FINAL TECHNICAL REPORT

Chemical Analysis of Lubrication Oil Samples from a Study to Characterize Exhaust Emissions from Light-Duty Gasoline Vehicles in the Kansas City Metropolitan Area

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ABSTRACT

This study compares the chemical composition of lubrication oils with corresponding composition of exhaust PM emissions obtained during the Kansas City Light Duty Vehicle Emissions Characterization Study. This test fleet consisted of 480 randomly selected, light-duty vehicles in the Kansas City Metropolitan Area. The study was conducted during July to September 2004 (summer/Round 1) and January to March 2005 (winter/Round 2). All vehicles were tested using the Unified Driving Cycle (UDC). A total of 26 individual/composite chemical profiles were obtained from 51 of 254 vehicles tested in Round 1 and another 26 composites from 51 of 230 vehicles tested in Round 2. Organic speciation included semi-volatile and particle phase polycyclic aromatic hydrocarbons (PAH), alkanes, hopanes and steranes, nitro-PAHs and polar compounds. Samples of the lubricating oil from each of the test vehicles were collected and stored for future analysis. We analyzed a subset of 15 used oil samples, combined into 9 composites, and three unused oils. Correlations of emissions of hopanes and steranes with organic carbon and PM emissions indicated that the organic fraction of particulate matter (PM) emissions of high emitters were associated mainly with consumption of lubricating oils. The rates of oil consumption were estimated from the exhaust emissions of hopanes and abundances of hopanes in the corresponding lubricating oil. Based upon consumption rates estimated from the correlation and chemical composition of the oils, we determined that the contributions of PAHs that were absorbed in the lubricating oil to PAHs in exhaust emissions were small. This limited dataset indicate that fuel-combustion was the primary source of PAHs.

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1 INTRODUCTION

The U.S. Environmental Protection Agency (EPA), U.A. Department of Energy through the National Renewable Energy Laboratory (DOE/NREL), U.S. Department of Transportation (DOT), Federal Highway Administration (FHWA), Coordinating Research Council (CRC, Project E-69), and the State and Territorial Air Pollution Program Administrators/Association of Local Air Pollution Control Officials (STAPPA/ALAPCO) conducted a program to evaluate exhaust emissions from 480 randomly selected, light-duty vehicles in the Kansas City Metropolitan Area (Kishan et al., 2006). EPA will use the data from this program to evaluate and update existing and future mobile source emission models, evaluate existing emission inventories and assess the representativeness of previous PM emissions studies. The project team consisted of the prime contractor, Eastern Research Group (ERG), and the following subcontractors: Bevilacqua Knight Inc (BKI), Desert Research Institute (DRI) and NuStats Partners L.P.

The Kansas City light duty vehicle exhaust characterization study was conducted during July to September 2004 (summer/Round 1) and January to March 2005 (winter/Round 2). Cars and light-duty trucks were recruited for testing in four model year groups (pre 1981, 1981-90, 1991-95 and 1996 and newer). The vehicle groupings for trucks and cars were designated strata 1-4 and 5-8, respectively. All vehicles were tested using the Unified Driving Cycle (UDC). Separate samples were collected for each of three phases of the UDC on Teflon filters for gravimetric mass and elements and on quartz filters for organic and elemental carbon. Samples for speciation of particulate organic compounds were collected over the entire cycle. Mass was determined for all samples and subsets of samples were selected for carbon analysis and chemical speciation and grouped into composites for the two newer model year groups. A total of 26 individual/composite chemical profiles were obtained from 51 of 254 vehicles tested in Round 1 and another 26 composites from 51 of 230 vehicles tested in Round 2. Organic speciation included semi-volatile and particle phase polycyclic aromatic hydrocarbons (PAH), alkanes, hopanes and steranes, nitro-PAHs and polar compounds. Complete speciation was also obtained for dilution tunnel blanks and field/transport blanks. Samples of the lubricating oil from each of the test vehicles were collected and stored for future analysis subject to availability of additional funding. This report summarizes the analysis of a subset of the lubricating oil samples. The chemical analysis of the lubricating oil samples was performed under Tasks 7 and 8 of Modification Number 1 for the National Renewable Energy Laboratory Subcontract Number ACI-5-55528-01. Support for this work was also provided by the Coordinating Research Council through Project E-69A.

1.1 Background and Study Objectives

Consumption of lubricating oil can be a substantial contributor to particle phase (PM) emissions in the exhaust of worn engines relative to fuel-related combustion particles. PM emissions from lubricating oil increases with engine wear due to larger gaps that result in more transport of lubricating oil into the combustion chamber and out the exhaust port. In contrast, properly maintained newer engines produce very little particulate matter from lubricating oil. The composition of PM emissions of new and worn engines can be very different chemically because their source and formation processes are different. These compositional differences may have important implications with regard to health impacts. For example, the study by Seagrave et al. (2000) indicated that high-emitting vehicles (both diesel and gasoline) contribute

disproportionately to the health hazards of engine emissions. A related paper by McDonald et al. (2004) concluded that lubricating oil-derived, particle-associated organic compounds may contribute strongly to the inflammatory effects of inhaled emission from high-emitting vehicles. Additionally, the size distributions differ for particles associated with oil consumption and fuel combustion. In CRC Project E-43 (Kittelson et al., 2002), the organic component of total diesel particulate matter and nuclei mode particles appeared to be mainly comprised of unburned lubricating oil for the engines and operating conditions sampled. The relative importance of high-emitting gasoline vehicles as a source of lubrication oil-derived PM is expected to increase over time after the introduction of particle traps on diesel trucks.

Compositional differences of PM emissions for motor vehicles are also important considerations in the application of source composition profiles for emission inventory development and source apportionment by receptor modeling. Spark ignition (SI) vehicles, whether low or high emitters, were found in the Kansas City tests and in prior studies (e.g., Fujita et al., 2006), to emit greater amounts of high molecular-weight particle phase PAHs (e.g., benzo(b,j,k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, and coronene) than compression ignition (CI) vehicles. These combustion-produced PAHs were found in used gasoline motor oil but not in fresh oil or in diesel engine oil. Diesel emissions contained higher abundances of dimethylnaphthalenes, methyl- and dimethylphenanthrenes, methylfluorenes and other semi-volatile methylated PAHs. Hopanes and steranes were present in lubricating oil with similar composition for both gasoline and diesel vehicles and were not present in gasoline or diesel fuels. SI exhaust contains higher abundances of higher molecular weight hopanes and steranes relative to CI exhaust. Recent studies (Zielinska et al., 2003; Fujita et al., 2006) also showed that the abundances of particle phase PAHs in SI exhaust tend to increase as the lubricating oil ages with use. New and used lubricating oils contain a variety of elements associated with antiwear, extreme pressure and detergent additives, and engine wear. Analysis and comparison of the composition of lubrication oils from the Kansas City Study with the corresponding exhaust compositions will allow more detailed examination of this correlation and other associations between the composition of lubrication oils and composition of tailpipe PM emissions.

The purpose of this work is to determine the relative contributions of oil consumption and fuel combustion to exhaust PM emissions from SI vehicles. How does the contribution of lubrication oils to exhaust PM emissions affect chemical composition? The results are also intended to provide further understanding of the variations in chemical composition of exhaust PM and their implications for interpreting the source attributions derived from receptor modeling and their associated uncertainties. Another purpose of this work is to characterize the relationships between the composition of "marker" organic species (primarily PAHs, hopanes, steranes) in lubrication oil and corresponding exhaust PM. The following hypotheses will be addressed:

1. The abundance of individual hopanes and steranes relative to their sums are the same in exhaust PM emissions and corresponding lubrication oils.

2. Abundances of hopanes and steranes in exhaust PM emissions are correlated to organic carbon and PM emissions.

3. The concentrations of high molecular weight PAHs in unused lubrication oils are negligible but increase with mileage accumulation of the oils.

4. The abundance of high-molecular weight PAH in exhaust PM emissions are correlated with their abundance in corresponding lubrication oils, which would suggest that lubrication oil is a significant source of PAHs for high emitters.

2 EXPERIMENTAL

Details of the vehicle testing program for the study in Kansas City are documented in the project final report (Kishan et al. 2006). Methods and procedures for the dynamometer testing and PM sampling are also documented in the project Quality Assurance Program Plan (QAPP) prepared by BKI and DRI, respectively. The following is a brief description of the experimental details of the Kansas City LDGV Exhaust Characterization Study.

2.1 Vehicle Testing

Vehicle driving simulation was conducted using EPA-ORD's transportable dynamometer, a Clayton Model CTE-50-0 chassis dynamometer mounted within a towable trailer. For this study, the dynamometer was set up in one quadrant of a large building. Large (14' x 14') bay doors on either end of the building were opened and provided natural ventilation to ambient conditions. A Positive Displacement Pump-Constant Volume Sampler (PDP-CVS) system was used to quantitatively dilute exhaust gas from the vehicle operating on the dynamometer. The PDP-CVS system employed an 8-inch diameter stainless steel dilution tunnel with particle filtered inlet air and a SutorBilt PDP operating at ~540 SCFM. The outside of the dilution tunnel was insulated with Insulwrap and the temperature of the diluted exhaust and dilution tunnel was maintained at a constant temperature of 47 C using a 27.3 kW, electric dilution air heater (Unique Products model # 507-574) whose feedback control thermocouple had been moved to a location near the PDP inlet. The dilution air was also treated to reduce humidity levels by placing a re-generative desiccant-type dryer (TempAir model TD400) at the dilution tunnel inlet. The dryer was used only during Round 1, treating the humid air typical of Kansas City in the summer time. Both the heater and the dryer were powered with a portable, diesel-fueled 50kW generator located outside and adjacent to the facility. Diluted exhaust exiting the CVS-PDP system was routed through 8-inch diameter ducting to an existing, wall-mounted exhaust fan to remove diluted exhaust from the building.

Cars and light-duty trucks were recruited for testing in the main study in four model year groups (pre-1981, 1981-90, 1991-95 and 1996 and newer. The vehicle groupings for trucks and cars were designated strata 1-4 and 5-8, respectively, with strata ordered from older to newer model years. BKI conducted the vehicle emission tests using a modified version of the LA92 Unified Driving Cycle. The cycle consists of a cold start Phase 1 (first 310 seconds), a stabilized Phase 2 (311-1427 seconds), a 600-second engine off soak, and a warm start Phase 3 (repeat of Phase 1). Vehicles were tested with dilution air to the dynamometer constant volume sampler (CVS) heated to 47 C. The CVS dilution tunnel was purged for a minimum of 30 minutes between each test. Aerosol samples were collected with Teflon filters (Pall Teflo) for measurement of gravimetric mass and elements and pre-fired quartz fiber filters for organic and elemental carbon (OC and EC) and ions. Teflon and quartz filters were collected for each of the three phases of the test cycle and analyzed for gravimetric mass and elemental and organic carbon fractions by the IMPROVE TOR method. Teflon-impregnated glass fiber filters with backup XAD resin (TIGF/XAD) were collected over the entire cycle excluding the 10-minute soak and analyzed for semi-volatile and particle phase organic species including polycyclic aromatic hydrocarbons (PAH), hopanes, steranes, alkanes, polar organic compounds and nitro-PAHs. Gravimetric mass was determined for all Teflon filters. Because of the expected lower

PM emission rates for newer vehicles, subsets of the other test samples were grouped into composites of up to five vehicles for strata 4 and 8 and up to three vehicles in strata 3 and 7. Selected samples for the remaining older vehicle strata were analyzed without compositing. A total of 26 individual/composite chemical profiles were obtained from 51 of 254 vehicles tested in Round 1 and another 26 composites from 51 of 230 vehicles tested in Round 2. Dilution tunnel blanks were collected daily around midday and field/transport blanks were returned to the laboratory weekly.

2.2   Sampling Methods

DRI installed and operated a suite of instruments and samplers to provide continuous PM analysis and to collect batch samples of particle and gaseous exhaust components for later analysis in accordance with the methods and procedures specified in the project QAPP. Samples were collected from the dynamometer dilution system via two isokinetic probes, provided by BKI, inserted prior to a 90-degree bend in the dilution tunnel. Heated conductive lines carried air from the probes to the continuous instruments. Sample air was drawn from the CVS via ½" insulated copper tubing to a small heated stainless steel chamber. The sample air exited via a $PM_{2.5}$ cyclone contained in the chamber to a heated plenum approximately 50 cm tall, containing a temperature and RH probe. From this chamber, the sample air exited through two filter cartridges. Up to eight cartridges could be installed in the base of the diffusing chamber, allowing four successive pairs of filters to sample without changing cartridges. Airflow through the cartridges was switched by means of microprocessor controlled relays and solenoid valves, that responded to TTL line signals from the dynamometer control. Flow rates for each filter were set to 56 lpm by adjustable valves to give a combined flow of approximately 113 lpm as required by the inlet cyclone, and monitored by TSI 4000 flowmeters with serial data outputs. A single oil-less pump was used to draw air through the sampler.

