Chapter 5

Organic Compounds from Gasoline-Powered Motor Vehicles

5.1 Introduction

Tailpipe emissions of volatile hydrocarbons from gasoline-powered motor vehicles have been studied extensively to determine the characteristics of the compounds emitted (1-5) and their contribution to photochemical smog formation (6-9). Likewise, a detailed analysis of the organic compounds in the particulate matter emitted in the exhaust from mid-1980's California on-road motor vehicles has been conducted (10), and this analysis has been used in air quality models to determine the direct primary contribution of motor vehicle exhaust to the fine particulate organic compounds and fine particle mass concentrations in the Southern California urban atmosphere (11,12). Very little, however, is known about the contribution of gasoline-powered motor vehicles to the urban concentrations of the high molecular weight vapor phase semi-volatile organic compounds that typically are too heavy to be analyzed by gas canister sampling and Teflon bag sampling. The role of these compounds in the atmosphere has not been addressed largely due to the lack of emissions data for these species.

Since some of the semi-volatile organic compounds are toxic air contaminants (i.e. PAH) and since the semi-volatile and heavy volatile organic compounds likely play a role in photochemical smog formation and in secondary organic aerosol formation, there is a need to understand the sources and fates of these compounds in the atmosphere. Air pollution models currently are being developed to asses the role of these compounds, and a corresponding need to measure the emissions of these compounds from urban air pollution sources exists.

In an effort to reduce the emissions of air pollutants, both motor vehicle designs and gasoline formulations have changed during the 1980's and 1990's. As a result, the composition of the emissions from gasoline-powered motor vehicles are expected to have changed as well. While considerable effort has been expended to determine the effect of reformulated fuels on the volatile organic compounds emitted from gasoline-powered vehicles (13, 14), much less is known about the effects of fuel reformulation and vehicle design changes on the semi-volatile and particulate organic compounds emitted. The most recent detailed measurements of particulate organic compound emissions from individual in-use motor vehicles in Southern California are from vehicles owned and operated in the mid 1980's (10, 15). The current study was undertaken to measure the more recent tailpipe emission rates of volatile organic compounds from gasoline-powered motor vehicles, to provide the first data on the distribution of semi-volatile organic compounds between the gas and particle phases, and to both update and extend the carbonyl and particle-phase organic compounds emissions data.

5.2 Experimental Methods

5.2.1 Comprehensive Source Sampling

The dilution sampler used in the present study consists of two stages, the pre-dilution tunnel and the primary sampling system. The pre-dilution tunnel is connected via a stainless steel hose directly to the tailpipe of the gasoline-powered motor vehicle being tested on a chassis dynamometer. At the entrance of the pre-dilution tunnel, HEPA-filtered and activated carbon-filtered dilution air is turbulently mixed with the vehicle exhaust. The pre-dilution tunnel is operated at a fixed combined flowrate, such that the exhaust concentration in this tunnel is always proportional to the total emission rate from the vehicle tailpipe. Most of the exhaust from the pre-dilution tunnel is expelled through a flow orifice at the downstream end of the tunnel while a small slipstream is removed isokinetically from the pre-dilution tunnel through a cyclone separator. Particles smaller than 10 μm in aerodynamic diameter exit the cyclone along with the gas-phase species and are passed through a venturi meter into the primary sampling system where the sample is further diluted with purified dilution air. The total dilution rate of the combined two-stage system is set at approximately 140 fold for the noncatalyst cars and 40 fold for the catalyst-equipped cars. All of 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 in a way that is completely free of grease coatings and rubber gaskets (Teflon o-rings are used as seals). The pre-dilution tunnel and the primary dilution tunnel are thoroughly cleaned prior to sampling.

The sampling system used in this experiment is a modified version of the portable dilution tunnel originally developed by Hildemann et al. (15, 16). The modifications made to this system have been previously described in Chapters 2 and 4. A diagram of the original dilution sampler is shown in Figure 1 of Hildemann et al. (16), its use with a pre-dilution tunnel to test motor vehicles is shown in Figure 1 of Hildemann et al. (15), and the new sample collection systems are shown in Figure 2.1 of Chapter 2. At the back end of the dilution sampler is the residence time chamber where the sampling trains are connected. Semi-volatile and fine particle-phase organic compounds are collected using both a denuder/filter/PUF sampling train and a filter/PUF sampling train. These sampling configurations are described in Chapter 2. In addition, a third type of cyclone-based sampling unit is operated to collect fine particulate matter, carbonyls, organic acids, and gas-phase hydrocarbons. This sampling unit is also described in detail in Chapter 2.

MOUDI impactors and electronic particle sizing instruments are also used to obtain particle size distributions and particle chemical composition as a function of size for the diluted gasoline-powered vehicle exhaust. The size distribution measurements will be reported elsewhere.

5.2.2 Vehicle Selection

The vehicles tested in the current study are all sampled from the on-road vehicle fleet registered in Southern California. The catalyst-equipped motor vehicles are selected to represent the distribution of accumulated vehicle miles traveled (VMT) by automobiles and light trucks of various model years in Southern California as reported by Horie et al. (17). The nine catalyst-equipped motor vehicles tested are listed in Table 5.1. These vehicles span model years from 1981 through 1994 and consist of three light-duty trucks and six automobiles. The two noncatalyst equipped motor vehicles tested are typical vehicles of this type and are also listed in Table 5.1. No modifications or repairs were made to the vehicles; the vehicles were tested as received using the commercial gasoline fuels obtained with the vehicles.

5.2.3 Source Testing Procedure

The vehicles were tested at the California Air Resources Board (CARB) Haagen-Smit Laboratory in El Monte, California. The dynamometers used for

Table 5.1. Fine Particle Tailpipe Emissions from the Gasoline-Powered Motor Vehicles Tested

Model Year	Vehicle Manufacturer and Model	Engine (Displacement and Number of Cylinders)	Vehicle Mileage (miles)	Fine Particle Emission Rate (mg km^{-1})
Catalyst Equipped Motor Vehicles				
1994	Honda Civic	1.5 liters 4 cyl	17,458	0.8 ± 0.4
1994	Ford Taurus	3.0 liters 6 cyl	26,731	7.8 ± 0.3
1992	Toyota Pick-Up Truck	3.0 liters 6 cyl	41,283	6.1 ± 0.9
1992	Chevy Astrovan	5.0 liters 8 cyl	49,439	3.0 ± 1.1
1990	Toyota Celica	2.2 liters 4 cyl	54,911	2.9 ± 0.5
1990	GMC Pick-Up Truck	5.0 liters 8 cyl	21,073	3.2 ± 0.5
1986	Chrysler Reliant K	2.2 liters 4 cyl	78,656	2.3 ± 0.3
1984	Toyota Tercell	1.5 liters 4 cyl	76,656	5.4 ± 0.6
1981	Honda Accord	1.8 liters 4 cyl	106,722	36.4 ± 2.2
Noncatalyst Equipped Motor Vehicles				
1970	Volkswagon Vancamper	1.6 liters 4 cyl	30,000[a]	200 ± 5
1969	Chevy Camaro	5.0 liters 8 cyl	371,780	985 ± 3

[a] Indicated mileage since engine was rebuilt

testing were twin-roll hydraulic dynamometers. The dynamometers were loaded at settings specified by the vehicle manufacturers by the Haagen-Smit Laboratory staff, and the vehicles were driven on the dynamometers by the CARB dynamometer operations staff. The cold start Federal Test Procedure (FTP) urban driving cycle used for all of the tests is shown in Figure 5.1.

Upon receipt of each vehicle, a sample of the gasoline present in the vehicle fuel tank was withdrawn for analysis. The vehicles were warmed-up on a dynamometer and then placed in storage at 24 °C for 16 to 24 hours. After cold storage the vehicles were rolled onto the dynamometer and first were tested using the standard FTP urban driving cycle (Figure 5.1) and constant volume sampler (CVS) specified by the Federal Register for routine volatile organic compound (VOC), CO and NOx compliance testing of motor vehicles. The two stage dilution sampler was not used for these tests. At the completion of the FTP/CVS emissions test, each vehicle was returned to storage at 24 °C for an additional 16 to 24 hours. After the second storage period each vehicle was returned to the dynamometer and was tested using the same FTP urban driving cycle but with the vehicle exhaust routed to the two-stage dilution sampler.

Flows were established through the dilution sampler 1 minute prior to starting the engine on the FTP cycle. The sampler was run continuously through the first two stages of the FTP cycle, the cold start and the hot running section of

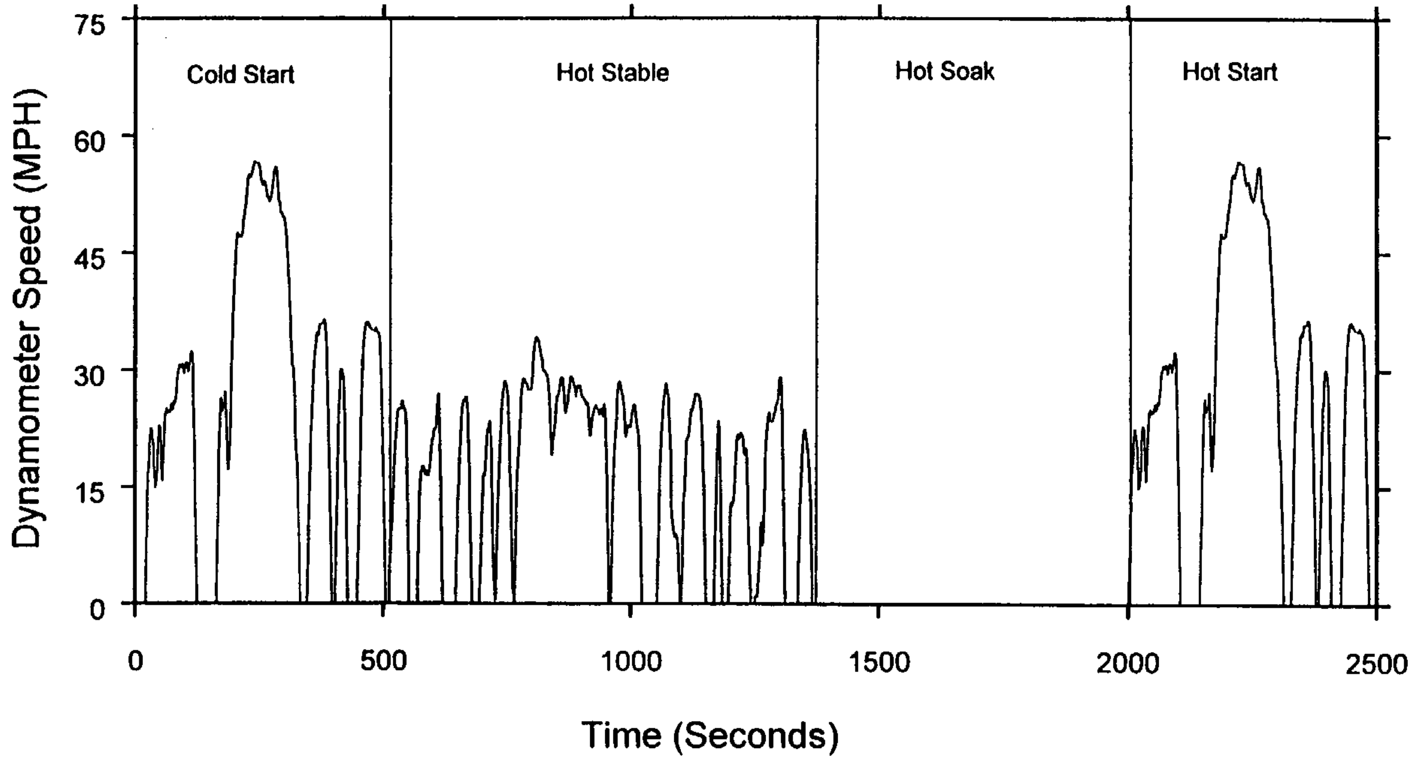


Figure 5.1. Federal Test Procedure (FTP) Urban Driving Cycle.

the cycle. One minute after the engine was turned off during the hot soak section of the FTP cycle, all of the flows through the dilution sampler were stopped. Likewise, one minute before the engine was restarted on the hot start section of the cycle, all of the flows were re-established through the dilution sampler, and the sampler was shut down one minute after the end of the FTP cycle. This protocol was employed to minimize pulling clean air over the sample collection substrates which could potentially lead to evaporation of semi-volatile organic compounds from the substrates causing sampling artifacts due to recollection on downstream substrates.

The catalyst-equipped gasoline-powered motor vehicles were tested in groups of three. Between each of the vehicles in a group, the XAD-coated denuders and one Teflon filter were replaced with new substrates. All other sample collection substrates, cartridges, and canisters were used to collect composites of the emissions from the three vehicles. This approach allowed enough mass collection for detailed organic chemical analysis while also providing for measurement of the individual fine particle mass emission rate for each vehicle tested. The same approach was used for the noncatalyst equipped motor vehicles except that only two vehicles were tested in this group.

Nitrogen oxides, carbon monoxide, methane, and total non-methane hydrocarbons were measured during the FTP/CVS tests. In addition, molecular weight vapor phase hydrocarbon emissions were sampled for detailed compound speciation for three vehicles, the 1992 Chevy Astrovan, the 1990 Toyota Celica, and the 1990 GMC Pick-Up Truck. These three vehicles were tested as a group using the two-stage dilution source sampler with the VOC emissions composited into one gas canister. This allows a comparison of the standard FTP hydrocarbon emissions speciation measurement to the measurements made from the canister-based sample collected by the two-stage dilution source sampler.

5.2.4 Organic Chemical Analysis

The same analytical techniques were used to quantify the semi-volatile and particulate organic compounds in the emissions from the gasoline-powered motor vehicles as was used in the diesel truck source test experiment. These procedures are described in Chapter 2.

Total non-methane organic gases (NMOG, EPA method TO12) and individual organic vapor phase hydrocarbons ranging from C_1 to C_{10} are analyzed from the SUMA canisters by gas chromatography/flame ionization detection (GC/FID) (see Chapter 2). Carbonyls collected by the C_{18} impregnated cartridges are analyzed by liquid chromatography/UV detection (see Chapter 2).

5.3 Results

5.3.1 Comparison of Speciated Volatile Hydrocarbon Emissions Measurements

The speciation of the volatile non-methane hydrocarbons was determined for emissions collected by the FTP/CVS sampler from three of the vehicles in the test fleet: the 1992 Chevy Astrovan, the 1990 Toyota Celica, and the 1990 GMC Pick-Up Truck. Since these three vehicles were tested as a group by the two-stage dilution source sampler, the average emissions rates of volatile hydrocarbons for these three vehicles can be compared for the two different sampling systems. Shown in Figure 5.2 is a comparison of the emissions of 53 volatile hydrocarbons measured by gas chromatography/flame ionization detection according to the FTP/CVS hydrocarbon speciation method and according to the methods described for use with the two-stage dilution sampler. Excellent agreement is observed for volatile hydrocarbon compounds emitted at rates > 1.0 mg km^{-1}. For hydrocarbons emitted at rates < 1.0 mg km^{-1} there is greater scatter in the data. This scatter at lower emission rates is due to the fact that the dilution air contains small amounts of contaminants in both sampling systems. The dilution air contaminant concentrations are measured and subtracted from the emissions in both sampling systems, but this correction produces a greater relative uncertainty at low emission rates.

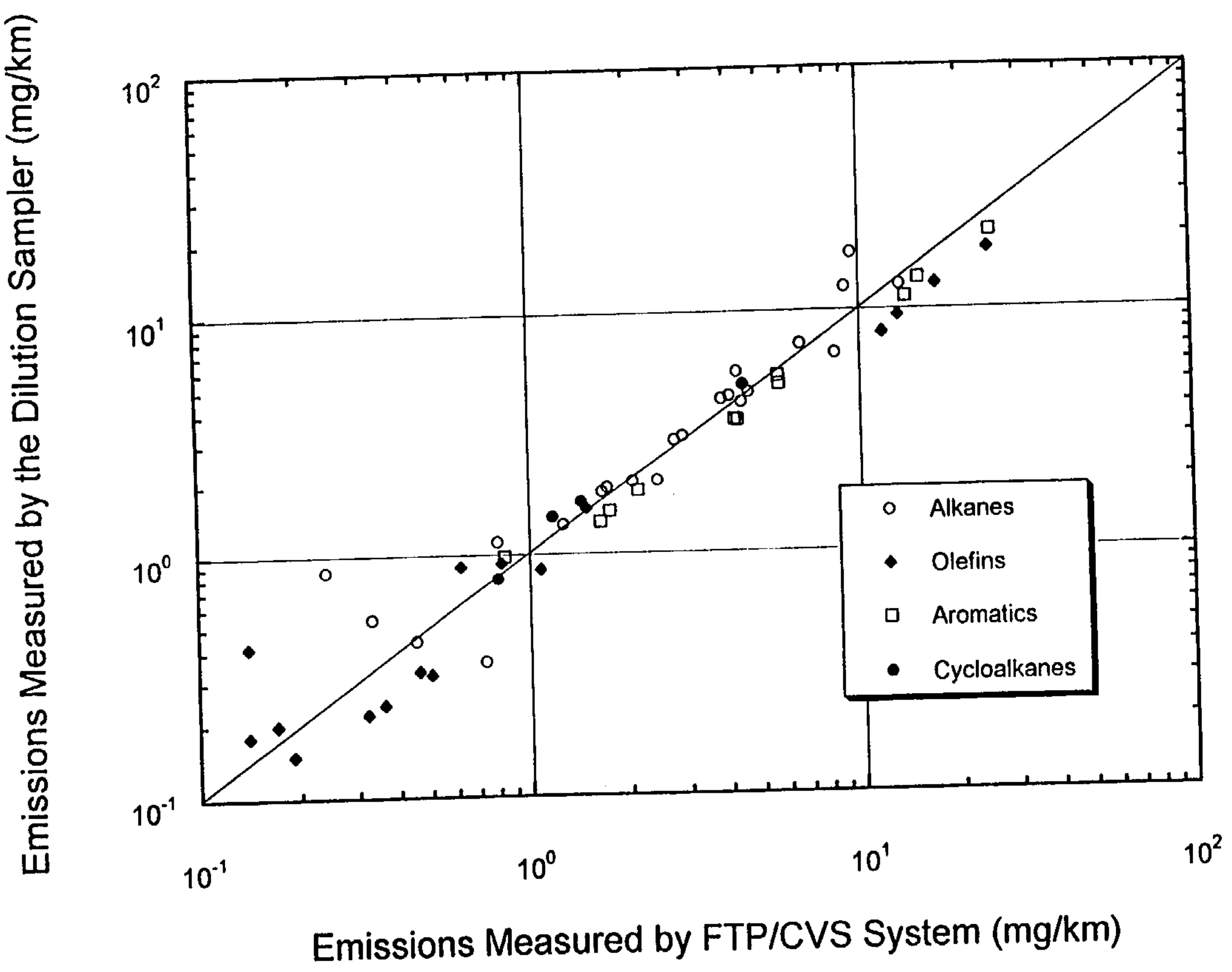


Figure 5.2. Individual hydrocarbon compounds emitted from a composite of 3 light-duty vehicles tested on the FTP Urban Driving Cycle as measured by the FTP/CVS sampler compared to measurements made for the same species and vehicles using the 2-stage dilution sampler.

The excellent agreement between the two source sampling methods is significant. Most gasoline-powered motor vehicle emissions data are collected using the FTP/CVS Teflon bag technique, while most ambient atmospheric data are collected in stainless steel canisters like those used by the two-stage dilution sampler. Data taken by these different sampling techniques are compared whenever air pollution models driven by CVS-based emissions data are compared to ambient atmospheric data collected by canister sampling. These results indicate that there is no systematic bias inherent in these comparisons.

5.3.2 Fine Particle Mass and Chemical Composition

The fine particle mass emissions rate for each of the motor vehicles tested is given in Table 5.1. Averaging over all nine of the catalyst-equipped gasoline-powered motor vehicles tested, the mean fine particle mass emission rate over the FTP driving cycle was 7.5 ± 2.7 mg per kilometer. It should be noted that the 1981 Honda Accord had an emissions rate that was significantly higher than any of the other eight vehicles at 36.4 ± 2.2 mg per kilometer. The average emission rate, not including the high emitter, is 3.9 ± 1.1 mg per kilometer.

Hildemann et al. (15) tested a fleet of catalyst-equipped gasoline-powered vehicles in the mid 1980's and also found that one high emitting vehicle among the group tested had a significant effect on the average fine particle emission rate from the group as a whole. The average fine particle emission rate from all catalyst-equipped cars tested by Hildemann et al. (15) was 18 mg per kilometer. Not including the high emitter, the average fine particle emission rate during the mid 1980's tests was 11 mg per kilometer. A comparison of the present emission rates to the emissions measured in the mid 1980's shows a reduction of fine particle emissions by approximately 60% over this ten year period.

The fine particle emission rates for the two noncatalyst gasoline-powered motor vehicles were 200 mg per kilometer for the 1970 Volkswagon Vancamper and 985 mg per kilometer for the 1969 Chevy Camaro. These emission rates are significantly greater than the average emission rate of 59 ± 25 mg per kilometer from the noncatalyst cars tested by Hildemann et al. (15) in the mid 1980's. It should be noted that the average age of the noncatalyst equipped vehicles tested by Hildemann et al. (15) in the mid 1980's was 16 years old, and that the average age of the noncatalyst motor vehicles tested in the current study is 26 years old. This increase in average age arises from the fact that noncatalyst equipped cars were phased out in the mid-1970's. While the Volkswagon Vancamper has a rebuilt engine, the 1969 Camaro does not. With increasing age, the Camaro has accumulated 371,780 miles driven. Its fine particle emissions alone are equivalent to those of more than 130 of the in-use catalyst-equipped cars. As a result it may be that an extraordinarily small fraction of the vehicle fleet is responsible for the majority of the fine particle emissions from gasoline-powered light-duty vehicles in Southern California.

During each group of source tests fine particle organic and elemental carbon emissions were measured from one of the quartz fiber filters located downstream of the XAD-coated annular denuder and also from one of the quartz fiber filters which did not have the gas-phase semi-volatile organic compounds removed by the denuder prior to collection on the filter. The organic carbon measured on the filters downstream of the denuder averaged 73% of the organic carbon on the undenuded filter sample for the catalyst equipped gasoline powered motor vehicles. Since very little semi-volatile organic carbon was present on the PUF cartridges of the denuder/filter/PUF sampling train, it is reasonable to assume that the higher organic carbon mass measured on the undenuded filter sample was due to sorption of gas-phase semi-volatile organic compounds to the quartz fiber filter and to the particulate matter collected on the filter.

Using the denuder/filter/PUF particulate organic carbon measurement, the fine particle mass emitted from catalyst-equipped motor vehicles was found to be comprised of 31.8 ± 2.1 percent organic carbon and 10.3 ± 2.1 percent elemental carbon. The next largest constituent of the fine particle mass was ammonium ion at 2.15 ± 0.13 percent. Sulfate was the next largest component accounting for 1.1 ± 0.3 percent of the mass. Silicon, phosphorus, chlorine, calcium, iron, and zinc were also present in small but measurable quantities. The fine particle mass elemental and ionic composition is shown in Table 5.2.

The fine particulate organic carbon measured downstream of the denuder for the noncatalyst equipped motor vehicles was found to be 69.5% of the organic carbon on the undenuded filter sample. Using the fine particulate carbon determined by the denuder/filter/PUF sampling train, the fine particle mass emitted from the noncatalyst equipped motor vehicles tested is 58.3 ± 2.7 percent organic carbon and 1.4 ± 0.4 percent elemental carbon. The next largest constituent in the fine particulate mass emitted from noncatalyst equipped gasoline powered vehicles is sulfur making up 0.28% of the mass. Silicon, phosphorus, calcium, iron, zinc, and lead also contribute smaller but measurable proportions of the mass as shown in Table 5.2. The lead present in the fine particulate matter emitted is likely due to lead deposited in the engine and/or exhaust systems when the vehicles were operated with leaded gasoline in earlier years.

5.3.3 Distribution of Carbon Emissions

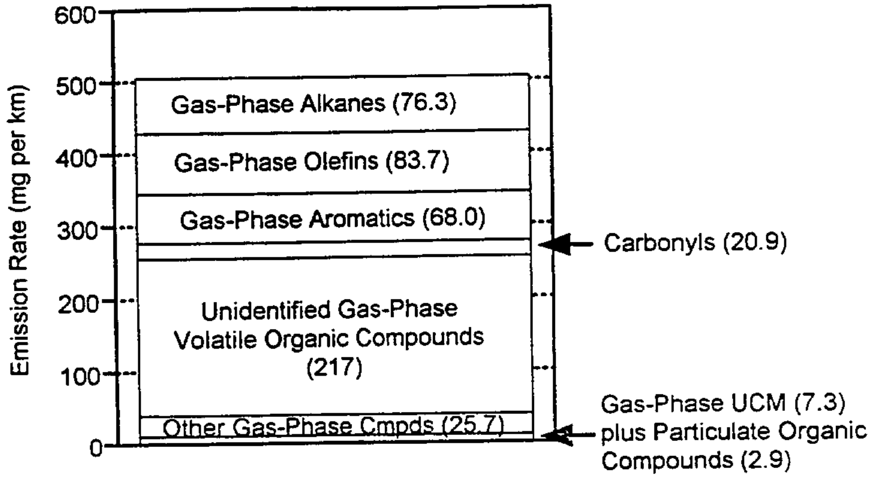
Gas-phase species dominate the organic compound emissions from both noncatalyst and catalyst-equipped motor vehicles. Figure 5.3 shows the distribution of non-methane organic compound emissions for both types of gasoline-powered motor vehicles. A detailed list of the emission rate and phase

Table 5.2. Average Fine Particle Emission Rate and Fine Particle Chemical Composition of Tailpipe Exhaust from Gasoline-Powered Motor Vehicles (Values shown in boldface are greater than zero by at least two standard errors).

	Catalyst-Equipped Gasoline-Powered Vehicles	Noncatalyst Gasoline Powered Vehicles
Fine Particle Emissions Rate (AVG ± STD)	**7.5 ± 2.7 mg km^{-1}**	**593 mg km^{-1}**
X-ray Fluorescence (Wt % of Fine Particle Mass)		
Aluminum	0.26 ± 0.23	0.00 ± 0.03
Silicon	**0.25 ± 0.11**	**0.12 ± 0.01**
Phosphorus	**0.31 ± 0.08**	**0.03 ± 0.01**
Sulfur	**0.48 ± 0.04**	**0.28 ± 0.01**
Chlorine	**0.44 ± 0.13**	0.01 ± 0.02
Potassium	0.04 ± 0.15	0.00 ± 0.01
Calcium	**0.35 ± 0.11**	**0.03 ± 0.01**
Titanium	0.01 ± 0.64	0.00 ± 0.06
Vanadium	0.00 ± 0.32	0.00 ± 0.02
Chromium	0.00 ± 0.09	0.00 ± 0.01
Manganese	0.00 ± 0.05	0.00 ± 0.00
Iron	**0.11 ± 0.03**	**0.01 ± 0.00**
Nickel	0.00 ± 0.03	0.00 ± 0.00
Copper	0.00 ± 0.03	0.00 ± 0.00
Zinc	**0.19 ± 0.02**	**0.03 ± 0.00**
Gallium	0.01 ± 0.05	0.00 ± 0.00
Arsenic	0.00 ± 0.06	0.00 ± 0.01
Selenium	0.01 ± 0.03	0.00 ± 0.00
Bromine	0.00 ± 0.03	0.00 ± 0.00
Rubidium	0.00 ± 0.03	0.00 ± 0.00
Strontium	0.01 ± 0.03	0.00 ± 0.00
Yttrium	0.00 ± 0.04	0.00 ± 0.00
Zirconium	0.00 ± 0.04	0.00 ± 0.00
Molybdenum	0.03 ± 0.09	0.00 ± 0.01
Palladium	0.00 ± 0.24	0.00 ± 0.02
Silver	0.06 ± 0.26	0.00 ± 0.02
Cadmium	0.00 ± 0.27	0.01 ± 0.03
Indium	0.12 ± 0.31	0.01 ± 0.03
Tin	0.03 ± 0.44	0.00 ± 0.04
Antimony	0.22 ± 0.52	0.02 ± 0.04
Barium	0.00 ± 1.73	0.00 ± 0.16
Lanthanum	0.31 ± 2.29	0.00 ± 0.22
Mercury	0.01 ± 0.07	0.00 ± 0.01
Lead	0.00 ± 0.09	**0.03 ± 0.00**
Elemental and Organic Carbon (Wt % of Fine Particle Mass)		
Organic Carbon	**23.2 ± 1.5^{a}**	**40.5 ± 1.9^{a}**
Elemental Carbon	**10.3 ± 2.1**	**1.4 ± 0.4**
Ionic Species (Wt % of Fine Particle Mass)		
Nitrate	0.47 ± 0.45	**0.07 ± 0.02**
Sulfate	**1.09 ± 0.30**	**0.05 ± 0.01**
Ammonium	**2.15 ± 0.13**	0.00 ± 0.01

Notes: (a) measured downstream of organics denuder. Organic carbon measured on undenuded filter is 31.8 % and 58.3 % of the fine particle mass for the catalyst-equipped and noncatalyst motor vehicle, respectively.

Catalyst-Equipped Gasoline Powered Vehicles



Non-Catalyst Gasoline Powered Vehicles

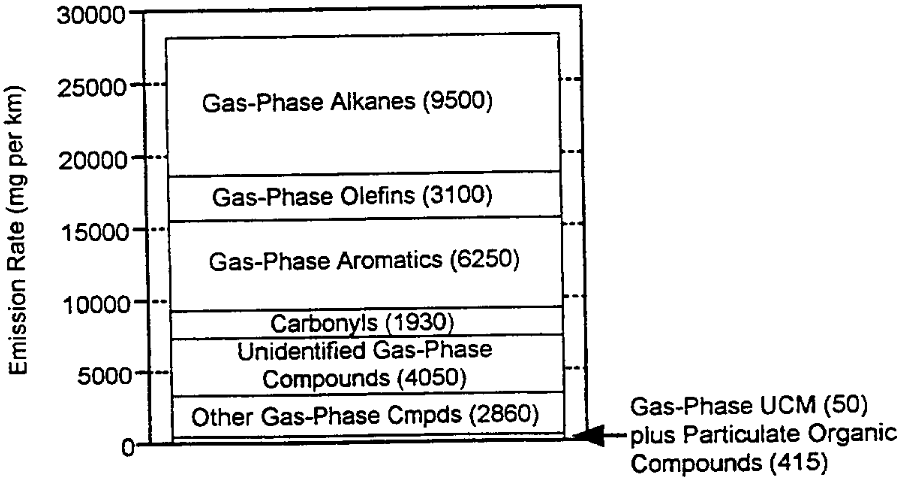


Figure 5.3. Mass balance on the non-methane organic compounds and elemental carbon emitted from catalyst-equipped and noncatalyst equipped gasoline-powered light-duty motor vehicles.

distribution of the organic compounds identified in the vehicle exhaust is given in Table 5.3. Also shown in Table 5.3 is the average composition of the commercial gasoline used by the vehicles in these source tests. n-Alkane and branched alkane gas-phase emissions are dominated by the same organic compounds which are present in noticeable quantities in gasoline. In contrast, ethene, propene, and ethyne make up a majority of the gas-phase olefinic compound emissions. These olefinic species are formed by the incomplete combustion of gasoline and are only present at trace levels in gasoline. The distribution of the monocyclic aromatic hydrocarbons emitted also is similar to the distribution of the aromatics present in the fuel, except that an enrichment in the benzene concentration is observed in the tailpipe emissions relative to the quantity of benzene in the gasoline burned.

Figures 5.4 and 5.5 show an expanded view of the semi-volatile and particle-phase organic compound emissions that form the lowest slice of the graphs in Figure 5.3 along with the elemental carbon emitted. Measurements shown are made by the denuder/filter/PUF sampling train. In this context, semi-volatile and particle-phase organic compounds are hydrocarbons with more than 11 carbons, carboxylic acids with more than 8 carbons, and all organic dicarboxylic acids. For the catalyst-equipped vehicles in Figure 5.4, the gas-phase unresolved complex mixture (UCM) of branched and cyclic hydrocarbons that appears as a wide hump that underlies the resolved peaks on

Table 5.3. Organic Compounds Present in Gasoline and in Gasoline-Powered Motor Vehicle Tailpipe Emissions

Compound	Catalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions ($\mu g\ km^{-1}$)		Noncatalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions ($\mu g\ km^{-1}$)		Gasoline Composition ($\mu g\ gm^{-1}$)	Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase		
n-Alkanes						
Methane	38000		330000			a, e
Ethane	7770		36900			a, e
Propane	650		9300		100	a, e
n-Butane	1620		191000		7620	a, e
n-Pentane	4290		536000		27600	a, e
n-Hexane	2900		410000			a, e
n-Heptane	1820		268000		9700	a, e
n-Octane	1070		131000		6380	a, e
n-Nonane	430		45300		2080	a, e
n-Decane	300		42600		1120	a, e
n-Undecane	*		*		*	
n-Dodecane†	83.9		1770		136	a, f
n-Tridecane†	48.2		1280		96.4	b, f
n-Tetradecane	18.4		212		13.8	a, f
n-Pentadecane	6.2		112		14.2	b, f
n-Hexadecane	6.4	0.2	92		8.3	a, f
n-Heptadecane	4.4		130		5.6	b, f
n-Octadecane	2.0	2.2	150	13	7.8	a, f
n-Nonadecane	2.0		92	75	4.7	b, f
n-Eicosane	1.8	0.8	100	190	2.5	a, f
n-Heneicosane	1.8	0 i	32.0	214	1.9	b, f
n-Docosane		0.8	29.8	228	1.5	b, f
n-Tricosane	0.5	1.9	11.9	191	2.2	b, f
n-Tetracosane		0.9	8.9	503	1.7	a, f
n-Pentacosane		2.7	14.3	489	1.7	b, f
n-Hexacosane		0.8	9.6	764	1.0	b, f
n-Heptacosane		0.6	2.4	391		b, f
n-Octacosane			3.0	119		a, f
n-Nonacosane			2.8	95		b, f
Branched alkanes						
i-Butane	130				1040	a, e
2,2-Dimethylpropane					110	a, e
i-Pentane	11300		1720000		79200	a, e
2,2-Dimethylbutane	800		195000		5720	a, e
2,3-Dimethylbutane	2140		298000		12900	a, e
2-Methylpentane	6310		827000		36900	a, e

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.

Sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details.

Additional Notes: † 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.

Table 5.3. (continued - page 2)

Compound	Catalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions ($\mu g\ km^{-1}$)		Noncatalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions ($\mu g\ km^{-1}$)		Gasoline Composition ($\mu g\ gm^{-1}$)	Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase		
Branched alkanes						
3-Methylpentane	3760		512000		22700	a, e
2,4-Dimethylpentane	2920		354000		15700	a, e
2-Methylhexane	2880		372000		15300	a, e
2,3-Dimethylpentane	5340		714000		29400	a, e
3-Methylhexane	2950		415000		16200	a, e
2,2,4-Trimethylpentane	8200		1080000		34600	a, e
2,5-Dimethylhexane	1500		205000		5070	a, e
2,4-Dimethylhexane	1650		219000		6460	a, e
2,3,4-Trimethylpentane	2510		412000		13000	a, e
2,3-Dimethylhexane	1040		148000		5600	a, e
2-Methylheptane	1340		159000		6260	a, e
3-Ethylhexane	1640		205000		810	a, e
2,2,4-Trimethylhexane					190	a, e
Norfarnesane†	65.5		638		106	b, f
Farnesane†	18.8		332		22	b, f
2,6,10-Trimethyltridecane	8.8		80		15.5	b, f
Norpristane	4.6	0.3	188	19.8	4.3	b, f
Pristane	7.8		225		12.1	a, f
Phytane	3.2		252		6.9	b, f
n-Alkenes						
Ethene	29200		716000			a, e
Propene	14900		436000		10	a, e
1-Butene					170	a, e
trans-2-Butene	2190		69300		630	a, e
cis-2-Butene	900		36100		720	a, e
1-Pentene	400		51800		1480	a, e
trans-2-Pentene	710		77400		4120	a, e
cis-2-Pentene	440		42300		2290	a, e
1-Hexene	430		18400		770	a, e
trans-2-Hexene	300		31600		1860	a, e
cis-2-Hexene	170		17300		1050	a, e
Branched alkenes						
Isobutene	15600		427000		170	a, e
3-Methyl-1-butene	350		22500		380	a, e
2-Methyl-1-butene	1120		84600		2690	a, e
2-Methyl-2-butene	2270		126000		6360	a, e
4-Methyl-1-pentene					300	a, e

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.
Sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details.
Additional Notes: †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.

Table 5.3. (continued - page 3)

Compound	Catalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions ($\mu g\ km^{-1}$)		Noncatalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions ($\mu g\ km^{-1}$)		Gasoline Composition ($\mu g\ gm^{-1}$)	Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase		
Branched alkenes						
2-Methyl-1-pentene	230		26600		1250	a, e
2-Methyl-2-pentene	480		50400		2700	a, e
Diolefins						
1,3-Butadiene	770		15600		10	a, e
Alkynes						
Ethyne	12800		865000			a, e
Saturated cycloalkanes						
Cyclopentane	780		85400		4110	a, e
Methylcyclopentane	4320		604000		26200	a, e
Cyclohexane	1440		238000		8900	a, e
Methylcyclohexane	1860		274000		7870	a, e
Ethylcyclohexane					930	a, e
Nonylcyclohexane			17		7.8	b, f
Decylcyclohexane	1.2		14		12.9	b, f
Undecylcyclohexane	0.84		16.7			b, f
Dodecylcyclohexane	1.4		15.9			b, f
Tridecylcyclohexane	0.91		22.4	21.5		b, f
Tetradecylcyclohexane	0.67		21.3	66.1		b, f
Pentadecylcyclohexane	1.3		20.4	162		a, f
Hexadecylcyclohexane				206		b, f
Heptadecylcyclohexane				362		a, f
Octadecylcyclohexane				265		b, f
Nonadecylcyclohexane				241		b, f
Eicosylcyclohexane				144		b, f
Heneicosylcyclohexane				75		b, f
Unsaturated cycloalkenes						
Cyclopentene	480		31700		1120	a, e
Aromatic hydrocarbons						
Benzene	11900		473000		7530	a, e
Toluene	21300		2360000		59500	a, e
Ethylbenzene	4180		434000		12800	a, e
m & p-Xylene	14300		1720000		50500	a, e
o-Xylene	5410		562000		19700	a, e
i-Propylbenzene					830	a, e
n-Propylbenzene	830		97900		3500	a, e
p-Ethyltoluene	4040		385000		6080	a, e
m-Ethyltoluene	1750		175000		14200	a, e

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.

Sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details.

Additional Notes: † 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.

Table 5.3. (continued - page 4)

Compound	Catalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions (μg km^{-1})		Noncatalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions (μg km^{-1})		Gasoline Composition (μg gm^{-1})	Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase		
Aromatic hydrocarbons						
1,3,5-Trimethylbenzene	1980		210000		7450	a, e
o-Ethyltoluene	1610		142000		4800	a. e
1,2,4-Trimethylbenzene	5720		602000		24600	a, e
Naphthalene†	≈ 1000		≈ 50000		1040	a, f
2-Methylnaphthalene†	≈ 1000		≈ 50000		1330	a, f
1-Methylnaphthalene †	≈ 500		≈ 30000		800	a, f
C_2-Naphthalenes†	183		28500		624	a, f
C_3-Naphthalenes†	62.5		5860		135	b, f
C_4-Naphthalenes†	25.3		950		55.7	b. f
Acenaphthylene†	37.0		2180			a. f
Acenaphthene†	6.55		177			a. f
Fluorene	9.72		358	20.1	4.35	a, f
C_1-Fluorene	6.34		398	388	10.0	b. f
C_2-Fluorene	10.5		490	384	17.1	b, f
Phenanthrene	21.7		622	434	9.24	a, f
Anthracene	3.69		148	106	4.35	a, f
3-Methylphenanthrene	2.92		236	181	6.01	b. f
2-Methylphenanthrene	3.35		291	195	9.64	b, f
2-Methylanthracene	1.14		94.1	66.7	5.54	a. f
9-Methylphenanthrene	2.47		131	107	4.49	b. f
1-Methylphenanthrene	1.63		122	65.1	3.91	a. f
C_2-MW 178 PAH	8.07		464	575	24.93	a. f
C_3-MW 178 PAH	1.51		176	216	10.76	b, f
Fluoranthene	4.25	0.069	160	152	1.15	a. f
Acephenanthrylene	0.58	0.012	50.8	57.8	0.04	b, f
Pyrene	4.28	0.077	160	217	3.38	a, f
C_1-MW 202 PAH	2.06		96.5	233	5.27	b, f
Benzo[ghi]fluoranthene	0.276	0.063	10.7	46.8		b, f
Cyclopenta[cd]pyrene		0.031	5.00	55.6		a, f
Benz[a]anthracene	0.181	0.097	4.80	51.9		a, f
Chrysene & Triphenylene	0.451	0.206	5.07	52.1		a, f
C1-MW 226 PAH		0.116				b, f
C1-MW 228 PAH		0.242	4.13	103		b, f
Benzo[k]fluoranthene		0.083		32.7	0.28	a, f
Benzo[b]fluoranthene				37.3		a, f
Benzo[j]fluoranthene		0.009		1.52		b, f
Benzo[e]pyrene		0.150		38.2	6.79	a, f

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.

Sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details.

Additional Notes: †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.

Table 5.3. (continued - page 5)

Compound	Catalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions (μg km^{-1})		Noncatalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions (μg km^{-1})		Gasoline Composition (μg gm^{-1})	Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase		
Aromatic hydrocarbons						
Benzo[a]pyrene		0.021		41.0		a, f
Perylene		0.031			2.79	a, f
Indeno[1,2,3-cd]fluoranthene		0.050		28.5		a, f
Indeno[1,2,3-cd]pyrene		0.436		92.0		a, f
Coronene				101		a, f
Tricyclic terpanes						
8β,13α-Dimethyl-14β-n-butylpodocarpane	1.13	0.20	46.9	119		c, f
8β,13α-Dimethyl-14β-[3'-methylbutyl]podocarpane	0.46	0.14	20.2	76.0		c, f
Diasteranes						
20S-13β(H),17α(H)-Diacholestane				73.6		c, f
20R-13β(H),17α(H)-Diacholestane				45.2		c, f
Hopanes						
18α(H)-22,29,30-Trisnorneohopane		0.038		125		c, f
17α(H)-22,29,30-Trisnorhopane				69.0		c, f
17α(H)-21β(H)-29-Norhopane		0.019		282		c, f
18α(H)-29-Norneohopane				75.6		c, f
17α(H),21β(H)-Hopane		0.033		321		c, f
22R&S,17α(H),21β(H)-30-Homohopane				259		c, f
22R&S,17α(H),21β(H)-30-Bishomohopane				196		c, f
Steranes						
20R-5α(H),14β(H),17β(H)-Cholestane				109		c, f
20R-5α(H),14α(H),17α(H)-Cholestane				119		c, f
20R&S-5α(H),14β(H),17β(H)-Ergostane				139		c, f
20R&S-5α(H),14β(H),17β(H)-Sitostane				136		c, f
Ethers						
MTBE	5700		1620000		109000	a, e
ETBE	200		34600			a, e
TAME	*		*		550	a, e
Aliphatic aldehydes						
Formaldehyde	8690		884000		*	a, g
Acetaldehyde	3940		301000		*	a, g
Propanal	640		60000		*	a, g
Butanal & Isobutanal	310		31000		*	a, g
Pentanal	250		22000		*	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.

Sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details.

Additional Notes: † 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.

Table 5.3. (continued - page 6)

Compound	Catalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions (μg km^{-1})		Noncatalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions (μg km^{-1})		Gasoline Composition (μg gm^{-1})	Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase		
Aliphatic aldehydes						
Isopentanal			31000		*	a, g
Hexanal	490		27000		*	a, g
Heptanal	300		19000		*	a, g
Octanal	120		7300		*	a, g
Nonanal	190		2600		*	a, g
Decanal	30		2300		*	a, g
Undecanal	50		2200		*	a, g
Dodecanal	40		2500		*	a, g
Tridecanal			870		*	a, g
Tetradecanal			5800		*	a, g
Olefinic aldehydes						
Crotonaldehyde	1760		114000		*	a, g
Acrolein	60		3800		*	a, g
Methacrolein	300		23000		*	a, g
Aliphatic ketones						
Acetone	1190		42000		*	a, g
Butanone / Methylacrolein	470		32000		*	a, g
Aromatic aldehydes						
Benzaldehyde	1270		159000		*	a, g
o-Tolualdehyde	390		45000		*	a, g
m&p-Tolualdehyde	1340		145000		*	a, g
2,5-Dimethylbenzaldehyde	240		35000		*	a, g
Naphthalenecarboxaldehydes	5.3					b, f
Aromatic ketones						
Indanone[†]	30.6		908		*	a, f
Fluorenone	15.7				*	a, f
Xanthone	2.00		30.8		*	a, f
9,10-Anthracenedione	0.849		25.4		*	a, f
Dicarbonyls						
Glyoxal	170		28000		*	a, g
Methylglyoxal	50		10000		*	a, g
Biacetyl	40		1800		*	a, g
Other carbonyls						
2-Furaldehyde			1700		*	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.

Sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details.

Additional Notes: [†] 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.

Table 5.3. (continued - page 7)

Compound	Catalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions (μg km^{-1})		Noncatalyst-Equipped Gasoline-Powered Motor Vehicle Tailpipe Emissions (μg km^{-1})		Gasoline Composition (μg gm^{-1})	Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase		
n-Alkanoic acids						
Octanoic acid	12.2		86.0			a, f, d
Nonanoic acid	27.9		80.6			b, f, d
Decanoic acid	9.3		54.7			a, f, d
Undecanoic acid			75.6			b, f, d
Heptadecanoic acid		0.26		90.6		b, f, d
Octadecanoic acid		4.32		147		a, f, d
Nonadecanoic acid				9.3		b, f, d
Eicosanoic acid		0.16		14.0		a, f, d
Alkanedioic acids						
Octadecanedioic acid		4.1		42.4		a, f, d
Nonadecanedioic acid		21.5		177		a, f, d
Aromatic acids						
Benzoic acid	124					b, f, d
Methylbenzoic acids		0.74		55.4		a, f, d
Other compounds						
Benzofuran			200	29.2		a, f
Dibenzofuran	5.6	3.43	42.2	4.0		a, f
Dibenzothiophene	0.32		25.6			a, f
Dibenzothiazole	12.3	0.40				a, f

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.

Sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. (*) not measured. See text for details.

Additional Notes: † 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.

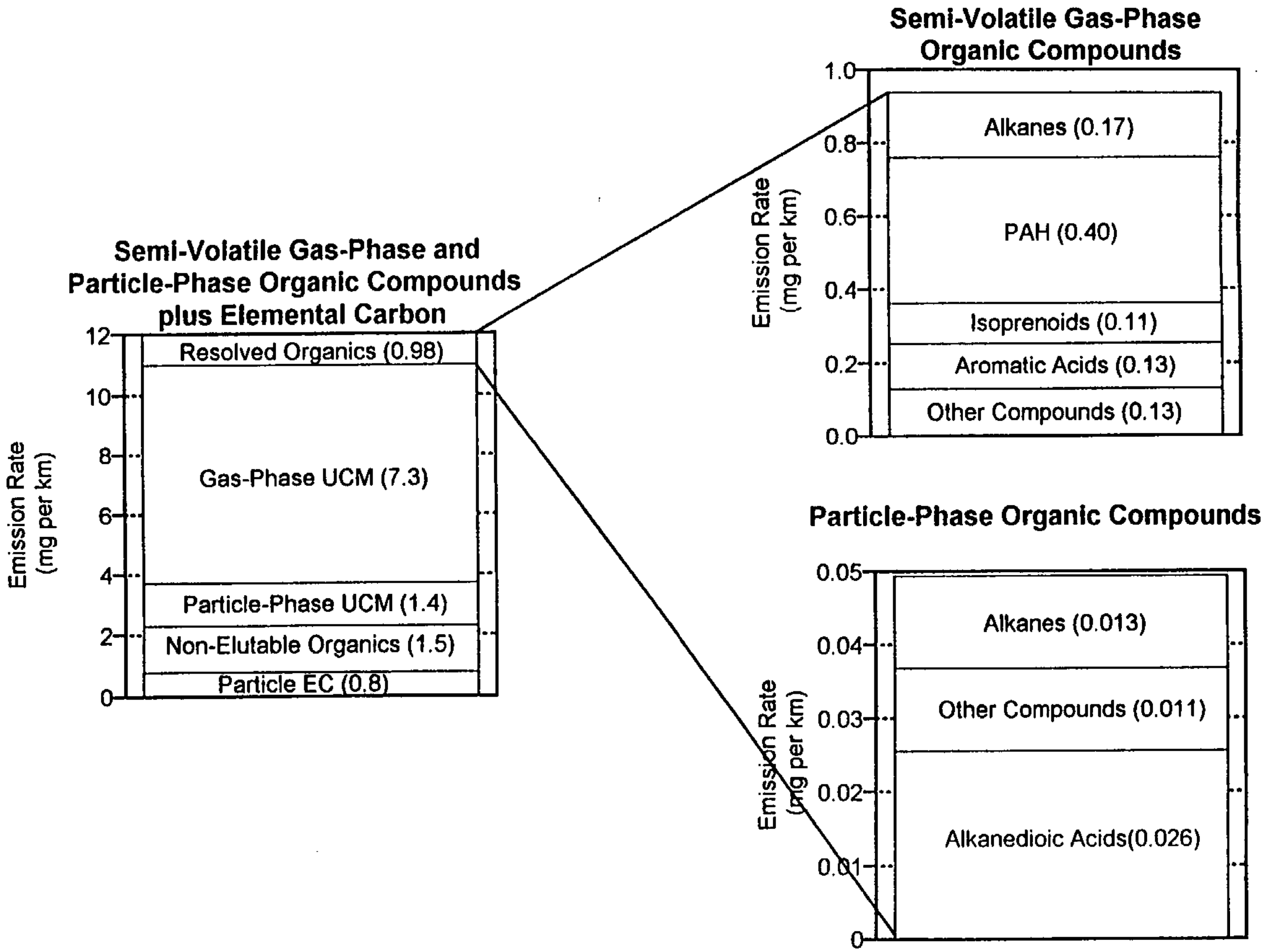


Figure 5.4. Mass balance on the semi-volatile and particle-phase organic compounds and elemental carbon emitted from catalyst-equipped gasoline-powered light-duty motor vehicles.

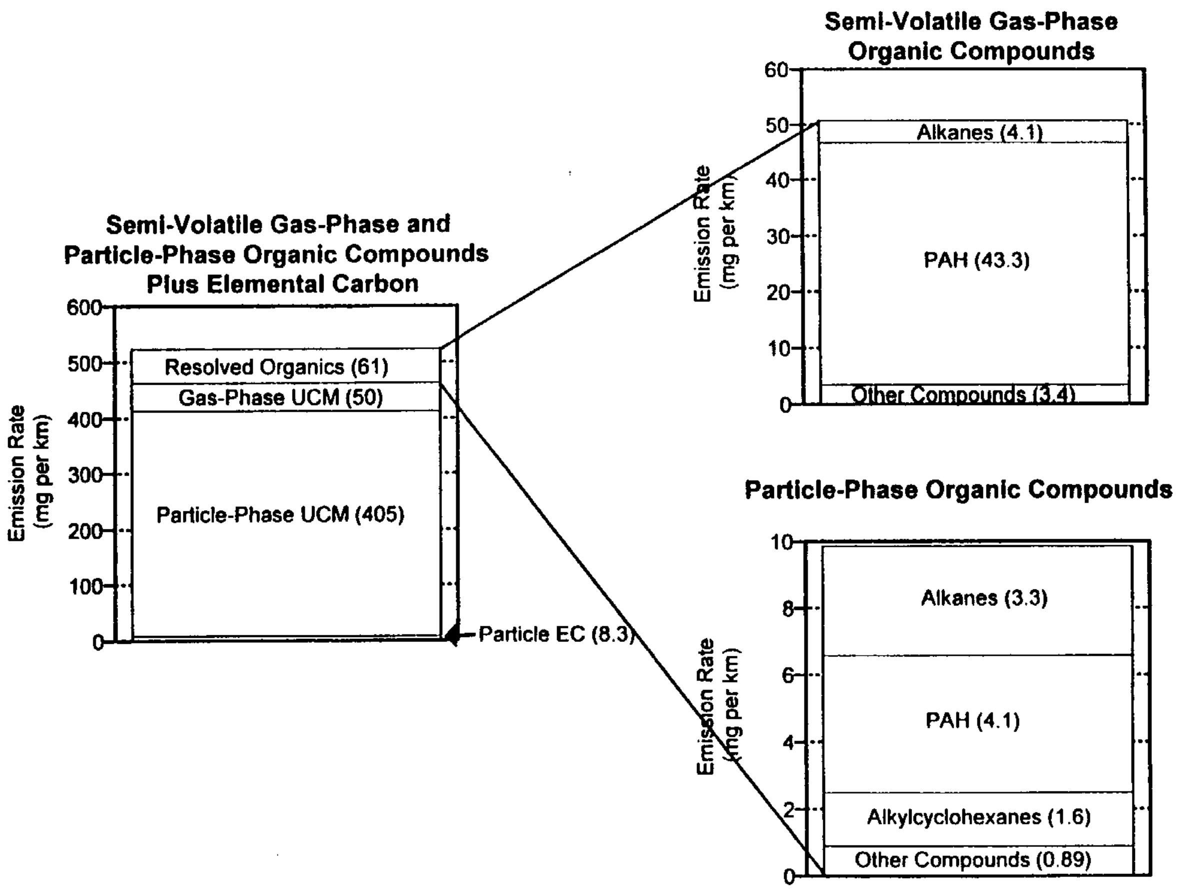


Figure 5.5. Mass balance on the semi-volatile and particle-phase organic compounds and elemental carbon emitted from noncatalyst-equipped gasoline-powered light-duty motor vehicles.

a GC trace makes up more than 7.3 mg per kilometer of the 12.0 mg of semi-volatile and particle-phase organic compounds plus elemental carbon emissions. The particle-phase UCM and particle-phase elemental carbon are emitted at 1.4 and 0.8 mg km^{-1}, respectively. Of the resolved organic compounds, alkanes and PAH make up most of the gas-phase semi-volatile species, and alkanes and alkanedioic acids make up most of the particle-phase species.

Figure 5.5 shows the emissions of the semi-volatile and particle-phase organic compounds plus elemental carbon emissions from the noncatalyst equipped cars tested as measured by the denuder/filter/PUF sampling train. For the noncatalyst equipped motor vehicle emissions, 77% of the semi-volatile and particle-phase emissions shown are present in the particle-phase UCM. For these noncatalyst gasoline-powered vehicles, essentially all of the particulate organic carbon mass is extractable from the filter sample and will elute from the GC column after derivatization. The organic carbon measured by thermal evolution and combustion balances with the mass of organic carbon quantified by GC/MS. Of the resolved organic compounds, PAH make up 85% of the gas-phase semi-volatile species, while alkanes and PAH make up most of the particle-phase organic compounds.

The n-alkanes and isoprenoids (see Chapter 4 for isoprenoid chemical structures) with more than 11 carbon atoms emitted from the catalyst-equipped gasoline-powered vehicles show a distribution according to carbon number and branching that is similar to that seen in the gasoline used to power the vehicles (Figure 5.6). The emissions from the noncatalyst equipped vehicles, however, show an increase in n-alkane emissions in the range of eicosane through heptacosane and significant flattening of the distribution of the isoprenoid emissions when compared to the composition of the gasoline burned. Since these heavier n-alkanes are not found in the engine motor oil in noticeable quantities (they are deliberately removed in the refining process) (18), it appears that these compounds are being formed in the engine during use by combustion or breakdown/recombination of the fuel components.

Figure 5.7 shows the distribution of PAH and alkyl-PAH ranging from fluorene through coronene in the gasoline fuel and in the vehicle emissions. Significant enrichment in the ratio of fluorene to methylfluorenes and dimethylfluorenes is observed in the catalyst-equipped vehicle exhaust when compared to the gasoline burned. The same trend is observed for the PAH with a molecular weight of 178 (phenanthrene plus anthracene). The increased dealkylation of the PAH in the catalyst equipped gasoline powered engine exhaust is likely due to increased thermal and catalytic processing in the engine and exhaust systems. It is also interesting to note that the distribution of the heavier PAH is significantly different in the fuel versus the tailpipe emissions. The parent fuel has increased relative concentrations of chrysene/triphenylene,

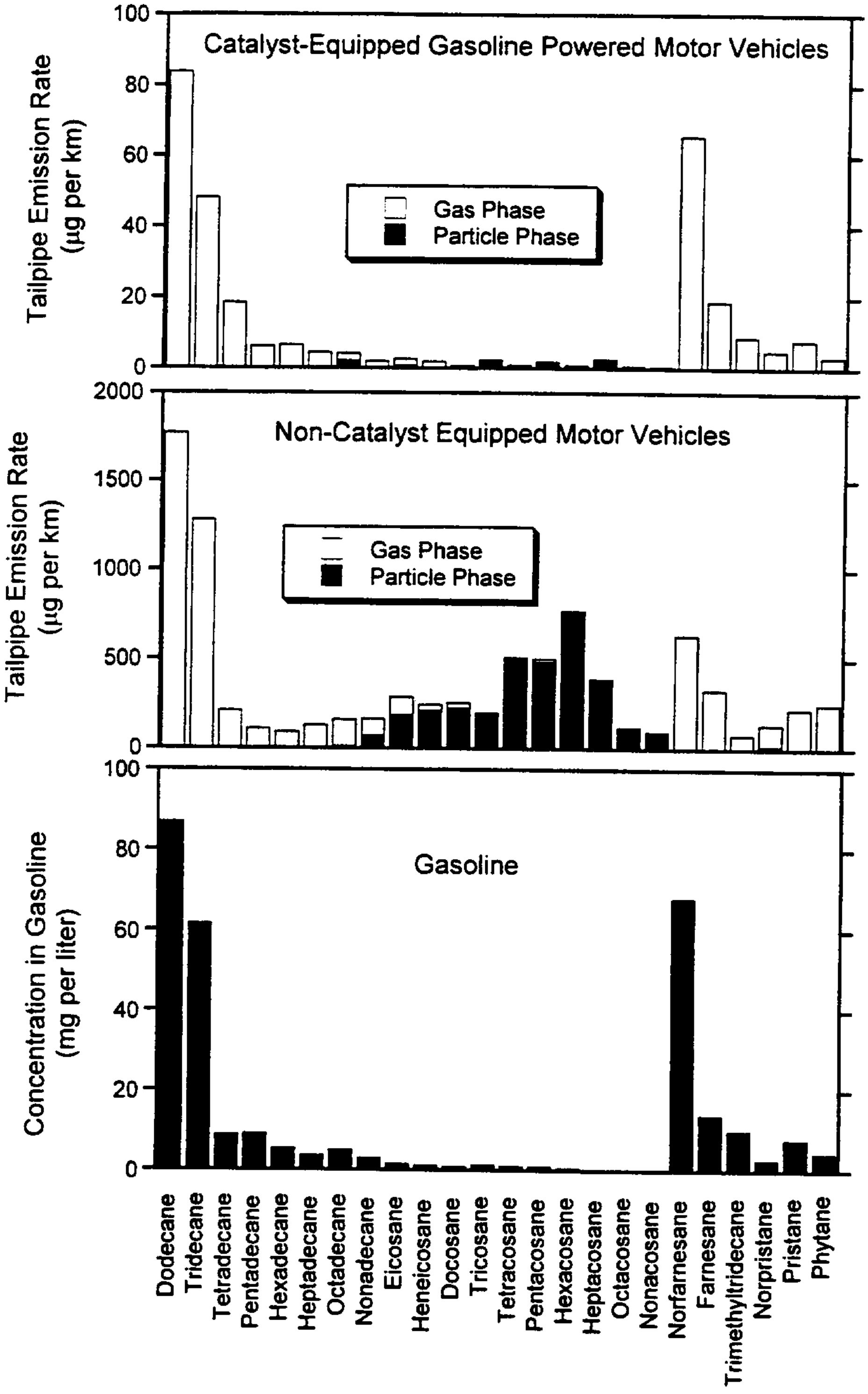


Figure 5.6. Emissions of n-alkanes and isoprenoids from gasoline-powered light-duty motor vehicles and the concentration of these compounds in gasoline.

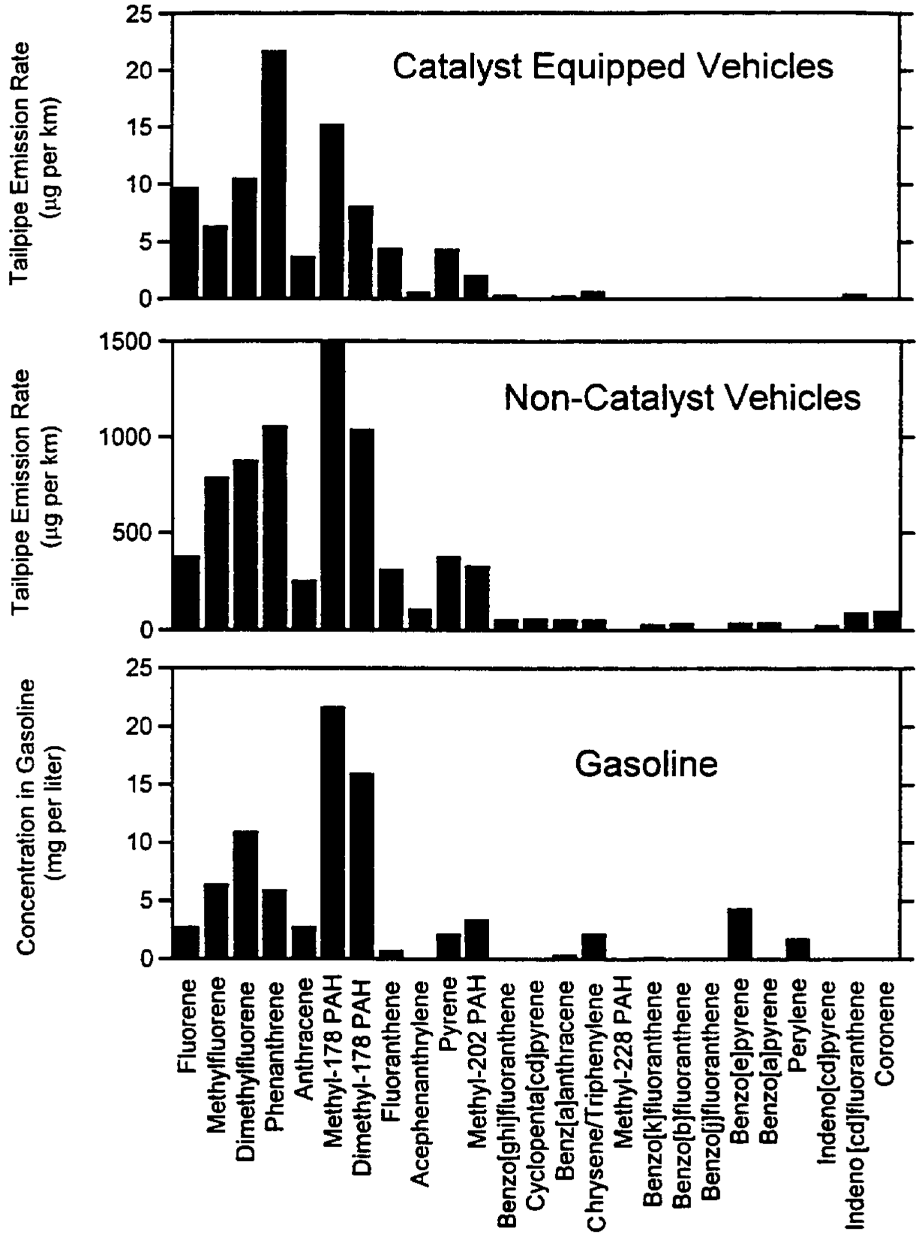


Figure 5.7. Emissions of PAH and alkyl-PAH from gasoline powered-motor light-duty vehicles and the concentration of these compounds in gasoline.

benzo[e]pyrene, and perylene while neither type of vehicle emissions shows this pattern.

As previously indicated the average fine particle emission rates from the catalyst-equipped gasoline-powered motor vehicles tested in the present study are about 58% lower than from a mid-1980's catalyst-equipped motor vehicle fleet made up of on-road vehicles in Southern California at that time. It is interesting to note that the emissions of fine particle organic carbon and elemental carbon are reduced even more than the reduction of fine particles between these tests. Fine particle organic carbon and elemental carbon average emission rate reductions are 73% and 81%, respectively. These reductions are likely due to improved combustion in the engines and improved organic compound destruction in the catalytic converters. The composition of the fine organic compound mass emitted from the catalyst-equipped cars has also changed. The ratio of hopanes plus steranes to organic carbon in the fine particle mass has dropped from 4.7 to 0.04 indicating either significant destruction of these compounds in either the engine or catalytic exhaust system. This reduction is not believed to be due to changes in the engine lubricant oil formulations as the same ratio in the noncatalyst equipped motor vehicles has increased over this time period from 2.4 to 5.3. The increase observed in the noncatalyst vehicles is likely due to the increased contribution of motor oil to the fine particle emissions resulting from engine wear. The relative destruction of the hopanes and steranes observed in the current catalyst-equipped motor vehicle emissions tests parallels the destruction of these compounds observed in the thermal and catalytic processing that occurs in the petroleum refinery (19). Likewise, the increased contribution of n-alkanoic acids and alkanedioic acids in the fine particle mass emitted from the current catalyst-equipped motor vehicle fleet suggests a more complete oxidation of the organic compounds in the vehicle exhaust.

5.3.4 Organic Compound Tracers for Gasoline-Powered Motor Vehicle Exhaust

Rogge et al. (12) and Schauer et al. (11) have shown that the hopanes and steranes emitted in vehicle exhaust can be used as molecular tracers for the fine particulate matter emitted from motor vehicles. Although acetylene and carbon monoxide have been proposed by others as tracers for the gas-phase emissions from vehicles, these compounds also are present in the emissions from other combustion sources such as wood burning (see Chapter 6). For this reason, there is a need to identify additional potential tracers for gas-phase and semi-volatile organic compounds present in motor vehicle exhaust that are not emitted when burning wood. The isoprenoids and tricyclic terpanes measured in the current study are distinctive compounds characteristic of petroleum that cannot be confused with wood combustion exhaust. Although these compounds have also been identified in the exhaust from diesel powered vehicles (see

Chapter 4), the ratio of the emissions of these compounds to other lighter gas-phase hydrocarbon emissions, such as n-hexane and iso-hexane, is very much lower for gasoline powered motor vehicles than for diesel powered motor vehicles. While the isoprenoids and tricyclic terpanes are present in gasoline as well as vehicle exhaust, again the entire compound assemblage found in vehicle exhaust differs from the gasoline alone as explained earlier. These differences are expected to be useful in receptor modeling applications (20, 21).

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Chapter 6

Organic Compounds from Fireplace Combustion of Wood

6.1 Introduction

Emissions from fireplace combustion of wood have been shown to be major contributors to air pollution during winter months in urban locations such as Portland, Oregon (1), Denver, Colorado (2), and Albuquerque, New Mexico (3). The relationships between direct primary emissions of wood smoke and ambient concentrations of particulate matter have been assessed in the past based on a variety of techniques. Non-mineral potassium is widely used as a tracer for wood smoke (3-5) but non-mineral potassium is contributed by several other major air pollution sources such as meat cooking exhaust (6, Chapter 2) and refuse incinerators (3). In addition, as is shown in the present study the emission rate of potassium from wood combustion varies widely among wood types. Khalil et al. (1) used the ratio of gas-phase methylchloride to particulate mass in the emissions from wood combustion to asses wood smoke concentrations in the Oregon atmosphere. Retene is the fully aromatized PAH resulting from thermal alteration of resin acids in conifer wood smoke. Ramdahl (7) proposed the use of retene as an organic tracer for wood smoke particles in the atmosphere. Others have used the ratios of polycyclic aromatic hydrocarbons (PAH) and substituted PAH in wood smoke and in other source emissions to determine the contribution of wood smoke to atmospheric particle concentrations (8, 9). These methods have limited application since methylchloride is a widely used industrial chemical and many of the PAH used as tracers react fairly rapidly in the atmosphere.

