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Comparison of Field versus Laboratory Generated Asphalt Fumes

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Studies conducted by the National Institute of Occupational Safety and Health (NIOSH) evaluated the carcinogenicity of fumes collected from a catalytically prepared roofing asphalt at 232°C and 316°C using a laboratory generator. The fume condensate from these studies was found to cause a carcinogenic response. However, the uniqueness of the roofing asphalt and the laboratory generation method make it difficult to assess the meaning of this study in the context of paving asphalt. The current study looked at how fumes from paving asphalt operations compare compositionally to the fumes generated and used in the NIOSH animal studies. Additionally, this study examined the impact of temperature on asphalt fume composition. The results showed that fume composition is greatly affected by the conditions under which the fume is generated, the design of the laboratory fume generator having the most significant effect on the type of fume produced. Fumes collected at field paving sites bear little resemblance chemically to the roofing fume used in the animal study. Most importantly, the study found that the compounds most likely responsible for the carcinogenicity in the animal studies were not present in fumes found in the field paving sites studied.

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Comparison of Field versus Laboratory Generated Asphalt Fumes

The National Institute of Occupational Safety and Health (NIOSH) conducted two animal skin painting studies *(1, 2, 3)* in the 1980's on asphalt fumes from a roofing asphalt produced at 232°C and 316°C. The fume generator used in these studies is shown in Figure 1. Both studies found that the fume condensate produced a carcinogenic response. NIOSH provided retained fume samples as well as the neat roofing asphalt for a study which sought to better define the chemicals responsible for the carcinogenic response.

This study investigated the chemical composition and biological effects of the laboratory-generated roofing fume condensate and compared it with fumes from paving asphalts. Initially, paving asphalt fumes were generated in an identical generator using conditions as outlined in the NIOSH protocol. This same paving asphalt was then fumed at two lower temperatures, including 191°C and 163°C, with 163°C being more consistent with typical paving operations, in order to determine what effect temperature would have on fume composition. Fumes were also collected from the vapor space above a storage tank containing this same paving asphalt held at the three temperatures used in the laboratory study. All fumes were compared to those collected from the worksite breathing zone air at a field site placing the same hot mix paving asphalt. This worksite fume was considered to be the most representative of actual worker exposure and are the samples to which others were compared.

MATERIALS

NIOSH Fume Condensate

NIOSH provided a sample of fume condensate dissolved in solvent. This solution was retained from the second skin painting study conducted by Sivak *(2).* The solutions were composed of 50% Whole Fume Condensate and 50% of a solvent mixture (50/50 cyclohexane/acetone). The roofing asphalt from which this fume was generated was an ASTM D312 Type III Asphalt *(4)* commercially produced by oxidizing Saudi Heavy Asphalt with $FeCl_3$ catalyst. The paving asphalt used in the study was a widely used commercially available AC-20 from Asphalt Materials, Inc. in Indianapolis, Indiana. The physical properties of the asphalt are listed in Table 1 and meet ASTM D3381 Table 2 asphalt *(5)*.

METHODS

Laboratory Fume Generation

Laboratory fume generation was conducted as described by Sivak *(2)* using the apparatus shown in Figure 1. Generation temperature was varied and included temperatures of 232°C, 191°C, and 163°C. The 232°C was selected because this temperature was used in the first NIOSH study. The 316°C fume was not evaluated because of safety concerns about fume generation at a temperature above the flash point of the asphalt cement. (Two early attempts resulted in implosions of the twelve liter generation flask.) Originally the 316°C temperature was used in the NIOSH studies since large quantities of condensate were required for dosing more than one thousand mice in the skin painting studies.

Fumes were collected in the laboratory by drawing air (10 liters/min) across the surface of a stirred (200 rpm) 12 liter glass reactor and into a series of cold traps, using 6.5 Kg of asphalt cement at temperature for 6 hours.

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Field Fume Tank Collection

Fumes from the same paving asphalt were collected from the vapor space above an oil-heated 57 m^3 (15,000 gallon) storage tank filled 2/3 full with asphalt cement. The collection system is shown in Figure 2. It uses the same cold traps and air flow (10 liters/min) used in the laboratory study. The fumes were collected at a point 15 cm above the surface. Initially, the tank was heated to 163°C and fumes were collected for 2.5 hours and retained for testing. The asphalt was then passed through a heat exchanger to raise the tank temperature to 197°C, after which fumes were collected another 2.5 hours. Finally, the asphalt was heated to 232°C and fumed for 2.5 more hours.

