the Investigation of Personal Breathing Zone and Dermal Exposure Using Levels of Polycyclic Aromatic Compounds (PAC) and PAC Metabolites in the Urine of Hot-Mix Asphalt Paving Workers

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As part of the design of a comprehensive study of hot-mix asphalt paving workers to investigate the relative contribution of personal breathing zone and dermal exposures to polycyclic aromatic compounds, a two-part pilot (Phase I) was performed. The pilot study was important to examine the sources of exposure, the chemical nature of these exposures, and their biological relevance through analysis of biomarkers in urine. Existing, modified, and new sampling and analytical techniques, used in concert with each other, were evaluated to help design the full-scale study (Phase II).

Although subject numbers were limited, the air, dermal, and urine sampling, analytical results and field experience provided valuable guidance in the design and implementation of Phase II. An overview of methods used and developed from this study is provided. More details of those methods selected for Phase II are presented in complementary manuscripts. Results of Phase II will be the subject of future publications.

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INTRODUCTION

Polycyclic aromatic compounds (PACs) are components of various materials that asphalt paving workers are exposed to during hot-mix asphalt (HMA) applications. The National Institute for Occupational Safety and Health (NIOSH) reviewed numerous HMA-related publications (1) prior to 2000 that reported increased levels of urinary 1-OH pyrene, suggesting an increased risk of exposures to PACs in workers around HMA as compared to individuals that have no exposure to HMA. 1-OH pyrene is a metabolite of pyrene, which commonly occurs in PAC mixtures. Studies that are more recent have also shown that elevated levels of urinary PAC metabolites are found in asphalt paving workers (2–5). The scientific community has increased research activities related to potential dermal exposure to asphalt emissions and related asphaltic materials with conflicting results. Based on a statistical lag model, McClean et al. estimated that workers were exposed to approximately eight times more pyrene through dermal absorption than through inhalation (6). However, Walter and Knecht (7) found that workers were exposed about equally through dermal absorption and inhalation. This conclusion was based on whole-body exposures to asphalt emission experiments where some subjects wore powered air purifying respirators and, as such, were primarily exposed by the dermal route and the remaining subjects were exposed both dermally and through inhalation. Airborne PAC exposure concentrations were then compared to the concentrations of PAC metabolites in the urine. A study conducted by Cirla et al. (8) showed a three-fold higher dermal exposure rate as compared to inhalation exposure rate but indicated that the relevance of dermal absorption is lower than inhalation absorption based on toxicokinetic information. Finally, the International Agency for Research on Cancer (IARC) epidemiological studies (9–11) were updated to include a dermal exposure component. Results of this study found "no consistent evidence of an association between indicators of either inhalation or dermal exposure to bitumen and lung cancer risk" (12).

Real-world HMA worker exposures are extremely complex not only because of the chemical complexity of the emission itself but also because of the presence of other organic exposure sources. For example, when asphalt cools it solidifies and must be removed from equipment; it is common practice to use diesel oil (a petroleum distillate ~C-10 through C-28) to clean tools and rinse down the paver. Recent studies have shown the importance of these mixed exposures. One study of road pavers in Hungary determined chromosome aberrations (CAs) in blood samples and concluded that increases in CAs could be attributed to the presence of genotoxic agents other than those in asphalt fumes, mainly compounds in diesel exhausts and in solvents used for cleaning the equipment (13). Another study by Boogaard concluded that co-exposures (such

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as asphalt fumes and diesel oil) were important contributors to elevated levels of urinary metabolites of PACs (14). In 2004, IARC initiated a nested case control epidemiology study (12) as a follow up to their previous mortality study (9–11) and concluded that confounders such as tobacco smoke and coal tar may have made significant contributions to the increased incidence of lung cancer mortality observed in European asphalt workers.

The focus of the current work was to develop new methods and evaluate existing methods for a comprehensive study intended to better understand potential sources of organic exposure and the chemical composition of these exposures within the HMA paving industry. Through detailed analysis of the physical and chemical properties of asphalt emissions related to worker exposures, the relative influence of dermal exposure compared to personal breathing zone (PBZ) exposure will be investigated in Phase II. This will be accomplished through evaluation of targeted urinary PAC metabolites using procedures and methods developed in this pilot study.

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STUDY DESIGN

An overview of the study design is portrayed in Figure 1. Phase I included six asphalt paving workers and three concrete control group workers and only two days of sampling for each of two parts (Parts A and B) and is consequently not intended to provide statistically definitive exposure assessment data. However, it did allow a preliminary assessment of environmental and biological measures to evaluate their usefulness in Phase II and provided an opportunity to identify and resolve logistical issues that may arise in the subsequent comprehensive study. Phase II is intended to understand the relative contributions of air and dermal exposures and their potential impact on dose and is a much more comprehensive and robust study design as fully described in a complementary article (15).

Phase I occurred in two steps: Parts A and B. Three members of an asphalt paving crew and three members of a concrete crew (control group) were used for Part A. Carried out in the fall of 2007, Part A included air monitoring, dermal sampling via cotton gloves, equipment wipes, and collection of pre-shift, post-shift, and bedtime urine samples. Part B, which was conducted in the spring of 2008, focused on the evaluation of dermal methods. It included three asphalt paving workers, limited air sampling, and limited urine sampling (pre- and post-shift only), primarily for comparison with the data obtained in Part A, and for use in the development of an immunoassay test used as a screening tool for PACs and their metabolites in urine. Two different dermal sampling approaches were evaluated in Part B. Unique to this study, the first approach utilized a newly developed passive organic dermal (POD) sampler, detailed in complementary articles (15–17). The second assessment involved hand wipe

