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## **NIOSH HEALTH HAZARD EVALUATION REPORT:**

### **HETA #2001-0536-2864**

# **Crumb-Rubber Modified Asphalt Paving: Occupational Exposures and Acute Health Effects**

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DEPARTMENT OF HEALTH AND HUMAN SERVICES  
Centers for Disease Control and Prevention  
National Institute for Occupational Safety and Health



## PREFACE

The Hazard Evaluations and Technical Assistance Branch (HETAB) of the National Institute for Occupational Safety and Health (NIOSH) conducts field investigations of possible health hazards in the workplace. Upon request, HETAB provides technical and consultative assistance to Federal, State, and local agencies; labor; industry; and other groups or individuals to investigate occupational health hazards and to prevent related trauma and disease.

This summary report completes a technical assistance to the Federal Highway Administration (FHWA). It contains the summation of the environmental and medical data gathered from a series of seven NIOSH Health Hazard Evaluations (HHEs) conducted between 1994 and 1997. Each of these HHEs measured airborne exposures among paving crews while using crumb-rubber modified asphalt and conventional (non-rubber containing) asphalt. Health assessments of acute effects was also conducted at each site. Mention of company names or products does not constitute endorsement by NIOSH.

## ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

The main authors of this composite report are Gregory Burr and Allison Tepper (NIOSH, Division of Surveillance, Hazard Evaluations and Field Studies [DSHEFS]), Larry Olsen (NIOSH, Division of Applied Research and Technology [DART]), and Aubrey Miller (Department of Health and Human Services-[DHHS], U.S. Public Health Service [USPHS], Region VIII). The statistical analysis was performed by Amy Feng (NIOSH, DART). Those responsible for the development of the initial research protocol included Aubrey Miller, Kevin Hanley, Larry Olsen, and Ken Wallingford. Individual project officers for the HHEs included Kevin Hanley, Aubrey Miller, Daniel Almaguer, Gregory Burr, and Gregory Kinnes, all of DSHEFS at the time. Analytical methods were developed by Larry Jaycox, Charles Neumeister, and Larry Olsen. Laboratory analyses were provided by Ardith Grote, Robert Kurimo, Larry Jaycox, Leroy May, Charles Neumeister, and Rosa Key-Schwartz, all of DART. Desktop publishing was by Robin Smith and Ellen Blythe of DSHEFS. Review and preparation for printing were performed by Penny Arthur of the Education and Information Division [EID].

Copies of this report have been sent to FHWA officials as well as to employer and employee representatives at each asphalt paving company. Copies have also been furnished to the appropriate OSHA Regional Offices. This report is not copyrighted and may be freely reproduced. Single copies of this report are available for a period of three years from the date of this report. To expedite your request, include a self-addressed mailing label along with your written request to:

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## Highlights of the NIOSH Health Hazard Evaluation

### Evaluation of Crumb Rubber Modified Asphalt Paving: Occupational Exposures and Acute Health Effects

Between 1994 and 1997, the National Institute for Occupational Safety and Health (NIOSH), with help from the Federal Highway Administration, studied asphalt paving workers at seven road paving sites in the U.S. Our plan included developing and testing new sampling methods, comparing workers' exposures to crumb-rubber modified (CRM) asphalt and conventional (CONV) asphalt, and evaluating potential acute health effects from CRM and CONV asphalt.

#### What NIOSH Did

- We took personal breathing zone (PBZ) air samples on both CRM and CONV asphalt paving workers during their workday.
- The jobs that were sampled included truck dumper; paver, screed, and roller operators; rakers; laborers, and site supervisors.
- We tested for total particulate (TP), benzene soluble particulate (BSP), polycyclic aromatic compounds (PACs), organic sulfur-containing compounds (OSCs), and benzothiazole. Only TP and BSP have occupational exposure limits.
- We sampled for solvents that are sometimes used during asphalt paving.
- We sampled for diesel exhaust and carbon monoxide (CO) at the paving site.
- We checked if the asphalt fume was mutagenic by testing it on bacteria.
- We asked paving and non-paving workers to complete a questionnaire about symptoms such as eye, nose, and throat irritation.
- We tested the workers' breathing capacity during their work day.

#### What NIOSH Found

- PBZ exposures were usually higher during CRM asphalt paving.
- The highest exposures were from jobs near the paver or asphalt delivery trucks.
- Eye, nose, and throat irritation were the symptoms most frequently reported.
- During CRM asphalt paving, eye, nose, and throat irritation were associated with TP.
- Four paving workers had breathing problems which may be work-related. All were exposed to CRM asphalt.
- Solvent levels were generally very low. Benzene was detected at several sites.
- High CO exposures (near the NIOSH ceiling limit of 200 parts per million) were measured near some workers.
- Diesel exposures were low.
- Benzothiazole was found at all sites. We do not know if these levels have health effects.
- None of the asphalt fume samples tested in this study were mutagenic.

## Conclusion

Our findings suggest that CRM exposures are potentially more hazardous than CONV exposures. Regardless of the type of asphalt being used, however, skin contact with asphalt and any clean-up solvents should be avoided and exposure to asphalt fume should be reduced whenever possible by the use of engineering and administrative controls.



**What To Do For More Information:**  
We encourage you to read the full report. If you would like a copy, either ask your health and safety representative to make you a copy or call 1-513-841-4252 and ask for HETA Report # 2001-0536-2864



# **NIOSH Summary Report of Crumb–Rubber Modified Asphalt Paving: Occupational Exposures and Acute Health Effects**

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## **SUMMARY**

In 1991, Congress enacted the Intermodal Surface Transportation Efficiency Act (ISTEA), which required each state to use a minimum quantity of "crumb–rubber modified" (CRM) hot–mix asphalt (HMA) paving material. Because of industry and labor concerns over the lack of available information on the environmental and human health effects resulting from the use of CRM–HMA, along with the higher initial cost of using this paving material, a temporary legislative moratorium was passed and the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Transportation, Federal Highway Administration (FHWA) were directed by Congress to evaluate the potential environmental and human health effects associated with the use of CRM asphalt. The National Highway System Designation Act of 1995 eliminated the mandate requiring the use of CRM asphalt but continued to require research concerning CRM asphalt paving.

In June 1994, the National Institute for Occupational Safety and Health (NIOSH) entered into an Interagency Agreement with the FHWA to evaluate occupational exposures among asphalt road workers. A study protocol developed by NIOSH included the following objectives:

- Develop and field test new methods to assess asphalt fume exposures.
- Characterize and compare occupational exposures to CRM asphalt and conventional (CONV) asphalt.
- Evaluate potential health effects associated with CRM asphalt and CONV asphalt.

The protocol called for up to eight individual site evaluations in different regions of the country. The intent was to allow NIOSH investigators to observe different asphalt pavement formulations, climatic conditions, and paving techniques. Seven site evaluations were completed between 1994 and 1997. The environmental and medical results discussed collectively in this report have been individually published in the following seven NIOSH Health Hazard Evaluation (HHE) final reports:

- HETA 94–0365–2563, Spartan Paving Company, Lansing, Michigan (March 1996)
- HETA 94–0408–2564, Granite Construction Company, Sacramento, California (March 1996)
- HETA 95–0118–2565, Martin Paving Company, Yeehaw Junction, Florida (March 1996)
- HETA 95–0307–2602, Koester Equipment Company, Evansville, Indiana (December 1996)
- HETA 96–0072–2603, Staker Paving Company, Casa Grande, Arizona (December 1996)
- HETA 96–0130–2619, Sim J. Harris Company, San Diego, California (December 1996)
- HETA 97–0232–2674, Barton–Trimount, Stoughton, Massachusetts (February 1998)

A new NIOSH method which simultaneously sampled for total particulate (TP) and benzene soluble particulate (BSP) was developed.<sup>1</sup> Polycyclic aromatic compounds (PACs) were sampled using a new analytical method that

included a PAC<sub>370</sub> group (2–3 ring compounds, many of which have irritative effects) and a PAC<sub>400</sub> group (4– and more ring compounds, some of which are carcinogenic).<sup>2</sup> In addition to PACs, organic sulfur–containing compounds (OSCs, present in crude petroleum or from the addition of rubber) and benzothiazole (a sulfur–containing compound present in rubber tires), were also sampled using a newly developed sampling and analytical method.<sup>3</sup> These compounds were of interest for their potential for respiratory irritation (OSCs) or for their use as an indicator of other chemicals present in CRM asphalt fume (OSCs and benzothiazole). Samples were collected for volatile organic compounds (VOCs, including toluene, xylene, benzene, and methyl isobutyl ketone [MIBK], and total VOCs [TVOCs, quantified as Stoddard solvent]. Both elemental carbon (EC) and organic carbon (OC) were measured and the ratio to total carbon (TC) was compared to ascertain if diesel exhaust was a likely contributor to the air contaminants measured at each site. Area air samples were collected to determine the respirable particulate concentrations. Direct–reading instruments were used to measure carbon monoxide (CO), hydrogen sulfide (H<sub>2</sub>S), sulfur dioxide (SO<sub>2</sub>), and ozone. Finally, high volume air samples of both CRM and CONV asphalt fume were collected from the emissions of asphalt cement storage tanks located at the hot–mix plants and analyzed to determine their mutagenic potential.

Area air sample results revealed that concentrations of TP, respirable particulate, BSP, PACs, OSCs, and benzothiazole varied between sampling locations and survey days but were generally higher during the CRM asphalt paving than during CONV asphalt paving. In all but two samples, the PAC<sub>370</sub> concentrations were greater than the PAC<sub>400</sub> concentrations. All of the air samples collected for EC above the screed auger on the paver vehicle had concentrations above the background levels. Since diesel exhaust has been reported to contain EC levels between 60 to 80% of the TC, the relatively low EC:TC ratios measured at all but one of the sites imply that diesel exhaust was not substantially contributing to the air sampling results.<sup>4</sup> None of the asphalt fume samples were found to be mutagenic using a spiral *Salmonella* mutagenicity assay.

Over 50 VOCs were detected in the asphalt emissions, but only the highest peaks were analyzed quantitatively. Although higher concentrations of toluene, xylene, and MIBK were measured during CRM asphalt paving, all concentrations were generally less than 1 part per million (ppm). Concentrations of TVOCs (as Stoddard solvent) ranged up to 224 milligrams per cubic meter (mg/m<sup>3</sup>). The NIOSH Recommended Exposure Limit (REL) for Stoddard solvent is 350 mg/m<sup>3</sup> for up to a 10–hour time–weighted average (TWA). Benzene was detected near the screed auger in area samples collected during CRM asphalt paving in concentrations up to 0.77 ppm. Lower, but still detectable, concentrations of benzene were measured during CONV paving. NIOSH classifies benzene as an occupational carcinogen with a REL of 0.1 ppm, 8–hour TWA, noting that exposures should be controlled to the lowest feasible level (LFL).

All personal breathing–zone (PBZ) TP exposures were below 1.4 mg/m<sup>3</sup>, expressed as TWAs for the workday. These PBZ results cannot be compared to the NIOSH REL for asphalt fume of 5 mg/m<sup>3</sup> for a 15–minute exposure since the samples in this study were collected over the full work–shift. For six of the eight job categories studied, the geometric mean (GM) PBZ exposures to TP during CRM asphalt paving (range 0.17 to 0.48 mg/m<sup>3</sup>) was higher than during CONV asphalt paving (range 0.06 to 0.81 mg/m<sup>3</sup>). However, only the screed operators and roller operators were exposed to significantly more TP during CRM asphalt paving than during CONV asphalt paving ( $p \leq 0.01$ ).

The GM BSP concentrations were higher for four of the six jobs evaluated during CRM asphalt paving (range 0.02 to 0.25 mg/m<sup>3</sup>) compared to CONV asphalt application (range 0.02 to 0.44 mg/m<sup>3</sup>). The average concentration by job was below the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV<sup>®</sup>) of 0.5 mg/m<sup>3</sup>, 8–hour TWA for asphalt fume. Some paver operators and truck dumpers, however, had individual exposures above the TLV. The BSP concentration differences by asphalt type were not significantly different for any job category.

The GM PBZ concentrations for PAC<sub>370</sub>, PAC<sub>400</sub>, OSCs, and benzothiazole were higher during CRM asphalt paving than CONV paving. As was observed in the area air samples, PAC<sub>370</sub> concentrations exceeded PAC<sub>400</sub> concentrations. Of the jobs evaluated, only the screed and roller operators had significantly higher PAC exposures during CRM asphalt paving when compared to CONV paving ( $p \leq 0.01$ ). The paver, screed, and roller operators

were all exposed to significantly more OSC during CRM paving than CONV paving ( $p \leq 0.01$ ). All paving jobs were exposed to significantly more benzothiazole during CRM paving than during CONV paving ( $p \leq 0.01$ ). With the exception of the first survey site in California, benzothiazole was only detected during CRM asphalt paving. There are currently no occupational exposure limits for PAC<sub>370</sub>, PAC<sub>400</sub>, OSCs, or benzothiazole, and little occupational exposure data exists for comparison beyond what is reported in this study.

TWA CO area concentrations ranged up to 24 ppm during paving, with peak values as high as 910 ppm. The NIOSH REL is 35 ppm for up to an 8-hour TWA, with a ceiling limit of 200 ppm. Concentrations of H<sub>2</sub>S, SO<sub>2</sub>, and ozone were well below their respective occupational exposure limits.

Prior studies of the acute toxic effects of asphalt fume exposures in workers have repeatedly reported eye and upper respiratory tract (nasal) irritation.<sup>5</sup> These health effects have been well documented in asphalt road pavers and typically appear to be mild and transient. In this study, both CRM and CONV asphalt workers experienced symptoms (eye, nose, and throat irritation being most commonly reported), but the occurrence rates of these symptoms were higher among the CRM asphalt-exposed group. With one exception during CRM asphalt paving, specific contaminant concentrations did not differ between days when eye, nose, or throat irritation or cough were present and days when these symptoms were absent. Concentrations of TP were nearly twice as high on days when eye, nose, or throat irritation was present compared to those days when eye, nose, or throat irritation was not reported ( $p \leq 0.01$ ). During CONV asphalt paving, concentrations of TP, BSP, and PACs were significantly higher on days when eye, nose, or throat irritation was present ( $p \leq 0.05$ ). Concentrations of BSP, OSC, and benzothiazole were significantly higher on days when cough was present ( $p \leq 0.05$ ). Although an exposure-response relationship has not been established in this study, the identification of health effects related to personal exposures to contaminants (measured as TP and BSP) during both CRM and CONV asphalt paving indicates that such a relationship may exist.

Exposures to TP, BSP, PACs, and OSCs were generally higher during CRM asphalt paving compared to CONV asphalt paving. The highest PBZ exposures were measured on paver and screed operators, and truck dumpers. Screed and roller operators were exposed to significantly more TP during CRM paving than during CONV paving, while no significant difference existed between CRM and CONV paving for BSP exposures. Workers on all paving jobs had significantly higher exposures to benzothiazole during CRM paving. Symptom occurrence rates were higher during CRM asphalt paving, and eye, nose, and throat irritation were the three most frequently reported symptoms among all asphalt fume exposed workers. At some paving sites, worker exposures to CO exceeded the NIOSH ceiling limit of 200 ppm. Area air samples measured generally low concentrations of selected VOCs at the paving sites, with the exception of benzene. Recommendations are included for lowering the asphalt application temperature; prohibiting eating, drinking, and smoking near asphalt fume emissions; providing washing and clothes-changing facilities at the work site; reducing the use of diesel fuel for tool cleaning; and wearing protective clothing or appropriate sun screen to protect exposed skin from harmful effects of sun exposure when working outdoors.

**Keywords:** SIC 1611 (Highway and Street Construction), asphalt fume, bitumen, crumb-rubber modified, CRM, recycled tires, paving, polycyclic aromatic compounds, PACs, polynuclear aromatic hydrocarbons, PAH, total particulate, respirable particulate, benzene soluble particulate, volatile organic compounds, TVOC, elemental carbon, eye irritation, throat irritation, respiratory irritation, mutagenicity.



