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16. ABSTRACT

In recent years, warm mix asphalt (WMA) technologies have been used to modify asphalt binders, with the aims of decreasing production and construction temperatures, reducing fumes and emissions, retaining the properties of the mix during long haul distances, and improving workability. Reduced production temperatures at the plant and during paving and compaction are believed to reduce emissions from the asphalt. The objective of this research study was to quantify the potential environmental benefits during paving operations with respect to the reduction of volatile and semi-volatile organic compounds and polycyclic aromatic hydrocarbons to confirm or refute this hypothesis. Asphalt plant stack emissions were not assessed as part of this study. A portable “flux” chamber was designed and fabricated to capture and directly measure emissions during paving operations. An analytical method was developed to identify and quantify alkane emissions using gas chromatography mass spectrometry (GC-MS). A separate method was developed for identification and characterization of trace level polycyclic aromatic hydrocarbon compounds in the asphalt fumes. The results demonstrated that the warm-mix asphalt technology type, plant mixing temperature, and level of compaction significantly influence emissions characteristics throughout paving operations. Depending on these variables, most warm-mix technologies appear to have potential for reducing emissions during transport and paving operations.

(Abstract continued on page 2)

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Key findings from the study include:

- The majority of the reactive organic gases are volatilized in the first hour after sampling initiation.
- There is a significant difference between emissions concentrations from loose mix and those recorded immediately after compaction.
- Gaseous phase PAH compounds in asphalt fumes are mainly low molecular weight compounds and are present at trace levels. The concentrations vary depending on the temperature of the mix at the time of sampling.
- Particulate phase PAHs were below the detection limit of this study for all the mixes. The results confirmed that typical asphalt production temperatures are not high enough to initiate significant PAH formation.
- The total alkane emissions from the warm-mixes were, in most instances, significantly lower than those measured from the hot-mixes (e.g., 117 µg/m3 from one of the warm-mixes compared to 2,516 µg/m3 from the hot-mix control).
- In some instances, specific warm-mixes had higher alkane concentrations than the hot-mix controls. Consequently, any generalization with regard to emissions reduction through the use of warm-mix asphalt is inappropriate.
- PAH concentrations correlated with initial mix production temperature, with those warm-mixes produced at the lowest temperatures showing the lowest PAH concentrations

June 2013
Research Report: UCPRC-RR-2013-03

Warm-Mix Asphalt Study: Evaluation of Rubberized Hot- and Warm-Mix Asphalt with Respect to Emissions

Authors:
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Partnered Pavement Research Center (PPRC) Contract Strategic Plan Element 4.41.2:
Environmental Impacts and Energy Efficiency of Warm Mix Asphalt

PREPARED FOR:

California Department of Transportation
Division of Research, Innovation, and System Information
Office of Materials and Infrastructure Roadway Research

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PROJECT OBJECTIVES

The objective of this study is to compare the potential environmental impacts in terms of fugitive emissions from conventional and rubberized hot-mix asphalt and warm-mix asphalt mixes during construction and paving activities. This will be achieved through the following tasks:

1. Review of the literature review
2. Design and develop a methodology for collecting emissions in the field
3. Develop an analytical method for characterization of emissions in the laboratory
4. Analyze the qualitative and quantitative characteristics of emissions
5. Investigate the chemical structural effects associated with WMA technologies
6. Prepare recommendations and guidelines

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The University of California Pavement Research Center acknowledges the assistance and interest of Ms. Nahid Hosseinzadeh (retired), Mr. Joseph Peterson, and Dr. T.Joe Holland from Caltrans; Mr. Nate Gauff and Mr. Robert Fujii from CalRecycle; and Dr. Peter Green and Dr. Isabel Faria, University of California, Davis.

EXECUTIVE SUMMARY

In recent years, warm mix asphalt (WMA) technologies have been used to modify asphalt binders, with the aims of decreasing production and construction temperatures, reducing fumes and emissions, retaining the properties of the mix during long haul distances, and improving workability. Reduced production temperatures at the plant and during paving and compaction are believed to reduce emissions from the asphalt. The objective of this research study was to quantify the potential environmental benefits during paving operations with respect to the reduction of volatile and semi-volatile organic compounds and polycyclic aromatic hydrocarbons to confirm or refute this hypothesis. Asphalt plant stack emissions were not assessed as part of this study.

This study developed and assessed equipment for accurately measuring surface emissions during hot- and warm-mix asphalt paving operations. A transportable flux chamber was fabricated to obtain direct measurements of reactive organic gas emissions and to estimate the fluxes of volatile and semi-volatile organic compounds for different asphalt mixes and production temperatures using gas chromatography mass spectrometry. A study to validate the applicability of the flux chamber/gas chromatography mass spectrometry method was carried out during placement and compaction of ten rubberized asphalt test sections (three hot-mix and seven warm-mix, all produced at different temperatures). The study verified the applicability of the method in characterizing organic compounds in emissions during paving and was therefore extended to assess other gaseous and particulate polycyclic aromatic hydrocarbon (PAH) emissions from four additional asphalt mixes produced at two different asphalt plants.

Based on the results of the study, the following general observations with regard to emissions during asphalt paving are made:

- There is a significant difference (a factor of two on average) between emissions concentrations in terms of total volatile organic compounds measured from loose mix (e.g., in a truck, windrow, or when tipped into the paver hopper) and those measured from the road surface immediately after compaction.
- The kinetics of emissions over time indicated that the majority of reactive organic gases are volatilized in the first hour after construction.
- Gaseous phase PAH compounds in asphalt fumes are mainly low molecular weight compounds and are present at trace levels. The concentrations varied depending on the temperature of the mix at the time of sampling.
- Particulate phase PAHs were found to be below the detection limit of this study (0.1 ng/μL) for all the mixes (hot and warm) assessed. The results confirmed that the temperature ranges at which the asphalt mixes were produced in this study (123°C to 166°C) were not high enough to initiate significant PAH formation.

The following observations were made with respect to the effect of WMA technologies on emissions during paving:

- Alkane emissions consisted of n-hydrocarbons ranging from C_8 to C_{18}. Depending on the type of mix and its temperature at the time of sampling, the total alkane emissions from the warm mixes were, in most instances, significantly lower than those measured on the hot mixes (e.g., 117 $\mu g/m^3$ from one of the warm-mixes compared to 2,516 $\mu g/m^3$ from the hot-mix control).
- In some instances, specific warm mixes had higher alkane concentrations than the hot-mix controls. Consequently, any generalization with regard to emissions reduction through the use of warm-mix asphalt is inappropriate and should be restricted to comparisons of specific warm-mix technologies against a hot-mix control.
- PAH concentrations correlated with initial mix production temperature, with those warm-mixes produced at the lowest temperatures showing the lowest PAH concentrations.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
BSM	Benzene soluble matter
Caltrans	California Department of Transportation
CalRecycle	California Department of Resources, Recycling, and Recovery
CARB	California Air Resources Board
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
CS_2	Carbon disulfide
EPA	Environmental Protection Agency
GC-MS	Gas chromatography/mass spectrometry
FID	Flame ionization detector
HAP	Hazardous air pollutants
HMA	Hot-mix asphalt
LOD	Limit of detection
LOQ	Limit of quantification
O_3	Ozone
NIOSH	National Institute for Occupational Safety and Health
NO_x	nitrogen oxides
PAH	Polycyclic aromatic hydrocarbon
PM	Particulate matter
PPRC	Partnered Pavement Research Center
PTFE	Polytetrafluoroethylene
ROG	Reactive organic gas
RAP	Recycled asphalt pavement
R-HMA	Rubberized hot-mix asphalt
R-HMA-G	Gap-graded rubberized hot-mix asphalt
R-OGFC	Rubberized open-graded friction course
R-WMA-G	Gap-graded rubberized warm-mix asphalt
SIM	Selected ion monitoring
SO_x	Sulfur oxides
SVOC	Semi-volatile organic compound
SPE	Strategic Plan Element
tpd	Tons per day
TPM	Total particulate matter
TOC	Total organic compounds
UCPRC	University of California Pavement Research Center
VOC	Volatile organic compound
WMA	Warm-mix asphalt

CONVERSION FACTORS

SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	Millimeters	mm
ft	feet	0.305	Meters	m
yd	yards	0.914	Meters	m
mi	miles	1.61	Kilometers	Km
		AREA		
in^2	square inches	645.2	Square millimeters	mm^2
ft^2	square feet	0.093	Square meters	m^2
yd^2	square yard	0.836	Square meters	m^2
ac	acres	0.405	Hectares	ha
mi^2	square miles	2.59	Square kilometers	km^2
		VOLUME		
fl oz	fluid ounces	29.57	Milliliters	mL
gal	gallons	3.785	Liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
	NOTE: volumes greater than 1000 L shall be shown in m^3			
		MASS		
oz	ounces	28.35	Grams	g
lb	pounds	0.454	Kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
		TEMPERATURE (exact degrees)		
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
		ILLUMINATION		
fc	foot-candles	10.76	Lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.45	Newtons	N
lbf/in^2	poundforce per square inch	6.89	Kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	Inches	in
m	meters	3.28	Feet	ft
m	meters	1.09	Yards	yd
km	kilometers	0.621	Miles	mi
		AREA		
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	Hectares	2.47	Acres	ac
km^2	square kilometers	0.386	square miles	mi^2
		VOLUME		
mL	Milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	Gallons	gal
m^3	cubic meters	35.314	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
		MASS		
g	grams	0.035	Ounces	oz
kg	kilograms	2.202	Pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
		TEMPERATURE (exact degrees)		
°C	Celsius	1.8C+32	Fahrenheit	°F
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	Poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380 (Revised March 2003)

1. INTRODUCTION

1.1 Background

Warm-mix asphalt is a relatively new technology. It was developed in response to the needs for reduced energy consumption and stack emissions during the production of asphalt concrete, to allow longer haul distances, lower placement temperatures, improved workability, and better working conditions for plant and paving crews. Studies in the United States and Europe indicate that significant reductions in production and placement temperatures, and potentially related emissions, are possible.

