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Sources of Fine Organic Aerosol. 2. Noncatalyst and Catalyst-Equipped Automobiles and Heavy-Duty Diesel Trucks

Wolfgang F. Rogge, Lynn M. Hildemann,[†] Monica A. Mazurek,[‡] and Glen R. Cass*

Environmental Engineering Science Department and Environmental Quality Laboratory, California Institute of Technology, Pasadena, California 91125

Bernd R. T. Simoneit

Environmental Geochemistry Group, College of Oceanography, Oregon State University, Corvallis, Oregon 97331

Gasoline- and diesel-powered vehicles are known to contribute appreciable amounts of inhalable fine particulate matter to the atmosphere in urban areas. Internal combustion engines burning gasoline and diesel fuel contribute more than 21% of the primary fine particulate organic carbon emitted to the Los Angeles atmosphere. In the present study, particulate ($d_p \leq 2$ μm) exhaust emissions from six noncatalyst automobiles, seven catalyst-equipped automobiles, and two heavy-duty diesel trucks are examined by gas chromatography/mass spectrometry. The purposes of this study are as follows: (a) to search for conservative marker compounds suitable for tracing the presence of vehicular particulate exhaust emissions in the urban atmosphere, (b) to compile quantitative source profiles, and (c) to study the contributions of fine organic particulate vehicular exhaust to the Los Angeles atmosphere. More than 100 organic compounds are quantified, including n-alkanes, n-alkanoic acids, benzoic acids, benzaldehydes, PAH, oxy-PAH, steranes, pentacyclic triterpanes, azanaphthalenes, and others. Although fossil fuel markers such as steranes and pentacyclic triterpanes can be emitted from other sources, it can be shown that their ambient concentrations measured in the Los Angeles atmosphere are attributable mainly to vehicular exhaust emissions.

Introduction

For more than four decades, exhaust emissions from gasoline- and diesel-powered vehicles have received attention because of their potential for producing adverse health effects, contribution to visibility deterioration, and dominant influence on atmospheric smog formation (1–7). Because of the complexity of primary particulate vehicular emissions, characterization of the chemical composition of vehicle exhaust aerosol is still under study. Much of the research to date on exhaust emissions from vehicles has been guided by the mutagenic and genotoxic potential of certain compound classes found in the particle phase, e.g., polycyclic aromatic hydrocarbons (PAH), oxygenated PAH (oxy-PAH), and nitroarenes (1, 8–21). Together, these compounds are considered to be among the most pervasive classes of potential environmental carcinogens (22).

Vehicle exhaust aerosols, however, contain a great variety of organic compounds in addition to those that have been studied for their mutagenic or carcinogenic potential. Among these compounds may be relatively stable molecules that could be used to trace and quantify the presence of vehicle exhaust in urban atmospheres. If unique tracer compounds or groups of distinct compound assemblages characteristic of exhaust from gasoline and diesel vehicles could be identified and these compounds could also be measured in ambient air, then the fractions of the ambient aerosol derived from gasoline and diesel vehicles could be accurately determined. In the past, the lead content of gasoline-powered vehicle exhaust was used to estimate the contribution of gasoline-powered cars to the ambient aerosol (23–26). Today, due to the near absence of lead in gasoline and the absence of a unique elemental marker in diesel fuel, it has become very difficult to apply receptor modeling methods to the analysis of vehicle-influenced urban air quality problems. Thus, it is quite important to future studies that alternative molecular tracer compounds be identified in both diesel and spark-ignition engine emissions.

In the present study, gasoline- and diesel-powered vehicle exhaust aerosol samples collected by Hildemann et al. (27, 28) are analyzed by gas chromatography/mass spectrometry (GC/MS) to characterize the organic particulate matter in vehicle exhaust at a molecular level.

Experimental Methods

Dilution Sampler. A dilution sampling device was used to measure the fine particulate matter ($d_p \leq 2$ μm) emissions from a fleet of automobiles and diesel trucks, including that portion of the vapor-phase organics that would have condensed onto preexisting particles as the exhaust is cooled by mixing in the atmosphere. The newly developed dilution source sampler was designed and tested by Hildemann et al. (29). The motor vehicle source sampling program, including measurement of exhaust aerosol size distributions and bulk chemical characteristics [22 elements, ionic species, elemental carbon (EC), and bulk organic carbon (OC)], has been described in detail elsewhere (27, 30). Only a brief description of the test procedures will be provided here.

The dilution source sampler configuration used for motor vehicle tests consisted of a dilution air purification system, a predilution tunnel, and the main dilution tunnel with its attached residence time chamber, followed by fine aerosol collection downstream of cyclone separators. Hot vehicle exhaust emitted from the tailpipe of the vehicle was introduced directly into the predilution tunnel and diluted (approximately 3-fold for the diesel trucks and an average of 11–23-fold for the automobiles) with a controlled stream of precleaned dilution air [high-efficiency particulate air (HEPA) filtered]. With a constant flow rate through the predilution tunnel, the exhaust concentration

Table I. Emission Characteristics of the Vehicle Fleet Tested

vehicle fleet	FTP fuel economy, miles/gal	fine particulate emissions		
		mg/km driven	% organics (1.2 × [OC])	% EC
6 noncatalyst autos[a]	15.7	59.4	78.6	8.0
7 catalyst-equipped utos[b]	23.3	18.0	60.1	22.6
2 heavy-duty diesel trucks[c]	7.6[d]	408.0	39.1	40.5

[a] Average of the following vehicls: 1965 Mercury Monterey, 1969 Ford Mustang, 1970 Buick Skylark, 1972 Chevrolet Caprice, 1974 Ford Pinto, and 1976 Volkswagen Beetle. [b] Average of the following vehicles: 1977 Chevrolet Vega, 1980 Honda Civic 150, 1980 Honda 1500, 1980 Toyota Corolla, 1981 Datsun 200SX, 1983 Chevrolet Malibu CL, and 1983 Dodge Omni. [c] Average of the following diesel trucks: 1987 GMC Truck (two-axle) and 1987 Ford Dump Truck (three-axle). [d] Fuel economy for the truck driving cycle as explained in text.

of the vehicle emissions varied according to the vehicle speed. This procedure guaranteed that the exhaust concentration in the predilution tunnel was proportional to the flux of exhaust from the tailpipe at any speed. A constant fraction of the prediluted vehicle exhaust was diverted into a second-stage dilution tunnel and diluted a second time, achieving on average a dilution of 80–90-fold for the diesel trucks and 300–600-fold for the automobiles. Aerosol samples were collected on filters located downstream of AIHL-designed cyclone separators (31) having a 50% cutoff at 2-μm aerodynamic particle diameter.

Dilution Sampler Preparation. All parts of the sampling system which might come into contact with exhaust emissions were carefully cleaned prior to use to guard against possible contamination. Smaller parts, including the cyclones and filter holders were rinsed with dionized water and then sequentially sonicated for 5 min each in glass-distilled methanol and glass-distilled hexane. The larger parts, including the predilution tunnel, were vapor-degreased with tetrachloroethylene and then baked out by wrapping electrical heating tape around the stainless steel pieces while purified air was drawn through the sampler. For further details, see Hildemann et al. (27).

Vehicle Testing Procedures. The vehicle fleet tested during this program consisted of 15 different automobiles and trucks that were in current use in the Los Angeles area, representing a wide range of vehicle ages and accumulated mileage. Six automobiles without catalytic converters, seven catalyst-equipped automobiles, and two heavy-duty diesel trucks listed in Table I were tested on chassis dynamometers at the California Air Resources Board's Haagen-Smit Laboratory. The 13 passenger cars were tested following the cold-start Federal Test Procedure (FTP) to simulate urban driving conditions. For the diesel trucks, a heavy-duty chassis dynamometer was used. The heavy-duty driving cycle included idle modes, constant driving speed at ca. 40 and 70 km/h, plus abrupt acceleration and decceleration modes; for more details see Hildemann et al. (27, 30). Five of the automobiles without catalytic converters were tested with leaded regular gasoline with a lead content of 0.34 g/gal, while the two other noncatalytic cars used premium gasoline with 0.22 g of Pb/gal. The heavy-duty diesel trucks were late-model, low-mileage trucks provided by the city of Pasadena and were operated with the diesel fuel normally purchased by the owner. Additional information regarding the vehicles

tested can be found in Table I; for a complete description see Hildemann et al. (27).

Fine particle exhaust samples were collected downstream of six parallel AIHL cyclone separators, each connected to three 47-mm-diameter filter holders which were used to sample particulate matter at a flow rate of 9.0–9.6 L/min per filter, yielding 18 separate fine particle samples. Sixteen filter holders were loaded with quartz fiber filters (Pallflex 2500 QAO), and the remaining two filter holders contained Teflon filters (Gelman Teflo, 2.0-μm pore size). All quartz filters were baked at 750 °C for 2–4 h before use in order to ensure low organic contamination levels on the blank filter material. After each experiment, three filter samples (two Teflon and one quartz fiber filter samples) were used for the determination of trace metals, ionic species, total organic, and elemental carbon. The remaining quartz fiber filters were reserved for organic compound analysis. All samples were stored at -25 °C shortly after completion of each source test.

Sample Extraction. Filter samples from the motor vehicle source tests were grouped to form three composite samples representing, respectively, seven catalyst-equipped automobiles, six automobiles without catalytic converters, and two heavy-duty diesel trucks. An extraction protocol was followed which is designed for the quantitative analysis of trace amounts of organic compounds found in particulate matter. The method is described extensively elsewhere (32–36). In brief, each filter composite was spiked prior to extraction with known amounts of perdeuterated tetracosane (n-$C_{24}D_{50}$), which served as a recovery standard. The samples were extracted twice with hexane, followed by successive extraction three times with benzene/2-propanol (2:1). After the extracts were combined and the extract volume was reduced in a multistep reduction process to 200–500 μL, one aliquot of the extract was derivatized by adding freshly produced diazomethane to convert organic acids to their methyl ester analogues and other compounds having active H atoms (e.g., phenols, enols) to their methoxy analogues.

Compound Identification and Quantification. Compound identification and quantification were conducted using a Finnigan 4000 quadrupole gas chromatograph/mass spectrometer (GC/MS) interfaced with an INCOS data system. The GC/MS system was operated in the electron impact mode (electron energy of 70 eV). The chromatographic procedure for GC/MS can be described as follows: (1) extract injection at 65 °C, (2) isothermal hold at 65 °C for 10 min, (3) temperature ramp program of 10 °C/min for 21 min, and (4) isothermal hold at 275 °C for another 49 min. Additional details are described elsewhere (32, 33, 35, 36).

Compound identification was performed with the help of the National Institute of Standards and Technology (NIST) standard library (incorporated in the INCOS data system) and, where available, by comparison with the retention times and mass fragmentation patterns of standard reference compounds. Organic compounds that remain undetected include the following: (a) compounds of molecular weight higher than ~500 (the upper limit of the spectrometer mass scan), e.g., polymeric compounds; (b) organics in very low yields; (c) compounds insoluble in the solvents used; and (d) compounds which do not elute from the chromatographic column used. Within these constraints, compound identification was deemed (a) *positive*, when the sample mass spectrum was identical

to that of an authentic standard plus the library spectrum and also the retention time data for the sample and standard agreed quite well; (b) *probable*, same as above except that no authentic standards were available; (c) *possible*, same as above except that the mass spectrum contained information from other compounds but with minor overlap; or (d) *tentative*, when the mass spectrum revealed additional fragment ions from several compounds (noise) with overlap.

