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Research Report – UCD-ITS-RR-09-60

# Environmental Impacts and Energy Efficiency of Rubberized Warm Mix Asphalt (R-WMA) for Sustainable Road Construction: Final Progress Report

December 2009

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# Final Progress Report

*Project Name*: Environmental Impacts and Energy Efficiency of Rubberized Warm Mix Asphalt (R-WMA) for Sustainable Road Construction
*Project #*: **S04-2** *PI Name*: **John Harvey**
*Project Start Date*: **9-1-2009** *Project End Date*: **12-15-2009**
*Project Award:$* **9087.33**

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If you have completed your research, please provide the following:

1) Final Progress Report: Update on personnel, presentations, publications and impacts involved in this research. Please fill out pp. 2-3.
2) Research Brief: 2-page summary of research, as explained on p. 4 and using the template provided on pp. 5-6.
3) Final Product: As described on pg. 7, every project is required to submit a final product, usually a research report published in the ITS online publications database. One or more peer-reviewed papers can serve as the final product, if equivalent information is provided. For some projects, other types of products may be appropriate.

Please complete the entirety of this worksheet and email it to Kevin Ward (kcward@ucdavis.edu) The report is due one month after project completion. Please note we will continue to ask for brief *Project Follow-ups* listing project-derived publications and presentations. These *Follow-ups* are due every March 1 and September 1. Thank you for your time in completing this important information.

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# Final Progress Report

## Personnel Information

*Please list all other personnel (researchers, grad students, etc.) who have been involved in this project. Include name & title. Please be sure to include any unpaid volunteer researchers or assistants.*

John Harvey
Frank Farshidi

## Technology Transfer

### Presentations

Please list any presentations resulting from this funding during this reporting period. The PI does not need to be the presenter. This information is needed for federal reporting compliance.

Provide the following for each listing: Presenter, Month/Year, Title, Event, and Location.

*Presentation*: **Frank Farshidi, January 2010, Direct Measurements of Volatile and Semivolatile Organic Compounds from Hot- and Warm-Mix Asphalt, TRB, Washington D.C.**

*Presentation*:

### Publications

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Please provide as much citation information as you can for each item: Author(s), Year, Title, Publication, Volume, Issue, Pages (or status such as “submitted to but not published”). Please also mark all applicable boxes for each listing.

1) Citation: Farshidi, F., Jones, D., Kumar, A., Green, P. and Harvey, J. (2011). " Direct Measurements of Volatile and Semivolatile Organic Compounds from Hot and Warm Mix Asphalt." Transportation Research Record

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For assistance or clarifications, please contact either of the following STC staff:

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slhandy@ucdavis.edu

Kevin Ward, Research Reporting Coordinator
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Environmental Impacts and Energy Efficiency of Rubberized Warm Mix Asphalt (R-WMA) for Sustainable Road Construction

PI: John Harvey, Civil & Environmental Engineering (jtharvey@ucdavis.edu)

## ISSUE

The production of asphalt mixes at high temperatures contributes to air quality problems due to emissions of reactive organic gases (ROGs) and particulate matter (PM). Emissions released through the plant stack are regulated and controlled in the United States according to U.S. EPA AP-42, section 11.1 Hot Mix Asphalt Plants (Kinsey 1986). According to the current regulation, HMA 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 ducted source of emissions is the rotary drum dryer. Emissions from the drum consist of water (as steam evaporated from the aggregate); Particulate Matter (PM); products of combustion (carbon dioxide [CO2], nitrogen oxides [NOx], and sulfur oxides [SOx]); carbon monoxide (CO); and small amounts of organic compounds of various species (including volatile organic compounds [VOC], methane [CH4], and hazardous air pollutants [HAP]). The CO and organic compound emissions result from incomplete combustion of the fuel which mostly comes from combustion of natural gas. The ducted sources of emissions at the plants are tested annually by an independent agency and the results are reported to EPA for compliance and permit renewal.

The source of fugitive emissions, on the other hand, is mainly from load-out during transportation and during paving operations and are not currently monitored and controlled. These emissions mainly consist of organic compounds of various species including VOCs, SVOCs, and Polycyclic Aromatic Hydrocarbons (PAHs). Ground-level ozone (O3) is produced by the photochemical reaction of oxides of nitrogen (NOx) and reactive organic gases (ROGs) including VOCs and SVOCs.

Urban smog or ozone (O3) is a persistent public health problem with serious economic consequences in the United States (ARB 2010). In the years 2005 through 2007, more than 400 counties had eight-hour average O3 concentrations higher than 75 ppb (the current U.S. EPA ozone criterion, soon to be reduced to 70 ppb [California's current eight-hour average standard] or lower) (ARB 2010). The six counties with the highest O3 concentrations were located in California.