The California Department of Transportation (Caltrans) has expressed interest in warm-mix asphalt with a view to reducing stack emissions at asphalt plants, to allowing longer haul distances between asphalt plants and construction projects, to improving construction quality (especially during nighttime closures), to improving working conditions during construction, and to extending the annual period for paving. However, the use of warm-mix asphalt technologies requires incorporating an additive into the mix, and/or changes in production and construction procedures specifically related to temperature, which could influence the short- and long-term performance of the pavement, as well as the emissions during production and placement. Consequently, Caltrans identified the need for research to address a range of concerns related to these changes before statewide implementation of the technology is approved.

1.2 Project Objectives

The research presented in this report is part of Partnered Pavement Research Center Strategic Plan Element 4.41.2 (PPRC SPE 4.41.2), titled "Environmental Impacts and Energy Efficiency of Warm Mix Asphalt," undertaken for Caltrans and the California Department of Resources, Recycling, and Recovery (CalRecycle) by the University of California Pavement Research Center (UCPRC). This study follows an earlier three-phase project (SPE 4.18), which assessed the performance of warm-mix asphalt in laboratory, accelerated loading, and full-scale field trials on California highways *(1-6)*.

The objective of this study is to compare the potential environmental impacts in terms of fugitive emissions from conventional and rubberized hot- and warm-mix asphalt during construction and paving activities. This will be achieved through the following tasks:

1. Review of the literature review
2. Design and develop a methodology for collecting emissions in the field
3. Develop an analytical method for characterization of emissions in the laboratory
4. Analyze the qualitative and quantitative characteristics of emissions

5. Investigate the chemical structural effects associated with the different WMA technologies assessed
6. Prepare recommendations and guidelines

1.3 Structure and Content of this Report

This report presents an overview of the work carried out to meet the objectives of the study, and is organized as follows:

- Chapter 2 provides an overview of studies on emissions from asphalt and identifies knowledge gaps in the literature.
- Chapter 3 describes the method developed in this study for sampling and characterizing alkane and PAH emissions from asphalt paving.
- Chapter 4 details the results of laboratory testing on the collected samples.
- Chapter 5 provides conclusions and preliminary recommendations.

1.4 Measurement Units

Although Caltrans recently returned to the use of U.S. standard measurement units, metric units have always been used by the UCPRC in the design and layout of experiments, for laboratory and field measurements, and for data storage. In this report, both U.S. Customary and metric units (provided in parentheses after the U.S. Customary units) are provided in general discussion. In keeping with convention, only metric units are used in laboratory data analyses and reporting. A conversion table is provided on page viii at the beginning of this report.

1.5 Terminology

The term “asphalt concrete” is used in this report as a general descriptor for asphalt concrete surfacings. The terms “hot-mix asphalt (HMA)” and “warm-mix asphalt (WMA)” are used as descriptors to differentiate between the control and the warm-mixes discussed in this study.

2. LITERATURE REVIEW

2.1 Emissions from Asphalt Production and Placement

The production of asphalt mixes at high temperatures can contribute to air quality problems due to the emission of reactive organic gases (ROGs) and particulate matter (PM). In the United States, emissions released through asphalt plant stacks are regulated and controlled by the Environmental Protection Agency (EPA AP-42, Section 11.1 Hot-Mix Asphalt Plants *[7]*). According to the current regulations, asphalt plants have two major categories of emissions:

- Ducted sources (those vented to the atmosphere through some type of stack, vent, or pipe), and
- Fugitive sources (those not confined to ducts and vents but emitted directly from the source to the ambient air).

The most significant source of ducted emissions is the rotary drum dryer. Emissions from the drum consist of water (as steam evaporated from the aggregate); particulate matter; products of combustion (carbon dioxide [CO_2], nitrogen oxides [NO_x], and sulfur oxides [SO_x]); carbon monoxide (CO); and small amounts of organic compounds of various species (including volatile organic compounds [VOC], methane [CH_4], and hazardous air pollutants [HAP]). The carbon monoxide and organic compound emissions result from incomplete combustion of the fuel, which is mostly natural gas. The ducted sources of emissions at asphalt plants are tested annually by an independent agency and the results are reported to the EPA for compliance and permit renewal.

Fugitive emissions come mainly from loading trucks, transportation to a construction site, and during paving operations. Fugitive emissions are not currently monitored and controlled. These emissions mainly consist of organic compounds of various species including VOCs, semi-volatile organic compounds (SVOC), and polycyclic aromatic hydrocarbons (PAHs). Ground-level ozone (O_3) is produced by the photochemical reaction of oxides of nitrogen and reactive organic gases, which include both VOCs and SVOCs.

Urban smog or ozone is a persistent public health problem with serious economic consequences in the United States *(8)*. Between 2005 and 2007, more than 400 counties in the United States had eight-hour average ozone concentrations higher than 75 ppb, the current U.S. EPA ozone criterion, which will soon be reduced to 70 ppb or lower. California's current eight-hour average standard is 70 ppb. The six U.S. counties with the highest ozone concentrations are all located in California. The operation of asphalt plants in nonattainment areas (i.e., those areas not meeting the national air quality standards established in 1997) can be restricted during daylight hours at certain times of the year when ozone levels are a concern.

Figure 2.1 shows a national map of areas that according to the U.S. EPA have been violating the eight-hour ozone 75 ppb limit. Many of these areas are in urban areas in California where most road maintenance and rehabilitation activities take place.

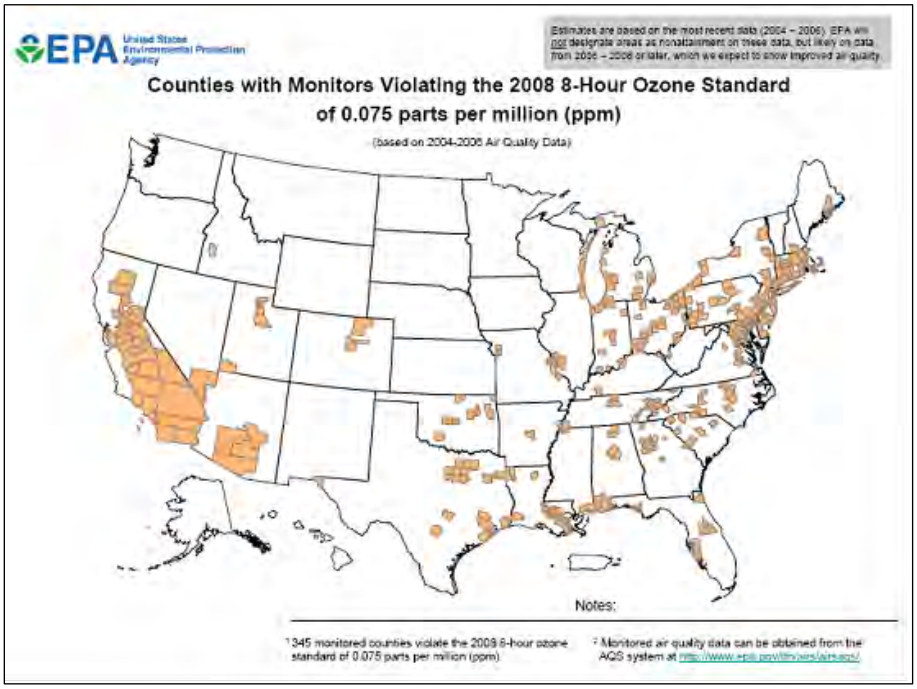

Figure 2.1: National map of 2008 Ozone Limit Violations *(8)*.

The use of rubberized hot-mix asphalt (R-HMA) is often limited in urban areas because it requires higher production and construction temperatures (between 320°F and 350°F [160°C and 176°C]) compared to conventional hot-mix asphalt (about 310°F [150°C]). These higher temperatures are required to overcome the effects of the higher viscosity of the rubberized binders to ensure adequate aggregate coating and mix workability). These higher temperatures lead to higher fuel consumption in the mixing plant, increased emissions, more smoke and haze, increased odors, and increased safety hazards during mixing/production, load-out/transfer, and during paving.

Reducing reactive organic gases and nitrogen oxide emissions will reduce ozone formation potential in urban areas and consequently this is a high priority nationwide. According to the California Air Resources Board (CARB) inventory, emissions from light-duty vehicles rank as the largest source of ROG and in 2005 accounted for 600 tons per day (tpd) or 24.6 percent of the total ROGs in the state. In recent years, these emissions have decreased and were projected to account for 400 tpd or 18.9 percent of the total ROGs in 2010. As emissions from these major sources decreased over time, reducing emissions from smaller sources has become a higher priority for achieving clean air standards. The CARB inventory listed

statewide asphalt paving and roofing ROG emissions as 31.3 tpd or 1.3 percent of the total for 2005, and projected an increase for 2010 to 32.2 tpd, or 1.5 percent of the total.

