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**HETA 95-0118-2565  
Martin Paving Company  
Yeehaw Junction, Florida**

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## PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

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## ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Daniel Almaguer, Aubrey Miller, and Kevin Hanley of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Donald Booher, Ann Krake, Dave Marlow, and Kenneth Wallingford. Analytical methods were developed by Larry Jaycox, Charles Neumeister, and Larry Olsen. Laboratory analysis provided by Larry Jaycox, Leroy May, Charles Neumeister, Rosa Key-Schwartz, Ardith Grote, and Robert Kurimo. This report was edited by Gregory Burr. Desktop publishing by Ellen Blythe.

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Martin Paving Company  
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March 1996**

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## **EXECUTIVE SUMMARY**

Approximately 285 million used tires are discarded in the United States each year, posing significant health, fire, and solid waste management problems. As one means of reducing these problems, considerable attention has been focused on the use of the 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 public concerns over the lack of available information on the environmental and human health effects resulting from the use of CRM-HMA, along with the high cost of using this paving material, a temporary legislative moratorium was passed which precluded enforcement of the penalty provisions of the ISTEA legislation. This legislation 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. The recently passed National Highway System Designation Act of 1995 has eliminated the mandate requiring the use of CRM asphalt but continues to require research concerning CRM asphalt paving.

Approximately 300,000 workers are currently employed in the asphalt paving industry in the U.S. 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 research protocol developed by NIOSH included the following objectives.

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

The protocol allows for up to eight individual site evaluations in different geographic regions of the country, enabling investigators to observe different asphalt pavement formulations, climatic conditions, and paving techniques.

One of the greatest challenges in conducting this study is the fact that asphalt is not a consistent product. Asphalt is composed of a highly complex mixture of paraffinic and aromatic hydrocarbons and heteroatomic compounds containing sulfur, nitrogen, and oxygen. The specific chemical content of asphalt products is dependent on the crude petroleum source, production techniques, and process temperatures. The addition of rubber further complicates the asphalt mixture as numerous additional substances present in tires (such as aromatic oils, accelerants, and antioxidants used during tire manufacturing) may become airborne during the asphalt heating and

mixing processes. Finally, there is a lack of available air sampling methods and occupational exposure limits for most of the compounds present in asphalt and the rubber tire components.

This report presents the findings from the site evaluation, conducted in Yeehaw Junction, Florida, during asphalt pavement construction on the Florida Turnpike. The purpose of this report is not to draw definitive conclusions about CRM and conventional asphalt exposures, but rather to provide the site-specific information obtained at the Yeehaw Junction, Florida project.

On February 10-11, 1995, approximately 999 metric tons of conventional asphalt were applied by ten workers of Martin Paving Company; 1,505 metric tons of CRM asphalt were placed on February 13-14 by the same workers. The rubber content was approximately 12% of the asphalt cement by weight. The workplace exposure and health assessment was performed during all four paving days. The evaluation included the collection of area air samples to characterize the asphalt fume emission, personal breathing-zone (PBZ) air samples to evaluate worker exposures, and a medical component that included symptom questionnaires and lung function tests.

Asphalt fume exposures have typically been measured as total particulate and the benzene soluble particulate fraction. However, since neither of these exposure markers measure exposure to a distinct chemical component or even a distinct class of chemicals, it is difficult to relate them to possible health effects. For example, many organic compounds are soluble in benzene, and any dust may contribute to total particulate levels. In an effort to address this problem, new or modified analytical methods were developed and included in this study to more definitively characterize asphalt fume exposures. For example, polycyclic aromatic compounds (PACs), which may be present in asphalt fume, were measured using a new analytical method. Some of the PACs are believed by NIOSH investigators to have irritative effects while other PACs are suspected to be carcinogenic. In addition to PACs, benzothiazole (a sulfur-containing compound present in rubber tires) along with other sulfur-containing compounds (suspected to be present as a result of the addition of rubber to the asphalt or from crude petroleum used for asphalt manufacturing) were also measured. Benzothiazole is of interest since it may be useful as a surrogate indicator for other CRM asphalt fume exposures while other sulfur-containing compounds may be associated with respiratory irritation. Samples were collected for selected volatile organic compounds (toluene, benzene, and methyl isobutyl ketone) and total hydrocarbons (as Stoddard solvent). Elemental carbon was measured to determine if diesel exhaust could have contributed to the air contaminants measured at the paving site. The airborne particulate at the paving site was analyzed to determine the concentration of particles which were respirable. Air samples were collected for 28 different metals and minerals and direct-reading instruments were used to measure carbon monoxide, hydrogen sulfide, sulfur dioxide, and ozone. Finally, bulk air samples of asphalt fume were collected at the asphalt cement storage tank located at the hot mix asphalt plant and submitted for mutagenicity testing.

The area air sample results indicate that concentrations of total and respirable particulate, benzene soluble particulate, and PACs were generally higher during the CRM asphalt paving as compared with the conventional asphalt paving. Total PAC concentrations above the paver screed on CRM asphalt paving days were generally about 5-10 times greater than total PAC concentrations measured at the screed on conventional asphalt paving days. Furthermore, CRM asphalt paving generated more benzothiazole and other sulfur-containing compounds than conventional asphalt paving. Factors that may impact the amount of asphalt fume generated were the amount of asphalt laid and the lay-down temperature. On average, more CRM asphalt was applied (approximately 253 metric tons more per day) than conventional asphalt, and the average application temperature of CRM asphalt was approximately 33°C higher than during conventional asphalt paving.

Over 50 volatile organic compounds (VOCs) were detected in the asphalt emissions; however, only the most significant peaks were analyzed quantitatively. A benzene concentration of 0.08 ppm was detected at the left side of the screed on the first day of CRM asphalt paving. While this benzene concentration does not represent a

personal exposure, it does suggest the potential for employee exposures. NIOSH considers benzene to be an occupational carcinogen and recommends that occupational exposures be reduced to the lowest feasible level. The concentrations of toluene, xylene, methyl isobutyl ketone, and total “other” hydrocarbons were orders of magnitude below their respective occupational exposure criteria. Extremely low or trace concentrations of the following were detected: aluminum, barium, calcium, iron, magnesium, manganese, silver, sodium, and zinc.

Personal breathing-zone air samples were collected on nine workers during two days of conventional asphalt paving and eight workers on the two days of CRM asphalt paving. The PBZ samples were analyzed for total particulates, and for some workers, a second sample was analyzed for total PACs, benzothiazole, and other sulfur compounds. Total particulate concentrations ranged from not detected (ND, less than 0.02) to 1.0 milligrams per cubic meter ( $\text{mg}/\text{m}^3$ ) during CRM asphalt paving, compared to ND ( $<0.05$ ) to  $0.16 \text{ mg}/\text{m}^3$  during conventional asphalt paving. These concentrations are well below the asphalt fume criteria of  $5 \text{ mg}/\text{m}^3$  (measured as total particulate) recommended by NIOSH.

Seven of the ten workers with exposure to the asphalt paving operation (pavers) participated in the health assessment. Additionally, seven workers not typically exposed to hot asphalt fume (non-pavers) were included in the health assessment for comparison. Serial symptom questionnaires were administered to obtain information concerning the prevalence of acute symptoms (i.e., respiratory, eye, nose, throat, and skin symptoms) in relation to worksite exposures. Serial measurements of peak expiratory flow rate (PEFR) were conducted to evaluate acute changes in lung function in relation to worksite exposures. Three pavers and three non-pavers were excluded from analysis of the medical data due to ongoing flu-like illness or incomplete survey data. Among the remaining four pavers, the most frequently reported symptoms (as a percentage of occurrences over all four days) were shortness of breath (55%), throat irritation (14%), nasal irritation (10%), and wheezing (10%). There were no appreciable changes between the conventional and CRM asphalt paving periods in the types of symptoms reported. There also were no appreciable differences between pavers and non-pavers in the number of reported symptoms or rate of symptom occurrences per completed questionnaire. While acute irritant symptoms, including lower airway symptoms, were reported by a number of workers in association with worksite exposures, none of the reported symptoms were accompanied by significant bronchial lability.

This study showed higher asphalt fume emissions at source locations, with higher area air sample concentrations of total particulate, respirable particulate, benzene soluble particulate, total PACs, benzothiazole, and other sulfur-containing compounds detected during the CRM asphalt paving period. All of the PBZ exposures measured in this survey (regardless of the composition of the asphalt) were below the current NIOSH REL for asphalt fume (measured as total particulate). Findings from the medical assessment suggest that pavers were not experiencing symptoms or bronchial lability associated with either the conventional or CRM asphalt paving operations. However, it is premature to draw any definitive conclusions from this single site evaluation. Data provided from this evaluation are based on a very small sample size and may reflect production and weather conditions specific to this site. Additional site evaluations may enable more definitive conclusions to be drawn. A final composite report will be prepared after these additional evaluations are completed.

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

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## PROCESS OVERVIEW

There are three basic steps in constructing an asphalt pavement - manufacture of the hot mix asphalt (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 which is usually a mixture of coarse and fine stones, gravel, sand, and other mineral fillers. The mix design establishes the proportions of the aggregate materials and sizes to the amount of asphalt cement to obtain the appropriate pavement properties (flexibility, drainage, durability, etc.).

The purpose of an HMA plant is to blend the aggregate and asphalt cement to produce a homogenous paving mixture at a hot temperature so that it can be easily applied and compacted. Asphalt cement is typically received from a refinery by tractor trailer tankers and is transferred into heated storage tanks. Aggregate of different materials and sizes is blended through a series of belt conveyors and a dryer (a heated drum mixer). Once the aggregate is sufficiently blended and dried, asphalt cement is applied so that a continuous thin film of cement covers the aggregate evenly. The finished HMA is then placed in a storage silo until it can be dispensed into trucks that haul the material to the paving site. At the paving site the following equipment is typically used:

**P Tack truck:** A vehicle which precedes the paver and applies a low viscosity asphalt ("tack" coat) to the roadway to improve adhesion prior to the HMA placement.

**P 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 in a line onto the road where it is picked up by a windrow conveyor and loaded into the paver

hopper; or (3) conveying the mix with a material transfer vehicle.

**P 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.

**P Rollers:** Typically two or three roller vehicles follow the paver to compact the asphalt.

Paving crews normally consist of eight to ten workers. Job activities include a foreman who supervises the crew; a paver operator who drives the paver; one or two screed operators who control and monitor the depth and width of the HMA placement; one or two rakers who shovel excess HMA, fill in voids and prepare joints; laborers who perform miscellaneous tasks; roller operators who drive the rollers; and a tackman who applies the tackcoat. The paver operators and roller operators do not usually perform different jobs, while the screed operators, rakers, and laborers may perform a variety of tasks throughout the workday.

For purposes of this report, workers associated with the asphalt paving operation (i.e., workers with potential exposure to HMA fume) will be referred to as "pavers." This definition may include workers not specifically employed by the paving contractor (i.e., state highway inspectors) but who are associated with the paving operation and could be exposed to HMA fume during paving. Additionally, some workers who performed jobs associated with road construction, but not exposed to HMA fume (i.e., foremen, laborers, heavy equipment operators, and road surveyors), participated as a control group for the pavers and will be referred to as "non-pavers."

## SITE DESCRIPTION

On February 10 - 14, 1995, NIOSH investigators conducted a study in Yeehaw Junction, Florida, during asphalt pavement construction on the Florida



Turnpike by the Martin Paving Company. During this survey, both the conventional hot mix asphalt (hereafter referred to as “conventional asphalt”) and crumb rubber modified hot mix asphalt (subsequently referred to as “CRM asphalt”) were manufactured at the same portable hot mix plant from the same petroleum crude source with the exception of the pulverized rubber and asphalt cement modifiers. The conventional asphalt was placed on February 10 and 11, while the CRM asphalt was used on February 13 and 14. All of the paving occurred on the North bound lanes of the Florida Turnpike.

A summary of the paving activities and equipment used on the Florida Turnpike paving site is contained in Table 1. Both projects required the placement of a 1.6 centimeter (5/8 inch) “FC-2” open graded friction course. Both mixes were of the same aggregate gradation (0.0075 to 0.95 centimeters) and were consistent with FDOT “FC-2” aggregate specifications. The aggregate contained 91% “FC-2” stone and 9% local sand from Fort Drum. The binder content of the mix was 6.34% “AC-30” grade asphalt cement. A liquid anti-strip additive derived from polyamines and fatty acids was blended to the AC-30 at 0.5% by weight at the asphalt supply terminal; its purpose is to promote adhesion of asphalt cement to aggregate and reduce stripping. Additionally, a very small amount of silicone fluid (25 cubic centimeters per 18,830 liters of asphalt cement) was added to the asphalt cement at the asphalt supply terminal. The silicone is typically added to decrease asphalt foaming and improve asphalt cement workability. The granulated rubber was manufactured by American Tire Recyclers Inc., Jacksonville, Florida, and the rubber content of the CRM asphalt was approximately 12% by weight of the asphalt cement. Aggregate sources and blend percentages were held constant for the production of both the conventional and CRM mixes.

