Environ. Sci. Technol. **1999**, *33,* 1578−1587

Measurement of Emissions from Air Pollution Sources. 2. C_1 through C_{30} Organic Compounds from Medium Duty Diesel Trucks

JAMES J. SCHAUER,[†,§]
MICHAEL J. KLEEMAN,[†,||]
GLEN R. CASS,[*,†] AND
BERND R. T. SIMONEIT[‡]

Environmental Engineering Science, California Institute of Technology, Pasadena, California 91125, and College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, Oregon 97331

Gas- and particle-phase tailpipe emissions from late-model medium duty diesel trucks are quantified using a two-stage dilution source sampling system. The diesel trucks are driven through the hot-start Federal Test Procedure (FTP) urban driving cycle on a transient chassis dynamometer. Emission rates of 52 gas-phase volatile hydrocarbons, 67 semivolatile and 28 particle-phase organic compounds, and 26 carbonyls are quantified along with fine particle mass and chemical composition. When all C_1-C_{13} carbonyls are combined, they account for 60% of the gas-phase organic compound mass emissions. Fine particulate matter emission rates and chemical composition are quantified simultaneously by two methods: a denuder/filter/PUF sampler and a traditional filter sampler. Both sampling techniques yield the same elemental carbon emission rate of 56 mg km^{-1} driven, but the particulate organic carbon emission rate determined by the denuder-based sampling technique is found to be 35% lower than the organic carbon mass collected by the traditional filter-based sampling technique due to a positive vapor-phase sorption artifact that affects the traditional filter sampling technique. The distribution of organic compounds in the diesel fuel used in this study is compared to the distribution of these compounds in the vehicle exhaust. Significant enrichment in the ratio of unsubstituted polycyclic aromatic hydrocarbons (PAH) to their methyl- and dimethyl-substituted homologues is observed in the tailpipe emissions relative to the fuel. Isoprenoids and tricyclic terpanes are quantified in the semivolatile organics emitted from diesel vehicles. When used in conjunction with data on the hopanes, steranes, and elemental carbon emitted, the isoprenoids and the tricyclic terpanes may help trace the presence of diesel exhaust in atmospheric samples.

Introduction

Since diesel fuel consists largely of aliphatic hydrocarbons containing 10−25 carbon atoms, it is expected that these components and their thermally altered breakdown products also will be present in diesel exhaust. The inorganic and organic composition of fine particulate matter emitted in the exhaust from diesel-powered motor vehicles has been characterized in the past (*1, 2*) at a level sufficient to determine the contribution of primary emissions from diesel engines to atmospheric fine particle mass concentrations via transport modeling and organic chemical tracer techniques (*3, 4*). Specific volatile and semivolatile gas-phase polycyclic aromatic hydrocarbons (PAH) emitted from diesel-powered motor vehicles also have been examined (*5−7*). However, a detailed analysis of the remaining semivolatile gas-phase emissions from contemporary diesel trucks has not been reported. These semivolatile organic compounds (SVOC) can play a role in photochemical smog formation and are likely candidates to become the precursors of secondary organic aerosol (SOA) (*8, 9*) that is produced from the low vapor pressure products of atmospheric chemical reactions. In addition, toxic air contaminants such as polycyclic aromatic hydrocarbons (PAH) are present in the SVOC emissions from diesel engines. The lack of emissions data for these compounds from diesel engines, however, has prevented current air quality models from assessing their importance in urban air pollution. In the present work, new measurements of exhaust emissions from contemporary diesel engines are undertaken with an emphasis on defining the mixture of semivolatile organic compounds emitted and their distribution between the gas and particle phases.

The ratio of methyl-substituted PAH to unsubstituted PAH has been used previously to help determine the origin of hydrocarbon contamination in aquatic environments (*10*) and in the atmosphere (*11*). Crude oils and many refined petroleum products have a higher ratio of methyl-substituted PAH to unsubstituted PAH than is found in engine exhaust emissions due to thermal dealkylation within the engine (*12*). In the present study, the composition of the commercial diesel fuel burned in the diesel trucks tested is compared to the composition of the organic compounds emitted from the diesel trucks during the source tests. The change in the degree of methyl substitution of the PAH in the exhaust emissions when compared to the fuel as well as other selective changes in the relative distribution of organic compounds is assessed, with an emphasis on quantifying those features that show potential for distinguishing diesel fuel vapors in the atmosphere from the organic compounds emitted from diesel truck exhaust as well as distinguishing diesel truck exhaust from gasoline-powered motor vehicle exhaust.

Experimental Methods

Comprehensive Source Sampling. A two-stage dilution sampler is used in the present study. It consists of two sections, a predilution tunnel followed by the primary sampling system. The predilution tunnel is connected directly to the tailpipe of the diesel truck being tested on the dynamometer via a stainless steel hose. At the entrance of the predilution tunnel, HEPA-filtered and activated carbon-filtered dilution air is turbulently mixed with the vehicle exhaust. The predilution tunnel is operated at a fixed combined flowrate of 9910 L min^{-1}, such that the exhaust concentration in this tunnel is always proportional to the total emission rate from the tailpipe. At the downstream end of the predilution tunnel, a small portion of the total flow is drawn through a cyclone separator which removes particles

---

[*] Corresponding author telephone: (626)395-6888; fax: (626)395-2940; e-mail: glen@eql.caltech.edu.

[†] California Institute of Technology.

[‡] Oregon State University.

[§] Present address: Water Chemistry Program, University of Wisconsin−Madison, Madison, WI 53706.

[||] Present address: Civil and Environmental Engineering Department, University of California at Davis, Davis, CA 95616.

10.1021/es980081n CCC: $18.00

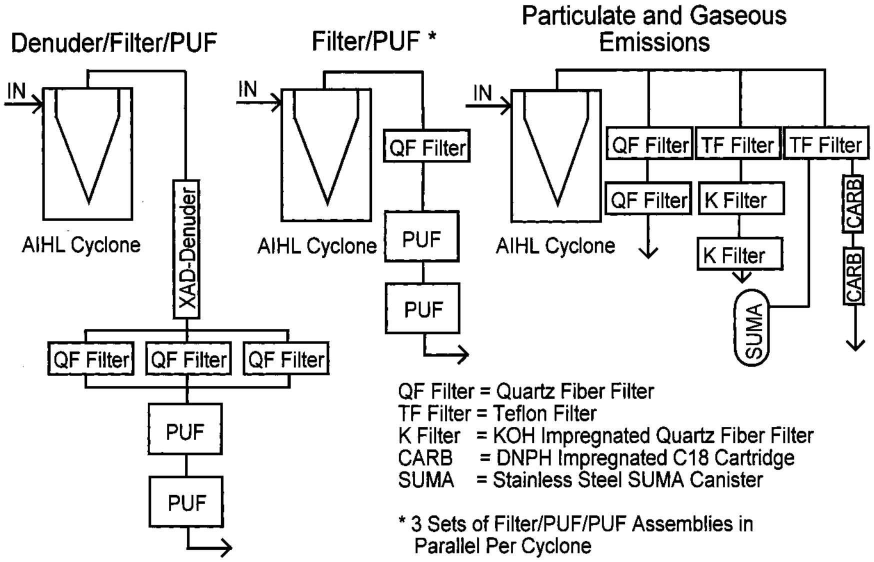

FIGURE 1. Schematic of sampling equipment connected to the comprehensive dilution source sampler.

larger than a nominal 10 μm in aerodynamic diameter. The gas-phase and particulate species that exit the cyclone pass through a venturi meter into the primary sampling system where they are diluted a second time. Stage 1 plus 2 of this system dilute the vehicle exhaust by a total average dilution factor of approximately 140-fold relative to combustion of a stoichiometric air/fuel mixture. The predilution tunnel is 246 cm in length and 20.5 cm in diameter. The primary dilution tunnel is 145 cm in length up to the entrance to the residence time chamber and 15.2 cm in diameter. The residence time chamber is 138.4 cm long and 30.5 cm in diameter.