Locker (10) used levoglucosan (1,6-anhydro-β-D-glucose) to determine the contribution of wood burning to ambient total suspended particulate mass (TSP) concentrations. Hawthorne et al. (11) measured the relative concentrations of guaiacol (2-methoxyphenol), syringol (2,6-dimethoxyphenol), and derivatives of these compounds in the plumes downwind of residential wood stoves and fireplaces. Hawthorne et al. (12) showed that guaiacol and its derivatives (but not the syringol family) could be used to estimate the contribution of wood smoke to PM-10 concentrations in the wintertime urban atmosphere at several locations. The studies by Locker (11) and Hawthorne et al. (12) have helped to elucidate the effect of wood combustion on atmospheric particulate mass concentrations. Standley and Simoneit (13) and Simoneit et al. (14) have shown that the distribution of resin acids, resin acid thermal alteration products, phytosterols, lignans, and phenolic compounds from lignins can be used to separately identify the smoke from the combustion of coniferous trees, deciduous trees, and grasses. Rogge et al. (15) quantified the distribution of organic compounds in the fine particles emitted from fireplace combustion of pine, oak, and synthetic logs. The data of Rogge et al. (15) were used by Schauer et al. (16) to show how to separately quantify the amount of wood smoke particles in the Southern California atmosphere in the presence of the effluent from eight other major source types.

The organic chemical tracer model of Schauer et al. (16) that originally addressed only particle-phase air pollutants currently is being extended to track volatile organic gases, gas-phase semi-volatile organic compounds as well as particle-phase organic compounds. In addition, advanced photochemical airshed models are being developed that can for the first time track gas-phase, semi-volatile and particle-phase organic compounds simultaneously, and compute their effect on photochemical smog formation and secondary aerosol formation. Air quality models of both of these types require emissions data for individual organic compounds that span the range from methane to heavy particle-phase organic compounds. The current research reports the C_1 through C_{29} gas- and particle-phase organic compound emissions from wood combustion.

6.2 Experimental Methods

6.2.1 Comprehensive Source Sampling

The source sampler used for the wood combustion source tests is configured in the same manner as was used in the meat charbroiling source tests discussed in Chapter 2. Details of the sampler are presented in Chapter 2. Briefly, hot exhaust from the fireplace chimney was drawn isokinetically through a cyclone separator to remove particles with aerodynamic diameters greater than 10 μm. The particles with aerodynamic diameters less than 10 μm along with the gaseous pollutants passed through a heated stainless steel tube and through a venturi meter after which they were turbulently mixed with HEPA-filtered and activated carbon-filtered dilution air within a portable dilution tunnel to bring the mixture to ambient temperature and pressure. Most of the diluted and cooled exhaust was passed through a pre-baked quartz fiber filter (10 inch X 12 inch, Pallflex Tissuequartz 2500 QAO) located at the downstream end of the dilution tunnel. The remaining portion of the diluted exhaust was sent to a residence time chamber where the semi-volatile compounds were allowed time to partition between the gas and particle phases. From the residence time chamber, diluted exhaust was drawn through four AIHL cyclone separators (17) operated in parallel at a flow rate of 30 lpm each to remove particles with aerodynamic diameters greater than 1.8 μm. Gases and fine particles with diameters less than 1.8 μm passed through the cyclones and were then directed to a series of sampling trains operated in parallel.

Semi-volatile and fine particle-phase organic compounds were collected continuously throughout the burn cycle by filter/PUF sampling trains operated downstream of the AIHL cyclone separators. A single filter/PUF unit consisted of a quartz fiber filter (47 mm diameter, Pallflex Tissuequartz 2500 QAO) 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. Particle-phase organic compounds were collected on the quartz fiber filter and gas-phase organic compounds were collected on the PUF cartridges located downstream of the quartz fiber filter. Compounds too volatile to be collected completely by the first PUF cartridge were then collected by the back-up PUF cartridge. If the mass of an individual organic compound on the second PUF cartridge was found to be more than 25% of the mass collected on the front PUF cartridge, then this compound was deemed to be too volatile to be measured by the filter/PUF sampling train under the given sampling conditions. Three filter/PUF units, each operating at a flowrate of 10 lpm, were connected to the outlet of each of two AIHL cyclone separator. These two complete AIHL cyclone filter/PUF assemblies were operated in parallel during each test.

In addition to the filter/PUF sampling trains, an organic compound denuder-based sampling train was employed to measure gas-phase, semi-volatile, and particle-phase organic compound emission rates during segments of the burn cycle. The capacity of the organic vapor denuders under the conditions of the present study limited denuder sampling times to a maximum of approximately 25 minutes, such that continuous sampling using the XAD-coated annular denuder was not practical. The organic vapor denuder-based sampling train operated at a flow rate of 30 lpm downstream of one AIHL fine particle cyclone separator and consisted of an XAD-coated annular denuder (URG, 400 mm, 4 channel) followed by three quartz fiber filters (47 mm diameter, Pallflex Tissuequartz 2500 QAO) operated in parallel which were in turn 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 semi-volatile organic compounds were collected by the annular denuder while particles and particle phase-associated organic compounds passed through the denuder and were collected on the filters downstream of the denuder. The PUF cartridge downstream of the filters collected any particle-phase semi-volatile compounds that blew off of the filters. The preparation of the XAD-coated denuders and additional details concerning denuder/filter/PUF sampling train operations and collection efficiency are discussed in Chapter 2. Denuder/filter/PUF sampling trains were operated for each of the wood combustion source tests but were only analyzed for the pine wood combustion source test.

A third type of cyclone-based sampling unit also was used during the wood combustion source tests. An AIHL cyclone separator was followed by sampling substrates configured to measure the emissions of fine particulate matter, carbonyls, vapor-phase organic acids, and gas-phase hydrocarbons. Three stacked filter units each operating at 10 lpm and one carbonyl sampling line operated at a flow rate of 0.3 lpm were connected in parallel at the outlet of this AIHL cyclone separator. The first stacked filter unit consisted of two quartz fiber filters (47 mm diameter, Pallflex Tissuequartz 2500 QAO) in series which were used for elemental carbon and organic carbon (EC/OC) determination by thermal evolution and combustion analysis as described by Birch and Cary (18). The second filter stack contained 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 was used for gravimetric determination of the fine particle mass emissions rate and was analyzed by X-ray fluorescence for 35 trace elements (19). The tandem KOH-impregnated quartz fiber filters were 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 contained one Teflon membrane filter which was used for a duplicate fine particle mass emissions measurement and for inorganic ion measurements by ion chromatography (20), atomic absorption spectroscopy and colorimetry (21). Downstream of that single Teflon filter the sample flow was divided, and a small portion of the flow was used to fill a 6 liter polished stainless steel SUMA canister for the collection of non-methane volatile hydrocarbons ranging from C_1 to C_{10}. The 6 liter SUMA canister was filled continuously at a constant flowrate set to fill the canister over the entire wood burning cycle. Carbonyls were collected at the outlet of the AIHL cyclone separator by two C_{18} cartridges impregnated with dinitrophenylhydrazine (DNPH) that were operated in series (22). Non-methane volatile hydrocarbon samples were collected only during the pine wood combustion test. All other samples were collected and analyzed for all three wood burning tests.

Electronic particle sizing instruments and a pair of MOUDI impactors also were connected to the residence time chamber during the wood combustion source tests to obtain particle size distributions and particle chemical composition as a function of size. The size distributions and the results obtained from the MOUDI impactors will be reported elsewhere.

6.2.2 Source Testing Procedure

The firewood burned in the wood combustion source tests was obtained from a large firewood distributor in the residential suburbs of Los Angeles in

Southern California. The three woods tested (pine, oak, and eucalyptus) represented the largest volumes of wood sold by this distributor. Kindling to start each fire was obtained by chopping up a log of the particular wood being tested and only a small number of sheets of newspaper (approximately five sheets per test) were burned to ignite the kindling. No other materials were used to start the fires or were burned with the wood. The mass of wood burned (logs plus kindling) was measured prior to each test, and the remaining mass of ashes was collected and weighed after each test. The difference between the mass of wood ignited and the mass of ashes remaining was defined as the mass of wood burned. In all tests, the mass of ash amounted to only a few percent of the original wood mass.

The firewood combustion source tests were conducted in a residential fireplace located in a two-story house. Emissions were withdrawn from a port installed in the chimney on the second floor level of the house approximately five meters above the fireplace grate. The total exhaust gas flow from the fireplace was measured at the chimney outlet and was monitored periodically throughout the wood burning cycle. In the pine wood test, 17.2 kilograms of wood were burned over a period of 189 minutes. In the oak wood combustion test, 15.4 kilograms of wood were burned over a period of 165 minutes, and in the eucalyptus wood combustion source test, 18.9 kilograms of wood were burned over a period of 218 minutes.

Denuder/filter/PUF samples were drawn for approximately 15 minutes directly after the fire was lit, and a second denuder-based sample was taken using a new set of substrates for another 15 minutes approximately midway through the burn cycle. All other sampling systems operated continuously through the entire length of each test.

6.2.3 Organic Chemical Analysis

The analytical procedures used in the present study for the identification and quantification of semi-volatile and particle-phase organic compounds in air pollution source emissions are presented in Chapter 2. Briefly, all of the quartz fiber filters, PUF cartridges, and XAD-coated denuders were spiked with a mixture of eight 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 benzaldehyde-d_6 prior to extraction. The quartz fiber filters were extracted under mild sonication twice with hexane (Fisher Optima Grade), followed by three successive benzene/isopropanol (2:1 mixture) extractions (benzene: E & M Scientific; isopropanol: Burdick & Jackson). The extracts were filtered, combined, reduced in volume to approximately 250 ml, and then split into two separate fractions. One fraction was then derivatized with diazomethane to convert organic acids to their methyl ester analogs which are amenable to GC/MS identification and quantification. Although substituted phenols, guaiacols, and syringols will convert to their methoxy analogs when reacted with diazomethane, these compounds were identified and quantified in the underivatized fraction to assure correct identification of the hydroxy and methoxy substitution patterns.

The denuders were extracted four times successively using at each step 40 ml 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 lightly for approximately 30 seconds per aliquot. The four aliquots from each of the two denuder samples were composited, reduced to a volume of approximately 250 μl and then split into two separate fractions. One fraction was derivatized with diazomethane as above.

The PUF cartridges were extracted by four successive aliquots of the dichloromethane/acetone/hexane (2:3:5) (Fisher Optima Grade) solvent mixture. The foam plugs were repetitively compressed during the extraction. 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.

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 system (GC Model 5890, MSD Model 5972) using a 30 meter long X 0.25 mm diameter HP-1701 capillary column (Hewlett-Packard). 1-Phenyl dodecane 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 wood combustion emissions. For a group of compounds with similar structure, such as the n-alkanes, standards were only prepared for some of the compounds within the series. Compounds within a homologous series for which standards were not available were identified by comparing their spectra to the standards for similar compounds within the series and by comparison to the NIST and Wiley mass spectral libraries. For these compounds, quantification was based on the response factors for the authentic standards of closely related compounds within the series. Compounds for which standards of similar compounds were not available were tentatively identified by comparison of their spectra to the mass spectral libraries and by fundamental interpretation of the mass spectra. The emission rates of such compounds were not 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. (23). Carbonyls collected by the C_{18} impregnated cartridges were analyzed by liquid chromatography/UV detection as described by Grosjean et al. (24).

6.3 Results

6.3.1 Fine Particle Emission Rates and Elemental Compositions

Table 6.1 shows the elemental composition of the fine particle mass emitted from the fireplace combustion of the three wood types. Those species with emission rates greater than twice the standard error of each determination are shown in boldface type. Fine particle mass emissions from the fireplace combustion of pine wood were measured to be 9.5 ± 1.0 grams per kilogram of wood burned. The fine particle mass emitted was found to be 56.0 ± 2.8 percent organic carbon and 1.4 ± 0.1 percent elemental carbon. Potassium and chloride were the next largest components comprising 0.28% and 0.18% of the

Table 6.1. Average Fine Particle Emission Rate and Fine Particle Chemical Composition of Emissions from Fireplace Combustion of Wood (Values shown in boldface are greater than zero by at least two standard errors).

	Fireplace Combustion of Pine Wood	Fireplace Combustion of Oak Wood	Fireplace Combustion of Eucalyptus Wood
Fine Particle Emissions Rate (AVG ± STD)	**9.5 ± 1.0 grams kg^{-1} of wood burned**	**5.1 ± 0.5 grams kg^{-1} of wood burned**	**8.5 ± 0.8 grams kg^{-1} of wood burned**
Elemental and Organic Carbon (Wt % of Fine Particle Mass)			
Organic Carbon	**56.0 ± 2.8**[a]	**59.1 ± 3.0**[a]	**43.7 ± 2.2**[a]
Elemental Carbon	**1.4 ± 0.1**	**3.2 ± 0.2**	**2.6 ± 0.2**
Ionic Species (Wt % of Fine Particle Mass)			
Chloride	**0.29 ± 0.04**	**0.20 ± 0.01**	**1.70 ± 0.05**
Nitrate	**0.19 ± 0.01**	**0.44 ± 0.01**	**0.45 ± 0.01**
Sulfate	**0.12 ± 0.01**	**0.41 ± 0.01**	**0.24 ± 0.01**
Ammonium	**0.09 ± 0.01**	**0.10 ± 0.01**	**0.45 ± 0.01**
Sodium	**0.09 ± 0.01**	**0.10 ± 0.01**	**0.18 ± 0.01**
X-ray Fluorescence (Wt % of Fine Particle Mass)			
Aluminum	0.004 ± 0.003	0.000 ± 0.010	0.006 ± 0.003
Silicon	**0.008 ± 0.001**	**0.016 ± 0.005**	**0.011 ± 0.002**
Phosphorus	**0.004 ± 0.001**	**0.007 ± 0.002**	**0.012 ± 0.002**
Sulfur	**0.059 ± 0.002**	**0.148 ± 0.004**	**0.056 ± 0.003**
Chlorine	**0.181 ± 0.003**	**0.127 ± 0.006**	**1.290 ± 0.008**
Potassium	**0.277 ± 0.003**	**0.647 ± 0.007**	**0.809 ± 0.005**
Calcium	0.004 ± 0.005	0.008 ± 0.011	0.007 ± 0.013
Titanium	0.000 ± 0.010	0.000 ± 0.017	0.000 ± 0.009
Vanadium	0.000 ± 0.006	0.000 ± 0.007	0.000 ± 0.003
Chromium	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.001
Manganese	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001
Iron	0.001 ± 0.001	0.000 ± 0.001	0.000 ± 0.001
Cobalt	0.000 ± 0.000	0.000 ± 0.001	0.000 ± 0.001
Nickel	0.000 ± 0.000	0.000 ± 0.001	0.000 ± 0.001
Copper	0.000 ± 0.001	0.000 ± 0.001	0.001 ± 0.001
Zinc	**0.006 ± 0.001**	**0.005 ± 0.001**	**0.005 ± 0.001**
Gallium	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
Arsenic	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
Selenium	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001
Bromine	0.000 ± 0.000	0.000 ± 0.001	**0.013 ± 0.001**
Rubidium	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001
Strontium	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.000
Yttrium	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001
Zirconium	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001
Molybdenum	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
Palladium	0.000 ± 0.003	0.000 ± 0.006	0.000 ± 0.003
Silver	0.000 ± 0.003	0.000 ± 0.007	0.001 ± 0.003
Cadmium	0.000 ± 0.004	0.000 ± 0.007	0.002 ± 0.004
Indium	0.000 ± 0.004	0.000 ± 0.008	0.000 ± 0.004
Tin	0.001 ± 0.006	0.001 ± 0.011	0.000 ± 0.005
Antimony	0.004 ± 0.007	0.000 ± 0.013	0.000 ± 0.006
Barium	0.000 ± 0.025	0.000 ± 0.048	0.002 ± 0.024
Lanthanum	0.001 ± 0.033	0.000 ± 0.065	0.000 ± 0.031
Mercury	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
Lead	0.000 ± 0.002	0.000 ± 0.003	0.000 ± 0.002

Notes: (a) measured on a undenuded filter.

fine particle emissions, respectively.

The fine particle emissions from the combustion oak firewood and eucalyptus firewood were 5.1 ± 0.5 and 8.5 ± 0.8 grams per kilogram of wood burned, respectively. The fine particles emitted from oak wood combustion were found to be comprised of 59.1 ± 3.0 percent organic carbon and 3.2 ± 0.2 percent elemental carbon, while the fine particle mass emitted from eucalyptus wood combustion was found to be 43.7 ± 2.2 percent organic carbon and 2.6 ± 0.2 percent elemental carbon. The potassium content of the fine particle mass emitted from burning eucalyptus and oak was much greater than the content of this element in the pine smoke. The potassium content of the eucalyptus smoke and oak smoke were determined to be 0.809 ± 0.005 percent and 0.647 ± 0.007 percent, respectively, while the concentration of potassium in pine smoke was 0.277 ± 0.003 percent. In addition, the chloride content of the fine particle mass emitted from eucalyptus was much higher than that found in the pine smoke or the oak smoke. Chloride comprised 1.29 ± 0.008 to 1.7 ± 0.05 percent of the fine particle mass emitted from eucalyptus combustion, while chloride only made up 0.127 ± 0.006 to 0.20 ± 0.01 percent of the fine particle mass emitted from oak wood combustion (comparison of two independent measurement methods). It is interesting to note that the sodium content of the fine particle emissions from eucalyptus wood combustion is 0.18 ± 0.01 percent which is only 80% higher than the sodium content in oak smoke, while the chloride content of the eucalyptus smoke is about ten times greater than that of oak smoke. These differences may be important if potassium and other inorganic elements are used as combined tracers for conifer and hardwood smoke particles.

6.3.2 Mass Balance on Organic Compound Emissions

Figure 6.1 shows a mass balance on the non-methane organic compound emissions from pine wood combustion. Gas-phase emissions make up most of the 23.8 grams of total non-methane organic compounds emitted from each kilogram of pine wood burned. The largest contributors to gas-phase organic compound emissions are aliphatic aldehydes which make up 4.1 grams kg^{-1} of the 14.9 grams kg^{-1} of identified organic compounds emitted. Gas-phase alkenes and alkynes, principally ethene and acetylene, also make up a significant fraction of the gas-phase emissions. Phenols and substituted phenols, as well as guaiacol (2-methoxyphenol) and substituted guaiacols with substituents at position 4, make up 1.46 and 1.33 grams per kilogram of the gas-phase emissions, respectively. Alkanes, aliphatic ketones, and dicarbonyls also make up noticeable portions of the gas-phase emissions.

Approximately half of the fine particulate organic compound mass emitted from the fireplace combustion of pine wood can be extracted and characterized by GC/MS. The largest single component of the extractable particle-phase

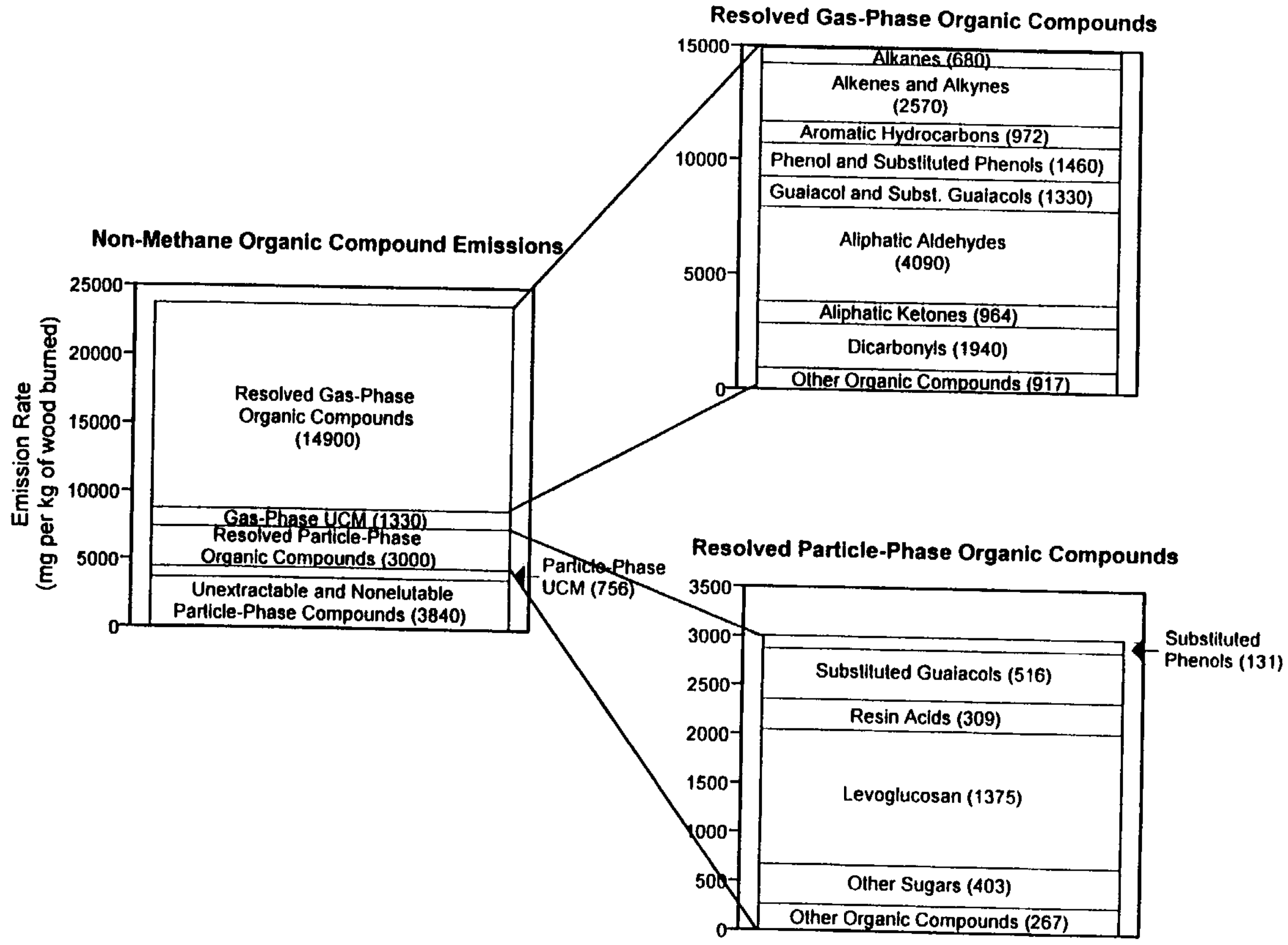

Figure 6.1. Mass balance on the non-methane organic compounds emitted from the fireplace combustion of pine wood.

organics mixture is levoglucosan (1,6-anhydro-β-D-glucose), which comprises 18% of the total fine particle organic compound mass emitted. The next largest component of the fine particle organics mass is contributed by the unresolved complex mixture (UCM) which consists of highly branched and cyclic organic compounds that appear as a wide hump on a GC/MS trace and that is not resolved by gas chromatographic techniques. Although the UCM cannot be characterized on a single compound level, the fine particle UCM is a well defined portion of the pine combustion emissions. Substituted phenols, substituted guaiacols, and resin acids also make up significant fractions of the fine particle mass emitted from fireplace combustion of pine wood. In addition to levoglucosan, other sugar derivatives were found in the pine wood smoke and are quantified as a group in Figure 6.1. Although the sugar derivatives have not yet been identified, they have mass spectra and GC retention times very similar to levoglucosan and have been quantified assuming the same response factor as for levoglucosan. These additional sugar-like compounds also make up a noticeable fraction of the fine particle mass emitted.

Since the C_2 through C_{10} gas-phase hydrocarbon emissions from the combustion of pine wood are dominated by the C_2 hydrocarbons, ethene, ethylene and acetylene which are not very source specific, gas canister samples were not taken for the oak and eucalyptus wood combustion source tests. Mass balances on the carbonyls, semi-volatile gas-phase and particle-phase organic compound emissions are shown in Figures 6.2 and 6.3 for the oak and eucalyptus wood combustion source tests, respectively. Gas-phase syringol (2,6-dimethoxyphenol) and the substituted syringols are emitted from the combustion of both oak and eucalyptus in significant quantifies, 0.84 grams and 0.56 grams per kilogram of wood combusted, respectively. Syringol and substituted syringols differentiate the gas phase emissions from hardwood combustion in which they are present, from the gas-phase emissions from conifer (pine) wood combustion in which these compounds are virtually absent. Gas-phase guaiacol and substituted guaiacols are emitted from the combustion of these hardwoods at approximately half of the rate that is seen in the emissions from pine wood combustion. Phenol and substituted phenols also are emitted from the combustion of hardwoods at approximately 50% of the rate measured during the softwood combustion experiment.

Turning to the fine particle-phase emissions from hardwood combustion in Figures 6.2 and 6.3, we see that the extractable portion of the fine particles which elutes from the GC column under the present analytical conditions accounts for approximately half of the fine particle organic mass emitted, as was the case for pine wood smoke. Levoglucosan, however, makes up a much larger fraction of the fine particle mass emitted from eucalyptus wood combustion (72% of the resolved fine particle organic compound mass and 31% of the total fine particle organics mass) than is the case for pine and oak

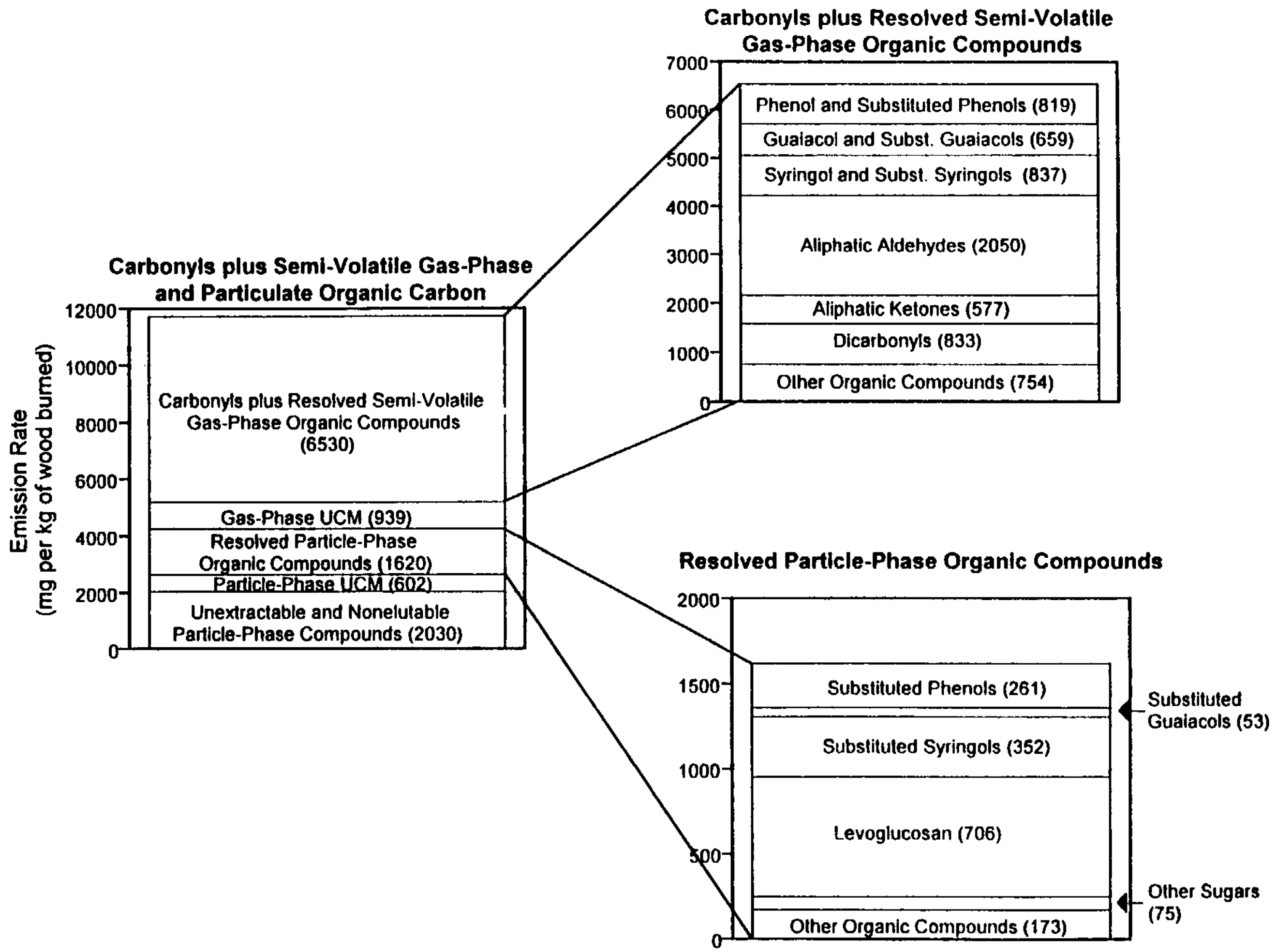

Figure 6.2. Mass balance on the carbonyl, semi-volatile, and particulate organic compounds emitted from the fireplace combustion of oak wood.

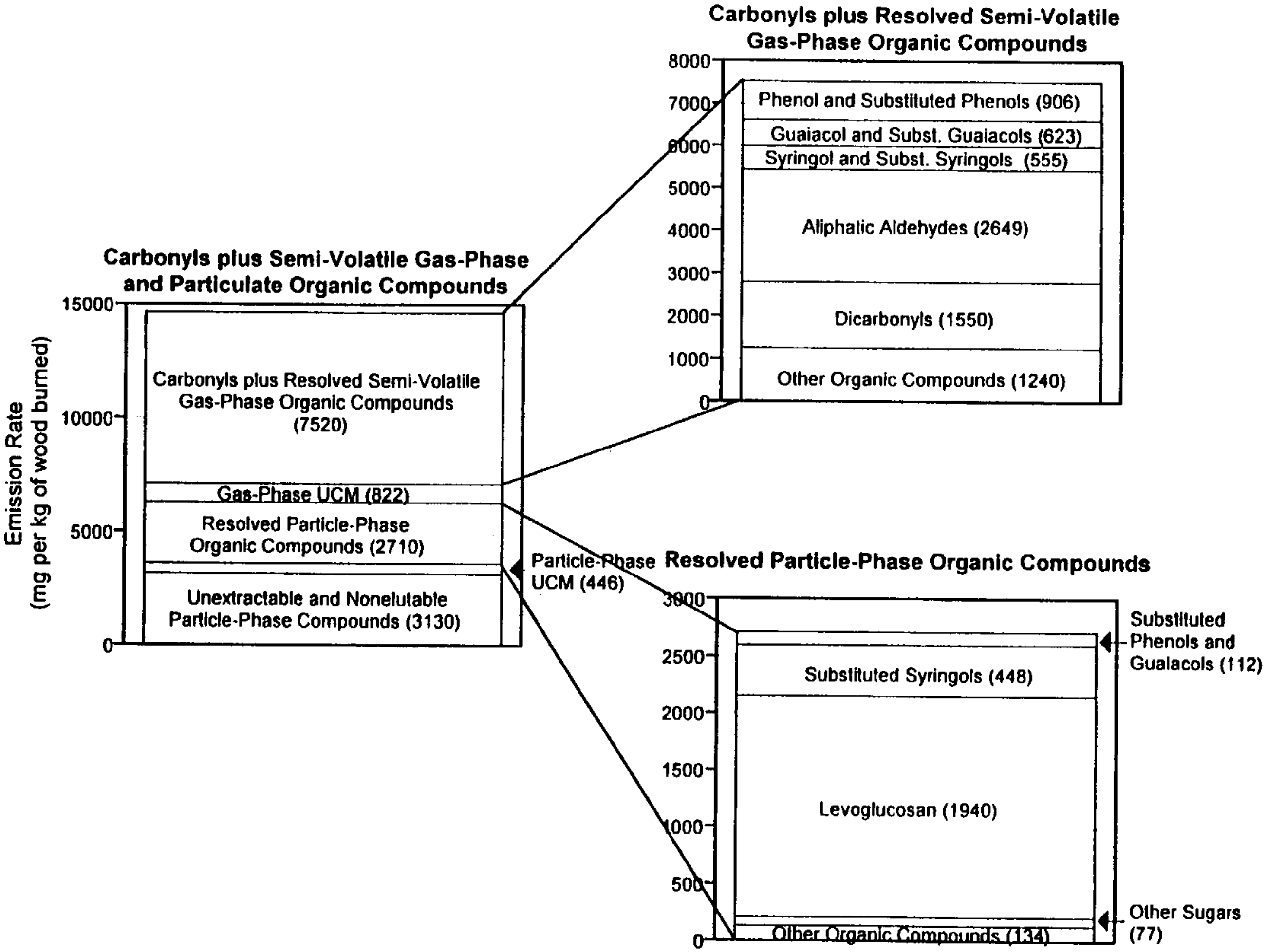

Figure 6.3. Mass balance on the carbonyl, semi-volatile, and particulate organic compounds emitted from the fireplace combustion of eucalyptus wood.

combustion. It is important to note that while the combined fine particle-phase emissions of substituted guaiacols and substituted syringols are very similar for all three woods burned in the present study at circa 400-560 mg kg^{-1} of wood burned, the pine wood smoke emissions are clearly distinguishable by their high resin acids and substituted guaiacol emission rates when compared to the hardwood smokes which contain substantial quantities of substituted syringol compounds. These differences in resin acids and guaiacols versus substituted syringol emission rates are due to fundamental differences in the chemical composition of conifers and deciduous trees as explained by Simoneit et al. (14), and can be used to distinguish hardwood smoke from softwood smoke in the atmosphere.