2.2 Health Concerns

Research on health concerns with respect to asphalt fume exposure has been carried out for many years with a recent focus on potential exposure to carcinogens. Polycyclic aromatic hydrocarbons potentially represent a very important group of chemical carcinogens in asphalt. Although the adverse effects of PAH compounds are recognized and have been documented in epidemiological studies *(9)*, they are mainly formed during combustion, which does not occur during asphalt production (typically performed at temperatures no higher than 340°F [170°C] compared to the combustion temperature of asphalt, which is around 932°F [500°C]) *(10)*. Consequently the impacts of PAH emissions on worker health is probably limited. Many of the lower molecular weight PAH compounds might also be removed during the refinery process, but this depends on the crude oil source and the process used to refine it. These studies, although limited to only a few asphalt binders tested in the laboratory, have demonstrated that factors such as binder source, type, temperature, and pitch content can lead to an extraordinary variation in composition and toxicity of fumes *(11,13)*.

2.3 Emissions Sampling

Studies concerned with reducing ROGs from asphalt production and placement require accurate quantification of the emissions both at the asphalt plant and during paving operations. A number of protocols exist for measuring stack emissions at asphalt plants and these are routinely undertaken. However, emissions at paving operations are generally limited to measurements from monitors attached to the paving equipment and/or workers, and are often inconsistent because of the influence of numerous variables.

Documented investigations of asphalt emissions in the laboratory are limited to small-scale studies testing locally available conventional neat binders *(11,13)*. In these studies, small amounts of asphalt binder were placed in special containers and heated to generate asphalt fumes, which were then subsequently analyzed. The drawbacks with these types of studies include:

- The fume generation methodology is not representative of the field conditions during production and construction of asphalt mixes.
- Studies are conducted with a limited number of neat binders.
- The studies are focused on a small range of temperatures, which are often not in the range that occurs in the field. With the widespread application of warm-mix asphalt technologies, there is a need to measure and evaluate emissions more accurately during paving and to include different mix

types produced at different temperatures (i.e., conventional, rubberized and polymer-modified asphalts, and dense-, gap-, and open-graded asphalt, etc.).

Gaudefroy et al. *(14)* developed a laboratory fume generation system composed of an asphalt mixer linked to a stainless steel stack, which enabled the collection of the emitted fumes. According to the experimental protocol, the asphalt mix is stirred for 30 minutes in the temperature-regulated mixer, while total organic compounds (TOCs) in the fumes are continuously analyzed with a flame ionization detector (FID). This study demonstrated that mix design and temperature have an influence on total organic compound emissions and the thicker the bitumen coat, the lower the quantity of total organic compound emissions emitted. In a similar study, total organic compound emissions were also found to increase with increasing heating time *(15)*. These studies, undertaken in France, were limited to two types of dense-graded hot-mix asphalt mixes produced according to French specifications. No comparison with actual field emissions was attempted.

Sampling of emissions during actual paving operations has been limited to personal devices used for detection of total particulate matter (TPM) and benzene soluble matter (BSM) *(16)*. These devices do not differentiate between emissions from the asphalt and those from equipment, passing traffic, and roadside activities. They are also limited in terms of wind speed, ambient temperature, and device location and exposure.

3. EMISSION SAMPLING METHOD AND PROGRAM

3.1 Emission Sampling Apparatus

To overcome the limitations of current emissions sampling methods during paving operations discussed in Chapter 2 (i.e., devices do not differentiate between emissions from the asphalt and those from equipment, passing traffic, and roadside activities, and are limited in terms of wind speed, ambient temperature, and device location and exposure), a portable flux chamber was designed and built at the UCPRC for collecting emissions in the field (Figure 3.1). The chamber consists of a half-cylinder made of stainless steel with dimensions of 1.0 m x 0.65 m x 0.33 m (3.3 ft. x 2.1 ft. x 1.1 ft.). The chamber inlet is connected to two zero-air generators that are used to evacuate the chamber prior to sampling. These generators have an ultra violet lamp for the control of microorganisms, an activated carbon/alumina mixture for the removal of trace quantities of nitrous oxide and ozone, a catalyst to convert carbon monoxide to carbon dioxide, and a 1.0 µm particulate filter with a 93 percent rating down to 0.1 µm to ensure that any airborne particles that may have been in the background air are removed. The generators are operated at 15 L/min. (3.3 gal./min.). Temperature inside the chamber is monitored during sampling with a thermocouple.

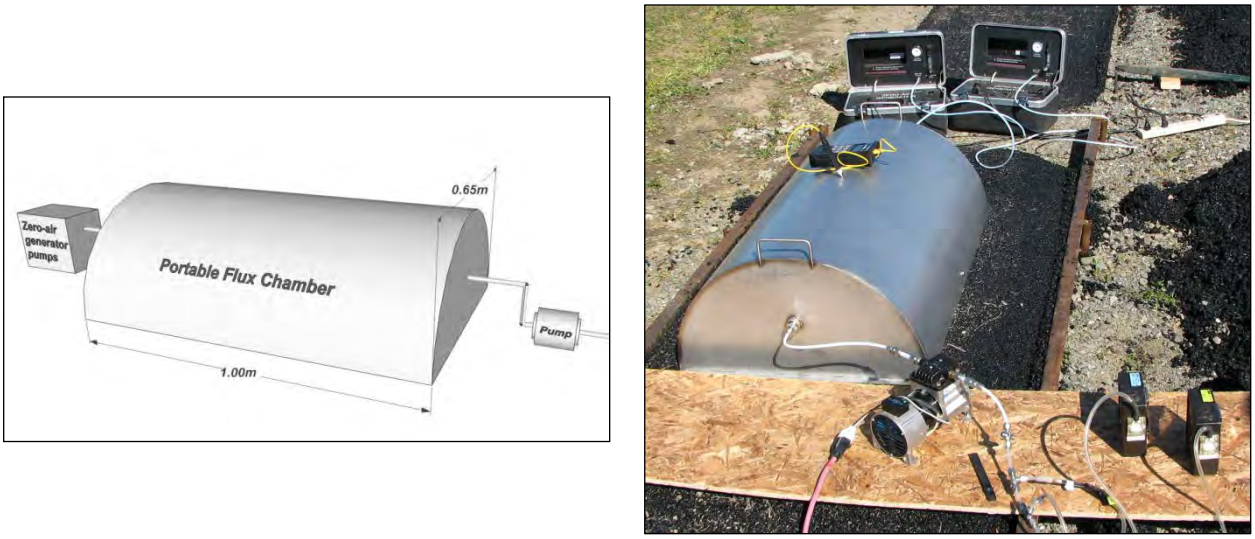

Figure 3.1: Portable flux chamber schematic and field sampling setup.

A pump samples at flow rates of 500 mL/min. and 1.5 L/min. (0.5 fl. oz. and 3.3 gal./min.) simultaneously, which are considered the most desirable for sampling volatile and semi-volatile organic compounds for extended periods. The sampling pump is calibrated with an electronic digital flow calibrator before and after collection of each sample.

A series of commercial sampling tubes and filters are installed after the pump outlet to collect the emissions (Figure 3.2). The first two branches consist of tubes that contain 400 mg and 200 mg (0.0014 and 0.007 oz.) of activated carbon in two successive sections, which are used for sample collection and breakthrough determination respectively (Figure 3.3). The charcoal tubes at the second branch train can be replaced at different intervals to understand the kinetics of the emission over time. The third sampling branch employs sampling through a polytetrafluoroethylene (PTFE) filter with a 0.45-µm pore size, followed by an XAD-2 resin tube for capturing both the particulate and gaseous phase of polycyclic aromatic hydrocarbons (PAHs). The fourth and fifth sampling branches consist of an XAD-2 trap and PTFE filter respectively as replicates and as a check to verify the technique.

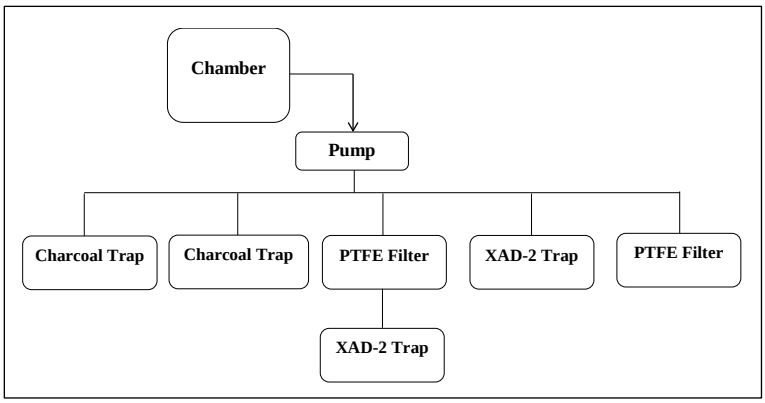

Figure 3.2: Schematic of asphalt emissions sampling.

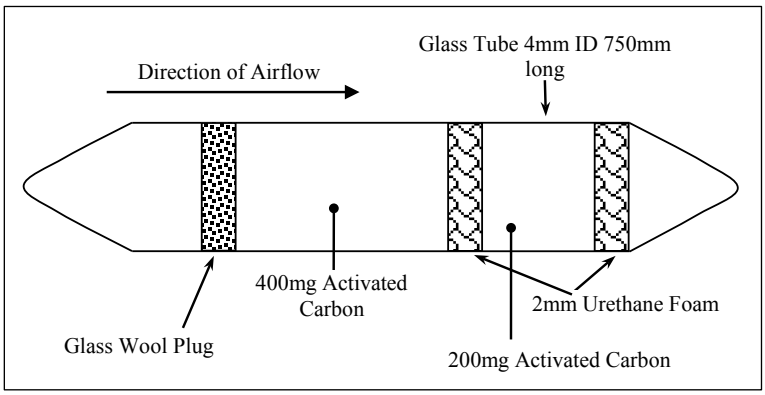

Figure 3.3: Activated charcoal adsorption sampling tube.