Quantification was based on the application of 1-phenyldodecane as coinjection standard and perdeuterated tetracosane as the internal surrogate standard. In order to correct for detector response, sets of relative response factors were determined from multiple injections and analyses of standard compounds with the analytical system.

Standard Compounds. Quantification and compound confirmation was achieved using prepared standards. The following standard mixtures were injected onto the GC/MS systems: (1) normal alkanes ranging from n-C_{10} to n-C_{36}; (2) normal alkanoic acids as methyl esters from n-C_6 to n-C_{30}; (3) a suite of 40 aromatic and polycyclic aromatic hydrocarbons (PAHs) including isopropylbenzene, indan; neopentylbenzene, 1,2,3,4-tetramethylbenzene, naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, 1,1′-biphenyl, 2,6-dimethylnaphthalene, hexamethylbenzene, 1,3,5-triisopropylbenzene, acenaphthylene, 2,3,4-trimethylnaphthalene, fluorene, 2-methylfluorene, 3-methyl-1,1′-biphenyl, 3,4′-dimethyl-1,1′-biphenyl, dibenzothiophene, phenanthrene, anthracene, fluoranthene, pyrene, 2,3-benzofluorene, 1,1′-binaphthalene, benz[a]anthracene, chrysene, triphenylene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, 9,10-diphenylanthracene, dibenz[a,h]anthracene, benzo[ghi]perylene, anthanthrene, coronene, 1,2,4,5-dibenzopyrene, cyclopenta[cd]pyrene, and indeno[1,2,3-cd]pyrene (4) a set of 10 polycyclic aromatic ketones and quinones including 9H-fluoren-9-one, dibenzofuran, phenyl p-tolyl ketone, benzophenone, 9,10-phenanthrenedione, 9,10-anthracenedione, anthrone, xanthone, 7H-benz[de]anthracen-7-one, and benz[a]anthracene-7,12-dione; (5) a set of 8 aromatic and polycyclic aromatic N- and S-substituted compounds including 4-hydroxyquinone, phenanthridine, carbazole, 5,6-benzoquinoline, 7,8-benzoquinoline, 1,2,3,4-tetrahydro-9-acridanone, dibenzothiophene, and 9-thioxanthenone; (6) a suite of 11 dicarboxylic acids (C_3–C_{10}) as dimethyl esters; and (7) others including 4-methylbenzaldehyde, 3,4-dimethoxybenzaldehyde, indanone, (20R)-5α(H),-14α(H),17α(H)-cholestane, 2-methoxypyridine, benzothiazole, 1-methyl-2-pyrrolidinone, N,N-dibutylformamide, 2-(2-butoxyethoxy)ethanol, and 2,3-dihydroxy-1H-indan-1-one.

Results and Discussion

Sources of Particulate Emissions from Combustion Engines. In order to understand how the molecular nature of vehicle exhaust aerosol may be related to vehicle operation, it is useful to consider the mechanisms within the internal combustion engine which contribute to the emissions of particle-phase organic compounds.

The composition and emission rate of particles from internal combustion engines vary with (a) engine parameters such as engine type and design, size, accumulated operation time, and emission control system; (b) engine operating conditions including length of cold start period, air/fuel ratio, engine load, lubricant oil type, and fuel composition; and (c) maintenance schedule for engine adjustment and lubricant oil replacement (*12, 19, 37–39*).

The contribution of fuels and lubricants to the aerosol production process can be further subdivided by tracing the molecular origin of the aerosol back to the following seven sources and processes: (1) unburned fuel components, (2) unburned lubricant oil components, (3) partially oxidized combustion products from the combustion of fuel, (4) partially oxidized products of the combustion of lubricant oil, (5) pyrolysis products of fuel constituents, (6) pyrolysis products from lubricant oil, and (7) combustion of fuel additives (*13, 37, 38, 40–46*). Gasoline fuels have a final boiling point of less than 220 °C and consist of a complex mixture of hydrocarbons ranging from C_4 to C_{10} in carbon numbers (*47, 48*). Typical diesel fuels on the other hand, show boiling points between 280 and 360 °C and hydrocarbon mixtures that range from roughly C_{10} to C_{25} (*37, 38, 43, 47, 49*). The higher boiling fraction of diesel fuel is largely responsible for the soot formation characteristic of diesel vehicles (*47*). In contrast, lubricating oils usually have final boiling points between 400 and 550 °C and consist of hydrocarbon mixtures from C_{14} to C_{45} (*40, 47, 49, 50*). A number of researchers have investigated the contribution of engine oil to the particulate exhaust emissions from diesel-powered vehicles. It was concluded that, depending on the operating conditions, 2–25% of the particulate mass emitted originated from the lubricating oil. This amounted to 10–88% of the solvent-extractable particulate mass emitted (*37–40, 42, 43, 46, 51*). Pedersen et al. (*39*) conducted a number of experiments on a gasoline-powered engine. They found that 90% of the engine oil consumed in the combustion chamber had passed the piston and piston rings while 10% passed through the positive crankcase ventilation system (PCV) to reach the combustion chamber. Further, they observed that using a lubricant oil with low viscosity markedly increased both oil consumption and particulate emissions. The oil consumption and therefore the particulate emissions from high-mileage automobiles are increased as oil mist is passed into the combustion chamber via worn-out intake valve guides (*39*). Since there are distinct differences between the chemical composition of fuels vs lubricants, it may be possible to identify the relative contribution of each of these sources to the exhaust aerosol during the present source testing program.

Vehicular Mass Emission Rates. Details of the vehicles tested have been published elsewhere, including the fine particle emission rates, the bulk chemical and elemental compositions of the fine particulate matter emitted, and the particle size distributions for the different vehicle types (*27, 30*). Table I summarizes the major vehicle fleet emission characteristics including fuel consumption, fine particle emission rates, and bulk content of organics and elemental carbon. Hildemann et al. (*27*) have shown that the fleet-average mass emission rates for these noncatalyst and catalyst-equipped autos compare well with previously published data. The fine particulate emission rates for the two fairly new heavy-duty diesel trucks tested are somewhat lower than have been found by other studies. The organic carbon emission rates from these diesel trucks are similar to earlier studies, but the
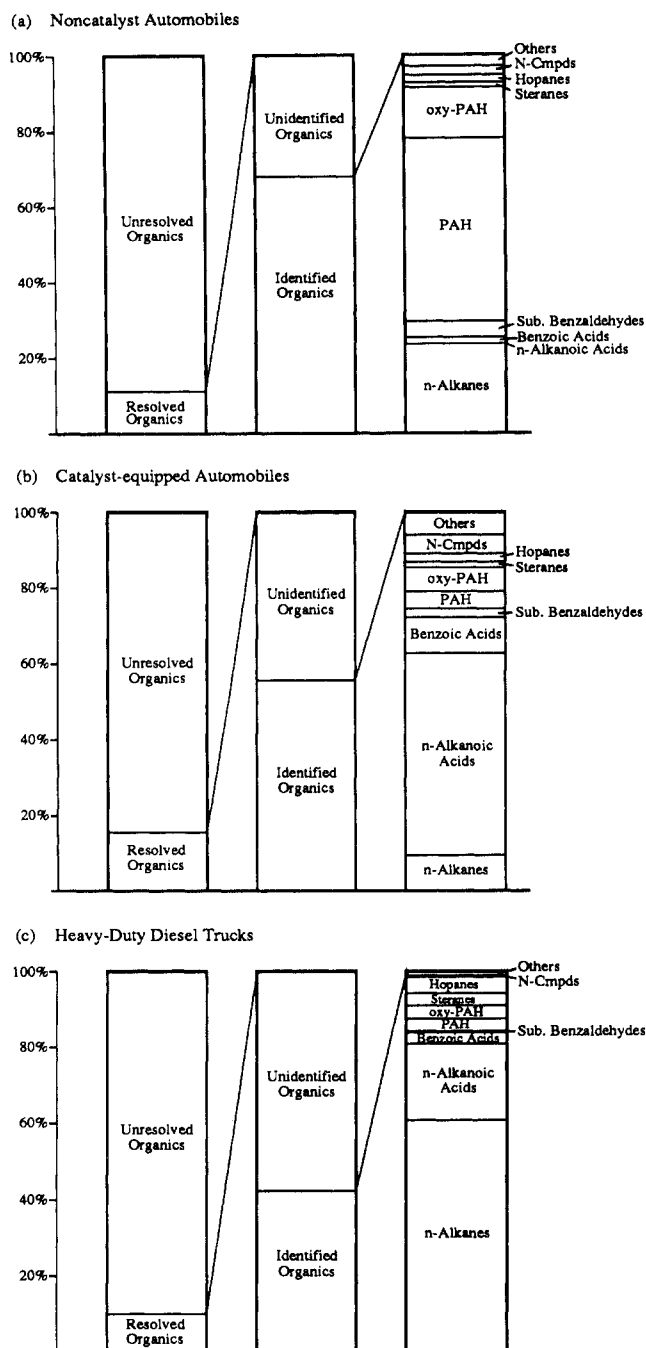
(a) Noncatalyst Automobiles

(b) Catalyst-equipped Automobiles

(c) Heavy-Duty Diesel Trucks

Figure 1. Mass balance for elutable organic matter in the fine particle emissions from (a) automobiles without catalytic converters, (b) catalyst-equipped automobiles, and (c) heavy-duty diesel trucks.

Figure 2. Total reconstructed ion current (RIC) for the fine particle organics emitted from the vehicles tested: (a) automobiles without catalytic converters, (b) catalyst-equipped automobiles, and (c) heavy-duty diesel trucks. I.S. is the internal standard (n-$C_{24}D_{50}$); 1-PD is the coinjection standard (1-phenyldodecane); X denotes a contaminant peak.

elemental carbon (e.g., black soot) emission rates are lower than for older trucks (27).

