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**Laboratory Generation and Evaluation of Paving Asphalt Fumes**

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**ABSTRACT**

A novel laboratory asphalt fume generator was developed and validated against fumes collected on personnel monitors from field paving sites and above paving asphalt storage tanks. Once the apparatus was validated, fumes were generated from the eight core Strategic Highway Research Program (SHRP) library of single crude asphalts, as well as from synthetically produced positive and negative control asphalts. The fumes were characterized using a number of analytical techniques including GC/FID, GC/MS, UV/Fluorescence and a short term bioassay called the Modified Ames Test. For comparison purposes, the same methods were applied to fume condensate preparations from the NIOSH animal skin painting studies. Based on the chemical and biological tests, these SHRP asphalt fumes were found to have a lower carcinogenic potential than a NIOSH fume fraction found to be non-carcinogenic in the NIOSH studies.

**Key Words:** Asphalt Fume, SHRP Asphalts, Asphalt Fume Fluorescence, Modified Ames Assay

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### **Laboratory Generation and Evaluation of Paving Asphalt Fumes**

Laboratory generation of asphalt fumes which mimic those found in real world exposure has been found to be more complicated than originally expected (1). Studies of fume generation parameters under controlled conditions have led to the development of prototype units, and to a set of criteria by which the fumes can be compared to those generated in field operations. In this study, a laboratory fume generator developed by Heritage Research was investigated and validated against field generated asphalt fumes collected in the breathing zone of paving asphalt road workers.

The new unit will allow the study of asphalts in a controlled laboratory setting where the effects of workplace confounders such as diesel exhaust, smoking, diesel fuel used for equipment rinsing, additives, etc. can be eliminated. A second advantage of the new generator is that it makes possible the controlled study of a variety of asphalts from different crudes - thereby furthering our understanding of fume chemistry variability and composition.

To get a good cross section of the asphalts used in the United States eight core (single crude) asphalts were obtained from the Strategic Highway Research Program (SHRP) library. The Heritage fume generator was used to produce fumes for analysis. Two synthetically produced asphalts were also fumed as positive and negative controls. During this study, fumes were also collected from a commercially available asphalt and the generator fumes were compared to those produced in a workplace environment from the same asphalt.

### **MATERIALS AND METHODS**

#### **Paving Asphalt**

This study used eight paving asphalts from the SHRP library of materials. These asphalts were selected because they represent a significant number of the major type crudes which are used to produce asphalt cements for paving in the United States. All eight paving asphalts are from

single crude sources and are straight run vacuum distilled. The fumes generated from these asphalts were compared to retained fume samples from the National Institute of Occupational Safety and Health (NIOSH) (2) animal skin painting studies of roofing asphalt fumes. These NIOSH fumes were essential for such a comparison since they represent the only fume condensates tested for carcinogenicity in animals.

The single crude paving asphalts produced for the SHRP program have been extensively studied for their engineering and chemical properties, but little has been published on their fume composition or potential health effects.

Five 20-liter (five-gallon) buckets of each asphalt were sent to an independent laboratory (ATEC Associates) for recoding and labeling to ensure a blind study. A positive and negative control were also included in the study.

In addition, an asphalt from an Indiana Department of Transportation (INDOT) paving project on U.S. 31 (1997) (a PG 64-22 performance graded paving asphalt) was also fumed. This asphalt was one of those used in developing the Heritage fume generator, and was included in the study to re-verify that the generator was producing fumes similar in composition to field fumes. This straight run vacuum distilled asphalt is a widely used commercial product sold in the Midwest part of the United States.

The negative control asphalt was synthetically produced in the laboratory by blending a solvent precipitated hard asphalt (80.2% by weight) and a lube oil (19.8% by weight) which has been solvent refined to meet lube oil labeling (non-carcinogenic) requirements. This asphalt has poor physical properties for paving asphalt and is not a practical commercial product. It was developed because it was expected to produce a fume which is biologically and chemically low in the 4-6 Ring Polynuclear Aromatic Compounds (PACs) which are known to be the principal mediators of carcinogenicity in animal skin painting studies (3).