A portable asphalt mix plant was used for this construction project and was located on leased land just to the west of the turnpike, approximately one-half mile north of the Yeehaw Junction exit between U.S. Route 441 and the Florida Turnpike. Asphalt

cement was received from a refinery by tractor trailer (tankers) and transferred into heated storage tanks at the asphalt mixing plant and maintained at 116-143°C (240-290°F). The finished asphalt mixture was placed in a storage silo until it was dispensed into trucks.

The conventional asphalt was used to construct the right traffic lane from mileage marker 190.6 to 196.5 and CRM asphalt was used to construct the right traffic lane from mileage marker 196.5 to 205.6. Approximately 451 metric tons (497 short tons) and 548 metric tons (604 short tons) of conventional asphalt were applied, respectively, on February 10 and 11. This compares to 845 and 660 metric tons (931 and 728 short tons) of CRM asphalt placed on February 13 and 14. The mean temperatures for the asphalt mixes at the paver were 99°C (211°F), 104°C (219°F), 136°C (277°F), and 137°C (278°F) for days 1-4. The depth of both the conventional asphalt and CRM asphalt mats was approximately 1.6 centimeters (5/8 inches); the width of the paving was typically about 3.7 meters (12 feet wide).

One paving vehicle was used during both the conventional and CRM asphalt paving. Back dump trucks placed the asphalt mixes directly into the hopper of the paver which contained a screed placement attachment. The same paving crew was evaluated throughout the survey. During the conventional asphalt paving days the 10-person crew at the Florida site consisted of a foreman, a paver operator, a screed operator, an apprentice screed operator, two screed laborers, a raker laborer, one roller operator, and a traffic control man. During the CRM asphalt paving days a nine person crew was used; an apprentice screed operator was not used.

## **INDUSTRIAL HYGIENE EVALUATION DESIGN**

Previous research efforts by NIOSH investigators and other researchers have attempted to characterize asphalt fume exposures among road paving workers. Asphalt fume exposures have typically been

measured as total particulates and benzene soluble particulate fraction. Correspondingly, occupational exposure criteria for asphalt fume have been expressed in terms of total particulates and the benzene soluble fraction of the particulates. However, since neither of these exposure markers measure exposure to a distinct chemical component or even a distinct class of chemicals, it is difficult to relate them to possible health effects. For example, many organic compounds are soluble in benzene, and road dust will contribute to total particulate levels. In an effort to address this situation, new or modified sampling and analytical methods were developed and included in this study. For example, polycyclic aromatic compounds (PACs) which may be present in asphalt fume were measured using a new analytical method. Some of the PACs are believed to have irritative effects while other PACs are suspected to be carcinogenic. In addition to PACs, benzothiazole (a sulfur-containing compound present in rubber tires) along with other sulfur-containing compounds (suspected to be present as a result of the addition of rubber to the asphalt or from high sulfur crude petroleum used for asphalt manufacturing) were also measured. Benzothiazole is of interest since it may be useful as a surrogate indicator for other CRM asphalt fume exposures while other sulfur-containing compounds may be associated with respiratory irritation. Selected organic solvents (toluene, xylene, benzene, and methyl isobutyl ketone) and total hydrocarbons (as Stoddard solvent) were sampled for to evaluate the extent that solvents may be released during asphalt paving. Elemental carbon was measured to determine if diesel exhaust could have contributed to the air contaminants measured at the paving site. The airborne particulate at the paving site was analyzed to determine the fraction of particles which were respirable. Air samples were collected for 28 different metals and minerals and direct-reading instruments were used to measure carbon monoxide, hydrogen sulfide, sulfur dioxide, and ozone. Bulk air samples of asphalt fume were collected at the asphalt cement storage tank located at the hot mix asphalt plant and submitted for mutagenicity testing.

## Weather Information

Since weather can influence the air sampling results, meteorological conditions were recorded at regular intervals to allow comparative inferences between survey days. The meteorological data included dry bulb and wet bulb temperatures (for subsequent calculation of relative humidity), wind speed and direction, plus wet bulb globe temperature (WBGT). Wind speed and direction were measured with a Climatronics<sup>®</sup> cup anemometer equipped with a strip chart recorder. Environmental measurements were obtained at 15 minute intervals using a Reuter Stokes RSS 214 Wibget<sup>®</sup> heat stress meter.

## Process Information

Process information and operational details were recorded daily by FHWA, State Department of Transportation (DOT), contractors, or NIOSH investigators. This information included the asphalt grade, type of application, crude source, percent rubber, additives, production quantities, application temperature, paving depth, average application rate, site description, and traffic density.

## Area Air Samples

To evaluate worst-case conditions and characterize the asphalt fume, area air samples were collected above the screed auger of the paving vehicle and adjacent to the paver hopper. Background area air samples were collected in the highway median to evaluate the possible impact from vehicle emissions. Area samples were collected for total and respirable particulate, PACs, sulfur-containing compounds (including benzothiazole), benzene soluble fraction (BSF), aromatic and aliphatic compounds (based on the qualitative identification of volatile organic compounds via mass spectroscopy), elemental and organic carbon, and elemental metals. Direct reading instruments were used to measure carbon monoxide, hydrogen sulfide, sulfur dioxide, and ozone.

Except for the samples obtained with direct-reading

instruments, air samples were collected using calibrated battery-operated sampling pumps with the appropriate sorbent tube or filter media connected via Tygon® 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 so that the sampling data could be compared between days that had unequal monitoring durations. 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.

High volume air samples of the asphalt fume were collected above an open hatch on the asphalt cement storage tank at the HMA plant and are being evaluated at various concentrations for mutagenic activity via a modified Ames testing protocol. The basic analytical procedure has been described by Maron and Ames [1983], except a spiral plater device described by Houk et al. [1989, 1991] is used. The results from these modified Ames tests of asphalt fume will be discussed in a future NIOSH report.

## Personal Breathing-Zone Air Samples

Personal breathing-zone monitoring was conducted on paving crew workers who were in close proximity to the hot asphalt as it was applied, including the paver operator, screed operator, rakers, and laborers. Additionally, other members of the construction crew who had less potential for asphalt fume exposure were monitored, including the roller operators and the traffic control person. In total, nine workers were selected for personal monitoring each day during two consecutive days of conventional asphalt paving, and eight workers were monitored on the two consecutive days of CRM asphalt paving. Total particulate samples were collected on all paving crew workers. Air samples for total PACs, or selected polynuclear aromatic hydrocarbons (PAHs)

were also collected on some workers.

## Air Sampling Methods

Table 2 summarizes all of the air sampling methods used in this evaluation. Since sampling for PACs involved a new analytical technique, Appendix A is included to provide additional detail on this method. Appendix B is the draft NIOSH Sampling and Analytical Method No. 5040 for elemental carbon.

## MEDICAL EVALUATION DESIGN

On February 9, NIOSH investigators began recruiting workers to participate in the health assessment, which included a general health and occupational history questionnaire, serial acute symptom questionnaires, and serial peak expiratory flow rate (PEFR) testing. PEFR testing was conducted to evaluate acute changes in lung function. Peak flow refers to the amount of air in liters per minute that can be exhaled through the flow meter in one complete breath.

All ten pavers were asked to participate in the study. Seven pavers volunteered and were included in the health assessment. Additionally, seven workers (six workers performing jobs associated with road construction at another construction site and one worker performing traffic control duties at the paving site) not typically exposed to hot asphalt fume (non-pavers) were included in the health assessment for comparison.

A general health questionnaire was privately administered to each health assessment participant once during the study. Each worker was asked about the presence of chronic respiratory, eye, nose, throat, and skin symptoms. Information concerning smoking history and work history was also solicited.

During the work shift, acute symptom questionnaires were periodically administered to all study participants to determine if eye, nose, throat, skin, or

respiratory symptoms (including cough, chest tightness, or wheezing) were associated with their job tasks. Whenever possible, the acute symptom questionnaires were administered before and after each work shift and three times during the work shift, at approximately two-hour intervals during each survey day.

PEFR measurements were made using Wrights portable peak flow meters just prior to the administration of the acute symptom questionnaire. Three exhalations were recorded each time, and the highest of the three recordings 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.

## EVALUATION CRITERIA

To assess the hazards posed by workplace exposures, NIOSH investigators use a variety of environmental evaluation criteria. These criteria are exposure limits to which most workers may be exposed for a working lifetime without experiencing adverse health effects. However, because of the wide variation in individual susceptibility, some workers may experience occupational illness even if exposures are maintained below these limits. The evaluation criteria do not take into account individual sensitivity, preexisting medical conditions, medicines taken by the worker, possible interactions with other workplace agents, or environmental conditions.

The primary sources of evaluation criteria for the workplace are NIOSH criteria documents and recommended exposure limits (RELs) [NIOSH 1994], the Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) [OSHA 1993], and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs<sup>®</sup>) [ACGIH 1995]. These occupational health criteria are based on the available scientific information

provided by industrial experience, animal or human experiments, or epidemiologic studies. It should be noted that RELs and TLVs are guidelines, whereas PELs are legally enforceable standards. The NIOSH RELs are primarily based upon the prevention of occupational disease without assessing the economic feasibility of the affected industries and, as such, tend to be conservative. The OSHA PELs are required to take into account the technical and economical feasibility of controlling exposures in various industries where the agents are present. A Court of Appeals decision vacated the OSHA 1989 Air Contaminants Standard in *AFL-CIO v OSHA*, 965F.2d 962 (11th cir., 1992); and OSHA is now enforcing the previous standards (listed as Transitional Limits in 29 CFR 1910.1000, Table Z-1-A), which were originally promulgated in 1971. However, some states with OSHA-approved state plans continue to enforce the more protective ("final rule") limits promulgated in 1989. For exposures with evaluation criteria, NIOSH encourages employers to use the 1989 OSHA PEL or the NIOSH REL, whichever is lower.

Evaluation criteria for chemical substances are usually based on the average PBZ exposure to the airborne substance over an entire 8- to 10-hour workday, expressed as a time-weighted average (TWA). Exposures can be expressed in parts per million (ppm), milligrams per cubic meter ( $\text{mg}/\text{m}^3$ ), or micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ). To supplement the TWA where adverse effects from short-term exposures are recognized, some substances have a short-term exposure limit (STEL) for 15-minute periods; or a ceiling limit, which is not to be exceeded at any time. Additionally, some chemicals have a "skin" notation to indicate that the substance may be appreciably absorbed through direct contact of the material or its vapor with the skin and mucous membranes.

It is important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these occupational health exposure criteria. A small percentage may experience adverse health effects because of individual susceptibility, preexisting medical

conditions, previous exposures, or hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, or with medications or personal habits of the worker (such as smoking) to produce health effects even if the occupational exposures are controlled to the limit set by the evaluation criterion. These combined effects are often not considered by the chemical-specific evaluation criteria. Furthermore, many substances are appreciably absorbed by direct contact with the skin and thus potentially increase the overall exposure and biologic response beyond that expected from inhalation alone. Finally, evaluation criteria may change over time as new information on the toxic effects of an agent becomes available. Because of these reasons, it is prudent for an employer to maintain worker exposures well below established occupational health criteria.

## Asphalt Fumes (Petroleum)

Asphalt, produced from refining crude petroleum, is commercially valuable for pavement construction because of its adhesive properties, flexibility, durability, water and acid resistance, and its ability to form strong cohesive mixtures with mineral aggregates. Asphalt pavement is the major paving product in commercial use and accounts for 85% of the total asphalt usage (and over 90% of the roadway paving) in the United States [AI 1990]. About 4,000 HMA facilities and 7,000 paving contractors employ nearly 300,000 workers in the United States [AI 1990].

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 organics. The chemical composition and physical properties of the asphalt products are influenced by the original crude petroleum and the manufacturing processes. The basic chemical components of asphalt include paraffinic, naphthenic, cyclic, and aromatic hydrocarbons as well as heteroatomic molecules

containing sulfur, oxygen, and nitrogen [AI 1990].

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 raw material origin and manufacturing processes. Approximately 80% of the carbon in coal tar is associated with the aromatic ring structures, whereas less than 40% of the carbon in asphalt is present in aromatic rings [Puzinauskas 1978]. Furthermore, analysis by nuclear magnetic resonance indicated that an asphalt fume condensate was <1% aromatic and >99% aliphatic, whereas a coal tar pitch condensate was >90% aromatic [Niemeier et al. 1988]. Coal tar has a greater reported carcinogenic activity than asphalt and is considered an occupational carcinogen by NIOSH [1992] and ACGIH [1995].

In a 1977 criteria document, NIOSH established a REL of 5 mg/m<sup>3</sup> (as a 15-minute ceiling limit) for asphalt fumes, measured as a total particulate. This level was intended to protect against acute effects, including irritation of the serous membranes of the conjunctivae and the mucous membranes of the respiratory tract [NIOSH 1977a]. Asphalt fumes can be absorbed through the lungs or the skin. Hansen [1991] and Maizlish et al. [1988] indicated that nonmalignant lung diseases such as bronchitis, emphysema, and asthma were also among the toxic effects of exposure to asphalt fumes. Norseth et al. [1991] reported that during road repair and construction, three groups of asphalt workers experienced abnormal fatigue, reduced appetite, eye irritation, and laryngeal/pharyngeal irritation.

Since publication of the criteria document [NIOSH 1977a], 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 [NIOSH 1988]. This recommendation was based on information presented in the 1977 criteria document [NIOSH 1977a] and a study by Niemeier et al.