6.3.3 Emission Rates of Individual Organic Compounds

The emission rates of individual organic compounds are listed in Table 6.2 from the combustion of all three types of wood tested in the present study. Gas-phase alkanes are dominated by the emissions of methane, ethane, and propane with emission rates of 4120, 428, and 169 mg per kilogram of pine wood burned. n-Butane and n-heptane emissions are smaller but still significantly larger than the emissions of any of the remaining alkanes. Alkene emissions are dominated by ethene and propene, which are emitted at rates approximately 3 times greater than their alkane analogs, at 1120 and 429 mg kg^{-1} of wood burned. Acetylene and 1,3-butadiene also are emitted at 702

Table 6.2. Organic Compound Emission Rates from Fireplace Combustion of Wood

Compound	Pine Wood (mg kg^{-1} of Wood Burned)		Oak Wood (mg kg^{-1} of Wood Burned)		Eucalyptus Wood (mg kg^{-1} of Wood Burned)		Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase	Gas Phase	Particle Phase	
n-Alkanes							
Methane	4120		*		*		a, e
Ethane	428		*		*		a, e
Propane	169		*		*		a, e
n-Butane	25.9		*		*		a, e
n-Pentane	4.7		*		*		a, e
n-Heptane	28.9		*		*		a, e
n-Octane	1.7		*		*		a, e
n-Nonane	3.9		*		*		a, e
n-Octadecane	0.356						a, f
n-Nonadecane	0.347		0.513		0.195		b, f
n-Eicosane	0.175	0.272	0.574		0.258		a, f
n-Heneicosane	0.111	0.473	0.264		0.179		b, f
n-Docosane	0.085	0.762	0.191		0.136		b, f
n-Tricosane	0.096	0.847			0.154		b, f
n-Tetracosane	0.086	0.727			0.088		a, f
n-Pentacosane		0.382					b, f
n-Hexacosane		0.423		0.330		0.259	b, f
n-Heptacosane		0.276		0.203		0.209	b, f
n-Octacosane				0.068			a, f
n-Nonacosane				0.231			b, f
Branched alkanes							
i-Pentane	5.6		*		*		a, e
2-Methylpentane	8.6		*		*		a, e
2-Methylhexane	2.6		*		*		a, e
n-Alkenes							
Ethene	1120		*		*		a, e
Propene	429		*		*		a, e
1-Butene	90.7		*		*		a, e
trans-2-Butene	66.5		*		*		a, e
cis-2-Butene	35.4		*		*		a, e
1-Pentene	8.6		*		*		a, e
trans-2-Pentene	16.0		*		*		a, e
cis-2-Pentene	10.4		*		*		a, e
trans-2-Hexene	8.6		*		*		a, e
Branched alkenes							
i-Butene	40.1		*		*		a, e
3-Methyl-1-butene	6.9		*		*		a, e
2-Methyl-1-butene	13.8		*		*		a, e
2-Methyl-2-butene	13.4		*		*		a, e
2-Methyl-2-Pentene	6.9		*		*		a, e

Identification notes: a) authentic quantitative standard. b) authentic quantitative standard for similar compound in series. c) identified by mass spectra. d) detected as a methyl ester.

Sample collection notes: e) collected in SUMA canister. f) collected on filter/PUF sampling train. g) collected on DNPH impregnated C_{18} cartridges. *) not measured. +) detected but not quantified. See text for details.

Table 6.2. (continued - page 2)

Compound	Pine Wood (mg kg^{-1} of Wood Burned)		Oak Wood (mg kg^{-1} of Wood Burned)		Eucalyptus Wood (mg kg^{-1} of Wood Burned)		Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase	Gas Phase	Particle Phase	
Alkynes							
Ethyne (Acetylene)	702		*		*		a, e
Diolefins							
1,3-Butadiene	117		*		*		a, e
Isoprene	41.0		*		*		a, e
Cycloalkanes							
Methylcyclohexane	8.6		*		*		a, e
Cycloalkenes							
Cyclopentene	7.8		*		*		a, e
Aromatic hydrocarbons							
Benzene	383		*		*		a, e
Toluene	158		*		*		a, e
Ethylbenzene	22.9		*		*		a, e
m-Xylene + p-Xylene	60.0		*		*		a, e
o-Xylene	18.1		*		*		a, e
Naphthalene	227		*		*		a, f
2-Methylnaphthalene	15.0		9.61		5.69		a, f
1-Methylnaphthalene	10.6		6.39		4.31		a, f
Dimethylnaphthalene	13.8		11.5		7.24		a, f
Acenaphthylene	18.6		10.8		9.99		a, f
Acenaphthene	2.02		1.15		0.893		a, f
Fluorene	4.44		3.83		2.61		a, f
Phenanthrene	15.7	0.673	9.19	0.0695	8.14	0.0683	a, f
Anthracene	3.44	0.228	2.13	0.0230	1.76	0.0061	a, f
3-Methylphenanthrene	1.21	0.289	0.983	0.054	0.802		b, f
2-Methylphenanthrene	1.86	0.412	1.31	0.088	1.00		b, f
2-Methylanthracene	1.06	0.298	0.680	0.035	0.517		b, f
9-Methylphenanthrene	1.50	0.466	1.22	0.065	0.881		b, f
1-Methylphenanthrene	2.22	0.579	1.04	0.050	0.720		a, f
C_2-178 MW PAH	3.58		1.57	0.326	1.05		a, f
Retene	1.38	8.52	1.21	1.12	0.151		a, f
Fluoranthene	3.05	3.95	3.61	1.20	3.75	0.509	a, f
Acephenanthrylene	0.961	1.88	1.16	0.575	1.35	0.292	a, f
Pyrene	1.87	3.78	2.40	1.23	2.70	0.585	a, f
C_1-202 MW PAH	0.749	5.56	1.22	2.43	1.59	1.60	a, f
Benzo[ghi]fluoranthene	0.082	0.838	0.048	0.419	0.007	0.354	a, f
Cyclopenta[cd]pyrene		0.974		0.430	0.025	0.324	a, f
C_1-226 MW PAH		1.37		0.201		0.357	b, f
Benz[a]anthracene		1.22		0.630	0.032	0.533	a, f
Chrysene/Triphenylene		1.14		0.755	0.027	0.593	a, f
C_1-228 MW PAH		1.76		0.437		0.489	b, f

Identification notes: a) authentic quantitative standard. b) authentic quantitative standard for similar compound in series. c) identified by mass spectra. d) detected as a methyl ester.
Sample collection notes: e) collected in SUMA canister. f) collected on filter/PUF sampling train.
g) collected on DNPH impregnated C_{18} cartridges. *) not measured. +) detected but not quantified. See text for details.

Table 6.2. (continued - page 3)

Compound	Pine Wood (mg kg^{-1} of Wood Burned)		Oak Wood (mg kg^{-1} of Wood Burned)		Eucalyptus Wood (mg kg^{-1} of Wood Burned)		Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase	Gas Phase	Particle Phase	
Aromatic hydrocarbons							
Benzo[k]fluoranthene		0.671		0.303		0.286	a, f
Benzo[b]fluoranthene		0.790		0.400		0.327	a, f
Benzo[j]fluoranthene		0.466		0.073		0.121	b, f
Benzo[e]pyrene		0.459		0.231		0.212	a, f
Benzo[a]pyrene		0.712		0.245		0.301	a, f
Perylene		0.111		0.019		0.020	a, f
Indeno[1,2,3-cd]fluoranthene		0.224		0.018		0.010	b, f
Indeno[1,2,3-cd]pyrene		0.518				0.168	a, f
Benzo[ghi]perylene		0.437				0.173	a, f
Anthanthrene		0.052				0.008	b, f
Phenol and substituted phenols							
Phenol	525		300		434		a, f
o-Cresol	89.6		47.7	0.018	37.8	0.006	a, f
m&p-Cresol	380	0.500	179	0.210	110	0.055	a, f
Dimethylphenols	110	0.451	50.7		30.2	0.029	a, f
o-Benzenediol	312		142		215		b, f
p-Benzenediol	17.2	20.9	14.1	13.1	18.3	15.1	a, f
m-Benzenediol	2.81	47.0	4.47	26.0	10.0	13.0	a, f
Methylbenzenediols	10.4	54.5	56.0	28.9	38.4	18.1	b, f
Hydroxybenzaldehydes	12.1	7.91	14.1	0.529	11.4	0.316	b, f
4-(2-Hydroxyethyl)phenol			11.1	192	1.38	14.7	b, f
Guaiacol and substituted guaiacols							
Guaiacol	279	0.359	172	0.149	183	0.094	a, f
4-Methylguaiacol	339	0.854	101	0.113	81.3	0.110	b, f
4-Ethylguaiacol	203	0.939	100	0.054	56.7	0.058	b, f
4-Propylguaiacol	69.6	0.593	31.6		11.9		b, f
Eugenol	57.2	0.381	20.7		10.8		a, f
cis-Isoeugenol	41.2	0.702	13.1		9.25		b, f
trans-Isoeugenol	118	6.68	23.6	0.276	45.9	0.217	b, f
Vanillin	105	138	50.7	2.40	51.9	0.851	a, f
Acetovanillone	31.2	19.6	23.2	1.11	29.4	1.44	a, f
Guaiacyl acetone	88.6	118	123	33.7	143	29.0	b, f
Coniferyl aldehyde		230		15.1		19.3	a, f
Syringol and substituted syringols							
Syringol			397	1.99	287	2.22	a, f
4-Methylsyringol	0.301		174	5.06	130	2.74	b, f
4-Ethylsyringol	0.226		184	11.6	93.8	3.09	b, f
4-Propylsyringol			65.5	15.4	22.1	1.28	b, f
Allylsyringol			1.32	4.95	2.89	0.534	b, f
4-Propenylsyringol			1.27	36.2	5.70	5.60	a, f

Identification notes: a) authentic quantitative standard. b) authentic quantitative standard for similar compound in series. c) identified by mass spectra. d) detected as a methyl ester.

Sample collection notes: e) collected in SUMA canister. f) collected on filter/PUF sampling train. g) collected on DNPH impregnated C_{18} cartridges. *) not measured. +) detected but not quantified. See text for details.

Table 6.2. (continued - page 4)

Compound	Pine Wood (mg kg^{-1} of Wood Burned)		Oak Wood (mg kg^{-1} of Wood Burned)		Eucalyptus Wood (mg kg^{-1} of Wood Burned)		Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase	Gas Phase	Particle Phase	
Syringol and substituted syringols							
Syringaldehyde			7.77	25.3	9.32	50.5	b, f
Acetosyringone			1.02	28.1	1.19	55.3	b, f
Syringyl acetone	0.259		5.33	196	2.62	239	b, f
Propionylsyringol				8.79		16.0	b, f
Butyrylsyringol				0.353		14.2	b, f
Sinapyl aldehyde				18.4		57.4	b, f
Aliphatic aldehydes							
Formaldehyde	1165		759		599		a, g
Acetaldehyde	1704		823		1021		a, g
Propanal	255		153		155		a, g
Butanal	96		62		31		a, g
Pentanal	32		88		28		a, g
Hexanal	418		90		189		a, g
Heptanal	419		77		626		a, g
Aliphatic ketones							
Acetone	749		462		79		a, g
Butanone	215		115		77		a, g
Olefinic aldehydes							
Acrolein	63		44		56		a, g
Crotonaldehyde	276		177		198		a, g
Methacrolein	23		9.1		44		a, g
Aromatic carbonyls							
Benzaldehyde	49		16		21		a, g
m&p-Tolualdehyde	12				27		a, g
Acetophenone	3.9		5.3		14		a, g
2.5-Dimethylbenzaldehyde	12		20		50		a, g
Dicarbonyls							
Glyoxal	670		439		616		
Methylglyoxal	943		321		520		a, g
Biacetyl	89		73		73		a, g
2-Oxobutanal	241				337		a, g
n-Alkanoic acids							
n-Tetradecanoic acid	0.357	0.764		1.36		1.12	a, f, d
n-Hexadecanoic acid	2.00	19.9		16.9		15.4	a, f, d
n-Heptadecanoic acid	0.082	2.86		0.903			b, f, d
n-Octadecanoic acid		4.32		2.77		1.95	a, f, d
n-Nonadecanoic acid		0.645		0.347			b, f, d
n-Eicosanoic acid		7.25		0.958		0.992	a, f, d
n-Heneicosanoic acid		0.565		0.674		0.512	b, f, d
n-Docosanoic acid		20.8		7.61		5.09	a, f, d

Identification notes: a) authentic quantitative standard. b) authentic quantitative standard for similar compound in series. c) identified by mass spectra. d) detected as a methyl ester.

Sample collection notes: e) collected in SUMA canister. f) collected on filter/PUF sampling train. g) collected on DNPH impregnated C_{18} cartridges. *) not measured. +) detected but not quantified. See text for details.

Table 6.2. (continued - page 5)

Compound	Pine Wood (mg kg^{-1} of Wood Burned) Gas Phase	Pine Wood Particle Phase	Oak Wood (mg kg^{-1} of Wood Burned) Gas Phase	Oak Wood Particle Phase	Eucalyptus Wood (mg kg^{-1} of Wood Burned) Gas Phase	Eucalyptus Wood Particle Phase	Notes
n-Alkanoic acids							
n-Tricosanoic acid		0.479		1.26		0.780	b, f, d
n-Tetracosanoic acid		10.2		17.6		11.2	b, f, d
n-Pentacosanoic acid		0.161		0.266		0.504	b, f, d
n-Hexacosanoic acid		0.573		2.23		11.8	b. f, d
n-Alkenoic acids							
n-9-Octadecenoic acid		59.0		11.7		13.9	a, f, d
n-9,12-Octadecadienoic acid		18.9		11.7		21.4	a, f, d
Resin acids							
Pimaric acid		5.09		0.212			b, f. d
Sandaracopimaric acid		3.40		0.242			b. f. d
Isopimaric acid		42.9		3.55			b, f, d
8,15-Pimaradien-18-oic acid		0.132					b. f. d
Dehydroabietic acid		43.6		2.07		0.424	a. f. d
Abietic acid		187		1.20			b. f, d
7-Oxodehydroabietic acid		2.34					b, f, d
Abieta-6,8,11,13,15-pentaen-18-oic acid		20.1					b, f. d
Abieta-8,11,13,15-tetraen-18-oic acid		4.46		0.055			b, f. d
Sugars							
Levoglucosan		1375		706		1940	a. f
Other sugars		403		75		77	b. f
PAH Ketones							
Indan-1-one	17.5	0.135	13.8		7.66		b, f
9H-Fluoren-9-one	6.68	1.95	6.00		3.92		b, f
1H-Phenalen-1-one	0.285	4.45		1.35	0.689	1.52	a, f
7H-Benz[de]anthracen-7-one		0.694		0.187		0.289	a, f
Other compounds							
Veratraldehyde	1.24	0.299					a, f
3,4-Dimethoxytoluene	12.7		38.2		3.25		a, f
Veratric acid		8.10	2.04	4.12	0.910	8.41	a, f
Hydroxymethylfurfural	142	62.3	145	64.5	439	30.8	a, f
2-Furaldehyde	111		200		161		a, g
2-Methylfuraldehyde	10		5.3		1.9		a, g
Divanillyl		+		+		+	c, f
Divanillyl methane		+		+		+	c, f
Vanillylmethylguaiacol		+		+		+	c, f

Identification notes: a) authentic quantitative standard. b) authentic quantitative standard for similar compound in series. c) identified by mass spectra. d) detected as a methyl ester.
Sample collection notes: e) collected in SUMA canister. f) collected on filter/PUF sampling train. g) collected on DNPH impregnated C_{18} cartridges. *) not measured. +) detected but not quantified. See text for details.

and 117 mg per kilogram of pine wood burned. Although the emissions of acetylene and ethene, which are often used as motor vehicle exhaust tracers, will likely be dominated by motor vehicle emissions in urban locations like Los Angeles in the summer when wood is not generally burned for home heating, the ambient concentrations of these compounds will be significantly affected by wood combustion at times and places where greater wood burning occurs, as will be demonstrated later in the present work.

Benzene makes up 60% of the mono-aromatic hydrocarbon emissions from the combustion of pine wood with an emission rate of 383 mg per kilogram of wood burned. Benzene from wood combustion also will be a significant contributor to ambient benzene concentrations in high wood burning areas, as will be shown shortly.

As previously indicated, aliphatic aldehydes are major contributors to the gas-phase emissions from wood combustion. Acetaldehyde was emitted at the highest rate of all of the carbonyls, with an emission rate averaged over all three tests of 1180 mg per kilogram of wood burned. Formaldehyde, methylglyoxal and glyoxal were emitted at the next highest rates with average emissions of 841, 595, and 575 mg per kilogram of wood burned, respectively. Emissions of crotonaldehyde were also relatively high from all three types of wood burned, averaging 217 mg per kilogram of wood burned over all three tests.

Polycyclic aromatic hydrocarbons (PAH) are also emitted from wood combustion. Emissions of phenanthrene and anthracene average 11.2 and 2.5 mg per kilogram of wood burned, respectively. The methyl and dimethyl substituted homologs of these PAH are also emitted in significant quantities with emission rates of 7.6 and 2.2 mg per kilogram of wood burned averaged over all three tests. Retene (1-methyl-7-isopropylphenanthrene) is the fully aromatized thermal alteration product of resin acids present in conifer wood and is typically associated with the emissions from conifer wood combustion. In the current tests, the emission rate of gas- plus particle-phase retene from pine wood combustion was 9.9 mg per kilogram of wood burned, which is greater than the emissions of any of the other substituted phenanthrenes. Retene was also found in small amounts in the emissions from the fireplace combustion of the oak wood and in much lower quantities in the emissions from the combustion of eucalyptus wood. Volatilization of retene previously deposited on the chimney walls in earlier wood burning operations in the same fireplace might explain the presence of retene at low-levels in the emissions during the hardwood combustion experiments.

The patterns formed by the emissions of benzenediols, guaiacols, syringols, and resin acids are shown in Figure 6.4. The chemical structures of guaiacol, syringol, and their derivatives are shown in Figure 6.5 and the chemical structures of the resin acids have been previously described (14). As

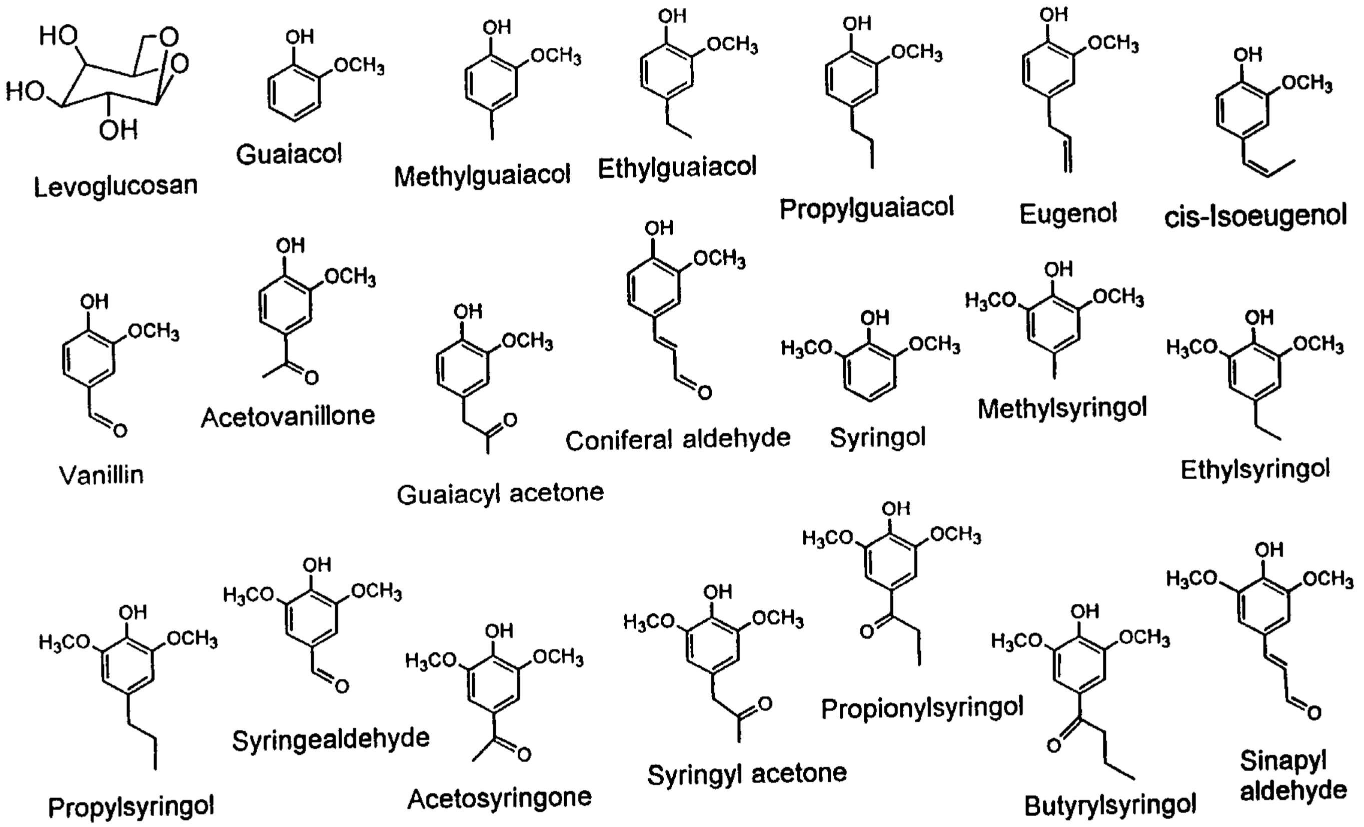

Figure 6.4. Chemical structure of levoglucosan, guaiacol, substituted guaiacols, syringol, and substituted syringols emitted from the fireplace combustion of wood.

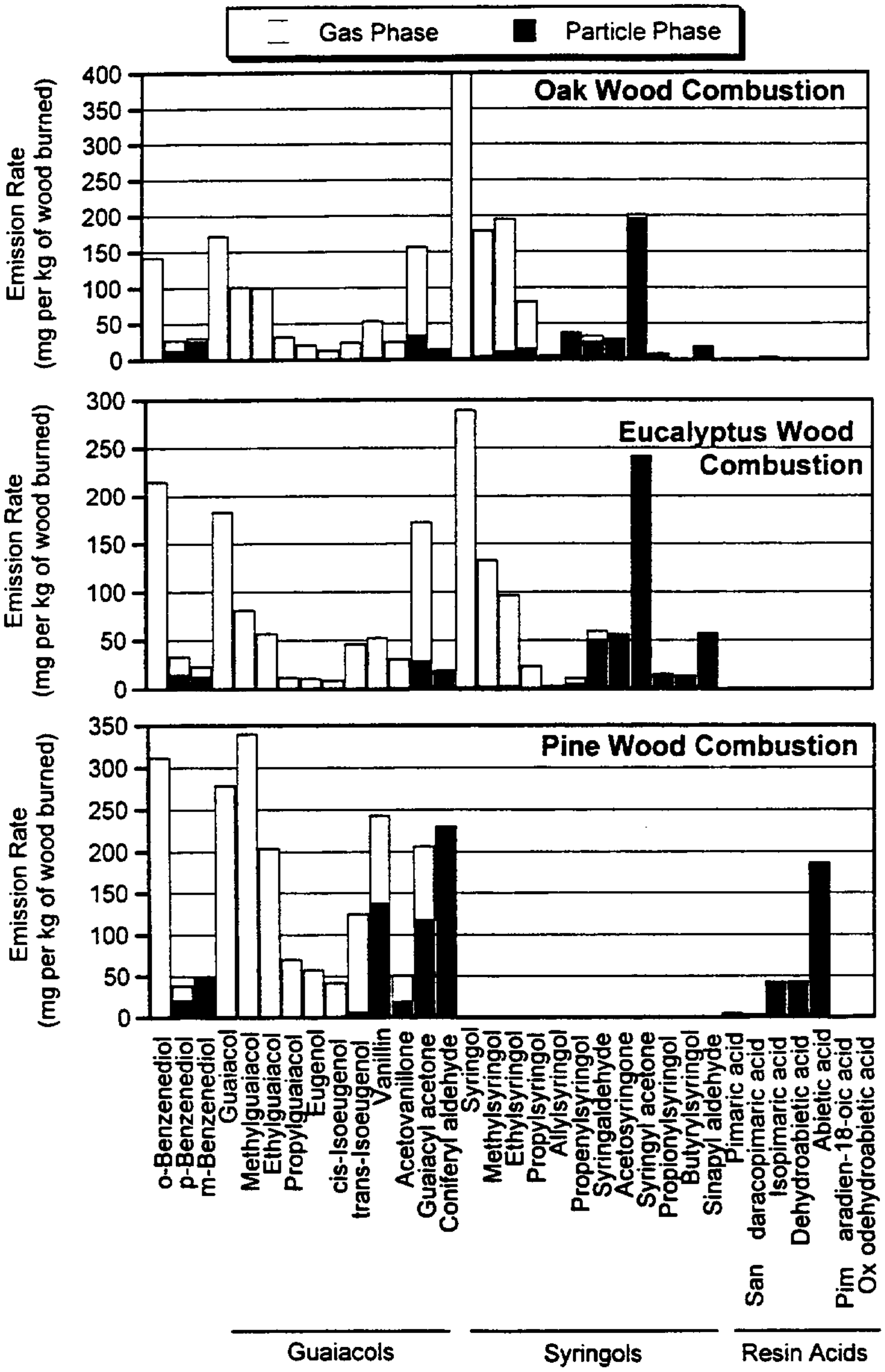

Figure 6.5. Emission rates of organic compounds from wood combustion and their gas/particle phase distributions in the diluted exhaust from a residential fireplace.

can be seen from Figure 6.4, significant differences exist in the emission profiles that distinguish pine wood combustion effluent from the emissions generated when the two hardwoods are burned. The emissions of resin acids from the combustion of pine wood can only be detected at trace levels in the emissions from the combustion of oak and eucalyptus firewood. The syringol and syringol derivatives which are present in the emissions from hardwood combustion are not detected at significant quantities in the softwood combustion emissions. Although trace concentrations of the pine smoke markers are found in the hardwood emissions possibly due to volatilization of deposits off of the chimney walls, only minute quantities of a few of the hardwood markers are found in the softwood emissions due to the fact that no hardwood was burned in the chimney used for the current source tests for at least three years prior to the pine wood combustion tests.

Guaiacols and the derivatives of guaiacol are emitted by the combustion of both the softwood and the hardwoods, but the emission rates of individual guaiacol derivatives are very different for the two types of wood. Coniferyl aldehyde and vanillin are emitted at significantly higher rates from pine wood combustion than from combustion of the hardwoods tested in the present study. The alkyl-substituted guaiacols and guaiacol are emitted at moderately higher rates from the pine wood combustion process but the relative distribution of these compounds in the emissions from pine wood combustion is not significantly different from that in the hardwood combustion emissions.

The relative distribution of total benzenediol isomer emissions shown in Figure 6.4 is not very different for the combustion of the three types of wood tested, but the distribution of these compounds between the gas and particle phases in the diluted emissions varies significantly for the different isomers. The ortho-substituted benzenediol is completely in the gas phase while the para-substituted species is split evenly between the gas and particle phases. The meta-substituted species is found mostly in the particle phase for the pine and oak smoke but is evenly split between the two phases in the eucalyptus smoke.

6.3.4 Gas/Particle Partitioning: Experiment Versus Theory

Gas/particle partitioning theory (25, 26) holds that the phase distribution of a semi-volatile organic compound is determined by its absorption into the particle phase matrix, and that this phase distribution can be described by a partitioning coefficient, $K_{p,opm}$, defined as:

$$K_{p,opm} = \frac{F/OPM}{A} \qquad (1)$$

where $K_{p,opm}$ is the gas/particle partitioning coefficient based on organic particulate matter as the receiving particle phase substrate in units of $m^3\ \mu g^{-1}$. F is the particle-associated mass concentration of the semi-volatile organic compound of interest ($\mu g\ m^{-3}$), OPM is the total organic particulate matter concentration into which the compound can partition ($\mu g\ m^{-3}$), and A is the gas-phase mass concentration of the compound of interest ($\mu g\ m^{-3}$). It is expected that the gas/particle partitioning coefficient, $K_{p,opm}$, will depend on the vapor pressure of the various organic compounds (27):

$$Log(K_{p,opm}) = m_{r,opm} Log(p_L^0) + b_{r,opm} \qquad (2)$$

where p_L^0 is the vapor pressure over a liquid pool of the semi-volatile organic compound of interest in torr, and $m_{r,opm}$ and $b_{r,opm}$ are coefficients that can be estimated by regressing a series of experimentally measured values of $K_{p,opm}$ on the corresponding liquid vapor pressure values, p_L^0, for the members of a given organic compound class. If the compounds have similar activity coefficients when present in the particulate organic matrix and the partitioning process has reached equilibrium, then $-m_{r,opm}$ should be close to unity. Under this condition, $b_{r,opm}$ is a constant characteristic of the partitioning for that class of compounds with the specific particle matrix.

As previously indicated the phase distribution of the emitted PAH was measured throughout the complete wood burning cycle by filter/PUF sampling trains during each source test, and 15-minute samples were analyzed that represent two different times during the pine wood combustion source test using the denuder/filter/PUF sampling technology. A plot of $K_{p,opm}$ as a function of p_L^0

is presented in Figure 6.6 for all of the available PAH data. Values of $m_{r,opm}$ and $b_{r,opm}$ for PAH as measured by the filter/PUF sampling train in the diluted exhaust from hardwood combustion are -1.4 ± 0.05 and -10.4 ± 0.22, respectively. For measurements made by the filter/PUF method in the diluted exhaust from the pine wood combustion, $-m_{r,opm}$ is -1.3 ± 0.07 and $b_{r,opm}$ is -9.4 ± 0.31. In both of these cases, $m_{r,opm}$ is significantly different from unity indicating that the partitioning of the PAH as determined by the filter/PUF sampling trains does not appear to be at equilibrium. However, also shown in Figure 6.6 are the $K_{p,opm}$ values determined by the denuder/filter/PUF measurement technique in the diluted exhaust from pine wood combustion. For the denuder/filter/PUF measurements, $m_{r,opm}$ is -0.93 ± 0.03 and $b_{r,opm}$ is -7.6 ± 0.16, which is in much better agreement with the partitioning theory described above. Measurements of the partitioning behavior of PAH by Liang and Pankow (27) using a filter/PUF sampler were found to have $b_{r,opm}$ values of -7.0 for tobacco smoke and -6.9 for urban particulate matter.

6.3.5 Determination of the Contribution of Wood Smoke to Ambient VOC Concentrations

Demonstration that the distribution of fine particle-phase organic compounds in wood smoke can be used to trace wood smoke contributions to atmospheric fine particle concentrations is provided by Schauer et al. (16) and will not be repeated here. The characterization of the gas-phase emissions from

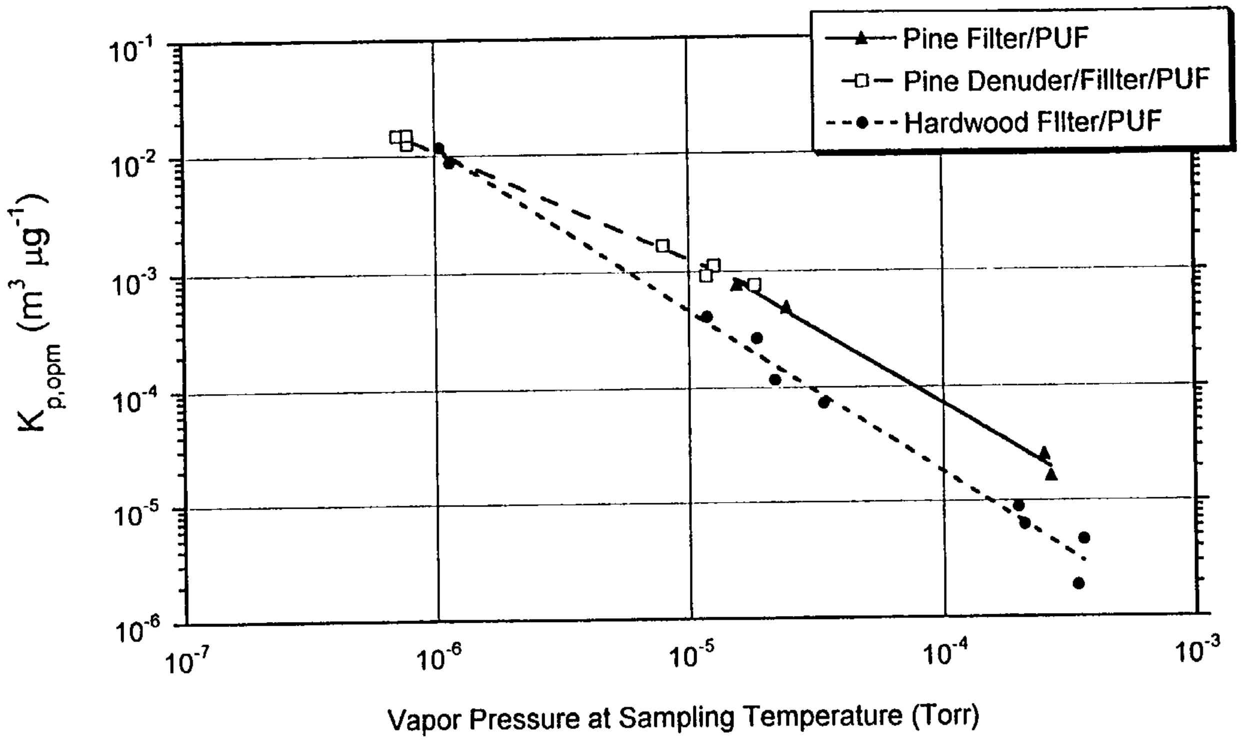

Figure 6.6. Gas/particle partitioning of PAH in the diluted exhaust from wood burned in a residential fireplace as a function of the vapor pressure of the pure compound.

wood combustion provided in the present study when combined with particle-phase wood smoke tracers now makes it possible to asses the contribution of wood combustion to ambient VOC concentrations. The concentrations of fine particulate organic compounds and gas-phase volatile hydrocarbons were measured in Fresno, California, in the winter of 1995-1996 as part of the San Joaquin Valley IMS95 air quality study. Ambient concentrations of benzene, ethene, acetylene, and levoglucosan for two episodes of 48 hours duration during the IMS95 study are listed in Table 6.3. Also included in this table are the emission rates of these compounds collected in the present study for pine wood combustion. Emissions and ambient concentrations that are normalized according to levoglucosan also are presented in Table 6.3. Given that the average emission rate of levoglucosan from hardwood combustion is close to that of the pine wood sample and given the fair similarity of the emissions rates of the lightest gas-phase compounds measured in all tests (e.g., the carbonyls) it is assumed that the levoglucosan and gas-phase emissions from pine wood combustion can be used to estimate the concentration of wood smoke-derived VOCs in the Fresno atmosphere. If levoglucosan is used as a tracer for woodsmoke, then the contributions of wood burning to the ambient concentrations of benzene, ethene, and acetylene can be estimated for these episodes. As shown in Table 6.3, the contributions from wood burning to the ambient benzene, ethene, and acetylene concentrations during the December 26-28, 1995, episode are 14%, 24% and 18%, respectively. This result is

Table 6.3. Estimate of the contribution from wood smoke to the ambient concentrations of benzene, ethene, and ethyne in Fresno, California, during two winter episodes using levoglucosan as a tracer for wood smoke

	Emission Rate from Firewood Combustion (mg per kilogram of wood burned)		Ambient Concentration ($\mu g\ m^{-3}$) Fresno, California Dec. 26-28, 1995	Ambient Concentration ($\mu g\ m^{-3}$) Fresno, California Jan. 4-6, 1996
Benzene	383	Benzene	15.1	12.0
Ethene	1120	Ethene	25.8	16.7
Acetylene	702	Acetylene	21.7	16.5
Levoglucosan	1375	Levoglucosan	7.59	2.13
	Ratio of Emission to Levoglucosan		Contribution from Wood Combustion ($\mu g\ m^{-3}$)	
Benzene	0.279	Benzene	2.1 (14.0 %)	0.6 (5.0 %)
Ethene	0.815	Ethene	6.2 (24.0 %)	1.7 (10.4 %)
Acetylene	0.510	Acetylene	3.9 (17.8 %)	1.1 (6.6 %)

significant because benzene, acetylene, and ethene are often used as motor vehicle exhaust tracers within VOC receptor models in which they are used to distinguish the differences between whole gasoline vapors and gasoline-powered motor vehicle exhaust within atmospheric samples. The omission of the contributions from wood smoke VOCs within receptor modeling calculations could lead incorrectly to an overestimate of the contribution of tailpipe exhaust and an underestimate of the contribution of whole gasoline vapors to ambient VOC concentrations in communities where a significant amount of wood burning occurs.