The positive control paving asphalt, like its negative counterpart, was synthetically produced in the laboratory. In this case a solvent precipitated hard asphalt (81.5% by weight) was blended with a catalytically cracked slurry (CCS) oil (18.5% by weight blended). CCS is the bottom residue of a catalytic cracker in a petroleum refinery and is both highly mutagenic and carcinogenic in skin painting studies due to its high levels of 4-6 Ring PACs (4). This asphalt, like the negative control, would not meet physical property requirements for paving asphalt cements in the United States.

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### **NIOSH Fume Fraction**

Sample retains from the NIOSH study conducted by Sivak (2) were provided by NIOSH. These samples included Whole Fume Condensates as well as Whole Fumes which had been separated using HPLC into five increasingly polar fractions. Fraction A (the least polar) was non-carcinogenic in animal skin painting studies. Fractions B and C which comprise about 18% of the whole fume were carcinogenic, and Fraction D and E (the most polar fractions) were non-carcinogenic.

Previous studies on these fractions found that the likely cause of the biological activity are 4-6 Ring PACs which include alkylated PAHs and sulfur heterocycles (thiophenes) (3).

### **Laboratory Fume Generator**

The Heritage laboratory fume generator is shown in [Figure 1](#). The unique features of the unit are designed to mimic the conditions found in asphalt paving projects. These include keeping the asphalt cement in an undisturbed (unmixed) condition in a storage vessel until it flows

across a plate as a thin film at a controlled rate of time. The thin film simulates coating of asphalt on aggregate in hot mix. As the asphalt flows across the plate, it releases fumes which are captured by incoming air and carried to adsorbent tubes for collection. The vessel and plate are carefully controlled to simulate paving asphalt temperatures (~155°C). The plate is 0.09 m<sup>2</sup> (1 ft<sup>2</sup>) and is warmer at the entrance than the exit to simulate paving conditions where cooling starts immediately. Flow rate across the plate is controlled at approximately 150 g/min. to simulate typical quantities of asphalt coming from the pavers per unit of area. In the initial studies fumes were generated from ~50,000g for an average of 284 minutes. Flow of asphalt cement is maintained continuously in the fume generator by refilling the heated storage with additional asphalt while generating fumes. The average amount of fume collected was 176 mg which represented about 3.5x10<sup>-4</sup> percent of the parent asphalt. This percentage is similar to that calculated for field operations. The extremely small amount of fume collected is barely enough for chemical analysis and mutagenicity testing.

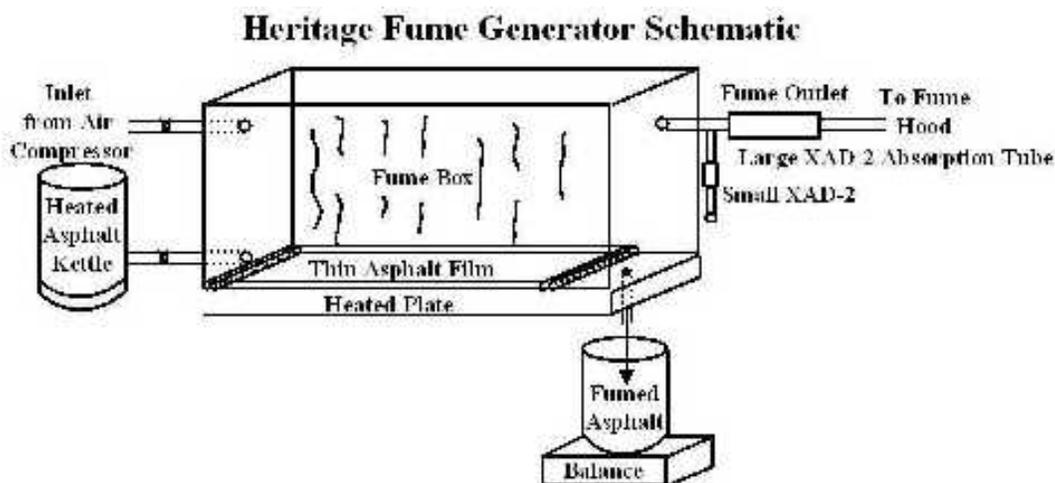


FIGURE 1 Heritage Fume Generator

Figure 1

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### Laboratory Fume Collection