Personnel Sampling of Field Paving Fumes

Fumes were collected from this same asphalt cement used as binder at a hot mix asphalt paving site. Samples were collected from individuals working on the paving crew, including the paver operator, two screedmen, and the first roller operator.

Sampling in the field used a modification of NIOSH Method 5506 *(6)*. The modification included pre-extracting the glass fiber and silver membrane with benzene to remove any organics. Secondly, a silver membrane was used instead of Teflon® . The outlet of the cassette was attached to an XAD-2 tube. The front chamber contained 400 mg of XAD-2 resin and the back half contained 200 mg. The XAD-2 tube was used to capture the total organic exposure in the workplace. This is important because the laboratory-generated fumes condense all the organic materials released from the heated asphalt surface. After exposure, the cassette filters and XAD-2 tubes were capped, wrapped in foil to avoid exposure to UV light, and placed in dry ice at the project.

Analytical Methods

Analyses of Total Particulate on Personnel Sampling

NIOSH Method 0500*(7)* was used for determination of total particulate.

Carbon Disulfide Soluble Material on Personnel Cassettes

NIOSH method 5023 *(8)* was followed, except that carbon disulfide was substituted for benzene as the extraction solvent. Cassettes from each team of four workers at a given site were combined to provide enough material for subsequent analysis. Carbon disulfide-soluble material on the filters and XAD-2 resins were combined to more accurately simulate total organic exposure in the breathing zone air. Carbon disulfide is an extremely dangerous material due both to its biological activity and because of its low autoignition temperature. It should be handled with extreme care in a well ventilated hood.

High Resolution Gas Chromatography/Mass Spectrometry (HRGC/MS)

Fume condensates were analyzed on a Hewlett-Packard mass spectrometer interfaced with a Hewlett Packard 5790 gas chromatograph. One microliter of sample dissolved in a suitable solvent was injected on a 30 m DB-1 capillary column in splitless mode. The injector and transfer line temperature were 280ºC, the oven was heated at 80ºC for 2 minutes and programmed to heat to 320ºC at 10ºC/min., and then held for 20 minutes. The mass spectrometer was scanned from mass 40 to 800 in approximately one second. One sample was derivatized to form the trimethylsilyl derivative by using a commercially available prepared cocktail.

as Chromatography with Flame Photometric Detection (GC/FPD)

Sulfur heterocycles were determined using the following procedure. Samples were dissolved in iso-octane and partitioned between iso-octane and dimethylsulfoxide. The DMSO extract was then diluted with water and back-extracted into iso-octane. The resulting iso-octane solution was analyzed using a Hewlett-Packard Model 5890 Series II gas chromatograph equipped with a 30 m x 0.54 mm DB-624 GLPC column and a flame photometric detector. External calibration standards contained 1.0, 5.0 and 10 mg/L each of benzothiophene, dibenzothiophene, thianthrene, and naphthobenzothiophene.

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Sulfur-containing compounds were arbitrarily divided into two groups: those eluting between the solvent peak and dibenzothiophene (<3-ring) SH(L), and those eluting at or after the retention time of dibenzothiophene ($\geq$3-ring) SH(H). Quantification was based on the assumption that all responses were similar to that of dibenzothiophene.

Gas Chromatography/Flame Ionization Detection (GC/FID) Simulated Distillation

Simulated distillation of the fume condensates was performed using ASTM Method D-2887 *(9)*.

RESULTS

Comparison of Field Tank Fumes and Laboratory Fumes at Three Temperatures

Table 2 shows a comparison of fumes generated at three different temperatures both in the NIOSH fume generator and in field storage tanks. The comparison is made using GC/FID Simulated Distillation of total fume and GC/FPD which evaluates the sulfur heterocycles. The results for sulfur heterocycles (Table 2) are graphically presented in Figure 3. These data show striking differences between the fumes collected from storage tanks and the laboratory-generated fumes. Most notable are the much higher boiling point distributions seen in the laboratory fumes. Comparison of fume generated in the laboratory at 232°C with that collected in the field storage tank at 163°C, shows virtually no overlap in composition, based solely on fume boiling point distribution. The data also show a trend of increasing volatility with decreasing temperature (see 50% B.P.) in both field and laboratory-generated fumes.