3.2 Sampling Handling after Collection

Samples are handled according to ASTM Method D3686 (Standard Practice for Sampling Atmospheres to Collect Organic Compound Vapors [Activated Charcoal Tube Adsorption Method]), in which the tubes are capped immediately after sampling, placed into individual sealed plastic bags, and then transferred to

the laboratory in a cooler with ice packs. Samples are refrigerated at 4°C (39°F) until processed to ensure that the compounds are stable before extraction and recovery.

3.3 Sampling Procedure

Given that there is limited knowledge about asphalt emissions during paving, a sampling plan focusing on the four different stages of production and paving operations was developed: These stages include:

- Stage 1. Transfer of the mix from the silo to the truck and transportation to the construction site. In this stage the flux chamber is placed on loose mix sampled directly from the silo. Emissions are monitored for a period of two hours.
- Stage 2. Transfer of the mix from the truck to the paver (either from windrows dumped onto the pavement or tipped directly into the paver hopper). In this stage, asphalt mix is sampled directly from the truck and placed on a suitable surface. The flux chamber is immediately placed on top of the loose mix to collect emissions during a 15-minute sampling period (Figure 3.4).
- Stage 3. Immediately after compaction. In this stage, the flux chamber can either be placed on the road surface immediately after compaction, or on a short dedicated separate compacted test section (Figure 3.5 and Figure 3.6). A 15-minute sampling period is used.

Figure 3.4: Stage 2 sampling on loose mix.

Figure 3.5: Test section compacting prior to sampling.

Figure 3.6: Stage 3 and 4 sampling on compacted surface.

- Stage 4. Postconstruction. In this stage, the flux chamber remains on the compacted surface for a period of two hours, after which a third set of samples is taken during a 30 minute sampling period to assess emissions after completion of construction and during opening to traffic.

3.4 Sample Preparation

Asphalt fumes are extracted from the tubes and filters ultrasonically. Individual sections of each charcoal trap are extracted in separate vials using 1.5 mL (0.05 fl.oz) of carbon disulfide (CS_2) solvent and 15 minutes of sonication. The PTFE filters and the XAD-2 resin tubes are extracted separately with 5 mL (0.17 fl.oz.) of dichloromethane – hexane (1:1 ratio). Ultrasonic extraction is performed for one hour for filter samples and 1.5 hours for the XAD-2 resin tube samples. Carbon disulfide was selected because it provides high recoveries of reactive organic gases and is prescribed for workplace hydrocarbon sampling in the National Institute for Occupational Safety and Health (NIOSH) manual of analytic methods (Method 1500-1501).

The charcoal is removed and transferred to an appropriately labeled vial. The supernatant phase of the solvent is then transferred into another vial and the compounds analyzed using gas chromatography/mass spectrometry (GC-MS). Control charcoal tubes that are taken to the sampling site but not used for sampling are also extracted to check the blank values. Analysis of both the front and end sections of all tubes is conducted after extraction and recovery to confirm that no breakthrough occurred in any of the samples (i.e., all emissions were captured in the first section of the tube).

3.5 Gas Chromatography/Mass Spectrometry

GC-MS analyses are undertaken with an appropriate gas chromatograph coupled with a mass spectrometer (this study used an Agilent 6890-5973 series gas chromatograph and Agilent 5973N mass spectrometer). The gas chromatograph, equipped with a 30 m x 0.25 mm (98 ft. x 9.8 mils) capillary column with 0.25 µm DB-5 film thickness, provides satisfactory separation of various compounds. The helium carrier gas is introduced at a rate of 1.0 mL/min. (0.03 fl. oz./min.) and linear velocity of 20 cm/sec (7.9 in./sec). The initial column temperature is maintained at 50°C (122°F) for four minutes, then raised to 125°C (257°F) at a rate of 2°C/min (3.6°F/min.), and finally to 280°C (536°F) at a rate of 10°C/min. (18°F/min.).

A full scan mode with splitless injection is used as the spectrometric technique for characterizing VOCs and SVOCs. A purge time of 1.5 minutes is specified in the method. A selected ion monitoring (SIM) mass spectrometer is used to detect individual priority PAHs at trace levels in the asphalt fumes. This mode of operation is dedicated to monitoring only a few ion currents and rapidly changes between the

m/z values where characteristic ions are expected, allowing for a higher sensitivity compared to the normal scanning mode *(17)*.

The instrument is calibrated with a standard solution containing 16 alkanes (C_8 through C_{23}) and 16 PAHs to ensure linearity of the system. The gas chromatograph is recalibrated if the response factor varies by more than 10 to 15 percent. The carbon disulfide solvent is also analyzed to ensure that it is free of contaminants.

Asphalt fumes are extremely complex and consist of aliphatic, heterocyclic compounds, polycyclic aromatic hydrocarbons, and some nitrogen-, oxygen-, and sulfur-containing compounds. In order to identify and characterize polycyclic aromatic hydrocarbon compounds more accurately, a simplified purification method was developed. In this technique, a column (250 mm x 10 mm [10 in. x 0.4 in.] inside diameter) packed with silica cartridge is used to separate the PAHs from saturated and polar compounds using dichloromethane – hexane (1:1 ratio) as the solvent. The extracts are filtered and preconcentrated by evaporating the solvent under a nitrogen blanket.

The GC-MS alkane extraction efficiencies from activated charcoal tubes are summarized in Table 3.1, which provides information regarding the detection limits as well as the accuracy for the alkane compounds.

Table 3.1: GC-MS Analysis Criteria for VOCs and SVOCs

Compound	Retention Time	Detection Limit (ng/m^3)	Recovery (%)
Decane	11.90	1.5	85
Undecane	14.25	2.0	94
Dodecane	16.35	2.1	90
Tridecane	18.26	1.9	93
Tetradecane	20.05	2.3	94
Pentadecane	21.72	1.8	92
Hexadecane	23.30	2.1	91
Heptadecane	24.79	2.0	90
Octadecane	26.22	1.9	95

3.5.1 GC-MS Detection for PAHs

Stable isotope dilution with anthracene (concentration of 10 ng/L) as an internal standard is used to evaluate the recovery of the PAH sample. This procedure improves the reliability of the analysis given that the relative recovery of the internal standard can account for losses of the analytes during sample preparation and detection processes. The recoveries of spiked PAHs from the XAD-2 tubes and the major ions that are monitored in the SIM mode are listed in Table 3.2.

Table 3.2: GC-MS Analysis Criteria for PAHs

Compound	Retention Time (min.)	Recovery from XAD-2 Resin (%)	Major Ions Monitored
Naphthalene	11.68	95	128, 102, 64
Acenaphthylene	12.45	92	152, 76, 63
Acenaphthene	14.74	91	153, 154
Fluorene	19.05	98	166, 139, 83
Phenanthrene	19.28	99	178, 89, 76
Anthracene	20.26	95	178, 89, 76
Fluoranthene	24.55	100	202, 101, 88
Pyrene	25.53	85	202, 101, 89
Benz(a)anthracene	31.24	92	228, 114, 101
Chrysene	31.39	91	228, 114, 102
Benzo(b)fluoranthene	35.94	85	252, 126, 113
Benzo(k)fluoranthene	36.05	89	252, 126, 114
Benzo(a)pyrene	37.19	91	276, 138, 124
Dibenz(a,h)anthracene	41.29	96	276, 138, 124
Benzo(ghi)perylene	41.44	93	278, 139, 125
Indeno(1,2,3-cd)pyrene	42.18	94	276, 138, 126

3.6 Sampling Program

Emissions samples were collected on four separate projects with mixes from four different asphalt plants as follows:

- Rubberized warm-mix asphalt test track construction at the University of California Pavement Research Center *(4,5)*. In this experiment, seven different warm-mix asphalt technologies were compared against two hot-mix asphalt controls. One control and three of the warm mixes were produced at the Granite Construction Bradshaw asphalt plant in Sacramento. The second control and remaining four warm mixes were produced at the George Reed Construction Marysville asphalt plant.
- Hot-mix asphalt production with 15 percent recycled asphalt pavement (RAP) produced at the Teichert Perkins asphalt plant in Sacramento.
- Rubberized warm-mix asphalt produced at the Teichert Perkins asphalt plant in Sacramento.
- Hot- and warm-mix asphalt produced at the Granite Construction Bradshaw asphalt plant in Sacramento.

Mix details are summarized in Table 3.3. All mixes used a PG 64-16 binder.