[1988] showing that exposure to condensates of asphalt fumes caused skin tumors in mice. Several epidemiologic studies concerning workers exposed to asphalt fumes have indicated a potential excess in mortality from cancer [Hansen 1989a,b, 1991; Maizlish et al. 1988; Engholm et al. 1991; Wilson 1984; Bender et al. 1989; Mommsen et al. 1983; Risch et al. 1988; Bonassi et al. 1989].

Currently there is no OSHA PEL for asphalt fume. In 1992, OSHA published a proposed rule for asphalt fumes that included a PEL of 5 mg/m<sup>3</sup> (total particulate) for general industry as well as for the maritime, construction, and agricultural industries [OSHA 1992]. OSHA is presently reviewing public comments. The current ACGIH TLV<sup>®</sup> for asphalt fumes is 5 mg/m<sup>3</sup> as an 8-hour TWA [ACGIH 1995]. This TLV was recommended to "maintain good housekeeping conditions and reduce the risk of possible carcinogenicity" [ACGIH 1992].

Table 3 summarizes the toxicity and exposure criteria information for asphalt fume and the other contaminants evaluated during this study, including total particulate, respirable particulate, benzene soluble particulate fraction, PACs, elemental carbon, and selected organic solvents.

## INDUSTRIAL HYGIENE RESULTS

### Weather

Table 4 summarizes the weather data recorded for each survey day. The high temperatures recorded for all four days ranged from 26° to 31°C (78° to 87°F), and the average temperatures ranged from 21° to 27°C (69° to 80°F).

Wind speed and direction were considered important factors that may influence the air sampling results. As shown in Table 4, the strongest winds were observed on February 11; the other three days were breezy. During the first three days the winds were out of the South-Southwest and on the last day the

winds were out of the East.

### Process Information

Table 1 summarizes the scope of the Florida Turnpike project. The most notable differences between conventional and CRM asphalt paving days were the amount of asphalt applied and the application temperature. On average, about 253 metric tons more CRM asphalt was laid per day, a factor that could influence asphalt fume exposures. Additionally, the average laydown temperature of the CRM asphalt was approximately 33°C (60°F) higher than the application temperature for conventional asphalt. Factors that remained the same for both conventional and CRM asphalt during all four paving days included the following: (1) back dump trucks were used to transport asphalt to the paving site; (2) asphalt was dumped directly into the paver hopper; (3) paving occurred in the right traffic lane; and (4) a 1/2 inch layer of friction course was laid down. The actual paving time for the two days of conventional asphalt paving ranged from approximately 5¾ to 6¾ hours, while the actual paving time on the two CRM asphalt paving days was approximately 6½ hours and 6 hours.

### Area Air Samples

#### *Total Particulate and Respirable Particulate*

Tables 5 and 6 present the results of area sampling for total and respirable particulate, respectively. Higher total particulate concentrations were measured during CRM asphalt paving than during conventional asphalt paving. The highest total particulate concentration, 5.0 mg/m<sup>3</sup>, was measured on the right side of the screed on the first day of CRM asphalt paving. A lower concentration (2.4 mg/m<sup>3</sup>) measured on the left side of the screed on this same day may be erroneous due to a sampling pump failure. All total particulate concentrations measured at locations other than at the screed were below 1 mg/m<sup>3</sup>.

The highest respirable particulate concentration (7.2 mg/m<sup>3</sup>) was measured over the left side of the screed on the first day of CRM asphalt paving. However, this reported concentration is likely erroneous since the concentration measured at a side-by-side total particulate sample was three times lower (2.4 mg/m<sup>3</sup>). Additionally, sampling pump failures occurred for both of these samples. The second highest respirable particulate concentration (3.8 mg/m<sup>3</sup> over the right side of the screed) was also measured on the first day of CRM asphalt paving. All respirable particulate concentrations measured at locations other than at the screed were either not detected or below 0.5 mg/m<sup>3</sup>.

### ***Benzene Soluble Particulate Fraction (BSF)***

As summarized in Table 7, the highest BSF concentrations (regardless of the hot mix asphalt composition) were measured over the screed. A trace concentration was measured at the highway background location the second day of conventional asphalt paving. BSF concentrations were not detected at the highway background location on the other three days. Trace concentrations were measured at the paver hopper and the screed during conventional asphalt paving compared with 0.34 to 5.1 mg/m<sup>3</sup> during the CRM asphalt paving.

### ***Polycyclic Aromatic Compounds (PACs), Sulfur-containing Compounds, and Benzothiazole***

A number of asphalt fume source samples from this study were analyzed by high pressure liquid chromatography (HPLC). The chromatograms obtained from these samples demonstrated the typical pattern associated with asphalt fume, which prevented quantitation. Hence, NIOSH method 5506 was modified to quantitate total PACs, as a class, via a flow injection technique with spectrofluorometric detection using emission wavelengths of 370 and 400 nanometers (nm). The 370 nm emission wavelength provides greater sensitivity to 2-3 ring

PACs and the 400 nm wavelength is more sensitive to 4-7 ring PACs.

Table 8 contains the results of area sampling for total PACs (both particulate and volatile [or semi-volatile]); and the benzothiazole and other sulfur compound concentrations obtained from hexane extracts of the PAC samples collected at the three asphalt fume emission locations and the highway background location. When compared to conventional asphalt, the CRM asphalt formulation generally produced greater PAC<sub>370</sub> concentrations, PAC<sub>400</sub> concentrations, total sulfur-containing compounds, and benzothiazole concentrations. The only exception was the sample collected at the left side of the screed on the second day of conventional asphalt paving. This sample had reported concentrations of PAC<sub>370</sub>, PAC<sub>400</sub>, and total other sulfur-containing compounds approximately 10 times greater than the other samples collected during conventional asphalt paving.

During both CRM and conventional asphalt paving, all samples collected had PAC<sub>370</sub> concentrations that were about 5-10 times greater than the PAC<sub>400</sub> concentrations. The smaller ring number PACs are believed to be associated with more irritative effects, whereas more concern exists for suspect carcinogenicity of the 4-7 ring size PACs. Occupational exposure criteria for total PACs, as a class, are presently unavailable from NIOSH, OSHA, or ACGIH. Specific quantitation of individual compounds is not possible for asphalt fume samples because of chromatographic interference.

During CRM asphalt paving days benzothiazole concentrations ranged from 3.3 to 20 µg/m<sup>3</sup> and were detected at the paver hopper and screed locations. Benzothiazole was not detected, however, at the highway background location during CRM asphalt paving or at any sample location on conventional asphalt paving days. The detected concentrations of benzothiazole were due to the vapor phase only; no particulate benzothiazole concentrations were detected.

Concentrations of sulfur compounds (not including benzothiazole) ranged from ND to 270  $\mu\text{g}/\text{m}^3$  at the paver hopper and screed sampling locations during CRM asphalt paving. With one exception, lower concentrations of sulfur compounds were measured during conventional asphalt paving. The exception was a concentration of 31  $\mu\text{g}/\text{m}^3$  which was measured at the left side of the screed on the second day of conventional asphalt paving; all remaining samples were not detected. Detected concentrations of sulfur compounds for samples collected at the screed were due to both the particulate and vapor phase, while all other samples with detected concentrations were due only to the vapor phase. Sulfur compounds were not detected at the highway background location on any of the four days of paving.

### ***Elemental (EC) and Organic Carbon (OC)***

Elemental and organic carbon analysis results are provided in Table 9. In general, a higher elemental carbon (EC) to total carbon (TC) ratio suggests that diesel engine exhaust may be contributing to other exposure measurements (such as the PAC results). The EC:TC ratio ranged from 0.02 to 0.47 near the hopper (which is adjacent to the paver engine), and from 0.006 to 0.47 above the two screed locations. Since diesel exhaust has been reported to contain EC levels between 0.6 to 0.8 of the TC [Blade 1989], these ratios imply that diesel exhaust was not excessively contributing to these air sampling results.

On all four sampling days the average EC:TC ratio above the two screed locations was lower than the ET:TC ratio for the hopper samples, suggesting that diesel exhaust may be contributing less to the screed samples than the hopper samples. Organic carbon was not detected on any of the highway background samples and elemental carbon was detected only the first day of conventional asphalt paving, so an EC:TC ratio can not be calculated and is not applicable for the highway background location.

### ***(VOCs) and Elements***

## ***Volatile Organic Compounds***

Table 10 lists all of the vapor concentrations for air contaminants collected during both the conventional asphalt and CRM asphalt paving days. The most significant peaks identified by the qualitative GC/MS analysis were benzene, toluene, xylene, methyl isobutyl ketone (MIBK), and total other hydrocarbons resembling a Stoddard solvent chromatogram pattern. Benzene was detected on the first CRM asphalt paving day (0.08 ppm at the left side of the screed and a trace concentration at the right side of the screed). While these benzene concentrations do not represent personal exposures, they do suggest the potential for employee exposures. NIOSH considers benzene to be an occupational carcinogen and recommends that occupational exposures be reduced to the lowest feasible level. The OSHA PEL for benzene is 1 ppm as an 8-hour TWA concentration. The remaining VOCs were either not detected or were orders of magnitudes below the occupational exposure criteria published by NIOSH, OSHA, or ACGIH.

Extremely low or trace concentrations were observed for aluminum, barium, calcium, iron, magnesium, manganese, silver, sodium, and zinc. All other elemental metals were not detected.

### ***Hydrogen Sulfide (H<sub>2</sub>S), Sulfur Dioxide (SO<sub>2</sub>), Carbon Monoxide (CO), and Ozone***

The highest CO concentration detected, 6 ppm, is well below the applicable occupational exposure criteria. The remainder of these compounds were all not detected.

## ***Personal Breathing-Zone Air Samples***

Table 11 presents the PBZ monitoring results for total particulates during conventional and CRM asphalt paving activities. The PBZ exposures to total



particulate during conventional asphalt paving ranged from ND to 0.16 mg/m<sup>3</sup>, and from ND to 1.0 mg/m<sup>3</sup> during CRM asphalt paving. The highest exposures recorded were obtained on the first day of CRM asphalt paving; the screed operator had an exposure concentration of 1.0 mg/m<sup>3</sup> and one of the laborers working near the screed had an exposure concentration of 0.59 mg/m<sup>3</sup>. The next highest concentrations were recorded on the second day of CRM asphalt paving; the shoulder roller operator had an exposure concentration of 0.45 mg/m<sup>3</sup> and the paver operator had an exposure concentration of 0.36 mg/m<sup>3</sup>.

Table 12 presents the results of PBZ air sampling for PACs. Two or three samples were collected per day for total PACs and sulfur compounds. The PAC<sub>370</sub> and PAC<sub>400</sub> concentrations for the screed operator were higher during CRM asphalt paving days than during conventional asphalt paving. The PAC<sub>370</sub> results for the screed operator were 1.8 µg/m<sup>3</sup> and 0.67 µg/m<sup>3</sup> on the first and second day of conventional asphalt paving, compared to 54 µg/m<sup>3</sup> and 18 µg/m<sup>3</sup> on the first and second day of CRM asphalt paving, respectively. The PAC<sub>400</sub> results for the screed operator showed a similar pattern, 0.29 µg/m<sup>3</sup> and 0.09 µg/m<sup>3</sup> on the first and second day of conventional asphalt paving, compared to 9.6 µg/m<sup>3</sup> and 2.7 µg/m<sup>3</sup> on the first and second day of CRM asphalt paving, respectively. PBZ exposures to benzothiazole and other sulfur-containing compounds were also higher for the screed operator during CRM asphalt paving compared to conventional asphalt paving.

## MEDICAL RESULTS

The seven pavers included in the health assessment were one paver operator, two screed operators, one roller operator, two rakers, and one assistant paving foreman. Three pavers (roller operator, raker, assistant foreman) were excluded from analysis of the medical data due to ongoing flu-like illness during the survey period. The remaining four pavers participated in the study for all four days. The seven non-pavers who were part of the health assessment

included two crew foreman, three heavy equipment operators, one laborer who worked at a different worksite than the pavers, and a traffic controller who worked at the same worksite as the pavers. Three non-pavers were excluded from analysis of the medical data; one worker was excluded due to illness (foreman) and two workers were excluded (two heavy equipment operators) due to insufficient survey participation (i.e., absent for half of the survey days and did not complete the general health questionnaire). Three of the remaining non-pavers participated in the study for all four days and one crew foreman was absent on the third day.

All results below pertain only to the four pavers and four non-pavers for whom data were analyzed. All four of the non-pavers were male and the average age of this group was 39 years (range 27-51 years). Three of the four pavers were male and the average age of the group was 38 years (range 35-40 years). Three of the non-pavers currently smoked cigarettes (all smoked during work) and one non-paver was a former smoker. All of the pavers currently smoked cigarettes (three smoked during work) although one did so infrequently.

The number of acute symptom questionnaires completed (i.e., the number of opportunities a worker had to report a health symptom) varied somewhat between survey days and among the non-pavers and pavers (Table 13). For each survey day, a maximum of 20 (four workers times five questionnaires/day) questionnaires could have been completed for each group (pavers and non-pavers). The non-pavers completed 33 questionnaires on the first and second study days (conventional asphalt paving period) and 34 on the third and fourth study days (CRM asphalt paving period). The pavers completed 35 questionnaires during the conventional asphalt paving period as compared to 39 questionnaires during the CRM asphalt paving period.