Filter samples were collected during each phase of the Unified Cycle tests. Pre-weighed polymethylpentane ringed, 2.0 mm pore size, 47 mm diameter PTFE Teflon-membrane Teflo filters (Pall #RPJ047) collected particles for measurement of gravimetric mass and elements. Pallflex 47 mm diameter pre-fired quartz-fiber filters (#2500 QAT-UP) were used for water-soluble chloride, nitrate and sulfate and for organic and elemental carbon measurements. Samples were collected by a separate sampler for determination of particle phase and semi-volatile organic compounds on Pallflex TX40HI20-WW 102 mm diameter Teflon-impregnated glass fiber (TIGF) filters followed by glass cartridges containing Aldrich Chemical Company, Inc. 20-60 mesh Amberliete XAD-4 (polystyrene-divinylbenzene) adsorbent resins at a flow rate of 112 lpm. A single filter and adsorbent pair were collected for each unified cycle, combining phases 1, 2 and 3. Sampling was suspended during the 10-minute soak period by turning off the pump.

Prior to the start of testing, all samplers were checked for leaks and the in-line flow meters were cross-calibrated using reference flow measurement devices. Leak testing was performed by capping the inlet lines leading to each sampler and turning on the pumps. If the flowmeter readings decreased to less than 10% of the nominal sampling flow rate in a reasonably short time the system was passed. If not, the leak was fixed and the test repeated. With the exception of the Teflon/Quartz filter sampler, all units achieved near-zero flow rates during the leak test. Due to the friable nature of the pre-fired quartz filters it is not possible to obtain a

perfect seal in the filter holders without damaging the media, but the <10% criteria were still met for each filter individually and for the system as a whole. In addition to the vacuum test, the sum of flows through each of the two filter cartridges was compared to the total flow entering the inlet and found to agree within 5%.

All flowmeters were calibrated using either a Gillibrator electronic bubble meter (Sensidyne Inc.) or a rotameter (Dwyer Instruments) that had been cross-calibrated with a Roots meter at DRI. Calibration flows were measured at the inlet point of each sampler (or outlet for the canister sampler) with appropriate sampling media installed. The resulting calibrations were used to determine the desired nominal flow rates, and these were marked on a label on each flowmeter so that the operator could observe any deviations during testing. Variations in nominal flow rate due to sampler problems were recorded in a logbook. For each integrated sample, the run number, start and stop time, elapsed time, initial and final flow rate, and any exceptional occurrences were recorded on log sheets which were kept with the media at all times. Bar coded stickers with unique media IDs were attached to all media and their corresponding log sheets for tracking. Immediately after the conclusion of each test cycle the media were repacked with the log sheets and stored in a refrigerator, except for the canisters, which were packed and shipped via 2-day express to DRI each day. All media were packed into coolers with ice packs and shipped overnight back to DRI where they were logged in and placed in cold storage until analysis. Media were shipped near weekly basis. Run number, date, time, and vehicle license plate number were attached to all files to identify the data.

Integrated sampling included Teflon with a backup quartz filters and TIGF filters with backup XAD cartridges. Teflon and quartz filters were collected separately for each replicate while all three replicates were collected on the same TIGF/XAD sample. Laboratory analysis by DRI included gravimetric mass on all Teflon filters and "elemental" and "organic" carbon (EC and OC) by the IMPROVE-TOR method. The TIGF/XAD samples were combined into four composite samples for each of the two dilution air temperatures for analysis of speciated organic compounds. The samples were combined based upon the PM mass loadings estimated from the DustTrak data and OC mass loadings derived from the differences between the DustTrak PM and photoacoustic black carbon data.

Approximately 100 ml of lubrication oil samples was collected from the crankcase of each vehicle after the pre-conditioning test drive. Relevant usage information (e.g. odometer reading, maintenance records) was also recorded if available. The oil samples were contained in labeled opaque polyethylene bottles and stored on site in a refrigerator until the conclusion of the testing program when they were shipped to DRI for analysis and cold storage.

2.3 Analytical Methods for Exhaust Samples

"Elemental" carbon (EC) and "organic" carbon (OC) were measured by the thermal optical reflectance (TOR) method using the IMPROVE (Interagency Monitoring of Protected Visual Environments) temperature/oxygen cycle (IMPROVE TOR). In this method, samples are collected on quartz filters. A section of the filter sample is placed in the carbon analyzer oven such that the optical reflectance or transmittance of He-Ne laser light (632.8 nm) can be monitored during the analysis process. The filter is first heated under oxygen-free helium purge gas. The volatilized or pyrolyzed carbonaceous gases are carried by the purge gas to the oxidizer

catalyst where all carbon compounds are converted to carbon dioxide. The CO_2 is then reduced to methane, which is quantified by a flame ionization detector (FID). The carbon evolved during the oxygen-free heating stage is defined as "organic" carbon. The sample is then heated in the presence of helium gas containing 2 percent of oxygen and the carbon evolved during this stage is defined as "elemental" carbon. Some organic compounds pyrolyze when heated during the oxygen-free stage of the analysis and produce additional EC, which is defined as pyrolyzed organic carbon (OP). The formation of OP is monitored during the analysis by the sample reflectance. EC and OC are thus distinguished based upon the refractory properties of EC using a thermal evolution carbon analyzer with optical reflectance correction to compensate for the pyrolysis (charring) of OC. Carbon fractions in the IMPROVE method correspond to temperature steps of 120 C (OC1), 250 C (OC2), 450 C (OC3), and 550 C (OC4) in a nonoxidizing helium atmosphere, and at 550 C (EC1), 700 C (EC2), and 850 C (EC3) in an oxidizing atmosphere. The IMPROVE method uses variable hold times of 150-580 seconds at each heating stage so that carbon responses return to baseline values.

The extracts from the TIGF or XAD for each composite were combined and analyzed by gas chromatography/mass spectrometry (GC/MS). TIGF and XAD were extracted and analyzed separately to determine the distribution of particle phase and semi-volatile organic carbon on the TIGF and backup XAD. Prior to extraction, the following deuterated internal standards were added to each sample: naphthalene-d8, acenaphthylene-d8, phenanthrene-d10, anthracene-d10, chrysene-d12, pyrene-d10, benz[a]anthracene-d12, benzo[a]pyrene-d12, benzo[e]pyrene-d12, benzo[k]fluoranthene-d-12, benzo[g,h,i]perylene-d12, coronene-d12, cholestane-d50, and tetracosane-d50. Filters and XAD-4 were extracted with dichloromethane, followed by acetone, using the Dionex ASE. The extracts were then combined and concentrated by rotary evaporation at 20 C under gentle vacuum to ~1 ml and filtered through 0.45 mm Acrodiscs (Gelman Scientific). The extract was concentrated to 1 ml and split into two fractions: (1) the first fraction was precleaned by the solid phase extraction technique using Superclean LC SI SPE cartridges (Supelco) with sequential elution with hexane, and hexane/benzene (1:1). The hexane fraction contained the non-polar aliphatic hydrocarbons and hopanes and steranes, and the hexane/benzene fraction contained the PAH. These two fractions were combined and concentrated to ~100 µL and analyzed by the GC/MS technique for PAHs. Samples were analyzed by GC/MS, using a Varian CP-3800 GC equipped with a CP8400 autosampler and interfaced to a Varian Saturn 2000 Ion Trap operating in electron impact (EI) ionization mode for PAHs. Concentrations were quantified by comparing the response of the deuterated internal standards to the analyte of interest.

2.4   Chemical Analysis of Lubricating Oil Samples

DRI performed chemical analyses of the lubrication oils collected from vehicles tested in the Kansas City study. Used lube oils corresponding to nine of the exhaust sample composites previously analyzed in the Kansas City program were selected for analysis. These were chosen to represent vehicles with low, medium, and high PM emissions (three of each) as shown in Table 1. We chose to analyze only Round 2 samples for this exploratory analysis in order to avoid seasonal variations as one additional potential variable in the analysis of the data. Relevant information on the vehicle make, model, year, odometer readings, most recent oil change, and oil condition was obtained from the Kansas City Study data archive and is presented in Table 2.

Three unused oils were also analyzed for comparison (Quaker State, Castrol and Penzoil). The species analyzed included PAHs, hopanes, steranes, and alkanes. The oils were cleaned and fractionated with 2.0 g LC-Si cartridge (Supelco) prior to analysis using the method described by Wang, et al.(1994a; 1994b) and detailed elsewhere (Zielinska et al., 2004). Additionally, oil samples were analyzed for the elements Na, Mg, Al, P, S, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Ag, Ba, W, and Pb by XRF equipped with a helium flush system for analysis of liquids.

Table 1. Summary of PM data for Round 2 composite exhaust samples. Gravimetric mass, OC,EC are in mg/mi and PAH, hopanes, and steranes are in µg/mi. The three PAHs that are potential markers for gasoline exhaust are indeno[123-cd]pyrene, benzo(g,h,i)pyrylene and coronene. Oil samples corresponding to the highlighted composite exhaust samples were selected for analysis.

Composites	Category	PM Mass	OC	EC	EC/TC	PAH gas markers	Sum of Hopanes	Sum of Steranes
Dilution Tunnel Blanks								
W0-1		0.85	0.68	0.14	0.17	0.01	0.03	0.01
W0-2		0.27	0.66	0.03	0.05	0.00	0.02	0.02
W0-3		0.50	0.65	0.16	0.20	0.01	0.02	0.01
W0-4		0.39	0.71	0.08	0.10	0.01	0.02	0.01
W0-5		0.90	0.90	0.17	0.16	0.00	0.03	0.00
W0-6		0.45	0.70	0.10	0.13	0.00	0.02	0.01
Trucks								
W1-1	High	113.12	74.96	14.09	0.16	111.67	88.99	24.66
W1-2	Med	43.21	31.26	10.01	0.24	26.50	28.36	1.70
W1-3		59.60	34.09	11.59	0.25	76.20	20.21	2.57
W2-1		52.30	25.69	22.84	0.47	100.50	54.53	4.96
W2-2		15.30	4.79	3.58	0.43	2.13	4.48	0.82
W3-1	Med	29.38	10.21	16.25	0.61	40.06	7.49	0.51
W3-2		23.57	7.94	9.00	0.53	0.02	1.23	0.24
W3-3		15.21	5.11	4.23	0.45	2.12	1.16	0.12
W4-1		6.89	2.09	3.35	0.62	0.00	0.93	0.03
W2-3		5.98	2.50	2.66	0.52	0.58	0.11	0.04
W4-2	Low	6.02	2.56	3.07	0.55	1.90	0.18	0.07
W4-3		11.65	5.30	5.24	0.50	2.63	0.73	0.08
Cars								
W5-1		16.82	8.54	7.39	0.46	2.20	1.02	0.09
W5-2		47.47	16.45	28.13	0.63	54.03	4.09	0.58
W5-3	Med	45.26	15.57	15.66	0.50	78.59	5.90	3.67
W6-1	High	56.31	32.13	20.39	0.39	61.48	50.82	14.88
W6-2		17.14	7.33	9.59	0.57	7.59	1.75	1.03
W6-3		9.97	5.00	3.22	0.39	2.78	1.18	0.62
W6-4	High	73.13	49.20	4.27	0.08	15.84	66.51	30.40
W7-1		5.08	2.70	2.82	0.51	1.55	0.12	0.04
W7-2		12.44	6.68	3.84	0.36	3.23	0.61	0.22
W7-3	Low	3.45	2.69	1.29	0.32	1.23	0.34	0.21
W7-4		4.65	2.58	1.49	0.37	1.73	0.12	0.07
W8-1		4.21	2.60	1.50	0.37	0.67	0.14	0.08
W8-2	Low	8.46	2.95	4.53	0.61	2.07	0.26	0.19
W8-3		27.78	2.52	3.34	0.57	0.00	0.19	0.05

Table 2. Information on the vehicle make, model, year, odometer readings, most recent oil change, and oil condition obtained from the Kansas City Study data archive for all vehicles selected for oil analysis. Blanks indicate missing information.