Mass Balance for Elutable Fine Organic Matter. Material balances that describe the chemical composition of the elutable organic mass as detected by GC/MS were constructed and are shown in Figure 1a–c. The elutable organic mass can be subdivided into resolved and unresolved organic mass. The unresolved organic mass, often referred to as an unresolved complex mixture (UCM) (52), consists mainly of branched and cyclic hydrocarbons and comprises 84.6% (catalyst-equipped autos) to 90.3% (heavy-duty diesel trucks) of the elutable organic mass. From the mass fraction that is resolved as discrete peaks by GC/MS (resolved organic mass), 42.3% (heavy-duty diesel truc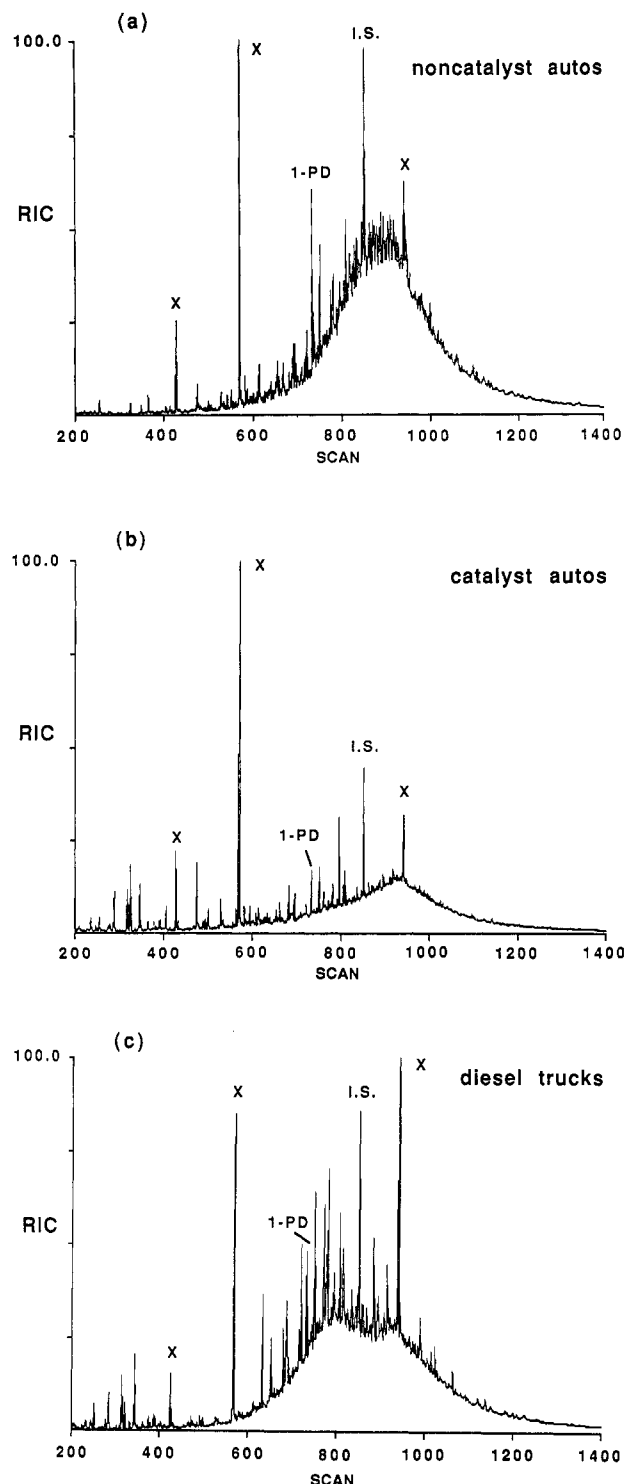ks) to 67.9% (noncatalyst autos) could be identified as specific organic compounds. For noncatalyst automobiles, the main portion (61.2%) of the identifiable mass consists of PAH and oxy-PAH such as polycyclic aromatic ketones (PAK) and polycyclic aromatic quinones (PAQ). In contrast, 53.4% of all the identifiable resolved organic mass being released from catalyst-equipped autos consists of n-alkanoic acids. For heavy-duty diesel trucks most of the identified resolved organic mass consists of n-alkanes (60.8%). Mechanisms and sources will be

Table II. Fine Aerosol Emission Rates for Single Organic Compounds from Noncatalyst and Catalyst Automobiles and from Heavy-Duty Diesel Trucks

| | emission rates,[a] μg/km | | | |
| | autos | | heavy-duty | |
	noncatalyst	catalyst	diesel trucks	compd ID[b]
n-Alkanes				
n-nonadecane	59.0	8.5	532.7	a
n-eicosane	103.9	13.3	991.3	a
n-heneicosane	95.2	12.1	673.0	a
n-docosane	79.8	10.9	363.6	a
n-tricosane	54.7	8.1	241.4	a
n-tetracosane	71.6	10.6	216.1	a
n-pentacosane	113.5	18.4	334.2	a
n-hexacosane	53.4	9.0	163.0	a
n-heptacosane	25.5	7.0	72.3	a
n-octacosane	6.8	2.4	32.1	a
n-nonacosane	7.6	2.7	37.2	a
n-triacontane	9.0	3.1	63.8	a
n-hentriacontane	4.8	1.4	21.9	a
n-dotriacontane	4.6	1.3	12.0	a
total class emission rate	689.4	108.8	3754.6	
n-Alkanoic Acids[c]				
n-hexanoic acid	3.6	65.8	159.2	a
n-heptanoic acid	0.8	8.4	99.4	a
n-octanoic acid	2.1	51.1	63.3	a
n-nonanoic acid	8.6	196.2	146.9	a
n-decanoic acid	3.2	72.7	77.4	a
n-undecanoic acid	8.8	77.3	269.9	a
n-dodecanoic acid	5.5	41.4	71.5	a
n-tridecanoic acid	0.56	3.3	21.2	a
n-tetradecanoic acid (myristic acid)	1.7	11.9	45.7	a
n-pentadecanoic acid	0.40	3.4	17.5	a
n-hexadecanoic acid (palmitic acid)	6.0	63.9	153.1	a
n-heptadecanoic acid	0.45	2.4	38.0	a
n-octadecanoic acid (stearic acid)	3.0	18.0	72.5	a
n-nonadecanoic acid	0.59	0.48	1.8	a
n-eicosanoic acid	0.27	nd	nd	a
n-heneicosanoic acid	0.11	nd	nd	a
total class emission rate	46.68	616.28	1237.4	
n-Alkenoic Acid[c]				
cis-9-octadecenoic acid (oleic acid)	1.2	5.0	8.0	a
total class emission rate	1.2	5.0	8.0	
Benzoic Acids[c]				
benzoic acid	4.2	99.9	170.7	b
4-methylbenzoic acid	0.62	7.7	14.4	a
total class emission rate	4.82	107.6	185.1	
Substituted Benzaldehydes				
2-methylbenzaldehyde	15.2	2.8	5.0	b
3-methylbenzaldehyde	3.5	0.53	1.6	b
4-methylbenzaldehyde	7.7	1.7	2.3	a
dimethylbenzaldehydes	56.4	10.9	8.6	b
trimethylbenzaldehydes	16.7	4.1	nd	b
1,4-benzenedicarboxaldehyde (4-formylbenzaldehyde)	19.2	5.2	1.5	b
3-methoxybenzaldehyde	5.4	1.7	nd	b
3,4-dimethoxybenzaldehyde	0.87	0.72	nd	a
total class emission rate	124.97	27.65	19.0	
Polycyclic Aromatic Hydrocarbons				
phenanthrene	17.3	0.88	12.2	a
anthracene	5.1	0.11	1.6	a
methylphenanthrenes, -anthracenes	42.2	1.9	31.3	b
dimethylphenanthrenes, -anthracenes	75.5	3.0	56.9	b
fluoranthene	48.3	2.0	13.0	a
pyrene	31.0	2.5	22.6	a
benzacenaphthylene	16.5	0.77	2.9	b
2-phenylnaphthalene	11.9	0.57	3.5	b
2-benzylnaphthalene	4.3	0.72	nd	b
methylfluoranthenes, -pyrenes	106.9	4.2	12.8	b
benzo[*a*]fluorene/benzo[*b*]fluorene	31.0	0.72	1.9	a
benzo[*ghi*]fluoranthene	24.7	1.3	6.9	b
cyclopenta[*cd*]pyrene	49.3	1.7	1.4	a
benz[*a*]anthracene	73.8	1.9	3.6	a

Table II (Continued)

	emission rates,^{a} μg/km			
	autos		heavy-duty	
	noncatalyst	catalyst	diesel trucks	compd ID^b
chrysene/triphenylene	55.8	3.8	9.9	a
methylbenz[a]anthracenes, -chrysenes, -triphenylenes	143.5	3.4	2.7	b
dimethylfluoranthenes, -pyrenes	161.1	4.1	14.6	b
benzo[k]fluoranthene	40.7	2.0	2.7	a
benzo[b]fluoranthene	37.9	2.9	2.9	a
benzo[j]fluoranthene	6.0	0.54	nd	b
benzo[e]pyrene	45.8	2.0	2.6	a
benzo[a]pyrene	43.5	1.9	1.3	a
perylene	14.0	0.60	1.0	a
methylbenzofluoranthenes, -benzopyrenes, -perylenes	6.4	0.47	nd	b
indeno[1,2,3-cd]pyrene	6.4	0.47	nd	a
indeno[1,2,3-cd]fluoranthene	32.6	1.7	nd	b
benzo[ghi]perylene	145.4	4.7	1.6	a
anthanthrene	9.4	0.08	nd	a
benzo[b]triphenylene	4.0	0.09	nd	b
dibenz[a,h]anthracene	8.3	0.33	nd	a
benzo[b]chrysene	2.3	0.02	nd	b
coronene	104.6	1.1	nd	a
total class emission rate	1405.5	52.47	209.9	
Polycyclic Aromatic Carboxaldehydes				
1-naphthalenecarboxaldehyde (1-formylnaphthalene)	13.5	5.5	nd	b
2-naphthalenecarboxaldehyde (2-formylnaphthalene)	68.0	22.2	nd	b
total class emission rate	81.5	27.7		
Polycyclic Aromatic Ketones (PAK) and Quinones (PAQ)				
9H-fluoren-9-one (fluorenone)	113.4	24.3	65.0	a
2-methylfluoren-9-one	9.7	1.9	17.2	b
9,10-phenanthrenedione (phenanthrenequinone)	31.6	3.8	63.1	a
9,10-anthracenedione (anthraquinone)	24.3	4.4	23.5	a
phenanthrone/anthrone	19.4	2.8	20.9	a
9H-xanthen-9-one (xanthone)	29.4	2.6	2.7	a
4-cyclopenta[def]phenanthren-4-one	7.9	1.0	5.1	b
1H-benz[de]anthracen-1-one	26.3	1.2	2.7	b
7H-benz[de]anthracen-7-one	27.9	1.3	5.6	a
6H-benzo[cd]pyren-6-one (benzo[cd]pyrenone)	20.0	0.78	1.2	b
total class emission rate	309.9	44.08	207.0	
Regular Steranes				
(20S and R)-5α(H),14β(H),17β(H)-cholestanes	8.4	3.6	39.6	b
(20R)-5α(H),14α(H),17α(H)-cholestane	9.3	4.0	43.0	a
(20S and R)-5α(H),14β(H),17β(H)-ergostanes	7.9	4.1	43.4	b
(20S and R)-5α(H),14β(H),17β(H)-sitostanes	11.4	5.4	63.4	b
total class emission rate	37.0	17.1	189.4	
Pentacyclic Triterpanes				
22,29,30-trisnorneohopane	6.8	3.0	23.1	b
17α(H),21β(H)-29-norhopane	10.7	5.9	39.6	b
17α(H),21β(H)-hopane	18.2	9.0	94.2	b
(22S)-17α(H),21β(H)-30-homohopane	8.3	3.1	38.0	b
(22R)-17α(H),21β(H)-30-homohopane	5.5	1.9	38.3	b
(22S)-17α(H),21β(H)-30-bishomohopane	4.7	1.5	22.7	b
(22R)-17α(H),21β(H)-30-bishomohopane	3.5	1.1	16.0	b
total class emission rate	57.7	25.5	271.9	
N-Containing Compounds				
quinoline	5.3	0.57	0.46	b
isoquinoline	4.9	3.4	4.1	b
1-methyl-2-pyrrolidinone (m-pyrol)	54.4	33.0	16.4	a
N,N-dibutylformamide	4.7	20.7	7.6	a
total class emission rate	69.3	57.67	28.56	
Other Compounds				
2-(2-butoxyethoxy)ethanol	42.6	53.6	55.0	a
5-methyl-1(3H)-isobenzofuranone (5-methylphthalide)	39.7	9.1	nd	b
2,3-dihydroxy-1H-indan-1-one (indanone)	4.9	2.5	10.8	a
total class emission rate	87.2	65.2	65.8	

^{a} nd, not detected; accuracy determinations were performed for both polar and nonpolar standard compounds, showing that the relative standard deviations were between 4 and 8% depending on the amount of the standard compounds injected. ^{b} For more details, see text: a, positive; b, probable; c, possible; d, tentative. ^{c} Detected as methyl ester.

discussed below which might explain the compositional differences found in the elutable organic mass emitted as fine aerosols from the vehicle types investigated here.