Table 3.3: Mix Details for Emissions Sampling Projects

Project	Mix	Binder Content (%)	Production Temperature (°C [°F])	Paving Temperature (°C [°F])	Emissions Collection[1]
UCPRC Mix Design #1	1/2 in. R-HMA-G (#1) 1/2 in. R-WMA-G (#1) 1/2 in. R-WMA-G (#2) 1/2 in. R-WMA-G (#3)	7.7 7.9 7.7 7.7	160 (320) 140 (284) 125 (257) 130 (266)	154 (309) 128 (262) 120 (248) 127 (261)	Stages 2, 3, and 4
UCPRC Mix Design #2	1/2 in. R-HMA-G (#2) 1/2 in. R-WMA-G (#4) 1/2 in. R-WMA-G (#5) 1/2 in. R-WMA-G (#6) 1/2 in. R-WMA-G (#7)	7.7 8.0 7.6 8.4 10.0	166 (331) 149 (300) 145 (293(145 (293) 140 (284)	140 (284) 140 (284) 137 (279) 136 (277) 126 (259)	Stages 2, 3, and 4
Teichert #1	3/4 in. HMA + 15% RAP	5.1	160 (320)	Not measured	Stage 1
Teichert #2	3/4 R-OGFC (WMA #8)	6.5	147 (297)	Not measured	Stage 1
Granite Construction	3/4 in. HMA 3/4 in. WMA (#9)	5.5 4.7	150 (302) 123 (253)	Not measured	Stage 1

[1] Stage 1 – Sampled from asphalt plant silo
Stage 2 – Sampled from loose mix removed from truck before tipping into paver
Stage 3 – Sampled from road surface immediately after compaction
Stage 4 – Sampled from road surface two hours after compaction

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4. TEST RESULTS

4.1 Emissions from R-HMA and R-WMA (UCPRC Study)

The alkanes identified by GC-MS consisted predominantly of straight chain and branched-chain paraffins ranging from undecane (C_{11}) to docosane (C_{22}) hydrocarbons. There is no universally agreed upon definition for how to separately categorize semi-volatile organic compounds (SVOCs) from volatile organic compounds (VOCs), but a common (and practical) cut-off is the chromatographic elution of the unbranched C16 alkane (n-hexadecane). Mixtures below this cut-off point are considered to be VOCs and those above it are considered to be SVOCs. Other definitions, such as boiling point, can be used when purified molecules are available but they are not appropriate for mixtures *(12)*. Although different VOCs and SVOCs have differing tendencies to react and form ozone, current EPA regulations do not differentiate between the two categories. Concentrations in micrograms per cubic meter ($\mu g/m^3$) and flux rates in micrograms per square meter per minute ($\mu g/m^2/min.$) were calculated for each identified compound for all of the mixes and sampling periods.

The total reactive organic gas (ROG) emission potentials of the different mixes were calculated by integrating the area underneath the chromatograph. The concentration of alkanes was calculated using the calibration factors determined from running the standard solution. Test chamber measurements were converted to flux rates using the following equation:

$$flux = \frac{CV}{\tau A} \qquad 4.1$$

where C is the measured concentration in the chamber
V is the chamber volume
τ is the time scale for air exchange
A is the exposed pavement surface area inside the chamber.

The total ROG emissions from the control and warm mixes before and immediately after compaction are shown in Figure 4.1 and Figure 4.2, respectively; they show that the emissions flux differs depending on the mix type and the temperature inside the chamber at the time of sampling. As expected, the emissions were significantly higher for the loose mix before compaction compared to the results obtained immediately after compaction. This was attributed to both the drop in temperature and the bound nature of the compacted surface. For example, the flux of the ROGs of the Mix Design #1 R-HMA control was 3,500 $\mu g/m^2/min.$ before compaction and 2,000 $\mu g/m^2/min.$ immediately after compaction.

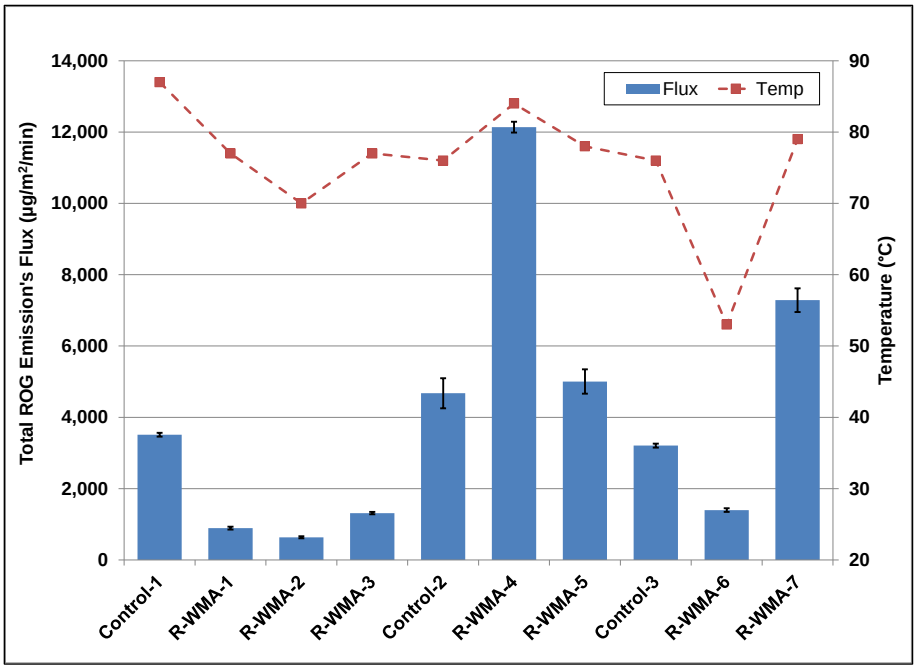

Figure 4.1: Total ROG emissions' flux (µg/m^2/min.) before compaction.

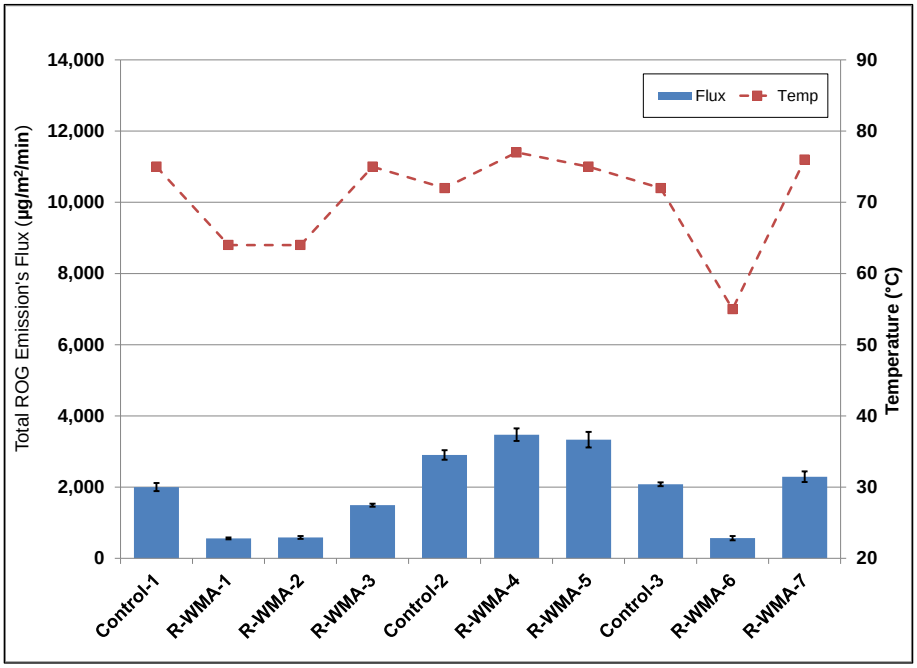

Figure 4.2: Total ROG emissions' flux (µg/m^2/min.) immediately after compaction.

The WMA technology type also had a significant effect on ROG emissions before compaction, while temperature had a more moderate effect (Figure 4.3). Depending on the warm-mix technology used, the increase in emissions was as much as three times higher with respect to total reactive organic gas emissions concentration compared to the hot-mix control at even lower loose mix temperatures. These

findings demonstrate the dependence of alkane emissions on the composition of the warm-mix technology and the temperature, and illustrate the importance of considering both factors in achieving reductions in emissions during asphalt paving.

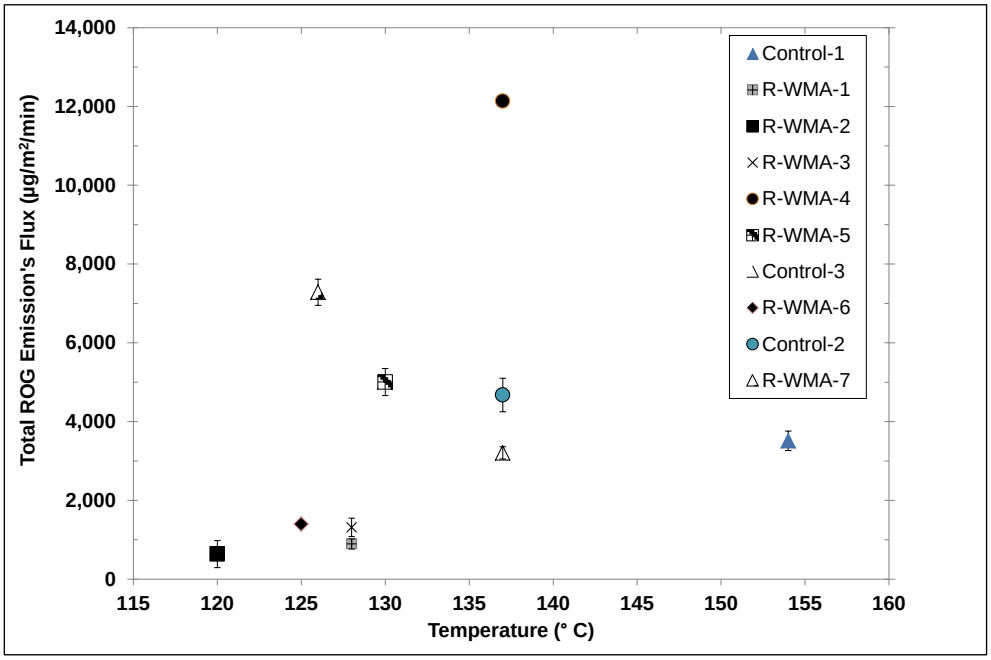

Figure 4.3: Total ROG emissions' flux versus temperature after laydown and before compaction.