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Chapter 7

Organic Compounds in Cigarette Smoke

7.1 Introduction

Organic compounds present in the emissions from air pollution sources and in ambient air can be used to determine the contribution of cigarette smoking to outdoor ambient fine particle concentrations. Calculations by Schauer et al. (1) show that cigarette smoke particles contributed approximately 0.7% of the fine particle mass in the Los Angeles area atmosphere in the early 1980's. The approach used in that analysis involved a chemical mass balance model in which high molecular weight iso- and anteiso-alkanes effectively acted as markers for cigarette smoke in ambient air while other chemical substances were used to simultaneously trace the presence of eight other fine particle source types. Although this technique has not yet been employed in indoor environments, the same approach can be used to determine the contributions to indoor fine particle concentrations from cigarette smoke, food cooking emissions, wood combustion, as well as other important air pollution sources.

The study by Schauer et al. (1) employed low volatility particle-phase organic compounds as environmental tracers, while others have pursued the use of more abundant semi-volatile organic compounds such as nicotine (2) as tracers for particulate matter emitted from cigarette smoke. Semi-volatile organic compounds exist simultaneously in both the gas and particle phases. If such compounds are to be followed in the environment it is valuable to assemble a source emissions data base that simultaneously quantifies both the gas-phase and particle-phase emissions.

Gas- and particle-phase organic compound emissions from air pollution sources including wood smoke, food cooking operations, and motor vehicle exhaust are presented in Chapters 2 through 6. Chemical profiles from these source tests can be used within a chemical mass balance source apportionment model to simultaneously determine the contributions of air pollution sources to ambient concentrations of organic gases and fine particulate matter. If a similar emissions profile is generated for cigarette smoke, then this approach can also be applied to indoor environments to apportion source contributions to gas- and particle phase-pollutants, as well as to identify the sources of individual organic compounds. To this end the current study has been undertaken to measure gas- and particle-phase organic compounds as well as the distribution of compounds between the gas and particle phases in the emissions from cigarette smoke.

7.2 Experimental Methods

7.2.1 Comprehensive Source Sampling

The source sampling system used for the present study consists of a dilution source sampler with a chamber that houses a human smoker built into the center of the apparatus. A cigarette customer steps inside the smoking chamber which is fabricated from a large sheet metal laboratory storage cabinet with the shelves removed. Commercially purchased high purity dilution air is purged to this chamber through two air inlet ports located near the top of the smoking chamber. A 152 cm diameter transfer line connects the side of the smoking chamber to the residence time chamber of the dilution source sampler described in Chapter 2. An ashtray was placed at the inlet of the transfer line such that virtually all of the sidestream smoke from a cigarette at those times when it was smoldering in the astray was drawn through the transfer line into the residence time chamber from which aged diluted cigarette smoke samples were taken. The smoker held the cigarette at the inlet to the transfer line when inhaling and exhausted the exhaled mainstream smoke directly into the transfer line. This procedure exhausted virtually all of the cigarette smoke through the transfer line without allowing the smoke to build up in the smoking chamber. The flow of high purity dilution air was set at 300 lpm while the flowrate through the transfer line was set at 240 lpm, thereby creating a slight over pressure within the cabinet. Additional air at a flowrate of 30 lpm were withdrawn from the lower section of the smoking chamber to a background air sampling train to quantify any back-mixing of emissions into the smoking chamber and to quantify whether or not any contaminants were present in the dilution air. The excess air going into the smoking chamber prevented intrusion of ambient air into the smoking chamber. All of the seals in the downstream transfer line and the residence time chamber of the sampler were air-tight.

The mainstream and sidestream cigarette emissions plus the dilution air passed through the transfer line into the residence time chamber, where the semi-volatile species in the diluted emissions were allowed to equilibrate between the gas and particle phases. From the residence chamber, the diluted exhaust was pulled through eight AIHL-design cyclone separators operated in parallel at a flowrate of 30 lpm each (3) that removed particles with aerodynamic diameters greater than 1.8 μm. Gases and particles with diameters less than 1.8 μm passed through the cyclones and were sampled by a series of sampling trains operated in parallel.

Semi-volatile and fine particle-phase organic compounds were collected continuously throughout the cigarette smoking cycle by the denuder/filter/PUF sampling train and the filter/PUF sampling train. Details of these sampling trains are provided in Chapter 2. One denuder-based sampling train was operated during each composite test in which two cigarettes were smoked. Four filter/PUF sampling trains were operated in parallel with the denuder-based sampling train during the cigarette smoking source tests.

The sixth cyclone-based sampling unit used during the cigarette smoking source tests was configured with sampling substrates to measure the emissions of fine particulate matter mass, carbonyls, organic acids, and gas-phase hydrocarbons. This sampling unit is described in Chapter 2 and is shown in Figure 2.1 of Chapter 2.

The background sampler, which was used to sample the air in the smoking chamber, consisted of three filter packs connected at the outlet of an AIHL cyclone separator. The first stacked filter unit consisted of two quartz fiber filters (47 mm diameter, Pallflex Tissuequartz 2500 QAO) in series which were used for elemental carbon and organic carbon (EC/OC) determination by thermal evolution and combustion analysis as described by Birch and Cary (4). The second filter pack contained a Teflon membrane filter (47 mm diameter, Gelman Teflo, 2 μm pore size) which was used for gravimetric determination of the fine particle mass emitted and also was analyzed by X-ray fluorescence for 35 trace elements (5). The third filter holder assembly contained one Teflon membrane filter which was used for a duplicate fine particle mass emissions measurement and for inorganic ion measurements by ion chromatography (6), atomic absorption spectroscopy and colorimetry (7). Downstream of the second

Teflon filter the sample flow was divided, and a small portion of the flow was used to fill a 6 liter polished stainless steel SUMA canister for the collection of non-methane volatile hydrocarbons ranging from C_1 to C_{10}. The 6 liter SUMA canister was filled continuously at the same flowrate as the SUMA canister used to collect the cigarette smoke samples.

Electronic particle sizing instruments and a pair of MOUDI impactors also were connected to the residence time chamber during the cigarette smoke tests to obtain particle size distributions and particle chemical composition as a function of size. The MOUDI impactors were connected to the 7th and 8th AIHL-design cyclone separator. The size distributions and the results obtained from the MOUDI impactors will be reported elsewhere.

7.2.2 Source Testing Procedure

Two cigarettes were smoked during each cigarette smoking source test. At the beginning of each source test the smoking chamber was purged with purified dilution air for 5 minutes and then the cigarette customer entered the smoking chamber. The chamber was then purged for an additional 3 minutes. All of the sampling train flowrates were established 30 seconds prior to lighting the first cigarette. The smoker inhaled and exhaled the cigarette smoke according to their customary smoking habits. The cigarette was left in the ashtray between inhalations. When the cigarette was completely smoked, the cigarette was extinguished in the ashtray and the sampling flows were continued for an additional 60 seconds. Typical cigarette smoking times were 5 minutes per cigarette, diluting the mainstream plus sidestream smoke from one cigarette to 1.2 m^3 of the flowing dilution air.

After the test of the first cigarette was complete, one Teflon filter and the quartz fiber filters designated for EC/OC analysis were replaced with new filters, permitting us to determine the mass emission rates and organic carbon emission rates for each cigarette. All other sampling collection devices were left in place for the second cigarette smoking test. At the beginning of the second cigarette smoking test, the smoking chamber was repurged with purified dilution air as was done for the first cigarette. Air flows through the sampling trains were reestablished 30 seconds before the second cigarette was lit, and the cigarette was smoked under the same conditions as described above. After the second cigarette was extinguished, the sampler flows were continued for 60 seconds and then all flows were stopped. All substrates were then unloaded for analysis except the SUMA canisters which continued to be filled over all six cigarettes smoked.

The cigarettes smoked in the present study are listed in Table 7.1. These six cigarettes were chosen to represent a market share average of the cigarettes smoked in the United States in the mid-1990's. The six cigarettes represent four

Table 7.1. Cigarettes Smoked in Present Study

Brand	Manufacturer	Length (mm)*	Filter	Regular or Light	Menthol
Camel	R. J. Reynolds	69	No	Regular	No
Kent Kings	Lorillard	63	Yes	Regular	No
Kool Filters	Brown & Williamson	63	Yes	Regular	Yes
Marlboro Light	Philip Morris	57	Yes	Light	No
Marlboro Regular	Philip Morris	60	Yes	Regular	No
Winston Filters	R. J. Reynolds	62	Yes	Regular	No

* Length of cigarette tobacco bed

of the major cigarette manufacturers, with one cigarette without a filter, one menthol flavored cigarette, one light cigarette, and three regular filter-tip cigarettes.

7.2.3 Organic Chemical Analysis

The analytical procedures used in the present study for the identification and quantification of semi-volatile and particle-phase organic compounds in air pollution source emissions are discussed in Chapter 2.

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.

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 non-quantitative secondary standard that could be used for unique identification of the organic compounds. An example of such a secondary standard is the use of petroleum wax as a source of high molecular weight *iso*-alkanes and *anteiso*-alkanes that were used to help identify these compounds in the cigarette smoke. Quantification of compounds identified using secondary standards has been estimated from the response factors for compounds having similar retention times and chemical structures.

Total non-methane organic gases (NMOG, EPA method TO12) and individual 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. (8). Carbonyls collected by the C_{18}-impregnated cartridges were analyzed by liquid chromatography/UV detection as described by Grosjean et al. (9).

7.3 Results

7.3.1 Fine Particle Emissions Rates and Compositions

Fine particle mass emission rates for the six cigarettes averaged 27.0 ± 1.3 mg per cigarette smoked. The fine particle mass collected in this fashion consisted of 62.5% organic carbon and 0.45% elemental carbon. Table 7.2 shows the elemental composition of the fine particle mass collected from cigarette smoking. Although nitrogen was not directly measured, the nitrogen associated with the specific organic compounds that were quantified in Table 7.3 accounts for 1.4% of the fine particle mass emitted. Potassium and chlorine were measured to be the next largest components of the fine particle mass comprising 0.64 ± 0.11 to 0.49 ± 0.07 percent and 0.44 ± 0.09 to 0.34 ± 0.06 percent of the fine particle mass, respectively (range of the two independent

Table 7.2. Average Fine Particle Emission Rate and Fine Particle Chemical Composition for Cigarette Smoking (Values shown in boldface are greater than zero by at least two standard errors).

Fine Particle Mass Emissions Rate (AVG ± STD)		**27.0 ± 1.3 mg per cigarette**	
Elemental and Organic Carbon (Wt % of Fine Particle Mass)			
Organic Carbon	**46.0 ± 1.8**[a]	Elemental Carbon	**0.45 ± 0.10**
Ionic Species (Wt % of Fine Particle Mass)			
Chloride	**0.44 ± 0.09**	Ammonium	**0.03 ± 0.01**
Nitrate	**0.06 ± 0.03**	Sodium	**0.03 ± 0.01**
Sulfate	**0.07 ± 0.02**	Potassium	**0.49 ± 0.07**
X-ray Fluorescence (Wt % of Fine Particle Mass)			
Aluminum	0.00 ± 0.03	Selenium	0.00 ± 0.00
Silicon	0.00 ± 0.02	Bromine	0.00 ± 0.00
Phosphorus	0.00 ± 0.01	Rubidium	0.00 ± 0.01
Sulfur	**0.13 ± 0.03**	Strontium	0.00 ± 0.00
Chlorine	**0.34 ± 0.06**	Yttrium	0.00 ± 0.00
Potassium	**0.64 ± 0.11**	Zirconium	0.00 ± 0.00
Calcium	0.00 ± 0.02	Molybdenum	0.00 ± 0.01
Titanium	0.00 ± 0.01	Palladium	0.00 ± 0.01
Vanadium	0.00 ± 0.01	Silver	0.00 ± 0.01
Chromium	0.00 ± 0.01	Cadmium	0.02 ± 0.02
Manganese	0.00 ± 0.01	Indium	0.00 ± 0.01
Iron	**0.03 ± 0.01**	Tin	0.01 ± 0.02
Nickel	0.01 ± 0.01	Antimony	0.00 ± 0.02
Copper	0.02 ± 0.01	Barium	0.00 ± 0.10
Zinc	0.01 ± 0.01	Lanthanum	0.00 ± 0.13
Gallium	0.00 ± 0.00	Mercury	0.00 ± 0.00
Germanium	0.00 ± 0.00	Lead	0.00 ± 0.00
Arsenic	0.00 ± 0.00		

Notes: (a) measured downstream of organics denuder. Organic carbon collected on undenuded filter is 62.5 percent of the fine particle mass.

Table 7.3. Organic Compounds Measured in Cigarette Smoke

Compound	Cigarette Smoking Emissions (µg per cigarette)		Notes
	Gas Phase	Particle Phase	
n-Alkanes			
Methane	4440		a, e
Ethane	1330		a, e
Propane	602		a, e
n-Butane	178		a, e
n-Pentane	52		a, e
n-Hexane	51		a, e
n-Heptane	31		a, e
n-Octane	16		a, e
n-Nonane	9		a, e
n-Decane	6		a, e
n-Pentacosane		4.52	b, f
n-Heptacosane		32.7	b, f
n-Octacosane		2.8	a, f
n-Nonacosane		35.4	b, f
n-Triacontane		11.2	b, f
n-Hentriacontane		148.2	b, f
n-Dotriacontane		17.9	a, f
n-Tritriacontane		49.9	b, f
Branched alkanes			
iso-Butane	277		a, e
iso-Pentane	46		a, e
2,2-Dimethylbutane	50		a, e
2-Methylpentane	22		a, e
2,4-Dimethylpentane	45		a, e
iso-Nonacosane		7.40	b, f
anteiso-Triacontane		25.8	b, f
iso-Hentriacontane		57.0	b, f
anteiso-Dotriacontane		52.0	b, f
iso-Tritriacontane		15.9	b, f
n-Alkenes			
Ethene	1590		a, e
Propene	1260		a, e
1-Butene	138		a, e
trans-2-Butene	159		a, e
cis-2-Butene	97		a, e
1-Pentene	91		a, e
trans-2-Pentene	54		a, e
cis-2-Pentene	39		a, e
1-Hexene	130		a, e
cis-2-Hexene	100		a, e

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.

Sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. *) not measured. See text for details.

Additional Notes: † Compound is too volatile for accurate determination of phase distribution by denuder/filter/PUF sampling train; reported emissions are from filter/PUF sampling train.

Table 7.3. (continued - page 2)

Compound	Cigarette Smoking Emissions (μg per cigarette)		Notes
	Gas Phase	Particle Phase	
Branched alkenes			
Isobutene	521		a, e
3-Methyl-1-butene	80		a, e
2-Methyl-1-butene	124		a, e
2-Methyl-2-pentene	87		a, e
Neophytadiene	59.8	31.2	b, f
Diolefins			
1,3-Butadiene	88		a, e
Isoprene	3000		a, e
Alkynes			
Ethyne	340		a, e
Saturated cycloalkanes			
Methylcyclopentane	36		a, e
Cyclohexane	12		a, e
Methylcyclohexane	21		a, e
Aromatic hydrocarbons			
Benzene	481		a, e
Toluene	829		a, e
Ethylbenzene	94		a, e
m & p-Xylene	469		a, e
o-Xylene	74		a, e
Styrene	132		a, e
iso-Propylbenzene	8		a, e
n-Propylbenzene	17		a, e
p-Ethyltoluene	58		a, e
m-Ethyltoluene	23		a, e
o-Ethyltoluene	27		a, e
1,3,5-Trimethylbenzene	14		a, e
1,3,4-Trimethylbenzene	111		a, e
Naphthalene†	41.0	0.39	a, f
2-Methylnaphthalene†	14.8		a, f
1-Methylnaphthalene†	17.3		a, f
C_2-Naphthalenes†	34.8	0.11	a, f
C_3-Naphthalenes†	13.9	0.08	b, f
Acenaphthylene†	6.23		a, f
Acenaphthene†	3.62		a, f
Fluorene	2.38	0.35	a, f
Phenanthrene	3.28	0.94	a, f
Anthracene	0.81		a, f
C_1 MW 178 PAH	2.48	4.12	a, f

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.
Sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. *) not measured. See text for details.
Additional Notes: † Compound is too volatile for accurate determination of phase distribution by denuder/filter/PUF sampling train; reported emissions are from filter/PUF sampling train.

Table 7.3. (continued - page 3)

Compound	Cigarette Smoking Emissions (μg per cigarette)		Notes
	Gas Phase	Particle Phase	
Aromatic hydrocarbons			
Fluoranthene	0.12	1.00	a, f
Acephenanthrylene	0.02	0.50	b, f
Pyrene	0.10	0.81	a, f
Benz[a]anthracene		0.40	a, f
Chrysene & Triphenylene		0.69	a, f
Aliphatic aldehydes			
Formaldehyde	165		a, g
Acetaldehyde	2120		a, g
Propanal	165		a, g
Butanal	114		a, g
Hexanal	82		a, g
Octanal	60		a, g
Nonanal	17		a, g
Decanal	10		a, g
Aliphatic ketones			
Acetone	736		a, g
Butanone	156		a, g
2-Pentanone	140		a, g
Olefinic aldehydes			
Crotonaldehyde	116		a, g
Acrolein	171		a, g
Olefinic ketones			
Solanone	14.0	3.2	b, f
Geranyl acetone	11.9		b, f
Aromatic aldehydes			
Benzaldehyde	59		a, g
Dicarbonyls			
Glyoxal	353		a, g
Methylglyoxal	575		a, g
Biacetyl	101		a, g
2-Oxobutanal	391		a, g
Furaldehydes			
2-Furaldehyde	81		a, g
5-Hydroxymethylfuraldehyde	45		a, g
Phenols			
Phenol†	409	6.12	a, f
o-Cresol†	24.9	0.435	a, f
m&p-Cresol†	73.1	1.50	a, f

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.

Sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. *) not measured. See text for details.

Additional Notes: † Compound is too volatile for accurate determination of phase distribution by denuder/filter/PUF sampling train; reported emissions are from filter/PUF sampling train.

Table 7.3. (continued - page 4)

Compound	Cigarette Smoking Emissions (µg per cigarette)		Notes
	Gas Phase	Particle Phase	
Phenols			
Ethylphenols[†]	19.6	1.40	a, f
Dimethylphenols[†]	44.2	1.61	a, f
Ethenylphenol	15.2	7.41	b, f
p-Benzenediol		147	a, f
m-Benzenediol		9.03	a, f
Methylbenzenediols		9.48	b, f
Ethenylbenzenediols		27.64	b, f
n-Alkanoic acids			
Tetradecanoic acid	0.50	17.0	a, d, f
Hexadecanoic acid	1.68	237	a, d, f
Octadecanoic acid		57.1	a, d, f
Eicosanoic acid		13.4	a, d, f
Heneicosanoic acid		2.98	b, d, f
Docosanoic acid		10.0	a, d, f
Tricosanoic acid		4.44	b, d, f
Tetracosanoic acid		5.01	a, d, f
Alkenoic acids			
9-Octadecenoic acid		64.4	a, d, f
9,12-Octadecadienoic acid		119	a, d, f
9,12,15-Octadecatrienoic acid		169	a, d, f
Carbonyl acids			
Glyoxylic acid		19	a, g
Pyruvic acid		11	a, g
N-Containing compounds			
1-Methyl-1H-pyrolo[2,3-b]pyridine[†]	60.7		b, f
Quinoline[†]	16.6		a, f
Isoquinoline[†]	8.35		a, f
Phenylpyridine	6.08		b, f
Myosmine	81.2	53.1	b, f
Indole[†]	79.4	6.08	b, f
Methylindoles	30.2	8.81	b, f
β-Nicotyrine	47.3	36.4	b, f
Nicotine	2040	2000	a, f
Bipyridyl	14.7	14.9	b, f
N-Methylsuccinimide	3.52	9.54	b, f
Carbazole	0.18	3.46	b, f
Cotinine	1.53	18.6	b, f
N-Oxynicotine		20.5	b, f

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.

Sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. *) not measured. See text for details.

Additional Notes: [†] Compound is too volatile for accurate determination of phase distribution by denuder/filter/PUF sampling train; reported emissions are from filter/PUF sampling train.

Table 7.3. (continued - page 5)

Compound	Cigarette Smoking Emissions (µg per cigarette) Gas Phase	Particle Phase	Notes
N-Containing compounds			
Nicotinic acid		12.7	b, f
Hydroxypyridine		41.5	b, f
Other compounds			
Furancarboxylic acid		19.4	b, f
Menthol[†]	179	31.1	a, f
Triacetin (glyceryl triacetate)	415	66.2	a, f
Levoglucosan		119	a, f
Vitamin E		11.1	a, f
6,7-Dimethoxy-coumarin		12.6	b, f
Phenylacetic acid		13.6	b, f

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series. (c) secondary standard. (d) detected as a methyl ester.
Sample collection notes: (e) collected in SUMA canister. (f) collected on denuder/filter/PUF sampling train. (g) collected on DNPH impregnated C_{18} cartridges. *) not measured. See text for details.
Additional Notes: [†] Compound is too volatile for accurate determination of phase distribution by denuder/filter/PUF sampling train; reported emissions are from filter/PUF sampling train.

determinations). Sulfur, sodium ion, and ammonium ion comprised smaller but measurable portions of the fine particle mass emitted from cigarette smoking.

7.3.2 Emissions of CO and CO_2

An overall carbon balance on the emissions from human smoking of cigarettes cannot be accurately closed since the CO_2 introduced from human respiration is larger than the production of CO_2 from a cigarette under normal smoking conditions. For this reason the CO_2 emission rate from smoking cannot be accurately measured by the techniques employed in this study. CO emissions, however, can be accurately measured from human smoking of cigarettes. CO emissions amounted to 98,000 μg per cigarette smoked, which is in good agreement with previously reported CO emissions for cigarettes (10, 11).

7.3.3 Mass Balance on Organic Compound Emissions

The sum of gas-phase plus particle-phase non-methane organic compounds emitted from the average cigarette smoked in the present experiment is 45.4 mg per cigarette, as shown in Figure 7.1. This accounts for approximately 6.2% of the mass of the tobacco found in the cigarettes smoked in the present study. Gas-phase species accounted for approximately 66% of the overall organic compound emissions. The largest fraction of the gas-phase emissions consisted of olefins and carbonyls, which made up 26% and 19% of

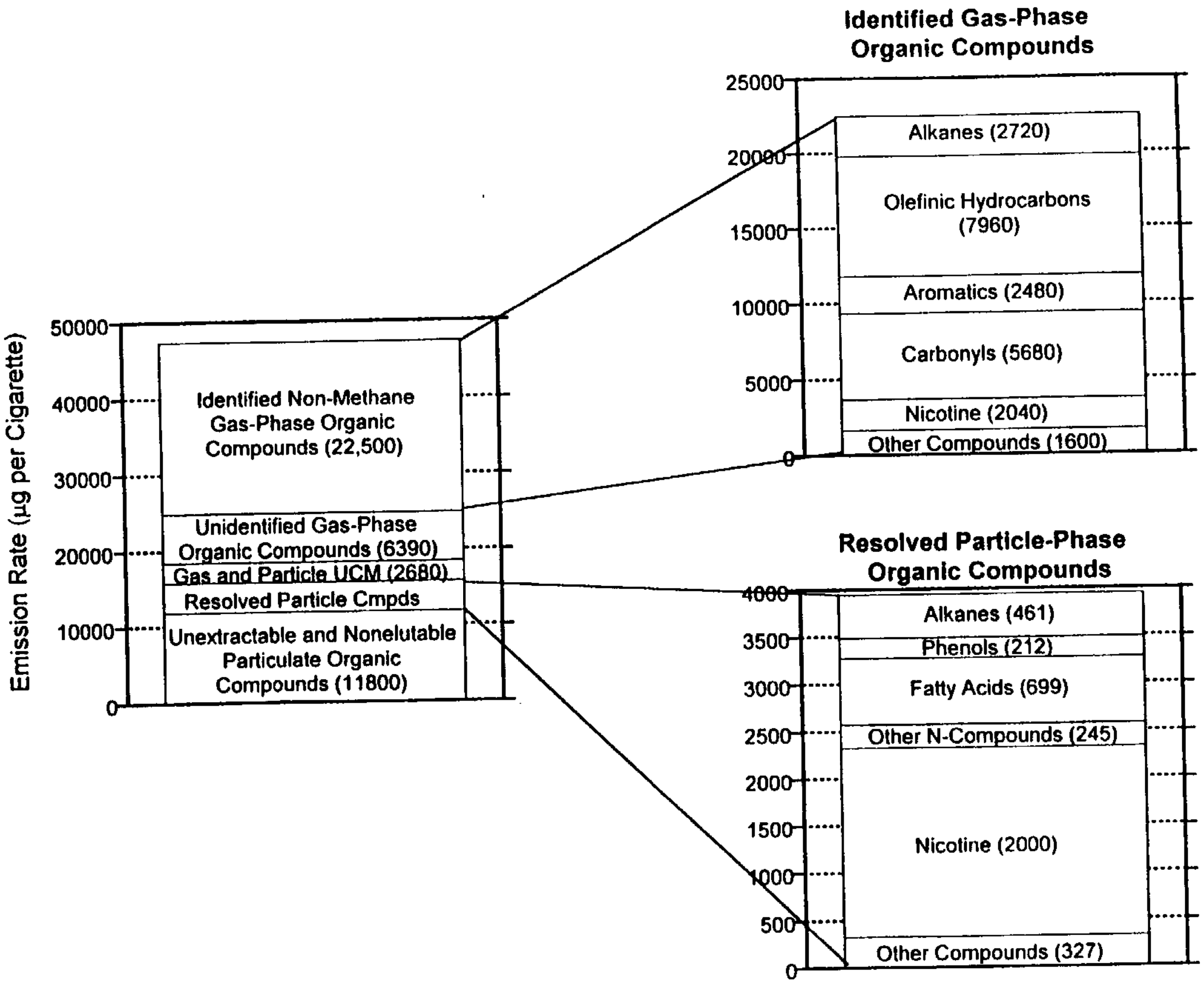

Figure 7.1. Mass balance on the non-methane organic mass emitted from the cigarette smoking.

the non-methane organic gas emissions, respectively. Alkanes and aromatic hydrocarbons each made up slightly less than 10% of the gas-phase emissions. Approximately 21% of the light gas-phase organic carbon mass was not identified at the single compound level and is believed to be comprised of low molecular weight alcohols, alkanoic acids, and nitrogen-containing species which are not detected by the analytical methods employed in the present study.

The unresolved complex mixture (UCM) appears as a wide hump that underlies the resolved compounds on a GC trace and consists of highly branched and cyclic organics that cannot be separated from each other by the present methods. The semi-volatile gas-phase UCM makes up a small portion of the gas-phase emissions, contributing only 3.6% of the gas-phase organic compound emissions. Likewise, the particle-phase UCM emissions are relatively small making up only 10% of the 15.4 mg of fine particulate organic mass emitted per cigarette. In contrast, the non-extractable and non-elutable fraction of the fine organic particulate matter mass emitted from cigarette smoking is relatively large, making up 77% of the fine particle organic mass.

The absolute mass emission rate of nicotine is split evenly between the gas and particle phases at the dilution rate used in the present study. Nicotine makes up over half of the organic compounds which can be extracted, eluted, and separated by the GC/MS techniques used here. Fatty acids (n-alkanoic acids and n-alkenoic acids) make up the next largest fraction of the organic compounds identified in the particle phase followed by the alkanes.

7.3.4 Emission Rates of Individual Organic Compounds

The gas- and particle-phase emission rates of 137 organic compounds quantified in the cigarette smoke are shown in Table 7.3. All of the semi-volatile and particle-phase organic compounds shown in Table 7.3 were quantified using the denuder/filter/PUF sampling train except for the 17 most volatile species which were quantified by the filter/PUF sampling train and are noted in Table 7.3 with a dagger. Nicotine is emitted at a rate of 4000 μg per cigarette smoked, the highest rate of any of the compounds identified, and is consistent with previously reported measurements (10). The compounds with the next highest emissions rates are isoprene and acetaldehyde which are emitted at rates of 3000 and 2120 μg per cigarette smoked, respectively.

Figure 7.2 shows the emission rates of the volatile hydrocarbons containing between 2 and 8 carbon atoms in the effluent from cigarette combustion, meat charbroiling, and wood combustion. As previously indicated the emissions rate of isoprene from cigarette smoking is very large compared to the emissions of other light hydrocarbons, almost twice the emissions rate of ethene and more than twice the emissions rate of propene. This is very different than the emissions of these compounds from meat charbroiling and fireplace combustion of wood where isoprene emissions are only a small fraction of the ethene and propene emissions. In addition the ratio of the emissions of ethene to propene in cigarette smoke is 1.3, compared to 5.1 and 2.6 for meat charbroiling and wood combustion, respectively. Although isoprene and propene are very reactive under many atmospheric conditions, the differences in these ratios could be useful in less reactive environments (i.e., nighttime, cold winter days, and some indoor environments) for the determination of the origin of gaseous pollutants. Isoprene has been used in the past to qualitatively distinguish cigarette smoke from the emissions of motor vehicles (12) and from the emissions of food cooking operations (13).

As can be seen in Figure 7.2, the abundance of the low molecular weight n-alkanes emitted from cigarette smoking decreases with increasing carbon number from ethane to n-pentane, a pattern which is also seen in the emissions from meat charbroiling and wood combustion. In contrast, however, the monoaromatic hydrocarbons in cigarette smoke show toluene emissions that exceed both benzene and xylene isomer emissions, while the emissions of the monoaromatic hydrocarbons from meat charbroiling and wood combustion both decrease with increasing carbon number from benzene to toluene to the xylenes.