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## INTRODUCTION

Approximately 285 million tires are discarded in the United States each year, posing significant health, fire, and solid waste management problems.<sup>6</sup> One means of reducing these problems is to use scrap tire rubber in highway paving materials. In 1991, Congress enacted the Intermodal Surface Transportation Efficiency Act (ISTEA), which required each state to use a minimum quantity of "crumb-rubber modified" (CRM) hot-mix asphalt (HMA) paving material, beginning at 5% of the HMA used in federally funded paving in 1993, and increasing to 20% in 1997 and thereafter.

Because of concerns over the lack of available information on the environmental and human health effects resulting from the use of CRM-HMA, along with the higher initial cost of using this paving material, a temporary legislative moratorium was passed which precluded enforcement of the penalty provisions of the ISTEA legislation. It also directed the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Transportation, Federal Highway Administration (FHWA) to evaluate the potential environmental and human health effects associated with the use of CRM asphalt. Although the National Highway System Designation Act of 1995 eliminated the mandate requiring the use of CRM asphalt, it still required research concerning CRM asphalt paving.

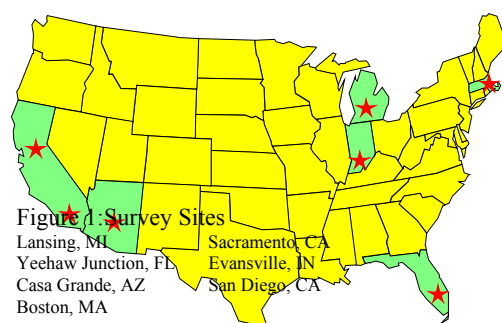
## BACKGROUND

In June 1994, the National Institute for Occupational Safety and Health (NIOSH) entered into an Interagency Agreement with the FHWA to evaluate occupational exposures among asphalt workers. A study protocol was developed by NIOSH investigators to address the following goals:

- Develop and field test new methods to assess asphalt fume exposures.
- Characterize and compare occupational exposures to CRM asphalt and conventional (CONV) asphalt.

- Evaluate potential acute health effects associated with CRM asphalt and CONV asphalt.

The initial protocol called for up to eight individual site evaluations, in different regions of the country. The intent was to allow NIOSH investigators access to different asphalt pavement formulations, climatic conditions, and paving techniques. A total of seven site evaluations were completed between 1994 and 1997 (Figure 1). A description of the paving characteristics and weather conditions at the survey sites is presented in Table 1. Although the goal at each site was to evaluate four consecutive days of paving by the same crew (two days of CRM asphalt, and two days of CONV asphalt formulated from the



same supply of asphalt cement), in a few instances there was a gap of several days to several weeks between paving projects.

The environmental and medical results discussed collectively in this report have been individually published in the following seven NIOSH Health Hazard Evaluation (HHE) final reports:

- HETA 94-0365-2563, Spartan Paving Company, Lansing, Michigan (March 1996)<sup>7</sup>
- HETA 94-0408-2564, Granite Construction Company, Sacramento, California (March 1996)<sup>8</sup>
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- HETA 96-0072-2603, Staker Paving Company, Casa Grande, Arizona (December 1996)<sup>11</sup>
- HETA 96-0130-2619, Sim J. Harris Company, San Diego, California (December 1996)<sup>12</sup>
- HETA 97-0232-2674, Barton-Trimount, Stoughton, Massachusetts (February 1998)<sup>13</sup>

## PAVING PROCESS OVERVIEW

There are three basic steps in constructing an asphalt pavement – manufacture of the HMA, placement of the mix onto the ground, and compaction. The asphalt mix contains two primary ingredients: a binder (which is typically an asphalt cement) and an aggregate (a mixture of coarse and fine stones, gravel, sand, and other mineral fillers).

Asphalt cement is typically received from a refinery by tractor trailer tankers and is transferred into heated storage tanks at the HMA plant. At the HMA plant, aggregate of different materials and sizes is blended and dried, then coated with a thin film of asphalt cement to produce a homogeneous paving mixture. This finished HMA paving mixture, which is kept heated so that it can be easily applied and compacted, is eventually dispensed into trucks and hauled to the paving site where the following equipment is typically used:

- **Tack truck:** A vehicle which precedes the paver and applies a low viscosity asphalt ("tack" coat) to the roadway to improve adhesion of the HMA. This equipment was seen in use only briefly at one paving site. This tack truck driver was monitored for total particulate (TP).
- **Paver:** A motorized vehicle which receives the HMA from the delivery trucks and distributes it on the road in the desired width and depth. The HMA may be directly transferred from the delivery truck to the paver by: (1) directly pouring HMA into a hopper located in the front of the paver; (2) dumping HMA onto the road where it is picked up by a windrow conveyor and loaded into the paver hopper (note: this method would usually involve a "truck

dumper" to monitor the emptying of the delivery truck and the placement of the windrow in front of the paving vehicle); or (3) conveying the mix with a material transfer vehicle. All three techniques were evaluated in this study. Each study site had one paver operator. Four of the seven sites used truck dumpers.

- **Screed:** Located at the rear of the paver, the screed distributes the HMA onto the road to a preselected width and depth and grades the HMA mix to the appropriate slope as the paving vehicle moves forward. Each study site had one or two screed operators.
- **Rollers:** Typically two or three roller vehicles follow the paver to compact the asphalt. Roller operators were present at all of the study sites.

The size of the paving crews at the seven sites typically ranged from eight to ten workers. Job titles and activities included a crew foreman; a truck dumper (also called a "dump man"), who coordinated the arrival (and operated the hatches) of the bottom-dump trucks; a paver operator, who drove the paver; one or two screed operators, who controlled the depth and width of the HMA placement; one or two rakers (also called "lutemen"), who shoveled excess HMA, filled in voids, and prepared joints; laborers, who performed miscellaneous tasks; roller operators who drove the rollers; and a tack truck driver who applied the tack coat. The paver operators, screed operators, and roller operators did not usually work different jobs, while the others may have performed a variety of tasks throughout the workday.

## ENVIRONMENTAL STUDY DESIGN

Previous research efforts have attempted to characterize asphalt fume exposures among road paving workers by separately measuring TP and the benzene soluble particulate fraction (BSP), usually in side-by-side samples. However, neither TP nor BSP methods measure a distinct chemical component. In addition, measuring the BSP fraction of the TP is less accurate when using separate sample filters.

To address these limitations in sampling asphalt fume, new or modified sampling and analytical methods were developed and used in this study. A new NIOSH method which simultaneously sampled for TP and BSP was developed.<sup>1</sup> Polycyclic aromatic compounds (PACs) were sampled using a new analytical method that included a PAC<sub>370</sub> group (2–3 ring compounds) and a PAC<sub>400</sub> group (4–7 ring compounds). Although there is some overlap between these two PAC groups, NIOSH researchers believe that the 4–7 ring PACs may have a greater likelihood for carcinogenesis, while the smaller molecular weight 2–3 ring PACs may have more irritative effects.<sup>2</sup> In addition to PACs, organic sulfur-containing compounds (OSCs, present in crude petroleum or from the addition of rubber) and benzothiazole (a sulfur-containing compound present in rubber tires), were also sampled.<sup>3</sup> As a group, the OSCs are well known for their irritative effects. Benzothiazole was of interest since it could be an indicator of exposure to CRM asphalt or to other compounds present in CRM asphalt.<sup>14</sup> Furthermore, recent results indicate benzothiazole is a potent inducer of the P450 and the phase II metabolizing enzymes.<sup>15</sup> The induction of these enzymes means that compounds in the asphalt fumes can now be metabolized in ways that would not have occurred if these enzymes were not induced. For example, the P450 enzymes are believed to be responsible for metabolizing benzo[a]pyrene to the carcinogenic epoxide.<sup>15</sup>

Air samples were collected for volatile organic compounds (VOCs, toluene, xylene, benzene, and

methyl isobutyl ketone [MIBK]) and total VOCs (TVOCs, quantified as Stoddard solvent). Both elemental carbon (EC) and organic carbon (OC) were measured and compared to total carbon (TC) to ascertain if diesel exhaust was a likely contributor to the air contaminants measured at the paving site. Respirable particulate concentrations were measured and direct-reading instruments were used to check for carbon monoxide (CO), hydrogen sulfide (H<sub>2</sub>S), sulfur dioxide (SO<sub>2</sub>), and ozone. Finally, high volume air samples of both CRM and CONV asphalt fume were collected from the emissions of asphalt cement storage tanks located at the hot-mix plants and analyzed to determine their mutagenic potential.

Table 2 summarizes the air sampling methods used in this evaluation. Calibration of the air sampling pumps with the appropriate sampling media was performed daily, before and after each monitoring period. Field blanks were collected and submitted to the laboratory for each analytical method.

### Area Air Sampling at the Paving Sites

To estimate worst-case conditions for paving workers, as well as to evaluate the various air sampling methods used in this study, area air samples were collected at the point of emission above the screed auger of the paving vehicle. Background area air samples were also collected near the paving site to determine if ambient concentrations of these contaminants existed. Area samples at both locations were collected for TP, respirable particulate, PACs, OSCs (including benzothiazole), BSP, VOCs (based on their qualitative identification via mass spectroscopy), TVOCs, and carbon (EC, OC, and TC forms). Direct-reading instruments were used to periodically measure CO, H<sub>2</sub>S, SO<sub>2</sub>, and ozone.

Air samples were collected using calibrated battery-operated sampling pumps with the appropriate sorbent tube or filter media connected via Tygon<sup>®</sup> tubing. The area and personal breathing-zone (PBZ) sample concentrations were calculated based on the actual monitoring time (time-weighted average [TWA-actual]

concentrations) instead of calculating an 8-hour TWA concentration to allow comparison of unequal monitoring durations.

## Area Air Sampling for Mutagenicity Testing

At each of the seven sites, CRM and CONV asphalt fume air samples were collected above an open port of the heated asphalt cement storage tank, located at the hot-mix plants. These air samples were collected on 37-millimeter (mm) polytetrafluoroethylene (PTFE) filters using a high-volume flow rate of 28.3 liters per minute over approximately 8 to 10 hours. Under an Interagency Agreement (IAG) previously established with the U.S. EPA, samples were sent to their laboratory for extraction and total mass determination. Following these analyses, a spiral *Salmonella* mutagenicity assay was conducted using tester strains TA98 and TA100, with and without 10% metabolic activation to determine the mutagenic potential for each asphalt formulation.<sup>16</sup>

Because of problems with plating the samples from the first three sites, the experimental protocol was revised. As a result, asphalt fume samples from the last four paving sites were extracted in the NIOSH laboratory. After extraction, half of the asphalt fume material was fractionated to separate aliphatic compounds, PACs, and polar compounds according to NIOSH Method 5800.<sup>5</sup> Next, the mass of these three fractions and the remaining unfractionated asphalt fume were sent to the U.S. EPA laboratory where the spiral *Salmonella* mutagenicity assay was conducted.

## Personal Air Samples

At each site the PBZ monitoring was conducted on most of the members of the paving crew. Full-shift PBZ samples were collected for the following compounds: TP, BSP, PACs, and OSCs (including benzothiazole).

## Other Site Information

Meteorological data were recorded at each paving site. Temperature and wind speed were measured using a portable meteorological station. Process information and operational details such as the asphalt grade, type of asphalt application, crude source, percent rubber, application temperature, paving depth, average application rate, site description, and traffic density were obtained. This information is summarized in Table 1.

## MEDICAL STUDY DESIGN

### Data Collection

The medical study included a general health and occupational history questionnaire, serial acute symptom questionnaires, and serial peak expiratory flow rate (PEFR) testing. The PEFR testing was used to evaluate acute changes in lung function. Peak flow refers to maximum air flow rate (volume per time) during forced exhalation.

Two groups of workers were recruited at each survey site. One group was comprised of asphalt-exposed workers at the paving site, including workers not employed by the paving contractor (e.g., state highway inspectors) who could have been exposed to asphalt fume. Most of the asphalt-exposed workers were present for four days, two days paving with CONV asphalt and two days paving with CRM asphalt. A small number were present for only one type of asphalt exposure. The control group was comprised of road construction workers at other sites where no paving was being done. Job activities of these asphalt-unexposed workers included installing guard rails, controlling traffic, and operating heavy machinery such as graders and earthmovers. Most of the asphalt-unexposed workers were present for four days; for purposes of comparison we considered them as asphalt-unexposed for CONV for two days and asphalt-unexposed for CRM for two days.

A general health questionnaire was completed by each participant at the beginning of a site survey. This questionnaire asked about recent history of eye, nose, and throat irritation, cough, shortness of breath, and wheezing, and about chronic respiratory conditions.

Questions about cigarette smoking and work history also were included.

A questionnaire addressing acute symptoms was distributed repeatedly throughout the work shift. Each day, each worker was asked to complete this questionnaire before the work shift, three times during the work shift (at approximately two-hour intervals), and after the work shift. This questionnaire asked about symptoms since awakening (for the first questionnaire of the day) or since the last questionnaire (for subsequent questionnaires). The symptoms included the following.

- burning, itchy, painful, or irritated eyes
- burning, itchy, stuffy, or irritated nose
- sore, dry, scratchy, or irritated throat
- coughing
- chest tightness or difficulty breathing
- wheezing or whistling in your chest

Throughout the work day the participants' PEFR was measured just before they completed the acute symptom questionnaire. Measurements were made using a mini-Wright portable peak flow meter. Each participant was instructed in the use of the meter and performed the first set of measurements under the supervision of the NIOSH investigator. Three exhalations were recorded each time, and the highest of the three readings was accepted as the PEFR determination. Participants were considered to have significant bronchial lability if the difference between the minimum and the maximum PEFR on at least one day exceeded 20% of that day's maximum PEFR.

## Data Analysis

Because many workers contributed observations on multiple days, we counted symptoms per day, rather than symptoms per worker. We defined the occurrence rate of each symptom as the number of days a symptom occurred divided by the number of person-days of observation. For each worker, a symptom was considered present if it was reported

any time after the first questionnaire of the day. Thus, a symptom a worker reported only on the first questionnaire of the day was not counted.

The association between symptoms and exposure was assessed in several ways, as described below. All analyses were done using SAS® (Versions 6 and 7). When comparing groups and assessing associations, a p-value less than or equal to 0.05 was considered statistically significant.

## Comparisons between Exposure Groups

We compared CONV asphalt-exposed vs. CONV asphalt-unexposed workers. Likewise, we compared CRM asphalt-exposed to CRM asphalt-unexposed workers. The occurrence of symptoms in each group was expressed as a rate, specifically, the number of person-days a symptom was present per 100 person-days. The association between each symptom (present/absent) and each type of asphalt exposure was assessed using an odds ratio (OR) and 95% confidence interval (CI). The OR is the odds of a symptom in the exposed group divided by the odds of the symptom in the unexposed group. When the OR is greater than 1, the exposed group is said to be at increased risk of the symptom compared with the unexposed group. The 95% CI is a measure of certainty about our findings. When the 95% CI excludes 1, we are more confident that there is a true association between exposure and symptoms. These analyses were completed using a statistical method called logistic regression for repeated measures (SAS® Proc GENMOD). This method accounts for the fact that individual workers contributed multiple observations (one observation for each day they participated).

## Relationship between Symptoms and Specific Air Contaminants

Within each asphalt-exposed group (CRM and CONV) the mean contaminant levels were compared for person-days with a symptom present and person-days with a symptom absent. We used the natural logarithm of the value for each contaminant



measurement since the exposure data were log–normally distributed. We compared the means of the log–transformed exposure variables using the t–test. This analysis was done for eye, nose, or throat irritation (one group), and for cough.

## EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre–existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increases the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),<sup>17</sup> (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®),<sup>18</sup> and (3) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs).<sup>19</sup> Employers are encouraged to follow the more protective criterion.

An employer is required by OSHA to protect their employees from hazards and to furnish them a place of employment that is free from recognized hazards that are causing or are likely to cause death or serious physical harm [Occupational Safety and Health Act of 1970, Public Law 91–596, sec. 5.(a)(1)]. However, employers should understand that not all hazardous chemicals have specific OSHA exposure limits such as PELs and short–term exposure limits (STELs). In such a situation, an employer is still required by OSHA to protect their employees from hazards, even in the absence of a specific OSHA PEL.

A TWA exposure refers to the average airborne concentration of a substance during a normal 8– to 10–hour workday. Some substances have recommended STEL or ceiling values where there are recognized toxic effects from higher exposures over the short–term.