Comparison of Fumes Collected from the Laboratory Generator with Fumes Collected Above the Storage Tank and from Paving Workers

Field Storage and Laboratory

Fumes collected from the paving site at 150°C were compared to fumes taken from the storage tank at the same temperature. Fumes were also generated in the laboratory at 150°C using the NIOSH protocol. Table 3 gives the results of these comparisons. The boiling point distribution for the personnel cassettes is between that from the storage tank and the laboratory fume generation. This result is not surprising inasmuch as the most volatile components of the fumes present in the storage tank are lost in the hot mix process when the asphalt cement is coated on the heated aggregate. The laboratory-generated fume had properties consistent with previous studies *(10),* i.e. it had a significantly higher boiling point distribution than other field fumes.

The second part of the study compared paving fume condensates taken from the storage tank at 150°C, and the laboratory generator at 150°C with NIOSH laboratory roofing fume condensate generated at 316°C used in the NIOSH animal study. GC/MS data on DMSO-extracted samples are presented in Table 4. DMSO extraction, as discussed under the GC/FPD method, was used because it selectively extracts polynuclear aromatic compounds (PACs) and evidence from other studies *(11)* suggests that the carcinogenicity of petroleum materials is due to 4-6 ring PACs. A graph of the data by ring number is shown in Figure 4. These results clearly show that the NIOSH fume condensate has a significant amount of 3 ring or larger PACs, while the laboratory-generated paving asphalt fume contains mostly one-to three-ring aromatics, but still contains significant amounts of 4-ring PAHs. However, the field fume taken from the storage tank contains no detectable 4-ring PACs, as expected based on the boiling point distribution and GC/FPD sulfur heterocycle analyses.

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CONCLUSION

The purpose of this study was to investigate the relationship between asphalt fume composition and the method of fume generation. The findings from the study could then be used to help assess the relevance of the NIOSH mouse skin-painting bioassays to any assessment of the carcinogenic potential of workplace asphalt fumes.

This study found that the NIOSH laboratory fume generation protocol does not produce fumes representative of those found in the workplace environment of the paving operations studied.

There are several reasons why the NIOSH fume generator produced a fume so different from those found in the field. The first is the reduced pressure inside the fume generator. Our testing found vacuums as high as 50 mm below atmospheric pressure inside the chamber during testing, an effect apparently due to partial plugging of the filters used to clean the air before it enters the chamber. NIOSH noted this in their report on the animal study *(2)*.

The second factor influencing fume composition was stirring. To avoid localized overheating of the asphalt, NIOSH used a multiblade stirrer rotating at 200 rpm. One of the mixing blades was at the surface of the liquid asphalt which resulted in significant aerosol formation at the liquid-vapor interface (see Figure 1). Because of the reduced vacuum and stirring these aerosol droplets, which contain high molecular weight hydrocarbons, leave the surface and enter into the air stream, and are carried into the cold traps. In paving operations the asphalt film does not experience such agitation or reduced pressure, and most large aerosol droplets fall back to the paving surface and do not reach the worker's breathing zone.

Three classes of aromatic compounds were assayed in the characterization of fume condensates: aromatic hydrocarbons, sulfur-heterocycles, and oxygen heterocycles. The sulfur heterocycles were further subdivided into low (< 3-ring) and high ($\geq$ 3-ring) molecular weight groups. Detailed analytical characterization by HR-GC/MS of fumes from paving asphalt was also carried out.

The rationale for selection of sulfur heterocycles as one of the endpoints was the speculation by NIOSH that the carcinogenicity seen in their skin-painting assays may have been caused in large part by these compounds. The subdivision into low and high molecular weight groups reflects the belief that one- and two-ring sulfur heterocycles *(12,13)* are not carcinogenic, while some three-, and especially four- and five-ring species are known to be mutagenic. Similar considerations apply to the analysis of the GC/MS data on distribution of aromatic hydrocarbons and sulfur heterocycles by ring-number.

Taken as a whole, the analytical data confirm the conclusions drawn from the gravimetric and boiling range assays: (a) the original NIOSH fume condensates have significant levels of high molecular weight PACs and sulfur heterocycles (PASH). A subset of these compounds are the likely source of the carcinogenicity found in the animal study; (b) the field fumes contain much lower molecular weight aromatic hydrocarbons than NIOSH laboratory fumes; and (c) four-ring or larger polycyclic aromatic compounds, which are the likely carcinogens in the NIOSH studies, were undetectable in these field paving fumes.