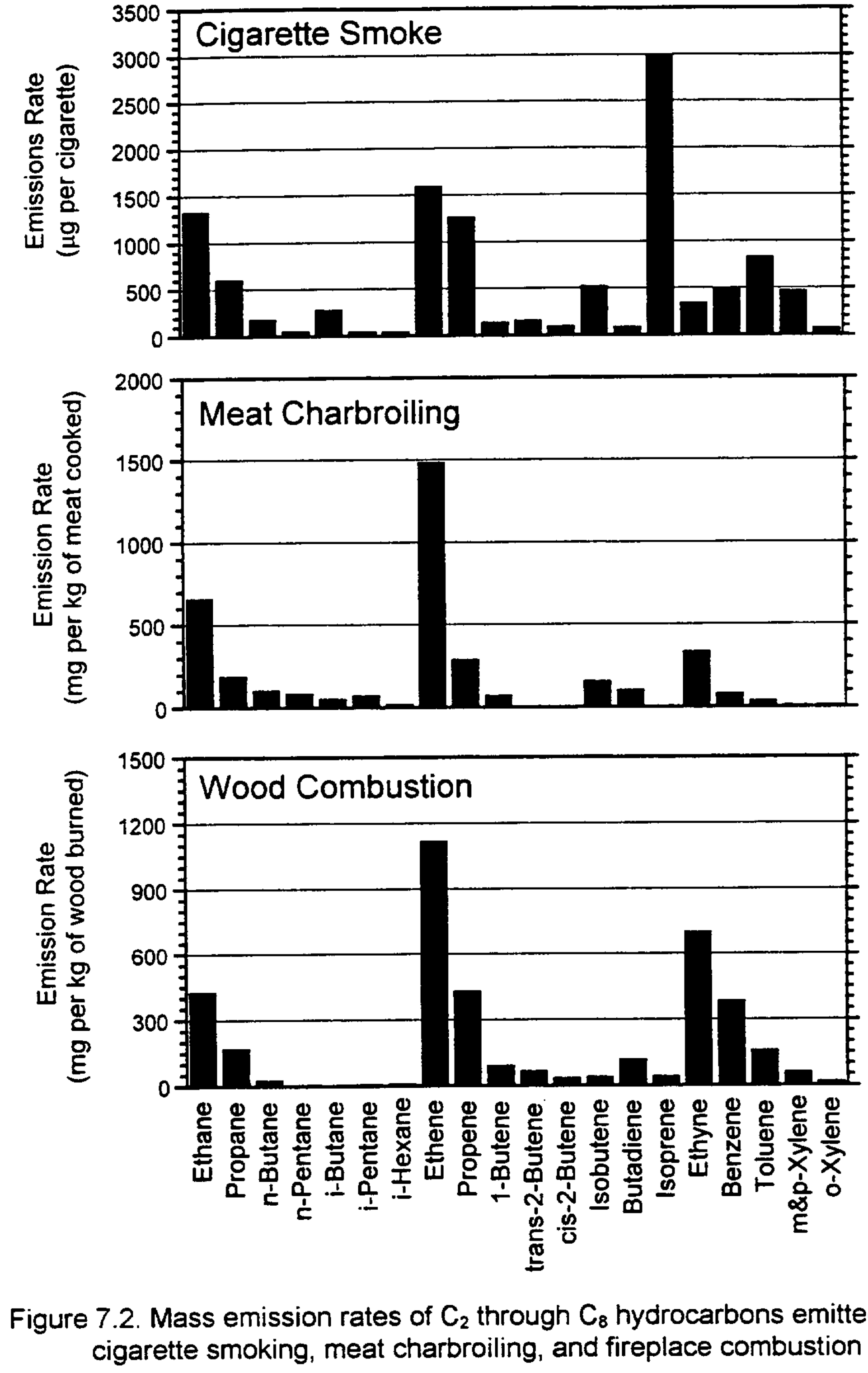

Figure 7.2. Mass emission rates of C_2 through C_8 hydrocarbons emitted from cigarette smoking, meat charbroiling, and fireplace combustion of wood.

The distributions of the light gas-phase carbonyls emitted from cigarette smoking, meat charbroiling, and wood combustion are shown in Figure 7.3. The ratio of the emissions of formaldehyde to acetaldehyde in cigarette smoke differs from that in wood combustion and meat charbroiling effluent. For cigarette smoke this ratio is 12.8 and for meat charbroiling and wood combustion this ratio is close to unity.

Several unusual semi-volatile and particle phase organic compounds have been identified and quantified in the emissions from cigarette smoking. The structures of these compounds are shown in Figure 7.4 and the gas- and particle-phase emission rates observed at the dilution rates of the present study are shown in Figure 7.5. As seen in Figure 7.5, nicotine emissions are more than 8 times greater than the emissions of any of the other semi-volatile organic compounds studied. Two other semi-volatile organics which are emitted at relatively high emission rates are triacetin and menthol. Both of these compounds are believed to be added to the cigarettes during manufacturing as triacetin is reported to be used as a flavor enhancer (14) and menthol is likely emitted from the menthol flavored cigarette. In contrast, neophytadiene, solanone, and geranyl acetone are derived from the tobacco content of the cigarettes smoked. They are not expected to be emitted from a large number of other sources. These three compounds are likely to suffer from high chemical reactivity under some atmospheric conditions due to the olefinic bonds and

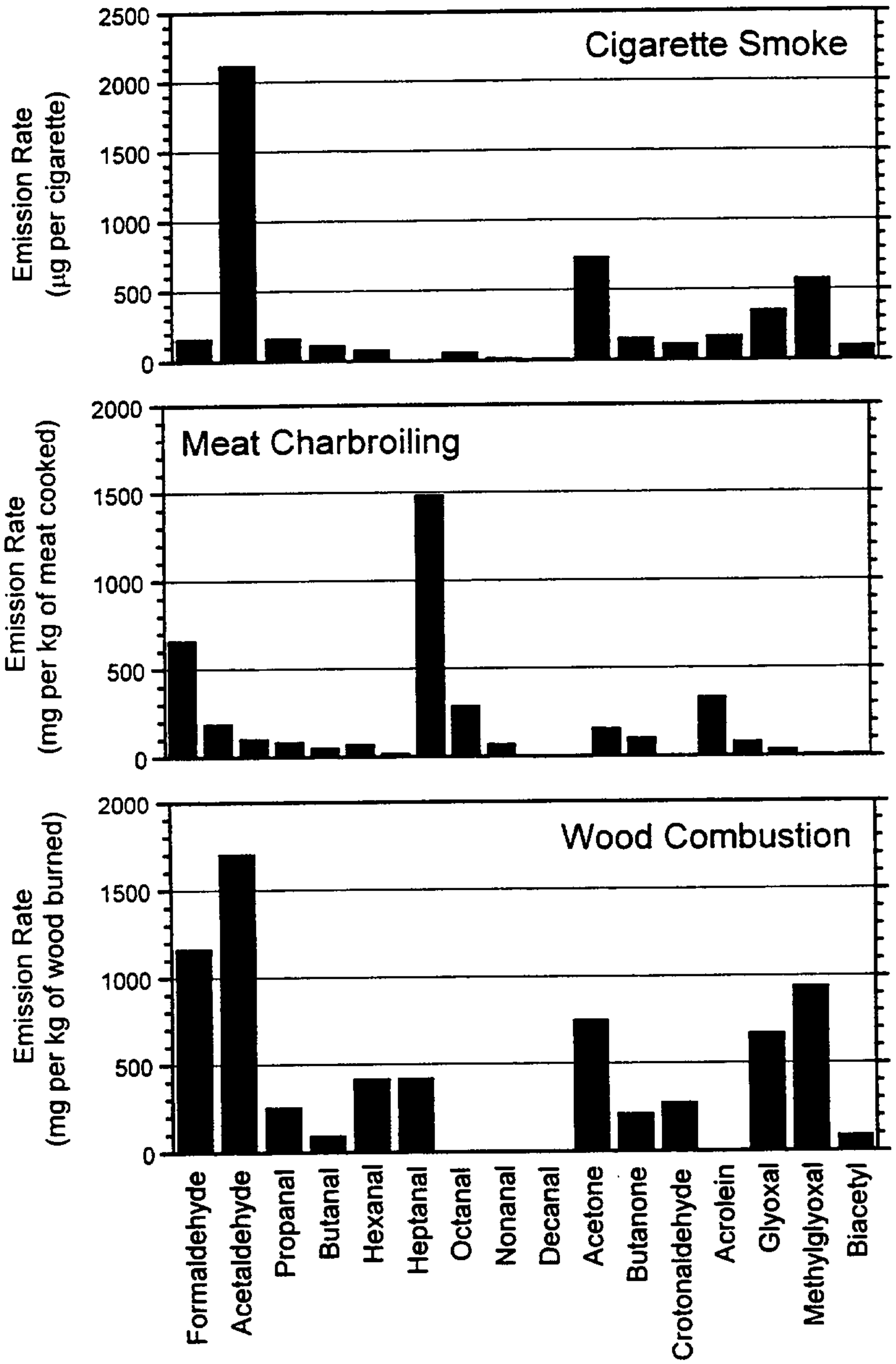

Figure 7.3. Mass emission rates of light gas-phase carbonyls emitted from cigarette smoking, meat charbroiling, and fireplace combustion of wood.

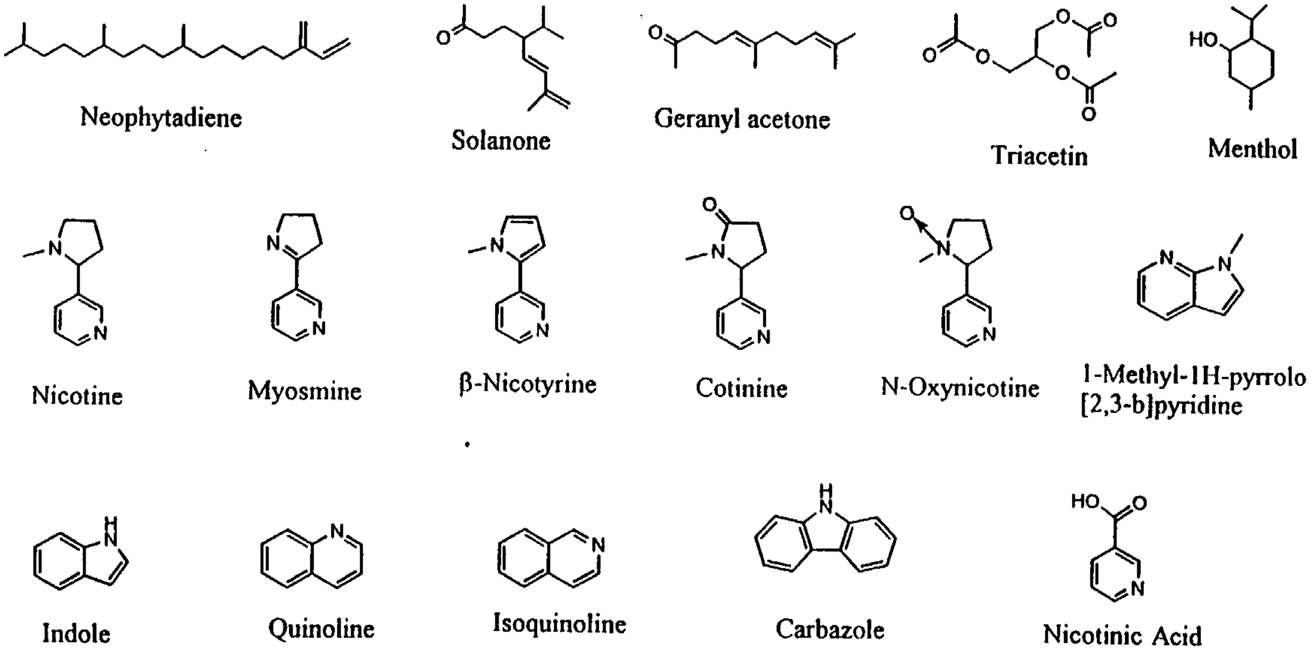

Figure 7.4. Chemical structures of selected semi-volatile organic compounds emitted from cigarette smoke.

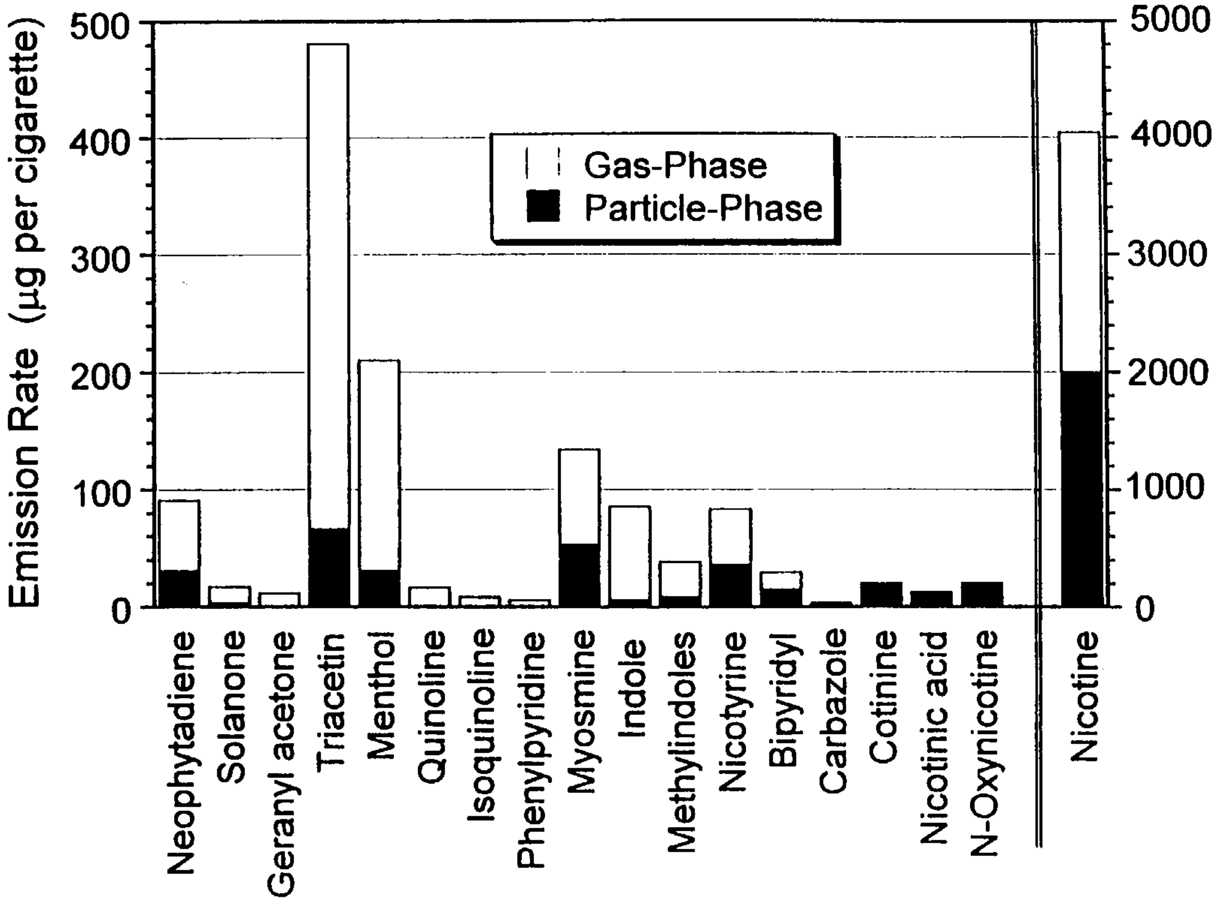

Figure 7.5. Gas and particle phase emission rate of semi-volatile organic compounds emitted from cigarette smoking.

carbonyl groups in these molecules. For this reason, these compounds should not be used routinely as tracers for cigarette smoke unless information is available that shows that these compounds will be adequately conserved in the air parcels of interest.

The remaining compounds shown in Figure 7.5 are organic compounds which contain nitrogen and tend to be characteristic of cigarette smoke. The most volatile of these, quinoline, isoquinoline, and phenylpyridine, are virtually entirely present in the gas-phase, whereas indole and the methyl-substituted indoles are found in noticeable quantities in the particle-phase but are still predominately in the gas phase. Myosmine, nicotyrine, and bipyridyl partition between the gas and particle phases to an extent similar to nicotine, with about half in the gas-phase and half in the particle-phase under the present experimental conditions. Carbazole, cotinine, nicotinic acid and N-oxynicotine are virtually completely in the particle phase and may supplement the use of the iso and anteiso-alkanes as atmospheric tracers for the particulate matter from cigarette smoke.

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Chapter 8

Organic Compounds from Industrial Spray Painting Operations

8.1 Introduction

Volatile organic compounds emitted from surface coating operations can be studied to determine their effect on urban air pollutant concentrations through the use of receptor-based air quality models that use organic compounds as tracers (1-4). Typically the source emissions profiles that describe the organic chemical composition of paint product vapors in these studies are based on the stated composition of the original product as reflected, for example, in the Material Safety Data Sheets (MSDS) that accompany the paint.

Certain aspects of the emissions from actual paint application simply cannot be reproduced from the manufacturer's ingredient list alone. In particular, selective segregation of some paint ingredients into the finished painted object, accompanied by removal of other ingredients by the emissions control system used on paint spray booths, argues that the direct measurement of the emissions from paint spray operations would be desirable. Further, when reported paint composition data are compared against atmospheric organic compound data often the only comparisons that can be made across both data sets are for the lowest molecular weight components of the paint vapors. Use of only the lowest molecular weight volatile organic compounds to trace the presence of the effluent from painting operations encounters difficulties because many of the most easily measured and most volatile components of paint mixtures are organic chemicals that are emitted from a wide variety of sources. Meanwhile, many of the more unusual compounds found in some paints (e.g., glycol-type compounds) are semi-volatile organics that are both difficult to collect and to analyze chemically in the atmospheric samples against which source samples must be compared. Data are needed on those unusual compounds found in paint formulations which are relatively easily assayed in an atmospheric sample. Finally, bulk analysis of the raw paint materials does not allow for measurements of the distribution of the emissions from paint spray coating operations between the gas and particle phases. For these reasons, the current study has been undertaken to directly measure the gas and particle phase emissions from paint spray coating operations using air pollutant sampling techniques that can be readily applied to characterize both air pollution source emissions and ambient atmospheric pollutant concentrations.

8.2 Experimental Methods

8.2.1 Source Sampling

Gas-phase and particle-phase emissions from paint spray coating operations were sampled at the outlet of the exhaust vent of a licensed paint spray booth located in the Los Angeles area. Sampling took place downstream of the particle filters in the paint booth exhaust system, which was operated at an air flowrate of 180,000 lpm. Solvent vapors and paint particle overspray from the spraying operation that exited the booth's emissions control system were accompanied by ambient air which was pulled into the paint booth by the ventilation system exhaust fan. Since the ambient air used for dilution contained atmospheric pollutants, the air entering the paint booth was sampled by the same sampling techniques as used for the exhaust emissions during these source tests. Emission rates were determined after background subtraction of the pollutant concentrations entering the paint booth.

Samples were withdrawn isokinetically from the outlet of the exhaust system into AIHL-design cyclone separators (5) that removed particles with aerodynamic diameters greater than 1.8 μm. Gases and particles with diameters less than 1.8 μm passed through the cyclones and were sampled by a series of sampling trains operated in parallel. Semi-volatile and fine particle-phase organic compounds were collected continuously downstream of these cyclone separators by the denuder/filter/PUF sampling train and a filter/PUF sampling train. Details of both sampling configurations are discussed in Chapter 2. One denuder based sampling train and one filter/PUF sampling train were operated during the paint spray booth source tests.

A third cyclone-based sampling train also was used to measure the emissions of fine particulate matter, carbonyls, organic acids, and low molecular weight gas-phase hydrocarbons. This sampling train is also discussed in Chapter 2.

The dilution air sampling units were located at the inlet of the paint booth ventilation system. Pollutant concentrations in the inlet air were measured using one cyclone/filter/PUF sampling unit and one cyclone/filter pack/SUMA canister/carbonyls sampling unit, as was used for measuring the paint booth exhaust emissions. As shown in Chapter 2, the total mass collected by the cyclone/denuder/filter/PUF sampling train and by the cyclone/filter/PUF sampling train show excellent agreement, such that minimal problems arise when air pollutant concentrations in the dilution air obtained by the filter/PUF sampling train are subtracted from the source samples collected with the denuder/filter/PUF sampling train.

8.2.2 Source Testing Procedure

The oil-based paint used in the present study was an oil-based primer (Z-Prime, Zehrung Corp., Portland, OR). The primer was cut with lacquer thinner (3:1 primer:lacquer thinner) and was sprayed with a high-volume low-pressure air gun which was operated at a paint gun cup pressure of 7 psig. A total of 1.9 liters of cut primer was sprayed by a professional painter over a period of 40 minutes. Sample collection commenced 1 minute prior to the start of spray painting and ended 1 minute after painting was finished.

Suprema Latex low gloss enamel (Dunn-Edwards Corp., Los Angeles, CA) was used as the water-based paint in the present study. The water-based paint was cut with water (3:2 paint:water) and was sprayed with the same air gun as used for the oil-based paint. Over a period of 40 minutes 2.4 liters of cut paint was sprayed. The same sampling protocol was used for both source tests.

8.2.3 Organic Chemical Analysis

The analytical procedures used in the present study for the identification and quantification of semi-volatile and particle-phase organic compounds in air pollutant source emissions are the same as was used for the other source tests described in Chapters 2 though 7. Details are provided in Chapter 2.

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.

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 non-quantitative secondary standard that could be used for unique identification of the organic compounds. An example of such a secondary standard is the use of the small amounts of 2,2,4-trimethyl-1,3-pentanediol diisobutyrate present in the Texanol standard as a secondary standard. Quantification of compounds identified using secondary standards has been estimated from the response factors for compounds having similar retention times and chemical structures.

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) (see Chapter 2). Carbonyls collected by the C_{18} impregnated cartridges were analyzed by liquid chromatography/UV detection (see Chapter 2).

8.3 Results

8.3.1 Fine Particle Emission Rates and Composition

Fine particle emission rates from the oil-based and the water-based spray coating operations were 104 ± 40 and 74.8 ± 29.0 mg per liter of cut-paint sprayed, respectively. Clearly, the fine particle mass emissions from these operations were reduced significantly by the filtration system present in the paint booth exhaust system. Due to the fact that the exhaust filters were located at the inlet to the exhaust system, samples of the unfiltered emissions could not be obtained from the exhaust duct. The elemental composition of the fine particle mass collected downstream of the exhaust filters are shown in Table 8.1.

Organic carbon and titanium are the largest contributors to the fine particle emissions from the water-based paint spraying operations. Assuming that the titanium is in the form of titanium dioxide and that the ratio of fine particle organic compound mass to organic carbon is 1.4, then the emissions of titanium dioxide plus particulate organic compound mass is not significantly different from the gravimetrically measured fine particle mass emission rate, indicating that indeed these species account for the entirety of the emissions from the water-based paint spraying test. The ratio of fine particulate organic compound mass to fine particle titanium dioxide is 2.4 in the water-based paint fine particle emissions.

Table 8.1. Average Fine Particle Emission Rate and Fine Particle Chemical Composition from Architectural Spray Coating Operations (Values shown in boldface are greater than zero by at least two standard errors).

	Oil Based Paint	Water Based Paint
Fine Particle Emissions Rate (AVG ± STD)	**104 ± 40 mg per liter sprayed**	**74.8 ± 29.0 mg per liter sprayed**
Elemental and Organic Carbon (Wt % of Fine Particle Mass)		
Organic Carbon	**22.4 ± 3.6**^{a}	**35.3 ± 4.2**^{a}
Elemental Carbon	1.0 ± 2.0	0.4 ± 2.3
X-ray Fluorescence (Wt % of Fine Particle Mass)		
Aluminum	**6.26 ± 0.88**	1.13 ± 1.84
Silicon	**7.57 ± 0.60**	0.05 ± 0.51
Phosphorus	0.00 ± 0.71	0.00 ± 0.72
Sulfur	0.00 ± 0.31	0.00 ± 0.35
Chlorine	0.49 ± 0.29	0.00 ± 0.79
Potassium	0.59 ± 0.74	0.00 ± 0.75
Calcium	**6.60 ± 0.49**	0.98 ± 0.50
Titanium	**38.5 ± 3.5**	**12.5 ± 3.9**
Vanadium	0.00 ± 2.60	0.00 ± 1.59
Chromium	0.00 ± 0.72	0.00 ± 0.36
Manganese	0.00 ± 0.33	0.00 ± 0.27
Iron	0.00 ± 0.10	0.10 ± 0.10
Cobalt	0.00 ± 0.18	0.02 ± 0.19
Nickel	0.00 ± 0.18	0.00 ± 0.18
Copper	0.00 ± 0.19	0.00 ± 0.19
Zinc	0.00 ± 0.20	0.00 ± 0.21
Gallium	0.00 ± 0.27	0.00 ± 0.31
Arsenic	0.00 ± 0.32	0.00 ± 0.35
Selenium	0.00 ± 0.17	0.00 ± 0.18
Bromine	0.00 ± 0.15	0.03 ± 0.17
Rubidium	0.02 ± 0.14	0.00 ± 0.16
Strontium	0.00 ± 0.16	0.01 ± 0.18
Yttrium	0.00 ± 0.20	0.00 ± 0.22
Zirconium	0.13 ± 0.24	0.00 ± 0.26
Molybdenum	0.00 ± 0.43	0.01 ± 0.48
Palladium	0.00 ± 1.17	0.00 ± 1.26
Silver	0.00 ± 1.40	0.00 ± 1.51
Cadmium	0.14 ± 1.50	0.00 ± 1.54
Indium	0.00 ± 1.71	0.00 ± 1.88
Tin	0.00 ± 2.14	0.00 ± 2.34
Antimony	0.00 ± 2.53	1.42 ± 2.85
Barium	0.00 ± 9.30	3.78 ± 10.3
Lanthanum	2.23 ± 12.3	3.41 ± 13.8
Mercury	0.00 ± 0.38	0.00 ± 0.42
Lead	0.00 ± 0.47	0.09 ± 0.53

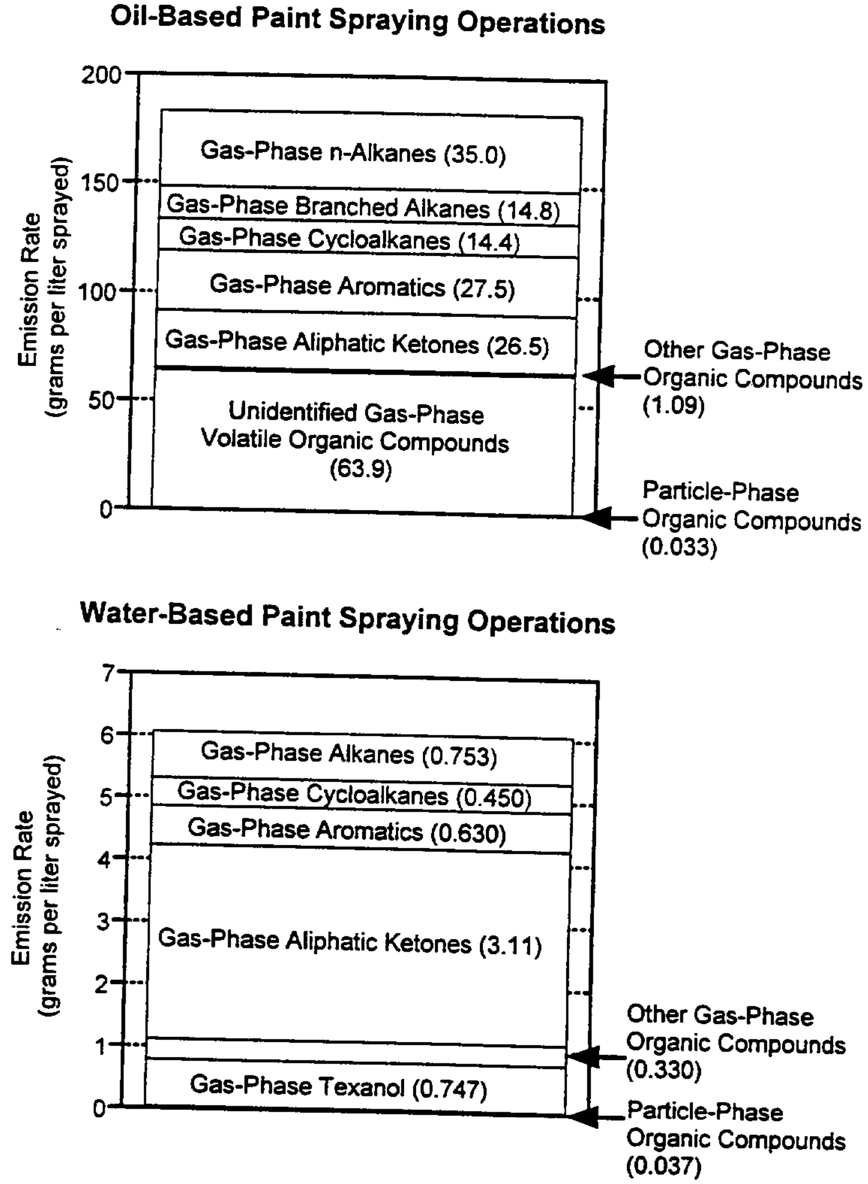
Notes: (a) measured on undenuded filter

Fine particle emissions from oil-based spray coating operations also are influenced largely by organic carbon and titanium which comprise 22.4% and 38.5% of the fine particle mass emissions, respectively. If the titanium once again is expressed as titanium dioxide and fine particulate organic carbon emissions are converted to an estimate of organic compound mass by multiplying by a factor of 1.4, then the ratio of organic compound mass to titanium dioxide mass is 0.5 for the fine particles emitted from spray coating with oil-based paint, much lower than in the fine particle emissions from the water-based paint spraying operations. In addition to organic compounds and titanium dioxide, the fine particle mass emitted from the oil-based paint spraying contains about 6 to 8 percent each of aluminum, silicon, and calcium.

The concentrations of water-soluble sulfate ion, ammonium ion, chloride ion, nitrate ion, and sodium ion in the exhaust emissions from the paint spray booth were not significantly different from the concentrations of these species in the dilution air input to the paint spray booth, such that the emissions of these species from the spray coating operations are lower than can be detected in this study.

8.3.2 Mass Balance on Organic Compound Emissions

Figure 8.1 shows a mass balance on the organic compounds measured during the spray coating source tests in the current study. It should be noted



Oil-Based Paint Spraying Operations

Water-Based Paint Spraying Operations

Figure 8.1. Mass balance on the non-methane organic compounds measured in the emissions from oil-based paint spray coating and water-based paint spray coating operations conducted in an industrial-scale paint spray booth.

that some highly polar volatile organic compounds such as ethylene glycol are not detected by the non-methane organic gas analysis (TNMOG, EPA Method TO-12) and therefore do not appear in the emissions from this study. Although the TO-12 method does not respond to formaldehyde and has only a reduced response for other carbonyls, the carbonyls can be properly accounted for since these compounds are measured by the DNPH-impregnated cartridges. While the absence of data on compounds like ethylene glycol appears to present a problem, it is important to note that the analytical methods used here are exactly the same as the methods commonly used to monitor ambient air quality, so these species are consistently absent from the ambient data sets as well. In the case of particle-phase carbon, the thermal evolution technique used here responds to all carbonaceous material and thus the entire mass emissions rate of fine particulate organic carbon is measured.

As seen in Figure 8.1, gas-phase emissions dominate the organic compounds released from both types of spray coating operations. The total organic compound emissions from the oil-based paint spraying source test amount to 183 grams per liter of solvent-cut paint sprayed, while particulate carbon emissions account for only 0.033 grams per liter of solvent-cut paint sprayed. Gas-phase emissions show significant contributions from n-alkanes, branched alkanes, cycloalkanes, aromatics, and ketones. The gas-phase organic compound emissions from the water-based paint spraying operations are significantly lower at 6.0 grams per liter of water-cut paint sprayed. These gas-phase emissions are about half from aliphatic ketones, accompanied by smaller but significant contributions from alkanes, cycloalkanes, aromatics, and Texanol. Particle phase organic carbon emissions from the water-based paint spraying operations are similar to the oil-based paint spraying at 0.037 grams of fine particulate matter per liter of water-cut paint sprayed.

8.3.3 Emission Rates of Individual Organic Compounds

The organic compounds quantified in the emissions from the spray coating operations studied here are listed in Table 8.2. The major components of the emissions for both water-based and solvent-based spray coating operations are shown in Figure 8.2. Emissions from the water-based spray coating operation are dominated by acetone, butanone, and Texanol. Acetone and butanone are both emitted at rates of approximately 1400 mg per liter of solvent-cut paint sprayed and Texanol is emitted at 763 mg per liter sprayed. The emissions of acetone and butanone from spray coating with the oil-based primer (11400 and 15100 mg per liter sprayed, respectively) are approximately ten times the emissions from water-based paint spraying (1410 and 1510 mg per liter sprayed, respectively). However, Texanol emissions are about ten times less from the oil-based paint spraying than from the water-based paint spraying. The oil-based paint spraying also results in significant emissions of C_7 through C_{10} n-alkanes, branched alkanes, aromatics and methylcyclohexane. Much of

Table 8.2. Organic Compounds Present in the Emissions from an Industrial-Scale Paint Spray Coating Booth.

Compound	Oil Based Paint (mg per liter of solvent cut paint sprayed)		Water Based Paint (mg per liter of solvent cut paint sprayed)		Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase	
n-Alkanes					
Propane	10				a, c
n-Butane	110		10		a, c
n-Pentane	10				a, c
n-Hexane	10				a, c
n-Heptane	6480		200		a, c
n-Octane	12000		20		a, c
n-Nonane	4660		20		a, c
n-Decane	9980		40		a, c
n-Undecane	1460		60		a, d
n-Dodecane	200		30		a, d
n-Tridecane	3		2		b, d
n-Tetradecane	1				a, d
Branched alkanes					
i-Butane	10				a, c
i-Pentane	10		10		a, c
2,4-Dimethylpentane	10				a, c
2-Methylhexane	460		40		a, c
2,3-Dimethylpentane	190		20		a, c
3-Methylhexane	1010		70		a, c
2,2,4-Trimethylpentane	1080		40		a, c
2,5-Dimethylhexane	1120		30		a, c
2,4-Dimethylhexane	840		30		a, c
2,3,4-Trimethylpentane	160				a, c
2,3-Dimethylhexane	590		10		a, c
2-Methylheptane	5440		40		a, c
3-Ethylhexane	3830		30		a, c
Saturated cycloalkanes					
Cyclohexane	30				a, c
Methylcyclohexane	14400		450		a, c
Aromatic hydrocarbons					
Toluene	9620		260		a, c
Ethylbenzene	2860		50		a, c
m & p-Xylene	8830		210		a, c
o-Xylene	4630		80		a, c
1,2,4-Trimethylbenzene	1590		30		a, c
Aliphatic aldehydes					
Formaldehyde	120		30		a, e
Acetaldehyde	200		210		a, e

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series.

Sample collection notes: (c) collected in SUMA canister. (d) collected on denuder/filter/PUF sampling train. (e) collected on DNPH impregnated C_{18} cartridges. See text for details.

Additional Notes: † 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.

Table 8.2. (continued - page 2)

Compound	Oil Based Paint (mg per liter of solvent cut paint sprayed)		Water Based Paint (mg per liter of solvent cut paint sprayed)		Notes
	Gas Phase	Particle Phase	Gas Phase	Particle Phase	
Aliphatic aldehydes					
Propanal	70		30		a, e
Hexanal	30		20		a, e
Aliphatic ketones					
Acetone	11400		1510		a, e
Butanone	15100		1410		a, e
4-Methyl-2-pentanone	420		190		a, e
Dicarbonyls					
Glyoxal	40		40		a, e
Methylglyoxal	10				a, e
Other compounds					
2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate (Texanol)	76.6	4.6	747	18.1	a, d
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	5.8	0.5	5.6		b, d
2-Butoxyethanol†	530		102		b, d
2-(2-Butoxyethanoxy)ethanol	40.5		12.7		b, d

Identification notes: (a) authentic quantitative standard. (b) authentic quantitative standard for similar compound in series.