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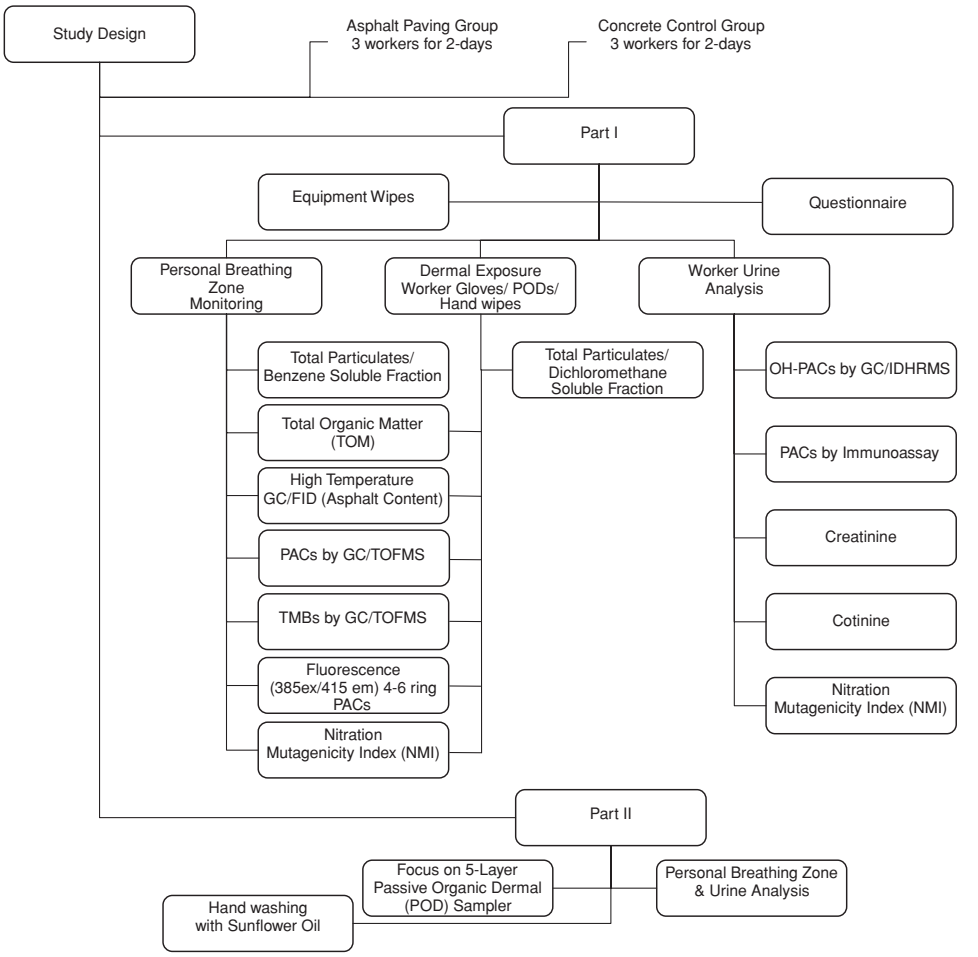

Figure 1: Overview of pilot study design. TMBs = Trimethylbenzenes, GC/FID = gas chromatography/flame ionization detection, GC/TOFMS = gas chromatography/time of flight mass spectrometry, GC/IDHRMS = gas chromatography/isotope dilution high-resolution mass spectrometry.

samples using sunflower oil (15, 17, 18) collected both pre- and post-shift. Although hand wipes have been used in the past, the battery of analytical tests conducted on these samples was more extensive than previously performed in other studies.

Asphalt worker volunteers included the operator, screedman, and raker for Parts A and B. The operator primarily sits on top of the asphalt paver while operating the equipment used to pave the roads. The screedman often stands on the back or next to the paver or screed area, and adjusts the equipment to deliver the asphalt mix at the proper depth and width. Finally, the raker generally rakes and shovels asphalt and adds finishing touches to the HMA after the mat has been laid but prior to compaction by the rollers. Within the

Figure 2: Hot mix asphalt paving of a parking lot during the pilot study (Color figure available online).

asphalt paving crew, these three tasks appear to have the greatest potential for exposure to HMA emissions. In addition, roller operators are a significant part of the asphalt paving crew and their function is to smooth and compact the laid-down asphalt to provide the finished product. Shuttle buggy operators are sometimes part of the crew when utilizing a hot asphalt transfer vehicle (shuttle buggy) that allows for non-contact continuous paving, although this equipment was not used in this particular study. Figure 2 shows the HMA paving process during Part A of this pilot study.

The study protocols for Phase I Parts A and B were reviewed and approved by the NIOSH Human Subjects Review Board. In addition, each study participant gave their informed consent before being allowed to take part in any aspect of the investigation.

SAMPLE COLLECTION

Air

For PBZ exposure monitoring, each worker wore a personal sampling train that included a 37-mm poly-tetrafluoroethylene (PTFE) membrane filter laminated to PTFE (2 μm pore size) housed in a cassette and a XAD-2 polymeric resin/charcoal tube connected in series as described in more detail in a companion article (15). The time of sample collection varied and continued over the entire shift for each worker. One background sample was collected each day, which was positioned upwind of the paving operation. Descriptive data were collected on potential confounders from the site, e.g., vehicle exhaust,

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construction dust, cleaning products, and any other potential background interferences. Field blanks were also collected, consisting of all sampling media that was opened in the field, then closed and stored with the worker samples.

Dermal

Gloves

Worker volunteers were asked to wear 100% cotton gloves, 12" in length (Cat No. RAD64057236; Airgas Inc.; Augusta, GA). Pre-rinsed with dichloromethane prior to use, dried and pre-weighed, these gloves were used as a sampler to understand better the types of dermal exposures on paving workers and were worn by each study volunteer for the majority of the day. None of the workers were observed wearing any other gloves during this phase of the study. At the end of the day when the asphalt paving workers cleaned up the equipment with diesel oil, a separate pair of gloves was provided to the appropriate workers. These gloves were referred to as the 15-min gloves, although the time varied slightly per day. Who and how many workers participated in the cleanup at the end of the day varied, and this information was documented. Workers removed their gloves and placed them into amber glass jars with Teflon® lined lids after use. Separate jars were used for the full workshift gloves and the 15-min gloves for equipment cleaning.

Extraction was performed on each pair of gloves by adding 200 mL of dichloromethane to each jar and sonicating for 30 min. They were then analyzed utilizing a battery of analytical tests as later described.

Hand Washing with Sunflower Oil (Dermal)

Wrists and hands were washed with sunflower oil to determine the quantity and composition of organic materials accumulated on the skin. Three mL of sunflower oil were added to the palm and, after rubbing the hands together in a washing motion for one minute, the workers then wiped the oil from their hands using Kimwipes® (Cat. No. 06–666c, Fisher Scientific; Pittsburgh, PA). This was performed at the beginning and end of the work shift. Full details are described in companion articles (15, 17, 18). Each Kimwipe® was stored in a Mylar bag and returned to that same labeled bag at the completion of the removal of oil. Workers were not observed washing their hands at any other times during the day. Unfortunately, there are rarely facilities available to do so in the construction world. Use of waterless hand cleaners or cloths was also not observed.