Fumes were collected on Amberlite XAD-2 resin, a hydrophobic adsorbent material. Offering excellent physical and chemical stability, it is a macroreticular, styrene-divinylbenzene copolymer, nonionic bead, composed of an agglomeration of microspheres. For this application, the resin required extensive cleaning and verification of purity. This grade of resin is commercially available through Supelco (Supelpak-2 Resin Cat. No. 20279).

A large 9-gram chromatography column was used for collection of fumes during the entire day's run. Pre-assembled smaller XAD-2 standard tubes (600 mg SKC Cat. No. 226-30-04) were used for one-hour collections at the beginning, middle, and end of the fuming process. The final residue sent for biological testing was the composite material from all tubes. There were two runs where the first 1-hour tube did not chemically resemble that of the large or other 1-hour tubes. In these instances, the first tube residue was not composited with the others. The majority of the material was collected on the large XAD. The analytical results showed that this material is representative of the composite.

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### Extraction of Laboratory Fumes from XAD

The asphalt fume residue was recovered from the XAD columns by elution with methylene chloride. Prior to elution, the beads were completely saturated with the solvent, then allowed to sit for either 30 minutes (9-gram tubes) or 10 minutes (600-mg tubes). The final elution volumes were 100 mL and 10 mL respectively. After completion of all chemical tests, the

methylene chloride was evaporated using a nitrogen evaporation system (with low heat), and sent for biological testing to obtain the Mutagenicity Index (MI).

### **Field Fume Collection**

Fumes from a paving project were collected on four paving workers using a modification of NIOSH Method 5506 (5). Workers carry small pumps which draw air from their breathing zone at 1.5-2.0 L/min. through a cassette. The modification included pre-extracting the filters with benzene. The outlet of the cassette was attached to an XAD-2 column. Both the filter and XAD-2 tube were combined and extracted as described above for the laboratory extractions. Fumes for Modified Ames testing were collected above a storage tank at the hot mix plant using a 9 g XAD-2 column.

### **GC/MS Analysis**

All extracts were analyzed by GC/MS using a Varian Ion Trap Gas Chromatograph/Mass Spectrometer. Two microliters of methylene chloride extract were injected on a 30 m DB-5 capillary column in splitless mode. The injector and transfer line temperature were 280°C, the oven was heated at 90°C for 3 minutes and programmed to rise to 320°C at 10°C/min., and then held for 11.5 minutes. The trap temperature was 230 °C.

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### **GC/FID Analysis**

The same extracts were also analyzed by gas chromatography with flame ionization detection (GC-FID) for mass determination and simulated distillation. Mass was calculated using an external standard method against a kerosene calibration curve. This method was validated for several asphalt fume samples by comparison to gravimetric data. The simulated distillation data was obtained by following ASTM D-2887 (6) protocol. Both determinations were obtained from the same chromatogram, which was generated by injection of a 2.0 microliter aliquot onto a Varian Model 3400 Gas Chromatograph equipped with a 1077 split/splitless injector at 290°C and the detector at 330°C, using helium as carrier gas. The column, a J&W DB-5, 30 m x 0.32 mm ID 0.45 micron film, was temperature programmed from 40°C (3 min.) to 305°C at 10°C/min and held for 12 minutes. The Varian STAR Simulated-Distillation Software was utilized for the calculations.

### **Fluorescence Analysis**

A known volume of the methylene chloride extract from each XAD tube or Filter + XAD tube was exchanged into cyclohexane and brought to a final volume of 10.0 mL for fluorescence analysis. A Perkin Elmer Luminescence Spectrometer LS50B was used to measure the fluorescence intensity in units of 'EU/g' (Emission Units per gram) at an excitation of 385 nm and an emission of 415 nm. Both slit widths were 3 nm. Scan speed was 1000 nm/minute.

