Aromatic Diesel Emissions as a Function of Engine Conditions

Trescott E. Jensen and Ronald A. Hites*

School of Public and Environmental Affairs and Department of Chemistry, Indiana University, Bloomington, Indiana 47405

The abundance and distribution of the alkyl homologues of polycyclic aromatic hydrocarbons (naphthalene, fluorene, phenanthrene, pyrene, fluoranthene, and phenylnaphthalene) and oxygenated polycyclic aromatic hydrocarbons (naphthalenecarboxaldehydes, fluoren-9-one, biphenylcarboxaldehydes, phenanthrenecarboxaldehydes, and thioxanthen-9-one) in the organic extractables of particulates produced by a diesel engine are reported. Samples were obtained at three engine loads and at three fuel injection timing conditions. The concentrations of alkyl homologues of PAH and oxy-PAH on the particulates were found to decrease as cylinder exhaust temperature increased. The degree of alkylation for the most abundant homologue of these compounds increased by one to two carbons as the cylinder exhaust temperature was decreased.

Diesel soot production in the United States is estimated to be 10^{11} g annually. These particulates are predominantly carbon; however, 10–40% by weight can be extracted with organic solvents (1). The Ames' *Salmonella* assay has indicated that this organic soluble material is mutagenic (2–4), and consideration of this activity has prompted an evaluation of the possible human health effects of diesel particulates (4–7). Identification of the compounds responsible for the observed mutagenic activity has been necessary to provide information about the magnitude of the environmental impact of diesel particulates.

Information about the composition of organic extractables from diesel particulates is becoming more complete (3, 4, 8–13). Besides unburned fuel, diesel particulate extracts contain polycyclic aromatic hydrocarbons (PAH), oxygenated-PAH, a few sulfur and oxygen heterocyclic compounds, and nitro-PAH. Over 250 different aromatic compounds, including alkyl homologues, have been identified in diesel emissions (3, 4, 8–13). Naphthalene, fluorene, phenanthrene, phenylnaphthalene, pyrene, and fluoranthene are the major PAH. Ketone and aldehyde derivatives of these PAH are the predominant components of the oxy-PAH fraction. Hydroxy, dihydroxy, and dicarboxylic acid anhydride PAH have also been reported (3). Thioxanthen-9-one, dibenzothiophene, and xanthen-9-one are the major heterocyclic components. Nitropyrene, found in diesel emissions, has been the focus of many studies because of the high direct mutagenic activity of nitro-PAH in the Ames' *Salmonella* assay (6, 13, 17). A summary of all these compounds is given in Table I.

Even though nitropyrene and benzo[a]pyrene are known mutagens, another group of PAH found in diesel exhaust are also very biologically active. 1-Methylphenanthrene, 2-methylphenanthrene, and 9-methylphenanthrene have all been found in diesel exhaust and are active in a bacterial mutagenicity bioassay. Their specific mutagenicities are 0.2–0.5 times that of benzo[a]pyrene (18). 9-Methylfluorene is also in diesel exhaust and was reported to be 0.2 times as mutagenic as benzo[a]pyrene; its higher alkyl homologue, 1,9-dimethylfluorene, was found to be 0.6 times as active as benzo[a]pyrene (19). On the basis of these biological activity findings, the alkyl homologues of the PAH are important

indicators of the environmental impact of diesel emissions. They are also more easily measured, because of their greater abundance (3) than are either benzo[a]pyrene or nitropyrene.

To decrease the potential impact of diesel exhaust on human health, engineering efforts have focused on improved fuel combustion. However, complete combustion has not been achieved. Many modern diesel engines burn 99.9% of their fuel (20). Thus, at least one thousandth of the fuel is discharged to the environment as partially burned or unburned material. Some improvement may yet be made that will increase fuel combustion efficiency, but it is not likely that exhaust emissions will be decreased significantly by using only this approach. Another approach would be the total removal of the soot from the exhaust. At the present time, however, the technology needed to remove all the particulates from diesel exhaust streams is neither economical nor practical.