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TABLE 1 AC-20 Physical Properties

	Result	Specification
Viscosity @60°C, P	1910	1600-2400
Viscosity @135°C, cSt.	365	300+
Penetration @25°C, 100g, 5s	66	60+
Flash Point, COC, °C	304	232+
Solubility, %	99.93	99.0+
Viscosity ATFOT, P	3860	10000-
Ductility @25°C, cm	100+	50+

TABLE 2 Field Tanks versus Laboratory

Asphalt Source/Type	Lab/Paving	Field/Paving	Lab/Paving	Field/ Paving	Lab/ Paving	Field/Paving
Temperature, °C	232	232	191	191	163	163
Air, Lpm.	10	10	10	10	10	10
Quantity of Asphalt, Kg.	6.5	38,000	6.5	38,000	6.5	38,000
Stirring, rpm.	200	No	200	No	200	No
Time in Generation, hrs.	6.0	2.5	6.0	2.5	6.0	2.5
Conditions	Lab	Field	Lab	Field	Lab	Field
Simulated Distillation,°C IBP 5% 10% 20% 30% 40% 50% 60% 70% 80% 90% 95%	252 264 286 312 327 349 363 378 397 416 429	161 189 216 225 234 253 267 273 289 348 399	262 271 294 309 327 338 353 368 385 407 425	168 187 205 216 224 232 243 251 262 287 356	247 252 264 260 269 271 287 302 317 338 361	174 193 208 216 227 232 241 247 251 263 271
Sulfur, %/ppm.						
Low Molecular Wt.	29.0/2100	87.6/3300	7.6/110	94.2/14,000	32.9/4000	97.2/13,000
High Molecular Wt.	71.0/5100	12.4/470	92.4/1300	5.8/850	67.1/8200	2.8/370
Sulfur Heterocyclic PACs, ppm						
Benzothiophene	4.6	38.0	0.26	110	1.0	100
Dibenzothiophene	810	82.0	740	200	2100	93.0
Thianthrene	BDL	4.5	BDL	7.3	BDL	3.1

BDL = Below Detection Limit

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TABLE 3 Field versus Lab Study/Indiana Paving Asphalt

Description	Field Cassettes	Field Tank	Lab
Sample #	1, 8, 19, 20	92340	92343
Temperature of Asphalt, °C	150	150	150
Sample Weight, CS_2 Soluble, mg., Filter	0.72	32 g	2.8 g
CS_2 Soluble, (Filter + XAD), mg.	4.31	NA	NA
Average Sampling Time, hrs.	7.75	7	54
Average Air Volume, liters	924	4200	32,400
TPM, mg/m^3	0.78	NA	NA
BSM, mg/m^3	0.03	NA	NA
Simulated Distillation,°C		174	252
5%	202	195	263
10%	217	207	269
20%	227	217	280
30%	236	227	285
40%	247	233	292
50%	253	246	297
60%	262	253	301
70%	267	264	314
80%	278	278	319
90%	300	299	333
95%	341		
Sulfur Heterocycles, ppm.			
Low Molecular Weight (%)	ND	96.7/2980	34.7/13,800
High Molecular Weight (%)	ND	3.3/100	65.3/26,100
Sulfur Heterocyclic PACs, ppm			
Benzothiophene	ND	12.1	12.1
Dibenzothiophene	ND	ND	ND
Thianthrene	ND	ND	ND
Naphthobenzothiophene	ND	ND	ND

NA = Not Analyzed
ND = Not Detected

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TABLE 4 High Resolution Mass Spec Whole Fumes DMSO Extracted

Compound ID*	Identification of Whole Fumes		
	NIOSH @316°C	Laboratory AX Paving @150°C	Field Tank AX Paving @150°C
Hydrocarbons, %			
Alkyl Benzene	2.00	7.7	26.0
Indene	2.11	ND	1.3
Alkyl Indenes	ND	1.10	ND
Indane	ND	0.19	1.30
Alkyl Indanes	ND	3.37	16.6
Diphenyl	ND	ND	0.74
Alkyl Diphenyl	ND	ND	3.26
Naphthalene	0.12	0.38	3.0
Alkyl Naphthalenes	7.88	16.1	40.77
Fluorene	0.81	1.14	ND
Alkyl Fluorenes	9.07	10.64	0.50
Anthracene	0.98	3.74	0.32
Alkyl Anthracenes	9.30	19.57	1.43
Pyrene/Fluoranthene	ND	5.51	ND
Chrysene	ND	1.19	ND
Alkyl Chrysenes	0.71	0.24	ND
Sulfur Compounds, %			
Benzothiophene	2.96	0.04	0.29
Alkyl Benzothiophene	23.36	19.4	3.79
Dibenzothiophene	1.05	1.75	ND
Alkyl Dibenzothiophene	33.43	7.85	ND
Naphtho Benzothiophene	3.31	ND	ND
Alkyl Naphthobenzothiophene	2.56	ND	ND
Oxygen Compounds, %			
Methyl Heptyl Ketone	0.50	ND	ND
Methyl Octyl Ketone	0.25	ND	ND
Phenol	0.30	ND	ND
Methyl Fluorenone	ND	ND	0.60
TOTAL	102	105	104