The primary sampling system is a modified version of the portable dilution sampler originally developed by Hildemann et al. (*13*). The modified sampling system has been previously described (*14*), but briefly consists of a dilution tunnel, which in the current study provides the second stage of dilution, followed by a residence time chamber that retains the diluted source sample while further condensation of organic gases onto the particles takes place. A diagram of the original dilution sampler as used in a motor vehicle test configuration is shown in Figure 1b of Hildemann et al. (*1*) and the added details of the particulate and gas-phase measurement systems now placed at the downstream end of the source sampler are shown in Figure 1 of this paper. At the downstream end of the dilution sampler, instruments for measuring fine particulate and gas-phase species concentrations and chemical composition are attached to the residence time chamber from which samples are withdrawn for chemical analysis. Samples are drawn through AIHL-design cyclone separators (*15*) which are operated at flowrates such that fine particles with aerodynamic diameters smaller than 1.8 μm pass through the cyclone separator along with gas-phase species. Semivolatile and fine particle-phase organic compounds are collected downstream of the cyclones using three types of sampling trains that are operated simultaneously in parallel at this location.

The first sampling train consists of an AIHL-design cyclone separator followed by a XAD-coated annular denuder (URG, 400 mm, four channel) which in turn is followed by three quartz fiber filters (47 mm diameter, Pallflex Tissuequartz 2500 QAO) operated in parallel that are then followed by two polyurethane foam (PUF) cartridges (Atlas Foam; density = 0.022 g cm^{-3}, ILD = 30, 5.7 cm diameter by 7.6 cm long) operated in series. The gas-phase semivolatile organic compounds are collected by the annular denuder while fine particles and particle-associated organic compounds pass through the denuder and are collected on the filters downstream of the denuder. The PUF cartridges downstream of the filters collect any semivolatile organic compounds that blow off of the filters. The denuders are operated at a flowrate of 30 L min^{-1} for the entire 22.8-min portion of the FTP urban driving cycle over which each truck was tested. The preparation of the XAD-coated denuders and additional details concerning denuder/filter/PUF sampling train operations and collection efficiency are discussed by Schauer et al. (*14*).

Four copies of a second sampling train configuration for collection of semivolatile organics and particle-phase material are operated simultaneously in parallel with the denuder/filter/PUF system. Each of these four filter/PUF sampling trains draws sample from the residence time chamber through an AIHL-design cyclone that is followed in each case by three filter/PUF units operated in parallel. A single filter/PUF unit consists of a quartz fiber filter (47 mm diameter, Pallflex Tissuequartz 2500 QAO) followed by two PUF cartridges (Atlas Foam; density = 0.022 g cm^{-3}, ILD = 30, 5.7 cm diameter by 7.6 cm long). Each filter/PUF assembly operates at a sample flowrate of 10 L min^{-1}.

In addition to the above sampling trains, a third type of cyclone-based sampling unit is operated to collect fine particulate matter, carbonyls, organic acids, and gas-phase hydrocarbons. Three stacked filter units each operated at flow rates of 10 L min^{-1} and one carbonyl sampling line are connected in parallel at the outlet of an AIHL-design cyclone separator. The first stacked filter unit consists of two quartz fiber filters (47 mm diameter, Pallflex Tissuequartz 2500 QAO) in series, which are used for elemental and organic carbon (EC/OC) determination by thermal evolution and combustion analysis as described by Birch and Cary (*16*). The second filter stack contains three filters, a Teflon membrane filter (47 mm diameter, Gelman Teflo, 2 μm pore size) followed by two KOH-impregnated quartz fiber filters in series. This Teflon membrane filter is used for gravimetric determination of the fine particle mass emissions rate and is analyzed by X-ray fluorescence for 35 trace elements (*17*). The tandem KOH-impregnated quartz fiber filters are used to collect vapor-phase organic acids which will be analyzed in association with other research activities and will not be reported here. The third filter holder assembly contains one Teflon membrane filter which is used for a duplicate fine particle mass emissions measurement and for inorganic ion measurements by ion chromatography (*18*), atomic absorption spectroscopy, and colorimetry (*19*). Downstream of that single Teflon filter the sample flow is divided, and a small portion of the flow is used to fill a 6-L polished stainless steel SUMA canister for the collection of non-methane volatile hydrocarbons ranging from C_1 to C_{10}. The 6-L SUMA canister is filled continuously at a constant flowrate set to fill the canister over the entire source test cycle. Carbonyls are collected at the outlet of the AIHL cyclone separator by two C_{18} cartridges impregnated with dinitrophenylhydrazine (DNPH) that are operated in series (*20*). The air flowrates through the DNPH impregnated cartridges are typically in the range 0.3 to 0.5 L min^{-1}.

The internally exposed area of the entire two-stage dilution sampler is constructed only of aluminum, Teflon, and stainless steel. The entire sampler is assembled with Teflon O-rings and is completely free of grease coatings and rubber gaskets.

Electronic particle sizing instruments and a pair of MOUDI impactors are also connected to the residence time chamber during the diesel vehicle source tests to obtain particle size distributions and particle chemical composition as a function of particle size. The size distributions and the results obtained from the MOUDI impactors will be reported by Kleeman et al. (*21*).

Source Testing Procedure. The two medium duty diesel trucks tested in the present study were both sampled during 1996 from the current in-use vehicle fleet in southern California and were fueled with commercially obtained California reformulated diesel fuel. The first vehicle tested was a 1995 model year Isuzu intercooled turbo diesel truck with a 3.8-L, four-cylinder engine. The second vehicle was a GMC Vandura 3500 full-sized commercial van with a 6.5-L, eight-cylinder diesel engine. The Isuzu truck and the GMC van had accumulated 39 993 miles and 30 560 miles of driving, respectively, prior to being tested.

Due to vehicle testing facility operating procedures, the diesel trucks could not be moved onto the dynamometer directly from cold storage. The truck has to be driven onto the dynamometer, which entails first starting the engine, so the diesel trucks had to be tested with a hot-start FTP cycle. Prior to the start of each source test, the truck tested was warmed on the dynamometer for approximately 10 min. The engine was then shut off, and the truck tailpipe was connected to the source sampler. The flows through the source samplers were established, and the truck was started and driven over the first two segments of the FTP dynamometer cycle (first 24 min shown in Figure 2a of Hildemann et al. (*1*)). For both vehicle tests the two roller hydraulic dynamometers were operated at a load of 7500 pounds (65% of maximum certified load for the Isuzu truck and 57% of the maximum certified load for the GMC truck) and an actual horsepower (AHP) of 17.5. The second diesel truck was tested directly after the first truck was finished. The filters used for fine particle mass and bulk chemical composition determination and the denuder were changed between tests, and all other samples destined for detailed analysis of individual organic compounds were collected as a composite sample of the exhaust from the two trucks.