Sample Composite	run#	Model Year	Make	model	Vehicle Type	odometer	Fuel Grade	Last Oil Change	Oil Brand	Oil Viscosity	Oil condition	Oil Additives	Oil Temp (F)
W1-1	84653	1977	Chevrolet	C-20 Pu	truck	37697	Regular	9 months	Quaker State	5W-30	clean	None	42
W1-2	84687	1976	Chevrolet	El Camino	truck	61809	Regular	4 months	Valvoline	10W-30	clean	None	44
W3-1	84487	1992	Mazda	B2200	truck	101090					dirty		
W3-1	84497	1995	Toyota	4 Runner	truck	85898	Regular	3.1 months	Quaker State	10W-30	clean	None	
W3-1	84510	1994	Chevrolet	Suburban	truck	187410	Regular	3 months	Castrol	10W-40	clean	Lucas Oil	
W4-2	84577	1998	Ford	Aerostar	truck		Regular	2.7 months	Valvoline	5W-30	dirty	None	49
W4-2	84580	2002	Chrysler	Town & Country	truck	84580	Regular	2.8 months	Kendall	10W-30	medium	None	
W4-2	84616	1999	Plymouth	Voyager	truck	113389	Regular	2.5 months	Penzoil	5W-30	clean	None	56
W5-3	84605	1977	Datsun	280Z	car	94782					dirty		43
W6-1	84474	1988	Honda	Civic	car	207265	Regular		Valvoline	10W-30		None	
W6-4	84635	1989	Ford	Crown Vic	car	62847	Regular	1000 miles	Quaker State	10W-40	medium	None	49
W7-3	84581	1995	Chevrolet	Corsica	car	78767	Regular	1.1 months	Unknown	5W-30	dirty	None	49
W7-3	84597	1994	Pontiac	Sunbird	car	145869					dirty		36
W8-2	84596	1997	Ford	Taurus	car	97601	Regular	3.1 months	Motorcraft	5W-30	dirty	None	41
W8-2	84599	1998	Toyota	Avalon	car	29575	Regular	1080 miles	Quaker State	10W-30	clean	None	

3   RESULTS

The purpose of this work study is to examine the relationship between the chemical compositions of lubricating oils and exhaust PM emissions. We analyzed a subset of 15 used oil samples combined into 9 composites from the Kansas City Light-Duty Vehicle Exhaust Characterization Study along with three unused oils to examine the associations between abundances of hopanes, steranes, alkanes, and PAHs in lubricating oils and the corresponding emission rates in the exhaust samples. We hypothesized that the abundance of individual hopanes and steranes relative to their sums are the same in exhaust PM emissions and corresponding lubricating oils (Hypothesis 1). We also hypothesized that the abundances of hopanes and steranes in exhaust PM emissions are correlated to organic carbon and PM emissions (Hypothesis 2). The degree of this correlation indicates the relative contributions of oil consumption and fuel combustion to exhaust PM emissions from SI vehicles. We also compared the concentrations of PAHs in used and unused lubrication oils and hypothesized that PAH concentrations in the oil increases with mileage accumulation of the oils (Hypothesis 3). The rates of oil consumption were estimated from the exhaust emissions of hopanes and abundances of hopanes in the corresponding lubricating oil. Based upon consumption rates and chemical composition of the oils, we estimated the contributions of PAHs absorbed in the lubricating oil to PAHs in exhaust emissions. We hypothesize that lubrication oil can be a significant source of PAH for high emitters and that this contribution is related to age of the oil (Hypothesis #4).

3.1   Chemical Composition of Lubricating Oils

The chemical compositions of used and unused lubricating oils are summarized in Table 3 by chemical groupings as percent of total mass of the oils. Data for individual species are provided in Appendix A. The data are displayed graphically in Figure 1a-h in concentrations units of µg of individual species per gram of oil and also as percentages of the sums of similar species. Figure 2 shows the percentages of total oil mass totaled by chemical groups. We highlight the following observations from the comparisons of the chemical composition of used and unused lubricating oils.

- Zn, P, Ca, and S were the predominant elements in lubricating oils. The abundances of these four elements were similar in used and unused oils in terms of both concentration and percentages to sums of the elements.

- Concentrations of total hopanes and total steranes in used oils were similar to unused oils for lower PM emitters, but were enriched in used oils for higher emitters by up to a factor of 20 for hopanes and a factor of 10 for steranes. Loss of more volatile components of the oil is one possible explanation for this enrichment. The magnitude of the enrichment suggests that there may be other contributing factors. The composition of hopanes, in percentage of individual hopanes relative to the sum of total hopanes, was similar among all oils.

- Concentrations of alkanes were higher in used oils by about a factor of 2-3 compared to unused oils. Enrichment of light alkanes (e.g., C12 and C13) is likely due to absorption of blow-by exhaust containing unburned gasoline. We speculate that thermal cracking of

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heavier alkanes in the combustion process might be the source of enrichment of the mid-range (C16-C28) alkanes.

- PAHs were generally undetectable in unused oil. PAHs were found in all used lubricating oil with no apparent relationship to exhaust PM emission rate. Insufficient information was available to determine the relationships between PAH concentrations in lubrication oil and mileage accumulation (Hypothesis 3). However, the absence of PAHs in unused lubricating oil indicates that their presence in used oil is due to absorption of blow-by exhaust containing fuel-combustion associated PAHs.

3.2   Chemical Composition of the Corresponding Exhaust Samples

Appendix B gives the chemically speciated emission rates for the individual and composite exhaust samples that correspond to the oil composition data in Appendix A. The exhaust emission data are displayed graphically in Figure 3a-h in units of µg/mi for individual species and also as percentages of the sums of species groups. The exhaust samples are ordered from left to right according to decreasing PM emission rates. We highlight the following observations from the comparisons of the exhaust compositions with the corresponding lubricating oils.

- The most abundant elements in lubricating oils, Zn, P, Ca and S, were also major elemental constituents in exhaust. The exhaust contained noticeably greater abundances of S and less of P than the corresponding lubricating oils. Significant, but variable amounts of Fe, Si and Na were also present in the exhaust. With the exception of the large amount of S in W1-1 and Si in W5-3 exhaust composites, total emissions of elements decreased with decreasing PM emissions.

- Hopanes and steranes were near nondetectable levels in the exhaust of low PM emitters and were substantially greater for high PM emitters. The compositions of hopanes and steranes were consistent among the exhaust samples, especially for the higher emitters, and matched the composition in lubricating oils.

- The composition of individually identified alkanes in the exhaust is shifted toward lighter alkanes relative to the corresponding oil samples. Higher PM emitters have greater total emissions of alkanes, but within a narrower range of emission rates than hopanes or steranes.

- Lower PM emitters have low emission rates of PAHs. While higher PM emitters tend to have higher rates of PAH emission, the correlation was not as strong as for hopanes and steranes.

3.3 Correlations of Oil-Derived Species with Corresponding Species in Exhaust and with PM, TC and OC Emissions

Exhaust emission rates of individual hopanes and steranes are correlated with concentrations in the corresponding lubricating oils in Figure 4a. Each data point is the mean of all composite samples for one compound. Similar plots are shown for elements and alkanes in Figure 4b and for particle phase PAHs and sum of naphthalenes in Figure 4c. The relationships between exhaust emission rates of sums of hopanes and steranes to PM, TC and OC are shown in the scatterplots in Figure 5a. Similar scatterplots are shown for particle phase PAHs and the three gasoline marker PAHs (benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, and coronene) in Figure 5b and Figure 5c, respectively. Sum of the emissions of hopanes and the three marker PAHs are plotted against EC in Figure 6. The key findings are as follows.

- The abundance of individual hopanes and steranes relative to their sums are the same in exhaust PM emissions and corresponding lubrication oils. Hypothesis #1 is true.

- Abundances of hopanes and steranes in exhaust PM emissions are correlated to organic carbon and PM emissions. Hypothesis #2 is true, but more so for hopanes than steranes. However, ratios of abundances in oil to emissions vary with individual vehicle composites.

- No consistency in speciation of inorganic elements or high-MW alkanes between oil and exhaust emission rates. Emissions of major XRF elements do not vary with concentration in oil.

- PAH emissions are moderately correlated with total PM or carbon. The correlation with total organic carbon is weaker, however, indicating a relationship between PAH and EC in the exhaust of higher-emitting vehicles.

3.4 Attributions of the Contribution of Oil Consumption to PAHs in Exhaust Emissions

We estimate lubricating oil emission rates for SI vehicles by assuming that all hopanes present in emissions are from the lubrication oil and are not destroyed during the combustion process. Since hopanes are created under high-temperature and pressure during geologic formation of crude oil, and do not exist in gasoline, these assumptions are justified. The lubrication oil emission rates (Oil Em) are estimated from the following equation:

$$\text{Oil Em (g/mile)} = H_{em} \text{ (µg/mile)}/H_{oil} \text{ (µg/g)} \tag{1}$$

where H_{em} is total hopane emission rate from the SI vehicles and H_{oil} is the total concentration of hopanes in the lubrication oil of the corresponding vehicle. The emissions of PAHs, or other chemical species, that originate from the lubrication oil can be estimated using equation (2):

$$\text{PAH emitted with oil (µg/mile)} = \text{PAH}_{oil} \text{ (µg/g) * Oil Em (g/mile)} \tag{2}$$

Table 4 lists the percent contributions of the lubricating oils to various species in the corresponding exhaust estimated by this method. The hypothesis that the lubricating oil can contribute substantially to exhaust emissions of PAHs is not supported by this analysis. Only a few percent of the volatile and particle phase PAHs are attributed to consumption of lubricating oil.

Essentially all of the phosphorus and zinc are attributed to lubricating oils and lesser, but significant, fractions of calcium and sulfur are also attributed to the oils. The other significant elements in some exhaust samples, iron, lead and silicon, are not associated with the oil and are presumed to result from deterioration of engine and/or exhaust system components. The attributions of alkanes to lubricating oils were mixed, with higher attribution to the oil for mid-range MW alkanes.

Table 3. Statistical summaries of the chemical composition of used and unused lubrication oil samples (percent of oil mass).

SAMPLEID	W1-1	W1-2	W3-1	W4-2	W5-3	W6-1	W6-4	W7-3	W8-2
Elements	1.062 + 0.029	1.152 + 0.015	1.178 + 0.013	1.072 + 0.014	1.323 + 0.021	1.358 + 0.021	1.172 + 0.034	0.867 + 0.027	1.096 + 0.013
total PAHs	0.409 + 0.004	0.256 + 0.002	0.554 + 0.007	0.330 + 0.003	0.654 + 0.007	0.491 + 0.004	0.246 + 0.002	0.275 + 0.004	0.372 + 0.003
Naphthalenes	0.269 + 0.003	0.229 + 0.002	0.405 + 0.005	0.212 + 0.002	0.543 + 0.007	0.407 + 0.003	0.193 + 0.002	0.192 + 0.002	0.266 + 0.003
volatile PAH	0.095 + 0.002	0.017 + 0.000	0.100 + 0.004	0.064 + 0.001	0.074 + 0.003	0.054 + 0.001	0.035 + 0.001	0.055 + 0.003	0.059 + 0.001
semi-vol PAH	0.041 + 0.001	0.008 + 0.000	0.045 + 0.001	0.046 + 0.001	0.033 + 0.001	0.027 + 0.001	0.016 + 0.000	0.023 + 0.000	0.041 + 0.001
particulate PAH	0.004 + 0.000	0.001 + 0.000	0.004 + 0.000	0.008 + 0.000	0.005 + 0.000	0.003 + 0.000	0.002 + 0.000	0.004 + 0.000	0.005 + 0.000
Hopanes	0.293 + 0.010	0.158 + 0.005	0.043 + 0.002	0.083 + 0.003	0.655 + 0.022	0.648 + 0.022	0.384 + 0.018	0.210 + 0.006	0.097 + 0.003
Steranes	0.160 + 0.007	0.032 + 0.001	0.021 + 0.001	0.021 + 0.001	0.164 + 0.007	0.136 + 0.006	0.140 + 0.008	0.111 + 0.005	0.026 + 0.001
Alkanes	0.712 + 0.016	0.475 + 0.014	0.681 + 0.033	0.539 + 0.014	0.794 + 0.024	0.733 + 0.018	0.752 + 0.023	0.402 + 0.012	0.561 + 0.015
Total Identified	2.636 + 0.036	2.074 + 0.022	2.477 + 0.036	2.044 + 0.020	3.589 + 0.040	3.365 + 0.036	2.694 + 0.046	1.865 + 0.031	2.152 + 0.020