The method was developed to provide a simple, yet sensitive and selective testing procedure that would provide information as to the level of fluorescence activity in an asphalt fume matrix. To assure linearity, the intensity was kept to less than 600 emission units by dilution if necessary. After obtaining the fluorescence of the initial solution, it was passed through a 12 mL cyanopropyl solid phase extraction (SPE) cartridge and the fluorescence re-measured. This SPE step removes some of the polar components that fluoresce, but do not significantly contribute to biological activity (3). The Pre-CN correlation of fluorescence with skin painting results was reasonably good ( $r^2 = 0.8$ ). The cyanopropyl step improved the correlation to an  $r^2$  of 0.95. The Pre-CN reading is therefore used to provide a maximum level, as well as to ensure that the SPE cartridge is not overloaded. When the Pre-CN value was extremely low, the cyanopropyl cleanup step was eliminated.

The fluorescence instrument was validated using a sealed water cell to monitor the Raman peak wavelength, signal to noise ratio, and the Rayleigh scatter for 350 nm and 550 nm. Instrument sensitivity and wavelength checks were also performed using a 0.004-mg/L solution of 9,10-Diphenylanthracene [DPA]. At an excitation of 385 nm, two maxima were observed: one at 408 nm and the second at 432 nm.

Standardization was accomplished using a minimum of three concentrations of the DPA ranging from 0.04 mg/L to 0.2 mg/L. The calibration was performed for both the Pre- and Post-CN samples. The average response factor was divided by a reference value to allow normalization of results between laboratories.

The Pre-CN endpoint is the fluorescence intensity of the solution multiplied by all dilution factors and the normalization factor, and divided by the weight of fume and an arbitrary factor of 10,000 in order to obtain simpler numbers. The Post-CN EU/g is calculated the same way, with the result multiplied by 0.7 to account for the reduced volume after cleanup.

### Modified Ames Test (MI)

The Modified Ames Test was performed in accordance with the procedures described in ASTM Standard Method E 1687-95 (7).

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## RESULTS

The results from the asphalt fume generation are presented in [Table 1](#). The eight SHRP core asphalts are labeled A-H. Asphalt fume C was not used in the correlation because too little was obtained to measure the MI reliably. I and J are the negative and positive controls. K and L are lab and field fumes collected from the same asphalt. Retained NIOSH fume samples were also evaluated in the same way on the SHRP asphalts and are reported in [Table 2](#). [Figure 2](#) compares graphically the UV/Fluorescence data with Mutagenicity Index ( $r^2 = 0.95$ ). This result suggests that the 4-6 Ring PACs detected by fluorescence are the same species responsible for mutagenicity and carcinogenicity. Also shown in [Figure 3](#) is the correlation between % fume boiling above 316°C ( $r^2 = 0.88$ ) and UV/Fluorescence. The high correlation ( $r^2 = 0.88$ ) is further evidence that the relatively high-boiling 4-6 Ring PACs are the principal sources of both fume fluorescence and biological activity.