4.2 Alkane Emissions During Paving

Concentrations of the different alkanes in the emissions from the R-HMA control mixes and R-WMA mixes during placement and immediately after compaction are shown in Figure 4.4 through Figure 4.7 (note that the y-axis scales differ between the two mix designs). The plots show significant differences between the two asphalt plants, which used two different asphalt binder sources, and between different warm-mix technologies in terms of composition and concentration. However, the trend in decreasing alkane emissions before and after compaction was similar for all mixes.

Alkane emissions as a function of sampling period for the Mix Design #2 R-HMA control are summarized in Figure 4.8, which shows the significant change over time between placement of the mix, compaction of the mix, and the two-hour period after compaction. These results suggest that most of the alkanes volatilize during the first hour of construction. The results also suggest that the chemistry of different warm-mix technologies will influence the concentration of alkanes in the emissions, and that emissions from certain warm-mix technologies will actually have higher concentrations of certain compounds than emissions from conventional hot-mix asphalt. Consequently, any generalization with regard to emissions

reduction during the placement of asphalt through the use of warm-mix technologies is inappropriate and should be restricted to comparisons of specific technologies against hot-mix asphalt controls.

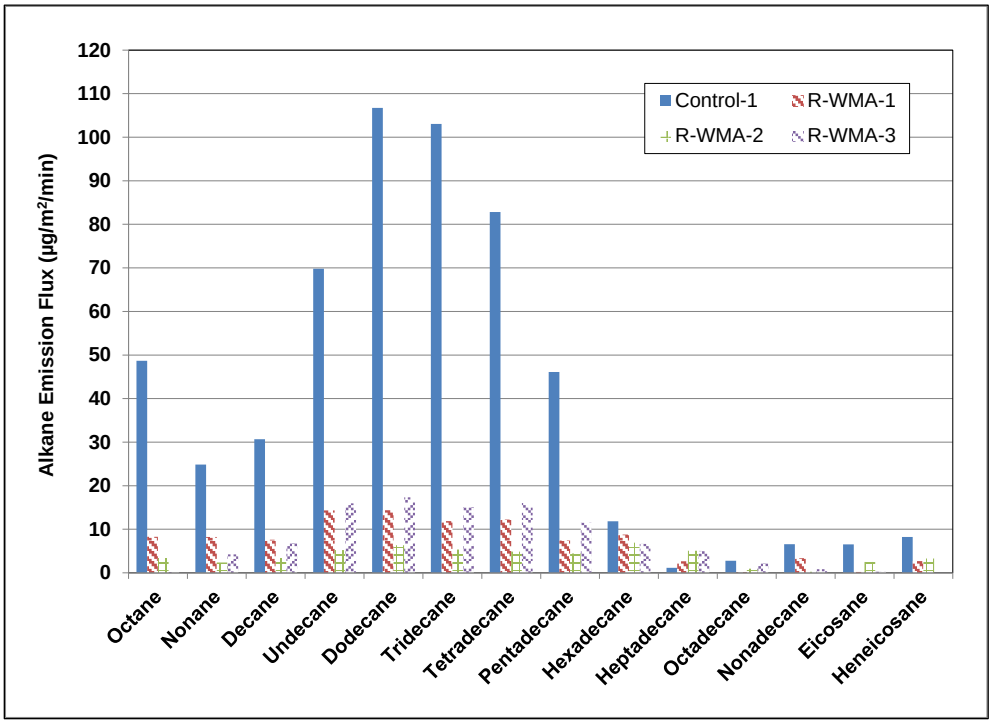

Figure 4.4: Mix Design #1 alkane emission flux before compaction.

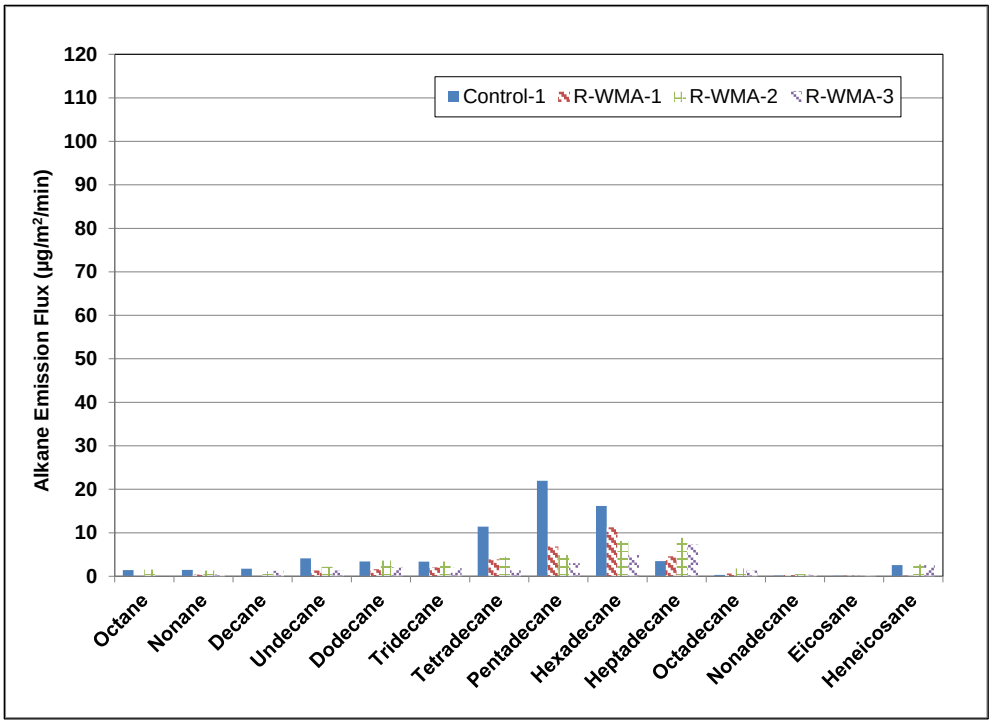

Figure 4.5: Mix Design #1 alkane emission flux after compaction.

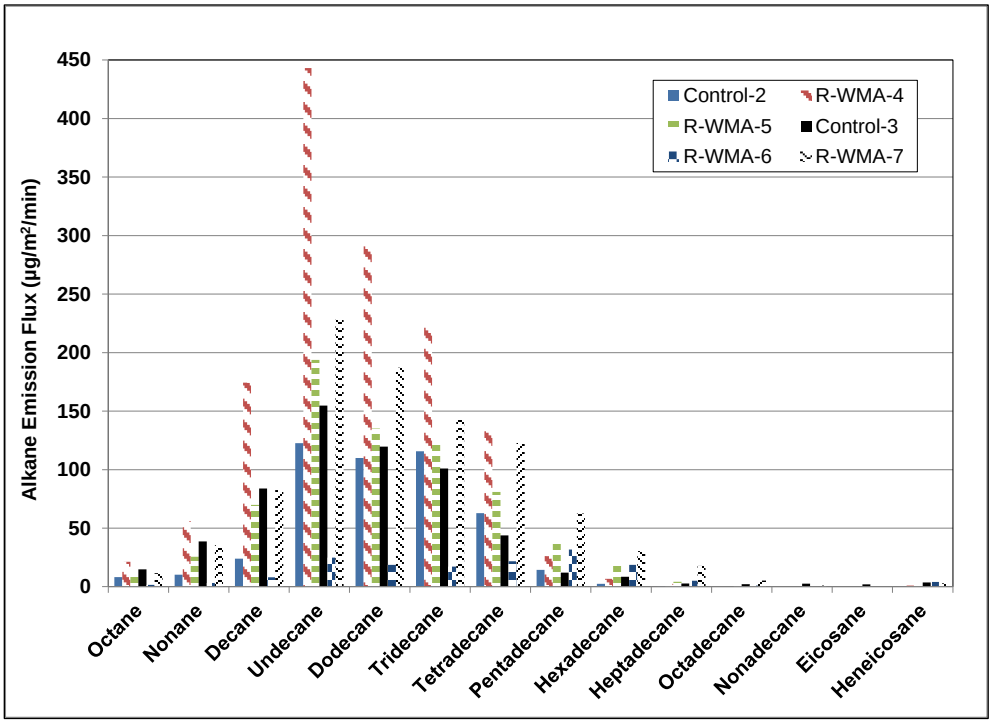

Figure 4.6: Mix Design #2 alkane emission flux before compaction.

