Composition of Light-Duty Motor Vehicle Exhaust Particulate Matter in the Denver, Colorado Area

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A study to characterize particulate matter emissions from 195 in-use gasoline and diesel passenger vehicles was conducted during the summer of 1996 and the winter of 1997 in the Denver, Colorado region. Vehicles were tested as received on chassis dynamometers using the Federal Test Procedure (FTP) Urban Dynamometer Driving Schedule (UDDS). Both PM-10 and regulated emissions were measured for each phase of the UDDS. Approximately 88% of the PM-10 collected was carbonaceous material, of which the average organic fraction was 0.7 for gasoline vehicles and 0.4 for diesel vehicles. This suggests that the organic carbon (OC) to elemental carbon (EC) split may be useful in separating light-duty gasoline from diesel PM emissions. Sulfate emission rates averaged 0.45 and 3.51 mg/mi for gasoline and diesel vehicles, indicating that the EPA's mobile emissions model overpredicts sulfate emission rates. Elements identified by X-ray fluorescence averaged between 3 and 9% of the PM-10 mass. Polynuclear aromatic hydrocarbon (PAH) profiles developed may help distinguish between gasoline and diesel vehicles in source apportionment studies. Total PAH emissions, however, were not a good candidate as a tracer of gasoline PM emissions. Hopane and sterane emissions were very similar across the fleet and may be useful tracers for mobile source PM emissions. Overall, emission rates varied significantly with vehicle classification and driving condition, suggesting that a single profile representing the entire fleet will need to carefully reflect the local fleet composition and the local weighting of cold, hot, and hot-stabilized emissions.

Introduction

The amount and composition of particulate matter (PM) emitted in the exhaust of light-duty gasoline vehicles (LDGVs) in the United States has changed over the last 25 years. Before 1975, all gasoline vehicles were designed to operate on leaded fuel. Approximately 75% of the lead consumed was emitted as PM, resulting in emission rates of 200–250 mg/mi (*1*). Leaded gasoline remained available, although at greatly reduced lead concentrations, until 1996.

Cars equipped with oxidation catalysts were introduced in 1975, necessitating the use of unleaded fuels. By 1977, essentially all new cars were catalyst equipped. Catalyst phase-in was slower for light-duty trucks, which were not totally catalyst equipped until 1982. The oxidation catalyst oxidized a small amount of the sulfur present in gasoline to sulfur trioxide, which was emitted as sulfuric acid particles. Typical sulfuric acid emission rates for vehicles equipped with and without air pumps were 16 and 5 mg/mi on the FTP (*2*). Since that time, changes in catalysts, the introduction of the three-way catalyst system, and improvements in the engine have reduced total PM emission rates to less than 2 mg/mi for late-model, properly functioning vehicles (*3*).

Light-duty diesel vehicles (LDDVs) typically account for less than 1% of the in-use fleet. However, since their PM emission rates are higher than those of gasoline vehicles, their contribution to the inventory cannot be ignored. Typical PM emission rates for LDDVs before 1981 were 700 mg/mi (*1, 2*). Improvements in diesel technology have decreased PM emission rates from current LDDVs, since they must meet the Federal Tier 1 FTP PM emission standard of 80 mg/mi, which phased-in from 1994 through 1996.

Relatively few studies have characterized the composition of PM exhaust emissions from the in-use vehicle fleet. Vehicle tunnel studies (*4–8*) have been used for this purpose, and are an excellent way of capturing PM emissions under specific driving conditions. However, it is difficult to separate the impact of diesel from gasoline PM emissions, and there are complications from reentrained road dust, and possibly tire and brake wear PM.

Other studies have utilized short tests on individual vehicles to obtain samples from in-use vehicles. Watson et al. (*9*) collected 14 samples of light-duty gasoline PM from an Arizona IM station using a loaded mode test. Sagebiel et al. (*10*) collected PM-10 samples from 23 in-use vehicles that were recruited as high emitters by remote sensing in Nevada. The IM240 driving cycle was used. In a subsequent study, Cadle et al. (*11*) collected PM-10 samples from 103 in-use high-emitting vehicles recruited in Orange County, California, also using the IM240 driving cycle. Since the loaded mode and IM240 tests are performed on vehicles in a hot, stabilized mode, no cold start emissions were collected in these studies. The complete study is described by Lawson et al. (*12*).

The Urban Dynamometer Driving Schedule (UDDS) of the Federal Test Procedure (FTP) represents 85% of the driving time in urban areas. There are three phases to the driving: cold start, hot stabilized, and hot start. The test averages 19.6 mph and has a top speed of 56.7 mph. Other driving cycles can be used to represent driving modes that do not occur in the FTP such as the HWFET (highway fuel economy test) and the US06, a high-speed, high-load driving cycle.

The purpose of this study was to characterize the PM emissions from the in-use, light-duty vehicle fleet in the Denver, Colorado area in a manner that could be used to

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improve both emission factor and source apportionment approaches to developing the PM emissions inventory. Emissions from 80 vehicles tested on the FTP were collected and analyzed. Forty-two of these vehicles were tested at ambient temperature during the winter, with the remainder tested during the summer. Analysis was performed separately for each of the three FTP phases. Measurements of carbonaceous matter and sulfate were made to facilitate an update of vehicle PM emission factor models such as PART5 or EMFAC7G (13). These measurements, together with additional data on trace elements, PAHs, steranes, and hopanes, have been used to create source profiles (14; currently available at http://charon.cira.colostate.edu) for the Northern Front Range Air Quality Study (NFRAQS). The vehicles discussed in this paper were part of a larger set of vehicles that were tested for PM emissions, particle size distributions, and particle number. These results have been reported elsewhere (15).

Experimental Section

The study was conducted at the Colorado Department of Public Health and Environment (CDPHE) Aurora Emissions Technical Center, in the eastern Denver metropolitan area. The summer portion of the study was conducted in July and August of 1996, while the winter portion was conducted in January and February of 1997. Two chassis dynamometers were used: one in the CDPHE facility and a transportable dynamometer that was supplied and operated by the EPA. Since experimental details have been given elsewhere (15, 16), they will only be summarized in this paper.

Vehicle Recruitment. A goal of the study was to obtain, as best as possible, an unbiased set of vehicles representing the in-use, on-road, light-duty vehicle fleet in the Northern Front Range area of Colorado. It was anticipated that the fleet PM emissions would be dominated by three categories of vehicles: smoking gasoline vehicles, diesel vehicles, and poorly maintained or malfunctioning vehicles. The latter are expected to occur most frequently in the older vehicle population. Thus, to ensure that a reasonable number of the higher emitting vehicles were acquired for testing, the total number of vehicles to be tested was allocated to six categories. These categories were 1991–1997 gasoline, 1986–1990 gasoline, 1981–1985 gasoline, 1971–1980 gasoline, 1971 or newer smoking gasoline, and 1971 or newer diesel-powered vehicles. Some of the diesel vehicles recruited during the summer were large pickup trucks that were classified as heavy-duty vehicles. Different vehicles were recruited for the summer and winter portions of the program.

Vehicle Testing. Vehicles were tested as received, including the use of the tank fuel. Only in instances where insufficient fuel was present to complete the testing, was a local commercial fuel added. During the summer, all vehicles were soaked indoors overnight at 72 °F. Half the gasoline vehicles were tested on the CDPHE chassis dynamometer, while the other half were tested on the EPA transportable chassis dynamometer, which was located outdoors under a canopy. All diesels in the summer were tested on the CDPHE dynamometer. Both dynamometers used 8.6 in. diameter dual rolls. Vehicles tested outdoors were pushed from the soak area onto the dynamometer immediately before testing.

During the winter, all vehicles were tested twice, once on each dynamometer. Half the vehicles were tested indoors first at 60 °F, and half outdoors first at the prevailing ambient temperature which ranged from 23.4 to 66.6 °F. The outdoor testing was done after an overnight outdoor soak at ambient temperatures. The average winter vehicle oil temperatures ranged from 28.2 to 39.9 °F for the six vehicle categories. The vehicles were driven on the UDDS of the FTP. Phases 1–3 of the UDDS represent cold start, hot stabilized, and hot start operation, respectively.

Fuel. The American Automobile Manufacturers Association (AAMA) collects and analyzes fuel samples in the summer and winter in the Denver area. Readers interested in the average fuel composition are referred to this report (17). One of the primary differences between the summer and winter portions of the study is that Denver has a winter oxyfuel program. Most summer fuels are not oxygenated. Fuel sulfur content was of special interest because it is expected to impact the sulfate emission rate. To supplement the AAMA survey, which emphasizes regular grade gasoline, 20 additional fuel samples were collected at gas stations during both the summer and winter portions of the study and analyzed for sulfur. The combined average fuel sulfur, unweighted for sales, was 0.036, 0.018, 0.014, and 0.034 wt %, respectively, for summer regular, mid-grade, premium gasoline, and #2 diesel fuel and 0.023, 0.018, 0.010, and 0.034 wt %, respectively, for the winter samples.