Responses to the acute health questionnaires were evaluated for symptoms potentially associated with worker tasks and exposures. A worker could report seven different types of symptoms during each survey time (including eye, nose, throat, and skin

irritation, cough, shortness of breath, and wheezing); each such symptom report will be referred to as a “symptom occurrence.” Thus, if a worker completed all five daily acute health questionnaires and reported all seven symptoms during each survey, they would have 35 symptom occurrences for that survey day.

Among non-pavers, 26 symptom occurrences were reported over the survey period. The number decreased markedly from 24 during the conventional asphalt paving period to 2 during the CRM asphalt paving period. Among pavers, 29 symptom occurrences were reported during the survey period. The number decreased from 17 during the conventional asphalt paving period to 12 during the CRM asphalt paving period. Seventy-six percent (22/29) of the symptoms among pavers were reported during ongoing or recent exposure to the asphalt paving operation. Ninety-three percent (27/29) of the symptoms reported by the pavers were rated as “mild” in severity (the choices were “mild,” “moderate,” or “severe”).

Among non-pavers, the most frequently reported symptoms (as a percentage of occurrences over all four days) were cough (58%), eye irritation (15%), nasal irritation (15%), and throat irritation (12%). Among pavers, the most frequently reported symptoms (as a percentage of occurrences over all four days) were shortness of breath (55%), throat irritation (14%), nasal irritation (10%), and wheezing (10%). There was no appreciable differences between the conventional and CRM asphalt paving periods in the types of symptoms reported.

Because of differences in the number of completed questionnaires, the number of symptom occurrences may not be the best measure for comparing health effects between exposure groups, and between conventional and CRM asphalt paving exposures. A more useful measure is the *rate* of symptom occurrences per completed questionnaire (defined as the *number of symptom occurrences* divided by the *number of completed questionnaires*). The rates of reported symptom occurrences per completed questionnaire among non-pavers and pavers for the

survey period and by period of exposure are presented in Table 14. Symptom reporting rates among non-pavers were approximately 1200% higher during the conventional paving period compared to the CRM paving period. Whereas, symptom reporting rates among pavers were approximately 60% higher during the conventional paving period compared to the CRM paving period.

The number of hours the road crew performed paving operations, and thus, were potentially exposed to asphalt fumes, varied between survey days and across jobs. Each paver estimated his or her own exposure time to the paving operation (typically in 15-minute increments) and this information was collected with each acute symptom questionnaire. Table 15 shows each pavers’ estimated exposure time to asphalt paving for each survey day. The average estimated hours of exposure to asphalt paving moderately increased over the survey period. Workers had a combined average of 5.5 hours of paving operation exposure/day during the conventional asphalt paving period compared to a combined average exposure of 6.2 hours/day during the CRM asphalt paving period. None of the non-pavers reported any exposure to asphalt paving during the survey period.

The *rate* of reported symptom occurrences per hour of estimated exposure to asphalt fume (defined as the *number of symptom occurrences* divided by the *number of hours of estimated exposure*) was calculated for the pavers for each survey day (Table 16). The rate of symptom occurrences per hour of exposure among pavers was approximately 60% higher during the conventional asphalt paving period (0.39 symptom occurrences per hour of exposure) as compared to the CRM asphalt paving period (0.24 symptom occurrences per hour of exposure).

Study participants occasionally reported symptoms of cough, shortness of breath, and wheezing during the survey period. However, the PEFr measurements did not reveal any workers with significant bronchial lability (i.e., difference between a day’s minimum and maximum PEFr exceeding

20% of that day's maximum PEFR) on any survey day.

## DISCUSSION

### Weather

Although there were many inconsistent factors that could affect results, some descriptive observations are presented. The wind can impact the air samples collected near the paver hopper more than those collected above the screed auger (the paver hopper was more open and emissions were more prone to effects from wind and other weather conditions than at the more sheltered screed area). Therefore, the screed sample results may be more useful for comparison between days with variable wind speed and (relative) direction.

### Process Information

The most significant differences between conventional and CRM asphalt paving on the Florida Turnpike asphalt paving construction project were the number of tons of asphalt laid and the lay-down temperature. On average, more CRM asphalt was applied (approximately 253 metric tons more per day) than conventional asphalt, and the average application temperature during CRM asphalt paving was approximately 33°C higher than during conventional asphalt paving. Both projects required the placement of a 1.6 centimeter 'FC-2' open graded friction course, both mixes were of the same aggregate gradation, the granulated rubber was supplied by the same manufacture, and the aggregate sources and blend percentages were held constant for the production of both the conventional and CRM mixes.

### Air Sampling

Air sampling concentrations for total and respirable particulates, BSF, PACs (370, 400, total sulfur compounds and benzothiozole), and VOCs were generally greater during CRM asphalt paving

compared to conventional asphalt paving. With the exception of one area sample for total particulate and one benzene concentration measured at the screed on the first day of CRM asphalt paving, most compounds detected during both CRM asphalt paving and conventional asphalt paving were below any existing occupational exposure criteria. However, occupational exposure criteria are presently unavailable for several groups of compounds (such as total PACs) present in asphalt fume.

No PBZ samples exceeded the current NIOSH REL for asphalt fume of 5 mg/m<sup>3</sup> (measured as total particulate). One area sample collected at the right side of the screed during the first day of CRM asphalt paving equaled the NIOSH REL (the corresponding respirable particulate concentration at this location was 3.8 mg/m<sup>3</sup>). A lower total particulate concentration (2.4 mg/m<sup>3</sup>) measured on the left side of the screed on this same day may be erroneous due to a sampling pump failure. All other area and PBZ samples for total particulate were below 5 mg/m<sup>3</sup>.

A benzene concentration of 0.08 ppm was measured in the area sample collected above the left side of the screed on the first day of CRM asphalt paving; a trace concentration was measured on the right side. Benzene was not detected on any other day of sampling. While the benzene concentrations measured over the screed were not personal exposures, they do suggest the potential for employee exposures. NIOSH considers benzene to be an occupational carcinogen and recommends that occupational exposures be reduced to the lowest feasible concentration. The OSHA PEL for benzene is 1 ppm for an 8-hour TWA.

NIOSH investigators assumed that comparison of the paver operator and screed operator total particulate PBZ exposure concentrations between days would be the most pertinent in regards to asphalt fume. The total particulate PBZ exposure concentrations for the paver and screed operators showed a pattern similar to the area sample concentrations collected above the screed [i.e., the exposures during CRM asphalt

paving were higher (0.15 to 1.0 mg/m<sup>3</sup>) than during the conventional asphalt paving (0.03 to 0.1 mg/m<sup>3</sup>). On conventional asphalt paving days total particulate PBZ concentrations for the paver operator and the screed operator were essentially the same as for those employees not working on the paver (such as the raker and screed laborer). However, during CRM paving days PBZ total particulate exposure concentrations were slightly higher for these employees. Naturally, the jobs that cause the worker to be in closer proximity to hot asphalt for prolonged durations have greater exposure potential to asphalt fume and are less likely influenced by general dust. In this regard, the paver and screed operators' PBZ exposure probably represents the highest asphalt fume exposure.

Table 17 summarizes the results obtained from the area air samples, arranged by location. Although there were many inconsistent factors that could affect results, the following descriptive observations are presented.

- P Total particulate, respirable particulate, and BSF area concentrations were higher during CRM asphalt paving.
- P Two detector emission wavelengths were used to provide greater sensitivity either to 2-3 ring PACs (370 nanometers [nm]) or to 4+ ring PACs (400 nm). Greater PAC concentrations were detected using the 370 nm wavelength, implying that the 2-3 ring PACs may be more abundant.
- P Total PAC concentrations above the screed were higher on CRM asphalt paving days than on conventional paving days. Furthermore, the CRM asphalt paving generated more benzothiazole and other sulfur containing compounds than the conventional paving.
- P VOCs concentrations above were generally greater during CRM asphalt paving days compared to conventional asphalt paving days.

## Medical

The results of the acute symptom survey revealed no appreciable difference in the *number* of reported symptoms or *rate* of symptom occurrences per completed questionnaire between pavers and non-pavers. Additionally, the rate of symptom occurrences per completed questionnaire among both pavers and non-pavers was lower during the conventional asphalt paving period than during the CRM asphalt paving period.

Evaluation of acute symptoms in combination with peak flow testing was performed to determine whether acute irritant effects of the airways (as measured by symptom reporting) were associated with intermittent or reversible bronchospastic responses. While acute irritant symptoms, including lower airway symptoms, were reported by a number of workers in association with worksite exposures, none of the reported symptoms were accompanied by significant bronchial lability. The inability to detect an association, if truly present, between reported symptoms or exposures and PEFr results at this study site may be due to the small number of workers tested and/or variability between worker exposures and individual responses to those exposures. Also, the two-hour PEFr testing interval may not be of sufficient frequency to detect intermittently occurring transient bronchospastic effects.

## CONCLUSIONS

Results presented here only apply to this survey and cannot be generalized to indicate the exposures or health effects associated with conventional or CRM asphalt paving. This study showed higher asphalt fume emissions at source locations, with generally higher area air sample concentrations of total particulate, respirable particulate, benzene soluble particulate, total PACs, benzothiazole, and other sulfur-containing compounds detected during the CRM asphalt paving period. However, all of the PBZ exposures measured in this survey (regardless of the composition of the asphalt) were below the current NIOSH REL for asphalt fume (measured as total particulate).

Findings from the medical assessment suggest that pavers were not experiencing symptoms or bronchial lability associated with either the conventional or CRM asphalt paving operations. It is premature to draw any definitive conclusions from this single site evaluation. Data provided from this evaluation are based on a very small sample size and may reflect production and weather conditions specific to this site. Additional site evaluations may enable more definitive conclusions to be drawn.

## RECOMMENDATIONS

The following recommendations are based on observations made during the survey and are intended to help ensure the safety and health of paving crew workers. These recommendations stem from our present understanding of the workers' occupational exposures and potential health effects associated with these exposures.

1. To minimize asphalt fume generation, the hot mix should be applied at the lowest temperature possible that can maintain quality control specifications.
2. To avoid contamination and possible ingestion of potentially harmful substances, workers should be

prohibited from consuming food and beverages and from using tobacco products in close proximity to asphalt fume emissions.

3. Workers should be provided with adequate washing facilities for use prior to eating and leaving the worksite.

4. To reduce potential contamination of workers' cars and homes, workers should be encouraged to change clothing prior to leaving the worksite and should be provided with adequate facilities for changing.

5. All workers should wear protective clothing or appropriate sunscreen to shield exposed skin surfaces from the harmful ultraviolet component of sunlight.

6. During this evaluation workers were observed performing a number of job tasks which could potentially lead to musculoskeletal injury. Employees performing manual lifting and shoveling should be taught appropriate lifting techniques and be provided with the appropriate equipment to minimize musculoskeletal strain.

## ABBREVIATIONS AND TERMS

ACGIH	American Conference of Governmental Industrial Hygienists	IH	Industrial hygiene
BSF	Benzene soluble (particulate) fraction	ISTEA	Intermodal Surface Transportation Efficiency Act
C	Ceiling, an exposure that shall not be exceeded during any part of the workday	LC	Liquid chromatography
CFR	Code of Federal Regulations	LOD	Limit of detection (analytical method)
cm <sup>2</sup>	Square centimeters	LOQ	Limit of quantitation (analytical method)
CO	Carbon monoxide	Lpm	Liters per minute
Control	A person working in road construction but not exposed to hot asphalt fume.	MCE	Mixed cellulose-ester filter
CRM	Crumb rubber modifier	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.
DOT	Department of Transportation	mg	Milligrams
EC	Elemental carbon	mg/m <sup>3</sup>	Milligrams per cubic meter of air
EPA	Environmental Protection Agency	MIBK	Methyl isobutyl ketone
FHWA	Federal Highway Administration	mL	Milliliter
FID	Flame ionization detector	mm	Millimeter
GC-MS	Gas chromatography-Mass Spectrometry	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.
H <sub>2</sub> S	Hydrogen sulfide	ND	Not detected
HHE	Health hazard evaluation	NIOSH	National Institute for Occupational Safety and Health
HMA	Hot mix asphalt		
IARC	International Agency for Research on Cancer		
ICP-AES	Inductively coupled (argon) plasma-atomic emission spectroscopy		

nm	Nanometer	TLV®	Threshold limit value (ACGIH exposure criteria)
OC	Organic carbon	TWA	Time-weighted average
OSHA	U.S. Occupational Safety and Health Administration	VOCs	Volatile organic compounds
PAC <sub>370</sub>	PACs monitored at an emission wavelength of 370 nanometers (representative of 2-ring and 3-ring compounds)	WBGT	Wet bulb globe temperature
PAC <sub>400</sub>	PACs monitored at an emission wavelength of 400 nanometers (representative of 4-ring and higher compounds)	°C & °F	Degrees Celsius and Degrees Fahrenheit
PACs	Polycyclic aromatic compounds	µg	Microgram (10 <sup>-6</sup> ), a unit of weight
PAHs	Polynuclear aromatic hydrocarbons	µg/m <sup>3</sup>	Micrograms of contaminant per cubic meter of air (a unit of concentration)
PBZ	Personal breathing-zone air sample		
PEFR	Peak expiratory flow rate		
PEL	Permissible exposure limit (OSHA)		
ppm	Parts (of a contaminant) per million parts of air		
REL	Recommended exposure limit (NIOSH exposure criteria)		
RP	Respirable particulate		
SCLD	Sulfur chemiluminescent detector		
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)		

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# APPENDIX A

## MODIFIED ANALYTICAL METHOD FOR POLYCYCLIC AROMATIC COMPOUNDS

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 PAC compounds 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 polycyclic aromatic compounds (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 43 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 was 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.