## Asphalt Fumes (Petroleum)

The specific chemical content of asphalt, a brown or black solid or viscous liquid at room temperature, is difficult to characterize because it is extremely complex and variable. In general, asphalt primarily contains high molecular weight cyclic hydrocarbon compounds as well as saturated organic compounds. Its chemical composition and physical properties are influenced by the original crude petroleum and the manufacturing processes; however, the basic chemical components of asphalt include paraffinic, naphthenic, and aromatic hydrocarbons as well as heteroaromatic compounds containing sulfur, oxygen, and nitrogen.<sup>5</sup>

Petroleum based asphalt and coal–tar pitch are often considered to be equivalent materials because of their similar physical appearance and construction applications. However, these materials are quite different chemically as a result of different raw material origins and manufacturing processes.<sup>20</sup> More than 90% of the carbon in coal–tar pitch condensates is in aromatic rings, while in asphalt fume condensates less than 1% of the carbon is in aromatic rings.<sup>21</sup> Furthermore, coal–tar has a greater reported carcinogenic activity than asphalt and is considered an occupational carcinogen. Petroleum–based asphalt was used at all seven paving sites.

Nonmalignant lung diseases such as bronchitis, emphysema, and asthma have been associated with exposure to asphalt fumes.<sup>22,23</sup> In a study of road repair and construction work, three groups of asphalt workers experienced abnormal fatigue, reduced appetite, eye irritation, and laryngeal/pharyngeal irritation.<sup>24</sup> Finally, several epidemiologic studies concerning workers exposed to asphalt fumes have indicated a potential excess in mortality from cancer.<sup>23,25,26,27,28,29,30</sup>

In 1977, NIOSH established a REL of 5 milligrams per cubic meter ( $\text{mg}/\text{m}^3$ ) as a 15-minute ceiling limit for asphalt fumes, measured as TP. This was intended to protect against acute effects, including irritation of the serous membranes of the conjunctivae and the mucous membranes of the respiratory tract.<sup>31</sup> Since then, data have become available indicating that exposure to roofing asphalt fume condensates, raw roofing asphalt, and asphalt-based paints may pose a risk of cancer to workers occupationally exposed. In 1988, NIOSH recommended that asphalt fumes be considered a potential occupational carcinogen.<sup>32</sup> In 2000, NIOSH completed work on a comprehensive Hazard Review on asphalt that neither found nor ruled out a carcinogenic risk from asphalt fumes generated during paving operations.<sup>5</sup>

Asphalt fume was initially regulated by OSHA under its coal tar pitch volatile standard. Beginning in 1982, OSHA chose to interpret the coal tar pitch volatile standard to exclude asphalt fume. Although there is currently no OSHA PEL, in 1988 OSHA published a proposed rule for regulating asphalt fumes in general industry and included a PEL for asphalt fume of  $5 \text{ mg}/\text{m}^3$ , measured as TP over an 8-hour TWA. In 1992 OSHA proposed a PEL for asphalt fume of  $0.2 \text{ mg}/\text{m}^3$  (measured as TP). The revised ACGIH TLV for asphalt fume is  $0.5 \text{ mg}/\text{m}^3$  as an 8-hour TWA, measured as benzene-soluble aerosol (or equivalent method).<sup>18</sup>

Table 3 summarizes the toxicity and exposure criteria information for TP, respirable particulate, BSP, PACs, benzothiazole, OSCs, OC, EC, selected VOCs, and TVOCs.

## ENVIRONMENTAL STUDY RESULTS

### Area Air Samples at Paving Sites

Tables 4 through 10 present the results obtained from area air samples collected on the asphalt paving vehicle (at the hopper and/or above the screed auger) as well as near the paving site (i.e., background samples). Area air concentrations of TP, BSP, PAC<sub>370</sub>, PAC<sub>400</sub>, and OSC collected on the paver vehicle were generally higher during CRM asphalt paving than during CONV asphalt paving. Benzothiazole, a chemical used in the vulcanization process for rubber and measured as an indicator of the complex exposures resulting from CRM asphalt paving, was found primarily during CRM paving. Benzothiazole concentrations were inexplicably found during both types of asphalt paving at the first California survey (see Table 5).

All of the air samples collected for EC above the screed auger on the paver vehicle had concentrations above the background levels. Since diesel exhaust has been reported to contain EC levels between 60% to 80% of the TC,<sup>4</sup> the relatively low EC:TC ratios measured at all but one of the survey sites imply that diesel exhaust was not substantially contributing to the air sampling results.

Qualitative analysis using gas chromatography/mass spectrophotometry (GC/MS) identified over 50 VOCs in the asphalt emission; however, only the most prominent VOCs (benzene, toluene, xylene, MIBK) were quantitatively analyzed using gas chromatography/flame ionization detection (GC/FID). Although higher concentrations were measured during CRM asphalt paving, the quantities of VOCs at all sites during both types of paving were, except for benzene, well below their respective occupational exposure limits published by NIOSH, OSHA, or ACGIH.



The average TVOC concentration (as Stoddard solvent) was 12 mg/m<sup>3</sup> (range 0.24 to 74 mg/m<sup>3</sup>) during CONV asphalt paving over all seven paving sites. During CRM asphalt paving, the average was 33 mg/m<sup>3</sup> (range 0.38 to 224 mg/m<sup>3</sup>). None of these area air samples, however, were collected in the breathing-zone of any paving worker. The NIOSH REL for Stoddard solvent is 350 mg/m<sup>3</sup>.

During CONV asphalt paving, benzene was generally detected at, or just above, the minimum quantifiable concentration (approximately 0.01 parts per million (ppm), TWA. However, during CRM asphalt paving, benzene was present in higher concentrations, ranging from 0.019 to 0.77 ppm, TWA. NIOSH, which classifies benzene as an occupational carcinogen, has established a REL of 0.1 ppm, TWA. The OSHA PEL for benzene is an 8-hour TWA of 1 ppm.<sup>19</sup> The ACGIH TLV for benzene is 0.5 ppm.<sup>18</sup>

Concentrations of H<sub>2</sub>S, SO<sub>2</sub>, and ozone were very low during both CRM and CONV asphalt paving. Much higher concentrations of CO, however, were measured at several paving sites. For example, CO concentrations at site four ranged up to 200 ppm in the vicinity of operators using gasoline powered equipment such as asphalt tampers. At sites two and seven, where portable gasoline-powered generators were used during night paving, 8-hour TWA CO concentrations ranged from 8 to 24 ppm during CRM paving, with peak values as high as 910 ppm. The NIOSH REL for CO is 35 ppm for up to a 10-hour TWA and 200 ppm for a ceiling limit.

## Area Air Sampling for Mutagenicity Testing

None of the asphalt fume samples were found to be mutagenic using a spiral *Salmonella* mutagenicity assay. This assay was conducted using tester strains TA98 and TA100 with and without 10% metabolic activation.

## Personal Air Samples

Tables 11 to 16 present, by paving job categories, the GM concentrations of TP, BSP, PACs, OSCs, and benzothiazole measured in PBZ air samples during both CONV and CRM paving operations. The highest PBZ TP exposure was 1.4 mg/m<sup>3</sup>, TWA for the work day (on a screed operator).<sup>a</sup> For both CONV and CRM asphalt, the job titles with the highest GM TP exposures generally included the following: truck dumper, paver operator, screed operator, and laborers. All of these jobs were ones which placed the workers in close proximity to asphalt fume emissions from either the paver vehicle or the delivery trucks. The GM TP concentration during CRM asphalt paving ranged from 0.13 to 0.48 mg/m<sup>3</sup>; during CONV asphalt paving the GM TP concentration ranged from 0.07 to 0.81 mg/m<sup>3</sup>. Of the job categories evaluated for TP, only the screed operators and roller operators were exposed to significantly more TP during CRM asphalt paving than during CONV asphalt paving ( $p \leq 0.01$ ).

As shown in Table 12, the GM BSP results followed a similar pattern as seen for the TP samples, with the highest concentrations associated with the jobs in closest proximity to fume emissions, such as the truck dumper, the paver operator, and the screed operator. In three of the six job categories where PBZ air samples for BSP were collected during both CRM and CONV paving, the GM BSP concentration during CRM asphalt paving ranged from 0.02 to 0.25 mg/m<sup>3</sup>, compared to 0.02 to 0.44 mg/m<sup>3</sup> during CONV asphalt paving. None of the differences by job were significantly different.

As shown in Tables 13, 14, 15 and 16, the GM exposures to PACs (measured at either the 370 or 400

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<sup>a</sup> The current NIOSH REL for asphalt fume is 5 mg/m<sup>3</sup>, measured as TP for a 15-minute exposure. All air samples in this study were collected over a full work shift and thus cannot be directly compared to the REL. The NIOSH sampling and analytical method used in this study for TP and BSP has typically been used for full-shift air sampling, and the applicability of this method for 15-minute sampling needs further study.

nanometer [nm] emission wavelength), OSC, and benzothiazole were higher during CRM asphalt paving than during CONV paving in most of the asphalt paving job categories. For all but one job category, the GM PAC<sub>370</sub> concentration was greater than the corresponding PAC<sub>400</sub> concentration, regardless of the asphalt type, implying that the smaller molecular weight, 2–3 ring PACs were more abundant in both the CRM and CONV asphalt. Of the jobs evaluated, only the screed and roller operators were exposed to significantly more PACs during CRM asphalt paving when compared to CONV paving ( $p \leq 0.01$ ).

The GM OSC concentrations ranged from 0.34 to 4.6 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) during CRM paving and from 0.24 to 2.3  $\mu\text{g}/\text{m}^3$  during CONV paving. Of the jobs evaluated, only the “other job” category (site supervisors, inspectors, and traffic control personnel) were exposed to significantly more OSC during CRM paving ( $p \leq 0.05$ ). For benzothiazole, the GM concentrations during CRM asphalt paving ranged from 1.3 to 40  $\mu\text{g}/\text{m}^3$ , compared to 0.2 to 1.1  $\mu\text{g}/\text{m}^3$  during CONV asphalt paving. The fact that, with the exception of one paving site, benzothiazole was only measured during CRM asphalt paving was not unexpected since it is present in rubber tires, a component used in CRM asphalt. All paving jobs were exposed to significantly more benzothiazole during CRM paving than during CONV paving ( $p \leq 0.01$ ).

## Other Site Information

Table 1 summarizes the similarities and differences among the seven asphalt paving sites. The crude supplier for the asphalt differed for all seven sites. Six of the sites involved at least some roadway paving of multi-lane, limited-access highways. The type of paving was either a base course (including shoulders and ramps) or a surface overlay (friction) course. The percent rubber content of the CRM asphalt ranged from 12% to 22%, and the rubber blending was done “wet,” meaning that the crumb rubber was mixed with the hot asphalt for a period of time to at least partially react with the asphalt. Following this, the modified asphalt binder was then added to the aggregate. In the dry process, the crumb

rubber was first added to the aggregate, then mixed with the asphalt. An alternate dry blending method would be to combine the three components (rubber, asphalt, and aggregate) together at the same time. The HMA was transported to the paving site either of two ways; four sites used bottom dump trailers or “flowboy” conveyor trucks, which emptied the HMA in a channel (called a windrow) in front of the paving vehicle, while the remaining three sites used dump trucks that directly transferred the HMA into a hopper on the paver vehicle. In the former, a truck dumper opened the hatch at the bottom dump trailers. The HMA application temperature ranged from approximately 255°F to 325°F (CRM HMA) to 211°F to 296°F (CONV HMA). These HMA temperatures were recorded after application by the screed auger, but prior to compaction by the roller. A daily estimate of the average production was made for each site (the amount of HMA applied in metric tons [mtons], divided by the number of hours of paving). Calculated in this manner, the production rate ranged from about 100 mtons/hour to over 300 mtons/hour. The highest production rates occurred with paving crews in several western states (California and Arizona) who were paving limited access highways

and were familiar with CRM asphalt paving material. The production rates were lower at the other sites due to unexpectedly cool or wet weather (Florida), intermittent HMA production problems (Indiana, Michigan), smaller roadway/more difficult terrain (Massachusetts and the second California site), and unfamiliarity with the CRM asphalt product (Indiana, Florida, and Massachusetts).

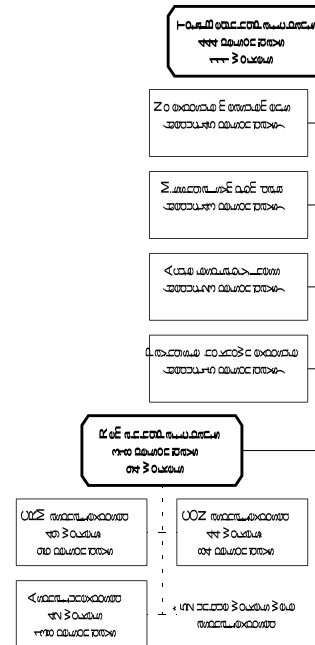
## MEDICAL STUDY RESULTS

### Demographics

A total of 111 workers participated in the medical evaluation (see Figure 2). After excluding workers with no exposure data, workers with no symptom data, workers with acute respiratory illnesses, and workers at a paving site who had no known asphalt exposure, 94 workers remained in the analyses described below. Forty-two of these workers were asphalt-unexposed; fifty-two were asphalt-exposed. The 94 workers included in the analysis represented 318 person-days of observations; 138 were asphalt-unexposed and 180 were asphalt-exposed.

Eighty-three workers (88%) were men; six women were asphalt-exposed and five were asphalt-unexposed. Seventy-one workers (76%) were below the age of 50. The age distribution of asphalt-exposed and asphalt-unexposed workers was similar. Fifty-seven of eighty-eight workers with smoking information (65%) were current cigarette smokers. The percentage of current smokers was higher among asphalt-exposed workers (34 of 48 workers, 71%) than asphalt-unexposed workers (23 of 40 workers, 58%), but was similar for both types of asphalt exposure. Cigarette smoking, however, was not associated with occurrence of any of the symptoms based on regression models, and was not considered further in the analyses described below.

The predominant job title among asphalt-exposed workers was roller operator (12 workers). Other job



**Figure 2:** The Number of Participants and Person-Days of Observations

titles represented were paver operator, screed operator, and raker (each with seven workers), laborer (five workers), supervisor/foreman (two workers), traffic control and tack truck driver (each with one worker), and other (six workers). Four were missing job information. The predominant job title among asphalt-unexposed workers was laborer (16 workers). The remainder in this group represented a wide variety of job titles.

## Association between Symptoms and Exposure

### Comparisons between Exposure Groups

With one exception, the pattern of symptoms was similar among the groups, although the occurrence rate of symptoms was not (Table 17). Eye, nose, and throat symptoms were the three most frequently reported symptoms in all groups; throat symptoms were the most frequently reported symptom in the

CRM asphalt-exposed group, but not in the other two groups (*note: nasal for the other 2 groups.*) The occurrence rate of all symptoms was lowest in the asphalt-unexposed group, intermediate in the CONV asphalt-exposed group, and highest in the CRM asphalt-exposed group. Due to small numbers of workers reporting chest tightness or difficulty breathing and wheezing or whistling in the chest, the odds of these symptoms by exposure group were not calculated. Although CONV asphalt-exposed workers reported all symptoms more frequently than asphalt-unexposed workers, the increase was statistically significant only for throat irritation, with an odds ratio of 3.6 ( $p \leq 0.03$ ). In contrast, the increase in the CRM asphalt-exposed group was statistically significant for all symptoms (all  $p$  values  $\leq 0.01$ ), with odds ratios of 4.0 for eye symptoms, 4.3 for nose symptoms, 5.6 for cough, and 20.1 for throat symptoms (Table 17).

### ***Relationship between Symptoms and Specific Air Contaminants***

With the exception of TP exposures, on the days of exposure to CRM asphalt contaminant concentrations did not differ between days when irritation or cough were present and days when these symptoms were absent (Tables 18 and 19). Total particulate concentrations were nearly twice as high on days when eye, nose, or throat irritation was present (geometric mean [GM] =  $0.30 \text{ mg/m}^3$ ) compared to days when eye, nose, or throat irritation was absent (GM =  $0.18 \text{ mg/m}^3$ ,  $p \leq 0.01$ ).