Gaseous Emissions. HC, CO, nitrogen oxides (NOx), and carbon dioxide (CO_2) were measured during all FTP tests. Diesel vehicles require the use of a heated flame ionization detector (FID) instrument, which did not operate properly during the summer portion of the study. Therefore, no HC data are reported for the diesels tested during the summer. The CDPHE measured gas-phase emissions using the standard bag collection system. The EPA used modal dilute exhaust measurement, rather than bag collection. In general practice, modal and bag measurement methods agree within 15%, with better precision for the higher emitters. During the winter, the dilution air for the EPA exhaust tunnel was preheated to 150 °F and the tunnel was wrapped with insulation to ensure that water condensation was not a problem. In addition, a heated sampling line was used between the dilution tunnel and the trailer that housed the analytical instruments and data acquisition computer. Some of the winter gaseous emission data from the EPA dynamometer was corrected for a leak in the sample pump. The magnitude of the correction was 30%. A detailed analysis of the problem and the correction is given in ref 16. The leak did not affect the PM measurements.

PM Emissions. PM samples were collected through two isokinetic probes inserted into each of the dilution tunnels. These probes were connected to University Research Glassware PM-10 cyclones, which operated at a flow rate of 28.3 lpm. Flow rates were held constant with mass flow controllers and were checked periodically with a dry gas meter. Each cyclone was attached to a 26.5-cm long straight tube for flow straightening. Solenoid valves activated by the test computer systems were used to switch between filters.

PM-10 samples were collected simultaneously on both 37-mm diameter, 2.0-μm pore size Gelman Teflo and Pallflex Tissue Quartz 2500 QAT-UP filters. Quartz filters were prefired at 900 °C for 3 h to remove any carbon. During the winter, either 47-mm Teflo filters or 37-mm or 47-mm T60A20 Pallflex filters replaced the 37-mm Teflo for the high-emitting gasoline vehicles and the diesels when filter plugging was anticipated to be a problem. All Teflo and Pallflex filters were weighed on a microbalance after equilibration at constant temperature (72 ± 4 °F) and humidity (32 ± 2% RH). Filters were stored in plastic Petri dishes in a refrigerator, and transported between laboratories using a cooler with blue ice packs. Tunnel blanks were collected, weighed, and analyzed for all species. All reported values are corrected for the average tunnel blank.

Sample Analysis. A representative subset of the samples from the study was selected for chemical analysis. Chemical analysis of PM samples was not performed on the winter indoor samples. QA/QC data from the sampling and analysis are given in the CRC final report (16). All analyses discussed in this report were performed at the Desert Research Institute (DRI). Samples were also provided to NIST for the deter-

mination of ^{14}C content. These analyses were performed as part of the CRC/NFRAQS-funded Project A-20: "Carbon Isotopic Analysis of the Northern Front Range Air Quality Study's Summer and Winter 1996−1997 Program." Results are given in the final report for that project (*18*), which is currently available at the NFRAQS website.

"Organic" carbon (OC) and "elemental" carbon (EC) were determined on 0.512 cm^2 punches removed from the quartz filters using the DRI thermal optical reflectance (TOR) technique (*19*). The TOR method was used in this study because it is commonly used in ambient studies, including the NFRAQS.

Quartz filters are known to adsorb small amounts of carbonaceous material during sampling. The magnitude of this problem can be estimated by analyzing the carbon collected on a backup quartz filter. Backup filters were collected for 20 samples. The amount of OC found on the backup filter was relatively insensitive to the front filter loading. Thus, the OC expressed as a percent of that found on the front filter varied from less than 1% for a heavily loaded sample to 34% for a lightly loaded sample. When quartz filters were run simultaneously behind both Teflon and quartz front filters, it was found that the quartz filters behind the Teflon collected twice as much carbon (28%) as those behind the quartz filters. Overall, it is concluded that quartz filters can capture substantially more OC than Teflon filters. However, since it is not possible to determine from these experiments if all of the adsorbed OC was initially present in the gas phase, or if some of it was released from particles collected on the front filter, no corrections were made to the OC values reported from the quartz filters.

Sulfate and nitrate were determined by ion chromatography (IC). Teflon or Pallflex filters were extracted in 15 mL of 40:60 water/isopropyl alcohol in an ultrasonic bath for 60 min, then in a mechanical shaker for 60 min. Teflon and Pallflex filters were analyzed for 38 elements by energy-dispersive X-ray fluorescence (XRF) analysis (*20*). Seventy PAHs were determined from the quartz filter/PUF/XAD samples by GC/MS in the selected ion monitoring mode. Samples have deuterated internal standards added before extraction to measure the recovery efficiency of the process. Hopanes and steranes were analyzed from these extracts by GC/MS as well. Authentic standards were available for five of the hopanes and steranes. The remaining hopanes and steranes were identified based on their mass spectra and retention time comparison with data available in the literature (*21, 22*). Deuterated PAHs were used as surrogate internal standards.

The primary purpose of measuring the PAHs was to create source profiles that can be used to determine the relative contributions of LDGV and LDDV exhaust PM emissions to the atmospheric particle burden. Some of the PAHs have also been designated by the EPA as air toxics. To limit the number of expensive PAH analyses, FTP runs from multiple vehicles were pooled on a FTP phase basis. Pooling was done on the basis of a similar PM emission rate, rather than by vehicle age. An insufficient number of PUF/XAD samples was collected to permit pooling by both vehicle age and emission rate. For the summer, a total of 29 FTP filter sets were pooled into 15 sets, each containing separate samples for the 3 FTP phases. These included three sets each in the following categories: diesels, smokers, low emitters, six medium emitters, and high emitters. Filter samples from all of the FTPs that were pooled for PAH analysis were also analyzed individually by IC, XRF, and TOR. This permitted the determination of the emission rates of the sulfate, nitrate, trace elements, OC, and EC on a vehicle model year category basis, while still allowing the calculation of the pooled sample emission rates for source profiles. For the winter, 42 FTP filter sets were pooled into the following 17 3-phase sample

TABLE 1. Average PM and Regulated Emission Rates

period	category	number	g/mi HC	g/mi CO	g/mi NOx	PM mg/mi
summer	1991−96	5	0.24	3.44	0.46	3.2
summer	1986−90	9	0.77	6.46	1.50	19.6
summer	1981−85	7	2.65	21.4	1.59	42.5
summer	1971−80	6	6.60	63.7	2.52	102
summer	smoker	7	8.43	44.7	2.21	351
summer	diesel	4	[a]	4.20	4.97	1176
winter	1991−96	5	1.39	17.0	0.73	39.9
winter	1986−90	6	1.17	14.9	1.38	25.0
winter	1981−85	6	4.05	45.3	2.07	62.3
winter	1971−80	6	4.42	59.6	1.82	109
winter	smoker	8	10.0	74.5	2.54	574
winter	diesel	11	1.14	1.80	1.64	538

[a] No data.

sets: 5 diesels, 3 smokers, 2 low emitters, 2 mid-low emitters, and 2 high emitters.

Results

Table 1 gives the number of vehicles in each of the six vehicle categories for the summer and winter whose PM samples were analyzed for carbon, anions, and elements. Also given are the average regulated and PM-10 emission rates. As expected, emissions tend to increase with vehicle age due to both changes in vehicle technology and the increased likelihood of poor maintenance or tampering. Emissions also tend to be higher in the winter than the summer due to the influence of the cold start portion of the FTP. Summer/winter differences are also due to the differences in the vehicles recruited in the two portions of the study.

Carbon. The bulk of the PM mass is expected to be carbonaceous material. Therefore, linear regressions were performed between mass and total carbon. For the summer the regression for the nonsmoking gasoline vehicles had a slope of 0.77 and an R^2 of 0.87 (with one outlier removed). This relationship was examined for each phase of the FTP for the summer nonsmoking vehicles as well. The slopes of the linear regressions for phases 1−3, respectively, were 0.79, 0.66, and 0.80, while the R^2 values were 0.84, 0.87, and 0.87. Results for the winter nonsmoking gasoline vehicles were similar, with a linear regression slope of 0.76 and an R^2 of 0.995. Results were poorer for the smoking vehicles and diesels. For the winter smokers and diesels, the slopes were 0.53 and 0.45 with R^2 values of 0.98 and 0.63. Removing the highest emitters improved the results, indicating that filter inhomogeneities with the heavily loaded samples may play a role.