* Percent of Total Sample Analyzed (DMSO Fraction Only)
ND = Not Detected

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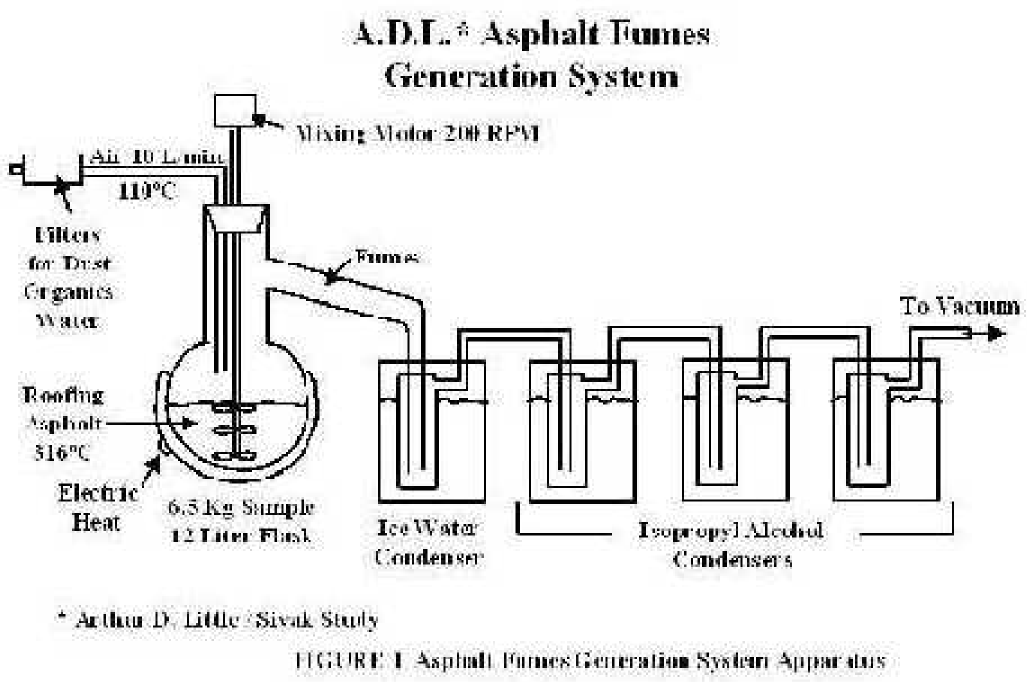