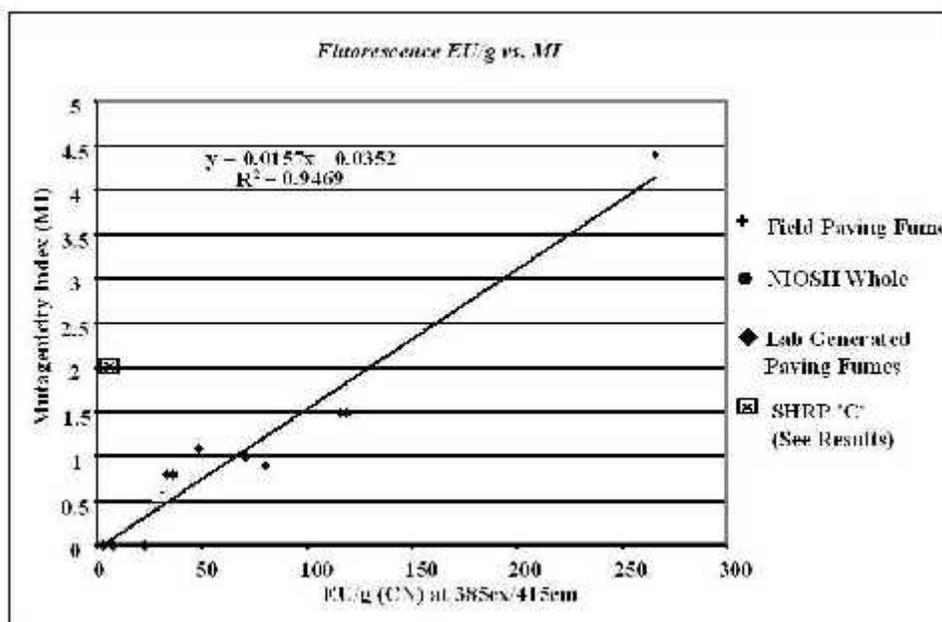


Figure 2

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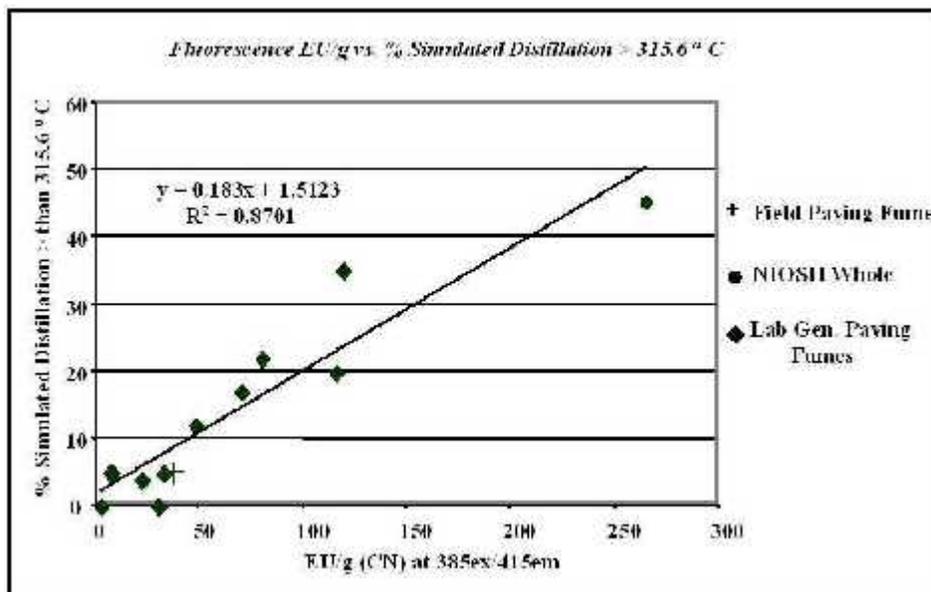


Figure 3

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## DISCUSSION

The roofing asphalt fume condensate and condensate fractions provided to Heritage Research by NIOSH, although not representative of the fumes to which workers are exposed (1), were invaluable reference standards for the studies described here. However, because of the broad range of biological responses found in these studies and a better understanding of the compounds responsible for the carcinogenicity, the results from these materials are extremely informative. Recent studies (3) of these NIOSH fumes found a subset of 4-6 ring PACs correlated well with the biological activity found in these studies. Only whole fumes and Fractions B and C were carcinogenic. Fractions A, D, and E were non-carcinogenic in five different skin painting studies when applied separately or in combination to the mouse skin. These results found in [Table 2](#) indicate that both MI and UV/Fluorescence track well with each other ([Figure 4](#)). A graphical plot of EU/g for both the NIOSH Whole fumes and the laboratory and field generated fumes is found in [Figure 2](#). The only laboratory fume greater than the UV/Fluorescence of Fraction A (highest non-carcinogenic fume) is the synthetic positive control which suggests that a measurable amount of the biologically relevant material was transferred to the fumes and properly evaluated.