SAMPLEID	Quaker	Castrol	Penzoil	Mean Clean
Elements	1.0936 + 0.0122	1.1409 + 0.0112	1.0504 + 0.0236	1.0950 + 0.0453
total PAHs	0.0031 + 0.0001	0.0034 + 0.0001	0.0034 + 0.0001	0.0033 + 0.0002
Naphthalenes	0.0002 + 0.0000	0.0007 + 0.0000	0.0003 + 0.0000	0.0004 + 0.0003
volatile PAH	0.0007 + 0.0000	0.0008 + 0.0000	0.0014 + 0.0001	0.0009 + 0.0004
semi-vol PAH	0.0018 + 0.0000	0.0013 + 0.0000	0.0013 + 0.0000	0.0015 + 0.0003
particulate PAH	0.0005 + 0.0000	0.0006 + 0.0000	0.0004 + 0.0000	0.0005 + 0.0001
Hopanes	0.0298 + 0.0010	0.0651 + 0.0031	0.0354 + 0.0012	0.0434 + 0.0190
Steranes	0.0120 + 0.0006	0.0297 + 0.0018	0.0181 + 0.0008	0.0199 + 0.0090
Alkanes	0.2974 + 0.0075	0.3462 + 0.0086	0.3933 + 0.0116	0.3456 + 0.0479
Total Identified	1.4359 + 0.0144	1.5854 + 0.0146	1.5005 + 0.0263	1.5073 + 0.0750
