United States
Environmental Protection
Agency

Air and Energy Engineering
Research Laboratory
Research Triangle Park, NC 27711

Research and Development

EPA/600/SR-94/135 November 1994

EPA

Project Summary

Evaluation of Emissions From Paving Asphalts

C.C. Lutes, R.J. Thomas, and R. Burnette

This work provides data from pilot-scale measurements of the emissions of specific air pollutants from paving asphalt both with and without recycled crumb rubber additives. The methods used in this work measured emissions from a static layer of asphalt maintained for several hours near the highest temperature likely to be encountered in a real paving operation (176° C). Although concentration levels observed for most species were in most cases near the detection limits of the analytical methods applied, statistically significant emissions of a variety of pollutant species were observed. Volatile organic compound (VOC) analyses showed significant amounts of benzene emitted from both types of asphalt studied. An analysis targeting 16 polycyclic aromatic hydrocarbons (PAHs) species of primary interest revealed significant emissions of 7 of the 16 species when the AC10 asphalt without rubber tests were compared to the facility blank tests. The emissions of 5 of 16 PAH species were significantly higher in the AC10 thin layer with rubber tests than in the facility blank tests. The concentrations observed, though significant, were close to the limit of detection. Statistically significant emissions of both total particulates and PM_{10} were found from both types of asphalt hot-mix material tested.

This Project Summary was developed by EPA's Air and Energy Engineering Research laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Paving asphalt is a widely used product with incompletely characterized emissions to the atmosphere. Approximately 20 million tonnes of asphalt were sold in 1976. Asphalt is most often used in paving applications as a "hot-mix" of petroleum-derived asphalt and aggregate material (crushed stone or gravel).

Typical elemental analyses of asphalt show the following approximate weight percentages: carbon, 80-90%; hydrogen, 5-11%; sulfur, 0.4-7.3%; nitrogen, 0.4-0.9%; and oxygen, 0.0-2.0%. Among the compounds identified in a soxhlet extract of an asphalt sample were dibenzothiophene, methyldibenzothiophene, phenanthrene, pyrene, and fluoranthene.

A previous study attempted to measure pollutant levels in the emissions, known as "blue smoke," from an asphalt hot-mix facility using a temporary enclosure to aid sampling. Concentrations measured (in ppm, vol) were methane (2-3 ppmv), C2-C6 hydrocarbons (< 1 ppmv), hydrogen sulfide (< 0.2-1.5 ppmv), sulfur dioxide (< 2 ppmv), carbon monoxide (3-6 ppmv), and nitrogen dioxide (0.05-0.08 ppmv). Concentrations were also reported for the following organic species (μg/1,000 m^3): pyrene (44-240), benzo(a)anthracene (5-38), benzo(a)pyrene (3-22), benzo-(e)pyrene (non-detectable -40), perylene (5-16). The particulate matter (PM) was determined to be composed of paraffins (28%), cycloparaffins (40%), aromatics (26%), and sulfur aromatics (6%). An evaluation of available literature shows