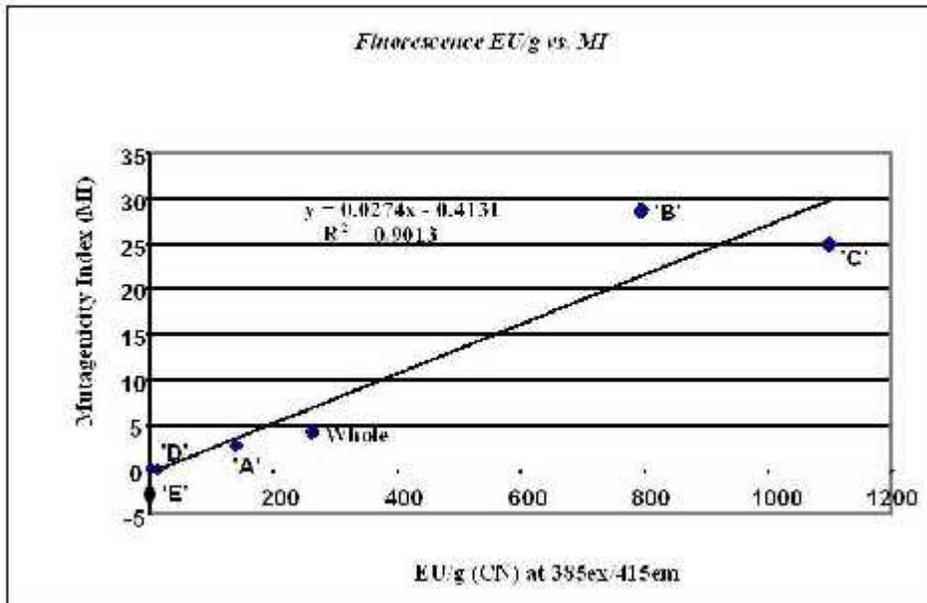


Figure 4

## CONCLUSION

1. The laboratory fume generator produced fumes similar to those generated in the field as judged by GC/FID (Simulated Distillation), Fluorescence (EU/g) and mutagenic activity comparisons of fumes from the same asphalt (Sample K and [Table 1](#)).
2. The laboratory-produced asphalts used as positive (Asphalt J) and negative (Asphalt I) controls produced results consistent with their compositions. Fume from the positive control was similar to the NIOSH carcinogenic fractions and would likely be positive in skin painting studies. Fume from the negative control had measured endpoints below those of Fraction A and would not be expected to produce tumors in animal bioassays.
3. Fume from the eight SHRP paving asphalts showed differences in chemical compositions, but had chemical and biological responses lower than those of NIOSH Fraction A, and therefore would not be expected to be carcinogenic in animal bioassays ([Figure 5A](#), [Figure 5B](#)).

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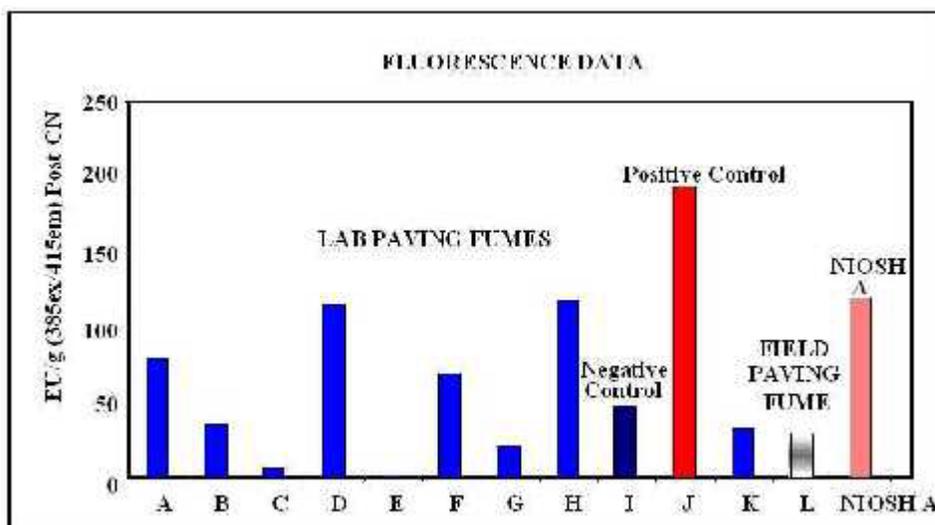