Very little information is available concerning the effects of fuel composition, fuel to air ratio, fuel injection timing, injection pressure, engine combustion temperature, oil age, exhaust temperature, and other engine operating conditions on the trace organic species in diesel emissions. Thus, we have examined the alkyl homologues of PAH and oxy-PAH in the soluble organic extract of diesel particulates which were produced using different engine operating conditions.

EXPERIMENTAL SECTION

Cummins Engine Co. (Columbus, IN) provided diesel soot samples produced using a single cylinder test engine that burned no. 2 diesel fuel. On the basis of the data presented below, we judge this engine to be similar to multicylinder engines in its emission characteristics. Five samples were obtained at the following engine conditions: advanced timing at full load, normal timing at full load, retarded timing at full load, normal timing at half load, and normal timing at no load. Full load was set at 36 braking horse power; injection timing was retarded or advanced by 6° off the normal setting of 10° of rotation before top dead center cylinder stroke. The temperature was measured 1.5 ft (46 cm) down the exhaust manifold from the cylinder exhaust port. The exhaust temperature was 590 °C at full load, 470 °C at half load, and 190 °C at no load.

Exhaust was diluted about 14:1 with filtered air in a dilution tunnel. Particulates were collected on 47 mm diameter, Teflon-coated, glass fiber filters (Pallflex T60-A20 or Pallflex TX40). The temperature of the filter was about 50 °C. Filters were Soxhlet extracted for 24 h with 150 mL of methylene chloride. An internal standard was added to each extract before extractant volume reduction; it consisted of 200 ng each of fluorene-d_{10}, anthracene-d_{10}, pyrene-d_{10}, and perylene-d_{12} (Merck Sharp and Dohme Canada, Limited), and 320 ng of fluoren-9-one-d_8 which was synthesized from fluorene-d_{10} by oxidation with sodium dichromate in concentrated acetic acid.

Extraction solvent volume was reduced to about 1 mL with a rotovap unit, then to about 20 μL with dry nitrogen purging. Prior to fractionation, the methylene chloride was exchanged with hexane by adding 100 μL of hexane followed by nitrogen purging to a volume of about 20 μL, repeated four times. Crude extracts were separated into five fractions on silicic acid (5% deactivated) columns (5 cm × 0.8 cm). The sequence of the eluents was hexane (3 mL), 1:1 hexane:toluene (3 mL), toluene (3 mL), methylene chloride (3 mL), and methanol (3 mL). All solvents were pesticide grade or better and were checked for purity.

Gas chromatographic mass spectrometry (GC/MS) was done with a Hewlett-Packard 5985B mass spectrometer. A capillary

Table I. PAH and Oxy-PAH Reported in Diesel Particulate Extracts

aromatic compound	alkyl homologue range reported	ref
naphthalene[a]	C_0-C_4	8, 14
fluorene[a]	C_0-C_4	8, 9
phenanthrene (and anthracene)	C_0-C_4	3, 8-11
phenylnaphthalene[a]	C_0-C_3	9
fluoranthene[a]	C_0-C_1	3, 8-11
pyrene[a]	C_0-C_1	3, 8-11
naphthalenecarboxaldehydes[a]	C_0-C_6	9-11
biphenylcarboxaldehydes[a]	C_0-C_2	9
phenanthrene (and anthracene[b]) carboxaldehydes[a]	C_0-C_2	3, 8-11
fluoren-9-one[a]	C_0-C_5	3, 8-11, 15
phenanthrone (and anthrone)	C_0-C_3	3, 10
4H-cyclopenta[def]phenanthren-4-one	C_0-C_2	8-11
fluorenequinone	C_0-C_2	3, 8
phenanthrene(and anthracene)quinones	C_0-C_2	3, 8-11
fluoranthene(and pyrene)quinones	C_0-C_1	3
hydroxyphenanthrenes	C_0-C_3	3
dihydroxyfluorenes	C_0-C_2	3
dihydroxyphenanthrenes	C_0-C_2	3
naphthalenedicarboxylic acids	C_0-C_2	3
naphthalenedicarboxylic acid anhydride	C_0-C_2	3, 8
dibenzothiophene	C_0-C_5	3, 9, 16
thioxanthen-9-one[a]	C_0-C_2	3, 10, 16

[a] Compounds discussed in this study. [b] Small abundance.