In contrast, on the days of exposure to CONV asphalt, concentrations of TP, BSP, PAC<sub>370</sub>, and PAC<sub>400</sub> were significantly higher when eye, nose, or throat irritation was present ( $p \leq 0.02$  for all comparisons, see Table 18). On the days of exposure to CONV asphalt, concentrations of BSP, OSC, and benzothiazole were significantly higher when cough was present ( $p \leq 0.05$  for all comparisons, see Table 19). However, the only appreciable benzothiazole concentrations measured during CONV asphalt paving occurred at just one survey site.

### ***Peak Flow***

For four workers, the difference between the minimum and the maximum PEFr on at least one day exceeded 20% of that day's maximum PEFr. All were asphalt-exposed. In three of the four, the pattern of PEFr variability was consistent with work-related bronchoreactivity.

## **DISCUSSION**

The study protocol developed in 1994 by NIOSH in conjunction with representatives from the FHWA was intended to address the following goals: (1) develop and field test new sampling methods to measure asphalt fume exposures; (2) characterize and compare occupational exposures to CRM asphalt and CONV asphalt; and (3) evaluate potential health effects associated with CRM asphalt and CONV asphalt.

### **Sampling Techniques**

Since asphalt is such a complex mixture, containing thousands of compounds, NIOSH investigators used a variety of existing, as well as new, sample collection and analytical methods to evaluate PBZ exposures (see Table 2). Two existing methods, for TP and BSP, were selected for PBZ air sampling because they had been used in many previous asphalt fume studies.<sup>5</sup> We also developed PBZ sampling techniques to measure potential irritants (PACs and OSCs) and an indicator compound for CRM asphalt fume (benzothiazole).<sup>3</sup>

All of the PBZ sampling methods used in these field studies were effective in measuring various components of the asphalt fume. Currently, however, only the results from the TP and BSP methods relate to existing occupational exposure limits for asphalt fume. The current NIOSH REL for asphalt fume is  $5 \text{ mg/m}^3$ , measured as TP for a 15-minute exposure. Since all of the air samples in this study were collected over a full work-shift, they cannot be directly compared to the REL. The NIOSH sampling and analytical method used in this study for TP and BSP has typically been used for full-shift air sampling, and the applicability of this method for 15-minute sampling needs further study. The revised

ACGIH TLV for asphalt fume is 0.5 mg/m<sup>3</sup> as an 8-hour TWA, measured as benzene-soluble aerosol (or equivalent method).<sup>18</sup> Since this is an 8-hour TWA exposure limit, the NIOSH sampling and analytical method for TP and BSP could be easily used.

The usefulness of the PAC and OSC methods is somewhat limited by the fact that there are currently no occupational exposure limits and little exposure data beyond what is reported in this study. Benzothiazole monitoring shares these same problems but may eventually prove useful as a measure of CRM asphalt fume exposures.

The low air concentrations of specific VOCs, such as toluene, xylene, and MIBK (all less than 1 ppm) suggest that PBZ sampling for these compounds may not be as useful as monitoring for TVOCs. However, sampling for benzene may be warranted, especially considering benzene's toxicity and low occupational exposure limits. Direct reading instruments were effective in identifying the high CO exposures to pavers under circumstances where gasoline-powered equipment was in use (such as during night paving).

## Occupational Exposures

During all types of paving the highest individual concentrations of TP, BSP, PAC<sub>370</sub>, PAC<sub>400</sub>, OSC, and benzothiazole were generally measured in those job activities that were closest to the paver vehicle (the paver and screed auger operators) or to the asphalt delivery trucks (the truck dumper). We compared GM exposures between CRM and CONV asphalt paving by grouping individual paving jobs into the following three categories, based on their proximity to the paver vehicle or asphalt delivery trucks (see Table 20). Group 1 included paver operators, screed operators, and truck dumpers (assumed to have the highest potential exposures since they worked on the paver vehicle or near the asphalt delivery trucks). Group 2 included rakers and laborers (moderate exposures, working near the paver vehicle), while Group 3 included roller operators, site supervisors, and state inspectors (lowest exposures, often working away from the paver vehicle and

asphalt delivery trucks). For TP, only Group 3 had a significant difference in exposure (0.15 mg/m<sup>3</sup> during CRM paving vs. 0.08 mg/m<sup>3</sup> for CONV paving,  $p \leq 0.01$ ). There were no significant differences for any of the groups for either BSP or OSC exposures. While both Group 1 and 3 had significant differences in exposure for PAC<sub>370</sub>, only Group 1 was significantly different for PAC<sub>400</sub>. Finally, there were significant differences in benzothiazole exposure for all three groups.

We also looked at asphalt fume exposures by individual jobs. For TP exposure by job, only the screed operators and roller operators were exposed to statistically more TP during CRM asphalt paving than during CONV asphalt paving ( $p \leq 0.01$ ). The GM PBZ concentrations for BSP (by job) were below the current ACGIH TLV of 0.5 mg/m<sup>3</sup>, although some paver and screed operators and truck dumpers had individual exposures near the TLV. No BSP concentrations were significantly different for any individual job category. Only the screed and roller operators were exposed to significantly more PACs during CRM asphalt paving when compared to CONV paving ( $p \leq 0.01$ ).

Regardless of the asphalt composition (CRM or CONV) or type of sample (PBZ or area), PAC<sub>370</sub> concentrations were higher than PAC<sub>400</sub>, indicating that the lower-molecular-weight (2-3 ring) PACs may be more abundant in the asphalt. These PACs, along with OSCs, are believed to be associated with irritative effects.<sup>2,3,14</sup> Benzothiazole concentrations were measured (with one exception) only during CRM paving, suggesting that the crumb rubber in the CRM asphalt formulation is the main source. Finally, except for one site (Florida) the EC:OC ratio at each of the paving sites suggests that diesel exhaust is not a primary contributor to BSP, PACs, and OSCs.

In area air samples collected above the screed auger of the paver vehicle (and away from workers' breathing zones), individual VOC concentrations were generally less than 1 ppm. All of these concentrations were, except for benzene, well below their respective occupational exposure limits published by NIOSH, OSHA, or ACGIH. The average TVOC concentration (measured as Stoddard solvent) was 12 mg/m<sup>3</sup> during

CONV asphalt paving; during CRM asphalt paving the average was 33 mg/m<sup>3</sup>. The NIOSH REL for Stoddard solvent is 350 mg/m<sup>3</sup>. Benzene concentrations ranged up to 0.77 ppm during CRM asphalt paving; concentrations were slightly lower during CONV asphalt paving. This suggests a potential occupational exposure to benzene for paving workers. The NIOSH REL for benzene is 0.1 ppm, TWA.

Full-shift CO exposures ranging up to 24 ppm were measured when workers were using gasoline-powered pavement tamping equipment. High short-term concentrations of CO (up to 910 ppm) were measured at a site where portable generators were placed on the paver vehicle to power lights used for night paving. Although it is possible that some of the CO may have resulted from cigarette smoke (over 60% of the study participants were smokers, and some workers smoked during work), these results suggest occupational CO exposures that could exceed the ceiling limit of 200 ppm.

## Health Effects

Prior studies of the acute effects of asphalt fume exposures in workers have repeatedly reported eye and upper respiratory tract (nasal) irritation.<sup>5</sup> These health effects have been well documented in asphalt road pavers and typically appear to be mild in severity and transient. In this study both CRM and CONV asphalt workers experienced symptoms (eye, nose, and throat irritation being most commonly reported), and the occurrence rate of these symptoms was highest among the CRM asphalt-exposed group. It is important to note, however, that workers were aware of the type of asphalt being used and some workers were known to be concerned about possible health effects from using CRM asphalt. Thus, it is possible that these results were affected by a reporting bias.

On the days of exposure to CRM asphalt, with the exception of TP, full-shift contaminant concentrations did not differ between days when irritation or cough were present and days when these symptoms were absent. However, TP concentrations were higher on days when eye, nose, or throat

irritation was present than on days when eye, nose, or throat irritation was not reported. In contrast, on the days of exposure to CONV asphalt, concentrations of TP, BSP, and PACs were significantly higher when eye, nose, or throat irritation was present and concentrations of BSP, OSC, and benzothiazole were significantly higher when cough was present.<sup>b</sup> Although an exposure-response relationship has not been established in this study, the identification of health effects related to exposures to asphalt fume during either CRM or CONV asphalt paving indicates that such a relationship may exist. This is further reinforced by data from a study of underground asphalt paving where TP and BSP measurements were up to 10 times higher than measurements taken during open-air paving and some workers experienced eye and nasal irritation, coughing, and shortness of breath in association with asphalt paving.<sup>33</sup>

## CONCLUSIONS

Overall, although no definitive results were obtained indicating that CRM exposures are more hazardous than CONV exposures, the trends are suggestive that CRM exposures are potentially more hazardous. With the exception of one site (California 1), results from the area air samples and PBZ samples indicated exposures to a variety of analytes were greater on the CRM paving days. The confidence intervals generally show that exposures can be considerably higher on CRM paving days and that some of these differences were statistically significant. For example, at the last site (Massachusetts) most exposures were significantly higher on CRM paving days. Also, in general, the reported number of symptoms was greater on the CRM paving days, including four paving workers who had a pattern of PEFr variability suggesting work-related broncho-reactivity only during CRM paving days. Furthermore, benzothiazole, found predominately only during CRM paving, may induce metabolic

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<sup>b</sup> There was only one survey where appreciable benzothiazole concentrations were measured during CONV asphalt paving, including the highway background sample.

pathways that may not otherwise be active in these workers, thus exposing them to potential new hazards.

## Sampling Techniques

- All of the PBZ sampling methods were effective in measuring various components of the asphalt fume. Currently, however, only the results from the TP and BSP methods can be compared to existing occupational exposure limits. The usefulness of the PAC and OSC methods is limited by the fact that there are currently no occupational exposure limits and little exposure data for comparison beyond what is reported in this study.
- The TVOC PBZ sampling method may prove to be a valuable technique to assess asphalt fume exposure and should be added to future study protocols.
- Benzothiazole monitoring may eventually prove useful as a surrogate measurement to evaluate CRM asphalt fume exposures.

## Occupational Exposures

- PBZ exposures to TP, BSP, PACs, OSCs, and benzothiazole were generally higher during CRM asphalt paving than during CONV paving. The highest exposures were often measured on those jobs near either the paver vehicle or the asphalt delivery trucks.
- For asphalt exposed, all full-shift TP PBZ exposures, regardless of asphalt type, were below 1.5 mg/m<sup>3</sup>, TWA over the period sampled.
- The GM PBZ concentrations for BSP (by job) were below the current ACGIH TLV of 0.5 mg/m<sup>3</sup>, although some paver and screed operators and truck dumpers had individual exposures above the TLV.<sup>12</sup>
- Benzene concentrations from area air samples ranged up to 0.77 ppm during CRM asphalt paving. These data suggest that a potential occupational exposure exists to benzene.

- The concentrations of PAC<sub>370</sub> (2–3 ring compounds, many of which have irritative effects) exceeded those of PAC<sub>400</sub> (4–7 ring compounds, some of which are carcinogenic).<sup>2</sup> Organic sulfur compounds, some of which may cause respiratory irritation, were measured during both CRM and CONV asphalt paving. There are no occupational exposure limits for PACs and OSCs.

- Benzothiazole was primarily detected during CRM asphalt paving, suggesting that the crumb rubber is a main source and that it may be useful as an indicator of CRM asphalt fume. It is not known if there are any health effects associated with benzothiazole at the air concentrations measured in this study and there are no occupational exposure limits for benzothiazole. However, a recent study indicates benzothiazole can induce enzymes which, in turn, could metabolize compounds in the asphalt fumes in ways that would not have occurred if these enzymes were not induced.<sup>15</sup>

- Diesel exhaust did not appear to contribute to BSP, PACs, and OSC concentrations at the paving sites, except for Florida.

- Area air concentrations of specific VOCs during both types of paving were very low (less than 1 ppm).

- Area air concentrations of TVOCs were generally higher during CRM paving, ranging up to 224 mg/m<sup>3</sup>.

- None of the asphalt fume samples tested in this study were found to be mutagenic using the spiral *Salmonella* mutagenicity assay.

## Health Effects

- Eye, nose, and throat irritation were the three most frequently reported symptoms for all asphalt workers in this study. For CRM asphalt workers, throat symptoms were the most frequently reported. For CONV asphalt workers, nasal symptoms were the most frequently reported. The occurrence rate of all symptoms was highest in the CRM asphalt-exposed group.



- During CRM asphalt paving, only TP concentration was associated with eye, nose, or throat irritation.
- During CONV asphalt paving, TP, BSP, PAC<sub>370</sub>, and PAC<sub>400</sub> concentrations were associated with eye, nose, or throat irritation, and BSP, OSC, and benzothiazole concentrations were associated with cough.
- Four CRM paving workers had a pattern of PEFV variability suggestive of work-related broncho- reactivity.

## RECOMMENDATIONS

The following recommendations are intended to help ensure the safety and health of all asphalt paving workers and are based on working conditions observed during our site evaluations. Many of these recommendations are in the NIOSH Hazard Review document entitled “Health Effects of Occupational Exposure to Asphalt.”<sup>25</sup>

1. Prevent dermal exposure to asphalt and to clean-up solvents.
2. Keep the application temperature of the heated asphalt as low as possible to minimize decomposition byproducts. This recommendation is based on good industrial hygiene practice.
3. Use engineering controls to minimize worker exposure to asphalt fumes, such as an exhaust ventilation system on the paver vehicle. More information on this topic may be found in the NIOSH document entitled Engineering Control Guidelines for Hot Mix Asphalt Pavers.<sup>34</sup>
4. To avoid contamination by, and possible ingestion of, potentially harmful substances, workers should not consume food or beverages or use tobacco products in close proximity to asphalt fume.
5. Workers should be provided with washing facilities for use prior to eating and leaving the work site and be encouraged to change clothing prior to leaving the work site.

6. Since asphalt paving is often done during daytime hours, workers should wear protective clothing or appropriate sun screen to shield exposed skin surfaces from the harmful ultraviolet component of sunlight.