Exhaust Aerosol Composition. Figure 2a–c shows the total reconstructed ion current (RIC) plots for (a) autos without catalytic converters, (b) catalyst-equipped autos, and (c) heavy-duty diesel trucks. The variety of compounds identified in vehicular exhaust emissions and their emission rates can be described as follows.

n-Alkanes. Crude oil, the primary source for gasoline, diesel fuel, and lubricating oil, contains n-alkanes ranging up to about C_{35} with no preference for odd vs even carbon numbers and shows a carbon preference index (CPI_{odd}) of ~ 1.0 (52–56). Because gasoline generally contains only the low-boiling crude oil distillates $\leq C_{10}$, virtually no particle-phase n-alkanes ($\geq C_{19}$) should be contributed from unburned gasoline. Diesel fuels contain n-alkanes up to C_{30} with more than 95% of these n-alkanes by mass having carbon numbers less than C_{19} (54, 57, 58). Newly refined lubricant oils show only trace amounts of n-alkanes (55, 59). To ensure trouble-free engine operation at low temperatures, a steady supply of lubricant oil is necessary at points of friction in the engine. Because the ability to pump lubricating oil through the engine depends strongly on the wax (n-alkanes) content of the oil, crude oil fractions used for lubricant oil production have to be dewaxed (59–61). Commercial dewaxing processes remove 92–98% of the n-alkane content of oils (59). Kissin (59) has shown that this dewaxing process does not remove the n-alkyl moieties in the oil such as n-alkyl-substituted naphthenic and naphtheno-aromatic compounds. At elevated temperatures ($\sim 250\,^{\circ}C$) encountered during engine operation, these n-alkyl hydrocarbons undergo mild thermocracking, preferably at the tertiary carbon atoms. This may explain how high molecular weight n-alkanes can appear in the exhaust of vehicles even when the fuels and or lubricants were originally deficient in those compounds.

By use of the sampling and analysis techniques described earlier, the emission rates of n-alkanes having carbon numbers ranging from C_{19} to C_{32} have been quantified in fine particulate vehicle exhaust as shown in Table II. Particulate n-alkane emissions for all vehicle classes tested show a more or less bimodal n-alkane carbon number distribution with elevated emission rates between C_{20}–C_{22} and C_{24}–C_{27} (Figure 3a,b). Essentially all of the particulate n-alkanes emitted from the gasoline engines come from unburned engine oil. The great relative increase of lower n-alkanes ($\leq C_{22}$) in the diesel exhaust particulate matter reflects the relatively higher lubricant oil consumption of diesel engines and results also from unburned diesel fuel itself. Further, it can be seen from Figure 3a that the n-alkane emission rate for noncatalyst autos is ~ 4 times higher than that of the catalyst-equipped cars. This difference could be due to one or both of the following factors. First, the noncatalyst autos tested have older, higher mileage engines (on average 1.5 times more accumulated mileage than the catalyst-equipped autos tested) with an increased probability that worn engine parts will pass more unburned lubricating oil through the engine. Second, these n-alkane emission differences could be due to changes in engine design and postcombustion oxidation in the catalytic converter systems of the newer catalyst-equipped automobiles.

n-Alkanoic Acids. Particle-bound n-alkanoic acids ranging from C_6 to C_{21} have been identified in the exhaust
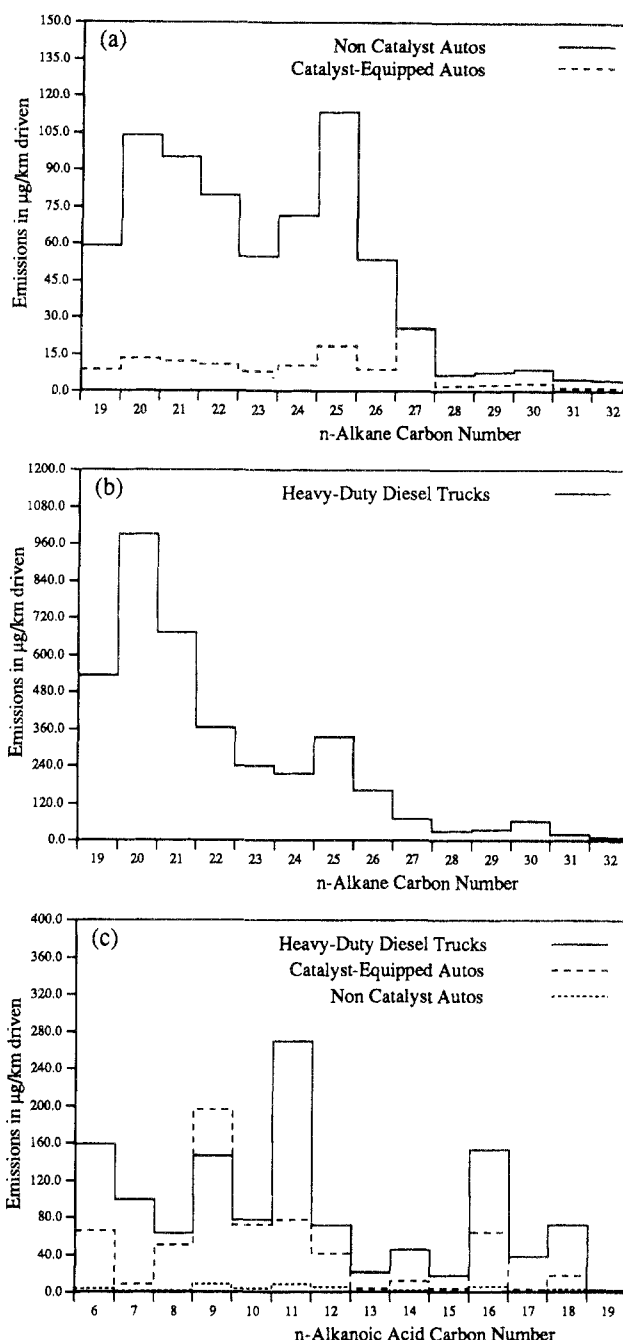

Figure 3. Vehicular emission profiles for fine particle associated n-alkanes and n-alkanoic acids: (a) n-alkanes from automobiles with and without catalytic converters, (b) n-alkanes from heavy-duty diesel trucks, and (c) n-alkanoic acids from the three vehicle types tested.

emissions from the vehicle types tested and are listed in Table II. The catalyst-equipped automobiles emitted more than 600 $\mu g/km$ of total n-alkanoic acids, ~ 13 times the amount emitted by the noncatalyst autos tested. Furthermore, the heavy-duty diesel trucks emitted about twice the quantity of n-alkanoic acids per kilometer driven when compared to the catalyst-equipped automobiles, or 26 times the amount emitted by autos that lack a catalytic converter (Figure 3c). Simoneit (56) reported a similar relationship when comparing n-alkanoic acid emissions (C_{10}–C_{20}) between a noncatalyst auto and a diesel truck. As a fraction of the total fine particle mass emitted, n-alkanoic acids are found to be highly enriched in catalyst-equipped vehicle exhaust (34 238 μg of n-alkanoic acids/g of fine aerosol emitted from catalyst-equipped cars vs 786

$\mu g/g$ from noncatalyst gasoline cars and 3033 $\mu g/g$ from diesel trucks).

Focusing on single compound emission rates, n-hexanoic (C_6), n-nonanoic (C_9), n-undecanoic (C_{11}), and n-hexadecanoic acid (C_{16}) are the most abundant normal fatty acids released from all three vehicle types (Figure 3c). Kawamura et al. (62) examined low molecular weight aliphatic organic acids ranging from C_1 to C_{10} in engine exhaust, new engine oil, and used engine oil. To sample the vehicle exhaust, they used a KOH-impregnated filter system to collect directly, without exhaust dilution, from the hot muffler of a gasoline-powered automobile. The most abundant n-alkanoic acids identified by Kawamura and co-workers (62) in the vehicle exhaust were the shorter C_1–C_3 n-alkanoic acids, found exclusively in the gas phase. Used engine oil contained, compared to new engine oil, enhanced concentrations of formic acid (C_1) and acetic acid (C_2). Because no n-alkanoic acids in the range C_5–C_{10} were found in engine oil and there is no indication that n-alkanoic acids are part of the fuels used, it is proposed that the higher alkanoic acids (C_6–C_{22}) quantified in vehicle exhaust (Table II) are formed during the combustion process (63) and/or catalytic oxidation process (catalyst auto only) (64). Given the relatively high emission rates of organic acids from the catalyst-equipped cars when compared to the noncatalyst cars, it is likely that the presence of the catalyst system enhances the formation of organic acids.

n-Alkenoic Acids. One unsaturated normal fatty acid, oleic acid ($C_{18:1}$), has been identified in all of the vehicular emissions. The emission rates are generally low and increase for catalyst-equipped autos by ~ 4 times when compared to noncatalyst automobiles. The emission rate for diesel trucks is enhanced by almost 7-fold when compared to the noncatalyst automobiles. Because gasoline fuels do not contain compounds equal to or higher than C_{10}, the oleic acid would be expected to have come from the combustion system including processing of lubricating oil constituents.

Substituted Benzoic Acids and Benzaldehydes. Benzoic acid and alkylbenzoic acids recently have been identified in vehicular source emissions (56, 62). Besides identifying benzoic acid in the exhaust of one noncatalyst auto, Kawamura and co-workers (62) also detected benzoic acid in used engine oil. New, unused oil did not show any benzoic acid. In the present study, benzoic acid and 4-methylbenzoic acid together with alkylbenzaldehydes, 4-formylbenzaldehyde, and methoxy- and dimethoxybenzaldehydes have been quantified in the vehicular sources tested (Table II). The emission rates for the two identified benzoic acids closely follow the emission pattern discussed earlier for n-alkanoic acids. Autos equipped with catalytic converters show a 22-fold higher emission rate than was found for automobiles without catalytic converters. This pronounced emission increase for the catalyst-equipped automobiles might indicate that postcombustion formation of benzoic acids in the catalytic converter system is an important factor. Substituted benzaldehydes show a reversed emission pattern, e.g., lower emissions for catalyst autos and diesel trucks than for noncatalytic automobiles.