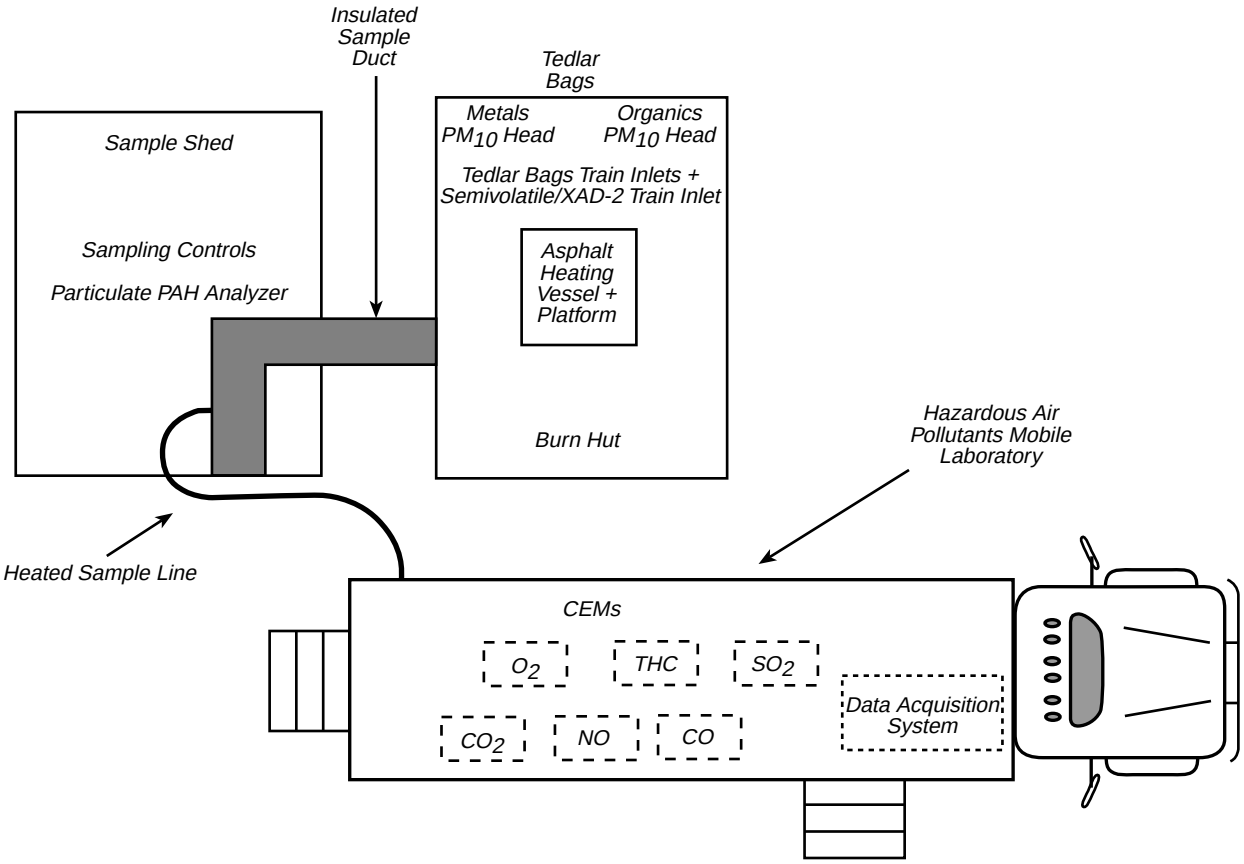

Figure 1. *Aerial view of the products of incomplete combustion facility.*

a lack of emissions data for specific pollutants measured in such a way that emissions from asphalt paving could be estimated.

The objective of this work, conducted through the guidance of an EPA-approved Quality Assurance (QA) Test Plan (AEERL QA Category II), was to provide quantitative data on the emissions of specific pollutants from paving asphalt. In addition, because paving asphalts with recycled crumb rubber additives are beginning to be used (The Intermodal Surface Transportation Efficiency Act requires the use of rubber additives), this project also compared the emissions of asphalt with and without this additive. The acquired data are intended to provide insight into the possible health effects of human exposure to asphalt emissions as well as to help assess the contribution of asphalt emissions to ozone non-attainment. This report also provides baseline data to which emissions from other modified asphalt products can be compared.

Approach

The project consisted of a replicate study to collect and qualitatively and quantitatively characterize organic and inorganic emissions from the asphalt paving processes. Although it was recognized that asphalt experiences a variety of temperature conditions and physical disturbances during a paving process, the investigators believed that it was impractical to simulate this temperature profile or agitation in a small-scale test. Therefore, a measurement of emissions from a static layer of asphalt, maintained for a period of several hours near the highest temperature likely to be encountered in a real paving operation, was used to provide a realistic basis for the estimation of emissions from an asphalt process. Samples of paving asphalts provided to EPA by asphalt vendors were heated in a specially designed stainless steel vessel within the Open Burning Simulation Test Facility (see Figures 1 and 2). Testing included two types of asphalt—an AC10 grade asphalt hot mix and an AC10 grade asphalt hot mix with a crumb rubber additive.

Air sampling was conducted within the facility through medium volume PM_{10} heads for semivolatile organics and particulate phase lead. Samples of volatile organics were removed directly from the facility and collected in Tedlar bags. A portion of the air within the facility was diverted to an adjacent sampling facility via an induced draft duct. A portion of the sample from the induced draft duct was also monitored for carbon dioxide (CO_2), carbon monoxide (CO), nitric oxide (NO), oxygen (O_2), sulfur dioxide (SO_2), particulate-bound polycyclic aromatic hydrocarbons (PAH), and total hydrocarbons (THC) by a series of continuous emission monitors (see Figure 1). The organic constituents were analyzed both qualitatively and quantitatively using gas chromatograph/mass spectrometer (GC/MS), the lead was quantified using a graphite furnace atomic adsorption method (GFAA). Hydrogen sulfide was measured using a colorimetric Dräger tube methodology.