5-Layer Passive Organic Dermal Samplers

Passive organic dermal (POD) samplers were designed specifically for this study. A detailed description of this sampler is provided in companion articles

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(15–17). Briefly, it entails the use of five layers to allow capture of the full range of potential HMA emissions and other workplace exposures, such as diesel oil. The outer polypropylene layer serves as barrier like that of human skin in that it is a selectively permeable membrane. Middle layers that capture what is likely to penetrate through the skin, include polyurethane foam (PUF) and a solid phase extraction (SPE) disk to capture the bulk of the organic exposures. The inner layer contains a carbon cloth to capture any volatiles that are not retained by the middle layers. Ethylene tetrafluoroethylene serves to isolate the SPE disk from the carbon cloth layer. During Part B, personal dermal samples from each study volunteer were collected during a full work shift at the jobsite. Sampling occurred over two days using PODs located on four regions of the body believed to have the greatest potential for dermal exposure: the lower pant leg above the boot, the wrist/forearm, the center of the upper chest in the PBZ area, and the center front of the worker's hard hat. All PODs were positioned on the exterior of the clothing/hat. Each POD was collected at the end of the work shift and placed in an appropriately labeled Mylar bag, and stored and analyzed as described later in the text.

Urine

In Part A, pre-shift, post-shift, and bedtime urine samples were collected to determine levels of urinary PAC metabolites. In Part B, the bedtime samples were not collected. Workers were asked to provide a urine sample in a sterile 120-mL urine collection cup. The urine was transferred to a 50-mL centrifuge tube (Cat. No. 352098; Becton Dickinson; Bedford, MA) labeled with the worker ID, date, and time. Samples were stored on ice until transported to the laboratory, where they were stored at -20°C until analysis. More details about the urine collection and storage are available elsewhere (15).

Worker Questionnaire and Log

Qualitative data were collected using a baseline questionnaire and a daily observation log. Answers pertaining to demographics, physiology, use of PAC-containing medicines/topical products, nutrition, smoking, and lifestyle were recorded. In Part A, a five-page questionnaire was distributed to each study volunteer for them to document these parameters including their daily diet. Use of PAC containing products in the workplace and at home and in the diet may be important relative to urinary PAC metabolites, providing insight for data interpretation. This questionnaire was intentionally not incorporated into Part B, since most of the information could be obtained through observation. For Parts A and B, field personnel completed the daily observation logs for each day of the study, which were included as part of Phase II.

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Equipment Wipe Sampling

In Part A only, contamination of surfaces that workers come in contact with was collected for chemical characterization and comparison to corresponding air and dermal samples. Here, sampling involved wiping the equipment with a dichloromethane pre-extracted cotton pad (Johnson & Johnson pure cotton rounds, 6 cm diameter, Cat. No. 08137008251) moistened with 3 mL of hexane. A known surface area was wiped. For the rake, shovel and paver railing, a 23 cm x 1.6 cm template was used (151 cm^2). The steering wheel and knobs were 147 cm^2 and 21 cm^2, respectively, while the screed handles were 251 cm^2. The pad was placed in a scintillation vial with a Teflon® or foil-lined lid. For extraction, 20 mL of dichloromethane were added to the vial, the sample was vortexed for 1 min and then sonicated for 20 min. Surface wipe samples were analyzed in accordance with the same methods used for the dermal sampling (analytical procedure published elsewhere (15)).

ANALYTICAL METHODS

A brief summary of each method used in this pilot study follows. Since companion articles fully describe many of these methods, only those methods not fully described elsewhere will be described in detail.

Gravimetric Methods

Traditional gravimetric procedures using NIOSH Method 5042 were used to quantify asphalt worker exposure as described elsewhere (15, 19, 20) for total particulates (TP) and benzene soluble fraction (BSF) determinations. Gloves were pre-weighed and re-weighed after use to determine the total particulate matter (organic and inorganic) collected during the workday. Results were reported as mg/gloves. Total particulate matter was also determined from the difference of pre-and post-weights obtained on the top layer of the POD sampler. Since 200 mL of solvent were required for extraction to provide complete coverage of the gloves, dichloromethane was selected as the solvent instead of benzene because it is less toxic and more volatile, enabling ease of sample concentration. Similar to the BSF, dichloromethane extracted samples of the gloves and the POD polypropylene layer were evaporated into pre-weighed boats to dryness to obtain the dichloromethane soluble matter (DSM).

Chromatographic Methods

Total Organic Matter (TOM)

Gas chromatography with flame ionization detection (GC/FID), as described elsewhere (15, 21, 22), provided the amount and the chromatographic

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profile (fingerprint) of these exposures. For example, if the sample shows a typical petroleum distillate pattern that has a boiling point range between C-10–C-28, that could provide important information about the source of the exposure. Unfortunately, asphalt emissions and diesel oil have overlapping chromatographic patterns that make them difficult to differentiate. However, lube oils and various other patterns are distinguishable providing valuable information. All TOM extracts from air samples, gloves, PODs, and hand wipes were analyzed using this technique, providing valuable qualitative information relative to source of exposure.

High Temperature GC/FID

A high temperature GC/FID (HTGC/FID) was used to determine asphalt cement content (defined as hydrocarbons > C-25 or 401°C) of dermal exposures, which enabled some distinction between dermal exposure fractions, i.e., asphalt binder versus asphalt emissions or other organic exposures. This method allowed the separation of the lower molecular weight hydrocarbons from the higher molecular weight compounds. The higher molecular weight region of the chromatogram > C-25 is compared to a known asphalt standard curve. Under the experimental conditions used, asphalt components co-elute rather than individual peaks and is integrated over a range such that all of the area under that curve is used to quantify asphalt.

Method details are described elsewhere (15, 23, 24). Air and POD sample extracts were analyzed using this instrument.

PACs by Gas Chromatography/Time of Flight Mass Spectrometry (GC/TOFMS)

PAC profiles, containing 33 specific PACs, were obtained using GC/TOFMS following the guidelines of EPA SW-846 8270C (25) and a published procedure (22, 26). Although naphthalene, fluorene, fluoranthene, phenanthrene, and pyrene are the predominant PACs detected in asphalt emissions (6), the determination of this extensive list of PACs may provide useful information about the source of confounding exposures.

Trimethylbenzenes by GC/TOFMS

Examination of the trimethylbenzenes (TMBs) was performed to determine the isomeric ratios in an attempt to enable distinction between diesel oil exposures versus asphalt emission exposure, since both materials contain TMBs at various levels. These ratios were expected to be different for asphalt emissions as compared to diesel oil. TMBs were analyzed by GC/TOFMS using the dichloromethane TOM fraction. Using a ZB-5, 30 m $\times$ 0.25 mm $\times$ 0.25 μm column, the 1,3,5-TMB, 1,2,4-TMB, and 1,2,3-TMB isomers were analyzed using the semi-volatile organic compound method SW846–8270C (25) that is

used for the 33 PAC analysis, with the oven at a lower initial temperature of 35°C instead of 50°C (26).