(30 m × 0.2 mm i.d.) fused silica column coated with a bonded silicone (J & W DB-5, equivalent to SE-54) stationary phase was used for GC separation. An injection of 1 μL at 30 °C was loaded splitless for 42 s. The initial temperature was held 4 min and then linear programming was begun at 4 °C/min to a final temperature of 280 °C and held for 55 min. Negative chemical ionization was done with methane as the reagent gas. All concentration values are reported as micrograms of component per gram of particulate. Concentrations were calculated by using the area for the mass chromatogram of the ions of interest, excluding interfering major components, ratioed to the appropriate internal standard. No attempt has been made to correct for the difference in mass spectrometer response factors for the higher alkyl homologues due to the lack of suitable standards.

The unsubstituted compounds were identified by comparison of the electron impact and negative chemical ionization mass spectra and gas chromatographic retention times with those of authentic compounds. Most of the methyl PAH and some of the methyl oxy-PAH were similarly identified. The other alkyl homologues were identified by a priori interpretation of their mass spectra and by extrapolation of their GC retention times obtained from mass chromatograms.

RESULTS AND DISCUSSION

Our analyses of the alkyl homologues in diesel particulates have focused on the hexane:toluene and toluene fractions. Both fractions have been examined by electron impact (EI) GC/MS, and the toluene fraction has also been studied with negative chemical ionization (NCI) GC/MS. The concentrations for naphthalene, fluorene, anthracene, phenanthrene, pyrene, fluoranthene, and phenylnaphthalene and their alkyl homologues are given in Table II. Table III lists concentration data for naphthalenecarboxaldehydes, fluoren-9-one, biphenylcarboxaldehydes, phenanthrenecarboxaldehydes, and thioxanthen-9-one and their alkyl homologues.

For full engine load samples, the fuel injection timing was either advanced, normal, or retarded. The cylinder exhaust temperature for full load was about 590 °C regardless of the timing. When the fuel injection timing is normal and the engine load is changed, the exhaust temperature varies from 590 °C for full load to 190 °C with no engine load. With this experimental design, it was possible to examine cylinder reaction products and compounds formed in the exhaust stream almost independently of each other. Unfortunately, there may be minor sources for the detected alkyl PAH compounds other
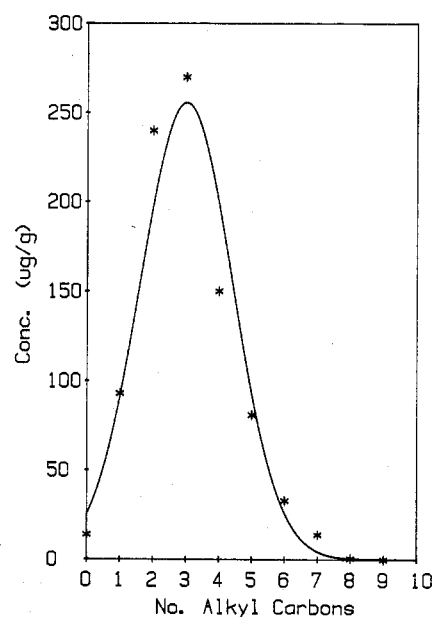

Figure 1. Concentration (in μg/g particulate) of the alkyl homologues of fluorenone as a function of the number of *alkyl* carbon atoms. The sample was emitted from a one cylinder diesel engine operating with normal timing and at no load. The curve is the best-fitting Gaussian function (average = 3.00, standard deviation = 1.40, normalization factor = 255.6).

than those desired. Potential sources are unconsumed fuel, lubricating oil, sample collection filter artifacts, and sample aging. For the purpose of this study, we believe these contributions are negligible.