Organic Chemical Analysis. The filter handling and extraction procedures employed in this study for particle-phase organic compounds collected on quartz fiber filters have been discussed previously (*14*). Briefly, the quartz fiber filters were baked at 550 °C prior to sampling for a minimum of 12 h to reduce residual carbon levels associated with new filters. Immediately after sampling, the filters were stored in a freezer at −21 °C until the samples were extracted. The filters were extracted within one to two weeks following sample collection. Before the quartz fiber filters were extracted, they were spiked with a mixture of seven deuterated internal recovery standards: *n*-decane-d_{12}, *n*-pentadecane-d_{32}, *n*-tetracosane-d_{50}, *n*-hexanoic acid-d_{11}, *n*-decanoic acid-d_{19}, phenol-d_5, benzoic acid-d_5, and benzadehyde-d_6. The samples were extracted twice with hexane (Fisher Optima Grade), followed by three successive benzene/2-propanol (2:1) extractions (benzene—E&M Scientific high purity lots; 2-propanol—Burdick & Jackson). Extracts were filtered, combined, and reduced in volume to approximately 250 μL, and were split into two separate fractions. One fraction was then derivatized with diazomethane to convert organic acids to their methyl ester analogues which are amenable to GC/MS identification and quantification.

The procedure for identification and quantification of organic compounds collected on XAD-coated annular denuders and PUF cartridges has been discussed previously (*14*). Briefly, the denuders used for sampling were extracted within 12 h after sample collection. During sample extraction, the denuder was first spiked with the same deuterated internal standard mix that was used for the filter extraction, and next was extracted successively with four aliquots of 40 mL each of a solvent mixture of dichloromethane/acetone/hexane 2:3:5) (Fisher Optima Grade) by pouring each aliquot into the denuder and shaking the Teflon capped denuder for approximately 30 s per aliquot. The four aliquots from each of the two denuder samples (i.e., one denuder sample from each of the two trucks tested) were composited and reduced to a volume of approximately 250 μL and then split into two separate fractions. One fraction was derivatized with diazomethane.

Prior to source sampling the PUF plugs were cleaned by four successive extractions with a solvent mixture of dichloromethane/acetone/hexane (2:3:5) (Fisher Optima Grade). The foam plugs were repetitively compressed during the extraction. After the cleaning procedure, the PUFs were air-dried in the dark in an organics clean room and were then stored in annealed borosilicate jars with solvent-washed Teflon lid liners in the freezer at −21 °C. After sampling, the PUF plugs were spiked with the same internal standard mix used for the filter and denuder extractions, and then were extracted with four successive aliquots of a mixture of dichloromethane/acetone/hexane (2:3:5). The extracts were filtered, combined, reduced in volume to approximately 250 μL, and then split into two separate fractions. One fraction was derivatized with diazomethane as is done with the filter extracts and the denuder extracts.

Filter, PUF, and denuder field blanks were analyzed with each set of source samples. The field blanks were prepared, stored, and handled by exactly the same procedures as used for the source samples.

Both the derivatized and underivatized sample fractions were analyzed by GC/MS on a Hewlett-Packard GC/MSD (GC Model 5890, MSD Model 5972) using a 30 m × 0.25 mm diameter HP-1701 capillary column (Hewlett-Packard). 1-Phenyldodecane was used as a co-injection standard for all sample extracts and standard runs. The deuterated *n*-alkanes in the internal standard were used to determine extraction recovery for the compounds quantified in the underivatized samples. The deuterated acids were used to verify that the diazomethane reactions were driven to completion. In addition, the deuterated *n*-alkanoic acid recoveries were used in conjunction with the recovery of deuterated tetracosane to determine the recovery of the compounds quantified in the derivatized fraction.

Hundreds of authentic standards have been prepared for the positive identification and quantification of the organic compounds found in the current source test program. When quantitative standards could not be obtained for a given compound or compound class, significant effort was made to obtain a nonquantitative secondary standard that could be used for unique identification of the organic compounds.

TABLE 1. Average Fine Particle Emission Rate and Fine Particle Chemical Compositionfor Medium Duty Diesel Truck Exhaust[a]

fine particle mass emissions rate (avg ± std): 185 ± 22 mg km^{-1}			
elemental and organic carbon (wt % of fine particle mass)			
organic carbon[b]	**19.7 ± 1.6**	elemental carbon	**30.8 ± 2.6**
ionic species (wt % of fine particle mass)			
chloride	0.00 ± 0.18	sulfate	**1.00 ± 0.25**
nitrite	0.01 ± 0.01	ammonium	**0.73 ± 0.11**
nitrate	0.23 ± 0.38		
X-ray fluorescence (wt % of fine particle mass)			
aluminum	0.08 ± 0.14	selenium	0.00 ± 0.01
silicon	**0.63 ± 0.04**	bromine	0.00 ± 0.01
phosphorus	0.01 ± 0.06	rubidium	0.00 ± 0.01
sulfur	**0.22 ± 0.02**	strontium	0.00 ± 0.01
chloride	0.00 ± 0.06	yttrium	0.00 ± 0.02
potassium	0.00 ± 0.09	zirconium	0.00 ± 0.02
calcium	0.03 ± 0.08	molybdenum	0.00 ± 0.04
titanium	0.00 ± 0.29	palladium	0.01 ± 0.10
vanadium	0.00 ± 0.12	silver	0.01 ± 0.11
chromium	0.01 ± 0.03	cadmium	0.06 ± 0.12
manganese	0.01 ± 0.02	indium	0.06 ± 0.14
cobalt	0.01 ± 0.01	tin	0.00 ± 0.18
iron	**0.05 ± 0.01**	antimony	0.00 ± 0.21
nickel	0.00 ± 0.01	barium	0.00 ± 0.79
copper	0.01 ± 0.01	lanthanum	0.00 ± 1.04
zinc	**0.07 ± 0.01**	mercury	0.00 ± 0.03
gallium	0.01 ± 0.02	lead	0.01 ± 0.04
arsenic	0.00 ± 0.03		

[a] Values shown in boldface are greater than zero by at least two standard errors. [b]Measured downstream of the organics denuder. Organic carbon measuredon undenuded filter is 30.4% of fine particle mass.

An example of such a secondary standard is the use of motor oil as a source of hopanes and steranes that was used to help identify these compounds in the fine particle diesel exhaust. Quantification of compounds identified using secondary standards has been estimated from the response factors for compounds having similar retention times and chemical structure. In the case of the hopanes and steranes an authentic standard of cholestane was used to estimate the response factors of the remaining hopanes and steranes that were quantified.

Total non-methane organic gases (NMOG, EPA method TO12) and individual organic vapor-phase hydrocarbons ranging from C_1 to C_{10} were analyzed from the SUMA canisters by gas chromatography/flame ionization detection (GC/FID) as described by Fraser et al. (*22*). Carbonyls collected using the DNPH-impregnated C_{18} cartridges were analyzed by liquid chromatography/UV detection as described by Grosjean et al. (*23*).

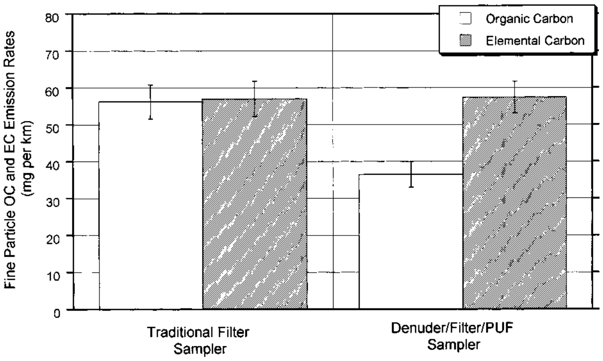

FIGURE 2. Comparison of fine particle organic and elemental carbon emitted from the diesel trucks tested as measured by a traditional filter sampler and a denuder/filter/PUF sampler.