Hydroxylated (OH-) PACs by GC/IDHRMS

All urine samples were extracted and analyzed, for 24 hydroxylated polycyclic aromatic hydrocarbon metabolites (OH-PACs) formed from eight different parent PAC compounds (naphthalene, fluorene, phenanthrene, pyrene, benzocphenanthrene, benzaanthracene, chrysene, and benzoapyrene), using a previously published method (27). The technology used for this evaluation was gas chromatography/isotope dilution high-resolution mass spectrometry (GC/IDHRMS). Since this provides definitive individual speciation, this test acts as the official reference method to which the newly developed methods are compared. This method was also selected due to the availability of large quantities of National Health and Nutrition Examination Survey data that were generated using this technique, which will allow comparisons with data from the more comprehensive study.

Spectroscopic Method

Total 4–6 Ring PAC Content

Fluorescence analysis was performed using the asphalt fume fluorescence (AFF) test protocol outlined in separate publications (15, 28). The instrument is calibrated using diphenylanthracene (DPA) and results are reported as DPA equivalents. This method was originally designed for asphalt fume emissions and the presence of asphalt binder and other confounders cannot be differentiated. Although the fluorescence response for asphalt binder is different from the asphalt fume response, this screening method provides relative differences. Low results indicate minimal exposure to any 4–6 ring PAC source, whereas high results, since mixed exposures are present, require further investigation to determine the source.

Biological Assay Methods

OH-PACs by Immunoassay

Urinary PAC-metabolites were assayed by modifying an existing commercial product designed for the measurements of PACs in water and used to measure PAC metabolites and parent PACs in urine. Details have been published elsewhere (15, 29). The goal of this method was to enable detection of the PACs and their metabolites using a faster and more economical approach relative to the individual speciation of the OH-PACs by GC/IDHRMS.

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Cotinine Analysis

Because tobacco combustion products contain PACs and therefore may contribute to daily PAC exposure, cotinine (nicotine-N-oxide), a metabolite of nicotine, was determined using a method previously described (15, 30, 31). The assay is an approved FDA method and is a common approach for differentiating passive and active tobacco users.

Creatinine Analysis

NIOSH analyzed all urine samples to quantify the amount of creatinine, which was used to normalize the urinary metabolite results using a previously described method (15, 32). Creatinine, a breakdown product of creatine phosphate in muscle, is commonly used to normalize concentrations in urine to account for the variations found with fluid intake since it is usually produced at a fairly constant rate by the body.

Nitration Mutagenicity Index (NMI)

Designed as a screening method indicative of the aggregate level of PACs, this Ames mutagenicity assay of chemically nitrated PACs (15, 33, 34) was used for air, dermal, and urine samples. This assay is a variation of that reported by Blackburn et al. (33, 34) and allows sensitive and selective detection of PACs and PAC metabolites. Sensitivity is achieved since the method involves nitration of PACs, which greatly enhances the signal of the PACs for detection (35). Although speciation is not determined, it can provide a useful relative comparison of urine samples from workers with closely related exposures. Uniquely, this method was also used for all of the non-urine industrial hygiene samples to provide similar screening data.

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RESULTS

Field Observations

Documentation of the potential factors that may influence worker exposures was a critical element of field monitoring. While sampling, many mixed exposures were observed including diesel oil used as a cleaning agent, smoking, asphalt emissions (vapors and fumes), asphalt binder, particulates, traffic exhaust, diesel exhaust from construction equipment, and solvents/lube oils while working on equipment. Exposure to organic compounds also occurred during equipment maintenance, breakdowns, and repairs when lube-oils and greases were used.

Because temperature is an important variable in the quantity and composition of the emissions released from asphalt (36), the asphalt mat temperatures just behind the screed were recorded daily. The average daily

temperatures were 129°C/140°C for the two days of sampling during Part A and 143°C/140°C for the two days of sampling during Part B.

During Part A, the operator and screedman smoked cigarettes, but the raker did not. Two of the concrete control group workers chewed tobacco products, but none of them smoked. During Part B, the three asphalt paving volunteers were all non-smokers.

One significant observation that will influence the future phases of the project was the use of diesel oil by many of workers. Diesel oil appeared to be a major contributor of both PBZ and dermal exposure and hence could potentially contribute to the dose of urinary PAC metabolites. One concrete control group worker used a substantial amount of diesel oil as a release agent for his equipment during this pilot study. The other two concrete control group workers did not use any diesel oil. All six asphalt workers used diesel oil during the course of their workday in varying amounts and times.

Based on observations made in Phase I, other variables were included in the data analysis of Phase II. Time working around HMA; tons of asphalt per minutes worked; asphalt type (performance grade specification); information about the relative amounts of diesel oil, grease, and lube oils usage or exposure; and information about the extent of dermal coverage (e.g., shirt or no shirt, long sleeves vs. short sleeves, hat or no hat, gloves or no gloves, and so forth) are among the variables under consideration.

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Air Sampling Results

Average PBZ exposure data are listed in Table 1. TP (which includes organic and inorganic particulates) and TMB average data were greater for the concrete control group workers than the asphalt group workers due to the substantial use of diesel oil by the one concrete crew volunteer. Dust levels were high during sawing concrete forms, which caused the high TP levels for the concrete control group. All other parameters showed greater results for the asphalt group as compared to the concrete control group. The sum of the 33 PACs was approximately 8 times higher for the asphalt group as compared to the concrete control group. Figure 3 shows chromatograms of two air monitoring samples (concrete control group worker 2 and the screedman) and a diesel oil reference sample. Although different sources of diesel oil were used, the chromatograms were similar (straight chain hydrocarbons in the C-10–C-28 range).