# APPENDIX B

## ELEMENTAL CARBON (DIESEL EXHAUST)

5040

C

MW: 12.01

CAS: none

RTECS: none

<b>METHOD:</b> 5040, Issue 1		<b>EVALUATION:</b> PARTIAL		<b>Issue 1:</b> 15 March 1996	
<b>OSHA :</b> <b>NIOSH:</b> see APPENDIX A <b>ACGIH:</b>		<b>PROPERTIES:</b> nonvolatile solid; MP >350 °C			
<b>SYNONYMS (related terms):</b> soot, black carbon, diesel emissions, diesel exhaust particles, diesel particulate matter					
<b>SAMPLING</b>			<b>MEASUREMENT</b>		
<b>SAMPLER:</b> FILTER (quartz fiber, 37-mm; size-selective impactor may be required, see INTERFERENCES)			<b>TECHNIQUE:</b> EVOLVED GAS ANALYSIS (EGA) by thermal-optical analyzer		
<b>FLOW RATE:</b> 1 to 4 L/min			<b>ANALYTE:</b> elemental carbon (EC)		
<b>VOL-MIN:</b> 106 L @ 40 µg/m <sup>3</sup> <b>-MAX:</b> 4300 L (for filter load ~ 20 µg/cm <sup>2</sup> )			<b>FILTER PUNCH SIZE:</b> 1.54 cm <sup>2</sup>		
<b>SHIPMENT:</b> routine			<b>CALIBRATION:</b> methane injection [1]		
<b>SAMPLE STABILITY:</b> stable			<b>RANGE:</b> 0.76 to 54 µg per filter portion		
<b>BLANKS:</b> 2 to 10 field blanks per set			<b>ESTIMATED LOD:</b> 0.2 µg per filter portion		
<b>ACCURACY</b>			<b>PRECISION (S<sub>r</sub>):</b> 0.10 @ 1 µg C, 0.01 @ 10 - 72 µg C		
<b>RANGE STUDIED:</b> 4.0 mg/m <sup>3</sup> (60-L sample) [1]					
<b>BIAS:</b> none [1]					
<b>OVERALL PRECISION (S<sub>r</sub>):</b> see EVALUATION OF METHOD					
<b>ACCURACY:</b> see EVALUATION OF METHOD					
<b>APPLICABILITY:</b> The working range is 4.4 to 312 µg/m <sup>3</sup> with an LOD of ~1.3 µg/m <sup>3</sup> for a 960-L air sample collected on a 37-mm filter with a 1.54 cm <sup>2</sup> punch from the sample filter. If a lower LOD is desired, a larger sample volume and 25-mm filter may be used (e.g., a 1920-L sample on 25-mm filter gives an LOD of 0.3 µg/m <sup>3</sup> ) [1]. The split between organic-based carbon (OC) and EC may be affected at higher EC loadings (e.g., >30 µg/cm <sup>2</sup> of filter), depending on type and amount of OC present. If pyrolysis correction is not required, an upper limit of ~800 µg/m <sup>3</sup> (90 µg/cm <sup>2</sup> ) can be determined, but post-analysis designation of OC-EC split may be necessary [1].					
<b>INTERFERENCES:</b> As defined by the thermal-optical method, EC is the carbon determined during the second stage of the analysis (after pyrolytic correction). If the sample contains no pyrolyzable material, all the carbon evolved during this stage is considered elemental. Carbonate and cigarette smoke do not interfere. Various EC sources (diesel engines, carbon black, coal dust, and humic acid) may be present [1]. For measurement of diesel-source EC in coal mines, an impactor with submicrometer cutpoint [2,3] must be used to minimize collection of coal dust.					
<b>OTHER METHODS:</b> Other methods for determination of EC and OC are described in the literature [4].					

**REAGENTS:**

1. Aqueous organic carbon solutions (e.g., sucrose), 0.10 to 2.4 mg C per mL solution.
2. Helium, prepurified.
3. Hydrogen, purified.
4. Oxygen (10%) in helium, premixed, purified.
5. Methane (5%) in helium, premixed, purified.

**EQUIPMENT:**

1. Sampler: Quartz fiber filter, precleaned (clean in low temperature ashers 2 to 3 h, or muffle furnace at ~ 800 °C), 37-mm, in a 3-piece, 37-mm cassette with support pad (stainless steel or cellulose).
2. Personal sampling pump, 1 to 4 L/min, with flexible tubing.
3. Thermal-optical analyzer, or other analyzer capable of EC speciation (see APPENDIX B).
4. Punch (e.g., cork borer) for removal of filter sample portion.  
NOTE: Portion  $\geq 0.5 \text{ cm}^2$  with diameter or width of  $\leq 1 \text{ cm}$  is recommended.
5. Syringe, 10- $\mu\text{L}$

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**SPECIAL PRECAUTIONS:** None

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**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.  
NOTE: Sampler should be used in open-face configuration.
2. Attach sampler outlet to personal sampling pump with flexible tubing. Remove top piece of cassette.
3. Sample at an accurately known flow rate between 1 and 4 L/min.
4. After sampling, replace top piece of cassette and pack securely for shipment to laboratory.  
NOTE: If the EC in the sample is more difficult to oxidize (e.g., graphite) than typical black carbon (e.g., soot), notify the laboratory of this fact.

**SAMPLE PREPARATION:**

5. Use punch to cut out a representative portion of the sample filter for analysis. Take care not to disturb deposited material and avoid hand contact with sample.

**CALIBRATION AND QUALITY CONTROL:**

6. Perform  $\text{CH}_4$  calibration injection at end of each sample analysis.
7. If a particular sample filter deposit appears uneven, take a duplicate portion (step 5) for analysis to check evenness of deposition. Analyze at least one duplicate and others as required to replicate 10% of the samples for sets of up to 50 samples and 5% of the samples over 50.  
NOTE: Precision in duplicate analyses of a filter is usually better than 2%.
8. Analyze three quality control blind spikes and three analyst spikes to ensure that instrument calibration is in control. Prepare spike as follows:
  - a. Using a microliter syringe, apply known volume of OC standard solution directly onto portion taken (step 5) from a precleaned blank filter.
  - b. Allow  $\text{H}_2\text{O}$  to evaporate and analyze with samples and blanks (steps 10 and 11).
9. Determine instrument blank (results of analysis with no sample present) for each sample set.

## MEASUREMENT:

10. Set analyzer according to manufacturer's recommendations (see APPENDIX B). Place sample portion into sample oven.

NOTE: Forms of carbon that are difficult to oxidize (e.g., graphite) may require increased analysis time to ensure that all EC in the sample is quantified.

11. Determine EC (and OC) mass,  $\mu\text{g}$ , as provided by analyzer and divide by sample punch area,  $\text{cm}^2$ , to report result in terms of  $\mu\text{g C per cm}^2$  of filter.

## CALCULATIONS:

12. Multiply the reported EC value by filter deposit area,  $\text{cm}^2$ , (typically  $8.55 \text{ cm}^2$  for a 37-mm filter) to calculate total mass,  $\mu\text{g}$ , of EC on each sample ( $W_{\text{EC}}$ ). Do the same for the blanks and calculate the mass found in the average field blank ( $W_{\text{b}}$ ). (OC masses may be calculated similarly.)
13. Calculate EC concentration ( $C_{\text{EC}}$ ) in the air volume sampled,  $V$  (L):

$$C_{\text{EC}} = \frac{W_{\text{EC}} - W_{\text{b}}}{V}, \text{ mg/m}^3$$

## EVALUATION OF METHOD:

Currently, a suitable EC standard reference material is not available for verification of the accuracy of the method in the determination of EC. For this reason, only the accuracy of the method in the analysis of various OC standards and carbonaceous dusts for total carbon could be examined [1]. A commercial instrument was used for method evaluation [5]. No discernable differences in the responses of five different compounds were noted. Linear regression of the data for all five compounds gave a slope and correlation coefficient near unity [ $m = 0.99 (\pm 0.01)$ ,  $r^2 = 0.999$ ,  $n = 43$ ]. Based on results for individual compounds, reported carbon values are expected to be from 98 to 100% of the actual amount present. In addition, results (total carbon) of analysis of different carbonaceous materials were in good agreement with those reported by two other independent laboratories. These findings indicate that instrumental response appears to be compound- and matrix-independent (i.e., carbon is accurately quantified irrespective of compound and matrix type). Such a response is required for accurate carbon determination.

To calculate the estimated LOD of the method (i.e.,  $\approx 0.24 \mu\text{g C}$  or  $0.15 \mu\text{g C/cm}^2$ ), ethylenediaminetetraacetic acid (EDTA) calibration standards covering a range from 0.23 to  $2.82 \mu\text{g C}$  (or from  $0.15$  to  $1.83 \mu\text{g C per cm}^2$  of filter) were analyzed. Results of linear regression of the low-level calibration data (i.e.,  $\mu\text{g C}$  reported vs. actual) were then used to calculate the LOD as  $3 \sigma_y/m$  (where  $\sigma_y$  is the standard error of the regression and  $m$  is the slope of the regression line). The calculated LOD shows good agreement with that estimated as  $\text{LOD} = (\text{blank} + 3\sigma_{\text{blank}})$ , which gives a value of  $\approx 0.22 \mu\text{g C}$ . The mean ( $n = 40$ ) instrumental blank was  $\approx .02 (\pm 0.07) \mu\text{g C}$ .

Because the split between EC and OC is method-dependent [1,4], and no suitable EC standard exists for assessment of a particular method's accuracy, various methods can be compared on a relative basis only. At present, the thermal-optical method is considered unbiased (i.e., it is the reference method), and the overall precision reflects the method accuracy. The  $S_r$  of the mean EC concentration ( $4 \text{ mg/m}^3$ ) found using fourteen samplers (two each of seven types) for collection of diesel exhaust was 5.6%. Although pumps were used for sample collection, a 5% pump error was added in the calculation of the overall precision of the method because of the relatively small sample taken (0.5 h, 60 L). Based on the 95% confidence limit (19%; 13 degrees of freedom,  $n = 14$ ) on the accuracy, results of this experiment indicate that the NIOSH accuracy criterion [6] is fulfilled. The amount of EC collected ( $240 \mu\text{g per sample}$ ) would be equivalent to sampling an EC level of  $250 \mu\text{g/m}^3$  for 8 h at 2 L/min.

The thermal-optical method is applicable to nonvolatile, carbon-containing species only. The method is not appropriate for volatile or semivolatiles, which require sorbents for efficient collection. A complete discussion on the evaluation of this method for monitoring occupational exposures to particulate diesel exhaust in general industry can be found in the literature [1]. Application of the method for monitoring exposures to diesel particulate matter in the mining industry may require use of a size-selective sampling strategy in some

situations [11]. In coal mines, a specialized impactor [2,3] with a sub- $\mu\text{m}$  cutpoint is required to minimize the contribution of coal-source EC [2].

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#### METHOD WRITTEN BY:

M. Eileen Birch, Ph.D., NIOSH/DPSE.

#### APPENDIX A.

Diesel exhaust has been classified by IARC as a probable human carcinogen [8]. NIOSH has recommended "...that whole diesel exhaust be regarded as a potential occupational carcinogen..." and that workers' exposures be reduced [9,10]. The American Conference of Governmental Hygienists (ACGIH) has proposed a TWA of  $0.15 \text{ mg/m}^3$  for diesel particulate (see Notice of Intended Changes for 1995-1996) [12]. The TLV applies to submicrometer particulate matter, which includes the solid carbon particle core and particulate-adsorbed components. A submicrometer size fraction was selected so that interference of other larger dusts is minimized. If other submicrometer particulate (e.g., cigarette smoke, fumes, oil mists) is present, it will interfere in the gravimetric determination of diesel particulate.