Dicarboxylic Acids. Kawamura and Kaplan (65) have identified dicarboxylic acids in the exhaust emissions from a diesel auto and one gasoline-powered automobile. The hot exhaust emissions were collected directly via KOH-impregnated filters from the muffler of each test auto while the engine was running at idle speed. They reported that dicarboxylic acids ranging from oxalic acid (C_2) to sebacic acid (C_{10}) were present in the emissions from both automobiles.

During the source test program conducted by dilution sampling in the present paper, the particulate emissions from all three vehicle types were examined for a set of 11 dicarboxylic acids (C_3–C_{10}) that we have previously identified as major compounds present in the Los Angeles atmosphere (36). None of the dicarboxylic acids found in ambient fine particulate matter could be detected in the fine particulate vehicular emissions. This suggests that no measurable particle-phase dicarboxylic acids were emitted from the vehicles tested here. Precursor compounds such as cyclic olefins are emitted from vehicle exhaust, which under ambient conditions (as well as under the sampling conditions employed here) are in the gaseous phase. Subsequent atmospheric oxidation (e.g., O_3) leads to some of the dicarboxylic acids observed in the atmosphere (66). There may be other gas-phase species in the vehicle exhaust (e.g., dialdehydes) that can subsequently form dicarboxylic acids in the atmosphere.

Polycyclic Aromatic Hydrocarbons. The concern that carcinogenic and mutagenic organic compounds could be released from diesel fuel and gasoline-powered engines has prompted research efforts on the formation, release, and ambient behavior of PAH and substituted homologues (8, 11, 12, 15, 16, 18, 67–69). As a result of this work, it has been shown that fuel aromaticity, engine load, PAH accumulation in lubricant oil, lubricant oil combustion, and cold start behavior influence the emission rates for PAH (20, 39, 44, 45, 48, 70–72).

At present, the exact mechanism of PAH formation during combustion is not understood in detail (73). Three different pyrolysis mechanisms are currently considered as possible: slow Diels–Alder condensations, rapid radical reactions, and ionic reaction mechanisms (73). Because the combustion process within the internal combustion engine has to occur very rapidly, the radical formation mechanism is considered to be favored (73). Gaseous hydrocarbon radicals are thought to rearrange quickly, providing the mechanism of PAH formation and growth. The addition of hydrocarbon radicals to lower molecular weight PAH then leads via alkyl-PAH to the formation of higher aromatized PAH (74).

During this study, the emission rates for more than 30 individual PAH and alkyl-PAH have been quantified in the vehicular emissions collected (Table II). Noncatalyst automobiles show the highest emission rates for each of the PAH detected. A more than 25-fold higher total PAH emission rate is observed for autos without catalytic converters than for autos equipped with catalytic exhaust emission control devices (1405.5 vs 52.5 $\mu g/km$). The two fairly new heavy-duty diesel trucks (average 4251 miles) tested showed an average total PAH emission rate per kilometer driven which is only one-seventh as large as seen for the noncatalyst automobiles. The emission rates for single PAH emitted from all vehicles are shown in Figure 4. While the heavy-duty diesel trucks tested show a preference for low molecular weight PAH (methyl- and dimethylphenanthrenes, anthracenes), the noncatalyst automobiles emit over the whole molecular weight spectrum investigated with greater emission rates for the higher molecular weight PAH such as benzo[ghi]perylene and coronene. Schuetzle and Frazier (45) reported that the
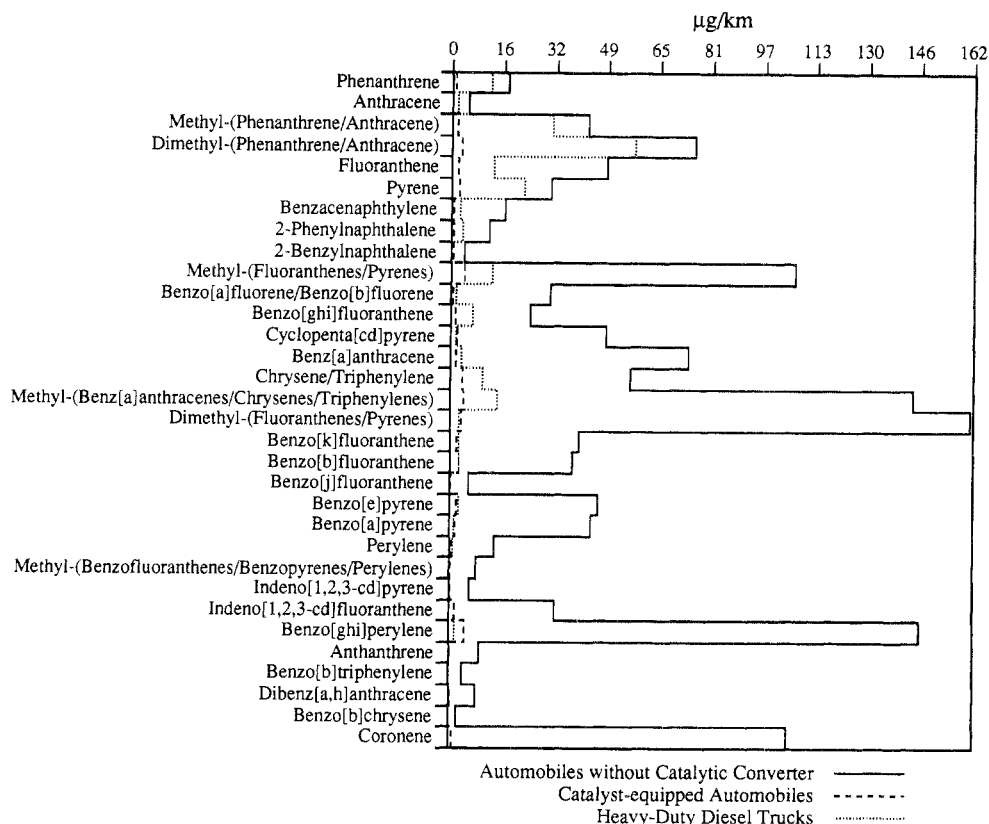
μg/km

0 16 32 49 65 81 97 113 130 146 162

Phenanthrene
Anthracene
Methyl-(Phenanthrene/Anthracene)
Dimethyl-(Phenanthrene/Anthracene)
Fluoranthene
Pyrene
Benzacenaphthylene
2-Phenylnaphthalene
2-Benzylnaphthalene
Methyl-(Fluoranthenes/Pyrenes)
Benzo[a]fluorene/Benzo[b]fluorene
Benzo[ghi]fluoranthene
Cyclopenta[cd]pyrene
Benz[a]anthracene
Chrysene/Triphenylene
Methyl-(Benz[a]anthracenes/Chrysenes/Triphenylenes)
Dimethyl-(Fluoranthenes/Pyrenes)
Benzo[k]fluoranthene
Benzo[b]fluoranthene
Benzo[j]fluoranthene
Benzo[e]pyrene
Benzo[a]pyrene
Perylene
Methyl-(Benzofluoranthenes/Benzopyrenes/Perylenes)
Indeno[1,2,3-cd]pyrene
Indeno[1,2,3-cd]fluoranthene
Benzo[ghi]perylene
Anthanthrene
Benzo[b]triphenylene
Dibenz[a,h]anthracene
Benzo[b]chrysene
Coronene

Automobiles without Catalytic Converter ———
Catalyst-equipped Automobiles - - - - - -
Heavy-Duty Diesel Trucks ·········

Figure 4. Vehicular emission profiles for fine particle polycyclic aromatic hydrocarbons (PAH).

ratio of pyrene/benzo[a]pyrene in exhaust emissions is ~10 times greater for diesel engines than for gasoline-powered engines, which is in good agreement with results stated here (ratio close to 13). Emissions of alkyl-substituted PAH are particularly high when compared to the emission rates for most individual unsubstituted PAH. This is in agreement with previous studies (75, 76). Alkyl homologues of some PAH show similar or even greater mutagenic activities than benzo[a]pyrene (77–80). Jensen and Hites (75) reported that decreasing the exhaust gas temperature (decreased engine load) increased the total emission rate for alkyl-PAH. In addition, they found that the number of alkyl functional groups on the PAH molecules increases with decreasing combustion temperature. Applying this result to urban traffic situations suggests that an increase in traffic congestion during rush hour (longer time periods of decreased engine load) could increase the alkyl-PAH emissions relative to unsubstituted PAH emissions for automobiles without catalytic exhaust control systems.

Polycyclic Aromatic Ketones, Quinones, and Carboxaldehydes. Oxygenated polycyclic aromatic hydrocarbons have been identified previously in particulate emissions from diesel and gasoline engines (8, 10, 14, 16, 75, 81–85). Oxy-PAH are believed to be formed during incomplete combustion by addition of oxygen free radicals or molecular oxygen to the PAH with subsequent rearrangements (85). To date only relative mass emission rates (μg/g) for a small number of oxy-PAH emitted from vehicles have been reported (75).

During the course of this study, the emission rates for 12 oxy-PAH were measured, including carboxaldehyde, ketone, and quinone derivatives as well as one oxyheterocyclic-PAH (9H-xanthen-9-one); see Figure 5. Jensen and Hites (75) reported that the diesel engine tested in
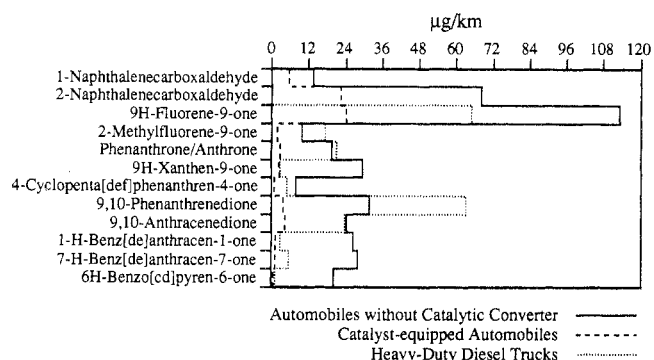
μg/km

0 12 24 36 48 60 72 84 96 108 120

1-Naphthalenecarboxaldehyde
2-Naphthalenecarboxaldehyde
9H-Fluorene-9-one
2-Methylfluorene-9-one
Phenanthrone/Anthrone
9H-Xanthen-9-one
4-Cyclopenta[def]phenanthren-4-one
9,10-Phenanthrenedione
9,10-Anthracenedione
1-H-Benz[de]anthracen-1-one
7-H-Benz[de]anthracen-7-one
6H-Benzo[cd]pyren-6-one

Automobiles without Catalytic Converter ———
Catalyst-equipped Automobiles - - - - - -
Heavy-Duty Diesel Trucks ·········

Figure 5. Vehicular emission profiles for fine particle oxygenated polycyclic aromatic hydrocarbons (oxy-PAH).

their experiment showed little evidence for the presence of naphthalenecarboxaldehydes. Fluoren-9-one and alkyl-fluoren-9-ones, the only ketone PAH identified in their diesel engine test, instead showed the highest concentrations. This observation is in reasonable agreement with our diesel truck data. The highest emission rate in our tests for a single oxy-PAH released from diesel trucks was found for fluoren-9-one (65.0 ng/km), followed by 9,10-phenanthrenedione (63.1 ng/km). In a manner similar to the PAH, the highest oxy-PAH emission rates were measured for automobiles without catalytic emission control systems (oxy-PAH emission ratios noncatalyst: catalyst:diesel = 5.5:1:2.9). The emission rate profile for oxy-PAH from heavy-duty diesel trucks shows a trend similar to that observed for PAH, low emission rates for high molecular weight oxy-PAH compared to noncatalyst automobiles (Table II).