A sample of the diesel oil used by the asphalt crew in Part A was also analyzed for PACs. In addition to hydrocarbons in air samples having a similar carbon number distribution to the diesel oil, results show that the same prominent PACs were present in similar abundances; i.e. naphthalene, phenanthrene, pyrene, fluoranthene, fluorene, anthracene, and trace levels of other

Table 1: Air sampling results

		Asphalt Paving Group		Concrete Control	
Analyte/Description	Units	Arithmetic Mean	sd	Arithmetic Mean	Sd
TP	mg/m^3	0.26	0.10	0.76	0.60
BSF	mg/m^3	0.08	0.05	$\leq$0.04	0.01
TOM	mg/m^3	1.68	1.01	0.61	0.69
4–6 Ring PACs	ng $_{as\ DPA/m^3}$	317	186	107	120
Asphalt Cement	mg/m^3	$\leq$0.18	na	$\leq$0.18	na
TMB	mg/m^3	1.97	1.03	4.55	2.90
NMI	revertants/μL	96.3	42.7	5.4	5.04
Phenanthrene	$\mu g/m^3$	2.19	1.28	0.05	0.09
Fluorene	$\mu g/m^3$	0.97	0.72	0.048	0.08
Naphthalene	$\mu g/m^3$	0.95	0.32	0.636	0.56
Acenaphthene	$\mu g/m^3$	0.53	0.30	0.018	0.04
Fluoranthene	$\mu g/m^3$	0.36	0.23	$\leq$0.01	na
Pyrene	$\mu g/m^3$	0.29	0.19	$\leq$0.01	na
Anthracene	$\mu g/m^3$	0.24	0.23	$\leq$0.01	na
Sum of 33 PACs	$\mu g/m^3$	6.58	3.56	0.834	0.48

sd = standard deviation, TP = total particulates, BSF = benzene soluble fraction, TOM = total organic matter, PACs = polycyclic aromatic compounds, DPA = 9,10-diphenylanthracene, TMB = trimethylbenzene and NMI = nitration mutagenicity index, *na* = not applicable.

PACs. Figure 4 contains pie charts of the overall PAC distribution for the air sampling data.

Dermal Results

Gloves

Seven pairs of gloves were spiked with 16.8 mg of diesel oil and showed recoveries between 85.7% and 96.9% (average = 15.0 mg/gloves, standard deviation = 0.6). Results are reported as mass/gloves. Hand exposures from the field are obvious from the photograph of the gloves worn by the screedman (Figure 5). Some of the contaminants observed on the gloves include asphalt binder, dirt, and oils. TOM and sum of the 33 PACs results are shown in Table 2. The TOM results undoubtedly overestimate the asphalt emissions on the gloves because the gloves also contained some of the diesel oil used, as shown by the chromatographic elution profile obtained during TOM analysis (Figure 3). Concrete control group worker 2 had an average of 55 times higher exposure on his hands as compared to the average of concrete control group workers 1 and 3 (2000 mg/gloves vs. 36.5 mg/gloves). These data are consistent with the field observation that worker 2 was the only concrete control group worker who used diesel oil, spraying it to clean the belt on the concrete paver. Within

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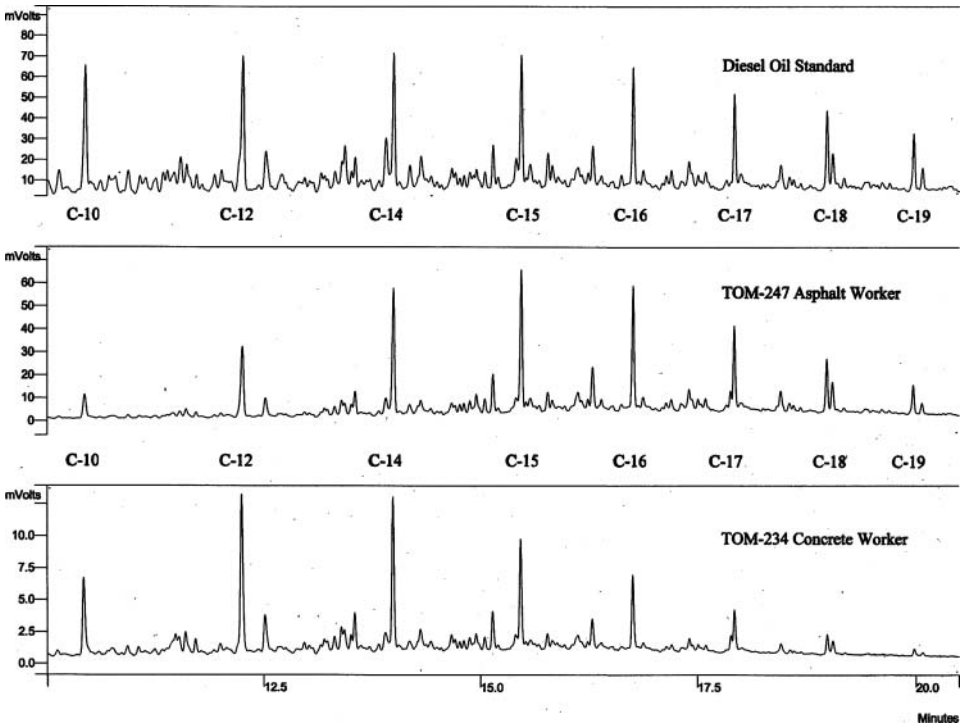

Figure 3: Chromatograms of two air monitoring samples and a diesel oil standard (x axis – elution time (minutes); y axis – intensity (mVolts). As an expanded view, the top chromatogram is that of a diesel oil standard, the bottom profile corresponds to the total organic matter exposures from concrete worker 2, while the middle chromatogram corresponds to that of the asphalt crew screedman. Although ratios are different, the same components are present despite the different sources of diesel oil used.

the asphalt group, the screedman used the most diesel oil for spraying down equipment and had the highest average all day TOM exposure at 262 mg/gloves and the highest all day TOM variability (166, 358 mg/gloves). The screedman also had the highest average TOM exposure for the 15-min gloves (463 mg/gloves) and highest TOM variability for the 15-min gloves (852, 73.2 mg/gloves).

The sum of 33 PAC data in Table 2 show similar trends to the TOM data. The all-day gloves of worker 2 contained approximately six times more PACs on day 1 than day 2 (1980 vs. 327 μg/gloves). PAC levels for the all day gloves used by the asphalt crew are consistent on both sampling days, with the screedman having the highest exposure.

As shown in Table 3 and consistent with the air monitoring samples, the TP is greater for the concrete control group over the asphalt crew. Fluorescence data indicated the presence of higher levels of 4–6 ring PACs for the asphalt group workers compared to the concrete control group (1170 vs. 240 μg

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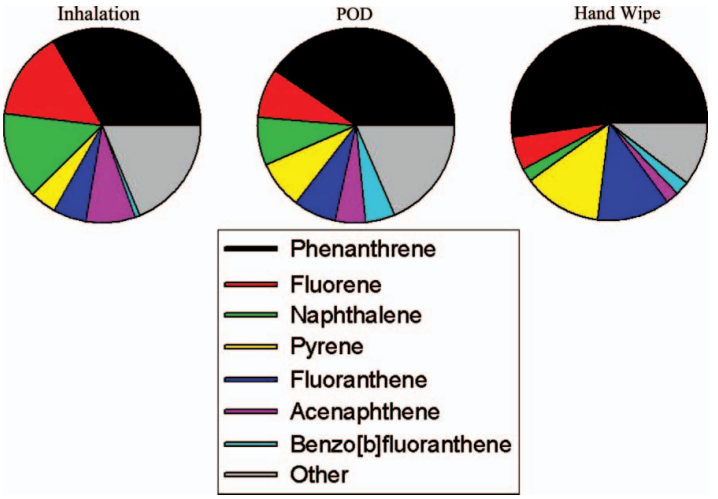

Figure 4: Pie charts showing distribution of the 33 PACs for asphalt paving air and dermal (Passive Organic Dermal (POD) and hand wipe) exposures, sum of all samplers (Color figure available online).