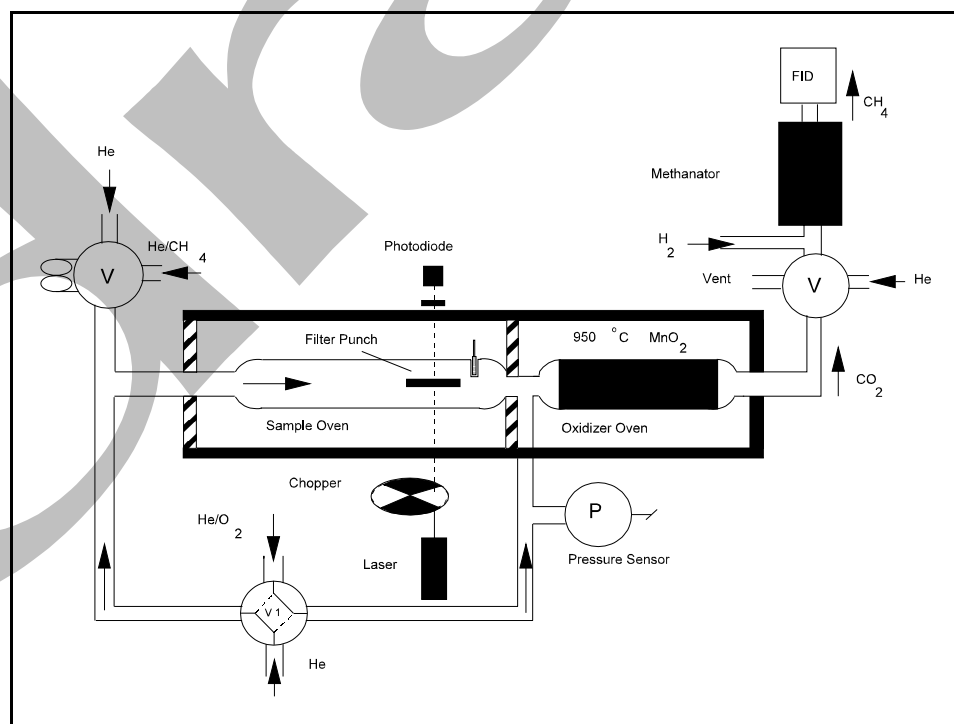
#### APPENDIX B. THERMAL-OPTICAL ANALYZER DESIGN AND OPERATION:



In the thermal-optical analysis of carbonaceous aerosols, speciation of various carbon types (organic, carbonate, and elemental) is accomplished through temperature and atmosphere control, and by continuous monitoring of filter transmittance. A schematic of the instrument is given below. The instrument is a modified version of a design previously described in the literature [11]. An optical feature corrects for pyrolytically generated elemental carbon (EC), or "char," which is formed during the analysis of some materials (e.g., cigarette smoke, pollen). He-Ne laser light passed through the filter allows continuous monitoring of filter transmittance. Because temperatures in excess of 850°C are employed during the analysis, quartz-fiber filters are required for sample collection. A punch from the sample filter is taken for analysis, and organic carbon (OC) and elemental carbon are reported in terms of  $\mu\text{g}/\text{cm}^2$  of filter area. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area. In this approach, a homogeneous sample deposit is assumed. At the end of the analysis (after the EC is evolved), calibration is achieved through injection of a known volume of methane into the sample oven.

Thermal-optical analysis proceeds essentially in two stages. In the first, organic and carbonate carbon (if present) are evolved in an inert helium atmosphere as the temperature is raised (stepped) to about 850°C. Evolved carbon is catalytically oxidized to  $\text{CO}_2$  in a bed of granular  $\text{MnO}_2$  (at 950°C),  $\text{CO}_2$  is reduced to  $\text{CH}_4$  in a Ni/firebrick methanator (at 450°C), and  $\text{CH}_4$  is quantified by an FID. In the second stage of the analysis, the oven temperature is reduced, an oxygen-helium mix (2%  $\text{O}_2$  in He) is introduced into the sample oven, and the oven temperature is again raised to about 850°C. As oxygen enters the oven, pyrolytically generated EC is oxidized and a concurrent increase in filter transmittance occurs. The point at which the filter transmittance reaches its initial value is defined as the "split" between EC and OC. Carbon evolved prior to the split is considered OC (or carbonate), and carbon volatilized after the split (excluding that from the  $\text{CH}_4$  standard) is considered elemental. The presence of carbonate can be verified through analysis of a second portion (punch) of the filter after its exposure to HCl vapor. In the second analysis, the absence of the suspect peak is indicative of carbonate carbon in the original sample.

Currently, only one commercial laboratory (Sunset Laboratory) performs thermal-optical analyses. To support the new method, a collaborative effort between NIOSH researchers and the instrument's developer is underway. During 1996, a thermal-optical instrument will be constructed and evaluated. This effort will assist in the transfer of this technology to other interested parties.



**Figure 1.** Schematic of Thermal-Optical Analyzer.



**Table 2**  
**Summary of Sampling and Analytical Methods**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Substance	Flow Rate (Lpm)	Sample Media	Analytical Method	Comments
<b>Total Particulate</b>	2.0	Tared PVC filter (37 mm diameter, 0.8µm pore size)	NIOSH Method No. 0500, Gravimetric analysis	Both personal breathing-zone and area samples collected
<b>Respirable Particulate</b>	1.7	Tared PVC filter (37 mm diameter, 0.8µm pore size)	NIOSH Method No. 0600, Gravimetric analysis	Dorr-Oliver nylon cyclone used as particle size selector
<b>Polycyclic Aromatic Compounds (PACs) and Sulfur Compounds</b>	2.0	Zefluor filter (37 mm diameter, 2µm pore size), followed by an ORBO 43 sorbent tube <i>(Note: an ORBO 42 sorbent tube was used in subsequent evaluations to reduce the pressure drop and pump failures.)</i>	NIOSH 5506, modified to quantitate 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. This method may be found in Appendix A.	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. A detailed description of this method may be found in Appendix A.
<b>Benzene Soluble Particulate</b>	2.0	Glass fiber filter (37 mm diameter)	OSHA Method No. 58. The filters were rinsed with benzene, the leachate collected and evaporated, and the residue weighed to report the <i>benzene soluble fraction</i> . Organic compounds are generally soluble in benzene, whereas inorganic compounds are not benzene soluble. This method has been applied as an indirect measure of exposure to polynuclear aromatic hydrocarbons (PAHs) to evaluate a variety of exposure matrices including asphalt fume.	Because the method is nonspecific, the results are not necessarily due to PAH compounds. This method was used since it has been reported in many asphalt investigations and will also allow comparison of the conventional and CRM asphalt paving operations.
<b>Elemental/Organic Carbon</b>	2.0	Quartz-fiber filters (37 mm diameter, open face)	A rectangular punch (1.54 cm <sup>2</sup> ) is taken from the quartz filter for a three stage thermal-optical analysis.	A draft copy of NIOSH Method 5040 is provided as Appendix B.
<b>Metals</b>	2.5	Mixed cellulose ester (MCE) membrane filters (37 mm diameter)	NIOSH Method No. 7300. The samples were wet-ashed with concentrated nitric and perchloric acids. The residues were dissolved in a dilute solution of the same acids and the resulting solutions were analyzed for metals and minerals via Inductively Coupled Argon Plasma, Atomic Emission Spectroscopy (ICP-AES).	Analyses included silver, aluminum, arsenic, barium, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, lithium, magnesium, manganese, molybdenum, sodium, nickel, phosphorous, lead, platinum, selenium, tellurium, thallium, titanium, vanadium, yttrium, zinc, and zirconium.
<b>Qualitative Volatile Organic Compound (VOC) Screen</b>	0.02	Thermal desorption tubes	Samples analyzed using the Tekmar thermal desorber interfaced directly to a gas chromatograph and a mass spectrometry detector (GC/MS).	Each thermal desorption (TD) tube contains three 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.

**Table 2**  
**Summary of Sampling and Analytical Methods**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Substance	Flow Rate (Lpm)	Sample Media	Analytical Method	Comments
<b>Quantitative Analysis for Selected Solvents</b>	0.2	Activated charcoal sorbent tubes (100 milligram front section/50 milligram back section)	Currently existing NIOSH methods were merged and modified (i.e. NIOSH Methods 1300 and 1301 for ketones, 1501 for aromatic hydrocarbons, and 1550 for petroleum distillates.) The activated charcoal was desorbed with carbon disulfide; an aliquot of this solution was analyzed using GC-FID.	Specific VOCs that were quantified included benzene, toluene, MIBK, and petroleum distillates (other hydrocarbons with retention times greater than toluene).
<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. 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 measurements were made throughout the work day around the paving site.
<b>Mutagenic Potential</b>	≈ 10	Zefluor filter (37 mm diameter)	Mutagenic activity evaluated via a modified Ames testing protocol. The basic analytical procedure used has been described by Maron and Ames except it was to be conducted using a spiral plater device as described by Houk et al. ( <u>Environ. Mol. Mut.</u> 1991, <u>17</u> , 112-121; and <u>Mut. Res.</u> 1989, <u>223</u> , 49-64).	Area samples were collected in the plume over an open port of a heated asphalt cement storage tank at the hot mix plant. The results of this modified Ames testing will be discussed in a separate NIOSH report.

The following are abbreviations which were not spelled out in the table.

PVC = Polyvinyl chloride sampling filter  
mm = millimeter  
µm = micrometer  
GC-FID = Gas chromatography-flame ionization detector  
H<sub>2</sub>S = Hydrogen sulfide  
HPLC = High pressure liquid chromatography

SO<sub>2</sub> = Sulfur dioxide  
CO = Carbon monoxide  
lpm = Liters per minute  
MIBK = Methyl isobutyl ketone  
Zefluor = Teflon® sampling filter  
nm = Nanometer

**Table 3**  
**Toxicity and Exposure Criteria Information**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Compound	Toxicity Review	Exposure Criteria
<b>Asphalt Fume</b>  <b>(As Total Particulate)</b>	<p>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. Current occupational exposure criteria from NIOSH and ACGIH for asphalt fume are expressed as total particulate. Asphalt fume has also been measured as the benzene soluble particulate fraction (BSF), a surrogate of exposure to polynuclear aromatic hydrocarbons (PAHs, see discussion below). Asphalt consists primarily of polycyclic aromatic compounds (PACs), many of which are soluble in benzene. These substances are of concern due to their irritancy and cancer-causing potential.</p>	<p>The NIOSH REL is 5 mg/m<sup>3</sup> for a 15-minute ceiling exposure.</p> <p>There is no current OSHA PEL for asphalt fume.</p> <p>The ACGIH TLV® is 5 mg/m<sup>3</sup> as an 8-hour TWA.</p>
<b>Respirable Particulate</b>	<p>In contrast to total particulate, 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.</p> <p>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], benzene solubles, and selected solvents) should be considered together when determining the degree of hazard.</p>	<p>No NIOSH REL</p> <p>The OSHA PEL is 5 mg/m<sup>3</sup>, 8-hour TWA.</p> <p>The ACGIH TLV® for particulates not otherwise classified is 10 mg/m<sup>3</sup> for inhalable particulate and 3 mg/m<sup>3</sup> for respirable particulate. Both are 8-hour TWAs.</p>
<b>Benzene Soluble Particulate</b>	<p>The benzene soluble particulate fraction (BSF) 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.</p> <p>Historically, the BSF 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. However, this method is non-specific and the BSF results are not necessarily due to polycyclic aromatic compounds (PACs) or polynuclear aromatic hydrocarbons (PAHs).</p>	<p>None established for BSF associated with asphalt fume</p>
<b>Polynuclear Aromatic Hydrocarbons</b>  <b>and</b>  <b>Polycyclic Aromatic Compounds</b>	<p>Analysis for unsubstituted PAHs has been applied to evaluate asphalt fume exposure. However, this approach provides limited information because asphalt fume contains numerous alkylated PACs that coelute, causing chromatographic interference, which prevents quantitation of specific compounds.</p> <p>Polycyclic aromatic compounds refer to a set of cyclic organic compounds that includes PAHs and also includes compounds that may 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 [Lunsford et al. 1989]. PAHs have received considerable attention since some have been shown to be carcinogenic in experimental animals.</p> <p>NIOSH investigators have hypothesized that PACs with 2 to 3 rings (referred to in this report as PAC<sub>370</sub>) are associated with more irritative effects, while the 4 to 7 ring PACs (termed PAC<sub>400</sub>) may have more carcinogenic and/or mutagenic effects. It is not currently possible to definitively distinguish between these two PAC groups analytically; however, using two different spectrofluorometric detector wavelengths (370 nanometer [nm] and 400 nm) allows the detector to be more sensitive to PACs based on ring number. A more complete discussion of the NIOSH analytical method for PACs may be found in Appendix A.</p>	<p>None established for PAHs and PACs as a class.</p>
<b>Benzothiazole</b>	<p>In its pure form, benzothiazole is a yellow liquid with an unpleasant odor [Sax 1987]. It is used as a rubber vulcanization accelerator [ILO 1971], as an antimicrobial agent [ITO 1978], and in dyes [Kirk-Othmer 1978]. Benzothiazole was identified in the air during rubber vulcanization [Rappaport 1977]. 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.</p>	<p>None established</p>