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**Table 1**  
**Description of Asphalt Paving Study Sites**

State	Michigan		California 1		Florida		Indiana		Arizona		California 2		Massachusetts	
<b>Paving Locations</b>	Lansing area, along I-96		Sacramento & Davis, along I-80 and U.S. 99		Yeehaw Junction on Florida Turnpike		Jasper area, along I-64		Casa Grande, along I-8		San Diego County Roads		Near Stoughton, at I-95; SR 138	
<b>Pavement Function</b>	Base course for traffic lanes, shoulders, ramps		Surface overlay of traffic lanes, shoulder elevation		Open graded friction course on traffic lanes		Base course and binder layers for traffic lanes		Base course for traffic and emergence lanes		Surface overlay of traffic lanes		Surface friction course; binder course	
<b>Crude Supplier</b>	Thompson/McCulley		Conoco Oil		Coastal Refining		Marathon Oil		Eott Paramount		Paramount		Bardon-Trimount	
<b>AC Grade (CONV)</b>	85/100		AR 4000		AC-30		AC-10		AC-40		AR 4000		AC-20	
<b>HMA Application Temp.‡</b>	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
<b>CRM temperature</b>	273 °F	296 °F	280 °F	288 °F	277 °F	278 °F	255 °F	270 °F	300 °F	300 °F	325 °F	320 °F	310 °F	305 °F
<b>CONV temperature</b>	287 °F	296 °F	288 °F	289 °F	211 °F	219 °F	257 °F	265 °F	285 °F	295 °F	280 °F	280 °F	285 °F	285 °F
<b>AC Grade (CRM)</b>	200/250		AR 4000		AC-30		AC-5		AC-10		AR 4000		AC-10	
<b>% Binder Content (CONV)</b>	Not determined		Not determined		Not determined		Not determined		5.2%		5.3%		5.6-6.2%	
<b>% Binder Content (CRM)</b>	Not determined		Not determined		Not determined		Not determined		6.2%		8.0%		6.6%	
<b>% Rubber (by weight)</b>	15%		20%		12%		22%		18.5%		20%		16%	
<b>Rubber Supplier</b>	Unknown		Baker Rubber		Unknown		Baker Rubber		Baker Rubber		Baker Rubber		NRB Materials	
<b>Rubber Blending</b>	Wet		Wet		Wet		Wet		Wet		Wet		Wet	
<b>HMA Conveyance (CONV asphalt)</b>	"Flow Boy" trailers & windrow pick-up		Bottom dump trailers & windrow pick-up		Dump directly into paver hopper		Dump directly into paver hopper		Bottom dump trailers & windrow pick-up		Bottom dump trailers & windrow pick-up		Dump directly into paver hopper	
<b>HMA Conveyance (CRM asphalt)</b>	Dump directly into paver hopper		Bottom dump trailers & windrow pick-up		Dump directly into paver hopper		Dump trucks into paver hopper		Bottom dump trailers & windrow pick-up		Bottom dump trailers & windrow pick-up		Dump directly into paver hopper	
<b>Avg. Production</b>	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
<b>CRM (mtons/day)</b>	109	167	240	227	151	150	103	160	311	329	190	175	198	181
<b>CONV (mtons/day)</b>	191	154	165	125	132	137	297	181	247	294	290	200	110	120
<b>Wind Conditions</b>	Low (0-5 mph)		Low (0-5 mph)		High (>10 mph)		Moderate (6-10 mph)		Moderate (6-10 mph)		Moderate (6-10 mph)		Moderate (6-10 mph)	
<b>Avg. Ambient Temp.</b>	71 - 80 °F		<70 °F		71 - 80 °F		>90 °F		<70 °F		>90 °F		81 -90 °F	

AC = asphalt cement    CRM = crumb-rubber modified hot mix asphalt    CONV = non-rubber hot mix asphalt    mtons/day = metric tons of asphalt per day  
‡ = HMA temperature after application by the screed auger, but prior to compaction by the roller

**Table 2**  
**Summary of Sampling and Analytical Methods**

Substance	Flow (Lpm)	Sample Media	Analytical Method	Comments
<b>Total Particulate</b>	2.0	Tared Zefluor filter (37 mm diameter, 2 µm pore size)	NIOSH Method No. 0500, Gravimetric analysis (first three surveys); NIOSH 5042 for remaining surveys.	A tared Zefluor filter replaced a tared PVC filter for sample collection after the first three site surveys.
<b>Benzene Soluble Particulate</b>	2.0	Tared Zefluor filter (37 mm diameter, 2 µm pore size) <i>Note: A glass fiber filter was used in the first three surveys.</i>	NIOSH Method No. 5042. The filters were rinsed with benzene, the leachate collected and evaporated, and the residue weighed to report the benzene soluble fraction.	This method was used since benzene solubles have been reported in other asphalt investigations.
<b>Respirable Particulate</b>	1.7	Tared PVC filter (37 mm diameter, 0.8 µm pore size)	NIOSH Method No. 0600, Gravimetric analysis	Dorr–Oliver nylon cyclone used.
<b>Polycyclic Aromatic Compounds (PACs), Organic Sulfur Compounds, and Benzothiazole</b>	2.0	Zefluor filter (37 mm diameter, 2µm pore size), followed by an ORBO 42 sorbent tube	NIOSH Method No. 5800. PACs via HPLC and a flow injection technique with spectrofluorometric detection. Two detector emission wavelengths were used: 370 nm (more sensitive to 2–3 ring PACs); and 400 nm (more sensitive to 4+ ring PACs). Sulfur compounds were analyzed by gas chromatography with sulfur chemiluminescence detection.	The collection method is similar to NIOSH method 5506, Polynuclear Aromatic Hydrocarbons. Opaque filter cassettes and sorbent tube holders were used to prevent the degradation of PACs by ultraviolet light. See Appendix A for more information.
<b>Elemental/Organic Carbon</b>	2.0	Quartz–fiber filters (37 mm diameter, open face)	Used NIOSH Method No. 5040	A rectangular punch (1.54 cm <sup>2</sup> ) is taken from the quartz filter for a three stage thermal–optical analysis.
<b>Qualitative Volatile Organic Compound (VOC) Screen</b>	0.02	Thermal desorption (TD) tubes	Samples analyzed using the Tekmar thermal desorber interfaced directly to a gas chromatograph and a mass spectrometry detector.	Each tube contained 3 beds of sorbent materials: (1) a front layer of Carbotrap C; (2) a middle layer of Carbotrap; and (3) a back section of Carbosieve S–III.
<b>Quantitative Analysis for Selected Solvents and Total Hydrocarbons</b>	0.2	Activated charcoal sorbent tubes (100 milligram front section/50 milligram back section)	Current NIOSH Methods 1300 and 1301 for ketones, 1501 for aromatic compounds, and 1550 for petroleum distillates were merged and modified. The activated charcoal was desorbed with carbon disulfide; then analyzed using a gas chromatograph with a flame ionization detector.	Benzene, toluene, xylene, MIBK, and “total hydrocarbons” (other hydrocarbons with retention times greater than toluene) were quantified.
<b>H<sub>2</sub>S, SO<sub>2</sub>, CO, and Ozone</b>	Diffusion	Toxilog® diffusion monitors for H <sub>2</sub> S, SO <sub>2</sub> , CO, and CEA® TG–KA Portable Toxic Gas Detector for ozone	Toxilog® diffusion monitors use individual electrochemical sensors specific for H <sub>2</sub> S, SO <sub>2</sub> , CO. The CEA® TG–KA Portable Toxic Gas Detector for ozone uses an electrochemical galvanic cell method.	Spot area measurements were made throughout the work day at several paving sites. Full–shift CO measurements were made at one site.
<b>Mutagenicity Assay</b>	28.3	37 mm Zefluor sampling filter, high–volume flow rate over approximately 8 to 10 hours	The Zefluor filters were extracted for a total mass determination. A spiral Salmonella mutagenicity assay was conducted using tester strains TA98 and TA100 with and without 10% metabolic activation to determine the mutagenic potential.	An Interagency Agreement (IAG) was set with the U.S. EPA, in Research Triangle Park, North Carolina, for the mutagenicity assay.

PVC = Polyvinyl chloride sampling filter  
mm = millimeter  
µm = micrometer  
GC–FID = Gas chromatography–flame ionization detector

SO<sub>2</sub> = Sulfur dioxide  
CO = Carbon monoxide  
Lpm = Liters per minute  
MIBK = Methyl isobutyl ketone

Zefluor = Teflon® sampling filter  
nm = nanometer  
H<sub>2</sub>S = Hydrogen sulfide  
HPLC = High pressure liquid chromatography

**Table 3**  
**Toxicity and Exposure Criteria Information**

Compound	Toxicity Review	Exposure Criteria
<b>Asphalt Fume</b>  <b>(TP, As Total Particulate)</b>	Although the composition of asphalt fume cannot be easily characterized, one evaluation technique has been to sample total particulate. Total particulate is a measure of all airborne particulate which was collected on the sample filter. The NIOSH REL for asphalt fume is expressed as total particulate. Asphalt fume can also be measured as the benzene soluble particulate fraction (BSP) of total particulate. <sup>1</sup>	The NIOSH REL is 5 mg/m <sup>3</sup> , 15-minute ceiling (C) exposure. No OSHA PEL. The ACGIH TLV® is 0.5 mg/m <sup>3</sup> , 8-hour TWA.
<b>Respirable Particulate (RP)</b>	A respirable particulate sample uses a selection device to obtain the fraction of the airborne particulate that is small enough to be retained in the respiratory system once inhaled. Any conclusions based on respirable (or total) particulate concentrations may be misleading since other potentially toxic substances may be present. These particulate concentrations, along with the results obtained from tests for individual components (such as polycyclic aromatic compounds [PACs], BSP, and selected solvents) should be considered together when determining the degree of hazard.	No NIOSH REL The OSHA PEL is 5 mg/m <sup>3</sup> , 8-hour TWA. The ACGIH TLV® is 3 mg/m <sup>3</sup> for respirable particulate, 8-hour TWAs.
<b>Benzene Soluble Particulate (BSP)</b>	The BSP fraction is that portion of the total particulate that is soluble in benzene. Organic compounds are generally soluble in benzene, whereas inorganic compounds are not benzene soluble. Historically, the BSP concentrations were measured in asphalt studies in an attempt to differentiate exposure between the asphalt fume and dirt or other dust present at asphalt construction operations.	No NIOSH REL No OSHA PEL The ACGIH TLV® for asphalt fume is 0.5 mg/m <sup>3</sup> , measured as BSP for an 8-hour TWA.
<b>Polynuclear Aromatic Hydrocarbons (PAHs)</b>  <b>and</b>  <b>Polycyclic Aromatic Compounds (PACs)</b>	PACs refer to a set of cyclic organic compounds that includes PAHs and also includes compounds that have sulfur, nitrogen, or oxygen in the ring structure and alkyl substituted cyclics. Hundreds of PACs with varying degrees of alkyl substitutions are typically associated with asphalt materials. PAHs have received considerable attention since some have been shown to be carcinogenic in experimental animals. <sup>1</sup>  PACs were sampled using a new analytical method that included a PAC <sub>370</sub> group (2–3 ring compounds, many of which have irritative effects) and a PAC <sub>400</sub> group (4–7 ring compounds, some of which are carcinogenic). <sup>2</sup> It is not currently possible to definitively distinguish between these two PAC groups analytically; however, using these two different emission wavelengths (370 nanometer [nm] and 400 nm) allows the detector to be more sensitive to PACs based on ring number. Also see Appendix A.	None established for PAHs and PACs as a class.
<b>Benzothiazole (BENZ)</b>	In its pure form, benzothiazole is a yellow liquid with an unpleasant odor. <sup>3</sup> It is used as a rubber vulcanization accelerator <sup>4</sup> , as an antimicrobial agent <sup>5</sup> , and in dyes. <sup>6</sup> Benzothiazole was identified in the air during rubber vulcanization. <sup>7</sup> Reports also indicate that benzothiazole is present in tires and CRM asphalt. Benzothiazole was selected for study since it may be useful as an indicator to represent the complex exposures resulting from CRM asphalt paving. It is not known if there are any health effects associated with benzothiazole at the air concentrations measured in this study.	None established
<b>Organic Sulfur-Containing Compounds (OSCs)</b>	The addition of tire rubber may increase sulfur compounds in asphalt. In this report “organic sulfur-containing compounds, OSCs” refer to aliphatic and aromatic organic compounds that contain sulfur. Although no specific occupational exposure limits exist for this group of sulfur compounds, it was hypothesized that some of these compounds may cause respiratory irritation. <sup>1</sup>	None established
<b>Organic and Elemental Carbon (OC, EC)</b>	Measuring organic, elemental, and total carbon concentrations (and determining a ratio between elemental and total carbon) provides an indication of diesel exhaust exposure. Any elemental carbon above background will most likely be from diesel exhaust. Unfortunately, this method cannot differentiate carbon sources (i.e., asphalt fume, diesel exhaust, cigarette smoke). There are no occupational exposure criteria for either elemental or organic carbon. This method was employed previously in several NIOSH trucking industry studies. <sup>8,9</sup>	None established



**Table 3**  
**Toxicity and Exposure Criteria Information**

<b>Compound</b>	<b>Toxicity Review</b>	<b>Exposure Criteria</b>
<b>MIBK</b>	Methyl isobutyl ketone (MIBK) is a colorless, flammable organic solvent used as an antioxidant in the tire manufacturing process. This solvent is absorbed primarily through inhalation and causes irritation of the eyes, mucous membranes, and skin. <sup>10</sup> At air concentrations much higher than were measured in this asphalt study, MIBK has caused central nervous system depression. Continued or prolonged skin contact can cause dermatitis. <sup>10</sup>	The NIOSH REL is 50 ppm for up to a 10-hour TWA; 75 ppm for a 15 minute STEL. The ACGIH TLV is 50 ppm, 8-hour TWA. The OSHA PEL is 100 ppm, 8-hour TWA.
<b>Benzene</b>	Acute overexposure can cause central nervous system depression with symptoms such as headache, nausea, and drowsiness. Chronic exposure to benzene has been associated with the depression of the hematopoietic system and is associated with an increased incidence of leukemia and possibly multiple myeloma. <sup>10</sup> NIOSH classifies benzene as a human carcinogen. <sup>11</sup> The ACGIH TLV® for benzene is 0.5 ppm, 8-hour TWA with a skin notation (indicating that skin exposure contributes to the overall dose and potential effects). <sup>12</sup>	NIOSH REL is 0.1 ppm. OSHA PEL is 1 ppm for an 8-hour TWA. ACGIH TLV is 0.5 ppm for an 8-hour TWA.
<b>Toluene</b>	Toluene can cause acute irritation of the eyes, respiratory tract, and skin and repeated or prolonged skin contact will remove the natural lipids from the skin which can cause drying, fissuring, and dermatitis. <sup>10,13</sup> Studies have shown that subjects exposed to 100 ppm of toluene for six hours complained of eye and nose irritation, and in some cases, headache, dizziness, and a feeling of intoxication (narcosis). <sup>14</sup> No symptoms were noted below 100 ppm in other studies. <sup>15</sup> The ACGIH TLV carries a skin notation, indicating that skin exposure contributes to the overall dose and potential effects. <sup>12</sup>	NIOSH REL is 100 ppm, up to a 10-hour TWA (15-minute STEL of 150 ppm). OSHA PEL is 200 ppm, 8-hour TWA; 300 ppm for a C limit. ACGIH TLV is 50 ppm, 8-hour TWA (skin).
<b>Xylene</b>	Structurally similar to toluene, xylene can also cause acute irritation of the eyes, respiratory tract, and skin. <sup>10</sup> In previous studies, humans exposed to concentrations ranging from 60 to 350 ppm (concentrations much higher than were measured in this asphalt study) experienced giddiness, anorexia (loss of appetite), and vomiting. <sup>10</sup>	NIOSH REL is 100 ppm, up to a 10-hour TWA (15-minute STEL of 150 ppm). OSHA PEL is 100 ppm, 8-hour TWA. ACGIH TLV is 100 ppm for an 8-hour TWA and 150 ppm for a 15-minute STEL
<b>Total volatile organic compounds (TVOCs), measured as Stoddard solvent)</b>	Effects from exposure to Stoddard solvent are primarily acute (such as upper respiratory irritation, nausea, headaches, and irritation of the eyes and nose), unless significant amounts of substances that have chronic toxicity are present, such as benzene or glycol ethers. <sup>10</sup> Epidemiologic studies have shown that exposure to similarly refined petroleum solvents (i.e., Stoddard solvent, mineral spirits) can cause dry throat, burning or tearing of the eyes, mild headaches, dizziness, central nervous system depression, respiratory irritation, and dermatitis. <sup>16</sup> The evaluation criteria are based upon the similarity of the mixture composition in relation to Stoddard solvent.	NIOSH REL is 350 mg/m <sup>3</sup> , up to a 10-hour TWA. The NIOSH C limit is 1800 mg/m <sup>3</sup> , 15 minutes. OSHA PEL is 2,900 mg/m <sup>3</sup> , 8-hour TWA. ACGIH TLV is 525 mg/m <sup>3</sup> , 8-hour TWA.