$_{\text{as DPA}}$/gloves). The presence of asphalt, as determined by HTGC/FID was confirmed on the asphalt group workers' gloves (average = 455 μg/gloves vs. non-detected for the concrete control group). Trimethylbenzenes were also detected on the gloves at a higher level for the asphalt group as compared to the concrete control group.

Figure 5: "All Day" gloves worn by the screedman of the asphalt paving crew (Color figure available online).

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Table 2: TOM and sum of 33 PACs detected on worker gloves

	Group	Worker ID	Glove ID	Day[a]	TOM mg/gloves	Sum 33 PACs μg/ gloves
All Day Gloves	Concrete Control	Worker 1	12	M	41.8	9.67
		Worker 1	22	R	27.4	12.8
		Worker 2	14	M	2460	1980
		Worker 2	19	R	1540	327
		Worker 3	21	M	38.5	21.7
		Worker 3	20	R	38.4	24.8
All Day Gloves	Asphalt Paving Group	Operator	2	M	52	49.7
		Operator	3	R	66.2	43.2
		Screedman	4	M	166	167
		Screedman	7	R	358	182
		Raker	6	M	165	94.5
		Raker	9	R	143	71.3
15-Minute Spray Down Gloves	Asphalt Paving Group	Operator	1	M	85.7	70.8
		Operator	11	R	39.6	52.5
		Screedman	5	M	852	17600
		Screedman	8	R	73.2	62.3
		Raker	10	M	6.95	26.2

[a] M = Monday, R = Thursday, TOM = total organic matter, PACs = polycyclic aromatic compounds.

POD Samplers

POD samplers were used in Part B to simulate dermal exposure for workers of the asphalt group and to capture PACs. The function of the five layers of the POD sampler was to facilitate capture of the chemically complex mixtures apparent in asphalt paving worker exposures. The outermost polypropylene layer served as a barrier to emulate that of human skin. Two middle layers included polyurethane foam and a C-18 solid-phase extraction disk to absorb and adsorb organic compounds that tend to migrate through the outer polypropylene layer. Finally, the inner-most layer consisted of activated carbon cloth to

Table 3: Arithmetic mean results from asphalt worker and concrete control group gloves

Test	Units	Asphalt Paving Group	Concrete Control Group
TP	g/gloves	1.86	6.32
TOM	mg/gloves	158	36/2002*
Fluorescence	μg $_{as\ DPA}$/gloves	1168	240
Asphalt Cement	μg/gloves	455	133
TMB	mg/m^3	424	24
NMI	revertants/μL	12,800	19,380

*concrete worker that used diesel oil (excluded from average) TP = Total Particulates, TOM = Total Organic Matter, TMB = trimethylbenzenes and NMI = Nitration Mutagenicity Index.

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capture volatile organics not retained by the middle layers. This sampler is fully described elsewhere (16). Samplers were located on the workers' head, chest, wrist, and leg to aid in the selection of the most suitable position of one POD sampler during Phase II. Organics were detected in the carbon cloth layer of the sampler at levels consistent with the field blanks. Therefore, the total dermal exposure of the seven most prominent PACs is taken from the polypropylene and PUF/SPE layers. The distribution of PACs within these two layers is further discussed in a companion article (16).

Figure 4 shows the percentages of individual PACs in relation to the sum of the 33 PACs for air, POD and hand wipe samples. Slices of these pie charts include phenanthrene, fluorene, naphthalene, pyrene, fluoranthene, acenaphthene, benzobfluoranthene, and "other", which represents the sum of the remaining detectable compounds (primarily 4–6 ring PACs). Remaining PACs (other) account for less than 6% of the total PACs. More detailed results for the POD samplers are presented in a separate publication (15–17).

Hand Wipes

Although the sunflower oil appeared to efficiently remove the materials that had accumulated on the hands throughout the work day, the oil did pose complications for the extensive analytical tests performed. For GC/MS analysis of the PACs, the injection port liners had to be changed daily due to the deposits of sunflower oil. For GC/FID fingerprint of the TOM, a solid-phase extraction cleanup was employed prior to analysis to remove the sunflower oil component. Results show dermal exposures similar to gloves.

In Part B, hand wipes were taken from three asphalt workers (operator, screedman, and raker) before and after their shift for two days. For the operator, the post-shift PAC concentrations (sum of 33) were 69.2 ng/cm^2 and 14.5 ng/cm^2, for day 1 and day 2, respectively. The screedman post-shift concentrations were similar for both days at 31.0 ng/cm^2 and 28.7 ng/cm^2. The raker post-shift concentrations varied for each day at 20.4 ng/cm^2 and 5.96 ng/cm^2. An examination of the GC/FID chromatograms indicated that many of the samples contained materials (exposures) from organic sources that were not fully consistent with asphalt emissions.

Urine

Cotinine levels were consistent with the field observations between smokers, chewers and non-smokers, with ng/mL concentrations averaging 7540, 3480 and 14, respectively.

Urine PAC-Metabolite Analysis by GC/IDHRMS

In Part A, urine samples were collected from workers of the asphalt paving and concrete control crews pre-shift, post-shift, and before bedtime and

Table 4: Summary data for all urine samples

Test	Units	Shift	Paving Group	Control Group
Cotinine	ng/mL	All	5027	2220
OH-PACs	$pg/mL_{creatinine}$	Pre-shift	23157	9040
		Post-shift	45265	15343
		Bed-time	39972	12664
NMI	revertants/μL	Pre-shift	186	183
		Post-shift	205	159
		Bed-time	196	204
Immunoassay	μg/g creatinine	Pre-shift	39.4	20.4
		Post-shift	107.3	28.9
		Bed-time	144.3	18.1

OH-PACs = hydroxylated polycyclic aromatic hydrocarbon metabolites, NMI = Nitration Mutagenicity Index.

analyzed by GC/IDHRMS to quantify the hydroxylated PAC metabolites as μg/g of creatinine. Detected OH-PACs included 2-, 3-, and 9-hydroxyfluorene, 1- and 2-naphthol, 1-, 2-, 3-, and 4-hydroxyphenanthrene, and 1−hydroxypyrene. The other 14 PAC metabolites were not detected; this was expected because these metabolites are excreted mostly via the feces (37). The limit of detections (LODs) were < 7 pg/mL for most analytes; however, the LODs were 18 and 12 pg/mL for 1- and 2-naphthol, respectively. Creatinine corrected PAC metabolite concentrations in pavers were about 2–10 times higher than the concrete control group, as seen in Table 4.