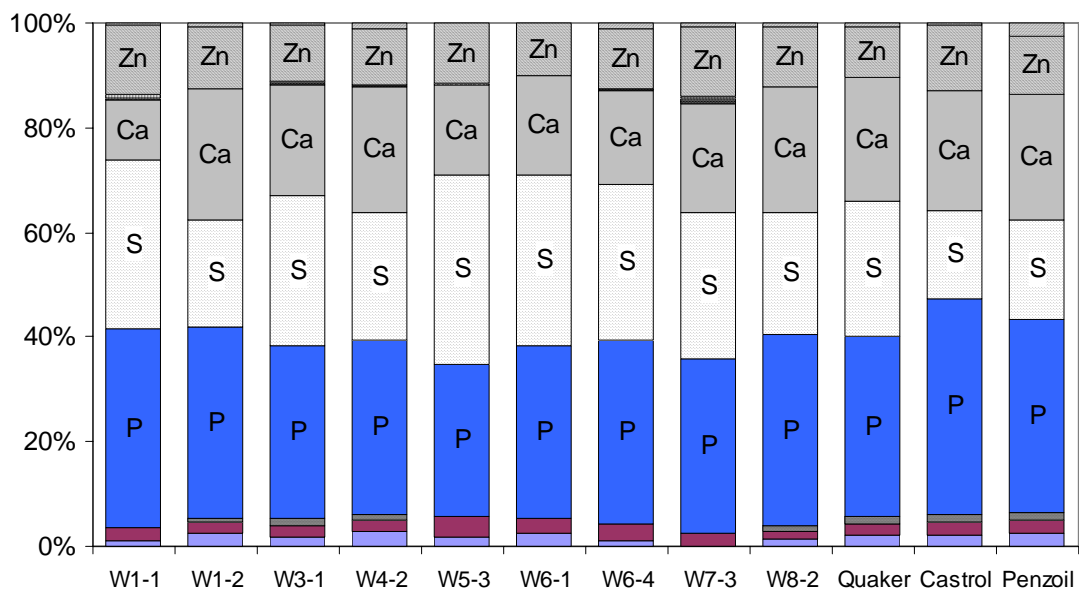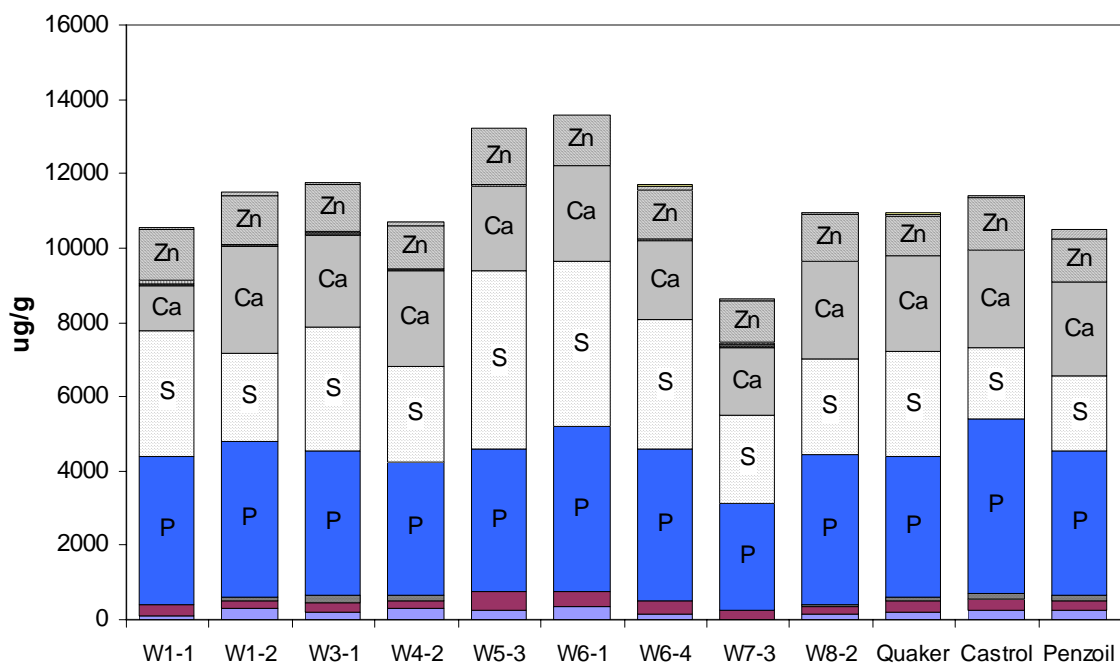
Figure 1a. Abundances of elements in used and unused lubricating oils in µg/g and percent.
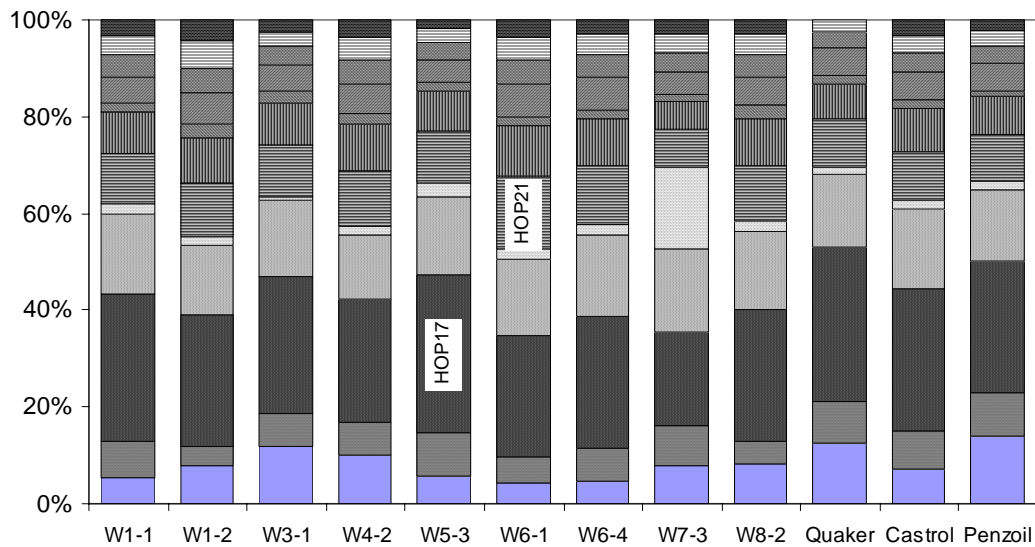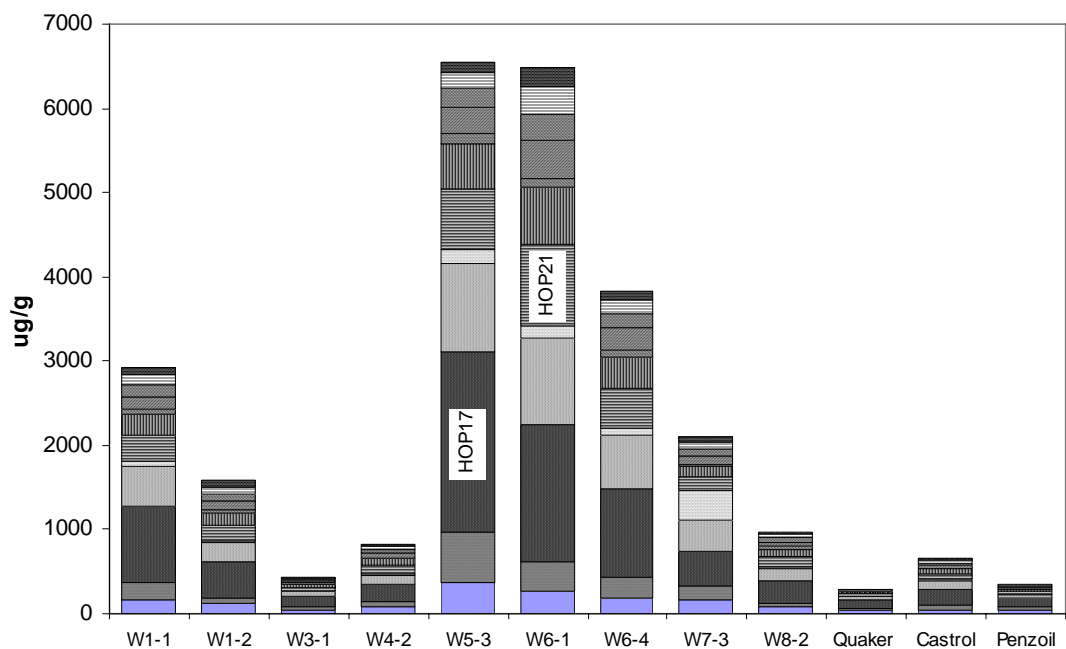
Figure 1b. Abundances of hopanes in used and unused lubricating oils in µg/g and percent.
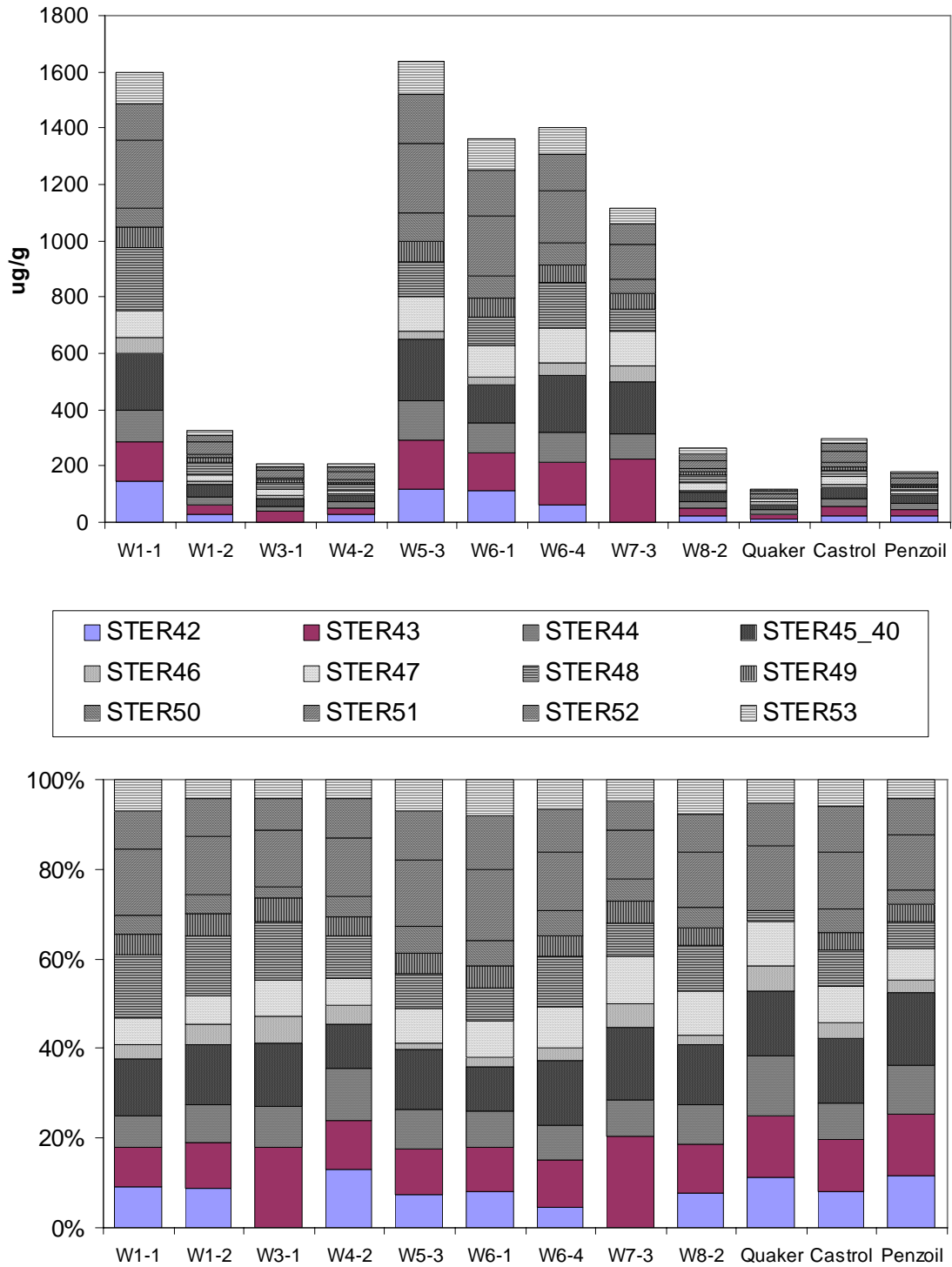
Figure 1c. Abundances of steranes in used and unused lubricating oils in µg/g and percent.
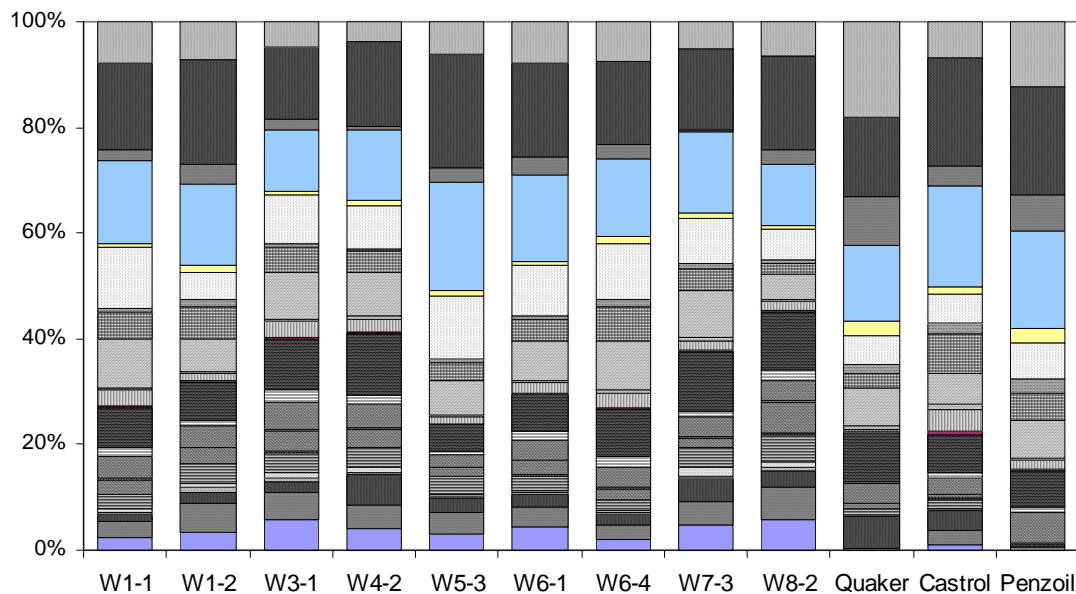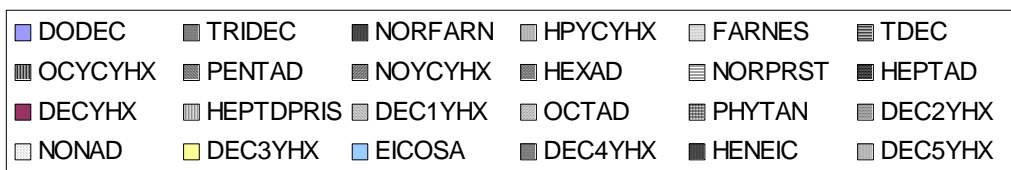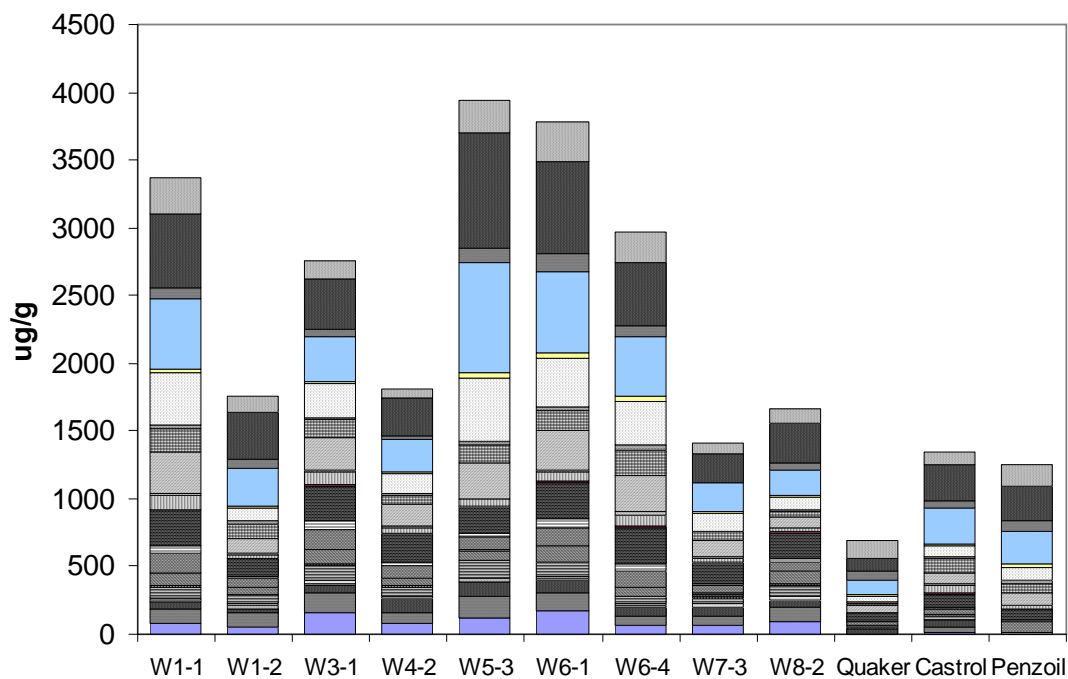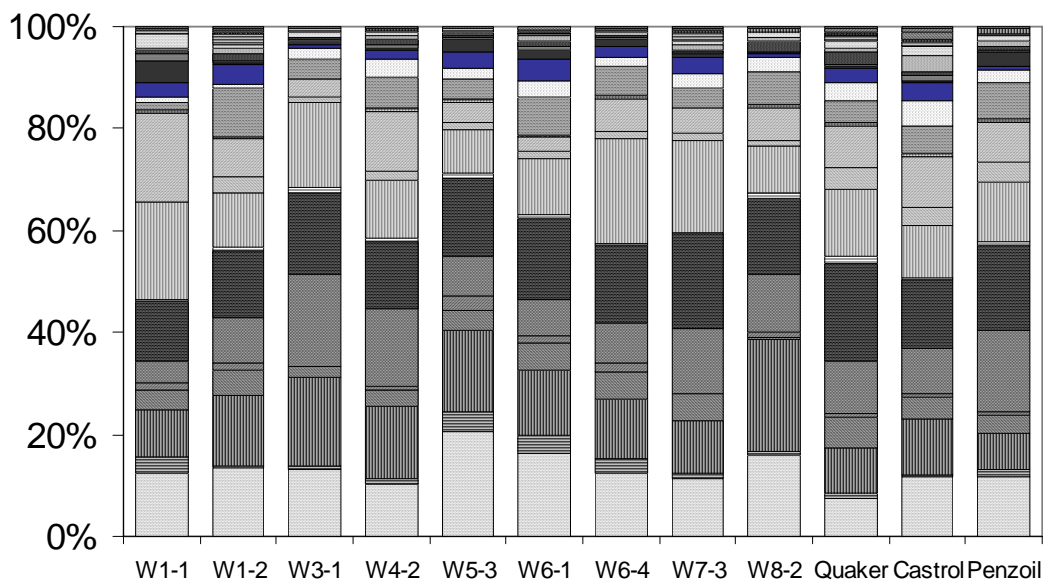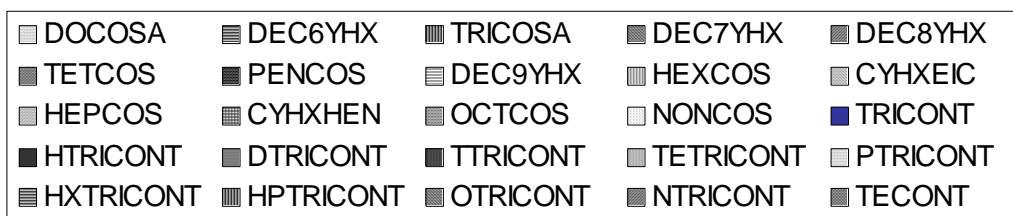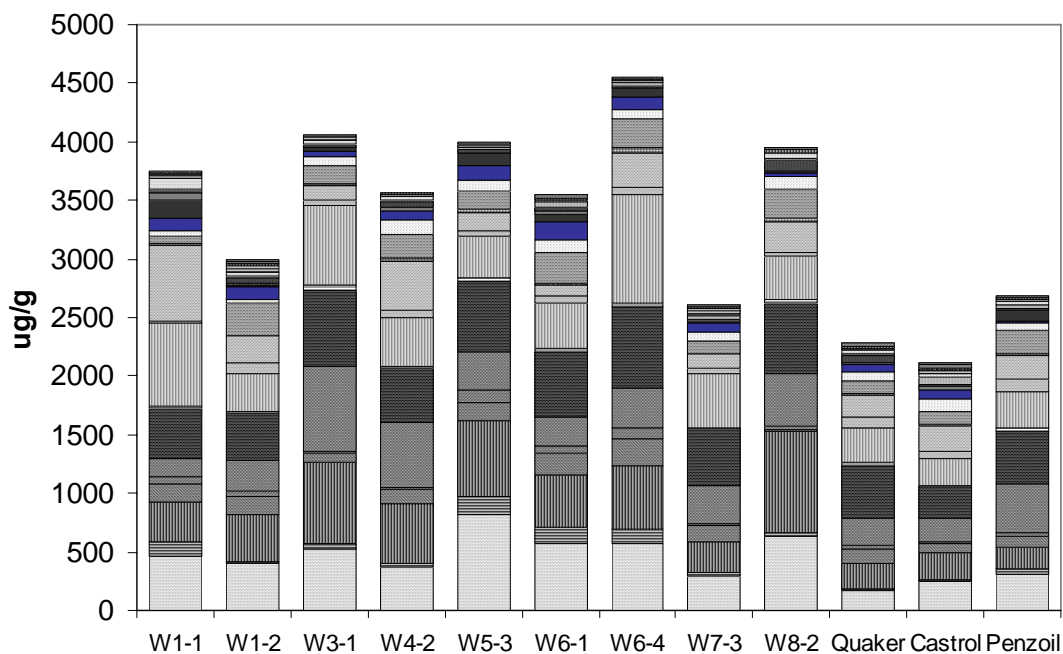
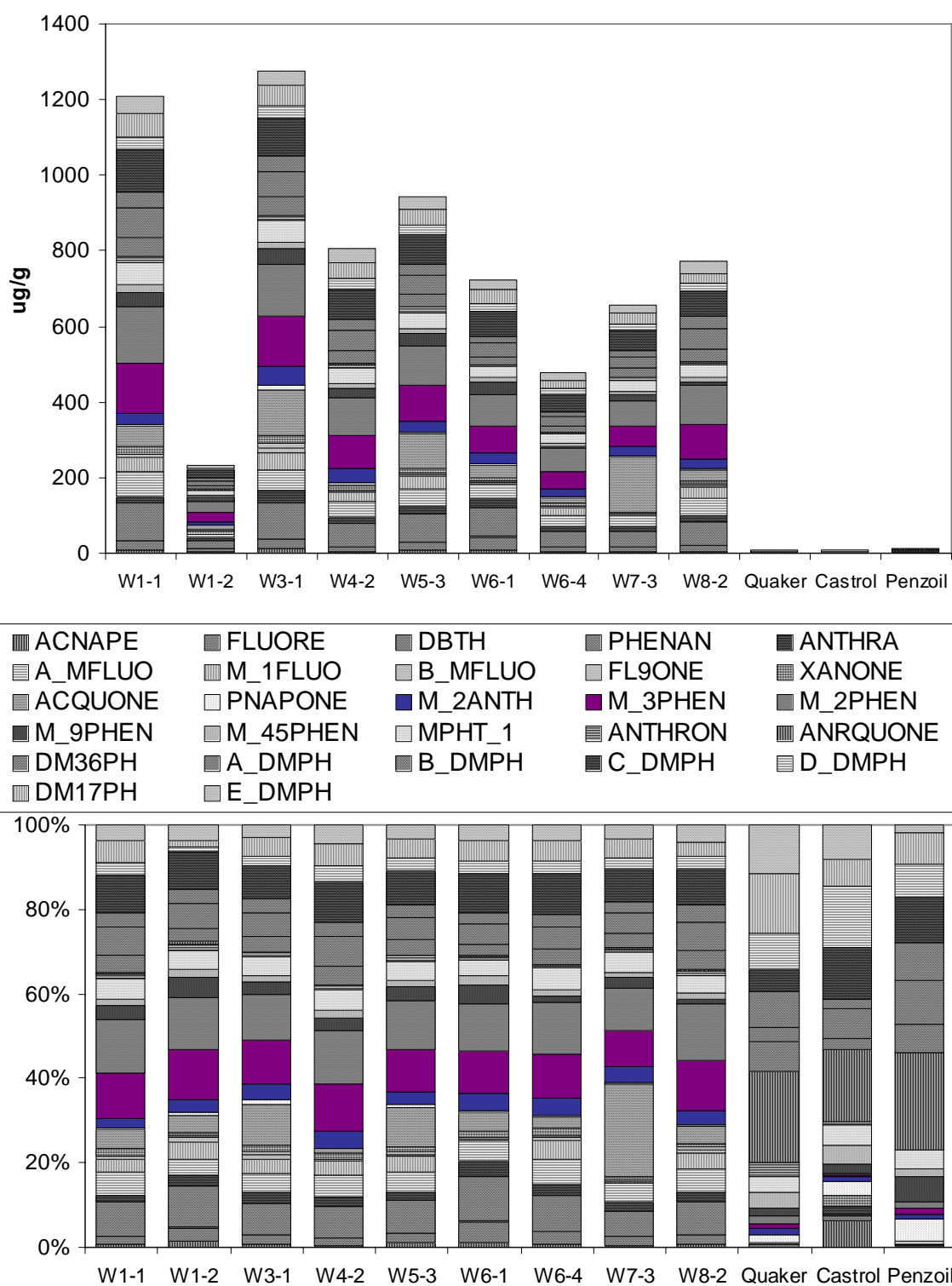Figure 1d. Abundances of <C22 alkanes in used and unused lubricating oils in µg/g and percent.