Representation of the data in Tables II and III as plots of the number of alkyl carbons in the compound vs. the concentration of the homologue gives an alkyl homologue plot (see Figure 1 for an example). A Gaussian distribution can be fit to such data by calculating the first and second moments. The first moment gives the average number of alkyl carbons for a specific compound type, and the second moment gives a measure of the width of the distribution. These calculations give the curve shown in Figure 1. Similar calculations for each of the other 48 data sets gave the average

Table II. Amount of Unsubstituted PAH and its Alkyl Homologues Expressed as μg/g Particulate Found in the Hexane:Toluene Fraction

compound	sample (engine condition)				
	1 (advanced)[a]	2 (normal)[a]	3 (retarded)[a]	4 (half load)[b]	5 (no load)[b]
naphthalene (C_{10})	0	4.8	0	0	1.0
C_{11}	0	13	0	0.8	2.5
C_{12}	0	47	c	6.2	4.0
C_{13}	0	46	0.4	26	8.6
C_{14}	0	13	3.4	1.2	16
C_{15}	0	1.7	0.2	0	5.0
C_{16}	0	0	0	0	0
fluorene (C_{13})	0	2.9	0.2	0.4	0.3
C_{14}	0.2	4.9	1.5	18	1.2
C_{15}	0.4	13	7.8	62	3.8
C_{16}	2.3	14	12	63	42
C_{17}	1.4	5.6	2.3	10	56
C_{18}	0.3	0	0.1	c	15
C_{19}	0	0	0	0	3.1
C_{20}	0	0	0	0	0.8
C_{21}	0	0	0	0	0
anthracene (C_{14})	0	1.2	0.9	6.4	4.1
phenanthrene (C_{14})	8.3	91	86	110	140
C_{15}	35	180	150	340	160
C_{16}	50	120	120	170	310
C_{17}	16	33	32	43	290
C_{18}	0.4	9.1	7.2	11	110
C_{19}	0	1.8	1.3	9.8	8.6
C_{20}	0	0	0	0	0.2
C_{21}	0	0	0	0	0
pyrene (C_{16})	1.5	5.3	0.8	17	40
fluoranthene (C_{16})	43	39	24	28	35
C_{17}	4.0	6.7	3.2	6.0	79
C_{18}	0.4	0.7	0	0.1	55
C_{19}	0.1	0	0	0	31
C_{20}	c	0	0	0	15
C_{21}	0	0	0	0	2.3
C_{22}	0	0	0	0	0
phenylnaphthalene (C_{16})	3.1	9.1	6.6	13	12
C_{17}	9.5	20	13	15	92
C_{18}	4.5	8.5	7.7	7.4	110
C_{19}	0.2	3.2	0.9	1.8	74
C_{20}	0	0	0	0	22
C_{21}	0	0	0	0	5.7
C_{22}	0	0	0	0	0

[a] Full engine load. [b] Normal injection timing. [c] Alkyl homologue detected at a concentration <0.1 μg/g.

alkyl carbon numbers given in Table IV. In almost all cases, the second moment was about 1 alkyl carbon; thus, this parameter will not be discussed further.