PACs and OH-PACs by Immunoassay

The method ranged from 0–720 ng/mL 1-OH pyrene equivalents with a lower limit of detection (LOD) of 14 ng/mL. Results are summarized in Table 4. Immunoassay data versus GC/IDHRMS PAC metabolite measurements gave consistent values at the individual level with an R^2 of 0.86. Total urinary PACs and PAC-metabolites as measured by the immunoassay method are increased for the asphalt paving group as compared to the concrete control group. At 95% confidence interval, the asphalt group levels were between 49.3–126 μg/g creatinine and the concrete control group levels were between 11.6–29.1 μg/g creatinine. The influence of diesel oil is evidenced in that the concrete control group worker that used diesel oil, had the highest level (143 μg/g creatinine) and the screedman, who used the most diesel oil, had the highest level for the asphalt group (517 μg/g creatinine).

Nitration Assay (NMI)

Urinary extracts for the concrete control group of workers averaged 159 revertants/μL for their post-shift samples. Asphalt worker averages were slightly higher (205 revertants/μL), but the differences were not statistically

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significant. Sample collection, transport, and storage indicated that this assay was feasible to include in the more comprehensive study. Results are shown in Table 4 and are discussed in greater detail in a subsequent publication.

Equipment Wipes

Surprisingly, the equipment wipes were relatively clean (individual data are not shown) perhaps due to removal by workers since they were wearing gloves. TOM results from the equipment were similar for the concrete control group and the asphalt group (16.2 vs. 7.1 μg TOM/cm^2). PACs also showed similar results (28.2 vs. 21.9 μg/wipe). Asphalt cement content by HTGC/FID averaged 23 μg/cm^2 on the asphalt paving equipment and was non-detected on the concrete equipment wipes. TMB data were slightly higher for the asphalt group as compared to the concrete control equipment (16.7 vs. 4.27 ng/cm^2). Both the fluorescence and the NMI data indicate that the asphalt paving equipment contained higher levels of total 4–6 ring PACs as compared to the concrete control group by one order of magnitude (1040/123 μg $_{\text{as DPA}}$/Wipe and 103/18 revertants/μL, respectively) likely from the presence of asphalt binder, known to contain these compounds. The personal scraper (a hand-held putty knife) showed the highest levels of contamination.

DISCUSSION

Air exposures in this pilot study were consistent with other recent industrial hygiene studies of asphalt workers for TP, BSF, and TOM (38–40). In the air monitoring samples of the asphalt paving work site, the sum of 33 PACs averaged 6.58 μg/m^3; similar to findings in other studies (1.1–9.1 μg/m^3 (6) and 5.03 μg/m^3 (41)). GC/HRMS results in the pilot study were similar in order of magnitude to results previously reported by the Division of Laboratory Sciences, National Center for Environmental Health, Centers for Disease Control and Prevention (37). However, as shown in Table 5, asphalt paver results were higher than concrete control group results; both of which were higher than the US adult and general population (37).

Analytically, most tests appeared to work well in concert with each other to help answer the questions posed for Phase II. Table 6 outlines a summary of methods evaluated in this pilot study and their fate as part of Phase II: accepted, accepted with modifications or rejected.

Accepted

The collection methods appeared to work well and were included in Phase II. The new POD sampler appeared to be very efficient at collecting the variety of compounds experienced in asphalt paving worker exposures and was

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Table 5: Comparison of concentrations of urinary PAC metabolites

Creatinine corrected geometric mean concentrations (ng/g creatinine)				
	Li et al., 2008 (37)		Pilot Study	
	US Adult (N = 1626)	General Population (N = 2748)	Concrete Control (N = 3)	Asphalt Paving (N = 3)
1-Naphthol	2070	1910	1913	11008
2-Naphthol	2480	2310	4131	7773
9-Hydoxyfluorene	217	205	423	1337
3-Hydoxyfluorene	131	125	179	1220
2-Hydoxyfluorene	314	298	538	3377
3-Hydroxyphenanthrene	99	98	264	1230
1-Hydroxyphenanthrene	137	132	250	1086
2-Hydroxyphenanthrene	54	51	143	582
1-Hydroxypyrene	45	46	212	2025

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included in Phase II. TP, BSF, TOM, 4–6 ring PACs and 33 PACs were all accepted for inclusion into Phase II for air samples. TOM and 33 PACs were retained for Phase II for the dermal samples.

Urine test results for the PAC-metabolite analysis by GC/IDHRMS, PACs, and OH-PACs by immunoassay, and NMI appear to be relevant and feasible for use in Phase II. Creatinine and cotinine evaluations also were helpful parameters in understanding the concentration and smoking contribution as related to the results. Additionally, the process developed for urine collection, transfer to the proper containers for the five urine tests, storage, and shipment during the Pilot study was all helpful in preparing for Phase II. This process was particularly important because of the large number of specimen collected in Phase II. It provided a better understanding of the personnel required, organization of vials containing any necessary preservatives, labeling, splitting samples, and delivering the proper amounts to each vial, thus allowing a smooth process for Phase II.

Accepted with modification

Despite the analytical complications from sunflower oil, hand washing data were valuable and incorporated into Phase II. Complications from the sunflower oil with the HTGC/FID analysis resulted in the development of an HPLC method for the determination of asphalt cement content used in Phase II as described elsewhere (15).