Figure 1e. Abundances of >C21 alkanes in used and unused lubricating oils in µg/g and percent.
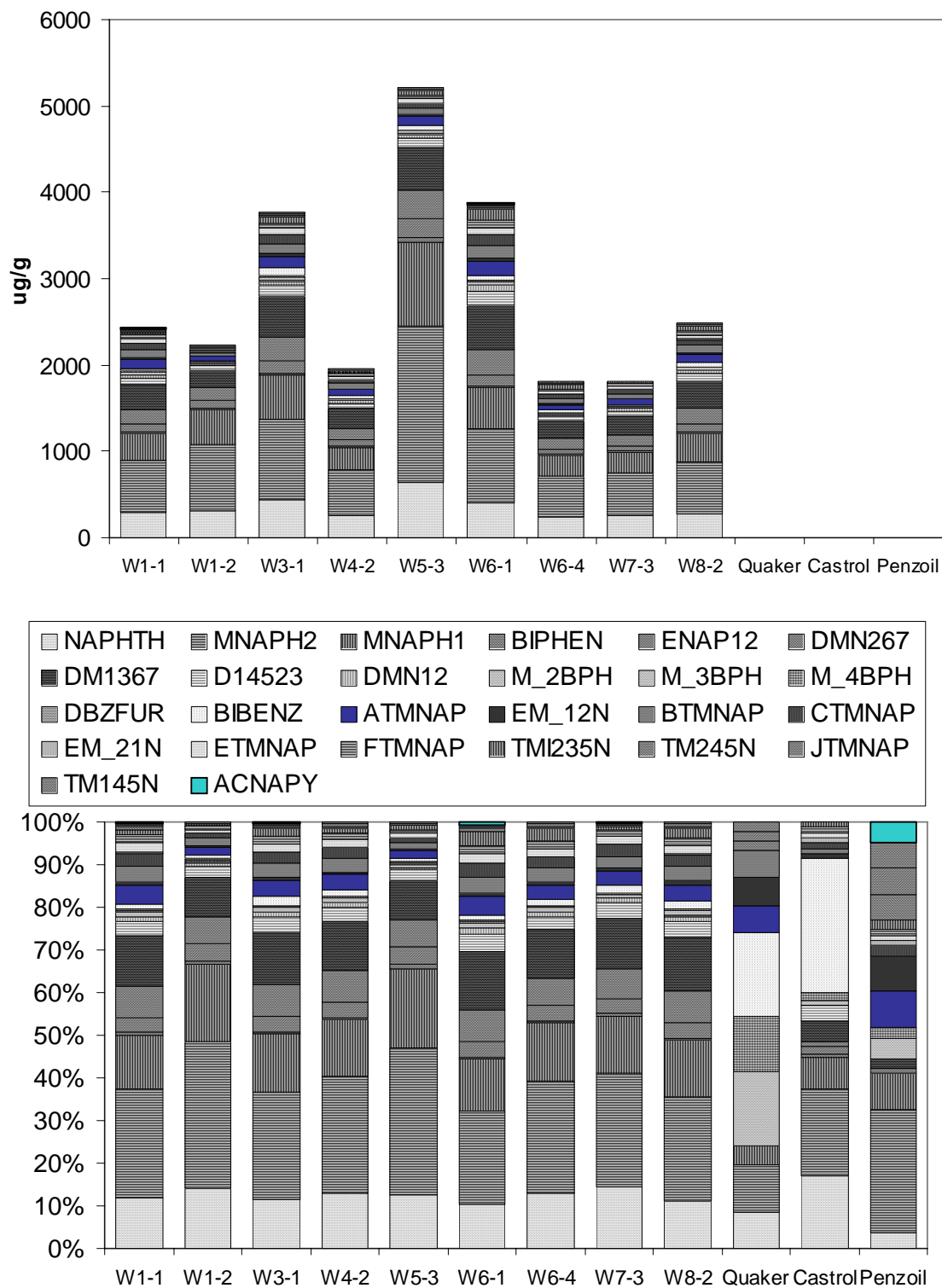
Figure 1f. Abundances of naphthalenes in used and unused lubricating oils in µg/g and percent.