Results and Discussion

Fine Particle Mass and Chemical Composition. Fine particle mass measurements made by directly filtering a known volume of the diluted cooled vehicle exhaust without the use of the semivolatile organic vapor denuder system are shown in Table 1. Chemical species for which the emissions rates are significantly greater than zero are shown in bold-face type. Fine particle mass emission rates for the medium duty diesel trucks tested averaged 185 ± 22 mg per kilometer driven on the FTP urban driving cycle (195.6 ± 3.1 mg km^{-1} for the Isuzu truck and 173.7 ± 16.1 mg km^{-1} for the GMC van). The fine particle mass collected in this fashion by the filter/PUF sampling train consisted of 30.4% organic carbon (equivalent to approximately 36.5% organic compounds) and 30.8% elemental carbon. Sulfate and ammonium ion were found to compose 1.0% and 0.73% of the mass, respectively, accompanied by detectable amounts of silicon, iron, and zinc. The identity of the additional 31% of the fine particulate mass that cannot be attributed to organic compounds, elemental carbon, sulfate ion, ammonium ion, plus trace metals is unknown. Water that is retained in the sample despite desiccation, and which cannot be measured by the methods used here, is one of the few candidates that could explain a portion of the mass that remains to be identified chemically.

Organic and elemental carbon also were measured on the quartz fiber filters located downstream of the XAD-coated denuders. The emission rate of fine particle elemental carbon as measured on the filter downstream of the denuder showed good agreement with the undenuded filter sample at 56 mg of elemental carbon per kilometer driven. Significantly less organic carbon was collected on filters located downstream of the denuders than was the case for the undenuded filter sample taken in parallel. Figure 2 shows the emission rates of organic and elemental carbon measured by the two sampling techniques. A detailed analysis of the organic carbon distribution between the collection substrates of the denuder/filter/PUF sampling system indicated that there was very little organics mass on the two PUF plugs located downstream of the XAD-coated denuder/filter combination as compared to the difference between the undenuded filter and the denuded filter measurement of the fine particle organic carbon concentration. This indicates that the lower particulate organic carbon mass on the filter in the denuder/filter/PUF system could not be due to organic carbon volatilizing off that filter as the volatilization of organic aerosol would have resulted in higher concentrations measured on the PUF located downstream. These facts indicate that the larger quantity of organic carbon collected on the undenuded filter was due mainly to sorption of semivolatile gas-phase organic compounds to the undenuded filter and not due to vaporization of particulate matter from the filter located downstream of the denuder.

Distribution of Organic Compounds. The quantities of individual gas-phase plus particle-phase organic compounds and elemental carbon emitted from the medium duty diesel trucks are shown in Table 2 and are summarized in Figure 3. The composition of diesel fuel also is given in Table 2, as measured by diluting diesel fuel with extraction-grade solvents and then analyzing the diluted fuel by the same GC/MS techniques as are used for the exhaust samples in this study. Light gas-phase carbonyls make up the largest fraction of the gas-phase exhaust emissions; they are emitted at a rate of 169 mg per kilometer driven. Over half of the carbonyl emissions consist of formaldehyde, acetaldehyde plus acetone, accompanied by significant quantities of propanal, butanone, and crotonaldehyde. It is known from previous work (*24, 25*) that the carbonyl emissions from diesel trucks are substantial. The present study is unique because

TABLE 2. Organic Compounds Present in Diesel Fuel and in Medium Duty Diesel Truck Exhaust

compound	diesel-powered medium duty truck emissions (μg km^{-1})		diesel fuel composition (μg g^{-1})	notes[a–g]	compound	diesel-powered medium duty truck emissions (μg km^{-1})		diesel fuel composition (μg g^{-1})	notes[a–g]
	gas phase	particle phase				gas phase	particle phase		
_n_-Alkanes									
n-butane	3830		*h*	*a, e*	*n*-octadecane	601	2.84	9212	*a, f*
n-pentane	1860		*h*	*a, e*	*n*-nonadecane	411	3.82	7020	*b, f*
n-heptane	470		*h*	*a, e*	*n*-eicosane	206	95.7	6530	*a, f*
n-octane	260		*h*	*a, e*	*n*-heneicosane	65.8	40.5	5220	*b, f*
n-nonane	160		*h*	*a, e*	*n*-docosane		52.0	4340	*b, f*
n-undecane	*h*		*h*		*n*-tricosane		45.5	2670	*b, f*
n-dodecane[i]	503		15500	*a, f*	*n*-tetracosane		40.7	1680	*a, f*
n-tridecane	477		15700	*b, f*	*n*-pentacosane		26.1	730	*b, f*
n-tetradecane	629		13500	*a, f*	*n*-hexacosane		34.9	290	*b, f*
n-pentadecane	398	2.12	10500	*b, f*	*n*-heptacosane		25.7	180	*b, f*
n-hexadecane	711	8.62	10100	*a, f*	*n*-octacosane		19.7	36	*a, f*
n-heptadecane	614	5.92	5700	*b, f*	*n*-nonacosane		6.1		*b, f*
Branched Alkanes									
isopentane	2740		*h*	*a, e*	2,4-dimethylhexane	50		*h*	*a, e*
2,2-dimethylbutane	310		*h*	*a, e*	2,3,4-trimethylpentane	310		*h*	*a, e*
2,3-dimethylbutane	570		*h*	*a, e*	2,3-dimethylhexane	160		*h*	*a, e*
2-methylpentane	930		*h*	*a, e*	2-methylheptane	100		*h*	*a, e*
3-methylpentane	670		*h*	*a, e*	3-ethylhexane	210		*h*	*a, e*
2,4-dimethylpentane	410		*h*	*a, e*	norfarnesane[i]	360		16300	*b, f*
2-methylhexane	570		*h*	*a, e*	farnesane[i]	434	4.1	9220	*b, f*
2,3-dimethylpentane	720		*h*	*a, e*	2,6,10-trimethyltridecane	367	1.2	8830	*b, f*
3-methylhexane	310		*h*	*a, e*	norpristane	566	4.9	8670	*b, f*
2,2,4-trimethylpentane	1240		*h*	*a, e*	pristane	443		5840	*a, f*
2,5-dimethylhexane	50		*h*	*a, e*	phytane	439		5770	*b, f*
_n_-Alkenes									
ethene	8560		*h*	*a, e*	*trans*-2-pentene	50		*h*	*a, e*
propene	780		*h*	*a, e*	*trans*-2-hexene	160		*h*	*a, e*
trans-2-butene	520		*h*	*a, e*	*cis*-2-hexene	100		*h*	*a, e*
cis-2-butene	260		*h*	*a, e*					
isobutene	1140		*h*	*a, e*					
3-methyl-1-butene	160		*h*	*a, e*					
Branched Alkenes									
2-methyl-1-butene	260		*h*	*a, e*	2-methyl-2-pentene	210		*h*	*a, e*
Diolefins									
1,3-butadiene	310		*h*	*a, e*					
Alkynes									
ethyne	4600		*h*	*a, e*					
Saturated Cycloalkanes									
cyclopentane	410		*h*	*a, e*	undecylcyclohexane	23.9		430	*b, f*
methylcyclopentane	620		*h*	*a, e*	dodecylcyclohexane	16.8		200	*b, f*
cyclohexane	210		*h*	*a, e*	tridecylcyclohexane	16.5	4.34	170	*b, f*
methylcyclohexane	520		*h*	*a, e*	tetradecylcyclohexane	15.9	3.96	160	*b, f*
pentylcyclohexane	83.9			*b, f*	pentadecylcyclohexane	12.8	9.88	150	*a, f*
hexylcyclohexane	14.9		830	*b, f*	hexadecylcyclohexane		12.9		*b, f*
heptylcyclohexane	20.0		730	*b, f*	heptadecylcyclohexane		16.7		*a, f*
octylcyclohexane	26.2		500	*b, f*	octadecylcyclohexane		11.5		*b, f*
nonylcyclohexane	24.7		490	*b, f*	nonadecylcyclohexane		9.0		*b, f*
decylcyclohexane	38.2		420	*b, f*					
Unsaturated Cycloalkenes									
cyclopentene	210		*h*	*a, e*					
Aromatic Hydrocarbons									
benzene	2740		*h*	*a, e*	C_1-fluorene	65.2	83.0	190	*b, f*
toluene	3980		*h*	*a, e*	phenanthrene	93.1	47.0	57	*a, f*
ethylbenzene	470		*h*	*a, e*	anthracene	12.5	10.9	5	*a, f*
m- and *p*-xylene	2330		*h*	*a, e*	3-methylphenanthrene	30.3	29.4	51	*b, f*
o-xylene	830		*h*	*a, e*	2-methylphenathrene	42.0	35.6	45	*b, f*
n-propylbenzene	100		*h*	*a, e*	2-methylanthracene	10.4	10.4	6	*a, f*
p-ethyltoluene	520		*h*	*a, e*	9-methylphenanthrene	22.9	22.0	35	*b, f*
m-ethyltoluene	210		*h*	*a, e*	1-methylphenanthrene	17.0	17.8	28	*a, f*
1,3,5-trimethylbenzene	260		*h*	*a, e*	C_2-MW 178 PAH	196	57.2	2080	*a, f*
1,2,4-trimethylbenzene	880		*h*	*a, e*	C_3-MW 178 PAH	97.4	97.5	120	*b, f*
naphthalene[i]	617		600	*a, f*	fluoranthene	53.0	56.6		*a, f*
2-methylnaphthalene[i]	611		980	*a, f*	acephenanthrylene	12.0	16.2		*b, f*
1-methylnaphthalene[i]	378		580	*a, f*	pyrene	71.9	88.5	64	*a, f*
C_2-naphthalenes	542		2050	*a, f*	C_1-MW 202 PAH	39.0	81.0	290	*b, f*
C_3-naphthalenes	240	130	1360	*b, f*	benzo[*ghi*]fluoranthene	5.82	19.8		*b, f*
C_4-naphthalenes	97.3	98.6	760	*b, f*	cyclopenta[*cd*]pyrene	2.06	3.50		*a, f*
acenaphthylene	70.1			*a, f*	benz[*a*]anthracene	2.98	7.76		*a, f*
acenaphthene	19.3			*a, f*	chrysene and triphenylene	3.35	15.6		*a, f*
fluorene	34.6	9.5	52	*a, f*	C_1-MW 228 PAH		6.54		*b, f*