Four trends are observed from the data given in Tables II and III and condensed in Table IV. First, with the possible exception of naphthalene and biphenylcarboxaldehydes, injection timing does not have an effect on the extractable component profiles of the reported compounds. Second, the most abundant alkyl homologue of the aromatic compounds reported, with the exception of phenanthrenecarboxaldehydes, extends to a greater number of carbons as the engine cylinder exhaust temperature decreases (decreased load). Third, there is an increase of the absolute concentration of all alkyl homologues, with the exception of naphthalene and fluorene, as the exhaust temperature decreases (decreased load). Fourth, the alkyl homologues of all compounds reported, except fluoranthene and thioxanthen-9-one, are more abundant than the unsubstituted aromatic compound. For fluoranthene and thioxanthen-9-one, the unsubstituted aromatic is less abundant than the methyl alkyl homologue for the no load sample.

Effect of Length of Combustion Time. For naphthalene, the shift from 2.4 to 4.0 alkyl carbons as the injection is retarded may be an artifact. Naphthalene and its smaller alkyl homologues have low boiling points (naphthalene, bp 218 °C,

and 1-methylnaphthalene, bp 242 °C). The absence of these compounds in the extract may be due to the air flow through the sample filter, temperature of the filter, vapor particle partitioning, or loss during sample workup. Therefore, it is not possible to draw conclusions about the significance of the length of combustion time for the alkyl naphthalene series.

Combustion time *may* be a factor in the biphenylcarboxaldehydes alkyl homologue distribution. For the advanced injection timing sample for these compounds, the most abundant homologue is one carbon greater (2.4) than for normal or retarded injection timing (1.3). The absolute abundance of the alkyl biphenylcarboxaldehydes, however, is very small, and this difference may not be significant.

Since only two of the alkyl series appear to be influenced by length of cylinder reaction time, we conclude that formation of the remaining eight alkyl series is essentially complete irrespective of combustion time or are formed in the exhaust to a significant extent.

Effect of Exhaust Temperature. The most abundant alkyl homologue (for nine of the ten aromatics) extends to a greater number of carbons as the engine cylinder exhaust temperature decreases. Phenanthrenecarboxaldehydes alkyl homologues increase in absolute concentration as exhaust temperature decreases, but there is no shift observed at no load for the most abundant homologue (1.3 vs. 1.4 alkyl

Table III. Amount of Unsubstituted Oxy-PAH and Its Alkyl Homologues Expressed as μg/g Diesel Particulate Found in the Toluene Fraction

compound	sample (engine condition)				
	1 (advanced)[a]	2 (normal)[a]	3 (retarded)[a]	4 (half load)[b]	5 (no load)[b]
naphthalenecarboxaldehydes (C_{11})	0.8	0.9	1.8	6.3	0
C_{12}	1.3	1.2	2.0	33	0
C_{13}	1.2	0.9	1.3	50	20
C_{14}	0.3	0.3	1.1	26	84
C_{15}	0.1	0.1	1.0	12	44
C_{16}	c	0	0.5	3.7	9.1
C_{17}	0	0	0	0.3	5.7
C_{18}	0	0	0	0	0
fluoren-9-one (C_{13})	29	25	43	26	14
C_{14}	45	41	72	82	93
C_{15}	41	35	56	120	240
C_{16}	27	18	30	84	270
C_{17}	11	7.2	12	23	150
C_{18}	5	2.8	7.8	6.4	81
C_{19}	2.3	1.1	1.9	2.2	33
C_{20}	0.7	0.4	0.7	0.8	14
C_{21}	0	0	0	0	0.6
C_{22}	0	0	0	0	0
biphenylcarboxaldehydes(C_{13})	0.3	0.4	0.6	1.1	0.1
C_{14}	0.6	2.1	3.0	6.2	5.2
C_{15}	1.2	1.8	1.6	13	120
C_{16}	0.9	c	0.2	4.3	130
C_{17}	0.8	0	0	1.2	75
C_{18}	0.1	0	0	c	20
C_{19}	0	0	0	0	0
phenanthrenecarboxaldehydes (C_{15})	1.1	0.8	1.0	3.0	70
C_{16}	3.1	1.5	1.4	4.9	84
C_{17}	1.5	0.7	0.8	2.2	41
C_{18}	1.2	0.3	0.5	1.2	23
C_{19}	0.8	0.3	0.4	0.7	12
C_{20}	0.5	0.1	0.2	0.3	5.3
C_{21}	0	0	0	0	1.4
C_{22}	0	0	0	0	0
thioxanthen-9-one (C_{13})	4.9	3.1	7.1	15	58
C_{14}	4.1	2.1	4.3	12	87
C_{15}	1.6	0.8	1.9	3.2	37
C_{16}	0.9	0.2	0.5	0.4	7.7
C_{17}	0.2	0.1	0.2	0.2	2.9
C_{18}	c	0	0.1	0	1.1
C_{19}	0	0	0	0	0.6
C_{20}	0	0	0	0	0