The concentration data for all analytes were converted to emission rates expressed on a per time and per surface area basis. These rates were calculated from the volumes sampled by each train, the volumes of air flowing into the test facility, the measured mass or concentration of analyte, the surface area of the asphalt heating vessel, and the duration of the sampling period.

Results and Conclusions

Successful triplicate tests were conducted of an AC10 asphalt hot-mix material, of an AC10 asphalt hot-mix material with a rubber additive, and of a facility blank test condition. Though concentration levels were, in most cases, near the detection limits of the analytical methods applied, statistically significant emissions of a variety of pollutant species were observed (data summarized in Tables 1 and 2).

VOC analyses showed statistically significant amounts of benzene emitted from both types of asphalt studied. None of the other 55 volatile compounds targeted for quantitative analysis were observed in statistically significant concentrations. A wide variety of volatile compounds, not specifically targeted for quantitative analysis, were also seen in various samples although no consistent set of compounds could be established.

Analysis of vapor-phase semivolatile species showed statistically significant concentrations of 2-methylphenol from the AC10 with rubber tests and significant emissions of diethyl phthalate from both hot-mix materials. Observations of phthalate emissions should be treated with extreme caution because phthalates are notorious as analytical artifacts because they are present in a very wide variety of plastic materials.

None of the other semivolatile species targeted showed statistically significant emissions in the vapor-phase analyses.

Analysis of particulate-phase semivolatile species by full scan mass spectrometry showed statistically significant concentrations of bis(2-ethylhexyl)phthalate. To reiterate, observations of phthalate emissions should be treated with extreme caution because phthalates are notorious as analytical artifacts and are present in a very wide variety of plastic materials. None of the other semivolatile species targeted showed statistically significant emissions in the PM analyses.

Because some PAH species were observed at concentrations near the detection limit in the full scan mass spectrometry analyses and analytical interferences from hydrocarbon coeluters were suspected, an additional analysis of semivolatile particulate-phase samples was conducted by a more sensitive selected ion monitoring method. This analysis targeted 16 PAH species of primary interest to the project and revealed statistically significant emissions of 7 of the 16 species when the AC10 thin layer without rubber tests were compared to the facility blank tests. The emissions of 5 of 16 PAH species were significantly higher in the AC10 thin layer with rubber tests than in the facility blank tests. The emissions of two species were significantly higher in the tests without the rubber additive than in the tests with the additive.

No statistically significant emissions of hydrogen sulfide were found in these tests. A very low level of lead may have been emitted in the AC10 thin layer without rubber tests. Statistically, significant emissions of both total particulates and PM_{10} were found from both types of asphalt hot-mix material tested.

The estimated emission values measured in this work could be combined with appropriate fate and transport data to model the exposure of populations (either occupational or general) to pollutants generated in the asphalt paving process. To facilitate such a modeling effort, the emissions results have been presented as a function of asphalt surface area so that emissions from the paving of an area of road could be estimated based on the road length and width. Modelers should, however, recall the limitations of this pilot-scale study, especially those discussed in Section 3.1 of the full report. The facility air concentrations reported in this work **should not** be used directly to evaluate risk to exposed populations because exposure scenarios will vary widely.

Although some statistically significant differences were found between the emissions from the asphalt materials tested with and without rubber, these differences were not in general dramatic. In addition, although the emissions for some pollutants, such as benzene, were significantly higher in the rubber-containing asphalt, the emissions of other pollutants, such as benzo(k)fluoranthene, were higher in the non-rubber-containing asphalt. Therefore, the data gathered in these experiments indicate that the addition of rubber to asphalt hot-mixes does not have a dramatic impact on the air emissions generated in the paving process.