The fraction of the carbonaceous material defined as organic and elemental is also of interest for several reasons. First, differences in OC and EC ratios may be useful in source apportionment studies to identify mobile source emissions or even to help distinguish between diesel and gasoline vehicle emissions. Second, elemental carbon is strongly light-absorbing, and thus has a different impact on visibility than the organic carbon. Third, OC may be useful as a surrogate for specific compounds of interest. Figure 1 gives the OC/EC splits for phase 1 of the FTP for the winter vehicles. The bars are grouped by vehicle category (nonsmoking gasoline, smoker, diesels), and within these categories the vehicles are arranged in order of increasing FTP Phase 1 emissions from left to right. There is clearly a great deal of variability between vehicles. Overall, the percent OC is highest for the smoking vehicles and lowest for the diesels. Similar variability was observed for the other FTP phases and for the summer samples. The complementary figures for these can be found elsewhere (*16*). Table 2 gives the average OC by FTP phase
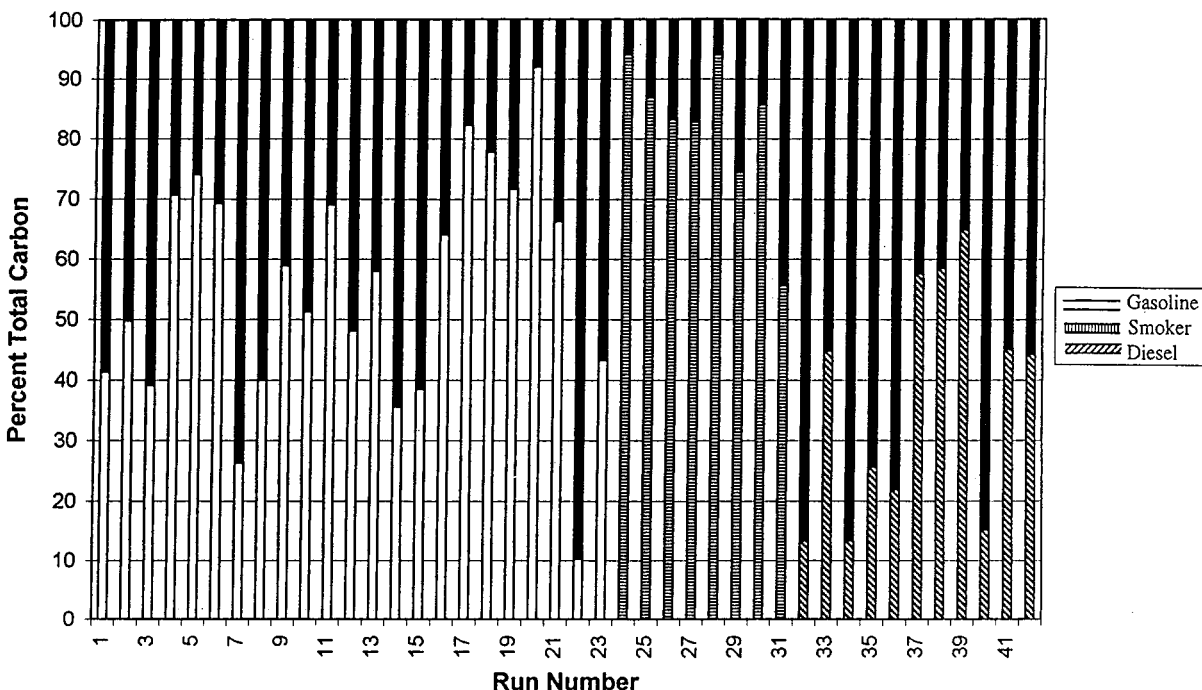
FIGURE 1. Phase 1 OC/EC split for winter vehicles. Solid bar is the EC percentage.

TABLE 2. Organic Carbon Percentage of the Total Carbonaceous Material

period	category	FTP phase 1	FTP phase 2	FTP phase 3
summer	1991−96	52.0	73.9	58.4
summer	1986−90	66.8	86.2	65.1
summer	1981−85	69.2	77.0	68.4
summer	1971−80	84.6	88.4	83.4
summer	smoker	89.7	89.0	83.1
summer	diesel	43.0	58.7	44.3
winter	1991−96	59.3	78.1	72.1
winter	1986−90	58.2	79.8	62.5
winter	1981−85	40.7	33.2	53.2
winter	1971−80	64.4	71.3	65.8
winter	smoker	82.2	88.3	83.5
winter	diesel	36.7	34.1	34.7

for both the summer and winter samples. There is a tendency for the newer, lower emitting vehicles to have lower percent OC emissions in phases 1 and 3 than in phase 2. This may be the influence of enrichment during starting. The summer vehicles show a clear trend of increasing organic percentage with age; however, this trend is not present for the winter vehicles. In both the summer and winter vehicles, the smokers consistently have the highest OC percentage, presumably due to motor oil emissions. Diesels consistently have the lowest OC percentage.

It is generally assumed that the organic carbon measurement for a source sample should be multiplied by a factor of 1.2 to account for the mass of other elements, primarily hydrogen and oxygen. Since 77% of the PM from nonsmoking gasoline vehicles was carbonaceous material, and approximately 70% of that is organic carbon, it is estimated that the carbonaceous material accounted for 88%, on average, of the PM from these vehicles.

Sulfate and Nitrate Emission Rates. Table 3 gives average FTP sulfate and nitrate emission rates by vehicle category for both the summer and winter studies. Minimum detection limits for sulfate and nitrate were approximately 0.04 mg/mi. Sulfate was detectable in most samples, although at very

low levels. The highest sulfate emission rate for a nonsmoking gasoline vehicle was 8.76 mg/mi, for a 1976 model car. The next two highest emission rates for nonsmoking gasoline vehicles were 1.55 and 1.27 mg/mi, for 1971 and 1984 vehicles, respectively. The average sulfate emission rate for the 51 nonsmoking vehicles tested was 0.45 mg/mi. The average with the highest emitter removed was 0.28 mg/mi. Five of the 14 smoking vehicles had a sulfate emission rate greater than 1.0 mg/mi. The average rate was 1.18 mg/mi, although this decreased to 0.73 mg/mi upon removal of the highest emitter (7.03 mg/mi). Diesel vehicles had the highest sulfate emission rate, averaging 3.51 mg/mi for 15 vehicles. Removal of the highest emitter (17.8 mg/mi) decreased the average to 2.49 mg/mi.

Since the number of cold and hot starts may be different in real world operation from the weighting factors used for the FTP, it is useful to examine the emission rates by FTP phase. Table 3 also gives the average sulfate emission rates for each vehicle category by FTP phase. Emissions are highest in phase 1 (cold start operation) and lowest in phase 2 (hot stabilized operation) during both the summer and winter.

Total sulfur measured by XRF can be compared to the IC sulfate measurements. Linear regressions were performed separately on the summer and winter data, including results from all three FTP phases and all vehicles. The IC sulfate results were adjusted to remove the mass of the associated oxygen. The summer and winter linear regressions had slopes of 0.35 and 0.39 and R^2 values of 0.74 and 0.92, respectively. Removing the diesels and/or smokers from the comparisons had little effect on the results. Average ratios of IC sulfur to XRF sulfur for the summer and winter were also computed. Summer average ratios were 0.40, 0.50, and 0.45 for FTP phases 1−3, respectively. Those for the winter were 0.44, 0.39, and 0.40, respectively. Thus, while the total sulfur is well correlated with the IC sulfur, the majority of the sulfur is not emitted as water-soluble sulfate. The nonsoluble sulfur may derive from organosulfur compounds present in fuel and motor oil and from zinc dithiophosphate, which is a standard additive to motor oil. Motor oil is clearly a major contributor to the PM mass in many of the samples.

TABLE 3. Average FTP Sulfate and Nitrate Emission Rates

period	category	sulfate (mg/mi)	phase 1 SO$_4^{2-}$ (mg/mi)	phase 2 SO$_4^{2-}$ (mg/mi)	phase 3 SO$_4^{2-}$ (mg/mi)	nitrate (mg/mi)
summer	1991−96	0.05	7.51 (0.69)[a]	0.13	0.20	0.00
summer	1986−90	0.15	0.27	0.08	0.11	0.02
summer	1981−85	0.14	0.28	0.15	0.24	0.00
summer	1971−80	1.67 (0.26)[a]	0.08	0.05	0.03	0.09
summer	smoker	0.34	0.33	0.20	0.34	0.04
summer	diesel	5.61 (1.54)[a]	9.19 (3.76)[a]	2.31 (0.81)[a]	9.16 (1.28)[a]	1.26 (0.25)
winter	1991−96	0.30	1.57	0.26	0.35	0.04
winter	1986−90	0.28	0.91	0.29	0.94	0.04
winter	1981−85	0.60	0.45	0.17	0.35	0.08
winter	1971−80	0.55	0.83	0.12	0.29	0.09
winter	smoker	1.80 (1.05)[a]	6.03 (2.24)[a]	0.61	0.94	[b]
winter	diesel	2.74	7.51	1.37	1.76	[b]

[a] Values in parentheses are the average with the highest emitter removed. [b] No data.

TABLE 4. Average Emission Rates of Elements

period	category	mg/mi PM	Mg	Al	Si	P	S	Cl	Ca	Fe	Cu	Zn	Br	Pb	K	Cr	sum
summer	1991−96	3.0	0.0	0.01	0.183	0.005	0.019	0.002	0.003	0.036	0.001	0.006	0.0	0.003	[a]	[a]	0.27
summer	1986−90	85.8	0.046	0.041	0.129	0.115	0.225	0.012	0.17	0.088	0.025	0.186	0.0	0.027	[a]	[a]	1.07
summer	1981−85	42.5	0.009	0.01	0.211	0.071	0.147	0.007	0.136	0.06	0.011	0.108	0.0	0.006	[a]	[a]	0.78
summer	1971−80	102.2	0.029	0.018	2.516	0.094	0.512	0.23	0.071	0.113	0.012	0.099	0.012	0.043	[a]	[a]	3.75
summer	smokers	281.7	0.148	0.029	0.249	0.241	0.629	0.039	0.312	0.085	0.019	0.369	0.009	0.035	[a]	[a]	2.17
summer	diesel	1175	0.402	0.303	3.189	0.634	4.504	0.139	1.329	3.151	0.019	1.731	0.009	0.15	[a]	[a]	15.6
winter	1991−96	39.9	0.046	0.035	0.11	0.097	0.316	0.014	0.139	0.293	0.013	0.19	0.001	0.019	0.012	0.007	1.29
winter	1986−90	25.0	0.051	0.098	0.132	0.079	0.217	0.041	0.126	0.236	0.009	0.149	0.002	0.019	0.015	0.01	1.18
winter	1981−85	42.6	0.064	0.103	0.371	0.15	0.505	0.028	0.181	1.074	0.015	0.236	0.028	0.103	0.02	0.017	2.89
winter	1971−80	108.7	0.078	0.09	0.714	0.225	0.581	0.068	0.241	1.013	0.018	0.246	0.057	0.222	0.027	0.021	3.60
winter	smoker	574.1	[a]	[a]	[a]	[a]	2.114	0.127	0.401	1.885	0.064	[a]	0.036	0.282	[a]	[a]	4.91
winter	diesel	537.5	[a]	[a]	[a]	[a]	2.343	0.217	0.137	0.476	0.025	[a]	[a]	0.142	[a]	[a]	3.34

[a] Emission rate below detection limit.