[a] Full engine load. [b] Normal injection timing. [c] Alkyl homologue detected at a concentration of <0.1 μg/g.

carbons).

Homologue Concentration Inversely Related to Temperature. The total concentration of all of the alkyl homologues of a series increases as the cylinder exhaust temperature decreases. The no load sample has the greatest concentration (micrograms per gram of particulate) with the exception of naphthalene which was discussed previously.

Partitioning of fluoranthene and pyrene between the particulate and gas phase has been reported. At 37 °C, the median partitioning coefficients (particulate/gas-phase mass ratio) are 0.75 and 0.95 for pyrene and fluoranthene, respectively (21). For the samples in this study, the pyrene to fluoranthene ratio increases from 0.14 to 1.1 with decreasing cylinder exhaust temperature. A similar but smaller change is seen with the phenanthrene to anthracene ratio (0.013 to 0.029). Irrespective of the temperature or sample, the fluoranthene concentration is almost unchanged. From this we infer that fluoranthene is formed in the cylinder, and from the partition coefficient, we would expect to find most of the fluoranthene associated with the particulate.

For all compounds except fluorene, this third trend [a general increase of the absolute concentration of all alkyl homologues as the cylinder exhaust temperature decreases (decreased load)] is distinct. Fluorene, however, shows a

decrease in concentration for the no load sample. At least two explanations for this observed difference in compound production are possible. Conversion of precursors to alkyl fluorenes may occur in the exhaust and is thermophilic, therefore, not occurring to a significant extent at a lower exhaust temperature. Alternatively, the alkyl fluorenes may be converted to alkyl fluorenones (9). The concentration of the alkyl fluorenones does increase and a homologue shift (1.7 to 2.1 to 3.0) does occur as engine temperature decreases.

The concentrations of alkyl homologues of most the compounds reported are exhaust temperature dependent. Unfortunately, our ability to describe the increase or decrease of these compounds as a function of formation, partitioning, or thermal stability is still limited.

Low Concentration of Unsubstituted Compounds. For all samples and for most compounds, the concentration of the unsubstituted PAH or oxy-PAH is lower than that for the alkyl homologues. There are several possible explanations for this distribution of homologues. (a) Formation of the unsubstituted compounds may not be favored. (b) Alkylation of the unsubstituted compound may be extensive. (c) Smaller (C_0–C_3) alkyl PAH may be more readily oxidized to oxy-PAH. Since the relative abundance of the oxy-PAH is about twice the concentration of the PAH, the oxy-PAH are probably more

Table IV. Average Number of Alkyl Carbons for Each Compound Type in Diesel Particulate Extracts as a Function of Operating Condition