Sample collection notes: (c) collected in SUMA canister. (d) collected on denuder/filter/PUF sampling train. (e) collected on DNPH impregnated C_{18} cartridges. See text for details.

Additional Notes: † 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.

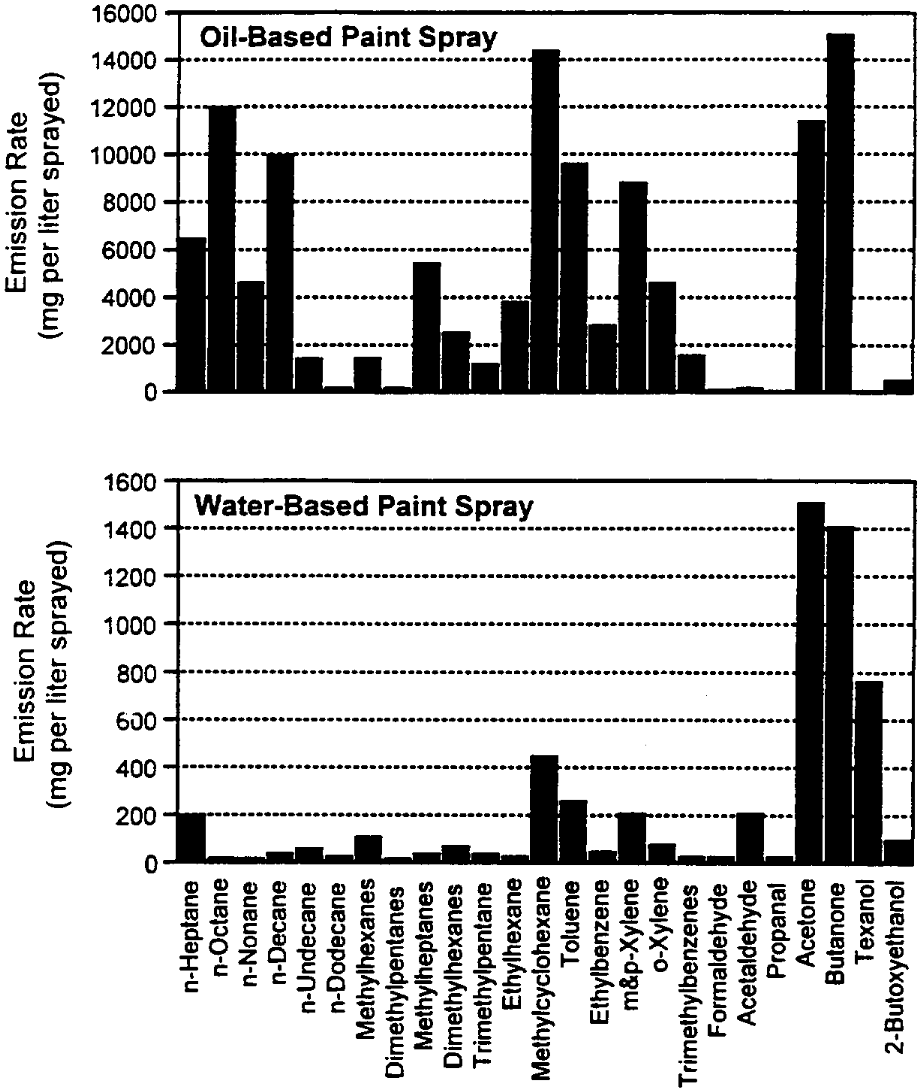


Figure 8.2. Mass emission rates for selected individual organic compounds emitted from oil-based paint spray coating and water-based paint spray coating operations.

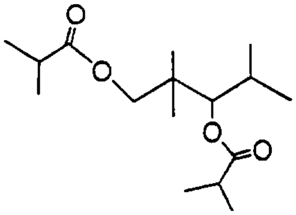
these emissions are due to the cutting solvent needed to properly spray the paint with a spray gun.

The only organic compounds identified in the particle phase were Texanol and the diisobutyrated analog of Texanol, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. The remainder of the organic mass in the particle-phase is unextractable and non-elutable under the conditions of this experiment.

8.3.4 Texanol as a Tracer for Water-Based Spray Coating Operations

Texanol is produced by Eastman Kodak and is added to water-based paint to enhance the coating properties of the paint (6). Texanol has two isomers both of which are found in technical grade Texanol. The chemical structures of these two isomers are shown in Figure 8.3. In addition, the diisobutyrate analog of Texanol was found in smaller but noticeable quantities in a sample of technical grade Texanol purchased from ChemService Inc. (West Chester, PA). The structure of the diisobutyrate form also is shown in Figure 8.3. Analysis of the water-based paint used in this study showed that the relative concentration of the two monoisobutyrate and the diisobutyrate species in the paint was similar to the relative abundance of these compounds found in the technical grade Texanol sample that was analyzed. It is therefore expected that all three forms will be present in the urban atmosphere. As previously noted, Texanol has not been reported in the ambient atmosphere, largely due to

2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate



2,2,4-Trimethyl-1,3-pentanediol diisobutyrate

Figure 8.3. Chemical structures of the organic compounds present in technical grade Texanol.

the fact that sampling techniques for semi-volatile organic compounds must be employed to properly collect this semi-volatile species. Smaller concentrations of Texanol were measured in the solvent-cut paint used for the oil-based spray painting source tests and in the emissions from this test. It is unclear if Texanol was used as an ingredient in the primer manufacturing process or if contamination of the primer occurred in the paint shop.

8.4 References

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Chapter 9

Source Reconciliation of Atmospheric Gas-Phase and Particle-Phase Pollutants Using Organic Compounds as Tracers

9.1 Introduction

Most chemical mass balance (CMB) receptor models applied to air quality problems have been employed to calculate either the source origin of particle-phase pollutants (Miller et al., 1972; Friedlander, 1973; Cass and McRae, 1983) or the source origin of gas-phase pollutants (Harley et al., 1992; Scheff and Wadden, 1993; Fujita et al.,1994). In a few cases, particle-phase tracers have been incorporated into the gas-phase pollutant models to allow additional sources to be resolved by the receptor modeling calculations. For the same reasons, gas-phase species occasionally have been incorporated into receptor models for particulate matter (Harrison et al., 1996; Hawthorne et al., 1992; Khalil et al., 1983), but these models have not been expanded to simultaneously determine the source contributions to entire suites of gas-phase and particle-phase pollutants.

The ability to simultaneously identify the origin of gas- and particle-phase pollutants is desirable since regulatory agencies are often faced with the task of developing combined emission control strategies that will both reduce gaseous and particulate pollutant concentrations. In addition, the comprehensive and simultaneous apportionment of atmospheric gaseous and particulate pollutants allows maximal source separation since the information contained in the emissions profiles included for the low molecular weight gas-phase species, the semi-volatile species, and the non-volatile particle-phase species all can be exploited. To this end, in the present study a comprehensive organic compound-based receptor model for gas-phase, semi-volatile and particulate air pollutants is developed and applied to atmospheric data collected during a severe photochemical smog episode in Southern California during the summer of 1993. The present study is the first application of an organic compound-based receptor model to determine the source contributions to fine particulate matter concentrations during a severe photochemical smog episode.

9.2 Experimental Methods

9.2.1 Ambient Samples

The ambient data used in the present study were collected during the summer of 1993 in the South Coast Air Basin of California that surrounds Los Angeles. The concentrations of hundreds of gas-phase, semi-volatile and particle-phase organic compounds were measured over a two-day smog episode during which peak 1-hour ozone concentrations reached 0.29 ppm. Conditions during this study are described in detail elsewhere (Fraser et al., 1996; Fraser et al., 1997; Fraser, 1998) and are briefly summarized here. Data were collected during the period September 8-9, 1993, at four urban air monitoring sites: Long Beach, Central Los Angeles, Azusa, and Claremont, California. These sites are shown in Figure 1 of Fraser et al. (1996). Data were taken over eight 4-hour sampling periods centered within consecutive 6-hour time intervals during the 48-hour study. The ambient data used in the present model evaluation effort were averaged by site thereby providing time-averaged ambient concentration data for the 48-hour sampling study at each of the four monitoring sites. The data collected by Fraser et al. (1996) which were used in the present study consist of ambient measurements of total non-methane organic gases, gas-phase volatile hydrocarbons, gas-phase semi-volatile organic compounds, fine particle-phase organic compounds, and fine particle mass and elemental composition. Gas-phase hydrocarbons and non-methane organic gases were collected in polished stainless steel SUMA canisters and were analyzed by gas chromatography/flame ionization detection (GC/FID). Fine particulate mass concentrations and bulk chemical composition were determined from filter samples collected downstream of AIHL-design cyclone separators (John and Reischl, 1980). Teflon membrane filters (47 mm diameter Teflo, Gelman) were used for collecting fine particle samples for gravimetric mass determination and for measurement of trace metals by X-ray fluorescence analysis and inorganic ions by ion chromatography and colorimetry. Fine particle samples collected on quartz fiber filters (47 mm diameter Tissuequartz 2500 QAO, Pallflex) were used for organic and elemental carbon analysis as described by Birch and Carey (1996). The concentrations of individual fine particle organic compounds and semi-volatile organic compounds were measured by gas chromatography/mass spectrometry (GC/MS) from samples collected using a high volume dichotomous virtual impactor (Solomon et al., 1983) that was modified by Fraser et al. (1997) for the collection of semi-volatile organic compounds along with particulate matter. Using this sampler fine particle mass is collected on a quartz fiber filter (102 mm diameter Tissuequartz 2500 AQO, Pallflex) and semi-volatile organic compounds are collected downstream of the quartz fiber filter on five consecutive polyurethane foam (PUF) cartridges (7.6 cm diameter by 2.5 cm long, density = 0.022 g cm^{-3}, ILD = 30, Atlas Foam).

The sample handling and extraction procedures employed to quantify semi-volatile vapor-phase and particle-phase organic compounds in atmospheric samples have been discussed previously (Fraser et al., 1997). Before the quartz fiber filters and PUF cartridges were extracted, they were spiked with deuterated internal recovery standards. Extracts were filtered, combined, and reduced in volume to approximately 250 ml, and were split into two separate fractions. One fraction was derivatized with diazomethane to convert organic acids to their methyl ester analogues which are amenable to GC/MS identification and quantification. Both the derivatized and underivatized sample fractions from all of the sample substrates were analyzed by GC/MS. 1-Phenyldodecane was used as a co-injection standard for all sample extracts and standard runs. Hundreds of authentic standards have been prepared for the positive identification and quantification of the organic compounds found in the ambient samples.

The semi-volatile and fine particle hydrocarbons data from Fraser et al. (1997) are scaled upward across all non-aromatic compounds by a factor of 1.7 to correct an error in the reported air volumes sampled.

9.2.2 Source Samples

Emissions from major urban air pollution sources were measured including gas-phase, semi-volatile, and particle-phase organic compounds, plus fine particle emission rates and fine particle elemental composition (Chapters 2-8). A dilution source sampler was employed to dilute hot exhaust emissions with HEPA-filtered and activated carbon-filtered dilution air to bring the source effluent to near ambient temperatures and pressures. The sampler was equipped with a residence time chamber that provides time for the cooled semi-volatile gases to equilibrate between the gas and particle phases under conditions similar to those in the plume downwind of the stack. The diluted exhaust was sampled from the residence time chamber by the same analytical techniques used for the ambient air pollutant measurements discussed above.

A detailed description of the dilution source sampler has been presented previously (Chapter 2). Using the dilution sampler, fine particle organic compound emissions were sampled by two simultaneous sampling trains, a denuder/filter/PUF system and a filter/PUF system. In both sampling trains, diluted exhaust was withdrawn from the residence time chamber of the source sampler through AIHL-design cyclone separators that are designed to remove coarse particles. The denuder/filter/PUF sampling train uses an XAD-coated annular denuder (4 channel, 400 mm long, URG) followed by three quartz fiber filters (47 mm diameter Tissuequartz 2500 QAO, Pallflex) operated in parallel followed by two PUF cartridges (5.7 cm diameter by 7.6 cm long; density = 0.022 g cm^{-3}, ILD = 30, Atlas Foam) operated in series. In the denuder/filter/PUF sampling train, semi-volatile organic compounds are collected on the XAD-coated denuder and particulate matter and particle-associated semi-volatile organic compounds are collected on the filter. The downstream PUF cartridges collect any particle-associated semi-volatile organic compounds that volatilize off of the quartz fiber filter. The filter/PUF sampling unit operates according to the same principle as the ambient filter/PUF samplers discussed above. Chemical analysis to quantify individual organic compounds in the source emissions was conducted by gas chromatography/mass spectrometry (GC/MS) as described previously for the ambient samples. As shown in Chapter 2 the total mass of semi-volatile and particle-phase organic compounds collected by the denuder/filter/PUF and filter/PUF sampling trains are in good agreement.

Also connected to the residence chamber of the dilution source sampler was a cyclone-based sampling unit for the collection of fine particulate matter and gas-phase hydrocarbons. In this sampling train, fine particulate matter collected on a quartz fiber filter (47 mm diameter, Pallflex Tissuequartz 2500 QAO) was used for EC/OC determination by the same method as described for the ambient samples. Fine particle samples collected on Teflon membrane filters (47 mm diameter, Gelman Teflo, 2 μm pore size) were used for gravimetric determination of the fine particle mass emissions rate and for analysis of trace metals and inorganic ions by the same analytical techniques as used for the ambient samples. Downstream of one of the Teflon filters, the sample flow was divided and a small portion of the flow was used to fill a 6 liter polished stainless steel SUMA canister for the collection of non-methane volatile hydrocarbons ranging from C_1 to C_{10}. The 6 liter SUMA canister was filled continuously at a constant flowrate set to fill the canister over the entire source test cycle. The analysis of the volatile hydrocarbons in the source emissions again were analyzed by the same analytical techniques as described for the ambient samples.

The composition of the emissions from gasoline-powered motor vehicle engines, diesel engines and meat cooking operations measured by the source sampling system just described form the basis for the organic chemical composition source profiles used for these sources by the organic tracer model. The gasoline-powered motor vehicle tests and the diesel-powered motor vehicle tests were conducted in the summer of 1996 by Schauer et al. (Chapters 4 and 5) using commercial fuels and 13 motor vehicles taken from the in-use fleet in Southern California. The diesel trucks tested in Chapter 4 were medium-duty diesel trucks which showed lower fine particle elemental carbon emission rates than the heavy-duty diesel trucks measured earlier by Hildemann et al. (1991). In the present receptor modeling study, organic compounds emitted from diesel trucks are represented by the diesel engine source profile of Chapter 5 but the elemental carbon content of diesel engine exhaust is increased to give the same EC/OC ratio as measured by Hildemann et al. (1991) for heavy duty diesel trucks. The meat charbroiling source profile described in Chapter 2 is used to represent commercial and residential meat charbroiling .

In addition, several other source emissions profiles were required for use in the present receptor modeling study. The chemical composition of fine particle paved road dust was measured by resuspending road dust collected in the south coast region of Southern California into a cleaned glove box followed by sampling through AIHL-design cyclone separators to remove coarse particles and collection on quartz fiber filters and Teflon filters, with chemical analysis as described above for elemental composition and organic compound quantification. Gas-phase pollutant measurements were not made for the road dust sample as road dust is not a significant source of gas-phase pollutants. (Road dust emissions profiles are included in Appendix B). Particulate emissions profiles for vegetative detritus and residential natural gas combustion were taken from Rogge et al. (1993a, 1993b). Gas-phase hydrocarbon and VOC emissions data from these sources were not available, but these emissions are thought to be relatively small. Commercial diesel fuel obtained in Southern California in the summer of 1996 was analyzed by the same analytical techniques as used for semi-volatile and particle-phase organic compounds to obtain an emissions profile for whole diesel fuel vapors. The composition of a 1995 sample of Southern California gasoline, constructed as a market share weighted average of the product of the five largest gasoline retailers in Southern California, was used to define the organic compound distribution in whole gasoline vapors. The 1995 gasoline composition data were modified to match conditions during the summer 1993 atmospheric experiments; these changes reflect the reduction in benzene and the increase in MTBE content of gasoline that occurred between the summer of 1993 and the summer of 1995.

A gasoline headspace vapor profile corresponding to the estimated 1993 gasoline composition and a natural gas leakage profile also are needed for the present study. Conner et al. (1995) have shown that the composition of the headspace vapors above a liquid pool of gasoline can be accurately calculated from the liquid gasoline composition and the Raoult's law coefficients for the gasoline components in a gasoline mixture. The gasoline headspace vapor composition for this study was therefore calculated from the composition of the whole gasoline sample described above using Raoult's law coefficients calculated from the data collected by Aulich et al. (1994). (Whole gasoline and gasoline headspace vapor emissions profiles are included in Appendix A). The natural gas leakage profile was taken from Harley et al. (1992).

9.3 Source/Receptor Reconciliation

9.3.1 Chemical Mass Balance Approach

Chemical mass balance (CMB) receptor models that use organic compounds as mass balance species have been demonstrated on several occasions (Harley et al., 1992; Scheff and Wadden, 1993; Fujita et al.,1994; Schauer et al., 1996). In the CMB model, the source contributions are calculated by determining the linear combination of source fingerprints that best reconstruct the ambient concentration data set. The chemical mass balance model can be represented by a set of linear equations as follows:

$$c_{ik} = \sum_{j=1}^{m} a_{ij} s_{jk} \qquad (1)$$

where c_{ik}, the concentration of chemical species i at receptor site k, equals the sum over m source types of the product of a_{ij}, the relative concentration of chemical constituent i in the emissions from source j, and s_{jk}, the increment to the total pollutant mass concentration at receptor site k originating from source j. The system of equations (1) states that the ambient concentration of each mass balance species must result only from the m sources included in the model and that no selective loss or gain occurs in transport from the source to the receptor site. Therefore, the selection of mass balance compounds must be limited to: (1) species in which all major sources are included in the model, (2) species that do not undergo selective removal by chemical reaction or other mechanisms between the source and the receptor site, and (3) species which are not significantly formed by chemical reactions in the atmosphere.

In the present study, the system of equations (1) is solved using the CMB7 receptor modeling computer program (Watson et al., 1990). That algorithm employs an effective variance weighted least-squares solution to the problem of determining the unknown source contributions, s_{jk}, given the relative concentrations of the chemical substances in the emissions from the sources (a_{ij}) and the atmospheric pollutant concentrations, c_{ik}.

9.3.2 Selection of Sources and Organic Compounds

The selection criteria for the particle-phase organic compounds which are used as tracers in the current study are based on the previous work (Schauer et al., 1996). Selection of the gas-phase hydrocarbon tracers used in the combined gas and particle phase tracer model is based on the criteria outlined by Harley et al. (1992). As previously indicated the motor vehicle source tests used in this analysis were conducted using commercially distributed fuels approximately 3 years after the atmospheric measurements were made. In this time period, no significant changes in diesel fuel formulation were reported but changes were made to the composition of gasoline. Changes in the benzene and MTBE content of gasoline between 1993 and 1995 are well documented and corrections have been made to the emissions profiles used in this study for whole gasoline vapors and gasoline headspace vapors, but the effect of these fuel composition changes on tailpipe emissions are more difficult to address. Data from the 1993 Van Nuys tunnel study conducted by Fraser et al. (1998) also show methylcyclopentane and methylcyclohexane concentrations in tunnel air that are much lower in the 1993 than would be expected from the tailpipe exhaust and gasoline vapor profiles obtained in 1996 and 1995, respectively. The apparent increase in the methylcyclopentane and methylcyclohexane content of gasoline between 1993 and 1995 is likely due to the direct introduction of these compounds into gasoline accompanied by the removal of these compounds from the catalytic reformer feedstock in the petroleum refinery in order to prevent the formation of benzene from these methylcyloalkanes. For these reasons, methylcyclopentane, methylcyclohexane, benzene, and MTBE are not used as mass balance species in the model.

Methane is used to help trace the leakage of natural gas to the Southern California urban atmosphere. The background air entering the South Coast Air Basin of Southern California contains methane at a concentration of approximately 1700 ppb (Harley et al., 1992) which was subtracted from the measured methane values at each air monitoring site.

9.4 Results

9.4.1 Comprehensive Apportionment of Organic Compounds in the Atmosphere

The comprehensive source apportionment model calculates the contributions of individual air pollution source types to the sum of gas-phase plus particle-phase organic compounds in the atmosphere. The total organic compound concentration in the atmosphere studied here due to a given source is the sum of the volatile organic compounds (VOC) concentrations due to that source as measured by EPA method TO-12, plus the sum of all gas-phase semi-volatile organic compounds and fine particulate organic compounds from that source. Since the ratio of the VOC's, the semi-volatile organic compounds, and the fine particle organic compounds to the sum of these three categories of organic compounds is known in the source emissions, the separate contributions of each source type to the VOC, the semi-volatile organic compounds and the fine particle organic compounds concentrations in the atmosphere can be extracted from the CMB model results.

In the present study, the atmospheric contributions from ten primary sources of organic compounds are calculated. The ten sources which have been included in the model are gasoline-powered motor vehicle exhaust, diesel engine exhaust, whole gasoline vapors, gasoline headspace vapors, whole diesel fuel vapors, fine particulate paved road dust, tire wear debris, vegetative detritus and meat cooking exhaust. Four additional sources, which have been previously included in organic compound-based CMB models, were not included either for lack of ambient data or because the contributions determined from the model were found not to be significantly different from zero using a 95% confidence interval. Cigarette smoke contributions could not be determined, since the anteiso- and iso-alkanes that are used to trace cigarette smoke particles were below detection limits in the summer 1993 ambient samples. Likewise, the contributions for wood smoke were too low to be determined on the days studied as the ambient sampling program was conducted during hot summer conditions when very little wood is burned. The minor mass contributions from residential natural gas combustion aerosol were not included in the model since the polcyclic aromatic compounds used to trace this source may not be sufficiently stable in the atmosphere during the extreme photochemical smog episode studied here. Sensitivity studies conducted with the model showed that when residential natural gas combustion was included in the model, the contribution from this source was found to be not significantly different from zero with 95% confidence. This inability to quantify the small contribution from residential natural gas combustion may be due to the decreased consumption of natural gas for home heating during this high temperature summer smog episode or may be due to the increased reactivity of the atmosphere which can destroy the PAH and oxy-PAH tracer species used to track the effluent from natural gas combustion. Emissions from paint spray coating operations were not found in the atmosphere at a level significantly different from zero with greater than 95% confidence and likewise they were removed from the model.

The calculated concentrations of the mass balance species in the receptor model and the measured concentrations of these species showed very good agreement at all four air monitoring sites studied. An example of the degree of agreement between the predicted and measured values of the mass balance species is shown in Figure 9.1 for atmospheric pollutants measured at Azusa. The only compound used as a mass balance species that appears to fit poorly in Figure 9.1 is n-triacontane. Although a comparatively large difference in the measured and calculated concentrations for that compound is seen in Figure 9.1, the difference shown is not significantly different from zero. There is a high uncertainty attached to the calculated value for this compound due to the relatively high uncertainty in the quantification of this compound present at low levels in the emissions from several sources such as motor vehicle exhaust and paved road dust. The CMB model results for this source apportionment study produce a R^2 value of greater than or equal to 0.94 at each of the four air quality monitoring sites studied.

9.4.2 Apportionment of Volatile Organic Compound Concentrations

Non-methane volatile organic compound concentrations are determined by EPA method TO-12. The TO-12 measurement is based on a flame ionization

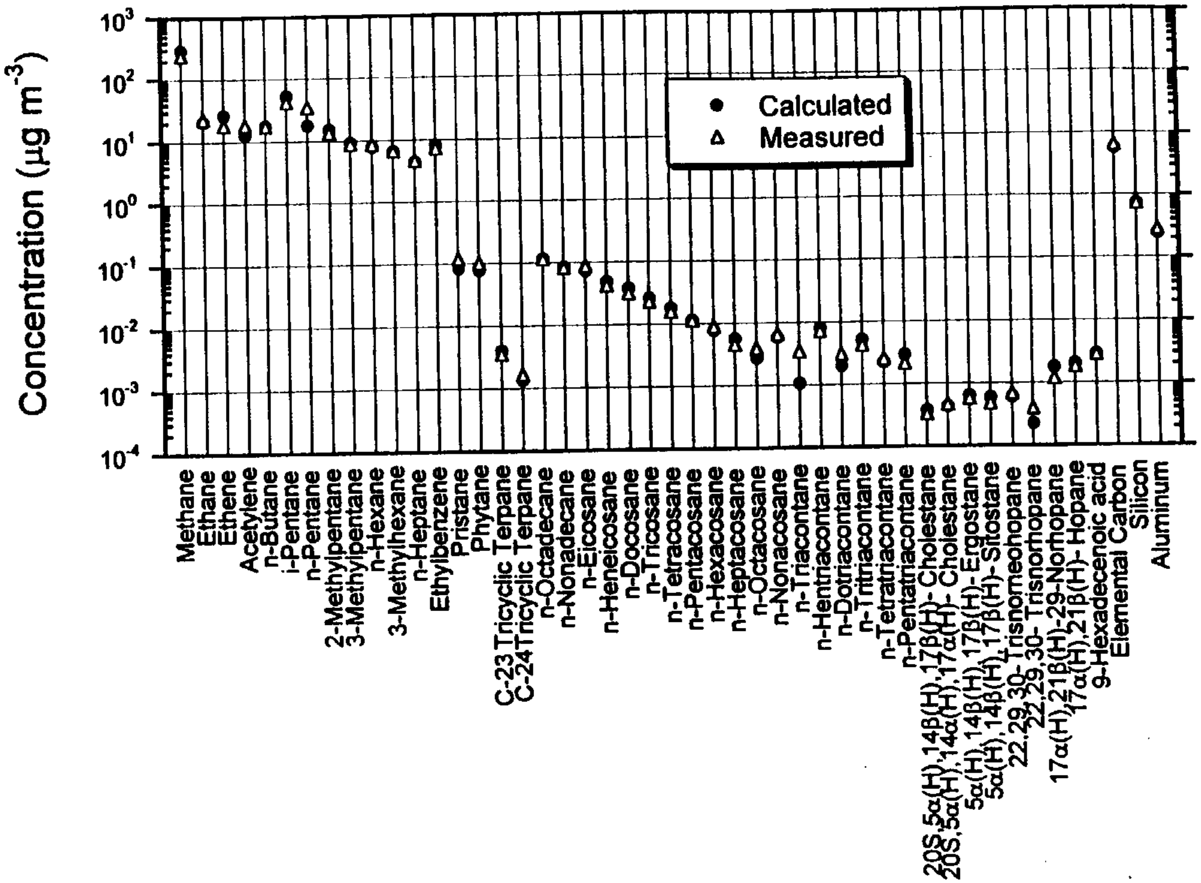

Figure 9.1. Comparison of the measured and calculated ambient concentrations of the mass balance species used in the fine particle CMB model at Azusa, California, September 8-9, 1993.

detection (FID) method which does not respond to all organic carbon in a completely quantitative fashion. For example a carbon atom in a carbonyl group does not respond to the FID analysis such that formaldehyde would give zero response and acetaldehyde would be counted as having half the number of carbon atoms that are actually present. In addition, some highly polar organic compounds such as glycols do not respond well to the TO-12 analysis as they tend to stick to the SUMA canister used for sample collection and to the TO-12 measurement apparatus. For these reasons, the TO-12 method does not truly measure all gas-phase organic carbon. Since all gas-phase organic compounds cannot readily be identified and quantified without exhaustive efforts, the VOC measurement used here still provides the best reproducible measure of the total gas-phase organic carbon present in an atmospheric sample. The fact that the TO-12 method does not respond to some of the oxidized products of gas phase photochemistry is noted since during the severe photochemical smog episode studied here the oxidation of hydrocarbons will tend to decrease the VOC concentration as measured by the EPA TO-12 method even if the total vapor-phase organic carbon content in the atmosphere has remained the same. For this reason, along with the fact that some gas-phase organic compounds will oxidize to form carbon monoxide as well as oxygenated semi-volatile and particle-phase organic compounds, the total quantity of VOC's apportioned from primary sources using non-reactive tracers is likely to be greater than that measured by method TO-12.

The source apportionment model results for volatile organic compounds are shown in Figure 9.2 and are listed in Table 9.1. Gasoline-powered motor vehicle exhaust is the largest single contributor making up over half of the VOC's at all sites. Gasoline vapors comprised of whole gasoline and gasoline headspace vapors are the next largest contributors to the VOC concentrations. At the Central Los Angeles site, the gasoline headspace vapors contribution was not found to be significantly different from zero, as was the whole gasoline vapor contribution at the Claremont site. Natural gas leakage also makes up a noticeable contribution to the ambient non-methane organic gas (NMOG) concentrations. In addition, the small contributions to NMOG from meat cooking operations and diesel engine exhaust are quantified.

As can be seen in Table 9.1, the apportioned contributions of VOC's at Long Beach, at central Los Angeles, and at Azusa are not significantly different from the measured values at the sites at the 95% confidence level. Although the measured and modeled values are not statistically different from each other, the ratio of apportioned VOC's to measured VOC's increases from approximately 1.1 at Long Beach and Central Los Angeles where much of the pollutant concentrations are due to local sources to 1.2 at Asuza which is at a downwind location that receives air pollution transported from Central Los Angeles. At Claremont, which is even farther downwind than Asuza and where gas-phase emissions experience significant gas-phase chemical reaction prior to arriving at this site, the ratio of predicted to measured VOC concentrations rises

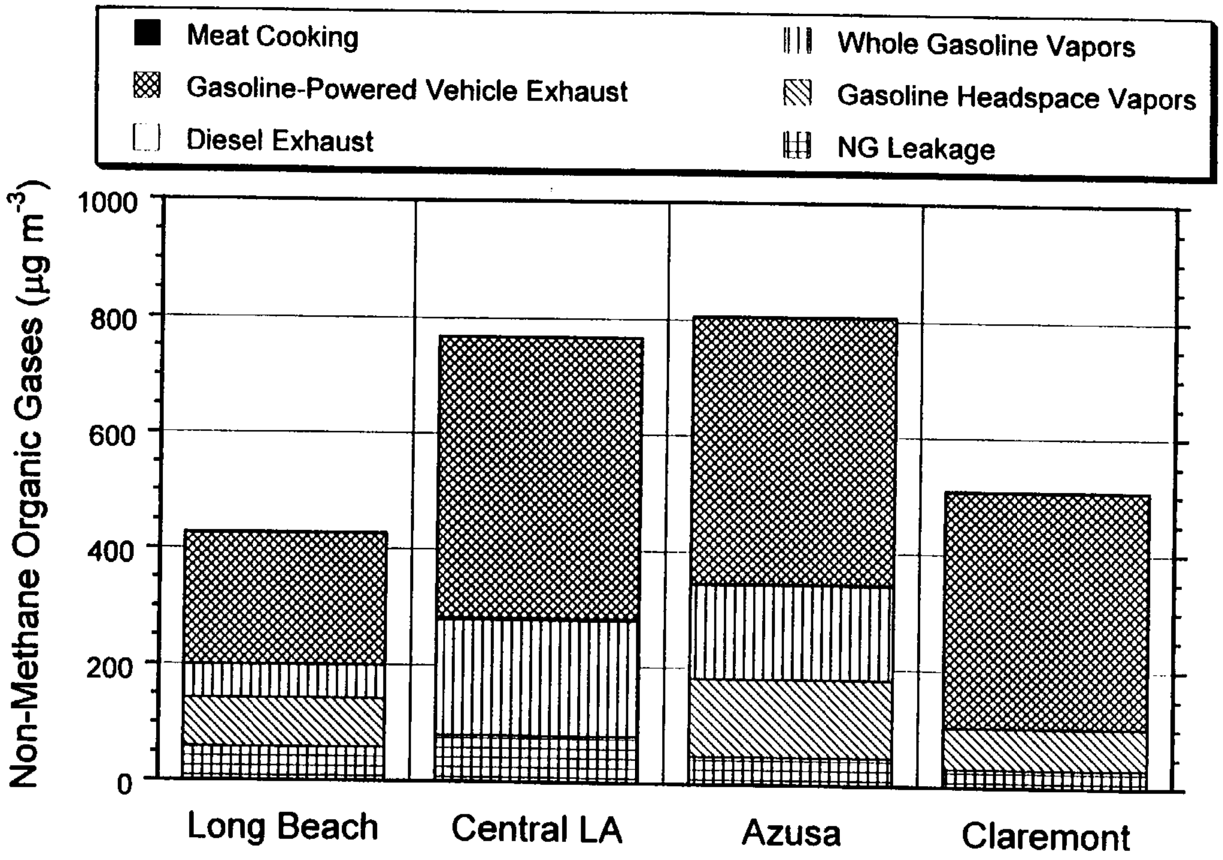

Figure 9.2. Source contributions to non-methane organic gases concentrations, September 8-9, 1993.

Table 9.1. Source apportionment of non-methane organic gas (TO-12) concentrations during the severe photochemical smog episode of September 8-9, 1993: determined by chemical mass balance

	Long Beach (avg ± std in μg m^{-3})	**Downtown LA (avg ± std in μg m^{-3})**	**Azusa (avg ± std in μg m^{-3})**	**Claremont (avg ± std in μg m^{-3})**
Gasoline-powered motor vehicle exhaust	226 ± 31.1	485 ± 64.6	459 ± 63.7	404 ± 35.6
Whole gasoline vapors	56 ± 20.4	198 ± 37.4	161 ± 40.1	[a]
Gasoline headspace vapors	84 ± 22.0	[a]	134 ± 33.2	71 ± 16.6
Diesel exhaust	1.4 ± 0.20	3.6 ± 0.39	2.7 ± 0.34	1.4 ± 0.35
Natural gas leakage	58.7 ± 8.1	80.8 ± 10.8	48.0 ± 8.0	31.9 ± 5.4
Meat cooking	1.5 ± 0.36	1.5 ± 0.45	1.4 ± 0.43	1.0 ± 0.34
Sum	428 ± 44.0	768 ± 75.4	807 ± 82.6	509 ± 39.6
Measured	401 ± 35.7	713 ± 76.0	666[b] ± 66.8	342[b] ± 27.0

[a] Not statistically different from zero with 95 percent confidence, and therefore removed from CMB model

[b] Note that the TO-12 method measurement underreports the VOC concentrations of oxygenated species such as carbonyls.

to 1.5. These trends are consistent with the characteristics of the TO-12 measurement method discussed above.