Sterane and Triterpane Hydrocarbons. During the geological maturation processes of source rocks and crude oils, organic material originally contributed by plants and
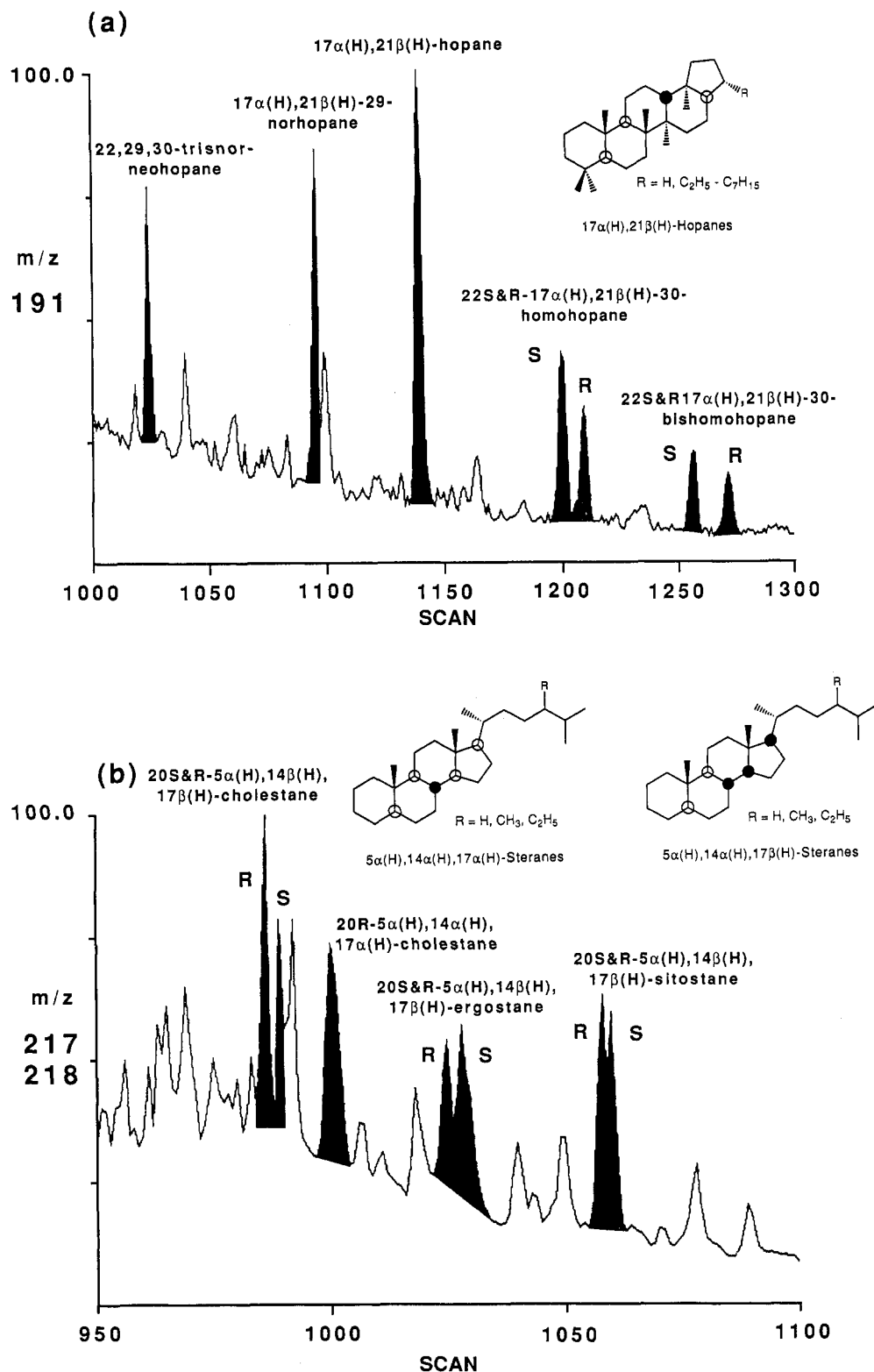
Figure 6. Selected mass fragmentograms for fine particle organic aerosol emissions from heavy-duty diesel trucks: (a) m/z 191, indicator for pentacyclic triterpanes; (b) m/z 217 + 218, key fragment ions for steranes.

animals is transformed by diagenesis and catagenesis over millions of years (52, 54, 58, 86–88). In petroleum geochemistry, steranes and triterpanes, found in petroleum, are used as marker compounds to determine the source rocks from which the crude oil migrated and also to assess the geological maturity of crude oils (54, 58). While a large spectrum of steranes and triterpanes are present in petroleum, only the major compounds present in vehicle exhaust were quantified during the course of

this study; see Figure 6a,b. The triterpanoid hopanes were all identified using information on elution order and the mass spectra of authentic standards (52, 55, 89). Among the steranes, (20R)-5α(H),14α(H),17α(H)-cholestane is identified and confirmed by injection of the authentic standard on the GC/MS system used in our study. The other steranes are identified according to published mass spectra and ion chromatograms for crude oils, engine oils, and particulate exhaust emissions (52, 55, 90, 91). Such

Table III. Comparison of the Present Study with Results from Previous Studies (Using Cold Start FTP Only): Organic Particulate Emissions from Noncatalyst and Catalyst-Equipped Automobiles

	emission rates, $\mu g/km$				
	noncatalyst autos			catalyst-equipped autos	
compound name[a]	this study[b]	ref 8[c,e]	ref 94[d,e]	this study[b]	ref 94[d,e]
phenanthrene	17.3	2.8		0.9	
anthracene	5.1	0.7		0.1	
methylphenanthrenes, -anthracenes	42.2	14.0		1.9	
dimethylphenanthrenes, -anthracenes	75.5	23.5		3.0	
2-phenylnaphthalene	11.9	2.5		0.57	
fluoranthene	48.3	17.0		2.0	
pyrene	31.0	29.5	11.7	2.5	6.2
benzo[ghi]fluoranthene	24.7	8.8		1.3	
cyclopenta[cd]pyrene	45.9	7.5		1.6	
benz[a]anthracene	73.8	5.8		1.9	
chrysene/triphenylene	55.8	7.7		3.8	
benzo[b]- and benzo[k]fluoranthene	78.6	5.5		4.9	
benzo[j]fluoranthene	6.0	1.0		0.54	
benzo[e]pyrene	45.8	4.4		2.0	
benzo[a]pyrene	43.5	3.2	9.1	1.9	2.0
perylene	14.0	0.4		0.60	
indeno[1,2,3-cd]pyrene	6.4	2.7		0.47	
indeno[1,2,3-cd]fluoranthene	32.6	0.6		1.7	
benzo[ghi]perylene	145.4	9.5		4.7	
anthranthrene	9.4	0.75		0.08	
coronene	104.6	9.3		1.1	

[a] Only those compounds measured in both the present study and at least one previous study are listed. [b] Six noncatalyst (av odometer reading 117 504 miles) and seven catalyst (av odometer reading 76 623 miles) automobiles were tested; for more detail see Hildemann et al. (27). Half the miles driven by noncatalyst vehicles in 1982 were driven by cars older than 10 years, and a typical 10-year-old car has an accumulated mileage of 117 300 miles (97). Emission rates are for compounds present in the fine particle fraction only. [c] Saab 900 Gl (noncatalyst) with a four-cylinder carbureted engine (odometer reading 2769 miles); commercial leaded fuel (0.15 g of Pb/L, 96 octane) was used. The vehicle was preadjusted by the manufacturer prior testing and samples were collected on Teflon-coated glass fiber filters (8). [d] Four noncatalyst (av odometer reading 44 848 miles) and 16 catalyst (av odometer reading 27 186 miles); model years from 1970 to 1981 (94). [e] Lubricant oils were drained and replaced before FTP testing.

ion chromatograms show essentially the same elution order and relative abundance for the steranes and hopanes as those for the vehicle exhausts investigated here. Simoneit (55) determined the complete spectrum of pentacyclic triterpanes and steranes in particulate exhaust emissions collected from diesel and gasoline engines and in lubricating oil. The relative abundance of the triterpanes for the vehicular emissions agreed well with the relative abundance found in lubricant oil. Because these fossil petroleum markers belong to the higher boiling fraction of crude oil, they are not found in gasoline or diesel fuel but instead are contributed to the vehicle exhaust from the lubricating oil (55). Dividing the vehicular emission rates for these fossil petroleum markers by the equivalent emission rates found for the catalyst-equipped automobiles, one can estimate that the noncatalyst autos tested emit 2.2–2.3 times the amount of unburned lubricating oil per kilometer driven when compared with the catalyst autos. The heavy-duty diesel trucks tested emit in the same manner 10.7–11.1 times the amount of unburned lubricant oil per kilometer driven as the catalyst autos (steranes–noncatalyst:catalyst:diesel = 2.2:1.0:11.1; triterpanes–noncatalyst:catalyst:diesel = 2.3:1.0:10.7). Applying the same technique to the higher molecular weight n-alkanes (C_{28}–C_{32}) which also are contributed by uncombusted engine oil, the relative lubricating oil contribution to the exhaust aerosol shows a similar pattern (noncatalyst:catalyst:diesel = 3.0:1.0:15.3).

N-Containing Compounds. Among the identified nitrogen-containing compounds found in vehicular exhaust emissions (Table II) are two azanaphthalenes, quinoline and isoquinoline. Recently, quinolines have also been identified in urban ambient fine particle samples (36).

They also are known to occur in crude oils and shale oil (92, 93). Therefore, it is possible that the two quinolines found in the vehicular exhaust emissions may be derived from unburned fuel or lubricant oil constituents. The other two N-containing compounds (1-methyl-2-pyrrolidinone and N,N-dibutylformamide) have not yet been reported in the vehicle exhaust literature.

Other Compounds. In addition to the compound classes discussed above, three other organic compounds [2-(2-butoxyethoxy)ethanol, 5-methylphthalide, indanone] present in the exhaust emissions have been quantified (Table II).