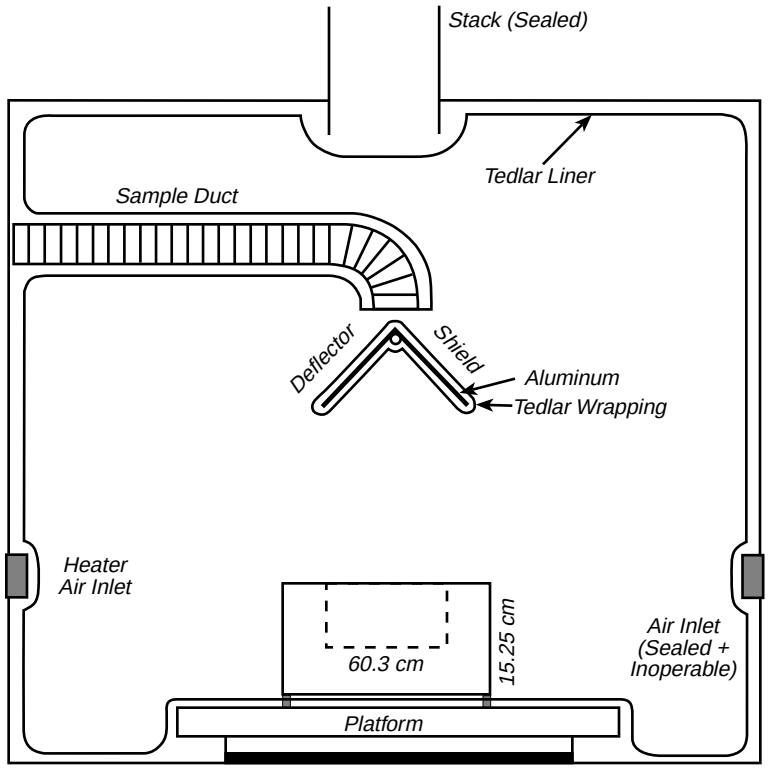

Figure 2. *Diagram of the burn hut as configured for the asphal heating tests; some sampling equipment not shown for clarity.*

Table 1. *List of Compounds with Statistically Significant Results*

Compounds for which AC10 without rubber emissions were significantly higher than the facility blank emissions:
Benzene
Diethyl Phthalate
Napthalene
Fluoranthene
Pyrene
Chrysene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3-cd)Pyrene
Lead
PM_{10} Particulate (as measured on both trains)
Total Particulate

Compounds for which AC10 with rubber emissions were significantly higher than the facility blank emissions:
Benzene
2-Methyl Phenol
Diethyl Phthalate
bis(2-Ethylhexyl)phthalate
Fluoranthene
Pyrene
Benzo(a)pyrene
PM10 Particulate (as measured on both trains)
Total Particulate

Compounds for which AC10 without rubber emissions were significantly higher than AC10 with rubber emissions:
Benzo(k)fluoranthene
Benzo(a)pyrene

Compounds for which AC10 with rubber were significantly higher than AC10 without rubber emissions:
Benzene
m,p-Xylene
2-Methyl Phenol

Table 2. *Summary of Levels of Significance and Estimated Emission Values*

	AC10 without rubber vs. facility blank		*AC10 with rubber vs. facility blank*	
Compound	*Level of significance*	*Estimated emissions (µg/(m²*min)*	*Level of significance**	*Estimated emissions µg/(m²*min)*
Benzene	*0.002*	*≤ 57*	*0.002*	*≤ 110*
2-Methyl Phenol	*NS*	*≤ 7.2*	*0.05*	*≤ 23.7*
Diethyl Phthalate	*0.10*	*≤ 32.7*	*0.10*	*≤ 34.37*
Bis(2-ethylhexyl)phthalate	*NS*	*≤ 5.1*	*0.10*	*≤ 5.3*
Naphthalene	*0.10*	*≤ 0.103*	*NS*	*≤ 0.063*
Fluoranthene	*0.10*	*≤ 1.648*	*0.10*	*≤ 1.178*
Pyrene	*0.10*	*≤ 1.469*	*0.10*	*≤ 1.612*
Benzo(a)anthracene	*NS*	*≤ 0.786*	*0.10*	*≤ 0.653*
Chrysene	*0.02*	*≤ 4.420*	*0.05*	*≤ 1.957*
Benzo(k)fluoranthene	*0.01*	*≤ 1.106*	*NS*	*≤ 0.306*
Benzo(a)pyrene	*0.05*	*≤ 0.660*	*0.10*	*≤ 0.204*
Indeno(1,2,3-c,d)pyrene	*0.05*	*≤ 0.141*	*NS*	*≤ 0.065*
Lead	*0.05*	*≤ 0.542*	*NS*	*≤ 1.10*
PM_{10} Particulate (organic train)	*0.05*	*26,850*	*0.05*	*12,710*
Total Particulate (organic XAD-2 train)	*0.05*	*27,700*	*0.05*	*12,950*
PM_{10} Particulate (metals train)	*0.05*	*37,710*	*0.10*	*19,810*

NS Not statistically significant at >90% confidence level.
* Level of significance is defined as the probability of making a type 1 error (i.e., of falsely rejecting the tested hypothesis, in this case the tested hypothesis is that the means are equal).

C. Lutes, R. Thomas, and R. Burnette are with Acurex Environmental Corp., P.O. Box 13109, Research Triangle Park, NC 27709.

Bobby E. Daniel is the EPA Project Officer (see below).

The complete report, entitled "Evaluation of Emissions from Paving Asphalts," (Order No. PB95-129110/AS; Cost: $36.50; subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
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