TABLE 2. (Continued)

compound	diesel-powered medium duty truck emissions (μg km^{-1}) gas phase	particle phase	diesel fuel composition (μg g^{-1})	notes^{a-g}	compound	diesel-powered medium duty truck emissions (μg km^{-1}) gas phase	particle phase	diesel fuel composition (μg g^{-1})	notes^{a-g}
Tricyclic Terpanes									
8β,13α-dimethyl-14β-*n*-butylpodocarpane	44.0	10.6	2.1	*c, f*	8β,13α-dimethyl-14β-[3′-methylbutyl]-podocarpane	13.8	4.50	0.6	*c, f*
Diasteranes									
20s-13β(H),17α(H)-diacholestane		1.37		*c, f*					
Hopanes									
18α(H)-22,29,30-trisnorneohopane		2.74		*c, f*	17α(H),21β(H)-29-norhopane		11.3		*c, f*
17α(H)-22,29,30-trisnorhopane		0.99		*c, f*	17α(H),21β(H)-hopane		11.4		*c, f*
Steranes									
20*R*,5α(H),14β(H),-17β(H)-cholestane		0.78		*c, f*	20*R*&*S*,5α(H),14β(H),-17β(H)-ergostane		3.15		*c, f*
20*R*,5α(H),14α(H),-17α(H)-cholestane		1.19		*c, f*	20*R*&*S*,5α(H),14β(H),-17β(H)-sitostane		2.61		*c, f*
Aliphatic Aldehydes									
formaldehyde	22300		*h*	*a, g*	octanal	3100		*h*	*a, g*
acetaldehyde	41800		*h*	*a, g*	nonanal	4400		*h*	*a, g*
propanal	14000		*h*	*a, g*	decanal	2800		*h*	*a, g*
butanal	1300		*h*	*a, g*	undecanal	2600		*h*	*a, g*
hexanal	2200		*h*	*a, g*	dodecanal	1200		*h*	*a, g*
heptanal	3200		*h*	*a, g*	tridecanal	2000		*h*	*a, g*
Olefinic Aldehydes									
crotonaldehyde	13400		*h*	*a, g*	methacrolein	4000		*h*	*a, g*
acrolein	3400		*h*	*a, g*					
Aliphatic Ketones									
acetone	22000		*h*	*a, g*	butanone	7500		*h*	*a, g*
Aromatic Aldehydes									
benzaldehyde	3800		*h*	*a, g*	2,5-dimethylbenzaldehyde	4100		*h*	*a, g*
acetophenone	5100		*h*	*a, g*					
Aromatic Ketones									
indanone[i]	69.5			*a, f*	xanthone	12.4			*a, f*
fluorenone	34.6	9.84		*a, f*					
Dicarbonyls									
glyoxal	2100		*h*	*a, g*	biacetyl	900		*h*	*a, g*
methylglyoxal	1700		*h*	*a, g*					
***n*-Alkanoic Acids**									
octanoic acid	125		*h*	*a, f, d*	tetradecanoic acid	5.3		*h*	*a, f, d*
nonanoic acid	240		*h*	*b, f, d*	heptadecanoic acid		22.3	*h*	*b, f, d*
decanoic acid	72.9		*h*	*a, f, d*	octadecanoic acid		362	*h*	*a, f, d*
undecanoic acid	206		*h*	*b, f, d*	nonadecanoic acid		5.7	*h*	*b, f, d*
dodecanoic acid	58.5		*h*	*a, f, d*	eicosanoic acid		14.2	*h*	*a, f, d*
tridecanoic acid	13.1		*h*	*b, f, d*					
Alkanedioic Acids									
octanedioic acid		138	*h*	*a, f, d*	nonanedioic acid		176	*h*	*a, f, d*
Aromatic Acids									
benzoic acid	1260		*h*	*b, f, d*	methylbenzoic acids	772	26.7	*h*	*a, f, d*
Other Compounds									
benzofuran	53.2			*a, f*	dibenzothiophene	1.98			*a, f*
dibenzofuran	28.7	6.0	29	*a, f*	dibenzothiazole	251			*a, f*
Unresolved Complex Mixture									
	53800	41400	*h*	*b, f*					

[a–g] Identification notes: (*a*) authentic quantitative standard; (*b*) authentic quantitative standard for similar compound in series; (*c*) secondary standard; (*d*) detected as a methyl ester. Exhaust sample collection notes: (*e*) collected in SUMA canister; (*f*) collected on denuder/filter/PUF sampling train; (*g*) collected on DNPH impregnated C_{18} cartridges. [h] Analysis was not performed. See text for details. [i] Compound is too volatile for complete collection by denuder at sampling conditions; mass of this compound reported in the gas-phase includes mass collected on PUF cartridge.

the emissions of high molecular weight carbonyls up to tridecanal are also quantified. Gas-phase alkanes are emitted at a rate of 11.2 mg per kilometer driven, accompanied by smaller quantities of aromatics, PAH, olefins, and other vapor-phase organic compounds. A noticeable quantity of the gas-phase alkane mass emitted is in the carbon number range from C_{12} through C_{20}, which is consistent with the composition of diesel fuel.