compound	full load			normal timing	
	advanced	normal	retarded	half load	no load
naphthalene		ı	4.0	2.8	3.4
fluorene	3.3	∠.4	2.6	2.4	3.8
phenanthrene	1.7	1.3	1.3	1.3	2.1
pyrene and fluoranthene	0.1	0.2	0.1	0.2	1.6
phenylnaphthalene	1.1	1.1	1.1	1.0	2.1
naphthalenecarboxaldehydes	1.4	1.3	1.9	2.1	3.4
fluoren-9-one	1.8	1.7	1.7	2.1	3.0
biphenylcarboxaldehydes	2.4	1.3	1.3	1.9	3.0
phenanthrenecarboxaldehydes	1.9	1.5	1.7	1.4	1.3
thioxanthen-9-one	0.9	0.8	0.8	0.7	1.1
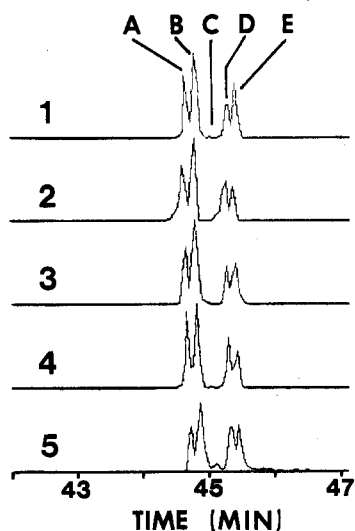
Figure 2. Mass chromatogram for methylphenanthrenes and methylanthracenes (peak A (3-methylphenanthrene), B (2-methylphenanthrene), C (2-methylanthracene), D (9-methylphenanthrene and 4-methylphenanthrene), and E (1-methylphenanthrene)) for hexane: toluene fraction of the advanced (1), normal (2), retarded timing (3), half load (4), and no load (5) samples.

stable in the exhaust or are formed in the exhaust. The low concentration of the unsubstituted compounds probably is not the result of exhaust temperature or boiling point of the compound because of the large range of exhaust temperatures and boiling points (naphthalene, bp 218 °C, and pyrene, bp 393 °C). At the lower engine exhaust temperature (no load), the amount of unsubstituted compound detected increased only for pyrene, phenanthrenecarboxaldehydes, and thioxanthen-9-one. For these compounds, the increase was 30 to 70 times the full load concentration but still not more than the alkyl homologues. Additional study will be required to more fully address this point.

CONCLUSIONS

Alkyl homologue analysis provides information about particulate bound diesel combustion products which are dependent on engine operating conditions. However, often only a few isomers of any single alkyl homologue have significant biological activity (23). Remembering that we desire to selectively decrease emission bioactivity as well as total extractable organics, we examined the individual methylphenanthrenes. The mass chromatograms for m/e 192 (methylphenanthrenes and methylanthracenes) of each sample are compared in Figure 2. Ratios for these alkyl homologue isomers do not indicate an obvious isomer specificity or dependence upon engine conditions. Thus, dependence of isomer concentration on engine condition is not a simple function of

engine condition or is nonexistent.

The inverse relationship between engine temperature and production of extractable organics suggests one possible emission control strategy. Reduction of particulate associated organics might be achieved by a post combustion reactor. To evaluate the feasibility of such an engine design modification, both particulate and vapor emissions need to be collected simultaneously. This will allow proper correlation of particulate vapor partitioning with engine condition. Alkyl homologue analysis of diesel emissions provides information which may lead to selection of engine operating conditions that will reduce the environmental impact of diesel emissions.

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Determination of Oxygenated Polycyclic Aromatic Hydrocarbons in Airborne Particulate Matter by Capillary Gas Chromatography and Gas Chromatography/Mass Spectrometry

Johann König,* Eckhard Balfanz, Werner Funcke, and Thomas Romanowski

Fraunhofer-Institut für Toxikologie und Aerosolforschung, Nottulner Landweg 102, D 4400 Münster-Roxel, Federal Republic of Germany

By use of a two-step column chromatographic separation of crude extracts from airborne particulate matter, a special fraction was separated which contained mainly oxygenated polycyclic aromatic hydrocarbons (OXPAH). The analysis was made by capillary gas chromatography (GC) and capillary gas chromatography/mass spectrometry (GC/MS). A total of 38 individual compounds belonging to five different groups of substances (ketones, quinones, anhydrides, coumarines, and aldehydes) were characterized by their retention indexes and mass spectra.