Comparison to Prior Source Emission Data. In Tables III and IV, the organic emission rates for the gasoline- and diesel-powered vehicles measured in the present work are compared to those few past studies where the cold start Federal Test Procedure was used in conjunction with dilution sampling (8, 94). The organic compound emission rates measured in the present study for noncatalyst cars are higher than in previous studies shown in Table III. The automobiles tested by the other researchers were usually preadjusted to meet their respective emission standards, and contaminated lubricating oils were replaced with new oil to guarantee intercomparison between consecutive experiments. Replacing the lubricating oil reduces emissions from accumulated combustion products present in used engine oils. In the present study, in order to determine emission rates for particle-phase organics that are as relevant as possible to air quality at an actual urban site, the automobiles were tested in as-received condition without tuning the engines or changing the lubricant oils. This approach was intended to ensure that the exhaust emission rates of the vehicle

Table IV. Comparison of the Present Study with Results from Previous Studies: Organic Particulate Emissions from Heavy Duty Diesel Trucks

compound name[a]	emission rates, μg/km			
	this study[b]	ref 72[c]	ref 21[d]	ref 95[e]
phenanthrene	12.2	11.0	29.0	
anthracene	1.6	2.7	3.3	
methylphenanthrenes, -anthracenes	31.3		159.0	
fluoranthene	13.0	22.0	17.0	
pyrene	22.6	22.0	11.0	
benzo[ghi]fluoranthene	6.9	6.2	1.5	
cyclopenta[cd]pyrene	1.3	2.2	0.18	
benz[a]anthracene	3.6	2.7	0.47	
chrysene/triphenylene	9.9	8.8	2.8	
benzo[b]- and benzo[k]fluoranthene	5.7	4.1	0.29	
benzo[e]pyrene	2.6	1.3	0.15	
benzo[a]pyrene	1.3	0.57	<0.06	1.5

[a] Only those compounds measured in both the present study and at least one previous study are listed. [b] 1987 GMC truck (two-axle), odometer 2920 miles, engine displacement 636 in.[3]; 1987 Ford dump truck (three-axle), odometer 5581 miles, engine displacement 636 in.[3]; chassis dynamometer test, emission rates are for compounds present in the fine particulate fraction only, for more details and the driving cycle used see Hildemann et al. (27). [c] Heavy-duty diesel truck (Volvo) with 157kW, engine displacement 403 in.[3]; truck was operated according to New York City cycle on chassis dynamometer. [d] Heavy-duty diesel truck (Scania 14311) with 331 kW, odometer 125 000 miles, engine displacement 866 in.[3]; truck was operated according to German city bus cycle. [e] Four heavy-duty diesel trucks [Caterpiller 3208 (1979), Mack ENDT 676 (1979), Cummins Formula 290 (1979), Detroit Diesel 8V-71 (1977)] were tested on the chassis version of the 1983 transient procedure (96); odometer 7000–69 000 (average 40 500) miles.

Table V. Estimate of the Mobile Source Emissions of Fine Aerosol Organic Carbon (OC) and Fine Aerosol Organics within an 80 × 80 km Urbanized Area Centered over Los Angeles (for 1982)

mobile sources	fine particulate emissions,[a] kg/day	
	OC	org compds[b]
gasoline-powered vehicles		
noncatalyst automobiles	2088	2506
other noncatalyst vehicles[c]	1372	1646
catalyst-equipped automobiles	780	936
other catalyst-equipped vehicles[d]	79	95
diesel-powered vehicles		
heavy-duty trucks	1242	1490
other diesel vehicles[e]	870	1044
total mobile source emissions	6431	7717
total primary emissions[a]	29822	35786

[a] Originally from Gray (97) as updated by Hildemann et al. (27). For a map of the geographic area see Rogge et al. (35). [b] Organic compounds estimated as 1.2 × [OC]. [c] Other noncatalyst vehicle types: light trucks, medium trucks, heavy trucks, motorcycles, off-highway vehicles, and stationary gasoline engines. [d] Other catalyst-equipped vehicles: light trucks and medium trucks. [e] Other diesel vehicles: diesel autos, light trucks, and off-highway vehicles as given by ref 27 plus diesel ships and railroad engines.

fleets tested were representative of the actual emission rates of the vehicles used within the greater Los Angeles area. Table IV compares organic compound emission rates for heavy-duty diesel trucks from this study with previous results (21, 72, 95). The data from this table show that the fairly new heavy-duty diesel trucks tested here have organic compound emissions per kilometer driven comparable to the heavy-duty diesel trucks tested by other researchers with much higher accumulated miles driven.

Molecular Tracers of Vehicular Exhaust. In order to use the steranes and pentacyclic triterpanes as molecular tracers in the atmosphere for the presence of particulate emissions from internal combustion engines, the ambient concentrations of such compounds must be dominated by emissions from the source types of interest. Using the emission inventory of Gray (97) and updated by Hildemann et al. (27) for all sources contributing fossil petroleum markers to the Los Angeles urban atmosphere, it is possible to estimate the mass of steranes and pentacyclic triterpanes emitted from internal combustion engines on a daily basis. Likewise, the emission strengths of these compounds from tire wear, resuspension of road dust, oil-burning industrial and residential boilers, roofing tar pots, and asphalt roof manufacturing also can be determined by measuring their content in the source samples taken by Hildemann et al. (27). For those minor sources that have not yet been tested, including surface coatings, organic chemical processes, and miscellaneous petroleum industry emissions, the fractional sterane and pentacyclic triterpane content of the organic aerosol emissions will be assumed to be the same as was found for roofing tar pot emissions (27). Then by totaling all of the known sources for fossil petroleum marker

emissions, it can be shown that roughly 85% of all particle-associated steranes and triterpanes emitted to the Los Angeles area atmosphere are contributed by internal combustion engines. Hence, it may be possible to use these compounds as markers for the contribution of vehicle-derived aerosols if it can be shown that they are sufficiently stable in the atmosphere. If organic compounds are to be used as tracers, their rate of reaction in the atmosphere must be slow relative to transport times from source to receptor (98, 99). Moderately reactive organic gases such as the alkanes, benzene, and certain chlorinated organics can be used as tracers in Los Angeles as their half-life with respect to chemical degradation here is of the order of 20 h or more (100). In the present paper we use fossil petroleum markers such as hopanes and steranes as tracers that have been stable over geological time scales and that are extensively used in geochemistry as marker compounds (54, 58). It is unlikely that these compounds will react in the atmosphere at rates fast enough to harm their use as an atmospheric tracer over the spatial scale of an urban area (i.e., time scales of a few hours).

Estimated Mobile Source Contributions to the Los Angeles Atmosphere. The compilation of vehicular source profiles from a fleet of vehicles actually driven in the greater Los Angeles area provides the opportunity to estimate source contributions from different types of combustion engines to the southern California atmosphere. Gray (97) compiled an extensive inventory for primary fine particulate organic carbon and elemental carbon emissions for the year 1982 within (a) the heavily populated central area of urban Los Angeles (an 80 × 80 km area) and (b) for the larger South Coast Air Basin comprising the populated portions of the four counties that surround Los Angeles. That same emission inventory was updated recently by using new data gained from a source testing campaign (27) that included the vehicles tested here plus source samples taken from other important urban sources of organic aerosol (Table V). Using this updated emission

Table VI. Fine Aerosol Emission Rates for Single Compound Classes Released from Noncatalyst and Catalyst-Equipped Automobiles and from Heavy-Duty Diesel Trucks within the Urbanized (80 × 80 km) Los Angeles Study Area for 1982

	emission rates, kg/day		
	gasoline vehicles[a]		
compound class	non-catal[b,e]	catal[c,e]	diesel vehicles[d,e]
n-alkanes	61.7	15.4	60.2
n-alkanoic acids	4.2	87.0	19.8
n-alkenoic acids	0.11	0.71	0.13
benzoic acids	0.43	15.2	3.0
substituted benzaldehydes	11.2	6.4	0.3
polycyclic aromatic hydrocarbons (PAH)	125.8	7.4	3.4
polycyclic aromatic carboxaldehydes	7.3	3.9	
polycyclic aromatic ketones (PAK) and quinones (PAQ)	27.7	6.2	3.3
steranes	3.3	2.6	3.0
pentacyclic triterpanes	5.2	3.9	4.4
N-containing compounds	6.2	5.2	2.6
other identified compounds	7.8	5.8	5.9
total identified	260.94	159.71	106.03

[a] Collective distance traveled daily within the 80 × 80 km area in 1982: noncatalyst autos 53.7 × 10^6 km; catalyst autos 140.0 × 10^6 km, and heavy-duty diesel trucks 9.4 × 10^6 km. [b] Includes the other noncatalyst vehicles as described in Table V. [c] Includes the other catalyst vehicles as described in Table V. [d] Includes the other diesel vehicles as described in Table V. [e] To include the emissions from the other noncatalyst, catalyst, and diesel vehicles these other vehicles were assigned mass emission rates based on source tests present in the literature reported in Table V. Then the chemical composition of those emissions was assumed to be like that of the closest analogous vehicle tested in the present study (i.e., "other" diesel engines were assumed to have the chemical nature of the diesel trucks tested here; noncatalyst trucks were assumed to have the exhaust composition of noncatalyst autos, etc.).

inventory for the 80 × 80 km urban Los Angeles area in conjunction with the emission rates from Table II for single organic compounds, it is possible to estimate the total mass emission rates of key compound classes representing all vehicle traffic within that urban area, as shown in Table VI (for more details see the footnotes). From Table VI, it is seen that more than 85% of the fine particle bound PAH, PAK, and PAQ vehicular emissions to the urban Los Angeles atmosphere in 1982 were contributed by automobiles without catalytic exhaust emission control systems. In contrast, the n-alkanoic acids in vehicle exhaust were emitted mainly from autos equipped with catalytic converters (>80%).

Vehicular particle-phase tracer compounds comprised of the steranes and triterpanes quantified in Table II are emitted within that 80 × 80 km urban area at an estimated rate of 22.4 kg/day. Figure 7a shows the emission rates for each of these fossil petroleum marker compounds within the 80 × 80 km Los Angeles study area. The highest emission rate for a single marker compound was found for 17α(H),21β(H)-hopane (1.75 kg/day). The emissions of fine primary particulate organic carbon from all sources combined for the area discussed was estimated to total 29 820 kg/day (Table V). Restated, this amounts to 35 800 kg/day equivalent organic compound mass ([organic compound] ≃ 1.2[organic carbon]). Thus, the fossil petroleum markers studied here, when combined, account for 0.063% of the fine particulate organic compound

emissions. From the OC data of Gray et al. (101), the ambient annual mean fine particulate total organic compound concentrations ($d_p \leq 2 \mu m$) can be calculated to be the following: West Los Angeles 6.94 $\mu g/m^3$, downtown Los Angeles 8.63 $\mu g/m^3$, and Pasadena 8.06 $\mu g/m^3$ during 1982. If 0.063% of the fine total organic compound concentrations at the three sampling sites were present as steranes and triterpanes, then ambient fine particle concentrations of these compounds totaling ~4.37 ng/m^3 at West Los Angeles, 5.43 ng/m^3 at downtown Los Angeles, and 5.08 ng/m^3 at Pasadena should be measured.

Comparison of Source and Ambient Data. Recently, Rogge et al. (36, 102) compiled an extensive data set on fine aerosol organic compound concentrations for the year 1982 for the 80 × 80 km greater Los Angeles study area discussed here. The aerosol sampling strategy and the analytical procedures used in that study were nearly identical to those used for vehicle testing. Hence, the results from both studies allow direct comparison. Most of the compounds identified in the particulate automobile exhaust emissions have also been quantified in the ambient aerosol. Indeed, hopanes and steranes have been quantified in the ambient fine aerosol collected at the three sampling sites mentioned above within the Los Angeles air basin. The ambient annual average concentration profiles for the sterane and hopane fossil petroleum markers for the three urban sites within the target area are plotted in parts b-d of Figure 7. Although absolute concentration levels of the fossil petroleum markers vary from sampling site to sampling site, the relative abundance of these markers is very similar at each site. Further, when the relative abundance of these fossil petroleum markers in vehicle emissions (Figure 7a) is compared to the ambient concentration profiles for the same fine particle compounds (Figure 7b-d), remarkably good agreement is seen. This indicates that the relative distribution between these fossil petroleum hydrocarbons is preserved from the source to the receptor sites.