REL = recommended exposure limit (NIOSH)    PEL = permissible exposure limit (OSHA)    TLV = Threshold Limit Value (ACGIH)  
TWA = Time-weighted average    STEL = Short-term exposure limit    ppm = parts per million  
mg/m<sup>3</sup> = milligrams per cubic meter    CRM = crumb-rubber modified asphalt    CONV = non-rubber containing asphalt

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**Table 4**  
**Summary of Area Air Concentrations**  
**Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94-0365-2563)**

Sampling Location	Analyte	TWA Concentration, expressed in micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ )			
		8/30/94 Conventional	8/31/94 Conventional	9/1/94 CRM	9/2/94 CRM
<b>Paver Hopper</b>	Total Particulate	80	380	170	220
	Respirable Particulate	50	60	80	ND (<40)
	Benzene Soluble Particulate	Trace	90	Trace	Trace
	PAC <sub>370</sub> (vapor and particulate)	14	4.8	3.0	1.4
	PAC <sub>400</sub> (vapor and particulate)	2.7	1.4	Trace	Trace
	Benzothiazole	Trace	Trace	5.6	11.4
	Organic Sulfur Compounds	ND (<0.6)	5.6	ND (<0.3)	ND (<0.5)
	TVOCs, retention time >Toluene	240	670	1200	750
<b>Paver Screed</b>	Total Particulate	190	450	2490	1050
	Respirable Particulate	160	80	520	300
	Benzene Soluble Particulate	90	220	380	970
	PAC <sub>370</sub> (vapor and particulate)	1.9	9.8	14	33
	PAC <sub>400</sub> (vapor and particulate)	1.4	3.1	4.1	12
	Benzothiazole	Trace	Trace	26	59
	Organic Sulfur Compounds	2.1	Trace	17	37
	TVOCs, retention time >Toluene	570	570	5600	3400
<b>Background</b>	Total Particulate	ND (<20)	ND (<20)	30	70
	Benzene Soluble Particulate	ND (<20)	ND (<30)	ND (<20)	ND (<40)
	Respirable Particulate	70	ND (<30)	40	ND (<80)
	PAC <sub>370</sub> (vapor & particulate)	0.31	Trace	0.27	1.5
	PAC <sub>400</sub> (vapor & particulate)	ND (<0.1)	ND (<0.1)	ND (<0.1)	Trace
	Benzothiazole	ND (<0.3)	ND (<0.3)	ND (<0.3)	ND (<0.5)
	Organic Sulfur Compounds	ND (<0.3)	ND (<0.3)	ND (<0.3)	ND (<0.5)
	TVOCs, retention time >Toluene	ND	ND	ND	ND

Trace = Concentration is between the Minimum Detectable and Minimum Quantifiable Concentrations

ND = Not Detected (below the Minimum Detectable Concentration)

() = The value which is shown in brackets is the minimum detectable concentration (MDC) for this sample. The MDC is calculated by dividing the analytical Limit of Detection by the air sample volume and is reported as a less than (<) value.

PAC<sub>370</sub> = Polycyclic aromatic compounds measured with the detector set at 370 nanometer

PAC<sub>400</sub> = Polycyclic aromatic compounds measured with the detector set at 400 nanometer

TVOC = total volatile organic compounds

**Table 5**  
**Summary of Area Concentrations of Air Contaminants**  
**Paving Site: Granite Construction Company, Sacramento, California (HETA 94-0408-2564)**

Sampling Location	Analyte	TWA Concentration, expressed in micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ )			
		10/7/94 Conventional	10/10/94 Conventional	10/6/94 CRM	10/11/94 CRM
<b>Paver Hopper</b>	Total Particulate	2300	6200	1500	4100
	Respirable Particulate	940	750	480	1000
	Benzene Soluble Particulate	1100	4700	1400	2000
	PAC <sub>370</sub> (vapor and particulate)	29	233	117	104
	PAC <sub>400</sub> (vapor and particulate)	62	56	21	21
	Benzothiazole	17	21	104	2.3
	Organic Sulfur Compounds	784	68	186	118
	TVOCs, retention time < toluene	18000	16000	3800	3400
TVOCs, retention time > toluene	3300	7600	7300	2800	
<b>Paver Screed</b>	Total Particulate	1300	3200	1500	1400
	Respirable Particulate	760	3100	810	610
	Benzene Soluble Particulate	1300	3000	Sample Lost	1500
	PAC <sub>370</sub> (vapor and particulate)	102	264	85	45
	PAC <sub>400</sub> (vapor and particulate)	19	59	17	10
	Benzothiazole	15	3.1	121	81
	Organic Sulfur Compounds	79	93	178	20
	TVOCs, retention time < toluene	2100	650	2800	510
TVOCs, retention time > toluene	6600	9000	10000	2500	
<b>Background</b>	Total Particulate	Sample Lost	40	90	190
	Benzene Soluble Particulate	Trace	ND (<10)	ND (<10)	Sample Lost
	Respirable Particulate	ND (<40)	60	ND (<20)	ND (<20)
	PAC <sub>370</sub> (vapor & particulate)	0.40	0.14	0.18	Trace
	PAC <sub>400</sub> (vapor & particulate)	0.14	0.02	0.03	ND (<0.01)
	Benzothiazole	14	ND (<0.3)	ND (<0.5)	ND (<0.3)
	Organic Sulfur Compounds	ND (<0.6)	ND (<0.3)	ND (<0.5)	ND (<0.3)
	VOCs, retention time > toluene	ND	ND	Trace	ND

PAC<sub>370</sub> = Polycyclic aromatic compounds measured with the detector set at 370 nanometer

PAC<sub>400</sub> = Polycyclic aromatic compounds measured with the detector set at 400 nanometer

ND = Not Detected (below the Minimum Detectable Concentration)

() = The value which is shown in brackets is the minimum detectable concentration (MDC) for this sample. The MDC is calculated by dividing the analytical Limit of Detection by the air sample volume and is reported as a less than (<) value.

TVOC = total volatile organic compounds

**Table 6**  
**Summary of Area Concentrations of Air Contaminants**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118-2565)**

Sampling Location	Analyte	TWA Concentration, expressed in micrograms per cubic meter (µg/m <sup>3</sup> )							
		2/10/95 Conventional		2/11/95 Conventional		2/13/95 CRM		2/14/95 CRM	
<b>Paver Hopper</b>	Total Particulate	ND (<30)		180		440		500	
	Respirable Particulate	140†		160		140		290	
	Benzene Soluble Particulate	Trace		Trace		1200		530	
	PAC <sub>370</sub> (vapor & particulate)	‡		3.3		28		23	
	PAC <sub>400</sub> (vapor & particulate)	‡		0.41		4.1		2.5	
	Benzothiazole	‡		ND (<0.30)		3.9		5.6	
	Organic Sulfur Compounds	‡		ND (<0.30)		11		9.4	
	TVOCs, retention time < toluene	210		130		180		210	
	TVOCs, retention time > toluene	2800		2300		2700		6400	
<b>Air Sample Position at Screenshot →</b>		Left	Right	Left	Right	Left	Right	Left	Right
<b>Paver Screenshot</b>	Total Particulate	130	180	380	450	2400	5000	1700	520
	Respirable Particulate	ND	220†	210	90	7200†	3800	1500	330
	Benzene Soluble Particulate	110	120	220	180	3500	5200	2100	370
	PAC <sub>370</sub> (vapor & particulate)	3.1	2.6	32	2.1	182	380	33	66
	PAC <sub>400</sub> (vapor & particulate)	0.42	0.41	4.1	0.33	30	73	5.6	11
	Benzothiazole	ND (<0.40)	ND (<0.40)	ND (<0.30)	ND (<1.7)	7.5	20	3.3	11
	Organic Sulfur Compounds	ND (<0.40)	ND (<0.40)	31	ND (<1.7)	270	200	ND (<0.80)	59
	TVOCs, retention time < toluene	190	310	160	130	990	810	340	Trace
	TVOCs, retention time > toluene	2500	2100	8200	4900	38000	26000	15000	8200
<b>Background</b>	Total Particulate	ND (<30)		40		40		30	
	Benzene Soluble Particulate	ND (<80)		Trace		ND (<60)		ND (<60)	
	Respirable Particulate	ND (<30)		ND (<20)		ND (<20)		ND (<20)	
	PAC <sub>370</sub> (vapor & particulate)	0.18		1.6		0.07		0.082	
	PAC <sub>400</sub> (vapor & particulate)	Trace		Trace		ND (<0.02)		ND (<0.02)	
	Benzothiazole	ND (<0.4)		ND (<0.3)		ND (<0.3)		ND (<0.3)	
	Organic Sulfur Compounds	ND (<0.4)		ND (<0.3)		ND (<0.3)		ND (<0.3)	
	TVOCs, retention time > toluene	ND		ND		ND		ND	

PAC<sub>370</sub> = Polycyclic aromatic compounds measured with the detector set at 370 nanometer  
PAC<sub>400</sub> = Polycyclic aromatic compounds measured with the detector set at 400 nanometer  
ND = Not Detected (below the Minimum Detectable Concentration)  
† = These concentrations should be considered suspect since the respirable particulate fraction exceeds the total fraction.  
‡ = Due to a sampling pump malfunction, no data is available at this location on this date for this substance.  
Trace = Concentration in between the Minimum Detectable and Minimum Quantifiable concentrations.  
TVOC = total volatile organic compounds

**Table 7**  
**Summary of Area Concentrations of Air Contaminants**  
**Paving Company: Koester Equipment, Evansville, Indiana (HETA 95-0307-2602)**

Sampling Location	Analyte	TWA Concentration, expressed in micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ )							
		8/22/95 Conventional	8/23/95 Conventional	7/13/95 CRM	7/14/95 CRM				
<b>Paver Hopper</b>	Total Particulate	220	180	240	200				
	Respirable Particulate	30	110	160	180				
	Benzene Soluble Particulate	ND	Trace	60	100				
	PAC <sub>370</sub> (vapor & particulate)	45◆	35	143	41				
	PAC <sub>400</sub> (vapor & particulate)	5.1◆	4.8	6.4	6.1				
	Benzothiazole	ND◆ (<1.3)	ND (<1.2)	31	89				
	Organic Sulfur Compounds	ND◆ (<1.3)	97	51	84				
	TVOCs, retention time < toluene	Trace	160	ND (<0.02)	ND (<0.02)				
TVOCs, retention time > toluene	4900	63000	500	380					
Air Sample Position at Screed Auger →		Left	Right	Left	Right	Left	Right	Left	Right
<b>Paver Screed</b>	Total Particulate	250	150	90	130	1000	1000	1200	1100
	Respirable Particulate	170	40	90	40	580	510	330	380
	Benzene Soluble Particulate	Trace	Trace	Trace	ND	560	400	980	700
	PAC <sub>370</sub> (vapor & particulate)	22	14	49	19	143	153	216	84
	PAC <sub>400</sub> (vapor & particulate)	2.9	1.9	6.0	2.4	22	26	35	16
	Benzothiazole	ND (<1.3)	Trace	ND (<1.2)	ND (<1.2)	61	67	127	125
	Organic Sulfur Compounds	70	70	105	47	255	296	792	164
	TVOCs, retention time < toluene	Trace	ND	170	Trace	210	170	ND	250
TVOCs, retention time > toluene	2000	1200	5000	2300	10000	8500	Trace	19000	
<b>Background</b>	Total Particulate†	100	50	160	150				
	Benzene Soluble Particulate	ND (<80)	ND (<80)	ND (<20)	ND (<30)				
	Respirable Particulate	ND (<30)	ND (<30)	140	ND (<30)				
	PAC <sub>370</sub> (vapor & particulate)	ND (<0.02)	Trace	0.2	0.4				
	PAC <sub>400</sub> (vapor & particulate)	ND (<0.02)	ND (<0.02)	Trace	0.04				
	Benzothiazole	Trace	ND (<1.1)	ND (<1.2)	ND (<1.5)				
	Organic Sulfur Compounds	11	ND (<1.1)	ND (<1.2)	ND (<1.5)				
	TVOCs, retention time > toluene	ND (<0.02)	ND (<0.02)	ND (<0.02)	ND (<0.02)				

† = Highest of three background samples collected.  
‡ = This sample should be considered suspect since it exceed the total particulate sample result.  
PAC<sub>370</sub> = Polycyclic aromatic compounds measured with the detector set at 370 nanometer  
PAC<sub>400</sub> = Polycyclic aromatic compounds measured with the detector set at 400 nanometer  
ND = Not Detected (below the Minimum Detectable Concentration).  
Trace = Concentration is between the Minimum Detectable and Minimum Quantifiable Concentration.  
◆ = Sampling pump failed twice during the workday. Concentration based on estimated sample volume.  
TVOC = total volatile organic compounds

**Table 8**  
**Summary of Area Concentrations of Air Contaminants**  
**Paving Site: Staker Construction Company, Casa Grande, Arizona (HETA 96-0072-2603)**

Sampling Location	Analyte	TWA Concentration, expressed in micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ )							
		2/27/96 Conventional		2/29/96 Conventional		3/20/96 CRM		3/21/96 CRM	
Air Sample Position at Screenshot →		Left	Right	Left	Right	Left	Right	Left	Right
Paver Screenshot	Total Particulate	290	2400	70	2500	3100	4000	6300	5300
	Benzene Soluble Particulate	150	2200	50	2400	3000	4000	6100	5300
	Total Particulate	4200	1300	5500	3000	5500	2700	3800	2800
	Benzene Soluble Particulate	4000	1100	5100	2900	5200	2600	3500	2600
	PAC <sub>370</sub> (vapor & particulate)	129	126	280	140	585	174	639	259
	PAC <sub>400</sub> (vapor & particulate)	19	43	80	22	108	30	113	39
	PAC <sub>370</sub> (vapor & particulate)	184	121	201	186	386	174	622	158
	PAC <sub>400</sub> (vapor & particulate)	30	19	64	19	69	28	108	23
	Benzothiazole	ND (<0.35)	ND (<0.35)	ND (<0.3)	Trace	21	51	28	83
	Organic Sulfur Compounds	133	224	258	110	313	246	739	373
	Benzothiazole	ND (<0.32)	2.7	ND (<0.32)	1.5	31	65	39	65
	Organic Sulfur Compounds	179	111	208	228	340	239	389	195
	TVOCs, retention time < toluene	420	840	1500	540	2900	1200	2700	1200
TVOCs, retention time > toluene	12000	19000	74000	15000	111000	34000	106000	36000	
Respirable Particulate	980	640	630	1400	1400	460	1800	1200	
Highway Backgd.	Total Particulate‡	30		10		30		80†	
	Benzene Soluble Particulate‡	10		ND (<20)		ND (<20)		ND (<20)	
	Respirable Particulate	ND (<20)		Sample Lost		40		ND (<30)	
	PAC <sub>370</sub> (vapor & particulate)	ND (<0.02)		ND (<0.02)		ND (<0.03)		ND (<0.03)	
	PAC <sub>400</sub> (vapor & particulate)	ND (<0.02)		ND (<0.02)		ND (<0.01)		ND (<0.01)	
	Benzothiazole	ND (<0.29)		ND (<0.28)		ND (<0.60)		ND (<0.70)	
	Organic Sulfur Compounds	ND (<0.29)		ND (<0.28)		ND (<0.60)		ND (<0.70)	
	TVOCs, retention time > toluene					Not collected at this site			

PAC<sub>370</sub> = Polycyclic aromatic compounds measured with the detector set at 370 nanometer  
PAC<sub>400</sub> = Polycyclic aromatic compounds measured with the detector set at 400 nanometer  
ND = Not Detected (below the Minimum Detectable Concentration which is shown in brackets)  
‡ = Average of three highway background samples  
† = The samples collected on 3/21/96 ranged from 20 to 210  $\mu\text{g}/\text{m}^3$ .  
TVOC = total volatile organic compounds



**Table 9**  
**Summary of Area Concentrations of Air Contaminants**  
**Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130-2619)**

Sampling Location	Analyte	TWA Concentration, expressed in micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ )							
		4/24/96 Conventional		4/25/96 Conventional		4/29/96 CRM		4/30/96 CRM	
Air Sample Position at Screenshot →		Left	Right	Left	Right	Left	Right	Left	Right
<b>Paver Screenshot</b>	Total Particulate	1700	2900	1700	2900	5700	6300	2100	1800
	Benzene Soluble Particulate	1200	2100	1100	1900	5400	5600	1700	1600
	Total Particulate	2900	2900	1900	3000	5200	6100	3000	1400
	Benzene Soluble Particulate	2400	2100	1100	2000	4700	5500	2800	1200
	PAC <sub>370</sub> (vapor & particulate)	102	132	65	116	228	224	140	103
	PAC <sub>400</sub> (vapor & particulate)	16	22	8.9	17	41	40	23	15
	PAC <sub>370</sub> (vapor & particulate)	130	136	65	119	222	233	151	105
	PAC <sub>400</sub> (vapor & particulate)	20	22	9.0	15	39	40	26	17
	Benzothiazole	ND (<1.1)	ND (<1.1)	ND (<1.1)	ND (<1.1)	44	52	39	28
	Organic Sulfur Compounds	139	113	48	88	65	62	47	25
	Benzothiazole	ND (<1.1)	trace	ND (<1.1)	ND (<1.1)	31	51	40	26
	Organic Sulfur Compounds	123	144	41	26	48	58	58	29
	TVOCs, retention time < toluene	700	1100	270	490	920	580	690	560
	TVOCs, retention time > toluene	25000	21000	6300	8400	34000	20000	26000	18000
Respirable Particulate	1190	1280	200	1210	9010	2280	1310	940	
<b>Highway Background</b>	Total Particulate	40		60		30		40	
	Benzene Soluble Particulate	ND (<40)		ND (<40)		ND (<40)		ND (<40)	
	Respirable Particulate	30		ND (<20)		30		20	
	PAC <sub>370</sub> (vapor & particulate)	1.2		ND (<0.02)		0.2		Trace	
	PAC <sub>400</sub> (vapor & particulate)	0.11		ND (<0.03)		Trace		ND	
	Benzothiazole	ND (<1.1)		ND (<1.1)		ND (<1.1)		ND (<1.1)	
	Organic Sulfur Compounds	ND (<1.1)		ND (<1.1)		ND (<1.1)		ND (<1.1)	
	TVOCs, retention time > toluene	Not collected at this site							