Nitrate concentrations were frequently below the detection limit. The combined summer and winter fleet FTP nitrate emission rate for nonsmoking gasoline vehicles was 0.04 mg/mi. The highest nitrate emission rate was 0.26 mg/mi for a 1971 model year vehicle.

No nitrate emission rate data were obtained for the winter smoking and diesel vehicles due to high nitrate blanks on the filters. The five summer smoking vehicles averaged only 0.04 mg/mi nitrate. The four summer diesels averaged 1.26 mg/mi nitrate, but this is highly influenced by one vehicle with a nitrate emission rate of 4.31 mg/mi. This is the same diesel vehicle that had a sulfate emission rate of 17.8 mg/mi, almost all of which was in the first phase of the FTP. Overall, it is concluded that nitrate is not a significant contributor to the PM mass emissions from motor vehicles.

XRF Elements. Emission rates of various elements are of interest since they constitute part of the mobile source PM source signature used in receptor modeling. Trace metals are of interest because one of the hypotheses for human health effects of PM involves reactions catalyzed by transition metals. Also, some metals are considered to be air toxics. Emission rates for 40 elements were obtained by XRF. Of these, only 12 elements had emission rates that averaged higher than the measurement uncertainty for the summer samples while 14 elements averaged higher than the measurement uncertainty for the winter samples. Uncertainties for the elements are presented elsewhere (16). The average FTP emission rates by vehicle category for quantifiable elements are listed in Table 4 for both the summer and winter. No data are available for several elements for smokers and diesels in the winter because of high filter backgrounds. The emission rates for each element averaged less than 1 mg/mi for the nonsmoking gasoline vehicles, with the exception of

silicon for the summer 1971−80 vehicles, and iron for the 1971−80 and the 1981−85 winter vehicles. The summer silicon emission rate of 2.5 mg/mi is dominated by one high-emitting vehicle. Smoking vehicles have higher emission rates for most of the elements, in line with their overall higher PM rate. Emission rates for the diesels were higher than for gasoline, with silicon, sulfur, calcium, iron, and zinc exceeding an average of 1 mg/mi in the summer.

The total emission rate for the elements as the percent of the average FTP PM mass was highest for the summer 1991−96 vehicles at 9.0%. For the winter, these elements only contributed to 3.2% of the mass. Much of this difference is due to the high silicon observed for the summer 1991−96 vehicles. The winter vehicles also had higher carbon emission rates due to the influence of the cold start. The average for the other nonsmoking vehicles was 2.25% during the summer and 4.94% during the winter. Overall, it is seen that these elements are a relatively small contributor to the PM mass.

Table 5 gives the average emission rates of the summer vehicle elements as a function of FTP phase. Emission rates tend to be highest during the cold start portion of the test, and lowest during hot, stabilized operation, the same general pattern that is observed for total PM mass emission rates.

Correlating the emission rates of the elements gives some information regarding their source. Zinc and phosphorus most likely are derived from motor oil, since zinc dithiophosphate is a standard anti-wear and anti-oxidant oil additive. Thus, it is not surprising that there was a high correlation between these species for both the summer and winter gasoline vehicles ($R^2 = 0.90$). Calcium and magnesium are present in motor oil as detergent additives, and copper is added as an antioxidant. These elements also correlate reasonably well with phosphorus, with R^2 values of 0.77, 0.68,

TABLE 5. Summer Average Emission Rates of Elements by FTP Phase

| | | | mg/mi | | | | | | | | | | | |
category	phase	mass	Mg	Al	Si	P	S	Cl	Ca	Fe	Cu	Zn	Br	Pb
1971–80	1	327	0.068	0.041	10.711	0.208	1.997	1.031	0.190	0.371	0.031	0.271	0.053	0.112
1971–80	2	43.4	0.019	0.010	0.426	0.051	0.111	0.025	0.032	0.030	0.006	0.034	0.002	0.015
1971–80	3	44.8	0.018	0.017	0.331	0.092	0.160	0.019	0.057	0.078	0.011	0.095	0.001	0.044
1981–85	1	108	0.031	0.017	0.326	0.162	0.393	0.017	0.264	0.129	0.030	0.260	0.001	0.016
1981–85	2	23.9	0.003	0.006	0.201	0.026	0.069	0.004	0.073	0.030	0.003	0.037	0.000	0.002
1981–85	3	28.4	0.005	0.011	0.141	0.088	0.111	0.006	0.162	0.066	0.011	0.129	0.000	0.006
1986–90	1	100	0.089	0.071	0.166	0.211	0.319	0.014	0.290	0.195	0.034	0.327	0.000	0.041
1986–90	2	13.0	0.033	0.028	0.136	0.073	0.237	0.014	0.141	0.046	0.019	0.123	0.000	0.020
1986–90	3	81.9	0.060	0.039	0.125	0.175	0.273	0.011	0.275	0.111	0.025	0.274	0.000	0.031
1991–96	1	6.35	0.000	0.012	0.231	0.010	0.034	0.008	0.011	0.092	0.003	0.013	0.001	0.005
1991–96	2	2.30	0.001	0.010	0.221	0.003	0.017	0.001	0.000	0.013	0.001	0.002	0.000	0.002
1991–96	3	1.94	0.000	0.007	0.075	0.004	0.010	0.002	0.002	0.036	0.001	0.006	0.000	0.002
smoker	1	335	0.126	0.059	0.258	0.304	0.911	0.057	0.305	0.119	0.022	0.403	0.029	0.116
smoker	2	225	0.178	0.022	0.225	0.175	0.472	0.037	0.181	0.031	0.022	0.279	0.004	0.010
smoker	3	235	0.133	0.021	0.282	0.291	0.672	0.040	0.342	0.110	0.018	0.488	0.008	0.031
diesel	1	2510	0.601	0.403	4.627	1.148	6.781	0.308	2.451	2.925	0.027	3.250	0.011	0.190
diesel	2	437	0.197	0.103	1.234	0.248	1.736	0.070	0.438	0.614	0.005	0.594	0.005	0.048
diesel	3	1568	0.639	0.607	5.819	0.982	8.040	0.144	2.185	8.133	0.039	2.756	0.015	0.313

and 0.63, respectively, for the summer and 0.95, 0.86, and 0.93, respectively, for the winter. On the other hand, sulfur is expected to be predominantly from the fuel, yet it also correlates moderately well with phosphorus ($R^2 = 0.63$) in the summer and winter ($R^2 = 0.79$).

This supports the earlier suggestion that a significant fraction of the sulfur in the PM may be derived from the motor oil. The correlation between phosphorus and PM mass was 0.29 and 0.52 in the summer and winter, respectively, suggesting that much more than oil consumption is involved in the production of PM.

Silicon is sometimes present as an additive to motor oil, but is not added to gasoline since it can damage emission control components. However, the silicon emission rate did not correlate with phosphorus ($R^2 = 0.03$ in the summer and $R^2 = 0.21$ in the winter). This could simply indicate that the silicon concentration in motor oil is highly variable. Silicon could also be present from the ingestion of road dust. PM-2.5 road dust composition was determined as part of the NFRAQS study (14). The ratio of silicon to iron, aluminum, and calcium averaged 1/0.19/0.32/0.15. The same ratios for the summer and winter exhaust PM-10 (which is mostly PM-2.5) were 1/0.35/0.11/0.80 and 1/1.97/0.25/0.36, respectively. The summer 1971–80 exhaust ratios were excluded from the average since the silicon appeared to be an outlier. The ambient and exhaust ratios indicate that road dust could be a significant contributor to all of these species. However, iron and aluminum, which are both in road dust, were weakly correlated ($R^2 = 0.44$ in the summer and 0.58 in the winter), and neither was correlated with silicon in the summer. Iron and aluminum were weakly correlated with silicon in the winter ($R^2 = 0.56$ for iron and 0.30 for aluminum). Thus, the relative importance of wear and corrosion products, oil consumption, and road dust ingestion cannot be determined from this analysis.