Figure 1g. Abundances of other volatile PAHs in used and unused lubricating oils in µg/g and percent.
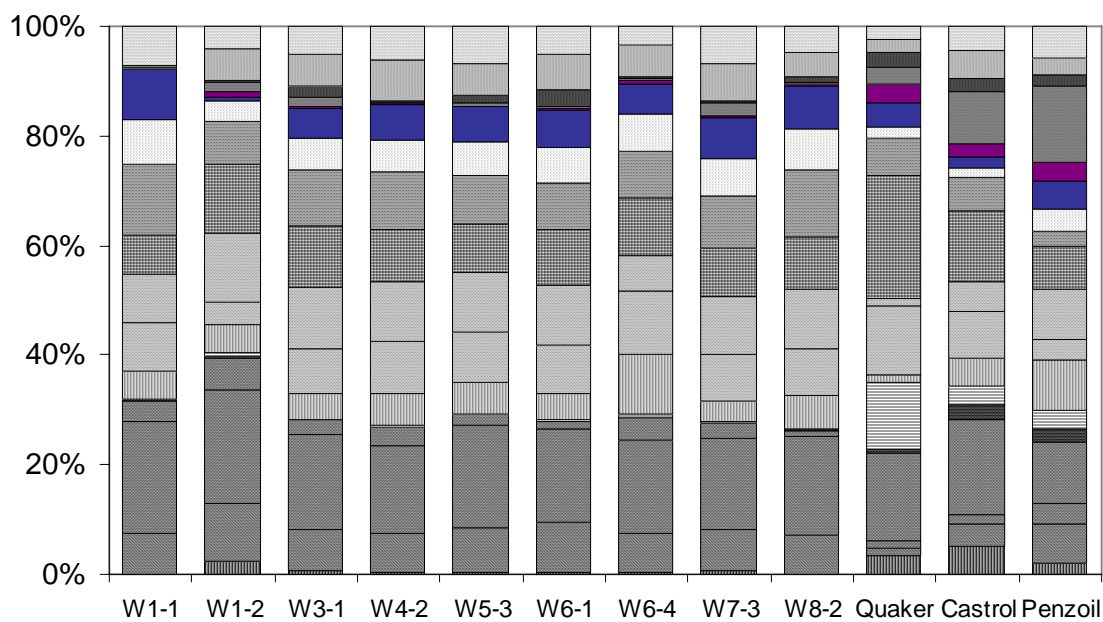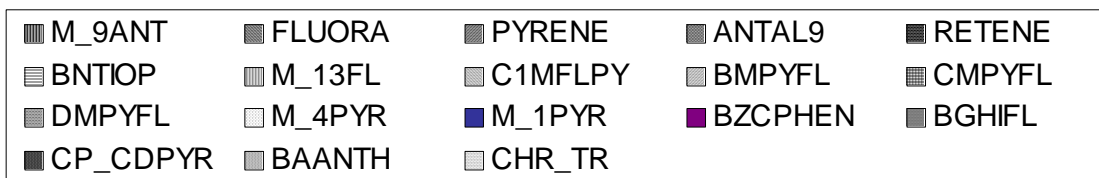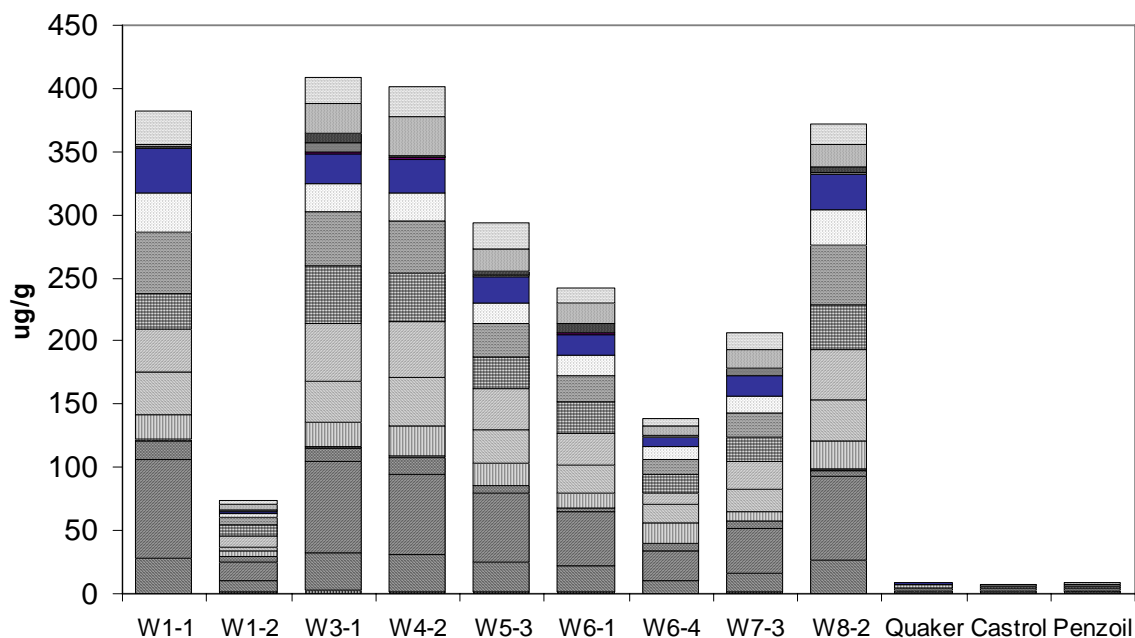
Figure 1h. Abundances of semi-volatile PAHs in used and unused lubricating oils in µg/g and percent.
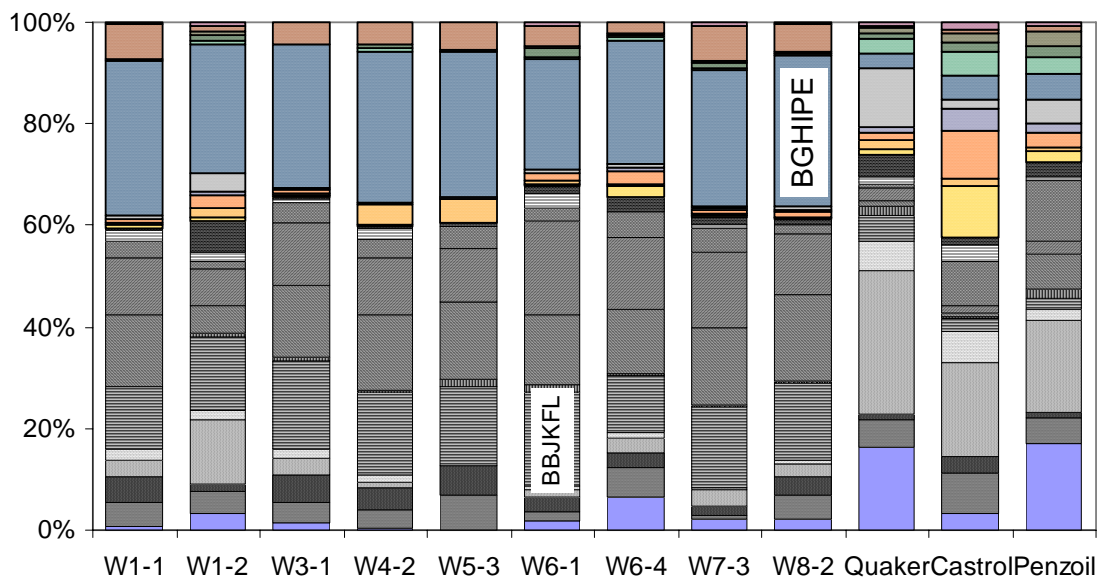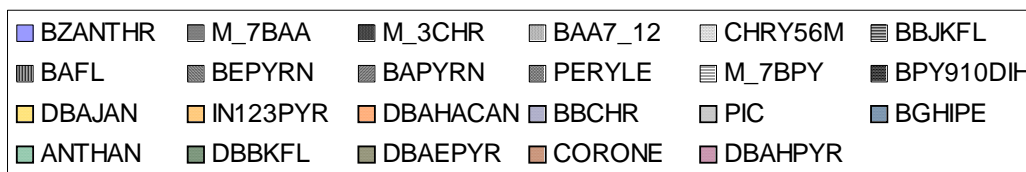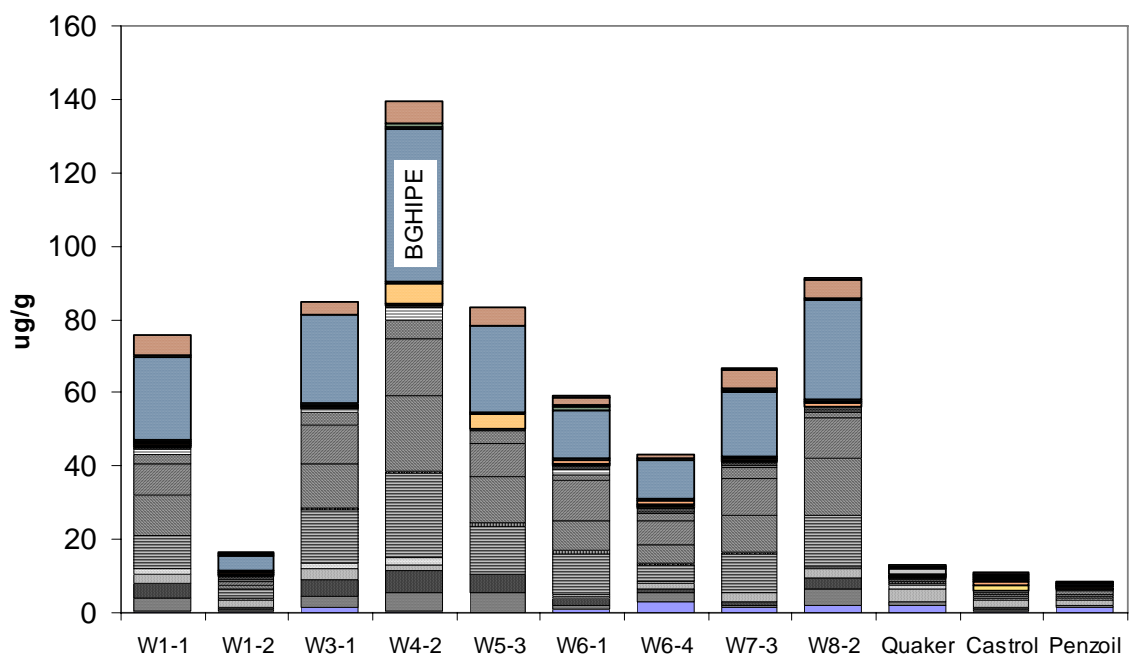
Figure 1i. Abundances of particle phase PAHs in used and unused lubricating oils in µg/g and percent.
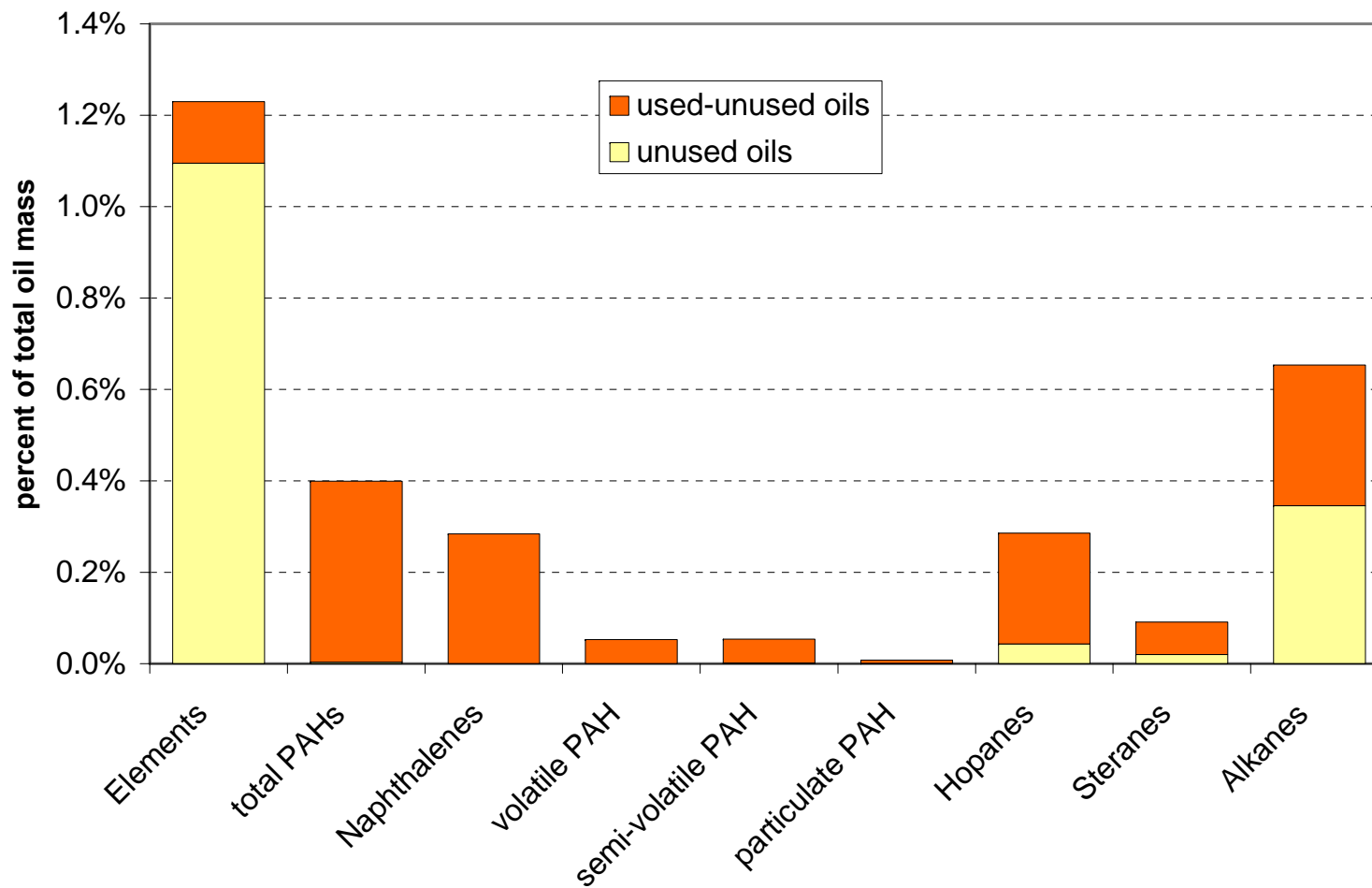