A major part of the remaining gas- and particle-phase organic compound emissions is made up of an unresolved complex mixture (UCM) comprised of aliphatic branched and cyclic hydrocarbons that are not separable as individual

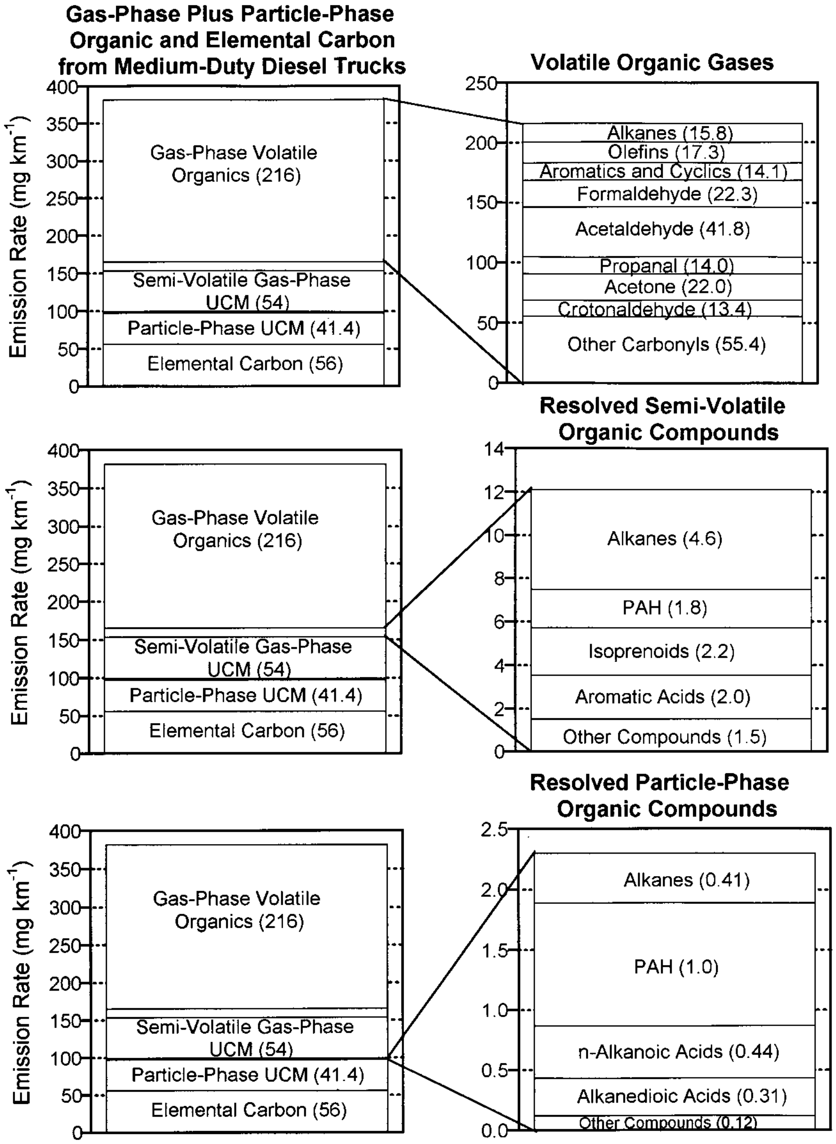

FIGURE 3. Material balance on the gas-phase, semivolatile, and particle-phase organic compounds emitted from medium duty diesel trucks driven over the hot-start Federal Test Procedure urban driving cycle on a chassis dynamometer.

GC peaks. The gas-phase portion of the UCM consists of high molecular weight semivolatile organics that are in the aggregate emitted at a rate of 54 mg km^{-1}, slightly less than half that of the total carbonyl mass emission rate, while the particle-phase UCM contributed an additional 41.4 mg km^{-1}.

The composition of the UCM found in the particle phase was very similar to motor oil when analyzed by GC/MS. The distribution of hopanes and steranes in the fine particle exhaust emissions and in motor oil was found to be very similar as well. For these reasons, the UCM contained in the fine particulate matter emitted was quantified according to a GC/MS response factor obtained by using motor oil as a standard. Quantifying the UCM by this method closes a mass balance on the organic carbon collected on the quartz fiber filters to within 20% as analyzed by thermal evolution and combustion analysis and by GC/MS analysis. The vapor-phase semivolatile UCM collected on the denuders and the PUF plugs was quantified by the same procedure, because the GC/MS response factor for motor oil was close to that of *n*-alkanes in the carbon number range from C_{14} to C_{24} on a total ion current (TIC) basis.

The remaining high molecular weight carbonaceous species emitted in the diesel exhaust include resolved vapor-phase semivolatile and particle-phase organic compounds plus elemental carbon, as summarized in Figure 3. Elemental carbon contributes 56 mg km^{-1}, while an additional 14.4 mg km^{-1} can be accounted for in terms of the individual organic compounds shown in Table 2. Included in the resolved organic compounds are *n*-alkanes, PAH, isoprenoids, saturated cycloalkanes, organic acids, hopanes, and steranes.

The *n*-alkane emission rates are greatest in the carbon number range from C_{12} through C_{20}, averaging over 400 μg km^{-1} for most individual *n*-alkanes in this range. *n*-Butane and *n*-pentane are also emitted at high rates at 3830 and 1860 μg km^{-1}, respectively. As the concentration of the C_4 and C_5 alkanes was not analyzed in the diesel fuel, it is unclear whether these compounds are formed in the diesel engine combustion process or if they were originally present in solution in the diesel fuel. Likewise, isopentane and other low molecular weight branched alkanes shown in Table 2 are emitted at relatively high rates. These unexpected high emission rates for butane, pentane, 2-methylpentane, and 2,2,4-trimethylpentane still only sum to less than 0.1 g per liter of diesel fuel burned.

Individual organic compounds in the class of branched C_{14} through C_{20} alkanes known as the isoprenoids are emitted

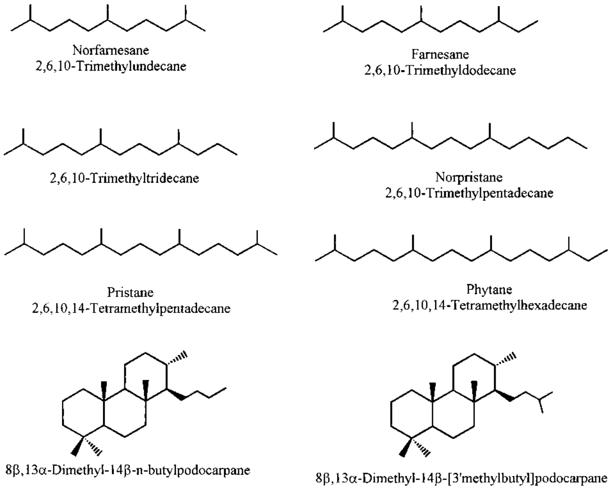

FIGURE 4. Chemical structures of isoprenoids and tricyclic terpanes present in diesel fuel and emitted from diesel trucks