Polynuclear Aromatic Hydrocarbons. As was noted earlier, PAH was determined on composited samples. Composites for nonsmoking gasoline vehicles were formed from vehicles having similar emission rates, regardless of age, and cannot be examined using the vehicle model year categories used in the rest of the report. These composites are identified as being either low emitters (L), medium low emitters (ML), medium emitters (M), or high (H) emitters. The carbon, anion, and elemental analyses discussed earlier were all performed on an individual vehicle basis. Thus, that data can be composited to match the PAH data.

Table 6 lists the individual PAH compounds measured for the summer vehicles. A slightly modified set of PAHs was measured for the winter vehicles as well. Compounds are listed in their gas chromatography elution order, which is equivalent to decreasing vapor pressure. Naphthalene was measured, but is not reported for the summer vehicles because of problems with a high blank. Naphthalene and monosubstituted naphthalenes are gas-phase compounds. Higher molecular weight PAHs up to chrysene are semi-volatile and will partition between the gas and particle phases. PAHs with molecular weights above chrysene are expected to be predominantly in the particle phase (5). Since the PUF and filter samples were analyzed together, it is not known how much of the PAH was present in the particle phase. In a previous study (10), PUF and filter samples were analyzed separately for 28 PAHs including naphthalene. For these vehicles, only 2.5% of the PAH was present on the filter samples. The actual partitioning between gas and particle phase depends on a number of sampling parameters. Therefore, even if the partitioning had been measured in this study, it might not be indicative of the partitioning that would occur in the atmosphere. For this reason, it is best to measure a broad range of PAH compounds when generating data for source apportionment purposes.

Figure 2 shows the emission rates of the compounds for the summer high emitter vehicles. Note that the emission rate scale is logarithmic. Compounds are in the same order as in Table 6, but only every other compound is labeled. There is a general trend toward lower emission rates for the lower volatility compounds. Table 7 gives the emission rates for a subset of the measured compounds for the different PM emission rate categories in the summer and winter. The emission rates of gasoline vehicle individual PAHs generally increase as the total PM emission rate increases. The exception is for the winter smoking vehicles, which have a higher PM emission rate than the winter high PM emitters, but lower PAH emission rates for most of the compounds. There were large differences in emission rates for some of the compounds between the summer and winter. The reason for the difference is not known. The total PAH emission rate (excluding naphthalene) is given in Table 8. Naphthalene emission rates for the winter low emitter (L) through diesel (D) categories were 1.46, 7.33, 6.74, 36.8, 29.9, and 4.9 mg/mi, respectively. Also included in Table 8, for comparison purposes, is the emission rate of the lower vapor pressure PAHs (anthracene through coronene in Table 6). As noted

TABLE 6. Measured PAH Compounds

| no.	compound	no.	compound	no.	compound
1	2-methylnaphthalene	24	H-trimethylnaphthalene	47	fluoranthene
2	1-methylnaphthalene	25	1,2,8-trimethylnaphthalene	48	pyrene
3	2,6 + 2,7-dimethylnaphthalene	26	acenaphthylene	49	A-methylpyrene
4	1,7+1,3+1,6-dimethylnaphthalene	27	acenaphthene	50	B-methylpyrene
5	2,3+1,4+1,5-dimethylnaphthalene	28	phenanthrene	51	C-methylpyrene
6	1,2-dimethylnaphthalene	29	fluorene	52	D-methylpyrene
7	1,8-dimethylnaphthalene	30	1-methylfluorene	53	E-methylpyrene
8	biphenyl	31	B-methylfluorene	54	F-methylpyrene
9	A-methylbiphenyl	32	C-methylfluorene	55	G-methylpyrene
10	2-methylbiphenyl	33	A-methylphenanthrene	56	retene
11	B-methylbiphenyl	34	2-methylphenanthrene	57	benzonaphthothiophene
12	3-methylbiphenyl	35	B-methylphenanthrene	58	benz(*a*)anthracene
13	4-methylbiphenyl	36	C-methylphenanthrene	59	7-methylbenz[*a*]anthracene
14	C-methylbiphenyl	37	1-methylphenanthrene	60	chrysene[a]
15	A-trimethylnaphthalene	38	3,6-dimethylphenanthrene	61	benzo(*b+j+k*)fluoranthene
16	1-ethyl-2-methylnaphthalene	39	A-dimethylphenanthrene	62	benzo[*e*]pyrene
17	B-trimethylnaphthalene	40	B-dimethylphenanthrene	63	benzo[*a*]pyrene
18	C-trimethylnaphthalene	41	C-dimethylphenanthrene	64	7-methylbenzo[*a*]pyrene
19	2-ethyl-1-methylnaphthalene	41	1,7-dimethylphenanthrene	65	indeno[123-cd]pyrene
20	D-trimethylnaphthalene	42	D-dimethylphenanthrene	66	dibenz(*ah+ac*)anthracene
21	E-trimethylnaphthalene	43	E-dimethylphenanthrene	67	benzo(*b*)chrysene
22	F-trimethylnaphthalene	44	anthracene	68	benzo(*ghi*)perylene
23	G-trimethylnaphthalene	45	9-methylanthracene	69	coronene
		46			

[a] May also include triphenylene.
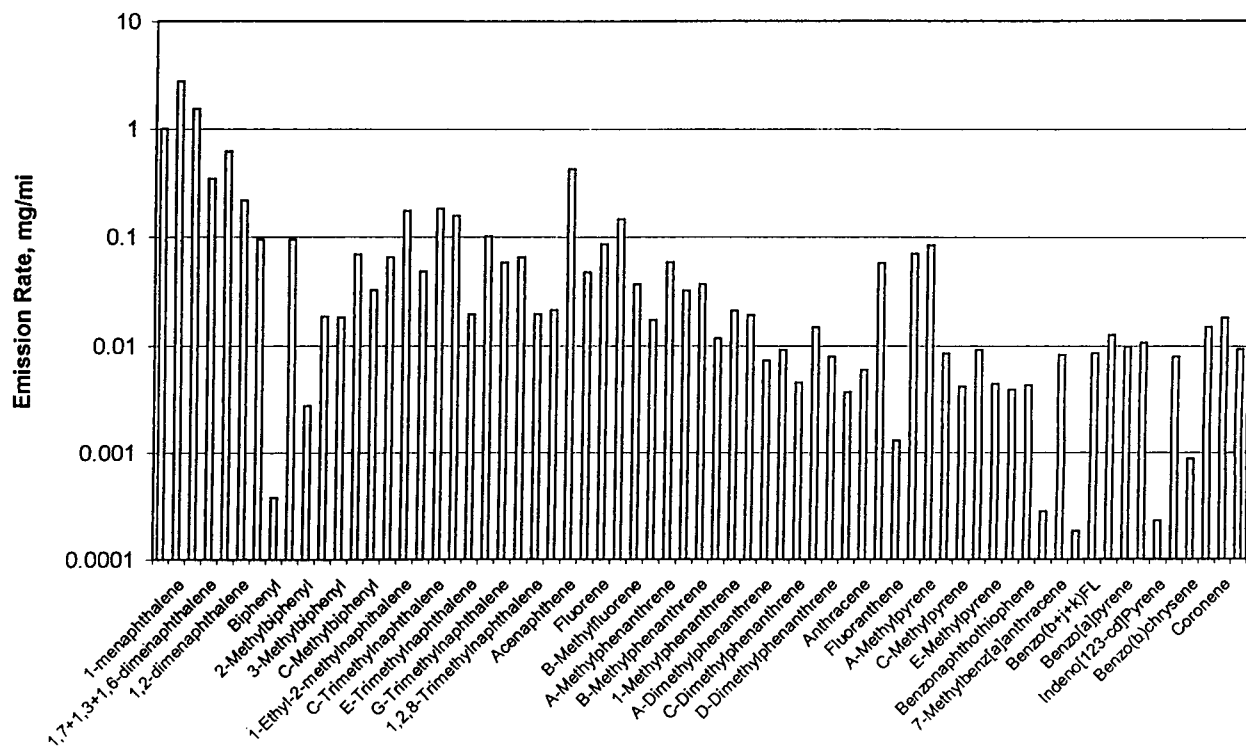
FIGURE 2. FTP average PAH emission rates for the summer high emitters.

with the individual compounds, PAH emissions tend to increase as the PM emission rate increases.

The gasoline vehicle PAH emission rate was compared to both the PM emission rate and the OC emission rate. For the summer, the correlation between individual samples was very weak, with an R^2 of 0.29 and 0.23 for PAH vs PM and PAH vs OC, respectively. The correlation was stronger with the winter samples, with an R^2 of 0.82 for PAH and PM and 0.47 for PAH and OC. The PAHs can be formed during combustion or can be unburned components of the fuel and motor oil. Thus, sources of variability in this comparison are expected to be the different fuels and motor oils used by each vehicle, and the engine combustion conditions. It is

concluded that total PAH is not a good candidate as a tracer of gasoline vehicle PM emissions.