Average annual ambient concentrations of the steranes and triterpanes of interest here were measured and found to be 6.53 ng/m^3 at West Los Angeles, 17.10 ng/m^3 at downtown Los Angeles, and 7.34 ng/m^3 at Pasadena for 1982. At West Los Angeles and Pasadena, the measured ambient concentrations compare rather well with the concentrations estimated above by scaling from the areawide emissions of these marker substances from vehicles. At downtown Los Angeles, the measured fossil petroleum marker concentrations are higher roughly by a factor of 3 compared to the concentrations predicted by assuming that the air column over that area could be represented by an air basin-wide mixture of source emissions. This local enrichment near downtown Los Angeles may be explained by the unusually high vehicle traffic densities near that site. In wintertime, the wind often stagnates and the ambient concentrations for many particle-bound organic compound classes peak over downtown Los Angeles (36). Indeed, as seen in Figure 8a,b, the ambient concentrations of the fossil petroleum markers studied here are markedly elevated in wintertime in downtown Los Angeles.

In Figure 9, the scaling technique described above was applied to single fossil petroleum markers released from internal combustion engines to estimate ambient concentrations in West Los Angeles. The ambient concentrations of fossil petroleum markers estimated due to
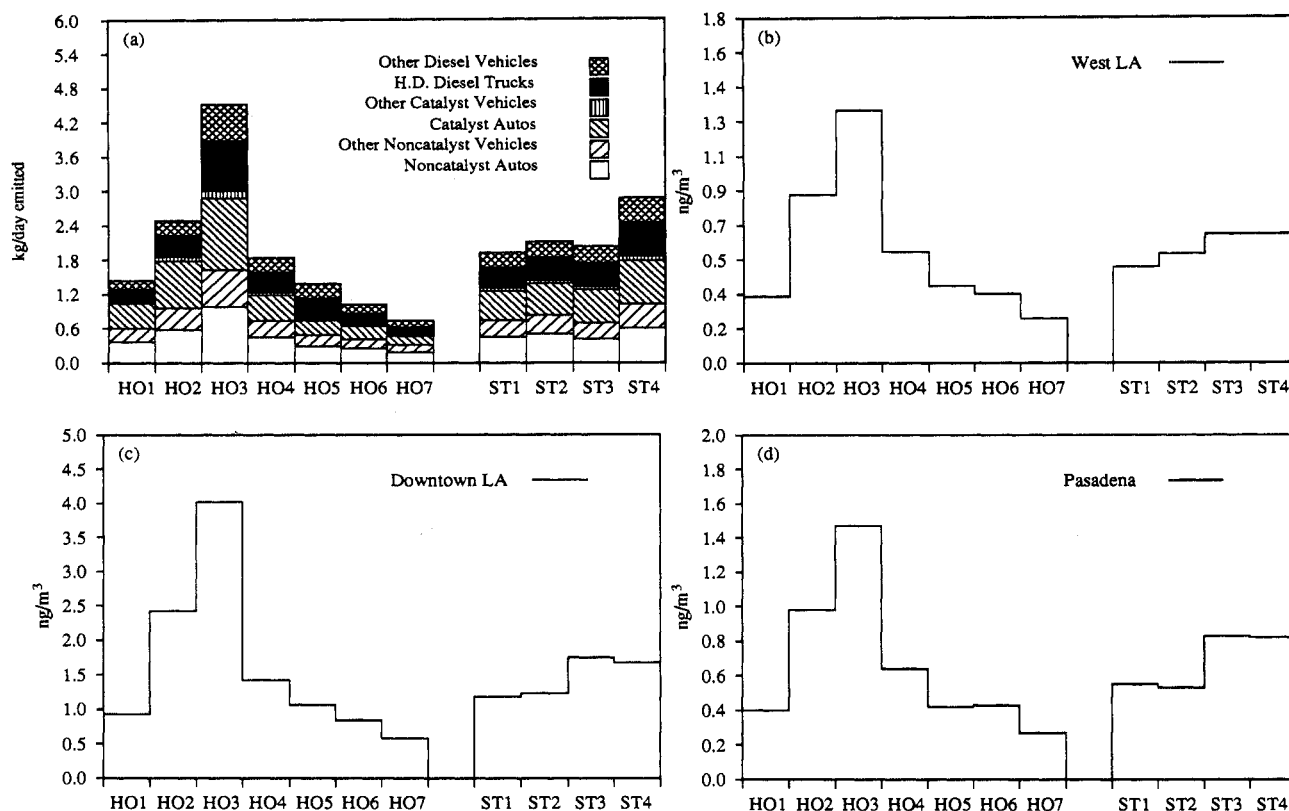
Figure 7. Vehicular emission profiles and ambient concentration profiles of fine particle fossil fuel markers: (a) 1982 emission rates for the 80 × 80 km greater Los Angeles area; measured 1982 annual average concentrations at (b) West Los Angeles, (c) downtown Los Angeles, and (d) Pasadena. HO1, 22,29,30-trisnorneohopane; HO2, 17α(H),21β(H)-29-norhopane; HO3, 17α(H),21β(H)-hopane; HO4, (22S)-17α(H),21β(H)-30-homohopane; HO5, (22R)-17α(H),21β(H)-30-homohopane; HO6, (22S)-17α(H),21β(H)-30-bishomohopane; HO7, (22R)-17α(H),21β(H)-30-bishomohopane; ST1, (20S and R)-5α(H),14β(H),17β(H)-cholestanes; ST2, (20R)-5α(H),14α(H),17α(H)-cholestane; ST3, (20S and R)-5α(H),14β(H),17β(H)-ergostanes; ST4, (20S and R)-5α(H),14β(H),17β(H)-sitostanes.

vehicle exhaust emissions follow the relative ordering of those marker concentrations measured in ambient air. These concentrations estimated from basin-wide emission data for vehicles fall short of matching the ambient concentrations in part because only ~85% of the mass emissions of these compounds to the Los Angeles atmosphere are from gasoline and diesel engines. Therefore, it is promising that ambient fossil petroleum marker concentrations can be used directly to estimate the contributions from vehicular source types to the ambient fine aerosol complex.

Conclusion

The chemical composition of organic fine particulate matter ($d_p \leq 2$ µm) emitted from noncatalyst and catalyst-equipped automobiles and from heavy-duty diesel trucks has been studied by GC/MS techniques. In the current study, more than 100 organic compounds were quantified including the series of n-alkanes, n-alkanoic acids, one n-alkenoic acid, benzoic acids, substituted benzaldehydes, PAH, oxy-PAH, steranes, pentacyclic triterpanes, aza-naphthalenes, and others. It has been shown that PAH and oxy-PAH emission rates are highest for automobiles without catalytic converter systems. The PAH emission rate measured for noncatalyst autos exceeds that for catalyst-equipped autos by more than 26-fold. In contrast, most of the n-alkanoic acids released from automobiles are released from catalyst-equipped autos. Heavy-duty diesel trucks show high emission rates for n-alkanes and n-alkanoic acids. PAH emission rates per kilometer driven

are ~4 times higher from diesel trucks than from catalyst-equipped automobiles, but nearly 7 times lower than from noncatalyst autos. Fossil petroleum markers such as steranes and pentacyclic triterpanes (hopanes) are readily identified in the exhaust emissions. Because they are not constituents of gasoline or diesel fuels, they are introduced into the exhaust via engine oil. For the greater Los Angeles area it has been found that these fossil petroleum markers are released mainly from internal combustion engines. Furthermore, the relative abundance of these marker compounds as seen in vehicular source emissions is preserved in the Los Angeles urban atmosphere. Thus, these fossil petroleum markers can be used as suitable tracer compounds to estimate the contributions from vehicular sources to the southern California atmosphere.
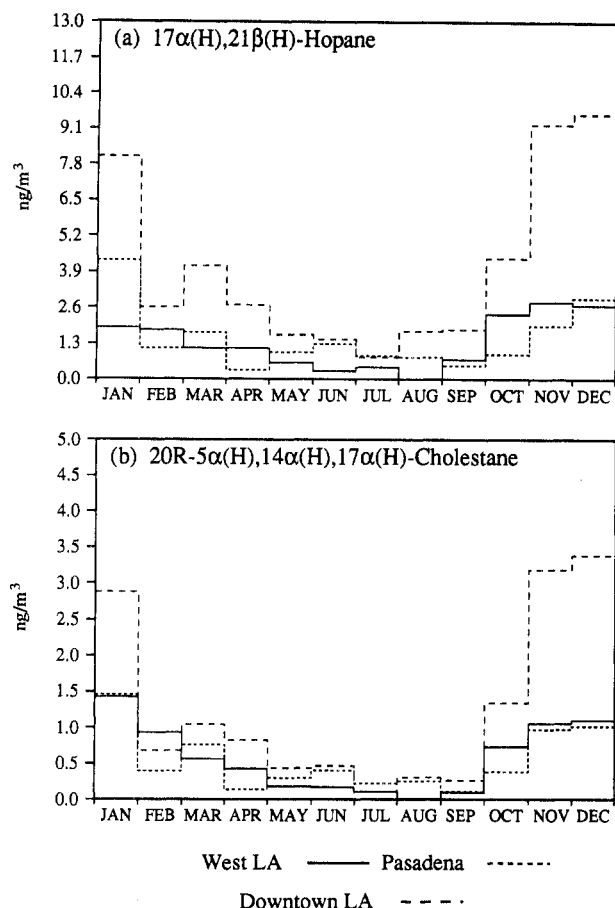
Figure 8. Measured monthly average ambient fine particle concentrations for two fossil fuel markers during 1982.
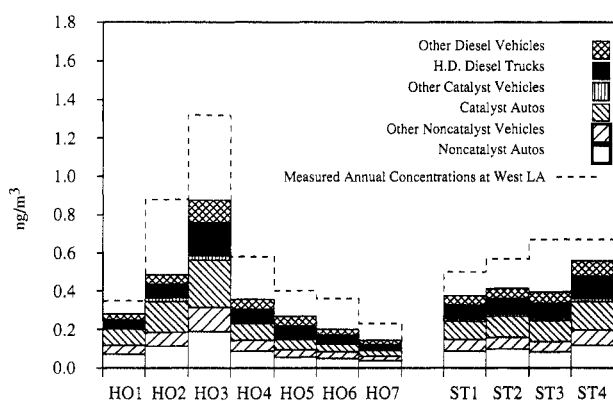

Figure 9. Estimated and measured ambient annual averaged concentrations of fine particle fossil fuel markers at West Los Angeles: HO1–HO7 and ST1–ST4 as in Figure 7.

Contract DE-AC02-76CH00016. The statements and conclusions in the report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products. This manuscript has not been subject to the EPA's peer and policy review, and hence does not necessarily reflect the views of the EPA.

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