Figure 5A

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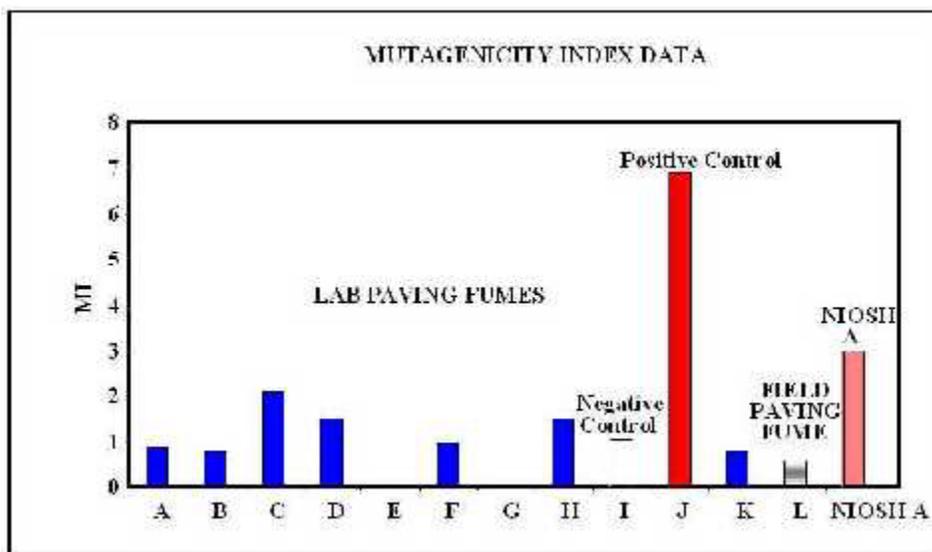


Figure 5B

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[FIGURE 4](#) NIOSH Whole Fumes and Fume Fractions

[FIGURE 5A](#), [FIGURE 5B](#) Comparison of Fluorescence and MI Data for Lab Generated Asphalt Fumes, a Field Paving Fume, and NIOSH A, a non-carcinogenic fraction in the NIOSH animal studies

**TABLE 1** Summary of Results

Description	Asphalt	EU/g after CN	Sim. Distillation % > 316 °C	MI	% Fume of Total Asphalt
SHRP Asphalt	A	80	22.0	0.9	$3.6 \times 10^{-4}$
SHRP Asphalt	B	36	5.0	0.8	$8.6 \times 10^{-4}$
SHRP Asphalt	C	7	5.0	2.1	$2.7 \times 10^{-4}$
SHRP Asphalt	D	116	20.0	1.5	$2.9 \times 10^{-4}$
SHRP Asphalt	E	3	0	0	$1.2 \times 10^{-4}$
SHRP Asphalt	F	70	19.0	1	$3.9 \times 10^{-4}$
SHRP Asphalt	G	22	4.0	0	$6.5 \times 10^{-4}$
SHRP Asphalt	H	119	35.0	1.5	$4.6 \times 10^{-4}$
Negative Control	I	48	12.0	1.1	$3.8 \times 10^{-4}$
Positive Control	J	194	33.0	6.9	$1.7 \times 10^{-3}$
Lab Validation to Field	K	33	5.0	0.8	$5.8 \times 10^{-4}$
Field PG 64-22	L	30	2.0	0.6	$3.5 \times 10^{-5}$

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**TABLE 2** NIOSH Roofing Asphalt Fume and Fume Fractions

	% of Whole	EU/g	Sim. Distillation % > 316°C	MI	% Fume of Total Asphalt
Whole	100	266	45	4.4	2.5
Fraction A	65.5	137	15	2.7	1.6
Fraction B	8.1	798	60	29	.2
Fraction C	10.6	1100	45	25	.3
Fraction D	11.4	44	15	0	.3
Fraction E	4.5	0	20	0	.1