Two effective tools in reducing ozone formation potential in urban areas are to reduce ROG emissions and to control NOx. The reduction of ROG emissions is a high priority nationwide. According to the California Air Resources Board (ARB) inventory, emissions from light-duty vehicles (LDV) rank as the largest source of ROG and accounted for 600 tonnes per day (tpd) or 24.6% of the total ROGs in the state of California in 2005, but have been decreasing and are projected to account for 400 tpd or 18.9% of the total ROGs in 2010. As emissions from the major sources decrease over time, reducing emissions from smaller sources becomes a higher priority for achieving the new clean air standards. The ARB inventory lists statewide asphalt paving and roofing ROG emissions as 31.3 tpd (1.3% of total) for 2005, with a projected increase for 2010 to 32.15 tpd or 1.5% of the total. Moreover, different compounds do not react equally; therefore reducing total mass may not reduce reactivity and hence not reduce ozone. Therefore, it is important to identify and quantify reactive organic compounds present in fumes resulting from fugitive emissions during production, load-out, and paving construction activities which are of the objectives of this thesis.

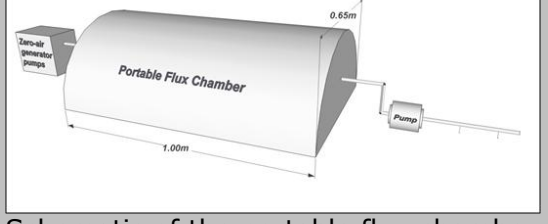
Studies into the reduction of ROGs from asphalt production and placement require accurate quantification of the emissions both at the asphalt plant and during paving operations. A number of protocols exist for measuring stack emissions at asphalt plants and these are routinely undertaken. However, emissions at paving operations are generally limited to measurements from monitors

attached to the paving equipment and/or workers, and because of the influence of numerous variables, are often inconsistent.

The investigations of asphalt emissions in the laboratory available in the literature are limited to small scale studies with small amounts of the asphalt binders only and are limited to a few conventional neat binders (Kito, Pirbazari et al. 1997; Vu-Duc, Huynh et al. 2007; Fernandes, Soares et al. 2009). Small amounts of asphalt binders are placed in special containers and heated to generate asphalt fumes. The drawbacks with these types of studies are (1) the fume generation methodology is not representative of the field conditions during production and construction of asphalt mixes; (2) studies are conducted with a limited number of neat binders from limited sources; (3) the studies are focused on a small range of temperatures and are not in the range that occurs in the field. With the widespread application of WMA technologies, there is a need to evaluate and measure emissions more accurately in the field and include different HMA, WMA, and other modified mixes (i.e. R-HMA and R-WMA).

Development and assessment of a protocol/procedure and a methodology for accurately measuring surface emissions during HMA and WMA paving operations is needed to quantify the potential environmental impacts of different HMA mixes and will enable engineers, practitioners, and regulators with a pragmatic tool for quantifying environmental impacts in decision making processes for alternative materials.

## KEY FINDINGS



Schematic of the portable flux chamber on the pavement surface

Emissions from the production and paving of hot-mix asphalt are being increasingly scrutinized. The introduction of a range of warm-mix asphalt (WMA) technologies could potentially lead to a reduction in these emissions. However, the measurement of these emissions is both complex and expensive. To overcome this, a simplified protocol was developed as part of this investigation that can be used in addition to conventional methods, and which allows direct comparison of emissions from different mixes measured at the pavement surface during construction. A portable "flux" chamber is used to capture and directly measure emissions before and immediately after compaction and then two hours after compaction. Emissions are collected in activated charcoal sorbent tubes and analyzed using gas chromatography mass spectrometry (GC/MS) in the laboratory to identify individual compounds. The protocol was evaluated during the construction of a test track, which was later used in an accelerated pavement test to compare the performance of three rubberized hot-mix asphalt (R HMA) controls against seven different rubberized warm-mix asphalt (R-WMA) sections. The measured reactive organic gases (ROGs) included selected volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). The results demonstrated that the warm mix asphalt technology type, temperature and level of compaction influence the emission characteristics significantly.

## POLICY IMPLICATIONS

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 organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) for different asphalt mixes and production temperatures. A comprehensive validation study was carried out during placement and compaction of three rubberized hot mix asphalt control test sections and seven rubberized warm mix asphalt test sections. The study verified the applicability of the method in characterizing organic compounds in emissions during construction.

Although trends in emission reduction from the time of placement until after final compaction were similar for all the mixes tested, significant differences were noted in the

alkanes' concentration of the emissions from the control mixes from the two asphalt plants and from the different warm mix technologies. In some instances, the warm mixes had higher concentrations than the control. 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 WMA technologies against HMA controls.

## METHODOLOGY

Emissions sampling, using the equipment and procedure shown above, was conducted on a designated area adjacent to the test track. Loose material was sampled from the first truck for each mix. Half of the sample was placed on the ground to measure emissions from the loose mix. The remainder was spread in an area of 15 m x 1 m and compacted to a thickness of 60 mm with small steel vibratory roller. Emissions were measured immediately after compaction and again after two hours.