A more robust approach to using the PAH data is to create source profiles using the individual compounds. The suitability of using the data from this study to create unique source profiles for different emitter categories was judged by examining plots of the ratios of all the compounds in different samples. Comparisons between individual samples within a PM emitter category showed considerable variability in the relative emission rates of the various PAHs, with the greatest variability occurring for the highest molecular weight species. Significant differences were also observed between the average emission rates in the different emitter classes,

TABLE 7. Emission Rates of Individual PAHs

		mg/mi					
period	compound	ave L	ave ML	ave M	ave H	ave S	ave D
summer	anthracene	0.022	b	0.0481	0.0572	0.147	0.562
summer	fluoranthene	0.0484	b	0.0474	0.0705	0.176	0.896
summer	pyrene	0.0556	b	0.0521	0.0840	0.301	1.0503
summer	benz(a)anthracene	0.00159	b	0.0038	0.00821	0.0287	0.0768
summer	chrysene	0.00126	b	0.00374	0.0085	0.0328	0.153
summer	benzo(b+j+k)fluoranthene	0.00007	b	0.00294	0.0125	0.0353	0.115
summer	benzo[a]pyrene	0.00052	b	0.00247	0.0107	0.0417	0.0392
summer	indeno[123-cd]pyrene	0.00033	b	0.00204	0.00791	0.0208	0.0476
summer	dibenz(ah+ac)anthracene	0.00007	b	0.00033	0.00087	0.00158	0.0038
summer	benzo(ghi)perylene	0.00089	b	0.00578	0.0183	0.0919	0.0829
winter	anthracene	0.124	0.128	0.280	0.543	0.609	0.225
winter	fluoranthene	0.218	0.267	0.435	1.018	0.587	0.181
winter	pyrene	0.257	0.356	0.559	1.464	0.753	0.209
winter	benz(a)anthracene	0.00153	0.00437	0.00504	0.0341	0.0355	0.0165
winter	chrysene[a]	0.00153	0.00479	0.0056	0.0378	0.0321	0.0238
winter	benzo(b+j+k)fluoranthene	0.00000	0.00728	0.00952	0.107	0.0890	0.0463
winter	benzo[a]pyrene	0.00073	0.00312	0.00353	0.0651	0.0455	0.0108
winter	indeno[123-cd]pyrene	0.00000	0.00188	0.00257	0.0439	0.0387	0.00797
winter	dibenz(ah+ac)anthracene	0.00000	0.0001	0.00007	0.00271	0.00343	0.00145
winter	benzo(ghi)perylene	0.00020	0.00548	0.00841	0.178	0.125	0.0151

[a] May include triphenlyene. [b] Asterisk indicates that the ML category was not used for the summer samples.

TABLE 8. Average FTP Emission Rates for the Composite PAH Samples

period	sample	no. of vehicles	PM (mg/mi)	PAH[a] (mg/mi)	high MW PAH[b] (mg/mi)
summer	L	7	6.1	2.03	0.14
summer	M	6	24.4	5.51	0.17
summer	H	6	70.5	8.05	0.29
summer	S	6	282	31.3	0.97
summer	D	4	1497	45.6	3.12
winter	L	3	7.2	2.98	0.51
winter	ML	5	28.3	10.3	0.7
winter	M	8	61.4	13.0	1.09
winter	H	2	213	38.9	3.3
winter	S	8	632	46.7	1.94
winter	D	11	557	23.7	0.61

[a] Naphthalene not included. [b] Compounds 47−69 from Table 6.

although the differences were no greater than the variability between samples within a single emitter category. The most significant difference was between the diesel vehicles and the gasoline vehicles. An example of this is shown in Figure 3, which plots the ratio of the summer average diesel PAH emission rates to those of the summer high emitters. The diesel is clearly enriched in the midrange compounds as compared to both the low- and high-end compounds. It was concluded that PAH profiles may help in separating gasoline from diesel emissions in source apportionment studies. More data would be required before it can be determined if PAH profiles can distinguish between gasoline vehicle emitter categories, such as smoking and nonsmoking vehicles.

Finally, differences in PAH emission rate profiles between the three FTP phases were examined. The differences were greatest for the low and medium emitting gasoline vehicles, which had relatively higher emissions of both the low and high molecular weight compounds during the cold start (phase 1) than during phases 2 or 3. For the high emitting vehicles, the mid-molecular weight range PAH emission rates were approximately half those of the low and high molecular weight PAHs in phase 1 compared to phase 2. For smoking vehicles, the differences between phases 1 and 2 were mostly in the high molecular weight compounds, which had rates approximately double those of the low and mid-molecular

weight PAHs. Thus, a composite PAH profile for source apportionment should reflect the local vehicle activity data rather than relying on the FTP weighting of the three phases. This also suggests that PAH profiles generated from vehicle tunnel studies or driving cycles that do not incorporate starting emissions may not be fully representative of in-use vehicle emissions.

Steranes/Hopanes. It has been suggested that steranes and hopanes make good marker compounds for mobile source PM, and that the emission rates for gasoline and diesel vehicles may be different enough that their PM emissions can be distinguished from each other (23). Steranes and hopanes were measured in the same sample extracts as the PAHs. Thus, their emission rates are for the same composite samples as the PAHs.

Table 9 gives the average FTP emission rates of the individual compounds by PM emitter category for the summer. The average ratio of the emission rate to the uncertainty in the measurement of the rate ranged from a high of 5.5 for sitostane to 1.9 for trisnorhopane-1. Several of the compounds' emission rates averaged only 2−3 times the uncertainty. Thus, it should be recognized that significant errors are probable in the rates. The sum of the measured species and their percent of the PM mass are also given. Their contribution to the PM mass is seen to decrease as the average emission rate increases. Concentrations of all the species were lower in the winter samples (not shown), resulting in a larger number of compounds that were not detectable. The sum of the average emission rates of the measured compounds for the L, ML, M, H, S, and D emitter classes was 0.014, 0.031, 0.045, 0.077, 0.19, and 0.12 mg/mi, respectively. These were 0.20, 0.11, 0.073, 0.036, 0.030, and 0.021% of the PM mass, respectively. Winter hopane and sterane emissions constituted a lower percentage of the PM than during the summer, by factors of 2−4. This difference cannot be attributed entirely to the greater number of nondetectable compounds in the winter. The cause of the difference is not known. The trend for the winter sterane and hopane contribution to the PM mass was the same as for the summer, a decreasing contribution as the mass emission rate increased.

The distributions of individual steranes and hopanes for the different emitter categories were compared. An example is shown in Figure 4, which plots the individual emission
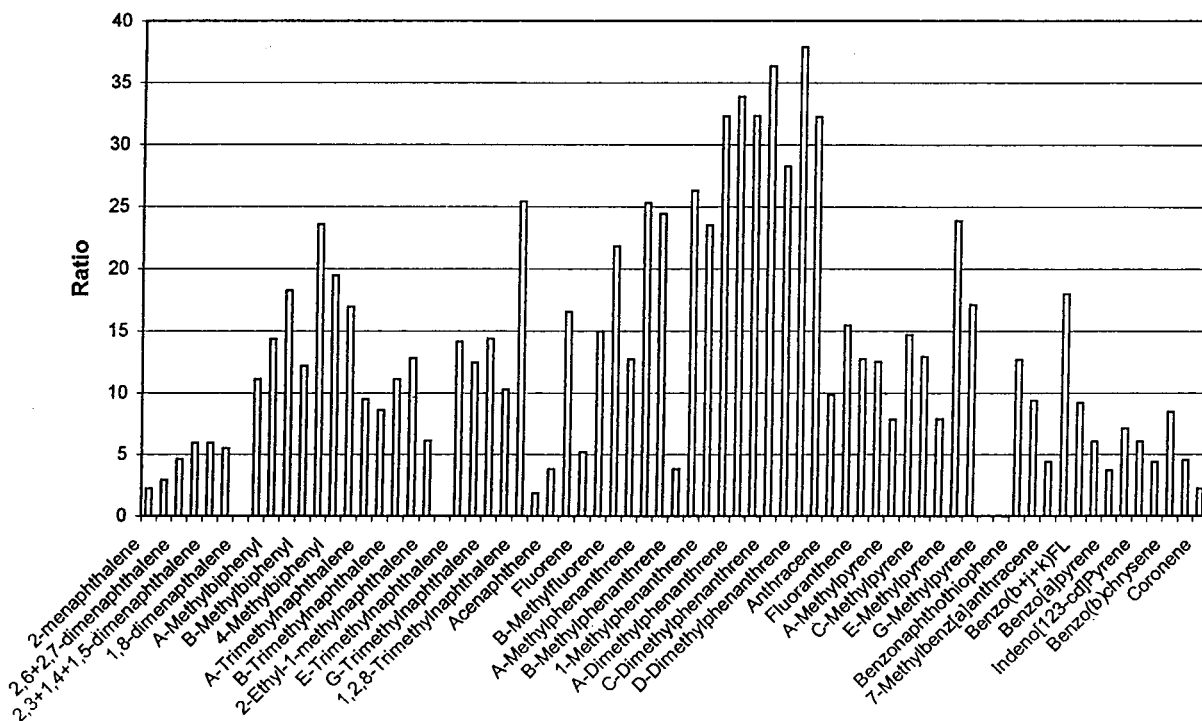
Ratio axis: 0, 5, 10, 15, 20, 25, 30, 35, 40

X-axis labels: 2-menaphthalene, 2,6+2,7-dimenaphthalene, 2,3+1,4+1,5-dimenaphthalene, 1,8-dimenaphthalene, A-Methylbiphenyl, B-Methylbiphenyl, 4-Methylbiphenyl, A-Trimethylnaphthalene, B-Trimethylnaphthalene, 2-Ethyl-1-methylnaphthalene, E-Trimethylnaphthalene, G-Trimethylnaphthalene, 1,2,8-Trimethylnaphthalene, Acenaphthene, Fluorene, B-Methylfluorene, A-Methylphenanthrene, B-Methylphenanthrene, 1-Methylphenanthrene, A-Dimethylphenanthrene, C-Dimethylphenanthrene, D-Dimethylphenanthrene, Anthracene, Fluoranthene, A-Methylpyrene, C-Methylpyrene, E-Methylpyrene, G-Methylpyrene, Benzonaphthothiophene, 7-Methylbenz2alanthracene, Benzo(b+j+k)FL, Benzo[a]pyrene, Indenol123-cd]Pyrene, Benzo(b)chrysene, Coronene

FIGURE 3. Ratio of summer average diesel to high emitter FTP PAH emission rates.