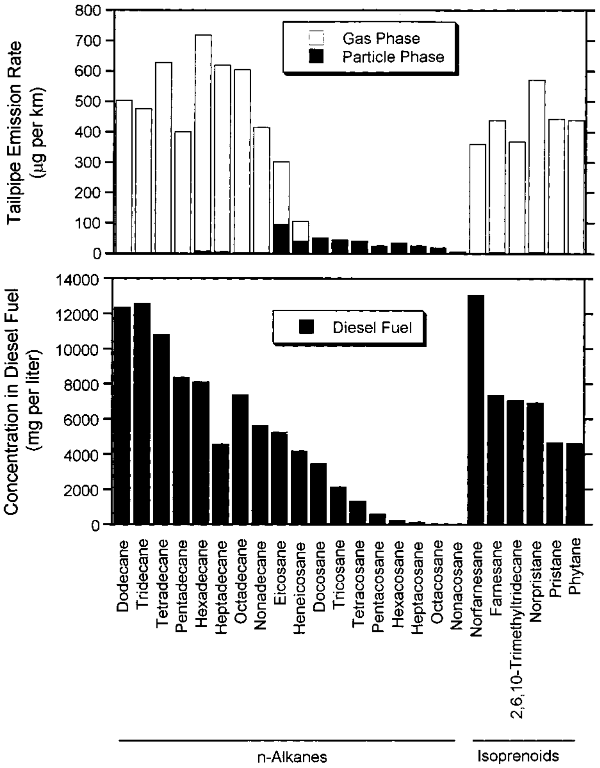

FIGURE 5. Comparison of the distribution *n*-alkanes and isoprenoids in medium duty diesel truck exhaust and present in the diesel fuel supplied to those trucks.

at rates in the range of 360 to 570 µg per vehicle kilometer traveled. The structures of selected isoprenoid hydrocarbons are shown in Figure 4. These compounds are naturally present in crude oil (*26*) and therefore would be expected to be found in lightly processed or straight run diesel fuel cuts in the petroleum refining process. The isoprenoids, in conjunction with certain PAH, hopanes, steranes, and elemental carbon as will be described shortly, have the potential to be used as tracers for diesel engine exhaust. Figure 5 shows the distribution of the *n*-alkanes and isoprenoids in the commercial California diesel fuel used in the current source tests compared to the emission rate and phase distribution of these compounds in the diesel truck exhaust. As can be seen in Figure 5, the tailpipe emissions are depleted in the lowest molecular weight homologues in each series of these branched and straight chain alkanes when compared to the parent fuel. It should be noted that the overall distribution of the organic compounds between the gas and particle phases summed over the entire FTP driving cycle may not behave according to gas/particle partitioning theory (*27*) applied to the bulk compound emission rate data averaged over the whole test. At any given point during the FTP cycle the organic compounds in the diluted exhaust should partition as expected by theory; however, the primary emission rates and organic compound compositions are changing continuously throughout the cycle such that the linear sum of these instantaneous equilibrated phase distributions may not add to produce gas/particle concentration ratios for the test as a whole that correspond to the equilibrium distribution at the average conditions during the test.

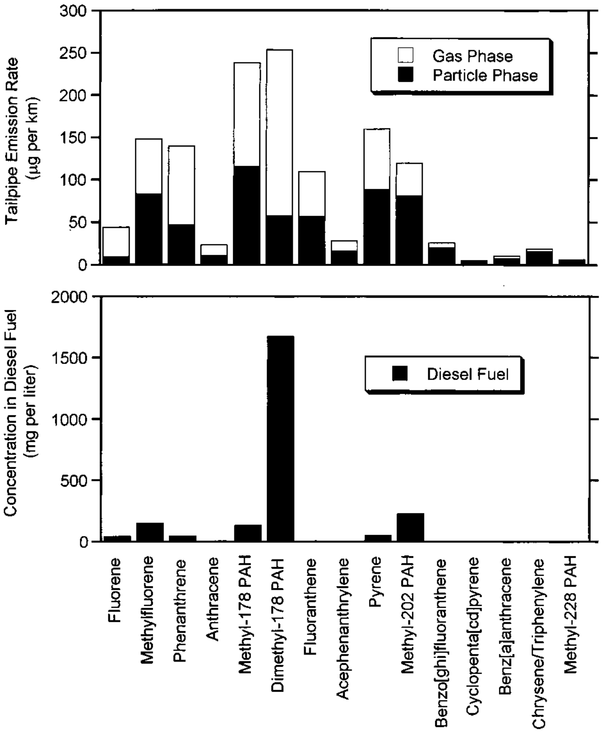

FIGURE 6. Polycyclic aromatic hydrocarbons (PAH) emitted from medium duty diesel trucks and present in diesel fuel.

A similar comparison between the PAH present in the fuel and in the diesel truck emissions is shown in Figure 6. Significant differences can be seen in the ratio of methyl-substituted PAH to unsubstituted PAH between the fuel and the tailpipe emissions. The dimethyl phenanthrenes and anthracenes (C_2-MW 178 PAH in Table 2) contribute the overwhelming majority of the PAH with three or more ring structures in the diesel fuel. The ratio of these compounds to phenanthrene plus anthracene decreases from 33.5 in the diesel fuel to 1.55 in the tailpipe emissions. An analogous but less extreme difference is observed for the methyl fluoranthenes, acephenanthrylenes, and pyrenes (C_1-MW 202 PAH in Table 2) when compared to the unsubstituted PAH with molecular weights of 202.

The particle-phase hopanes and steranes present in vehicle exhaust have been used in the past as tracers for motor vehicle exhaust contributions to atmospheric fine particle samples (*3, 4*). To this set of particle-phase exhaust molecular tracers we can now add two semivolatile tricyclic terpanes, 8*β*,13α-dimethyl-14*β*-*n*-butylpodocarpane and 8*β*,13α-dimethyl-14*β*-[3′-methylbutyl]podocarpane, which are quantified in the diesel truck exhaust and have been previously quantified in the atmosphere of Los Angeles (*28*).

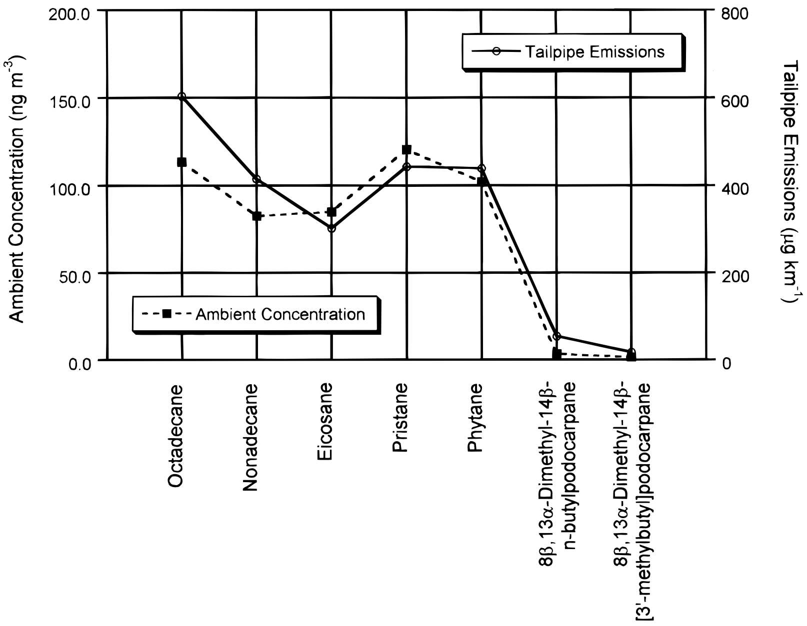

FIGURE 7. Semivolatile *n*-alkane, isoprenoid, and tricyclic terpane ambient concentrations measured in Azusa, CA, in the summer of 1993 compared to the tailpipe emission rates of these compounds from medium duty diesel trucks on the FTP hot-start driving cycle.