The temperature inside the chamber was monitored during sampling with a thermocouple. The chamber inlet was connected to two zero-air generators operated at 15 L/min. These generators have an ultra violet lamp for the control of microorganisms, an activated carbon/alumina mixture for the removal of trace quantities of NOx and O3, a carbon monoxide catalyst to convert CO to CO2, 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. Downstream on the outlet of the chamber, sampling on sorbent tubes was conducted at two different flow rates simultaneously (500 mL/min and 1.5 L/min). Coconut-based charcoal tubes, which are considered the most desirable to sample volatile and semi-volatile organic compounds for extended periods, were used for sampling. A 15 minute sampling duration was used for the first two measurements (i.e. before and immediately after compaction) and a 30 minute sampling duration for the third measurement (i.e. two hours after compaction).

Time integrated emissions samples were collected using activated charcoal tubes. Tubes containing 400 mg and 200 mg of activated carbon in two successive sections were used for sample collection and breakthrough determination respectively. The sampling pump was calibrated with an electronic digital flow calibrator before and after collection of each sample. Tubes were capped immediately after sampling, placed individually into sealed plastic bags, and then transferred to the laboratory in a cooler with ice packs (ASTM 1988). Samples were refrigerated at 4°C until they were processed to ensure that the compounds are stable before extraction and recovery.

Gas chromatography-Mass Spectrometry analyses were performed for the determination of VOCs and SVOCs employing an Agilent 6890-5973 series gas chromatograph coupled with a mass spectrometer (Agilent, 5973N). The gas chromatograph, equipped with a 30 m x 0.25 mm with 0.25 µm film thickness DB-5 capillary column, provided satisfactory separation of various compounds. The helium carrier gas was introduced at a rate of 1.0 mL/min and linear velocity of 20 cm/s. The initial column temperature was maintained at 50°C for 4 minutes, then raised to 125°C at a rate of 2°C/min, and finally to 280°C at a rate of 10°C/min.

The instrument was calibrated with a standard solution containing 16 alkanes (C8- C23) to ensure linearity of the system. The GC was recalibrated if the response factor varied by more than 10 to 15 percent. The carbon disulfide solvent was also analyzed to ensure that it was free of contaminants.

## RESULTS

The alkanes identified by GC-MS consisted predominantly of straight chain and branched-chain paraffins ranging from undecane (C11) to docosane (C22) hydrocarbons. There is no universally agreed definition for categorizing SVOCs from VOCs, but a common (and practical) cut-off is the chromatographic elution of the unbranched C16 alkane (n-hexadecane). Mixtures below this point are considered to be VOCs and those above this point are considered to be SVOCs. Other definitions, such as by boiling point, can be used

when purified molecules are available, but are not appropriate for mixtures (Vu-Duc, Huynh et al. 2007). Although different VOCs and SVOCs have differing tendencies to react and form ozone, current EPA regulations combine them all equally by mass. Concentrations in micrograms per cubic meter (µg/m3) and flux rates in micrograms per square meter per minute (µg/m2/min) were calculated for each identified compound for all of the mixes and sampling periods.

Total 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 from running the standard solution.

Total ROG emissions from the control and warm mixes before and immediately after compaction respectively showed that the emissions flux differs depending on the mix type and the temperature inside the chamber at the time of sampling. Moreover, the emissions are significantly higher for the loose mix before compaction compared to the results obtained immediately after compaction, as expected. For instance, the flux of the ROGs of the first R-HMA control was 3,500µg/m2/min before compaction and 2,000 µg/m2/min immediately after compaction. It is important to note that the temperature dropped from 85°C to 77°C inside the chamber while sampling before and after compaction respectively, and that both the temperature drop and compaction would influence the decrease in emissions.

The WMA technology type also had a significant effect on the ROG emissions before compaction, while temperature had a more moderate effect. Depending on the warm mix technology used, the increase in emissions was as high as three times with respect to total reactive organic gas emissions concentration compared to the control at even lower loose mix temperatures. These findings demonstrate the dependence of alkane emissions on the type of WMA technology and temperature, and illustrate the importance of considering both factors in achieving reductions in emissions during asphalt paving.

## PUBLICATIONS & PRESENTATIONS

Farshidi, F., Jones, D., Kumar, A., Green, P. and Harvey, J. (2011). " Direct Measurements of Volatile and Semivolatile Organic Compounds from Hot and Warm Mix Asphalt." Transportation Research Record

## NEW RESEARCH DIRECTIONS

*Preliminary results from this study indicate that the method developed is appropriate for accurately quantifying and characterizing VOC and SVOC emissions during asphalt paving. Based on the results obtained to date, the study needs to be extended to assess other gaseous and particulate polycyclic aromatic hydrocarbons (PAH) emissions during paving. Collection of PAHs through a fine particulate filter followed by a sorbent-backed filter with further Gas Chromatographic/Mass Spectrometric (GC/MS) analysis needs to be investigated*

*Find out more about the UC Davis Sustainable Transportation Center at http://stc.ucdavis.edu*

*The research was supported by a grant from the Sustainable Transportation Center at the University of California Davis, which receives funding from the U.S. Department of Transportation and Caltrans, the California Department of Transportation, through the University Transportation Centers program.*

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Please include a table of contents, list of tables, and list of figures showing corresponding page numbers.

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