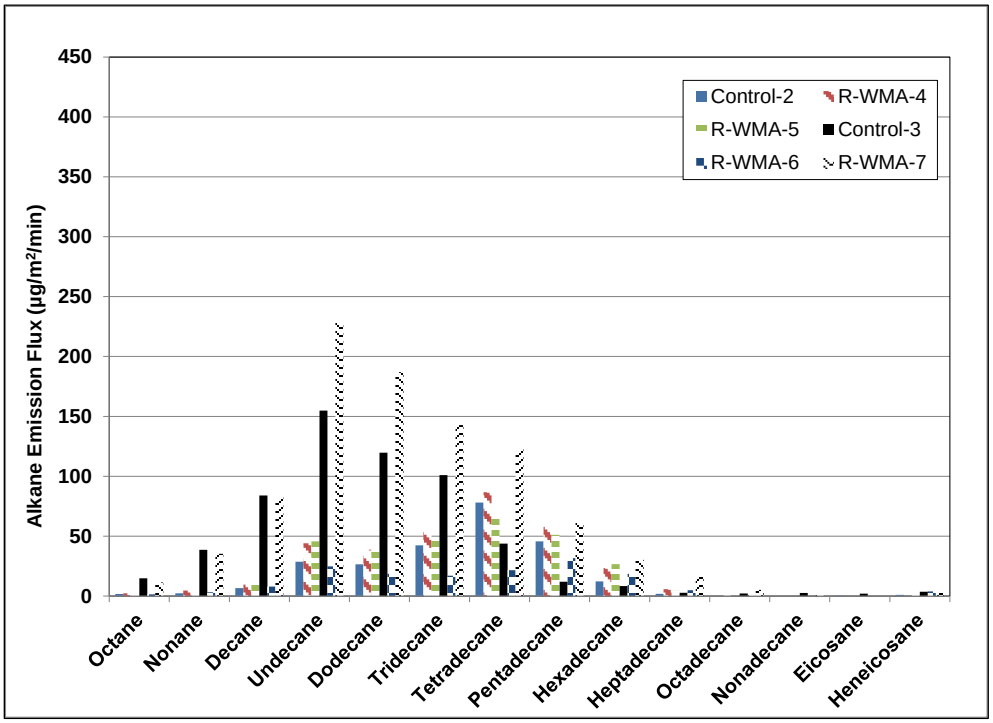

Figure 4.7: Mix Design #2 alkane emission flux after compaction.

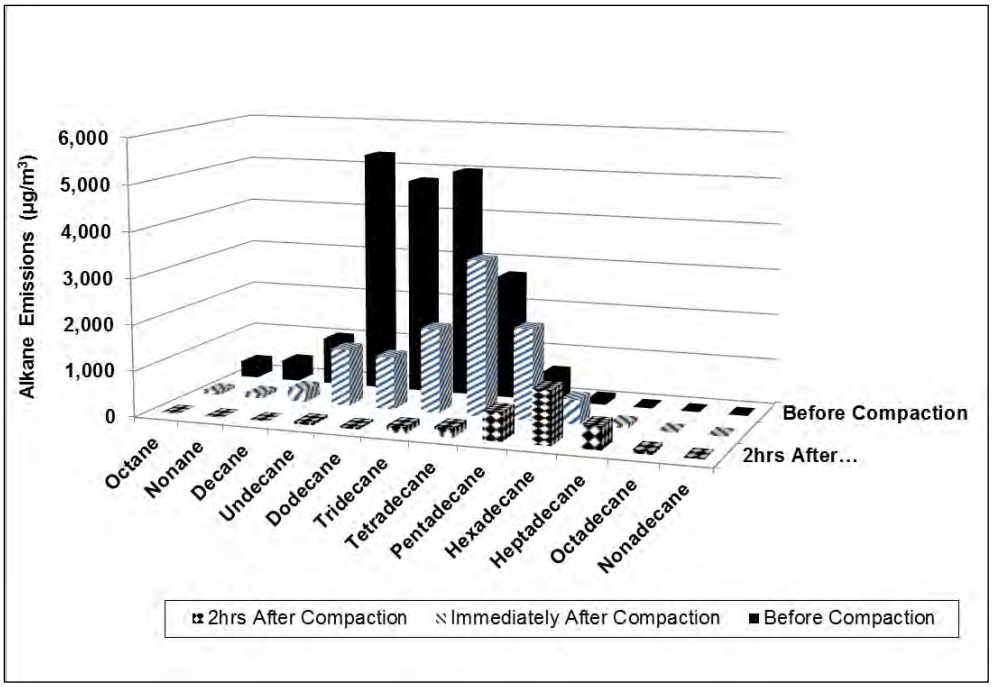

Figure 4.8: Alkane emission flux for Mix Design #2 control mix at three sampling periods.

4.3 Emissions from Asphalt Plant Studies (Teichert and Granite Construction)

4.3.1 Alkane Emissions

The total alkane emissions and individual alkanes from the four different mixes collected in activated charcoal tubes are shown in Figure 4.9 and Figure 4.10 respectively. The lower production temperatures of the warm-mixes had a significant influence on the total alkane emissions concentration.

The emission of alkanes as a function of sampling time is shown in Figure 4.11. During the first thirty minutes of sampling, alkane emissions were present in higher concentrations for all the mixes and especially the mixes with no warm-mix technology. Emissions decreased as time progressed with the second thirty minutes showing markedly lower concentrations of alkanes. The emissions in the third and fourth time intervals were significantly lower, demonstrating that most of the alkane emissions volatilized from the mix during the first hour after load out.

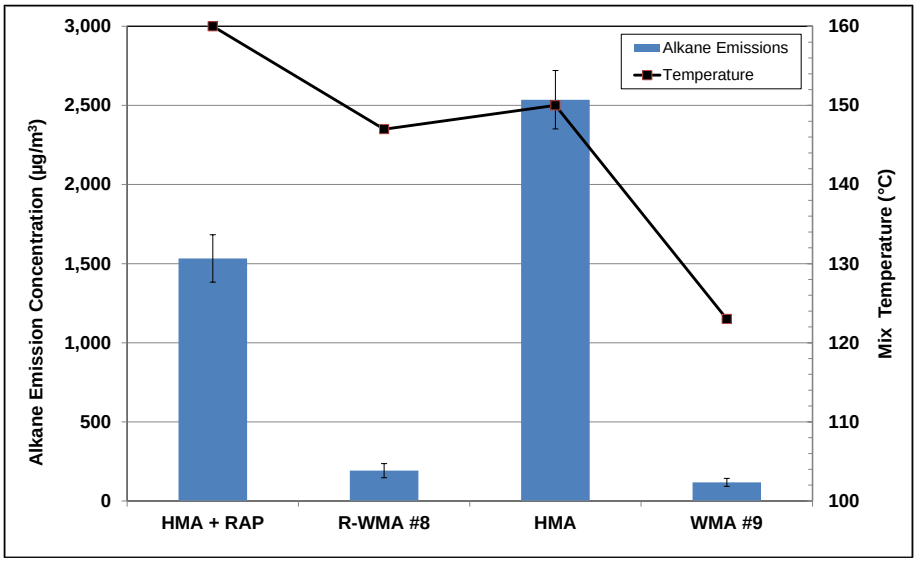

Figure 4.9: Total alkane emissions concentrations at asphalt plant load-out.

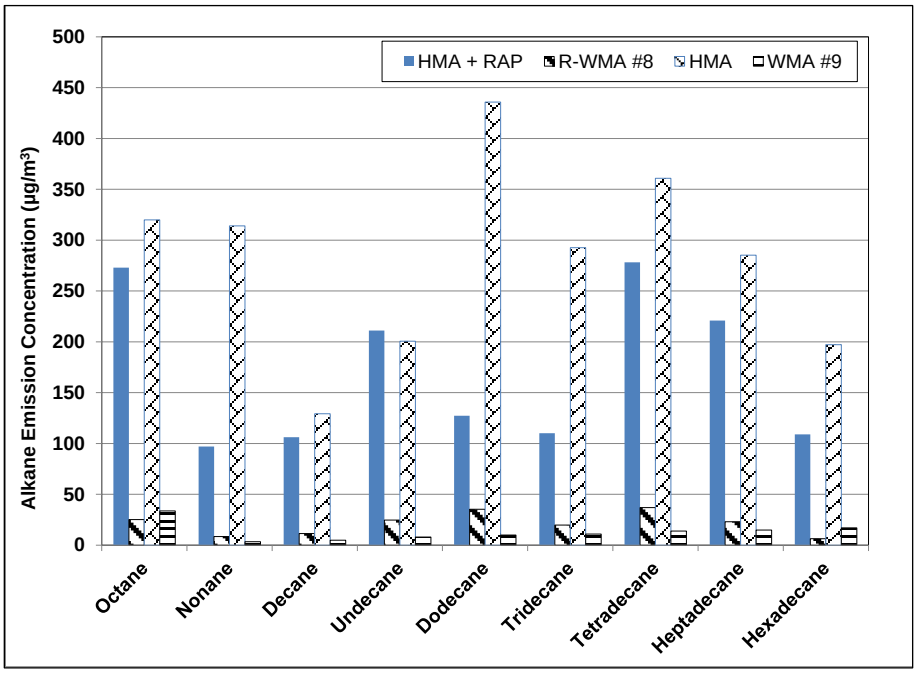

Figure 4.10: Individual alkane emissions concentrations at asphalt plant load-out.

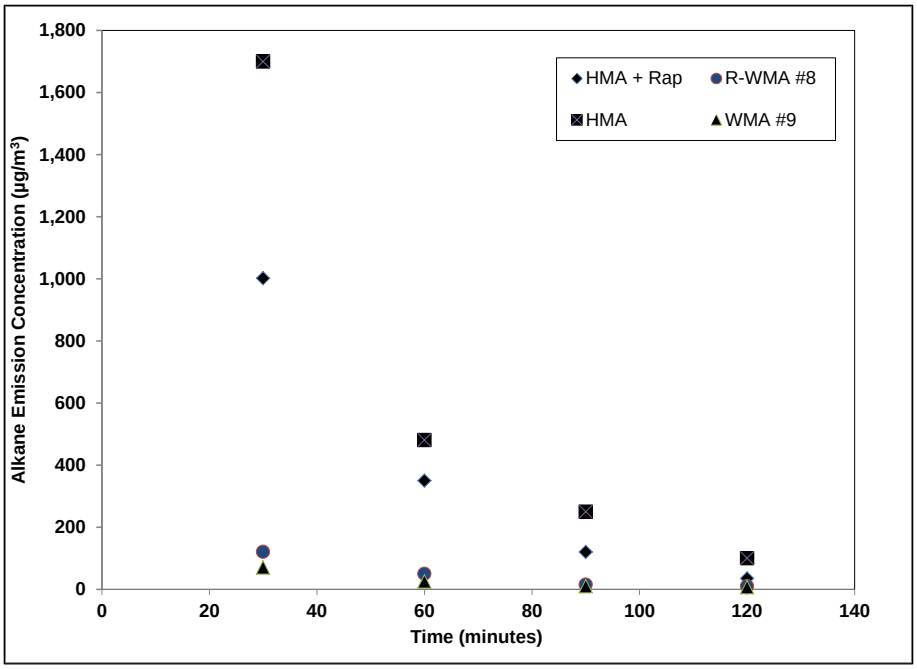

Figure 4.11: Alkane emissions over time at asphalt plant load-out.