9.4.3 Apportionment of Fine Particulate Organic Compound Mass and Fine Particulate Mass

Source contributions to fine particle organic compound concentrations are shown in Figure 9.3 and are listed in Table 9.2. Of the primary sources, motor vehicle exhaust is the largest single contributor to fine particle organic compound mass at all sites followed by meat cooking and road dust. Smaller but quantifiable contributions from vegetative detritus and tire wear debris are observed at all the sites except Central Los Angeles where tire wear debris concentrations were not found to be significantly different from zero with 95% confidence. One of the most notable features of Figure 9.3 is the significant amount of organic compound mass that cannot be attributed to the primary sources. The quantity of other organics that cannot be attributed to primary sources is calculated by subtracting the apportioned fine particle organic compound mass from the total fine particle organic compound mass measured at these sites. The organic compound mass at the ambient monitoring sites is estimated by multiplying the fine particle organic carbon measured by thermal evolution and combustion analysis by a factor of 1.4 to account for the H, O, N, and S present in organic compounds. Since there are no other potentially large sources of primary particulate organic carbon that have not been addressed here, it is reasonable to assume that much of the "other" organic material is

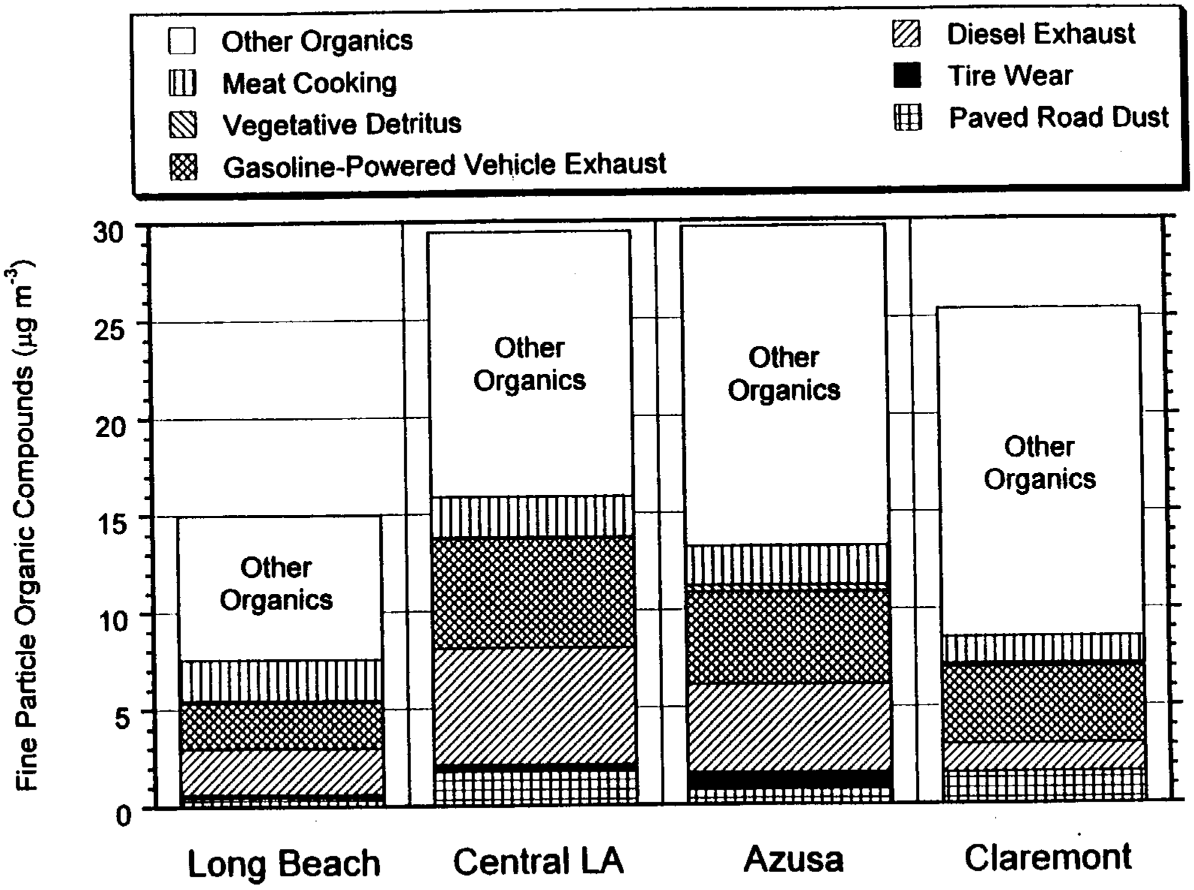

Figure 9.3. Source contributions to fine particulate organic carbon concentrations, September 8-9, 1993.

Table 9.2. Source apportionment of fine particulate organic compound concentrations during the severe photochemical smog episode of September 8-9, 1993: determined by chemical mass balance

	Long Beach (avg ± std in μg m^{-3})	Central LA (avg ± std in μg m^{-3})	Azusa (avg ± std in μg m^{-3})	Claremont (avg ± std in μg m^{-3})
Gasoline-powered motor vehicle exhaust	2.33 ± 0.27	5.62 ± 0.57	4.65 ± 0.54	3.90 ± 0.31
Diesel exhaust	2.36 ± 0.33	5.98 ± 0.66	4.51 ± 0.57	1.45 ± 0.36
Tire wear debris	0.17 ± 0.051	0.36 ± 0.11	0.87 ± 0.14	[*]
Paved road dust	0.48 ± 0.046	1.76 ± 0.055	0.78 ± 0.052	1.64 ± 0.057
Meat cooking	2.09 ± 0.50	2.07 ± 0.64	2.02 ± 0.60	1.39 ± 0.48
Vegetative detritus	0.10 ± 0.018	0.075 ± 0.024	0.33 ± 0.053	0.16 ± 0.028
Sum of identified primary sources	7.53 ± 0.66	15.9 ± 1.08	13.2 ± 1.00	8.54 ± 0.68
Measured	15.0 ± 1.50	29.5 ± 2.18	29.6 ± 2.02	25.4 ± 1.53

[*] Not statistically different from zero with 95 percent confidence, and therefore removed from CMB model

secondary organic aerosol (SOA) formed from the low volatility reaction products of gas-phase chemical reactions. As seen in Figure 9.3, the fraction of organic carbon that is not attributed to the primary sources increases as the air masses move inland. The lowest proportions of presumed SOA are seen at Long Beach and Central Los Angeles, with a higher fraction of SOA at Azusa and an even a greater proportion at Claremont. This behavior is consistent with the increased time for chemical reaction experienced by the emissions that arrive at the downwind sites.

Since the ratio of organic compound mass to overall fine particle mass in the emissions from the primary sources is known, the source contributions to the overall atmospheric fine particle mass concentrations can be calculated. The contributions of the primary fine particle emissions sources to the ambient fine particle concentrations are shown in Figure 9.4 and listed in Table 9.3 along with the secondary sulfate ion, nitrate ion, and ammonium ion measured at the four sampling locations. The quantity of “other” (presumably secondary organics) is determined above. As can be seen in Figure 9.4 the contributions of secondary inorganic ions to atmospheric fine particle concentrations during this particular smog episode show a spatial trend that is the reverse of that observed for the secondary organic aerosol. The contribution from secondary inorganic ions decreases as a function of distance from the coast on this occasion. This is likely due to the larger influence of sulfate from fuel combustion by ships at the harbor and from refineries near the coast accompanied by a decrease in

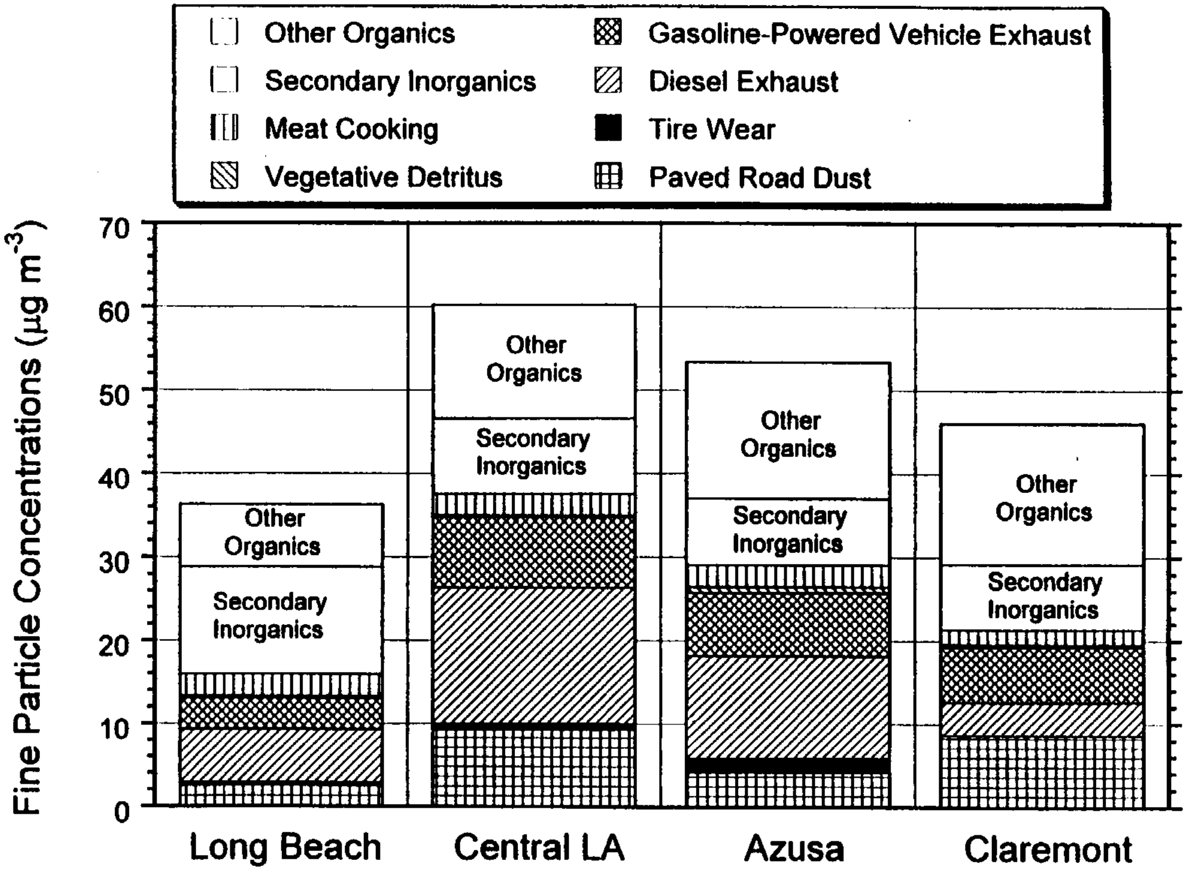

Figure 9.4. Source contributions to fine particle mass concentrations, September 8-9, 1993.

Table 9.3. Source apportionment of fine particle mass concentrations during the severe photochemical smog episode of September 8-9, 1993: determined by chemical mass balance

	Long Beach **(avg ± std in μg m^{-3})**	**Central LA** **(avg ± std in μg m^{-3})**	**Azusa** **(avg ± std in μg m^{-3})**	**Claremont** **(avg ± std in μg m^{-3})**
Gasoline-powered motor vehicle exhaust	3.75 ± 0.49	8.35 ± 1.02	7.59 ± 1.15	6.59 ± 0.66
Diesel exhaust	6.46 ± 0.91	16.4 ± 1.80	12.3 ± 1.56	3.97 ± 0.99
Tire wear debris	0.34 ± 0.10	0.71 ± 0.21	1.73 ± 0.27	*
Paved road dust	2.53 ± 0.24	9.31 ± 0.29	4.13 ± 0.28	8.68 ± 0.30
Meat cooking	2.64 ± 0.63	2.61 ± 0.84	2.55 ± 0.76	1.76 ± 0.61
Vegetative detritus	0.22 ± 0.039	0.17 ± 0.052	0.73 ± 0.12	0.35 ± 0.062
Other organics	7.45 ± 1.64	13.6 ± 2.43	16.4 ± 2.25	16.9 ± 1.67
Sulfate ion (secondary plus background)	7.21 ± 0.72	4.89 ± 0.33	4.43 ± 0.29	4.23 ± 0.28
Secondary nitrate ion[Δ]	2.93 ± 0.75	2.41 ± 0.32	1.84 ± 0.39	2.10 ± 0.13
Secondary ammonium ion[Δ]	2.73 ± 0.35	1.77 ± 0.12	1.68 ± 0.14	1.53 ± 0.10
Sum	36.3 ± 2.33	60.2 ± 3.35	53.5 ± 3.08	46.1 ± 2.16
Measured[Δ]	38.4 ± 5.55	47.9 ± 5.72	46.6 ± 5.79	59.3 ± 5.07

[*] Not statistically different from zero with 95 percent confidence, and therefore removed from CMB model

[Δ] Directly measured from fine particle Teflon filter ammonium nitrate concentrations at inland locations due to the very high ambient temperatures during the smog episode (greater than 40 °C peak temperature) that can drive the ammonium nitrate into the gas-phase. At all of the locations studied, except Claremont, the apportioned primary fine particle mass plus secondary aerosol concentrations are not significantly different from the measured fine particle mass concentrations with greater than 95% confidence. The uncertainties in the measured fine particle mass concentrations are in part due to the fairly small quantities of fine particle mass collected for gravimetric determination during a four-hour sampling period. At Claremont, the apportioned fine particle mass plus secondary aerosol falls short of the measured concentration by approximately 22%.

9.4.4 Apportionment of Semi-volatile Organic Compounds

Table 9.4 shows the contributions to the ambient concentrations of gas-phase semi-volatile organic compounds determined by the source apportionment model. Motor vehicle exhaust from the gasoline-powered and the diesel-powered engines along with diesel fuel vapors make up virtually all of the ambient concentrations of gas-phase semi-volatile organic compounds with only a small fraction resulting from meat cooking operations. Is should be noted that some or all of the unburned whole diesel fuel vapors may be from diesel exhaust emissions not represented by the hot-start dynamometer diesel emissions profile

Table 9.4. Source apportionment of gas-phase semi-volatile organic compound concentrations during the severe photochemical smog episode of September 8-9, 1993: determined by chemical mass balance

	Long Beach (avg ± std in μg m^{-3})	**Central LA** (avg ± std in μg m^{-3})	**Azusa** (avg ± std in μg m^{-3})	**Claremont** (avg ± std in μg m^{-3})
Gasoline-powered motor vehicle exhaust	3.41 ± 0.53	6.77 ± 1.09	7.02 ± 1.08	6.36 ± 0.60
Diesel exhaust	2.30 ± 0.32	5.84 ± 0.64	4.40 ± 0.56	1.41 ± 0.35
Diesel fuel vapors	6.89 ± 0.56	8.68 ± 0.83	7.69 ± 0.71	7.36 ± 0.61
Meat cooking	0.055 ± 0.013	0.054 ± 0.017	0.053 ± 0.016	0.036 ± 0.013
Sum	12.7 ± 0.83	21.3 ± 1.51	19.2 ± 1.41	15.4 ± 0.93

* Not statistically different from zero with 95 percent confidence, and therefore removed from CMB model

used in this study (i.e., unburned diesel fuel may be emitted in much larger quantities during cold starts).

9.4.5 Apportionment of Individual Organic Compounds

An additional result that can be calculated from the source apportionment model used in this study is the relative contribution of each primary source to the atmospheric concentrations of individual organic compounds. Figure 9.5 shows the contribution of each source to the atmospheric concentration of the mass balance species at the Azusa air monitoring site.

9.4.6 Comparison of Unapportioned Organic Compound Mass to Organic Acid Tracers

1,2-Benzenedicaboxylic acid is found in noticeable quantities in the atmosphere (Rogge et al., 1993; Fraser 1998) but has not been identified in the emissions from any of the major urban air pollution sources tested (Chapters 2-8). Therefore, it is likely that this non-volatile organic acid is formed in the atmosphere by gas-phase chemical reactions and is a secondary aerosol product. Shown in Figure 9.6 is the ambient concentration of 1,2-benzenedicarbolic acid compared to the “other” organics category determined in the present study and in a wintertime fine particle source apportionment study conducted in California’s San Joaquin Valley (Schauer, 1998). Data points are shown in Figure 9.6, only if the quantity of “other” organics determined from the source apportionment results were found to be

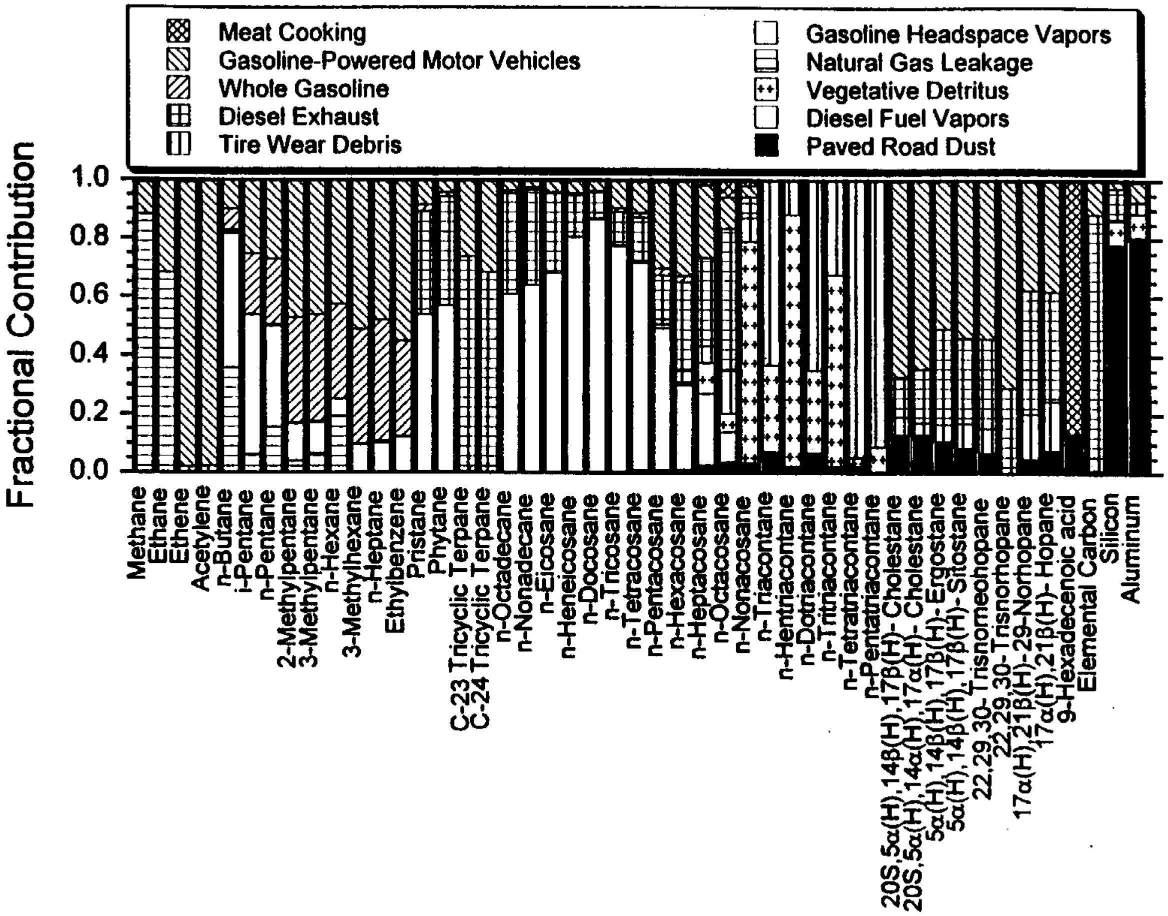

Figure 9.5. Source contributions to the atmospheric concentrations of the mass balance species used in the CMB model at Azusa, September 8-9, 1993.

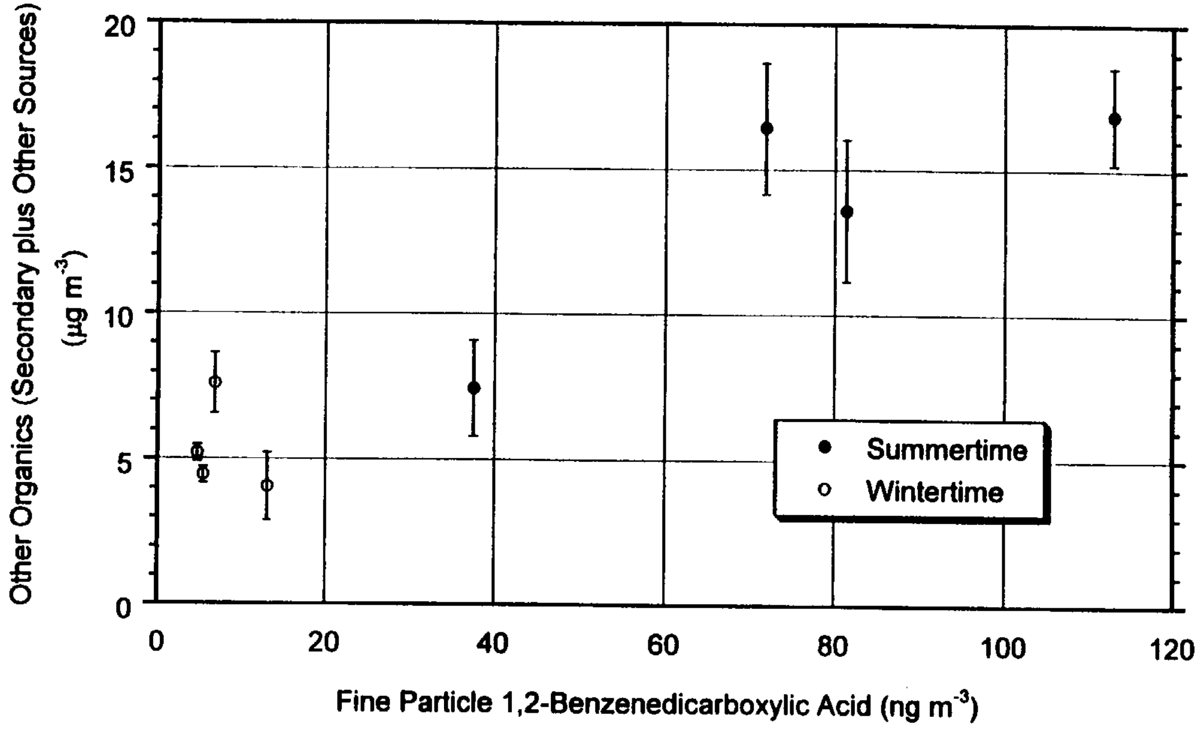

Figure 9.6. Comparison of the calculated "other" organics from the CMB model results and the fine particle 1,2-benzenedicarboxylic acid concentrations for the present summer study and from a fine particle source apportionment study of the wintertime aerosol in California's San Joaquin Valley.

significantly greater than zero with 95% confidence. The error bars shown in Figure 9.6 represent one standard deviation of the estimate of the quantity of "other" organics for the sampling events studied. As seen in Figure 9.6, the concentration of 1,2-benzenedicarboxylic acid present in the aerosol correlates fairly well with the calculated quantity of "other" organic compounds that cannot be assigned to a primary source and that thus are assumed to be largely due to secondary organic aerosol formation by atmospheric chemical reaction. The fact that a curve through the points in Figure 9.6 has an approximate intercept of about 4 μg m^{-3} of "other" organics when the 1,2-benzenedicarboxylic acid concentration is zero roughly matches the levels of background organic aerosol seen at remote air monitoring sites. Other small sources of primary organics which are not included in the model may also exist.

9.5 References

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Appendix A

Whole Gasoline Vapor and Gasoline Headspace Vapor Emissions Profiles

A 1995 gasoline sample was assembled as a market share weighted average of the gasoline products of the five largest gasoline retailers in Southern California. The 1995 sample was collected and analyzed to obtain a whole gasoline vapor emissions profile. In order to obtain a 1993 whole gasoline vapor emissions profile, the 1995 gasoline composition data were modified to match conditions during the summer 1993 atmospheric experiments; these changes reflect the reduction in benzene and the increase in MTBE content of gasoline that occurred between the summer of 1993 and the summer of 1995. The whole gasoline vapor profiles are provided in Table A.1.

Gasoline headspace vapor profiles which correspond to the associated whole gasoline emissions profiles were calculated. Conner et al. (1995) have shown that the composition of the headspace vapors above a liquid pool of gasoline can be accurately calculated from the liquid gasoline composition and the Raoult's law coefficients for the individual gasoline components in a gasoline mixture. The gasoline headspace vapor composition for this study was therefore calculated using Raoult's law coefficients from the data collected by Aulich et al. (1994). The gasoline headspace samples are also shown in Table A.1.

Table A.1. Whole Gasoline Vapor and Headspace Gasoline Vapor Emissions Profiles

Compound	1995 Southern California Market-Share Gasoline (Wt %)		1993 Southern California Market-Share Gasoline (Wt %)	
	Whole Gasoline	Headspace Gasoline[Δ]	Whole Gasoline[+]	Headspace Gasoline[Δ]
n-Alkanes				
Propane	0.01	0.2	0.01	0.2
n-Butane	0.79	6.2	0.91	6.5
n-Pentane	2.19	4.1	2.46	4.3
n-Hexane	1.41	0.3	1.59	0.3
n-Heptane	1.01	0.3	1.14	0.3
n-Octane	0.46	0.2	0.52	0.2
n-Nonane	0.24	0.1	0.27	0.1
n-Decane	0.12	0.0	0.14	0.0
Branched alkanes				
i-Butane	0.15	1.7	0.17	1.8
2,2-Dimethylpropane	0.01	0.1	0.01	0.1
i-Pentane	6.12	16.9	6.89	17.9
2,2-Dimethylbutane	0.22	0.2	0.25	0.2
2,3-Dimethylbutane	0.98	1.0	1.10	1.1
2-Methylpentane	3.01	1.3	3.39	1.4
3-Methylpentane	1.86	0.7	2.09	0.7
2,4-Dimethylpentane	0.90	0.3	1.01	0.3
2-Methylhexane	1.44	0.5	2.00	0.6
2,3-Dimethylpentane	1.73	0.5	1.95	0.6
3-Methylhexane	1.44	0.4	1.62	0.5
2,2,4-Trimethylpentane	2.55	0.8	2.87	0.9
2,5-Dimethylhexane	0.50	0.2	0.56	0.2
2,4-Dimethylhexane	0.52	0.2	0.59	0.2
2,3,4-Trimethylpentane	1.18	0.4	1.33	0.4
2,3-Dimethylhexane	0.14	0.0	0.16	0.0
2-Methylheptane	0.75	0.2	0.84	0.2
n-Alkenes				
1-Butene	0.02	0.2	0.02	0.2
trans-2-Butene	0.08	0.6	0.09	0.7
cis-2-Butene	0.08	0.5	0.09	0.6
1-Pentene	0.22	0.6	0.25	0.6
trans-2-Pentene	0.51	0.9	0.57	1.0

Notes: * Not Calculated

[+] The 1993 whole gasoline composition was estimated from the 1995 whole gasoline composition by reducing the MTBE content from 10.57 percent to 1.1 percent and by increasing the benzene content from 0.84 percent to 2.00 percent to reflect the changes that occurred in the average gasoline pool in southern California during this time period.

[Δ] Note that headspace gasoline vapor profiles do not represent all forms of gasoline evaporative emissions.

Table A.1. (continued - page 2)

Compound	1995 Southern California Market-Share Gasoline (Wt %)		1993 Southern California Market-Share Gasoline (Wt %)	
	Whole Gasoline	Headspace Gasoline[Δ]	Whole Gasoline[+]	Headspace Gasoline[Δ]
n-Alkenes				
cis-2-Pentene	0.27	0.5	0.30	0.5
1-Hexene	0.12	0.1	0.14	0.1
trans-2-Hexene	0.24	0.1	0.27	0.1
cis-2-Hexene	0.16	0.1	0.18	0.1
Branched alkenes				
Isobutene	0.02	0.2	0.02	0.2
3-Methyl-1-butene	0.05	0.2	0.06	0.2
2-Methyl-1-butene	0.25	0.5	0.28	0.6
2-Methyl-2-butene	0.25	0.4	0.28	0.4
4-Methyl-1-pentene	0.15	0.2	0.17	0.2
2-Methyl-1-pentene	0.15	0.1	0.17	0.1
2-Methyl-2-pentene	0.33	0.4	0.37	0.4
Saturated cycloalkanes				
Cyclopentane	0.34	0.3	0.38	0.4
Methylcyclopentane	2.46	0.7	2.77	0.8
Cyclohexane	0.75	0.5	1.99	0.6
Methylcyclohexane	1.14	0.3	1.28	0.4
Unsaturated cycloalkenes				
Cyclopentene	0.13	0.2	0.15	0.2
Aromatic hydrocarbons				
Benzene	0.84	0.7	2.00	1.7
Toluene	6.67	1.9	7.50	2.0
Ethylbenzene	1.46	0.7	1.64	0.7
m & p-Xylene	6.17	2.4	6.94	2.5
o-Xylene	2.29	1.3	2.58	1.4
i-Propylbenzene	0.10	0.1	0.11	0.1
n-Propylbenzene	0.54	0.4	0.61	0.4
p-Ethyltoluene	0.73	0.6	0.82	0.6
m-Ethyltoluene	1.67	1.3	1.88	1.3
1,3,5-Trimethylbenzene	0.84	0.7	0.95	0.7
o-Ethyltoluene	0.58	0.4	0.65	0.4
1,2,4-Trimethylbenzene	2.90	2.7	3.26	2.7
Ethers				
MTBE	10.57	*	1.10	*

Notes: * Not Calculated

[+] The 1993 whole gasoline composition was estimated from the 1995 whole gasoline composition by reducing the MTBE content from 10.57 percent to 1.1 percent and by increasing the benzene content from 0.84 percent to 2.00 percent to reflect the changes that occurred in the average gasoline pool in southern California during this time period.

[Δ] Note that headspace gasoline vapor profiles do not represent all forms of gasoline evaporative emissions.

A1.1 References

Conner, T. A., Lonneman, W. A. and Seila, R. L. (1995) Transportation-related volatile hydrocarbon source profiles measured in Atlanta. *J. Air & Waste Manage. Assoc.* **45**, 383-394.

Appendix B

Paved Road Dust Emissions Profiles

Fine particle road dust emissions profiles were generated by separately resuspending a road dust sample and then introducing the road dust/air mixture into the residence time chamber of the dilution source sampler. Samples were drawn through AIHL-design cyclone separators to remove coarse particles larger than 1.8 μm in diameter and were collected on quartz fiber filters and Teflon filters and then analyzed chemically as described for the other sources tested. Gas-phase measurements were not made for the road dust sample as road dust is not thought to be a significant source of gas-phase pollutants. Paved road dust emissions profiles are shown in Table B.1.

Table B.1. Emissions Profiles for Paved Road Dust Fine Particulate Mass

	Long Beach	Central LA	Rubidoux
Compound	$\mu g\ g^{-1}$	$\mu g\ g^{-1}$	$\mu g\ g^{-1}$
n-Alkanes			
n-Tricosane	5.86	8.81	5.06
n-Tetracosane	4.76	9.53	4.40
n-Pentacosane	14.3	11.1	5.62
n-Hexacosane	8.62	13.9	6.15
n-Heptacosane	35.3	15.2	10.7
n-Octacosane	11.5	14.2	7.16
n-Nonacosane	53.1	13.2	20.4
n-Triacontane	11.4	10.8	6.01
n-Hentriacontane	42.4	11.2	15.7
n-Dotriacontane	9.26	9.00	3.16
n-Tritriacontane	28.0	10.3	5.37
n-Tetratriacontane	6.42		
n-Pentatriacontane	11.9		
Polycyclic aromatic hydrocarbons			
Fluoranthene	0.93	1.79	1.25
Pyrene	0.71	0.94	0.98
Benz[a]anthracene	0.73	0.98	1.41
n-Alkanoic acids			
n-Dodecanoic acid	30.8	66.4	78.2
n-Tridecanoic acid	5.18	6.57	6.44
n-Tetradecanoic acid	58.9	124	82.1
n-Pentadecanoic acid	21.0	61.7	27.5
n-Hexadecanoic acid	351	486	328
n-Heptadecanoic acid	11.8	20.1	12.7
n-Octadecanoic acid	156	173	143
n-Nonadecanoic acid	4.90	5.28	3.42
n-Eicosanoic acid	36.9	10.7	10.4
n-Heneicosanoic acid	6.35	1.69	2.62
n-Docosanoic acid	33.7	7.59	11.9
n-Tricosanoic acid	9.27	3.48	4.54
n-Tetracosanoic acid	53.4	18.2	21.0
n-Pentacosanoic acid	9.63		3.61
n-Hexacosanoic acid	50.9	8.60	18.6
n-Heptacosanoic acid	5.38		6.94
n-Octacosanoic acid	30.0		14.3
n-Triacontanoic acid	21.9		6.56

Table B.1. (continued - page 2)

Compound	Long Beach μg g^{-1}	Central LA μg g^{-1}	Rubidoux μg g^{-1}
n-Alkenoic acids			
n-9-Hexadecenoic acid	39.1	193.4	55.5
n-9-Octadecenoic acid	178	643	122
n-9,12-Octadecadienoic acid	36.9	70.8	28.2
Resin acids			
Dehydroabietic acid	15.6	14.7	44.7
Other compounds			
Squalene	25.7	303	23.4
Elemental composition			
Aluminum	40100	41200	50200
Silicon	142000	138000	155000
Organic carbon	153000	151000	103000
Elemental Carbon	18000	9000	3700