Figure 1 - A.D.I.* Asphalt Fumes Generation System

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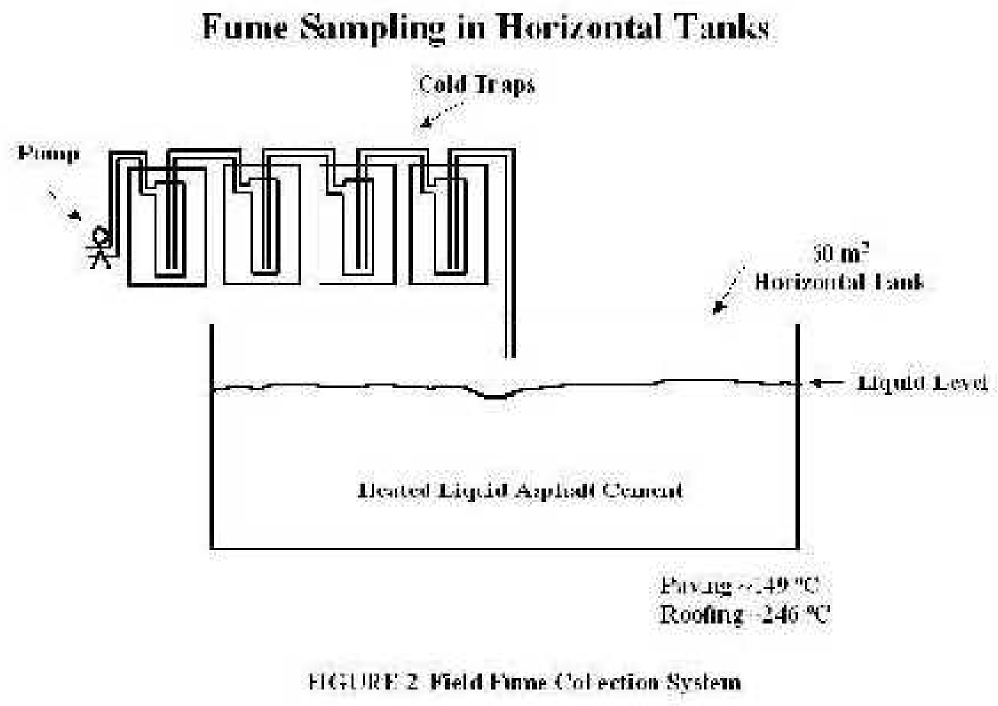
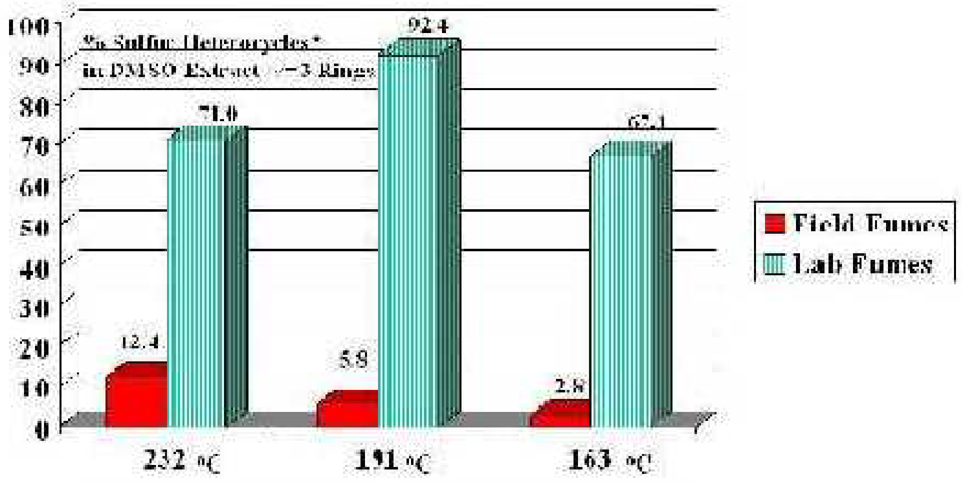


Figure 2 - Fume Sampling in Horizontal Tanks



* Result is based on % of all Sulfur Heterocycles in fume

FIGURE 3 Comparison of High Molecular Weight Sulfur Heterocycles in Field Tanks versus the Laboratory

<u>Figure 3 - Comparison of High Molecular Weight Sulfur Heterocycles in Field Tanks verses the Laboratory</u>

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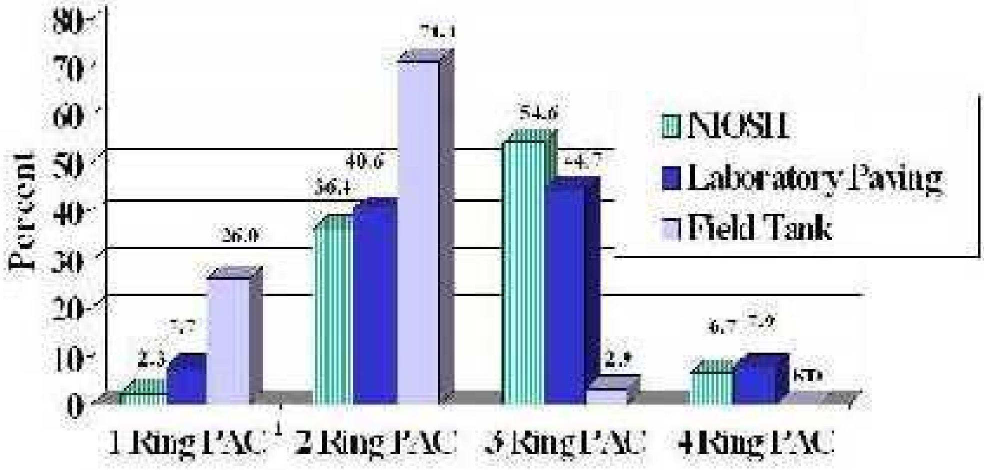

¹ PACs include Sulfur, Oxygen and Hydrocarbon PACs
ND = Not Detected

FIGURE 4 Percentage of Total PACs in Fume

Figure 4 - Percentage of Total PACs in Fume