PAC<sub>370</sub> = Polycyclic aromatic compounds measured with the detector set at 370 nanometer  
PAC<sub>400</sub> = Polycyclic aromatic compounds measured with the detector set at 400 nanometer  
ND = Not Detected; value is below the Minimum Detectable Concentration (MDC). MDCs are calculated by dividing the analytical Limit of Detection by the air sample volume.  
trace = Concentration was between the MDC and Minimum Quantifiable Concentration (MQC). MQCs are calculated by dividing the analytical Limit of Quantification by the air sample volume.  
TVOC = total volatile organic compounds

Note: The respective MDCs were 1.1  $\mu\text{g}/\text{m}^3$  for benzothiazole and organic sulfur compounds, 40  $\mu\text{g}/\text{m}^3$  for benzene solubles, 0.02  $\mu\text{g}/\text{m}^3$  for PAC<sub>370</sub>, 0.03  $\mu\text{g}/\text{m}^3$  for PAC<sub>400</sub>, and 20  $\mu\text{g}/\text{m}^3$  for respirable particulates. The MDCs for benzothiazole, organic sulfur compounds, PAC<sub>370</sub>, and PAC<sub>400</sub> were calculated assuming an average sample volume of 900 Liters, while the MDCs for benzene solubles and respirable particulates were calculated assuming average sample volumes of 835 and 940 Liters, respectively. Concentrations were between the respective MDCs and MQCs of 1.1 and 4.6  $\mu\text{g}/\text{m}^3$  for benzothiazole, 0.02 and 0.06  $\mu\text{g}/\text{m}^3$  for PAC<sub>370</sub>, and 0.03 and 0.10  $\mu\text{g}/\text{m}^3$  for PAC<sub>400</sub>. All values were calculated assuming an average sample volume of 900 Liters.

**Table 10**  
**Summary of Area Concentrations of Air Contaminants**  
**Paving Site: Bardon–Trimount, Stoughton, Massachusetts (HETA 97–0232–2674)**

Sampling Location	Analyte	TWA Concentration, expressed in micrograms per cubic meter (µg/m <sup>3</sup> )							
		7/22/97 Conventional		7/23/97 Conventional		6/25/97 CRM		6/27/97 CRM	
Air Sample Position at Screenshot →		Left	Right	Left	Right	Left	Right	Left	Right
Paver Screenshot	Total Particulate	1400	1400	1500	1800	6000	8800	11000	8400
	Benzene Soluble Particulate	1200	1200	1300	1600	5800	8500	9800	7500
	Total Particulate	1400	1500	1600	1900	6500	8100	12000	8700
	Benzene Soluble Particulate	1200	1200	1400	1600	6400	7700	10000	8100
	PAC <sub>370</sub> (vapor & particulate)	429	NS	393	281	2029	2832	2601	2027
	PAC <sub>400</sub> (vapor & particulate)	72	NS	77	60	130	279	192	181
	PAC <sub>370</sub> (vapor & particulate)	440	466	450	486	2062	2666	1853	2257
	PAC <sub>400</sub> (vapor & particulate)	81	97	83	88	145	273	203	177
	Benzothiazole	ND (<0.06)	NS	ND (<0.05)	ND (<0.05)	88	81	90	157
	Organic Sulfur Compounds	95	NS	78	106	112	264	207	165
	Benzothiazole	ND	ND	ND	ND	100	233	104	179
	Organic Sulfur Compounds	50	70	103	104	133	233	295	232
	TVOCs, retention time < toluene	1300	2000	2300	2300	4800	16000	9900	6000
	TVOCs, retention time > toluene	15000	23000	24000	24000	71000	224000	126000	86000
Respirable Particulate	440	590	580	770	2500	4800	4600	3000	
Highway Background	Total Particulate‡	29		30		74		33	
	Benzene Soluble Fraction‡	ND (<8.0)		12		ND (<10)		19	
	Respirable Particulate	880◆		110		72		ND (<30)	
	PAC <sub>370</sub> (vapor & particulate)	2.7		ND (<0.06)		10		7.0	
	PAC <sub>400</sub> (vapor & particulate)	0.32		ND (<0.06)		ND (<0.09)		ND (<0.07)	
	Benzothiazole	ND (<0.08)		ND (<0.06)		ND (<0.09)		ND (<0.07)	
	Organic Sulfur Compounds	ND (<0.08)		ND (<0.06)		ND (<0.09)		ND (<0.07)	
	TVOCs, retention time > toluene	Not collected at this site							

- PAC<sub>370</sub> = Polycyclic aromatic compounds measured with the detector set at 370 nanometer  
PAC<sub>400</sub> = Polycyclic aromatic compounds measured with the detector set at 400 nanometer  
ND = Not Detected (below the Minimum Detectable Concentration which is shown in brackets)  
‡ = Average of three highway background samples  
◆ = This background sample is suspect because it is 8 to 29 times higher than other respirable particulate samples collected at this site.  
TVOC = total volatile organic compounds  
NS = no sample collected

**Table 11**  
**Total Particulate Results from Personal Breathing–Zone Samples, by Job Category**

Job Category	Total Particulate, expressed in milligrams per cubic meter (mg/m <sup>3</sup> )									
	CONV Asphalt Paving					CRM Asphalt Paving				
	N	GM	SD	Min	Max	N	GM	SD	Min	Max
Truck dumper	7	0.36	2.0	0.15	0.89	10	0.48	1.5	0.21	0.84
Tack truck driver	2	0.21	1.5	0.16	0.27	2	0.24	1.3	0.20	0.30
Raker	16	0.20	1.9	0.05	0.51	12	0.25	1.6	0.14	0.68
Roller operator †	19	0.07	2.2	0.02	0.35	19	0.13	2.4	0.02	1.3 ■
Laborer	2	0.81	1.7	0.55	1.2	2	0.18	2.3	0.10	0.33
Screed operator †	15	0.14	2.2	0.04	0.47	22	0.28	2.9	0.01	1.4
Paver operator	10	0.31	3.6	0.03	1.3	14	0.27	2.2	0.08	0.91
Other *	7	0.10	4.0	0.01	0.46	6	0.24	1.8	0.15	0.67

N = number of person days in sample set  
 GM = geometric mean  
 SD = standard deviation  
 \* = site supervisors, inspectors, and traffic control personnel  
 Min = minimum value in sample set  
 Max = maximum value in sample set  
 † = difference between CRM and CONV is significant ( $p \leq 0.05$ )  
 ■ = maximum value from Michigan site and may not be from asphalt fume

**Table 12**  
**Benzene Soluble Particulate Results from Personal Breathing–Zone Samples, by Job Category**

Job Category	Benzene Soluble Particulate, expressed in milligrams per cubic meter (mg/m <sup>3</sup> )									
	CONV Asphalt Paving					CRM Asphalt Paving				
	N	GM	SD	Min	Max	N	GM	SD	Min	Max
Truck dumper	6	0.15	2.7	0.04	0.49	6	0.25	1.8	0.10	0.51
Raker	6	0.08	1.4	0.05	0.12	5	0.15	1.9	0.07	0.36
Roller operator	9	0.02	1.8	0.01	0.05	8	0.02	2.3	0.0	0.06
Screed operator	4	0.15	2.2	0.07	0.37	10	0.19	3.8	0.01	1.1
Paver operator	4	0.44	1.7	0.23	0.82	6	0.16	4.5	0.01	0.75
Other *	3	0.11	3.4	0.03	0.35	2	0.05	1.1	0.05	0.06

N = number of person days in sample set  
 GM = geometric mean  
 SD = standard deviation  
 Min = minimum value in sample set  
 Max = maximum value in sample set  
 \* = site supervisors, inspectors, and traffic control personnel

**Table 13**  
**PAC<sub>370</sub> Results from Personal Breathing–Zone Samples, by Job Category**

Job Category	PAC <sub>370</sub> Concentration, expressed in micrograms per cubic meter (ug/m <sup>3</sup> )									
	CONV Asphalt Paving					CRM Asphalt Paving				
	N	GM	SD	Min	Max	N	GM	SD	Min	Max
Truck dumper	6	13	1.5	8.3	22	9	22	5.1	3.1	466
Raker	6	7.8	1.5	5.0	16	9	12	4.1	2.1	172
Roller operator ■	15	0.42	9.2	0.01	17	11	2.7	5.4	0.6	152
Screed operator †	10	4.0	6.8	0.65	191	17	29	4.4	6.4	372
Paver operator	5	12	4.2	1.1	49	9	30	5.5	5.7	540
Other *	6	1.4	4.9	0.30	14	5	5.2	1.9	2.9	11

PAC<sub>370</sub> = polycyclic aromatic compound measured with the detector set at 370 nanometers  
 N = number of person days in sample set  
 GM = geometric mean  
 SD = standard deviation  
 † = difference between CRM and CONV is significant (p ≤ 0.01)  
 ■ = difference between CRM and CONV is significant (p ≤ 0.05)  
 Min = minimum value in sample set  
 Max = maximum value in sample set  
 \* = site supervisors, inspectors, and traffic control personnel

**Table 14**  
**PAC<sub>400</sub> Results from Personal Breathing–Zone Samples, by Job Category**

Job Category	PAC <sub>400</sub> Concentration, expressed in micrograms per cubic meter (ug/m <sup>3</sup> )									
	CONV Asphalt Paving					CRM Asphalt Paving				
	N	GM	SD	Min	Max	N	GM	SD	Min	Max
Truck dumper	6	1.9	1.5	1.1	2.9	9	2.3	3.4	0.43	24
Raker	6	1.3	2.1	0.61	4.2	9	1.4	3.3	0.11	8.8
Roller operator	15	0.08	6.4	0.01	3.4	11	0.28	3.3	0.1	3.9
Screed operator †	10	0.58	6.4	0.12	25	17	3.0	3.1	0.71	15
Paver operator	5	1.8	4.1	0.16	6.5	9	3.3	3.6	0.82	27
Other *	6	0.26	4.1	0.07	2.1	5	0.68	2.0	0.36	1.6

PAC<sub>400</sub> = Polycyclic aromatic compound measured with the detector set at 400 nanometers  
 N = number of person days in sample set  
 GM = geometric mean  
 SD = standard deviation  
 † = difference between CRM and CONV is significant (p ≤ 0.01)  
 Min = minimum value in sample set  
 Max = maximum value in sample set  
 \* = site supervisors, inspectors, and traffic control personnel

**Table 15**  
**OSC Results from Personal Breathing–Zone Samples, by Job Category**

Job Category	OSC Concentration, expressed in micrograms per cubic meter (ug/m <sup>3</sup> )									
	CONV Asphalt Paving					CRM Asphalt Paving				
	N	GM	SD	Min	Max	N	GM	SD	Min	Max
Truck dumper	6	0.39	9.5	0.03	11	9	2.4	21	0.02	135
Raker	6	1.3	2.9	0.50	11	9	0.37	3.6	0.04	1.8
Roller operator	15	0.24	5.0	0.03	1.7	11	0.34	4.9	0.02	2.5
Screed operator	10	0.52	5.8	0.03	8.3	17	1.1	10	0.02	85
Paver operator	5	2.3	7.1	0.22	35	9	4.1	4.8	0.14	16
Other ■ *	6	0.93	2.9	0.24	3.5	5	4.6	3.3	1.2	18

OSC = organic sulfur compounds  
 N = number of person days in sample set  
 GM = geometric mean  
 SD = standard deviation  
 \* = site supervisors, inspectors, and traffic control personnel

Min = minimum value in sample set  
 Max = maximum value in sample set  
 ■ = difference between CRM and CONV is significant (p ≤ 0.05)

**Table 16**  
**Benzothiazole Results from Personal Breathing–Zone Samples, by Job Category**

Job Category	Benzothiazole Conc., expressed in micrograms per cubic meter (ug/m <sup>3</sup> )									
	CONV Asphalt Paving					CRM Asphalt Paving				
	N	GM	SD	Min	Max	N	GM	SD	Min	Max
Truck dumper †	6	0.2	4.6	0.03	1.2	9	23	2.0	8.1	77
Raker †	6	1.1	1.7	0.5	2.7	9	8.9	4.1	0.3	26
Roller operator ■	15	0.24	4.7	0.03	1.7	11	1.3	6.2	0.04	7.8
Screed operator †	10	0.34	4.4	0.03	2.2	17	22	3.6	0.27	61
Paver operator †	4	0.72	2.2	0.22	1.1	9	40	2.1	12	108
Other * †	6	0.58	2.6	0.22	1.8	5	21	1.4	15	38

N = number of person days in sample set  
 GM = geometric mean  
 SD = standard deviation  
 † = difference between CRM and CONV is significant (p ≤ 0.01)

Min = minimum value in sample set  
 Max = maximum value in sample set  
 \* = site supervisors, inspectors, and traffic control personnel  
 ■ = difference between CRM and CONV is significant (p ≤ 0.05)

**Table 17**  
**Acute Respiratory Symptoms by Exposure Group**

Symptom	Control Asphalt–unexposed (138 person–days)			CRM <sup>a</sup> Asphalt–exposed (96 person–days)			CONV <sup>b</sup> Asphalt–exposed (84 person–days)		
	Person–days with symptom		OR (95% CI) <sup>c</sup>	Person–days with symptom		OR (95% CI)	Person–days with symptom		OR (95% CI)
	No.	%		No.	%		No.	%	
<b>Burning, itchy, stuffy, or irritated nose</b>	12	8.7	1.0 (referent)	27	28.1	4.3 (1.5, 12.6)	15	17.9	2.4 (0.8, 7.2)
<b>Burning, itchy, painful, or irritated eyes</b>	11	8.0	1.0	24	25.0	4.0 (1.4, 11.0)	9	10.7	1.4 (0.4, 4.7)
<b>Sore, dry, scratchy, or irritated throat</b>	5	3.6	1.0	41	42.7	20.1 (7.6, 53.5)	10	11.9	3.6 (1.1, 11.8)
<b>Cough</b>	5	3.6	1.0	16	16.7	5.6 (1.5, 21.4)	7	8.3	2.7 (0.6, 11.9)
<b>Chest tightness or difficulty breathing</b>	1	0.7	– <sup>d</sup>	12	12.5	–	3	3.6	–
<b>Wheezing or whistling</b>	0	0	–	2	2.1	–	2	2.3	–

a CRM Asphalt = crumb rubber modified hot mix asphalt

b CONV Asphalt = conventional (non–rubber containing) hot mix asphalt

c Odds ratio (95% confidence interval)

d Odds ratios were not calculated when the number of people in any one group was two or less

**Table 18**  
**Geometric Mean (Range) of Contaminant Levels by**  
**Presence of Eye, Nose, or Throat Irritation**  
**and Type of Asphalt Exposure**