**Table 3  
Toxicity and Exposure Criteria Information  
Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Compound	Toxicity Review	Exposure Criteria
<b>Other Sulfur-Containing Compounds</b>	The addition of tire rubber may increase sulfur compounds in asphalt. In this report "other sulfur-containing compounds" 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 by NIOSH investigators that some of them may cause respiratory irritation.	None established
<b>Organic and Elemental Carbon</b>	<p>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 be used to specifically differentiate carbon sources (i.e., asphalt fume, diesel exhaust, cigarette smoke).</p> <p>There are no occupational exposure criteria for either elemental or organic carbon. This method was employed previously in several NIOSH trucking industry studies [Zaebst et al. 1991, Blade 1989]. A copy of the draft NIOSH Method 5040 is provided in Appendix B.</p>	None established
<b>MIBK</b>	Tire rubber may be a source for methyl isobutyl ketone (MIBK) since this organic compound can be used as an antioxidant in the tire manufacturing process. In its pure form, MIBK is a colorless, flammable organic solvent that is typically used as a solvent in the surface coating and synthetic resin industries [ACGIH 1992]. This solvent is absorbed primarily through inhalation and causes irritation of the eyes, mucous membranes, and skin [Proctor 1989]. At air concentrations much higher than were measured in this asphalt study, MIBK has caused central nervous system depression [Proctor 1989]. Continued or prolonged skin contact with the liquid can cause dermatitis [Proctor 1989].	<p>The NIOSH REL and ACGIH TLV are 50 ppm, 8-hour TWA; and 75 ppm, 15 minute STEL.</p> <p>OSHA PEL is 100 ppm for an 8-hour TWA.</p>
<b>Benzene</b>	Acute benzene 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 [ACGIH 1992]. NIOSH classifies benzene as a human carcinogen [NIOSH 1992]. *Note: ACGIH has proposed to lower its TLV® for benzene to 0.3 ppm with a skin notation (indicating that skin exposure contributes to the overall absorbed inhalation dose and potential effects), and classify it as a proven human carcinogen [ACGIH 1995].	<p>NIOSH REL is to reduce exposures to the lowest feasible level.</p> <p>OSHA PEL is 1 ppm for an 8-hour TWA.</p> <p>ACGIH TLV is 10 ppm* for an 8-hour TWA.</p>
<b>Toluene</b>	Toluene can cause acute irritation of the eyes, respiratory tract, and skin. Since it is a defatting solvent, repeated or prolonged skin contact will remove the natural lipids from the skin which can cause drying, fissuring, and dermatitis [Proctor 1989, NIOSH 1973]. 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) [WHO 1981]. No symptoms were noted below 100 ppm in other studies [Bruckner 1981a,b]. The ACGIH TLV® carries a skin notation, indicating that skin exposure contributes to the overall absorbed inhalation dose and potential effects [ACGIH 1995].	<p>NIOSH REL is 100 ppm, 8-hour TWA (15-minute STEL of 150 ppm).</p> <p>OSHA PEL is 200 ppm, 8-hour TWA; 300 ppm for a ceiling limit (not to be exceeded at any time).</p> <p>ACGIH TLV is 50 ppm, 8-hour TWA (skin).</p>
<b>Xylene</b>	Structurally similar to toluene, xylene can also cause acute irritation of the eyes, respiratory tract, and skin [Proctor 1989]. 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 [Proctor 1989].	<p>NIOSH REL is 100 ppm, 8-hour TWA.</p> <p>OSHA PEL is 100 ppm, 8-hour TWA.</p> <p>ACGIH TLV is 100 ppm for an 8-hour TWA and 150 ppm for a 15-minute STEL</p>

**Table 3**  
**Toxicity and Exposure Criteria Information**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Compound	Toxicity Review	Exposure Criteria
<p align="center"><b>Total Hydrocarbons</b> <b>(as Stoddard Solvent)</b></p>	<p>In this study, total hydrocarbons (HC) refer to Stoddard solvent, a petroleum distillate mixture. Effects from exposure to Stoddard solvent are primarily acute, unless significant amounts of substances that have chronic toxicity are present, such as benzene or glycol ethers. 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 [NIOSH 1977b]. The evaluation criteria are based upon the similarity of the mixture composition in relation to the most commonly available products (in this case Stoddard solvent).</p>	<p>NIOSH REL is 350 mg/m<sup>3</sup>, 10-hour TWA (for all petroleum distillate mixtures, including Stoddard solvent). The a NIOSH ceiling limit is 1800 mg/m<sup>3</sup>, 15 minutes.</p> <p>OSHA PEL for Stoddard solvent is 2,900 mg/m<sup>3</sup>, 8-hour TWA.</p> <p>ACGIH TLV for Stoddard solvent is 525 mg/m<sup>3</sup>, 8-hour TWA</p>

**Abbreviations:**

REL = Recommended Exposure Limit (NIOSH)  
 TLV = Threshold Limit Value (ACGIH)  
 STEL = Short-term exposure limit  
 μm = micrometers

PEL = Permissible Exposure Limit (OSHA)  
 TWA = Time-weighted average  
 ppm = parts per million  
 mg/m<sup>3</sup> = milligrams per cubic meter

**Table 4**  
**Environmental Conditions**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Description	2/10/95 Conventional	2/11/95 Conventional	2/13/95 Crumb Rubber	2/14/95 Crumb Rubber
Summary	Windy, Clear	Windy, Clear	Windy, Overcast	Windy, Clear
Minimum Temp.	†	17°C (62°F)	16°C (60°F)	22°C (72°F)
Maximum Temp.	24°C (76°F)†	31°C (87°F)	28°C (83°F)	26°C (78°F)
Average Temp.	†	27°C (80°F)	21°C (69°F)	24°C (75°F)
Average Humidity	†	55%	76%	66%
Minimum WBGT <sup>1</sup>	†	62°F	58°F	68°F
Maximum WBGT	†	79°F	80°F	73°F
Wind Speed	Breezy	Windy	Breezy	Breezy
Wind Direction	S-SW	S-SW	S-SW	E
Traffic Density	Moderate	Moderate	Moderate	Moderate
<p>1 WBGT = Wet bulb globe temperature, a heat stress index.  † WBGT instrument did not work this day, no data available; one temperature reading recorded with Vaisala Model HM 34 battery powered, direct reading meter.</p> <p>Other Comments:</p> <p>Conventional = Non-rubber hot mix asphalt  Crumb Rubber = Crumb rubber modified hot mix asphalt</p>				



**Table 5**  
**Total Particulate Concentrations: Area Samples**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m <sup>3</sup> )
Conventional Asphalt 2/10/95	Paver Hopper	376	752	ND (<0.03)
	Screed (Right)	389	778	0.18
	Screed (Left)	401	800	0.13
	Highway Background	391	782	ND (<0.03)
Conventional Asphalt 2/11/95	Paver Hopper	527	1053	0.18
	Screed (Right)	528	1056	0.45
	Screed (Left)	516	1034	0.38
	Highway Background	561	1123	0.04
Crumb Rubber Asphalt 2/13/95	Paver Hopper	397	793	0.44
	Screed (Right)	149 <sup>PF</sup>	298	5.0 <sup>‡</sup>
	Screed (Left)	31 <sup>PF</sup>	62	2.4 <sup>P</sup>
	Highway Background	515	1029	0.04
Crumb Rubber Asphalt 2/14/95	Paver Hopper	427	855	0.50
	Screed (Right)	421	844	0.52
	Screed (Left)	420	841	1.7
	Highway Background	502	1008	0.03

Comments:  
mg/m<sup>3</sup> = Concentration, expressed in milligrams per cubic meter  
<sup>‡</sup> = Exceeds occupational criteria for asphalt fume  
<sup>P</sup> = Since the total particulate concentration for this sample is less than the corresponding side-by-side respirable particulate sample concentration, this value should be considered suspect. The total particulate concentration for this sample may have been influenced by the shorter sampling time (and lower sample volume) due to unexpected sample pump failure.  
<sup>PF</sup> = Pump faulted and was restarted at least once during the sample period.  
ND = Not Detected (below the Minimum Detectable Concentration)  
( ) = The value(s) which are 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.

**Table 6**  
**Respirable Particulate Concentrations: Area Samples**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m <sup>3</sup> )
Conventional Asphalt 2/10/95	Paver Hopper	376	640	0.14†
	Screed (Right)	389	686	0.22†
	Screed (Left)	401	682	ND (<0.03)
	Highway Background	378	678	ND (<0.03)
Conventional Asphalt 2/11/95	Paver Hopper	503 <sup>PF</sup>	859	0.16
	Screed (Right)	528	898	0.09
	Screed (Left)	516	877	0.21
	Highway Background	561	956	ND (<0.02)
Crumb Rubber Asphalt 2/13/95	Paver Hopper	397	674	0.14
	Screed (Right)	261 <sup>PF</sup>	444	3.8
	Screed (Left)	198 <sup>PF</sup>	358	7.2†
	Highway Background	515	877	ND (<0.02)
Crumb Rubber Asphalt 2/14/95	Paver Hopper	427	727	0.29
	Screed (Right)	421	714	0.33
	Screed (Left)	420 <sup>PF</sup>	712	1.5
	Highway Background	502	851	ND (<0.02)
Comments: mg/m <sup>3</sup> = Concentration, expressed in milligrams per cubic meter. † = Concentration is suspect since the respirable reported exceeds the total particulate concentration measured in a side-by-side sample (please see Table 5). PF = Pump faulted and was restarted at least once during sample period. ND = Not Detected (below the Minimum Detectable Concentration). ( ) = The value(s) which are 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.				

**Table 7**  
**Benzene Soluble Particulate Concentrations: Area Samples**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m <sup>3</sup> )
Conventional Asphalt 2/10/95	Paver Hopper	376	752	Trace
	Screed (Right)	389	778	Trace
	Screed (left)	401	802	Trace
	Highway Background	391	782	ND (<0.08)
Conventional Asphalt 2/11/95	Paver Hopper	527	1054	Trace
	Screed (Right)	528	1056	Trace
	Screed (left)	516	1032	Trace
	Highway Background	561	1122	Trace
Crumb Rubber Asphalt 2/13/95	Paver Hopper	397	797	1.2
	Screed (Right)	388	778	5.1
	Screed (left)	396	795	3.4
	Highway Background	515	1031	ND (<0.06)
Crumb Rubber Asphalt 2/14/95	Paver Hopper	427	855	0.53
	Screed (Right)	421	840	0.34
	Screed (left)	420	838	2.1
	Highway Background	502	1004	ND (<0.06)
Comments: mg/m <sup>3</sup> = Concentration, expressed in milligrams per cubic meter ND = Not Detected (below the Minimum Detectable Concentration) ( ) = The value(s) which are 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.				

**Table 8**  
**Polycyclic Aromatic Compounds (PACs) Concentrations: Area Samples**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration, micrograms per cubic meter			
				PACs @ 370 nm	PACs @ 400 nm	Total OSCs	Benzothiazole
Conventional Asphalt 2/10/95	Paver Hopper	†	†	†	†	†	†
	Screed (Right)	389	780	2.6	0.41	ND (<0.4)	ND (<0.4)
	Screed (Left)	401	805	3.1	0.42	ND (<0.4)	ND (<0.4)
	Highway Background	391	782	0.18	Trace	ND (<0.4)	ND (<0.4)
Conventional Asphalt 2/11/95	Paver Hopper	527	1053	3.3	0.41	ND (<0.3)	ND (<0.3)
	Screed (Right)	86 <sup>PF</sup>	172	2.1	0.33	ND (<1.7)	ND (<1.7)
	Screed (Left)	390 <sup>PF</sup>	781	32	4.1	31	ND (<0.3)
	Highway Background	561	1124	1.6	Trace	ND (<0.3)	ND (<0.3)
Crumb Rubber Asphalt 2/13/95	Paver Hopper	397	796	28	4.1	11	3.9
	Screed (Right)	245 <sup>PF</sup>	489	384	73	198	20
	Screed (Left)	396	791	182	30	270	7.5
	Highway Background	515	1030	0.07	ND (<0.02)	ND (<0.3)	ND (<0.3)
Crumb Rubber Asphalt 2/14/95	Paver Hopper	107	214	23	2.5	9.4	5.6
	Screed (Right)	421	844	66	11	59	11
	Screed (Left)	196	392	33	5.6	ND (<0.8)	3.3
	Highway Background	502	1006	0.082	ND (<0.02)	ND (<0.3)	ND (<0.3)

370 nm = 370 nanometers, including both vapor and particulate phase  
400 nm = 400 nanometers, including both vapor and particulate phase  
OSCs = Other Sulfur-containing Compounds  
Trace = Concentration is between the Minimum Detectable and Minimum Quantifiable Concentrations  
ND = Not Detected (below the Minimum Detectable Concentration)  
( ) = The value(s) which are 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.  
† = No data available for this sample location, pump failed within one minute.  
PF = Pump faulted and was restarted at least once during the sample period.

Other Comments:

Air samples were collected using 37 millimeter Zefluor® filters followed by an ORBO 43 sorbent tube.

**Table 9**  
**Elemental Carbon Concentrations: Area Samples**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration, micrograms per cubic meter			EC/TC
				Organic Carbon (OC)	Elemental Carbon (EC)	Total Carbon (TC)	
Conventional Asphalt 2/10/95	Paver Hopper	376	728	62	54	116	0.47
	Screed (Right)	389	756	95	84	179	0.47
	Screed (Left)	401	802	84	65	149	0.44
	Highway Background	391	760	ND (<2.3)	Trace	NA	NA
Conventional Asphalt 2/11/95	Paver Hopper	525 <sup>PF</sup>	1050	77	36	113	0.32
	Screed (Right)	528	1056	213	68	281	0.24
	Screed (Left)	516	1030	200	49	249	0.20
	Highway Background	561	1119	ND (<1.5)	ND (<1.7)	NA	NA
Crumb Rubber Asphalt 2/13/95	Paver Hopper	188 <sup>†</sup>	376	234	Trace	NA	NA
	Screed (Right)	185 <sup>†</sup>	371	3125	Trace	NA	NA
	Screed (Left)	206 <sup>†</sup>	412	4134	27	4160	0.006
	Highway Background	515	1030	ND (<1.7)	ND (<1.7)	NA	NA
Crumb Rubber Asphalt 2/14/95	Paver Hopper	427	853	302	34	336	0.10
	Screed (Right)	421	843	624	11	636	0.02
	Screed (Left)	420	840	1584	38	1621	0.02
	Highway Background	502	1006	ND (<1.7)	ND (<1.7)	NA	NA

Comments:

- EC/TC = Ratio of Elemental Carbon to Total Carbon
- NA = Not applicable, since one or both analytes were not detected
- 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.
- † = Morning samples lost in hopper and screed, replaced at 1:50 p.m.
- PF = Pump faulted at least once during the sample period.