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Table 6: Summary of methods accepted, accepted with modification and rejected for Phase II

Test	Methods	Breathing Zone	PODs	Hand Wipes	Urine
Total Particulates/ Benzene Soluble Fraction	NIOSH 5042	Accepted	Modified	Accepted (TP and DSF)	NA
Total Organic Matter	SW-846–8015B Mod.	Accepted	Accepted	Accepted	NA
High Temperature GC/FID (Asphalt Content)	Nynas Method	Rejected	Accepted	Accepted with Modification	NA
PACs by GC/TOFMS	SW 846 8270C	Accepted	Accepted	Accepted	NA
TMBs by GC/TOFMS	SW 846 8270C modified	Rejected	Rejected	Rejected	NA
Fluorescence (385ex/ 415 em) 4–6 ring PACs	Heritage Method	Accepted	NA	NA	NA
OH-PACs by GC/IDHRMS	CDC Method	NA	NA	NA	Accepted
OH-PACs by Immunoassay	ELISA kit (RaPID Assay PAH test kit Product Modified)	NA	NA	NA	Accepted
Cotinine Analysis	Immulite® 2000 immunoassay	NA	NA	NA	Accepted
Creatinine Analysis	Vitros Autoanalyzer (Ortho Clinical Diagnosis)	NA	NA	NA	Accepted
Nitration Muagenicity Index	Blackburn Method	Rejected	Rejected	Rejected	Accepted

NA = not applicable, TP = total particulate, DSF = dichloromethane soluble fraction, PODs = passive organic dermal samplers, GC/FID = gas chromatography/flame ionization detection, PACs = polycyclic aromatic compounds, GC/TOFMS = gas chromatography/time of flight mass spectrometry, TMBs = trimethylbenzenes, OH-PACs = hydroxylated polycyclic aromatic hydrocarbon metabolites, GC/IDHRMS = gas chromatography/isotope dilution high-resolution mass spectrometry. Also exclude from Phase II, but not listed in this Table were the equipment wipe sampling, use of gloves as dermal samplers and the questionnaire.

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Rejected

The HTGC/FID showed no detectable asphalt cement in the air samples, so it was deemed unnecessary to include in Phase II. Trimethylbenzene ratios were examined, but the complex nature of multiple sources of exposures did not allow conclusive source-related evidence for inclusion so it was deleted for both air and dermal testing. NMI testing was omitted from the air and dermal analysis in Phase II. Since other methods provided similar information, it was decided to use it for the urine samples only.

Cotton gloves as dermal samplers, although helpful in understanding the amount and composition of dermal exposures on the hands, were excluded in Phase II because they may prevent dermal exposure through the hands. Hypothetically, if saturated, they could increase exposure by acting as an absorbent that remains in contact with the skin. High variability existed in the glove results that appeared to correlate with the tasks performed and the variability in the amount of diesel oil used.

Because the surface wipe sample results were all very low, contamination of the asphalt paving equipment appears to be minimal. Therefore, equipment wipe sampling was excluded from the study design of Phase II.

Finally, the questionnaire was excluded in Phase II since most parameters that the workers documented could either be observed or measured by industrial hygiene personnel.

Results for the air, dermal, and urine samples all appeared to allow distinctions between the asphalt group and concrete control group of subjects, although the influence of diesel oil is a significant confounder. This confounder was considered in the study design of Phase II by removing it from use in one of the experimental scenarios (15).

Within the concrete control group, only the concrete equipment driver used the diesel oil for cleaning his machine. This provided a unique snapshot of a worker exposure to diesel oil only, in the absence of asphalt emissions. The other two concrete control group workers had no exposures to either diesel oil or asphalt emissions. The asphalt group exposures, on the other hand, were much more complicated because mixed exposures prevailed. Use of diesel oil by the asphalt group was not surprising, but the quantity used was greater than expected. Diesel oil may not only be absorbed through the skin itself, but may also act as a carrier (solvent) for other PAC containing materials like asphalt binder that otherwise would not be available systemically (42).

In air samples, PACs predominantly consisted of 2- and 3-ring compounds, whereas for dermal samples, the samples tended to contain a longer list of PACs including some of the 4–6 ring compounds. The presence of both naphthalene and acenaphthene were low for the hand wipes as compared to the POD samplers and the air monitoring samples. This observation may be attributed to the sorbent component of the XAD-2/charcoal tubes and POD

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samplers, which sequester the naphthalene and acenaphthene. Hand wipes capture only the exposures that remain on the hands and do not include what has evaporated or what has absorbed through the skin by the end of the workday. The PBZ TMB data were higher for the concrete control study group (from one worker) than the asphalt paving study group but the opposite was true for the TMB levels on the gloves. This suggests that the concrete worker had potentially greater airborne exposure to diesel oil fumes than the asphalt paving study group, whereas dermal exposure was greater for the asphalt paving crew.

Based on the results of this study, the POD samplers were positioned on each worker's wrist/forearm for Phase II (16).

Levels of urinary PAC metabolites were greater for the operator and screedman, who were both smokers, as compared to the raker, a non-smoker. Based on the GC/IDHRMS data, the immunoassay data and the NMI data, the asphalt paving group workers had higher levels of urinary metabolites as compared to the concrete control group workers.

Results were below the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value for asphalt fumes, which is 0.5 mg/m^3 (8-h time-weighted average) based on the benzene-soluble portion of inhalable particulates (TP) (43). ACGIH recommends using an IOM sampler, which was compared with the 37 mm closed-face cassette (NIOSH Method 5042 sampler) and shown to be equivalent to the BSF (44) as measured in this study.

This is one of five companion manuscripts mentioned previously. Results of Phase II are the subject of separate manuscripts either in progress (3) or under review (3) (45–47).

CONCLUSIONS

The pilot study was successful in evaluating various collection and analytical methods for use in Phase II. Accomplishments during the course of this study included: (1) demonstrating that a passive organic dermal (POD) sampler is a useful tool for collecting dermal exposure of such a complex nature and suitable for future studies; (2) validating an immunoassay method as a measure of aggregate exposure to PACs that showed good correlations with the GC/IDHRMS speciation of the individual PAC metabolites and the Ames mutagenicity results for nitrated PACs and their metabolites; and (3) optimizing analytical methods for POD and hand wipe samples.

TP, BSF, TOM, HTGC/FID, PACs by GC/TOFMS Fluorescence (air only) were all retained for use in the Phase II study. The HTGC/FID method was not used for the hand wipe samples; instead a new HPLC method was ultimately developed due to complications with the sunflower oil. Excluded methods included TMB analysis, asphalt cement content in air, equipment wipes, cotton gloves as dermal samplers, and the questionnaire.

Based on the frequency of diesel oil use observed in this pilot study, Phase II was designed to included an exposure scenario where diesel oil use was replaced with B-100 Biodiesel fuel (fatty acid methyl esters) to study HMA exposures without diesel oil as a confounder. This pilot study was also instrumental in working out the logistics in preparation for Phase II such as the large amount of equipment/samplers that would be needed, and field personnel required to handle sample mounting, monitoring and collection.

Overall, the asphalt paving group showed elevated OH-PAC exposures as compared to the concrete control group. Of the 33 PACs tested, the inhaled exposures were predominantly 2- and 3-ring, whereas the dermal exposures sometimes included the higher molecular weight PACs.

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