4.3.2 Polycyclic Aromatic Hydrocarbon Emissions

Polycyclic aromatic hydrocarbon emissions from the four mixes are shown in Figure 4.12. The PAH concentrations were only observed at trace levels for all mixes in the temperature range assessed in this study. The PAHs were distributed between the gaseous and particulate phases and represent the concentrations collected in the XAD-2 tubes (gaseous). The PAH concentrations decreased significantly as the temperature of the mix decreased, as expected. Consequently, there was also a significant difference between the PAH concentrations from the warm-mixes and those from the hot-mixes.

The particulate phase emissions collected on filters had concentrations below the detection level of the analytical method. The same trends were observed on both sampling branches. The detailed sample clean-up and use of the selected ion monitoring analysis method ensured that the compounds could be detected at ultra-trace levels.

The limit of detection (LOD) and limit of quantification (LOQ) were determined as three times and ten times the standard deviation of seven replicates of a low concentration standard, respectively. The limits of detection and limits of quantification for all the PAH compounds analyzed are listed in Table 4.1. Limits of detection ranged from 0.002 to 0.007 ng/µL (or 2 to 7 µg/L) while limits of quantification ranged from 0.005 to 0.02 ng/µL (or 5 to 20 µg/L).

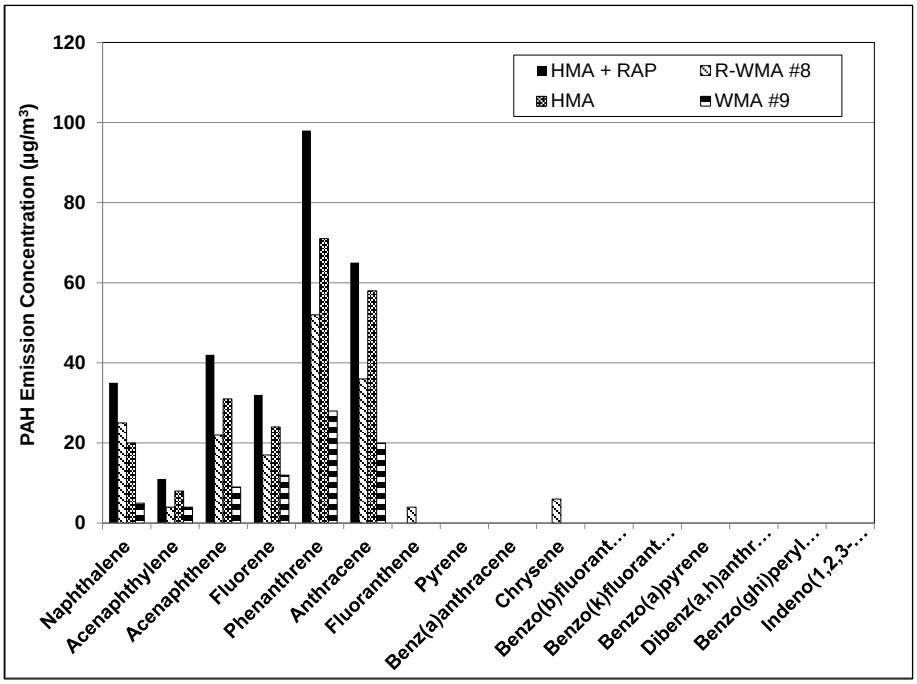

Figure 4.12: Concentrations of various PAHs at asphalt plant load-out.

Table 4.1: Limits of Detection and Quantification for the PAH Compounds

PAH Compound	Limits of Detection (ng/µL)	Limits of Quantification (ng/µL)
Naphthalene	0.002	0.008
Acenaphthylene	0.002	0.007
Acenaphthene	0.004	0.013
Fluorene	0.003	0.010
Phenanthrene	0.003	0.010
Anthracene	0.007	0.024
Fluoranthene	0.003	0.010
Pyrene	0.003	0.009
Chrysene	0.002	0.005
Benzo(a)anthracene	0.002	0.008
Benzo(b)fluoranthene	0.001	0.005
Benzo(k)fluoranthene	0.003	0.008
Benzo(a)pyrene	0.003	0.010
Indeno(1,2,3-cd)pyrene	0.002	0.007
Dibenzo(a,h)anthracene	0.006	0.019
Benzo(ghi)perylene	0.004	0.014

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5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary of Completed Tasks

The purpose of this study was to develop and assess equipment for accurately measuring surface emissions during hot- or warm-mix asphalt paving operations. A transportable flux chamber was fabricated to obtain direct measurements of reactive organic gas (ROG) emissions and to estimate the fluxes of volatile and semi-volatile organic compounds (VOCs and SVOCs) for different asphalt mixes and production temperatures. A study to validate the applicability of the flux chamber/gas chromatography mass spectrometry method was carried out during placement and compaction of ten rubberized asphalt test sections (three hot-mix and seven warm-mix, all produced at different temperatures). The study verified the applicability of the method in characterizing organic compounds in emissions during construction. Although trends in emissions reduction from the time of placement until after final compaction were similar for all the mixes tested, significant differences were noted between the concentration of alkanes in the emissions from the control mixes from the two asphalt plants and from the different warm mix technologies.

The preliminary results indicated that the method developed was appropriate for accurately quantifying and characterizing VOC and SVOC emissions during asphalt paving. The study was therefore extended to assess other gaseous and particulate polycyclic aromatic hydrocarbon (PAH) emissions from four additional asphalt mixes. Collection of PAHs through a fine particulate filter followed by a sorbent-backed filter with further gas chromatographic/mass spectrometric analysis was investigated. The results were used to quantify the potential benefits of using warm-mix asphalt technologies in reducing reactive organic gas emissions.

5.2 Conclusions

The following conclusions are drawn from the results of the work presented in this report with respect to the research issues identified:

- Accurate identification, quantification and measurement of emissions during HMA and WMA paving operations:
  - The developed methodology for characterizing emissions can be used to identify and quantify VOCs, SVOCs, and PAHs in asphalt fumes during production and paving activities.
- General observations about emissions during asphalt paving:
  - There is a significant difference (factor of two on average) between the concentrations of emissions in terms of total volatile organic compounds measured from loose mix (e.g., in a

truck, windrow, or when tipped into the paver hopper) and those measured from the road surface immediately after compaction.

  + The kinetics of emissions over time indicated that the majority of reactive organic gases are volatilized in the first hour after construction.
  + Gaseous phase PAH compounds in asphalt fumes are mainly low molecular weight compounds and are present at trace levels. The concentrations vary depending on the temperature of the mix at the time of sampling.
  + Particulate phase PAHs were found to be below the detection limit of this study (0.1 ng/µL) for all the mixes (hot and warm) assessed. The results confirmed that the temperature ranges at which the asphalt mixes were produced (123°C to 166°C) were not high enough to initiate significant PAH formation.
- Effect of WMA technologies on emissions during construction:
  + Alkane emissions consisted of n-hydrocarbons ranging from C_8 to C_{18}. Depending on the type of mix and its temperature at the time of sampling, the total alkane emissions from the warm-mixes were, in most instances, significantly lower than those measured from the hot-mixes (e.g., 117 µg/m^3 from one of the warm-mixes compared to 2,516 µg/m^3 from the hot-mix control).
  + In some instances, specific warm-mixes had higher alkane concentrations than the hot-mix controls. Consequently, any generalization with regard to emissions reduction through the use of warm-mix asphalt is inappropriate and should be restricted to comparisons of specific warm-mix technologies against a hot-mix control.
  + PAH concentrations correlated with initial mix production temperature, with those warm-mixes produced at the lowest temperatures showing the lowest PAH concentrations.

5.3 Recommendations

The following recommendations are made with regard to furthering the understanding of emissions generated during asphalt paving, and the effect of warm-mix technologies in reducing them:

- A laboratory procedure should be developed to simulate asphalt fume generation over a wide range of temperatures to better understand emission kinetics. Fumes generated using this procedure should be compared to those collected in the field using the procedure discussed in this report. The development of a laboratory procedure will allow the study of numerous different binders and production temperatures at very low cost compared to field collection. Determining the optimal temperature range that will minimize emissions concentrations without undermining performance properties will assist practitioners in deciding when to use warm-mix technologies and which type to use. Some unpublished initial research on this has been completed at the UCPRC and the results show considerable promise.
- The interactions between crumb rubber gradation, reaction time, and reaction temperature in rubberized asphalt binders, and the effect that warm-mix technologies have on these in terms of both performance and emissions properties should be further evaluated. The warm-mix technology chemistry, combined with lower production and paving temperatures, may lead to different crumb rubber/asphalt microstructure interactions that could result in different rheological properties and emissions characteristics.

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