In addition to the regular well-described polycyclic aromatic hydrocarbons (PAH), many oxygenated PAH (OXPAH) may be associated with particulate matter in ambient air. For instance, model experiments on chemical and, particularly, photochemical PAH stability suggest that several of the PAH that are emitted in sizable amounts from various natural and anthropogenic sources are degraded in the atmosphere by sunlight or by interactions with other reactive airborne species (1–10). To some extent, relatively stable oxidation products like quinones, ketones, aldehydes, coumarines etc. are generated by these reactions. Furthermore, analytical investigations of various source emissions have shown that oxygenated PAH may readily be formed by incomplete combustion of organic material (11–18). Recently, these compounds were investigated in more detail, particularly in the exhaust of diesel engines (12–15). Several components like quinones, ketones, dicarboxylic acid anhydrides, hydroxy compounds, etc. have been characterized. In spite of a variety of potential sources for these compounds, only a few OXPAH were actually detected, mostly associated with general airborne particulate matter (19–24). In most cases, they were not found as a result of systematic investigations but by chance. For instance, they were identified as part of the extract from airborne particulate matter in analyses of the polar fraction of the neutral portion collected by the classical extract separation into acidic, basic, and neutral portions (23, 24). By intent, only a few quinones of PAH in ambient air were investigated (19). Their concentrations were monitored over an extended period of time in order to assess the photochemical stability of the parent PAH by correlating the variations in concentration with meterological conditions. Obviously, a main reason for the lack of information on OXPAH in the atmosphere may be

that, from the environmental hygiene point of view, these were not of special interest, up to now.

However, recent investigations on diesel exhaust have shown that the so-called moderately polar fraction, which normally contains the OXPAH, exhibits a considerable direct-acting Ames mutagenicity (15). In contrast to most of the mutagenic parent-PAH (25), these substances require no activation by mammalian enzymes to cause mutagenic responses. It is easy to imagine that similar compounds may also occur in association with general airborne particulate matter. Thus, it would be of special interest to determine their airborne concentration and the direct-acting mutagenic activity.

The aim of the work described here is to set the stage for such investigations by extracting airborne particulate matter and separating an extract fraction that contains, as far as possible, OXPAH only. In this fraction, as many substances as possible will be characterized.

EXPERIMENTAL SECTION

Particulate Collection and Extraction. Airborne particulate matter was collected during the months of February to April of 1982 on the flat roof of a house in the center of Duisburg (Ruhr area) approximately 15 m above street level. The sampling device was a high volume air sampler (type HV 100, manufactured by Sartorius, Göttingen) equipped with a filter head containing a glass fiber filter (type SM 13400, supplied by Sartorius, Göttingen) with a surface area of about 520 cm². The filters were replaced weekly after passage of about 8000 m³ of air. Immediately following each collection period the filters with their deposits of particulate matter were subjected to a Soxhlet extraction by toluene for 8 h.

Liquid Chromatography. The extract contains various overlapping classes of substances, and the concentrations of oxygenated PAH are relatively low in comparison to substances of some other chemical groups in this fraction. Therefore, it is nearly impossible to characterize or identify more than a few, if any, individual substances without any further cleanup procedures. Thus, a two-step fractionation was performed prior to each analysis. For separating nonpolar substances like alkanes, PAH, etc. which are normally present in relatively high concentrations, the toluene extract was first prefractionated on a silica column (2.5 cm i.d., l = 20 cm; Kieselgel 60, 70–230 mesh, supplied by Merck, inactivated with 15% H₂O). For this purpose, 3 g of silica gel were added to the toluene extract. By rotary evaporation at 30 °C the solvent was removed under reduced pressure and the adsorbed residue was added to the top of the silica column. In the first step, the nonpolar substances were eluted with 450 mL of cyclohexane. Tests with several reference substances of the