TABLE 9. Summer Average FTP Emission Rates for Hopanes and Steranes

compound	mg/mi				
	ave L	ave M	ave H	ave S	ave D
ergostane	0.0031	0.0050	0.0123	0.0534	0.1168
sitostane	0.0043	0.0054	0.0082	0.0357	0.0874
20S-13β,17α-diasterane	0.0012	0.0047	0.0044	0.0336	0.3135
20R-13β,17β-diasterane	0.0014	0.0034	0.0041	0.0257	0.0471
20R-5α,14β,17β-cholestane	0.0033	0.0047	0.0089	0.0475	0.1009
20S-5α,14β,17β-cholestane	0.0014	0.0042	0.0028	0.0166	0.0355
20R-5α,14α,17α-cholestane	0.0027	0.0033	0.0070	0.0452	0.0915
17α(H),18α(H),21β(H)$-$25,28,30-trisnorhopane	0.0016	0.0041	0.0037	0.0173	0.0427
17α(H),21β(H),22,29,30-trisnorhopane	0.0010	0.0032	0.0033	0.0130	0.0309
17α(H),21β(H)$-$30-norhopane	0.0089	0.0087	0.0145	0.0598	0.1561
17β(H),21α(H)$-$30-norhopane	ND	0.0125	ND	0.0053	ND
17α(H),21β (H)-hopane	0.0071	0.0080	0.0100	0.0349	0.1074
17β(H),21α(H)-hopane	0.0020	0.0080		0.0036	0.0277
22S-17α(H),21β(H)$-$30-homohopane	0.0035	0.0036	0.0051	0.0148	0.0500
22R-17α(H),21β(H)$-$30-homohopane	0.0023	0.0032	0.0039	0.0106	0.0387
17β(H),21β(H)-hopane	ND	0.0028	ND	ND	ND
22S-17α(H),21β(H)$-$30,31-bishomohopane	0.0019	0.0023	0.0031	0.0079	0.0284
22R-17α(H),21β(H)$-$30,31-bishomohopane	0.0016	0.0024	0.0024	0.0054	0.0229
sum	0.047	0.090	0.094	0.43	1.30
% of PM	0.78	0.37	0.13	0.15	0.086

rates for the high, smoker, and diesel summer PM emitter categories. Overall, the pattern of emissions is very similar between the categories, especially considering the relatively high uncertainties in the measurements. This was observed for the summer lower emitter categories and all of the winter emitter categories as well. Overall, it is concluded that these compounds may be useful as tracers for mobile source particulate emissions. However, there is no indication in these data that they can be used to distinguish between light-duty diesel and gasoline vehicle PM emissions, or smoking gasoline vehicles from other gasoline vehicles.

The average emission rates of the hopanes and steranes by FTP phase for each emitter category were examined. As expected, many of the compounds show a distinct difference in rates between phases, with the highest emission rates during the cold start. Thus, it is important to include cold start emissions in profiles that represent urban fleet PM emissions.

Discussion

PM emissions from the light-duty vehicles included in this study are composed largely of carbonaceous material. The average contribution, including a correction for the mass of additional elements associated with the OC, was 88%. This is in agreement with most other studies. For example, when the OC correction factor is applied to the results from Rogge (23), the PM emissions from seven catalyst vehicles averaged 83% carbon. Similarly, Sagebiel et al. (10) found that carbon accounted for 83% of the PM emissions from 23 light-duty gasoline vehicles (LDGVs) with high CO and/or HC emission rates, and Cadle et al. (11) found that the PM emission from
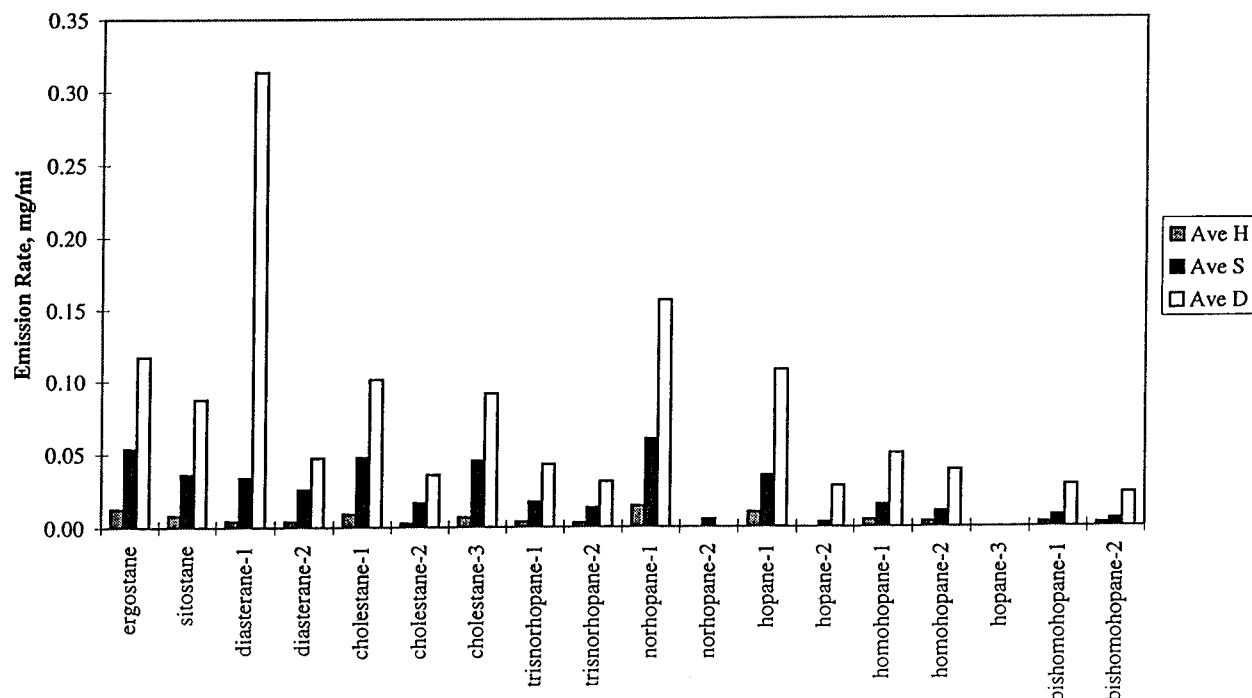
FIGURE 4. Comparison of high, smoker, and diesel average sterane and hopane emission rates for the summer.

67 LDGVs with high CO and/or HC emission rates was essentially all carbonaceous material.

PART5 is EPA's model for projecting PM emissions from on-road motor vehicles. PM emissions from gasoline vehicles operated on unleaded fuel are modeled as consisting of carbonaceous material and sulfate. The carbonaceous PM-10 emission rate is 4 mg/mi for all 1981 and later model year LDGVs, 6 mg/mi for 1970−80 model year LDGVs without air injection, and 25 mg/mi for 1970−80 model year LDGVs with air injection (13). In this study, the carbonaceous material emission rate, based on the total PM-10 emission rate and the 88% carbonaceous matter figure, was a strong function of vehicle age and maintenance condition as well as ambient temperature. Average carbonaceous material PM-10 emission rates for summer vehicles ranged from 90 mg/mi for 1971−80 vehicles to 2.8 mg/mi for 1991−96 vehicles. Vehicles recruited as having visible smoke emissions had an average carbonaceous matter emission rate of 309 mg/mi. The current PART5 carbonaceous matter emission rates for LDGVs underestimate the in-use vehicle fleet carbonaceous matter PM-10 emissions by not accounting for higher emissions from older vehicles or including the impact of cold start.

The OC fraction was found to be highly variable from vehicle to vehicle. This has been observed in previous studies as well (10, 11). On the other hand, average OC fractions reported in different studies have been quite consistent, ranging from 69% (9, 11) to 76% (10) for LDGVs. Smoking LDGVs averaged 91% (10). In this study, it was found that the OC percentage increases with PM emission rate, and varies by FTP phase (Table 2). For the summer LDGVs, 60% of FTP mass emissions occurred during phase 1 with 20% in each of phases 2 and 3. For the winter, an average of 72% of the FTP PM mass emissions occurred in phase 1, with 14% in phase 2 and 16% in phase 3, reflecting the increased importance of cold start at reduced temperature. Using these weighting factors, the FTP OC emissions for LDGVs in this study averaged 74% in the summer and 65% in the winter, in reasonable agreement with previous work. The OC percentages for the diesel vehicles in this study (45 and 35% in the summer and winter, respectively) were much lower than those for the LDGVs. This suggests that the OC/EC split

may be helpful in separating LDGV PM emissions from diesel PM emissions.