**Table 10**  
**Concentrations of Selected Volatile Organic Compounds (VOCs): Area Samples**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration, expressed in parts per million				Concentration, expressed in mg/m <sup>3</sup>	
				Benzene	Toluene	Xylene	MIBK	Total HC< Toluene <sup>†</sup>	Total HC > Toluene <sup>‡</sup>
Conventional Paving 2/10/95	Paver Hopper	376	71	ND	ND	ND	ND	0.21	2.8
	Screed (Right)	389	71	ND	ND	ND	ND	0.31	2.1
	Screed (Left)	401	77	ND	ND	ND	ND	0.19	2.5
	Highway Background	391	78	ND	ND	ND	ND	0.23	ND
Conventional Paving 2/11/95	Paver Hopper	527	106	ND	ND	Trace	ND	0.13	2.3
	Screed (Right)	528	106	ND	ND	Trace	ND	0.13	4.9
	Screed (Left)	516	103	ND	ND	Trace	ND	0.16	8.2
	Highway Background	561	113	ND	ND	ND	ND	Trace	ND
Crumb Rubber Paving 2/13/95	Paver Hopper	397	79	ND	ND	Trace	ND	0.18	2.7
	Screed (Right)	388	76	Trace	Trace	0.01	Trace	0.81	26
	Screed (Left)	397	76	0.08	Trace	0.02	ND	0.99	38
	Highway Background	515	102	ND	ND	ND	ND	ND (<0.03)	ND
Crumb Rubber Paving 2/14/95	Paver Hopper	427	85	ND	ND	Trace	ND	0.21	6.4
	Screed (Right)	421	84	ND	ND	ND	ND	Trace	8.2
	Screed (Left)	420	83	ND	ND	0.08	ND	0.34	15
	Highway Background	502	99	ND	ND	ND	ND	ND (<0.3)	ND

mg/m<sup>3</sup> = Concentration, expressed in milligrams per cubic meter

<sup>†</sup> = Total hydrocarbons with a gas chromatograph retention time less than (<) toluene. These concentrations are expressed in milligrams per cubic meter (mg/m<sup>3</sup>).

<sup>‡</sup> = Total hydrocarbons with a gas chromatograph retention time greater than (>) toluene. These concentrations are expressed in milligrams per cubic meter (mg/m<sup>3</sup>).

MIBK = Methyl isobutyl ketone

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

ND = Not Detected (below the Minimum Detectable Concentration)



**Table 11**  
**Total Particulate Concentrations: Personal Breathing Zone Samples**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Sampling Date	Activity	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m <sup>3</sup> )
<b>Conventional Asphalt</b>  <b>2/10/95</b>	Paver Operator	513	1028	0.05
	Screed Operator	511 <sup>PT</sup>	1024	0.08
	Screed Operator Trainee	351	702	0.10
	Raker	397	797	0.05
	Laborer (screed)	436	872	0.09
	Laborer (screed)	402 <sup>PT</sup>	806	0.10
	Front Roller Operator	405 <sup>PF</sup>	788	0.05
	Shoulder Roller Operator	223 <sup>a,b</sup>	446	ND (<0.05)
	Traffic Control	315 <sup>a</sup>	630	0.06
<b>Conventional Asphalt</b>  <b>2/11/95<sup>WS</sup></b>	Paver Operator	584	1101	0.03
	Screed Operator	483	965	0.08
	Screed Operator Trainee	620	1238	0.07
	Raker	341 <sup>PF</sup>	681	0.14
	Laborer (screed)	578 <sup>PT</sup>	1159	0.16
	Laborer (screed)	317 <sup>PF</sup>	634	0.11
	Laborer (screed)	560	1119	0.13
	Front Roller Operator	604	1212	0.05
	Traffic Control	361 <sup>b</sup>	722	0.09

**Comments:**

mg/m<sup>3</sup> = Concentration, expressed in milligrams per cubic meter

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.

PF = Pump faulted and was restarted at least once during the sample period.

PT = Pump turned off during periods when no paving was being performed (i.e., lunch and/or work break).

a = worker started later than the other crew members.

b = worker left paving site earlier than other crew members.

WS = all pumps turned off for approximately one hour (except traffic control), because of work stoppage with intent to switch to rubber asphalt.



**Table 11 (Continued)**  
**Total Particulate Concentrations: Personal Breathing-Zone Samples**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Sampling Date	Activity	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m <sup>3</sup> )
<b>Crumb Rubber Asphalt</b>  2/13/95	Paver Operator	437 <sup>PT</sup>	875	0.17
	Screed Operator	436 <sup>PT</sup>	874	1.0
	Raker	275 <sup>a,b</sup>	552	0.12
	Laborer (screed)	435 <sup>PT</sup>	871	0.12
	Laborer (screed)	338 <sup>a,PF,PT</sup>	675	0.19
	Laborer (screed)	404 <sup>PT</sup>	807	0.59
	Front Roller Operator	442 <sup>PT</sup>	885	ND (<0.02)
	Traffic Control	607	1216	0.14
<b>Crumb Rubber Asphalt</b>  2/14/95 <sup>WS</sup>	Paver Operator	143 <sup>†</sup>	296	0.36
	Screed Operator	390	783	0.24
	Screed Operator-Right	377	757	0.15
	Raker	381 <sup>c</sup>	761	0.02
	Laborer (screed)	373	746	0.25
	Front Roller Operator	392 <sup>PF</sup>	783	0.12
	Shoulder Roller Operator	195 <sup>PF</sup>	391	0.45
	Traffic Control	574	1151	0.15
Comments: mg/m <sup>3</sup> = Concentration, expressed in milligrams per cubic meter 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. † = Employee declined to continue wearing sampling pump after equipment was repaired. PF = Pump faulted and was restarted at least once during the sample period. PT = Pump turned off during periods when no paving was being performed (i.e., lunch and/or work break). a = worker started later than the other crew members. b = worker left paving site earlier than other crew members. c = worker left paving site for approximately 25 minutes (with pump running) and then returned. WS = all pumps turned off for approximately one hour (except traffic control), because of work stoppage due to damaged equipment.				

**Table 12**  
**Concentrations of Polycyclic Aromatic Compounds (PACs): Personal Breathing Zone Samples**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Sampling Date	Job	Sampling Time (minutes)	Sample Volume (Liters)	Concentration, micrograms per cubic meter			
				PACs @ 370 nm	PACs @ 400 nm	Other SulCom	Benzothiazole
Conventional Asphalt 2/10/95	Screed Operator Trainee	352	704	3.4	0.36	ND (<0.4)	ND (<0.4)
	Screed Operator	439	881	1.8	0.29	ND (<0.3)	ND (<0.3)
Conventional Asphalt 2/11/95	Raker	341	682	1.1	0.17	12	ND (<0.4)
	Screed Operator Trainee	359	720	1.1	0.16	ND (<0.4)	ND (<0.4)
	Screed Operator	526	1052	0.67	0.09	Trace	ND (<0.3)
Crumb Rubber Asphalt 2/13/95	Screed - laborer	405	810	16	2.9	16	7.0
	Screed Operator	188	376	54	9.6	85	17
Crumb Rubber Asphalt 2/14/95	Screed Operator	389	779	18	2.7	3.0	ND (<0.4)
	Shoulder Roller Operator	314	627	0.67	0.15	ND (<0.5)	ND (<0.5)

370 nm = 370 nanometers, including both vapor and particulate phase  
400 nm = 400 nanometers, including both vapor and particulate phase  
SulCom = Other sulfur-containing compounds  
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.  
PF = Pump faulted and was restarted at least once during the sample period.

Other Comments:

Air samples were collected using 37 millimeter Zefluor® filters followed by an ORBO 43 sorbent tube.

**Table 13**  
**Number of Acute Symptom Questionnaires Completed by Workers**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Work Group		Acute Questionnaires Completed			
		Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Rubber Asphalt	Day 4 CRM Rubber Asphalt
Pavers (n = 4)		15/20	20/20	20/20	19/20
Non-pavers (n = 4)		17/20	16/20	15/15	19/20
Paving Period Totals	Pavers	35/40		39/40	
	Non-pavers	33/40		34/35	
‡ = Number of completed questionnaires/potential number of questionnaires					

**Table 14**  
**Rate of Symptoms Occurrence Per Questionnaire Among Pavers and Non-pavers by Survey Day**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Symptoms	Work groups (Pavers = 4) (Non-pavers = 4)	Rate of Symptoms Occurrence Per Questionnaire			
		Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Rubber Asphalt	Day 4 CRM Rubber Asphalt
Completed Questionnaires	Pavers	15	20	20	19
	Non-pavers	17	16	15	19
Symptom Occurrences	Pavers	9	8	6	6
	Non-pavers	14	10	2	0
Symptom occurrence rate per questionnaire	Pavers	0.49		0.31	
	Non-pavers	0.73		0.06	

**Table 15**  
**Estimated Hours of Exposure to Asphalt Fume Among Pavers by Job Title and Survey Day**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Job Title (n=4)	Estimated hours exposure to asphalt fume			
	Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Rubber Asphalt	Day 4 CRM Rubber Asphalt
Paver Operator	5.75	5.75	6.5	6.5
Screedman	6.0	5.75	6.75	4.75
Screedman	4.25	5.5	6.5	6.0
Raker	6	4.75	6.25	6.0
Daily Total Hours (Average)	22	21.75	26	23.25
Total Hours by Asphalt Paving Material (Average)	43.75		49.25	

**Table 16**  
**Rate of Symptoms Per Hour of Exposure Among Pavers by Survey Day**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

Pavers (n=7)	Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Rubber Asphalt	Day 4 CRM Rubber Asphalt
Estimated Exposure to Asphalt (total hours)	22	21.75	26	23.25
Number Symptom Occurrences	9	8	6	6
Rate (symptom occurrence/hr exposure)	0.41	0.37	0.23	0.26
	0.39		0.24	

**Table 17**  
**Summary of Area Concentrations of Air Contaminants**  
**Paving Site: Martin Paving Company, Yeehaw Junction, Florida (HETA 95-0118)**

	Analyte	TWA Concentration, expressed in micrograms per cubic meter							
		2/10/95 Conventional	2/11/95 Conventional	2/13/95 Crumb Rubber	2/14/95 Crumb Rubber				
<b>Paver Hopper</b>	Total Particulate	ND	180	440	500				
	Respirable Particulate	140†	160	140	290				
	Benzene Soluble Particulate Fraction	Trace	Trace	1190	530				
	PAC <sub>S370</sub> (vapor & particulate)	‡	3.3	28	23				
	PAC <sub>S400</sub> (vapor & particulate)	‡	0.41	4.1	2.5				
	Benzothiazole	‡	ND	3.9	5.6				
	Other Sulfur Compounds	‡	ND	11	9.4				
	Total Hydrocarbons with a retention time < toluene	210	130	180	210				
Total Hydrocarbons with a retention time > toluene	2800	2300	2700	6400					
<b>Air Sample Position at Screenshot →</b>		Left	Right	Left	Right	Left	Right	Left	Right
<b>Paver Screed</b>	Total Particulate	130	180	380	450	2380	5030	1710	520
	Respirable Particulate	ND	220†	210	90	7240†	3830	1480	330
	Benzene Soluble Particulate Fraction	110	120	220	180	3460	5160	2090	370
	PAC <sub>S370</sub> (vapor & particulate)	3.1	2.6	32	2.1	182	384	33	66
	PAC <sub>S400</sub> (vapor & particulate)	0.42	0.41	4.1	0.33	30	73	5.6	11
	Benzothiazole	ND	ND	ND	ND	7.5	20	3.3	11
	Other Sulfur Compounds	ND	ND	31	ND	270	198	ND	59
	Total Hydrocarbons with a retention time < toluene	190	310	160	130	990	810	340	Trace
Total Hydrocarbons with a retention time > toluene	2500	2100	8200	4900	38000	26000	15000	8200	
<b>Highway Backgnd.</b>	Total Particulate	ND	40	40	30				
	Respirable Particulate	ND	ND	ND	ND				

PAC<sub>370</sub> = Polycyclic aromatic compound measured with 370 nanometer wavelength detector  
PAC<sub>400</sub> = Polycyclic aromatic compound measured with 400 nanometer wavelength detector  
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.  
Note = Highway background concentrations for benzene soluble fraction, PAC370 and PAC400 are not reported in this summary table. Please refer to the previous tables for these concentrations.  
Trace = Concentration in between the Minimum Detectable and Minimum Quantifiable concentrations.