The structures of these compounds are shown in Figure 4. These compounds are also present in the diesel fuel used in these experiments at 2.1 and 0.6 µg g^{-1}, respectively, as shown in Table 2.

The question posed at the outset of the study is now revisited: "How can the semivolatile organic compound components of diesel fuel vapors and diesel engine exhaust be tracked in the atmosphere?" Since diesel exhaust contains unburned diesel fuel, whole fuel vapors share many features in common with the tailpipe exhaust, as we have just seen. However, the diesel truck exhaust is clearly distinguished from unburned fuel by its high black elemental carbon content, by its hopanes and sterane content, by its higher ratio of unsubstituted PAH to methyl-PAH, and by its high aldehyde content (although the aldehydes are too reactive to be considered as tracer species for diesel exhaust). The hopanes and steranes are not present in large amounts in the fuel (e.g., see Table 2) but are present in motor oil (see discussion of standards in text) and thus must be contributed largely by the lubricant oil used by the engines. In addition, diesel exhaust is readily distinguished from gasoline-powered auto exhaust by its higher elemental carbon content and by the relatively high quantity of pristane and phytane in diesel exhaust. Auto exhaust in turn can be distinguished from non-tailpipe-derived gasoline vapors because there is a limit placed on the atmospheric concentration of the sum of the gasoline plus diesel engine tailpipe emissions by the total quantity of hopanes and steranes in the atmosphere (*3*).

Ambient concentrations of semivolatile *n*-alkanes, isoprenoids, the tricyclic terpanes were measured by Fraser et al. (*28*) in southern California during the summer of 1993. Shown in Figure 7 is the 2-day average ambient concentration of *n*-octadecane, *n*-nonadecane, *n*-eicosane, pristane, phytane, and the tricyclic terpanes as measured by Fraser et al. (*28*) at Azusa, CA, along with the diesel engine emission rates of these compounds from the present study. The data from Fraser et al. (*28*) are scaled upward across all compounds by a factor of 1.7 to correct an error in the reported air volumes sampled. Good agreement is observed between the relative distribution of these compounds measured in the atmosphere and the emission rates of these compounds from the diesel trucks tested in the present study, which further indicates that these compounds will likely be useful as part of the group of tracers for motor vehicle exhaust.

Acknowledgments

We thank Rapheal Susnowitz, Thu Vo, Pons Lazo, and the staff at the California Air Resources Board's Haagen-Smit Laboratory in El Monte, CA, for their assistance and cooperation in conducting the diesel truck source tests, Eric Grosjean and Daniel Grosjean (DGA, Inc.) for preparation and analysis the C_{18} cartridges used for carbonyls, Rei Rasmussen (Oregon Graduate Institute) for preparation and analysis of the SUMA canisters used for measurement of C_{10} and smaller vapor-phase hydrocarbons, Judy Chow and Cliff Frazier at the Desert Research Institute for X-ray fluorescence measurements, Bob Cary at Sunset Labs for EC/OC measurements, and Lynn Salmon (Caltech) for conducting the ion chromatography and atomic absorption spectroscopy analyses. This research was supported by the California Air Resources Board under Agreement number A93-329.

Literature Cited

(1) Hildemann, L. M.; Markowski, G. R.; Cass, G. R. *Environ. Sci. Technol.* **1991**, *25*, 744−759.
(2) Rogge, W. R.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1993**, *27*, 636−651.
(3) Schauer, J. J.; Rogge, W. R.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Atmos. Environ.* **1996**, *30*, 3837−3855.
(4) Rogge, W. R.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *J. Geophys. Res.* **1996**, *101*, 19379−19394.
(5) Lowenthal, D. H.; Zielinska, B.; Chow, J. C.; Watson, J. G.; Gautum, M.; Ferguson, D. H.; Neuroth, G. R.; Stevens, K. D. *Atmos. Environ.* **1994**, *28*, 731−743.
(6) Westerholm, R. N.; Almen, J.; Hang, L.; Rannug, J. U.; Egeback, K. E.; Gragg, K. *Environ. Sci. Technol.* **1991**, *25*, 332−338.
(7) Wilson, N. K.; McCurdy, T. R. *Atmos. Environ.* **1995**, *29*, 2575−2584.
(8) Hoffmann, T.; Odum, J. R.; Bowman, F.; Collins, D.; Klockow, D.; Flagan, R. C.; Seinfeld, J. H. *J. Atmos. Chem.* **1997**, *26*, 189−222.
(9) Benner, B. A.; Gordon, G. E.; Wise, S. A. *Environ. Sci. Technol.* **1989**, *23*, 1269−1278.
(10) Fernandez, P.; Vilanova, R.; Grimalt, J. O. *Polycyclic Aromat. Hydrocarbons* **1996**, *9*, 121−128.
(11) Simo, R.; Grimalt, J. O.; Albaiges, J. *Environ. Sci. Technol.* **1997**, *31*, 2697−2700.

(12) Tancell, P. J.; Rhead, M. M.; Pemberton, R. D.; Braven, J. *Environ. Sci. Technol.* **1995**, *29*, 2871−2876.
(13) Hildemann, L. M.; Cass, G. R.; Markowski, G. R. *Aerosol Sci. Technol.* **1989**, *10*, 193−204.
(14) Schauer J. J.; Kleeman M. J.; Cass G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1999**, *33*, 1566−1577.
(15) John, W.; Reischl, G. *JAPCA* **1980**, *30*, 872−876.
(16) Birch, M. E.; Cary, R. A. *Aerosol Sci. Technol.* **1996**, *25*, 221−241.
(17) Dzubay, T. G. *X-ray Analysis of Environmental Samples*; Ann Arbor Science: Ann Arbor, MI, 1977.
(18) Mueller, P. K.; Mendoza, B. V.; Collins, J. C.; Wilgus, E. A. Application of Ion Chromatography to the Analysis of Anions Extracted from Airborne Particulate Matter. In *Ion Chromatographic Analysis of Environmental Pollutants*; Sawicki, E., Mulik, J. D., Wittgenstein, E., Eds.; Ann Arbor Science: Ann Arbor, MI, 1978; pp 77−86.
(19) Solorzano, L. *Limnol. Ocenaogr.* **1969**, *14*, 799−801.
(20) Grosjean, E.; Grosjean, D. *Int. J. Environ. Anal. Chem.* **1995**, *61*, 343−360.
(21) Kleeman, M. J.; Schauer, J. J.; Cass, G. R. *Environ. Sci. Technol.* **1998**, submitted for publication.
(22) Fraser, M. P.; Grosjean, D.; Grosjean, E.; Rasmussen, R. A.; Cass, G. R. *Environ. Sci. Technol.* **1997**, *31*, 2356−2367.
(23) Grosjean, E.; Grosjean, D.; Fraser M. P.; Cass G. R. *Environ. Sci. Technol.* **1996**, *30*, 2687−2703.
(24) Wagner, T.; Wyszynski, M. L. *Proc. Inst. Mech. Engrs.* **1996**, *210*, 109−122.
(25) Sagebiel, J. C.; Zielinska, B.; Pierson, W. R.; Gertler, A. W. *Atmos. Environ.* **1996**, *30*, 2287−2296.
(26) Philp, R. P. *Mass Spectra* **1985**, *4*, 1−54.
(27) Pankow, J. F. *Atmos. Environ.* **1994**, *28*, 185−188.
(28) Fraser, M. P.; Cass G. R.; Simoneit B. R. T.; Rasmussen R. A. *Environ. Sci. Technol.* **1997**, *31*, 2356−2367.

Received for review January 27, 1998. Revised manuscript received January 19, 1999. Accepted February 4, 1999.

ES980081N