Nonsmoking LDGV sulfate emission rates in this study were very low, averaging 0.15 and 0.44 mg/mi for the summer and winter, respectively. Sagebiel et al. (10) found a 0.12 mg/mi average sulfate emission rate from 19 high-CO and/or HC emission vehicles tested on the IM240. This average excludes one vehicle with a sulfate emission rate of 13.6 mg/mi. Fuel sulfur content averaged 0.011 and 0.019 wt % at the two test locations employed. Mulawa and Dasch (24) found average FTP emissions of 0.67 mg/mi for eight LDGVs tested on the FTP. Fuel sulfur content was not reported. Watson et al. (9) report that the PM emissions from LDVGs tested on a loaded mode IM test average 2.3% sulfate. Fuel sulfur content and mass emission rates were not reported. Overall, it appears that sulfate emission rates from the in-use fleet are low.

The EPA PART5 model estimates sulfate emission rates from LDGVs. At FTP speeds with national average fuel sulfur content (0.034 wt %), the model uses a sulfate emission rate for catalyst-equipped LDGVs without air injection of 5 mg/mi and a sulfate emission rate of 16 mg/mi for catalyst LDGVs with air injection. These emission rates include the mass of water that is predicted to be associated with sulfate, which is assumed to be present as sulfuric acid. Thus, these values need to be reduced by a factor of 0.43 to compare to the sulfate emission rates reported in this and other studies. Even after adjusting for water content and reducing the sulfate emission rate to reflect a lower fuel sulfur content, it appears that PART5 overpredicts LDGV sulfate emissions.

Elemetal analysis results can be compared to those from other studies. Mulawa and Dasch (24) used neutron activation and XRF to identify elements in the PM from 14 vehicles. Fe, Ba, Cr, and Zn were the most abundant elements. Ce was present in PM from most vehicles, and Zr was identified in the PM from five of the vehicles. Fe, on average, was 12.4% of the total PM mass, which averaged 18 mg/mi. None of the other elements accounted for more than 0.5% of the mass. Since total PM was measured, some of the elements may have been present in large particles. Cadle et al. (11) used XRF to identify elements in the PM from 63 vehicles. The

TABLE 10. Comparison of PAH Emission Rates

compound	this study, summer FTP	air toxics[a] low emitter, FTP	air toxics high emitter, FTP	roadside[b] high emitters, IM240	roadside smoking, IM240	tunnel[c]
			mg/mi			
naphthalene	[f]	(2.1)[d]	(21.9)	28.5	61.5	62
1-methylnaphthalene	0.34–6.11	(0.42)	(6.04)	5.86	16.3	4.74
biphenyl	0.037–0.34	(0.055)	(0.82)	0.43	0.76	[f]
fluorene	0.025–0.44	(0.021)	(0.20)	0.30	0.86	0.12
phenanthrene	0.01–0.4	(0.020)	(0.035)	0.47	1.11	0.47
anthracene	0.022–0.15	(0.0065)	(0.011)	0.12	0.37	0.070
fluoranthene	0.048–0.18	(0.0002)	(0.0018)	0.22	0.88	0.074
pyrene	0.056–0.30	0.0018	0.039	0.27	1.12	0.097
chrysene[e]	0.0013–0.033	0.0009	0.018	0.022	0.17	0.0035

[a] Air toxics data of Siegl et al. (26). [b] Roadside data of Sagebiel et al.(10). [c] Tunnel data of Fraser et al.(8). [d] Values in parentheses are gas phase only. [e] May include triphenylene. [f] No data.

same elements were identified as in this study. The average contribution to the PM was 3.5%, with individual vehicle contributions ranging from 0.41 to 12.3%. Si, Cl, Fe, S, and P were the most abundant elements measured. Ball (25) used XRF to identify elements in the PM from four vehicles driven on three different cycles. The PM emission rates ranged from 0.48 to 9.5 mg/mi. Fe, Si, and S were the most abundant elements, followed by Ca, Cl, and Al. Small amounts of Ba, Ti, and Sn were also identified in some samples. It was concluded that 10–30% of the PM mass is composed of metals, sulfur and silicon. Watson et al. (9) reported percent mass abundances for elements from the PM collected during loaded-mode I/M tests. Si, S, Ca, Fe, Al, Cl, Zn, K, and P were the most abundant elements, with percent contribution to the PM of 1.64, 1.01, 0.71, 0.68, 0.41, 0.34, 0.27, 0.25, and 0.11, respectively.

It is concluded that inorganic species can be a significant fraction of the mass from some vehicles, primarily those with low emission rates. Their contribution to the in-use fleet LDGV exhaust emission is small, however. None of the individual elements are of particular environmental concern at these low emission rates. In addition, all of these species have other significant sources, and thus are not useful as unique tracers for motor vehicle emissions.

PAH emission rates determined in this study are compared to other LDGV measurements in Table 10. The range shown is for the average emissions for the different LDGV emitter categories, including smoking vehicles. Only the summer data were included since other studies have been done in the laboratory or in the field during warm periods. Data from three other studies are included in Table 10. The Siegl et al. (26) air toxics study measured PAHs from two vehicles operated on the FTP. One was a properly functioning 1989 LDGV, while the other was a high emitter 1987 LDGV. Most of the PAHs were measured in the gas phase only, although pyrene was measured in both the gas and particle phases and chrysene was measured in the particle phase only. Thus, the emission rates of those compounds expected to partition between the gas and particle phases (fluorene–fluoranthene) are expected to be low compared to a total PAH measurement. The Sagebiel et al. roadside study (10) measured gas- and particle-phase PAHs for 17 vehicles recruited as high-CO and/or HC emitters, and for 6 vehicles recruited because they had visible smoke emissions. Vehicles were tested using the IM240. The Fraser et al. (8) study measured gas and particle PAHs in the Van Nuys Tunnel in 1993. Traffic during sample collection included 6482 LDGVs and 186 diesel-powered heavy-duty vehicles. Thus, there was probably a significant diesel influence on the PAH distribution. These emissions clearly occur under different driving conditions than those in the other studies, and lack influence from cold and hot start emissions. Emission rates were reported as

micrograms per liter of fuel consumed. To facilitate a comparison to distance-based emission rates, a fuel economy of 20 mpg was assumed. A number of other tunnel studies have characterized PAH emissions (5), but are not included in this comparison because the fleets are older, and all tunnel study results are confounded by the diesel traffic and the lack of cold and hot start emissions.

Many factors can influence PAH emission rates, including fuel composition, PAH content of the lubricating oil, and engine operating mode (load, cold start, etc.). Thus, variations in PAH emissions are expected between these studies. For this study, naphthalene emission rates were not available for the summer. Winter naphthalene emission rates ranged from 1.46 to 36.8 mg/mi, which are similar to those found in the other studies. In general, the emission rates from the other studies fall within the large range of those found in Denver. This consistency is encouraging for the use of PAH profiles to help identify gasoline combustion emissions in source apportionment studies. The wide range of emission rates together with the differences observed in the profiles for different emitter categories and the different FTP phases suggest that a single profile representing the entire fleet will have to be carefully assembled based on the frequency of high emitters, smokers, and the appropriate local weighting of cold, hot, and hot-stabilized emissions.

Hopanes and steranes were measured solely due to their potential as vehicle emission tracers. Rogge et al. (23) measured the emission rates of several of these compounds for seven LDGVs. Fraser et al. (8) measured this class of compounds in the Van Nuys Tunnel. As noted above, the tunnel study includes the contribution from heavy-duty diesels as well as LDGVs, but is lacking in cold and hot start emissions. A few of the compounds measured were common to all three studies and can be compared. The $20R$-$5\alpha,14\alpha$,-17α-cholestane emission rates ranged from 0.0027 to 0.045 mg/mi in this study for the summer, was 0.0033 mg/mi in the tunnel (assuming a 20 mpg fuel economy), and was 0.0064 for the seven LDGVs. Emission rates for $17\alpha(H),21\beta(H)$-hopane were 0.0071–0.035, 0.016, and 0.014 mg/mi, in the three studies, respectively. Emission rates for $22S$-$17\alpha(H)$,-$21\beta(H)$-30-homohopane were 0.0035–0.015, 0.0066, and 0.0050 mg/mi, respectively, for the three studies. It is encouraging that the emission rates in the three studies are similar. Thus, it is likely that these will be useful as vehicle emission tracers. As was noted earlier, the emission rate profiles between gasoline emitter categories and LDDVs are very similar, and thus cannot be used to distinguish between these sources.

Overall, this study has provided a comprehensive characterization of the bulk composition of exhaust PM emissions from in-use vehicles in the Denver, Colorado area. These data are expected to be useful in improving emission

inventories and have already been used for source apportionment in the NFRAQS study (*14*). Future work will consider examining the composition of exhaust PM emissions collected from vehicles operated on driving cycles other than the FTP to determine if there are any significant differences that have to be considered when developing inventories.

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