Contaminant <sup>c</sup>	CRM Asphalt <sup>a</sup>			CONV Asphalt <sup>b</sup>		
	Eye, nose, or throat irritation			Eye, nose, or throat irritation		
	Absent	Present	p <sup>d</sup>	Absent	Present	p
<b>TP</b>	0.18 (0.01–0.78)	0.30 (0.04–1.38)	<0.01	0.13 (0.02–1.20)	0.23 (0.01–1.26)	0.02
<b>BSP</b>	0.08 (0.01–0.61)	0.13 (0.00–1.10)	0.26	0.05 (0.01–0.49)	0.16 (0.01–0.82)	<0.01
<b>OSC</b>	1.50 (0.02–135)	0.93 (0.02–85)	0.40	0.51 (0.03–11)	0.67 (0.03–35)	0.62
<b>BENZ</b>	8.30 (0.04–108)	17.64 (0.30–77)	0.10	0.43 (0.03–2.70)	0.29 (0.03–1.20)	0.39
<b>PAC<sub>370</sub></b>	10.31 (0.60–540)	17.27 (0.77–466)	0.25	1.28 (0.01–22)	9.13 (0.18–191)	<0.01
<b>PAC<sub>400</sub></b>	1.07 (0.10–27)	1.94 (0.10–24)	0.11	0.22 (0.01–4.20)	1.33 (0.04–25)	<0.01

a CRM Asphalt = crumb rubber modified hot mix asphalt

b CONV Asphalt = conventional (non-rubber containing) hot mix asphalt

c TP = total particulate, mg/m<sup>3</sup> (milligrams per cubic meter); BSP = benzene-soluble particulate, mg/m<sup>3</sup>; OSC = organic sulfur compounds, µg/m<sup>3</sup> (micrograms per cubic meter); BENZ = benzothiazole, µg/m<sup>3</sup>; PAC<sub>370</sub> = polycyclic aromatic compounds, 370 nm (nanometers), µg/m<sup>3</sup>; PAC<sub>400</sub> = polycyclic aromatic compounds, 400 nm, µg/m<sup>3</sup>

d For comparing means on days symptom was present with means on days symptom was absent, based on a t-test of the log of the concentration



**Table 19**  
**Geometric Mean (Range) of Contaminant Levels by**  
**Presence of Cough and Type of Asphalt Exposure**

Contaminant <sup>c</sup>	CRM Asphalt <sup>a</sup>			CONV Asphalt <sup>b</sup>		
	Cough			Cough		
	Absent	Present	p <sup>d</sup>	Absent	Present	p
TP	0.22 (0.01–1.35)	0.33 (0.08–1.38)	0.10	0.15 (0.01–1.26)	0.26 (0.05–1.03)	0.19
BSP	0.10 (0.00–0.88)	0.17 (0.01–1.10)	0.28	0.07 (0.01–0.49)	0.33 (0.14–0.82)	0.04
OSC	1.20 (0.02–135)	0.97 (0.05–13)	0.76	0.48 (0.03–11)	2.86 (0.89–35)	0.05
BENZ	11.43 (0.04–108)	18.34 (3.7–77)	0.23	0.34 (0.03–2.70)	1.18 (0.89–1.80)	<0.01
PAC <sub>370</sub>	13.38 (0.60–540)	14.99 (0.77–466)	0.84	2.28 (0.01–191)	5.90 (0.30–49)	0.40
PAC <sub>400</sub>	1.45 (0.10–27)	1.66 (0.10–24)	0.77	0.37 (0.01–25)	0.91 (0.07–6.50)	0.38

a CRM Asphalt = crumb rubber modified hot mix asphalt

b CONV Asphalt = conventional (non-rubber containing) hot mix asphalt

c TP = total particulate, mg/m<sup>3</sup> (milligrams per cubic meter); BSP = benzene-soluble particulate, mg/m<sup>3</sup>; OSC = organic sulfur compounds, µg/m<sup>3</sup> (micrograms per cubic meter); BENZ = benzothiazole, µg/m<sup>3</sup>; PAC<sub>370</sub> = polycyclic aromatic compounds, 370 nm (nanometers), µg/m<sup>3</sup>; PAC<sub>400</sub> = polycyclic aromatic compounds, 400 nm, µg/m<sup>3</sup>

d For comparing means on days symptom was present with means on days symptom was absent, based on a t-test of the log of the concentration

**Table 20**  
**Comparison of Geometric Mean of Contaminant Levels by Job Category**

Contaminant	Exposure Category *	CRM Paving			CONV Paving		
		n	GM	SD	n	GM	SD
<b>Total Particulate</b> <i>(concentration expressed in mg/m<sup>3</sup>)</i>	High	46	0.31	2.4	32	0.22	2.8
	Medium	14	0.24	1.7	18	0.23	2.1
	Low † ■	25	0.15	2.3	26	0.08	2.6
<b>Benzene Soluble Particulate</b> <i>(concentration expressed in mg/m<sup>3</sup>)</i>	High	22	0.20	3.3	14	0.20	2.5
	Medium	5	0.15	1.9	6	0.08	1.4
	Low	10	0.03	2.3	12	0.03	2.8
<b>PAC<sub>370</sub></b> <i>(concentration expressed in µg/m<sup>3</sup>)</i>	High † ■	35	27	4.6	21	7.3	4.8
	Medium †	9	12	4.1	6	7.8	1.5
	Low † ■	16	3.3	4.3	21	0.60	8.1
<b>PAC<sub>400</sub></b> <i>(concentration expressed in µg/m<sup>3</sup>)</i>	High † ■	35	2.9	3.2	21	1.1	4.6
	Medium	9	1.4	3.3	6	1.3	2.1
	Low †	16	0.37	3.1	21	0.11	6.0
<b>Organic Sulfur Compounds</b> <i>(concentration expressed in µg/m<sup>3</sup>)</i>	High	35	1.9	10	21	0.68	7.3
	Medium	9	0.37	3.6	6	1.3	2.9
	Low	16	0.77	6.7	21	0.36	4.6
<b>Benzothiazole</b> <i>(concentration expressed in µg/m<sup>3</sup>)</i>	High † ■	35	26	2.8	20	0.34	4.1
	Medium † ■	9	8.9	4.1	6	1.1	1.7
	Low † ■	16	3.2	7.4	21	0.31	4.2

\* High exposure category included paver operators, screed operators, and truck dumpers. The medium exposure category included rakers and laborers. The low exposure group included roller operators, site supervisors, and traffic control personnel.

CONV = conventional (non-rubber containing) asphalt

CRM = crumb rubber modified asphalt

PAC<sub>370</sub> = polycyclic aromatic compound measured with 370 nanometer emission wavelength detector

PAC<sub>400</sub> = polycyclic aromatic compound measured with 400 nanometer emission wavelength detector

n = number of samples in group

GM = geometric mean

SD = standard deviation

† Difference between CRM and CONV concentrations is significantly different ( $p \leq 0.05$ )

■ Difference between CRM and CONV concentrations is significantly different ( $p \leq 0.01$ )

# APPENDIX A

## MODIFIED ANALYTICAL METHOD FOR POLYCYCLIC AROMATIC COMPOUNDS

Larry Jaycox, Charles Neumeister, and Larry Olsen

Historically, attempts to characterize asphalt fume have focused on the analysis of 16 standard unsubstituted polynuclear aromatic hydrocarbons (parent PAHs). This approach has been successful in most of the other matrices where PAH exposure occurs; however, asphalt fume is composed of a multitude of aliphatic and alkylated polycyclic aromatic compounds (PACs) that is so complex that the mixture cannot be separated into discrete compounds. The analytical results obtained from analyzing asphalt fume samples by simply monitoring the 16 parent PAHs typically does not yield useful information regarding worker exposure.

Individual PACs typically are not quantifiable from asphalt fume if the current NIOSH liquid chromatography (LC) and gas chromatography (GC) methods (NIOSH methods 5506 and 5515) for PACs are used. This is due to the enormous number of substituted PACs in asphalt fume that are present in minute quantities which create signal interference from compounds that chromatographically co-elute at the same retention time. This has been previously shown in conventional asphalt fume studies when only the standard 16 unsubstituted PACs were evaluated.

Furthermore, the current method for detecting PACs does not evaluate the asphalt fumes for the compounds believed to be the most likely human health hazards. The health hazards associated with asphalt fume exposure are usually attributed to PACs that contain three to seven annulated rings with side chains of one to two carbons in length (with a maximum of four saturated carbons), or to PACs containing nitrogen, oxygen, and sulfur. For these reasons, a new method has been developed to separate the asphalt fume samples into aliphatic, aromatic, and polar fractions.

Since the published NIOSH methods do not account for all of these different compound types, the current methods were modified to provide a better indication of the total PAC content of the asphalt fumes. A new liquid chromatographic method was developed to give a better indication of the total PAC content in asphalt fume. This was achieved by adapting existing methods, reported in the literature, to initially remove the saturated compounds and the highly polar organic compounds. The remaining PACs can then be analyzed by LC with fluorescence detection. This modification should not only allow for the detection of the standard 16 PACs, that are usually analyzed, but should also allow measurement of the total PAC content present in each sample (i.e. sum of the peak areas). The total PAC content in the sample can then be compared to a PAH reference standard mixture to determine which fume samples have the most PACs. The total PAC content of the crumb-rubber modified (CRM) asphalt fume can be compared to the total PAC content of the conventional asphalt collected from each sample location.

A commercially available standard mixture of 16 PACs was used in a recovery study to show that these compounds are not lost during sample preparation and that the remaining materials can be analyzed. Asphalt fume collected from an earlier pilot investigation has been used to test the possible methods. The sample preparation used solid phase extraction columns and solvent extraction steps. The material remaining after the sample preparation (PACs) was analyzed by means of a reversed-phase high performance liquid chromatographic column with fluorescence detection. After this study was successfully accomplished, the asphalt fume samples collected from paving construction sites were analyzed.

The air sampling collection methods for PACs are very similar to those published in NIOSH method 5506, Polynuclear Aromatic Hydrocarbons. The sampling train consisted of 37-mm, 2 µm pore size, Teflon® filter to collect particulate PACs, connected in series with an ORBO 42 sorbent tube to collect volatile or

semi-volatile PACs. Air was sampled at a pump flow rate of 2 liters per minute (Lpm). Opaque filter cassettes and sorbent tube holders were used to prevent the degradation of PACs by ultraviolet light.

After collection, the asphalt fume sample was extracted from the sampling filter with hexane. The hexane extract was then eluted through a cyano solid phase extraction column. The polar material will be retained on the column, and the aliphatic and the aromatic compounds will elute with hexane. Dimethyl sulfoxide (DMSO) is added to the hexane solution; the aromatic compounds will partition into the DMSO layer while the aliphatics will remain in the hexane layer. Next, the polar compounds are eluted from the column with methanol. The aromatic compounds in the DMSO fraction are analyzed by means of reversed-phase liquid chromatography with fluorescence detection. Since the excitation and emission wavelengths are not the same for all PACs, two sets of excitation and emission wavelengths were utilized. One set of wavelengths is more sensitive for the 2-ring and 3-ring compounds (254 nm excitation, 370 nm emission), and the other set of wavelengths is more sensitive for the 4-ring and higher compounds (254 nm excitation, 400 nm emission). Finally, the total fluorescent response was normalized with a commercially available standard of 16 unsubstituted PAHs.

This methodology was applied to a representative number of CRM and conventional asphalt samples that were obtained from emission locations. The results obtained from this procedure confirmed that the chromatograms were due to widespread signal responses, elapsing over 20 minutes of column retention time indicative of co-elution interference. Upon completion of the chromatography, the samples were analyzed with a flow injection (FI) technique where the LC column was bypassed; an aliquot of the DMSO/asphalt fume extract was injected directly into the fluorescence detection system. The advantage of this modification is that it is a much quicker procedure and the signal response is a single, reproducible peak due to all PAC compounds that fluoresce at the selected wavelength producing a more sensitive and precise signal. The total fluorescent response was also normalized with the same commercially available standard of 16 unsubstituted PAHs that was used in the chromatography methods.

Furthermore, an investigation of the compounds that contain sulfur was conducted. If a significant difference exists between conventional and CRM asphalt, it may be evident in the number and type of sulfur compounds in each asphalt formulation because of the vulcanizing process used during rubber tire production. Preliminary analyses by GC/MS have indicated that the CRM asphalt does contain more sulfur-containing compounds than the conventional asphalt mix. Additionally, higher levels of benzothiazole were present in the CRM asphalt samples. To exploit this potential difference in the asphalt compounds, a sulfur chemiluminescent detector (SCLD) was used in conjunction with a gas chromatograph (GC). This detector is sulfur specific and enables the analysis of sulfur in the low picogram range. The GC/SCLD system was used to analyze hexane extracted sample aliquots prepared from each asphalt fume sample.

## GLOSSARY OF TERMS

ACGIH	American Conference of Governmental Industrial Hygienists
BSP	Benzene soluble particulate fraction
C	Ceiling, an exposure that shall not be exceeded during any part of the workday
°C	Degrees Celsius
CFR	Code of Federal Regulations
cm <sup>2</sup>	Square centimeters
CO	Carbon monoxide
Control	A person working in road construction but not exposed to hot asphalt fume.
CONV	Conventional (non-rubber) asphalt
CRM	Crumb-rubber modified asphalt
DOT	Department of Transportation
EC	Elemental carbon
EPA	Environmental Protection Agency
°F	Degrees Fahrenheit
FHWA	Federal Highway Administration
FID	Flame ionization detector
GC-MS	Gas chromatography-mass spectrometry
H <sub>2</sub> S	Hydrogen sulfide
HHE	Health hazard evaluation
HMA	Hot mix asphalt
IARC	International Agency for Research on Cancer
ISTEA	Intermodal Surface Transportation Efficiency Act
LC	Liquid chromatography
LOD	Limit of detection (analytical method)

LOQ	Limit of quantitation (analytical method)
Lpm	Liters per minute
MCE	Mixed cellulose–ester filter
MDC	Minimum <i>detectable</i> concentration (the smallest amount of a material which can be reliably detected). The MDC is calculated by dividing the analytical LOD by a representative air volume.
mg	Milligrams
mg/m <sup>3</sup>	Milligrams per cubic meter of air
MIBK	Methyl isobutyl ketone
mL	Milliliter
mm	Millimeter
MQC	Minimum <i>quantifiable</i> concentration (the smallest amount of a material which can be reliably measured). The MQC is calculated by dividing the analytical LOQ by a representative air volume.
ND	Not detected
NIOSH	National Institute for Occupational Safety and Health
nm	Nanometer
OC	Organic carbon
OSC	Organic sulfur compounds
OSHA	U.S. Occupational Safety and Health Administration
PAC <sub>370</sub>	PACs monitored at an emission wavelength of 370 nanometers (representative of 2–ring and 3–ring compounds)
PAC <sub>400</sub>	PACs monitored at an emission wavelength of 400 nanometers (representative of 4–ring and higher compounds)
PACs	Polycyclic aromatic compounds
PAHs	Polynuclear aromatic hydrocarbons
PBZ	Personal breathing–zone air sample
PEFR	Peak expiratory flow rate
PEL	Permissible exposure limit (OSHA exposure criteria)

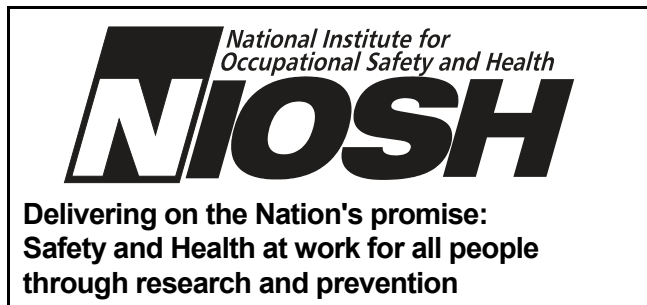
ppm	Parts (of a contaminant) per million parts of air
REL	Recommended exposure limit (NIOSH exposure criteria)
RP	Respirable particulate
Screed	During road paving, the screed levels the hot-mix asphalt to the desired thickness and slope as the paving vehicle moves forward
SO <sub>2</sub>	Sulfur dioxide
STEL	Short-term exposure limit
TC	Total carbon (elemental + organic carbon)
TLV <sup>®</sup>	Threshold limit value (ACGIH exposure criteria)
TWA	Time-weighted average
VOCs	Volatile organic compounds
WBGT	Wet bulb globe temperature
μg	Microgram (10 <sup>-6</sup> ), a unit of weight
μg/m <sup>3</sup>	Micrograms of contaminant per cubic meter of air (a unit of concentration)



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