Figure 2. Fractional sums of chemical groupings in lube oil. The dark bars represent the difference between the average of all used oil analyses and the average of all clean oil analyses.
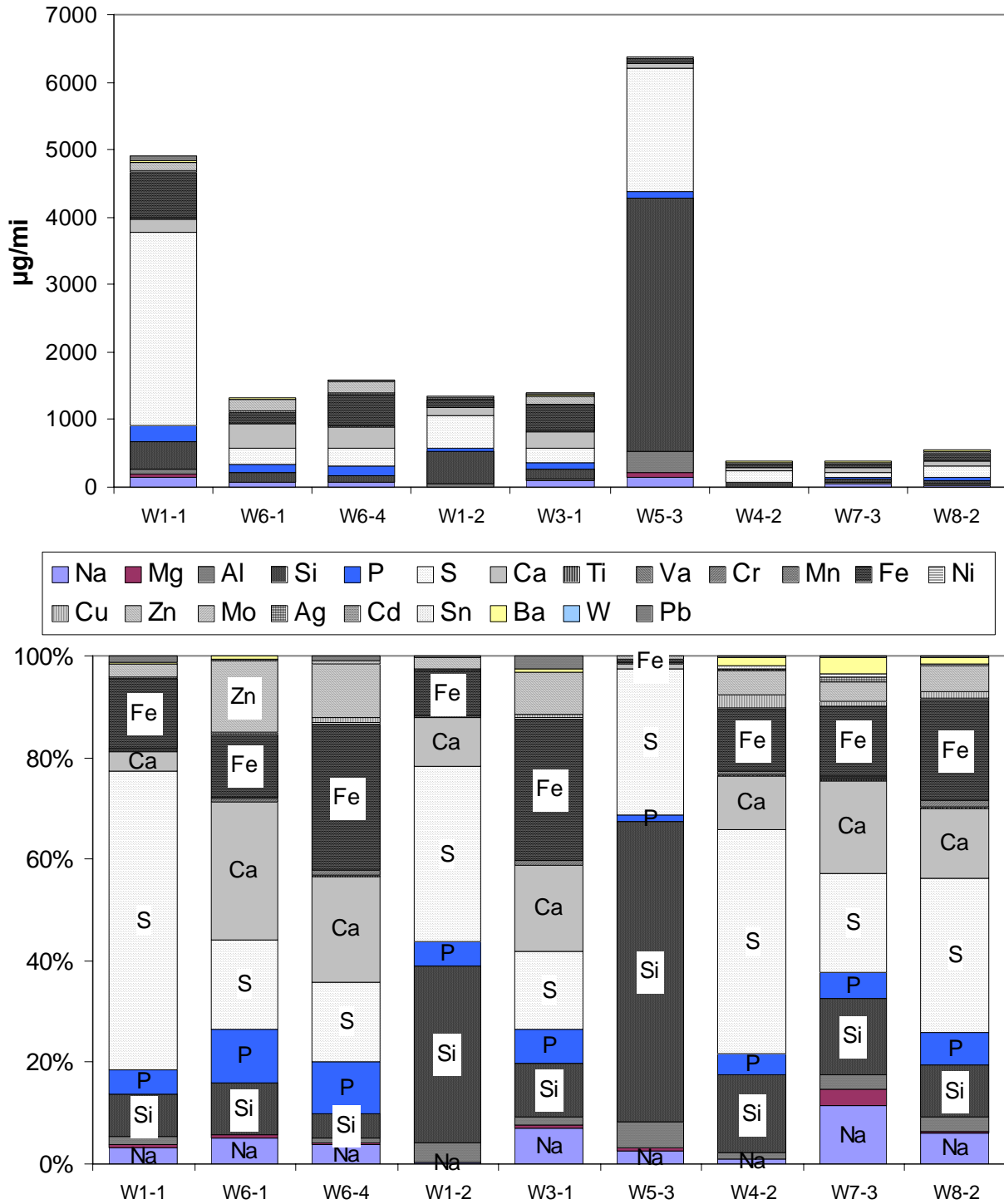
Figure 3a. Abundances of elements in exhaust emissions in µg/mi and percent.
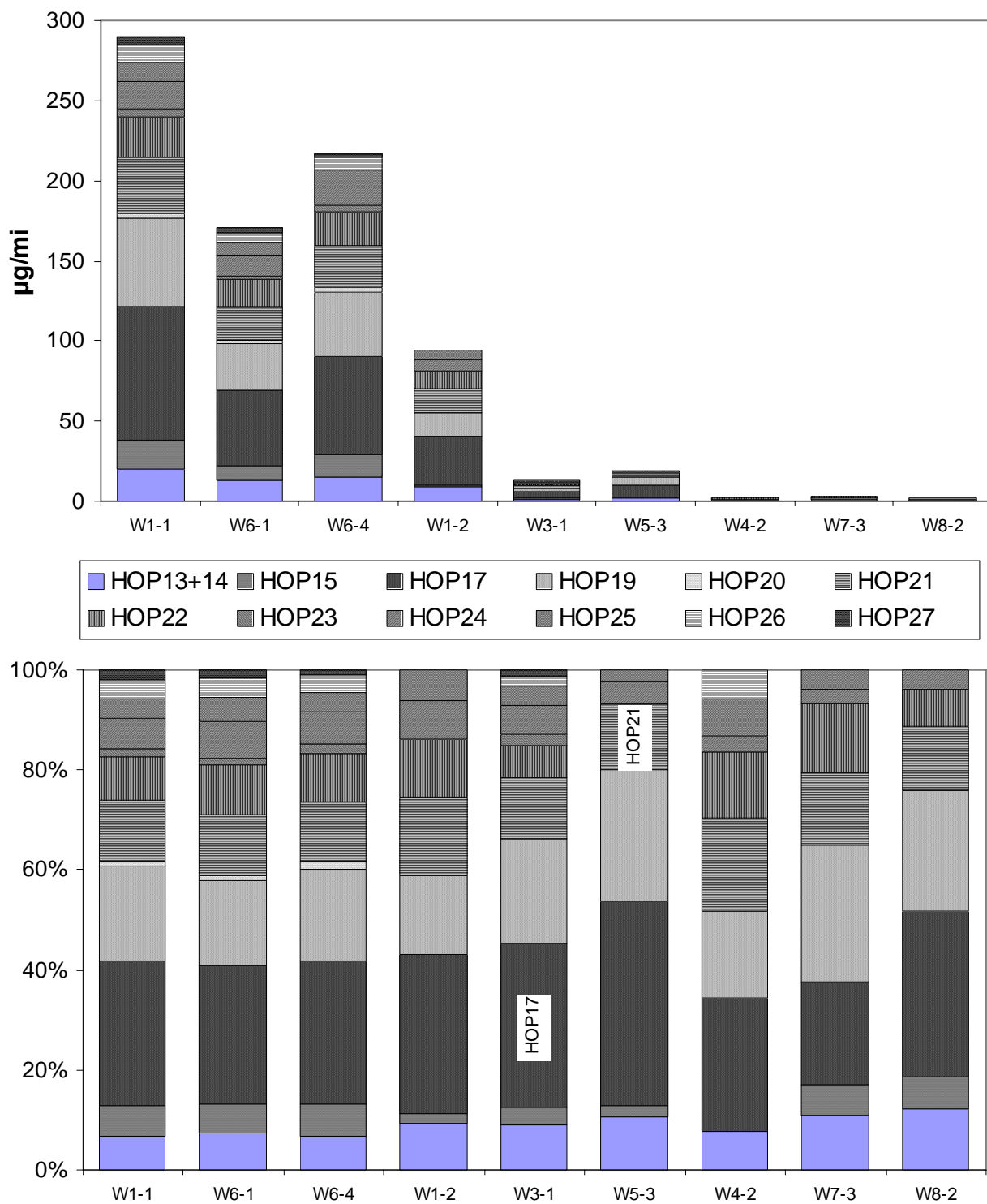
Figure 3b. Abundances of hopanes in exhaust emissions in µg/mi and percent.
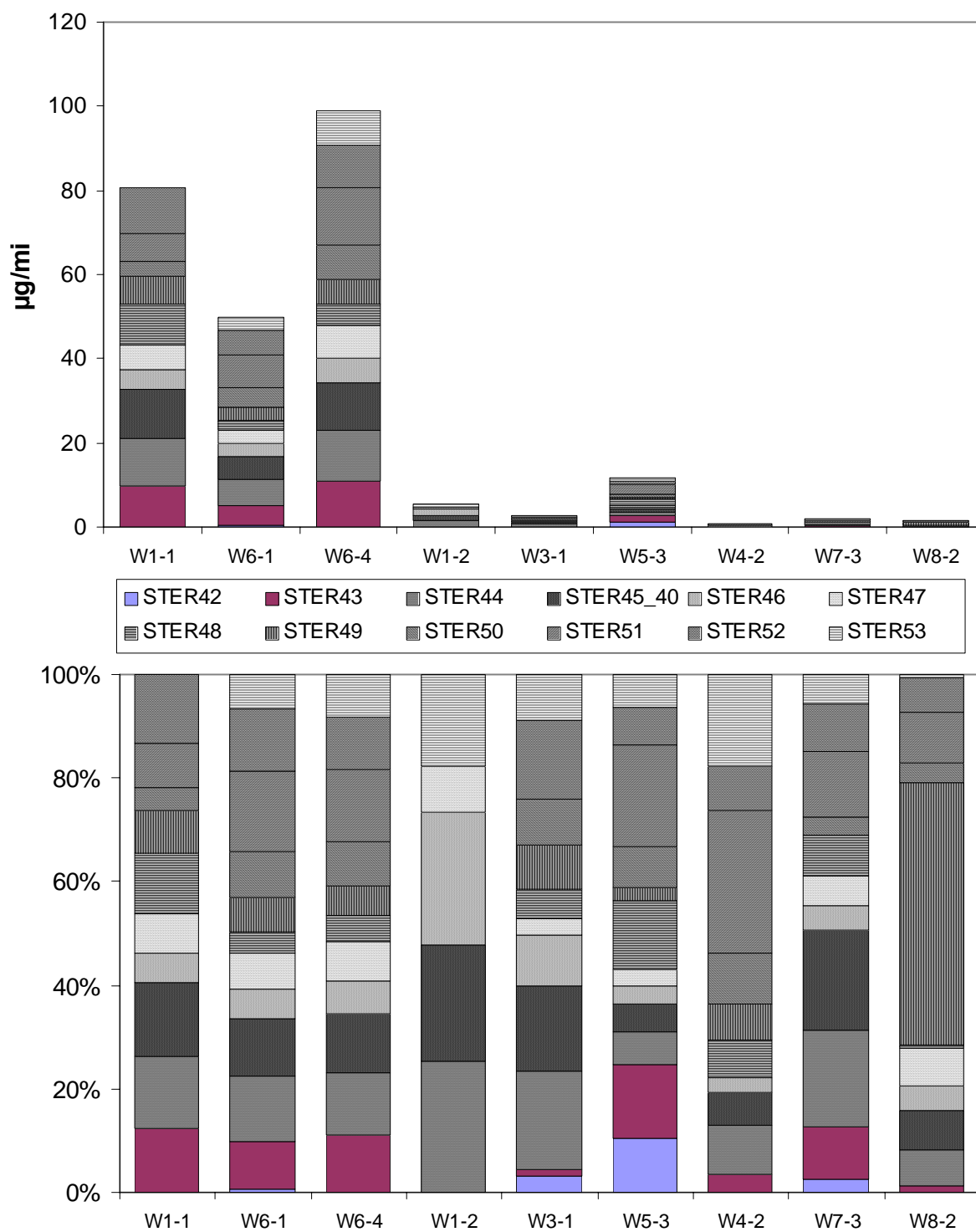
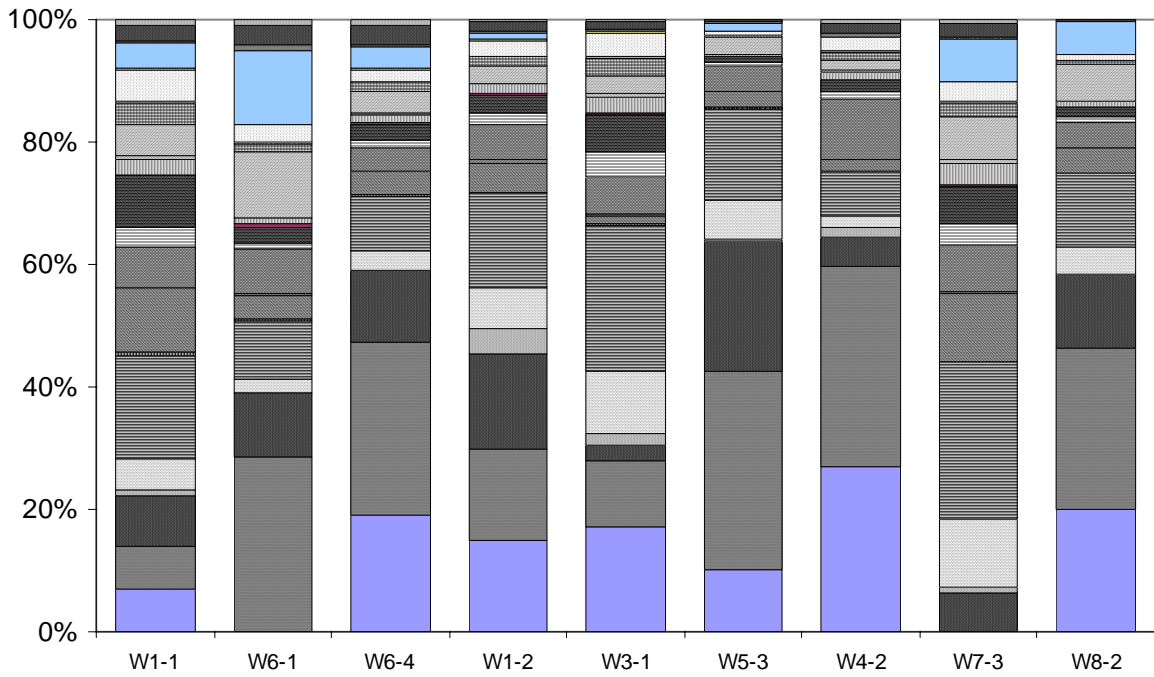Figure 3c. Abundances of steranes in exhaust emissions in µg/mi and percent.
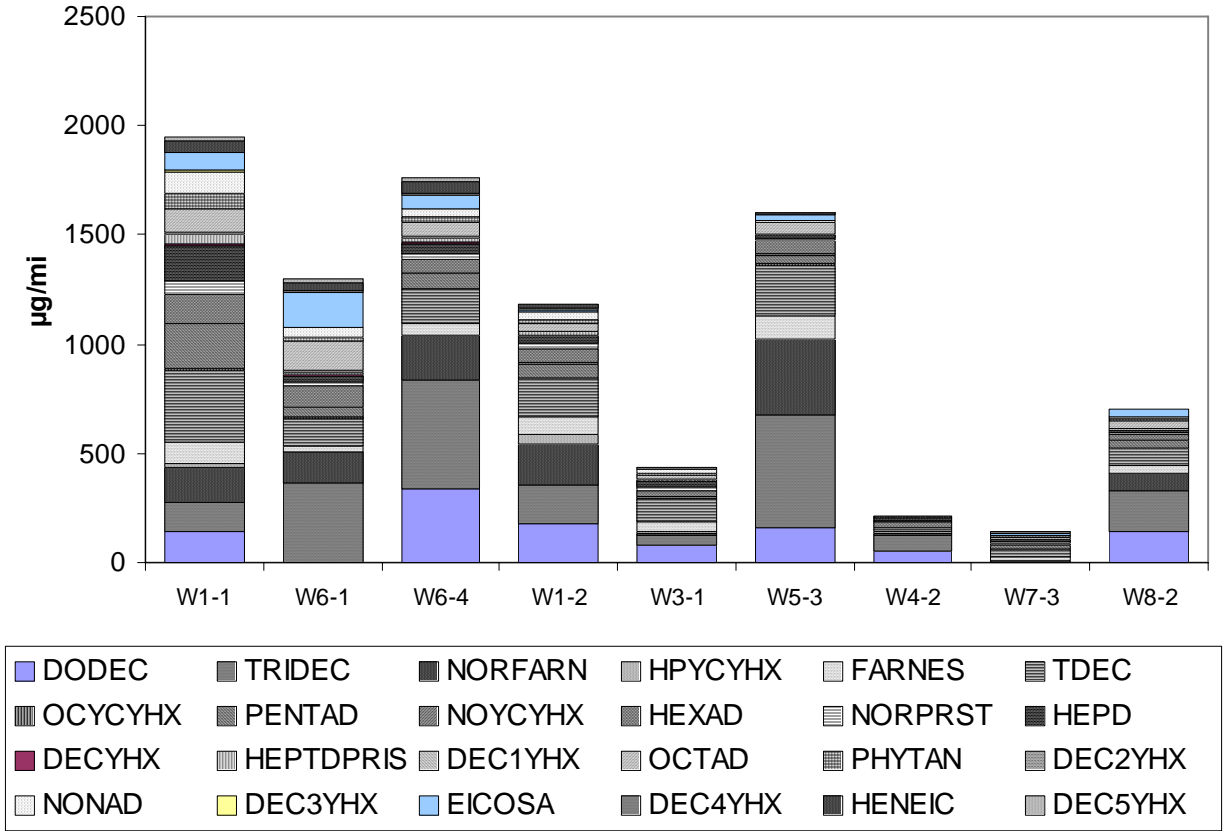
Figure 3d. Abundances of <C22 alkanes in exhaust emissions in µg/mi and percent.
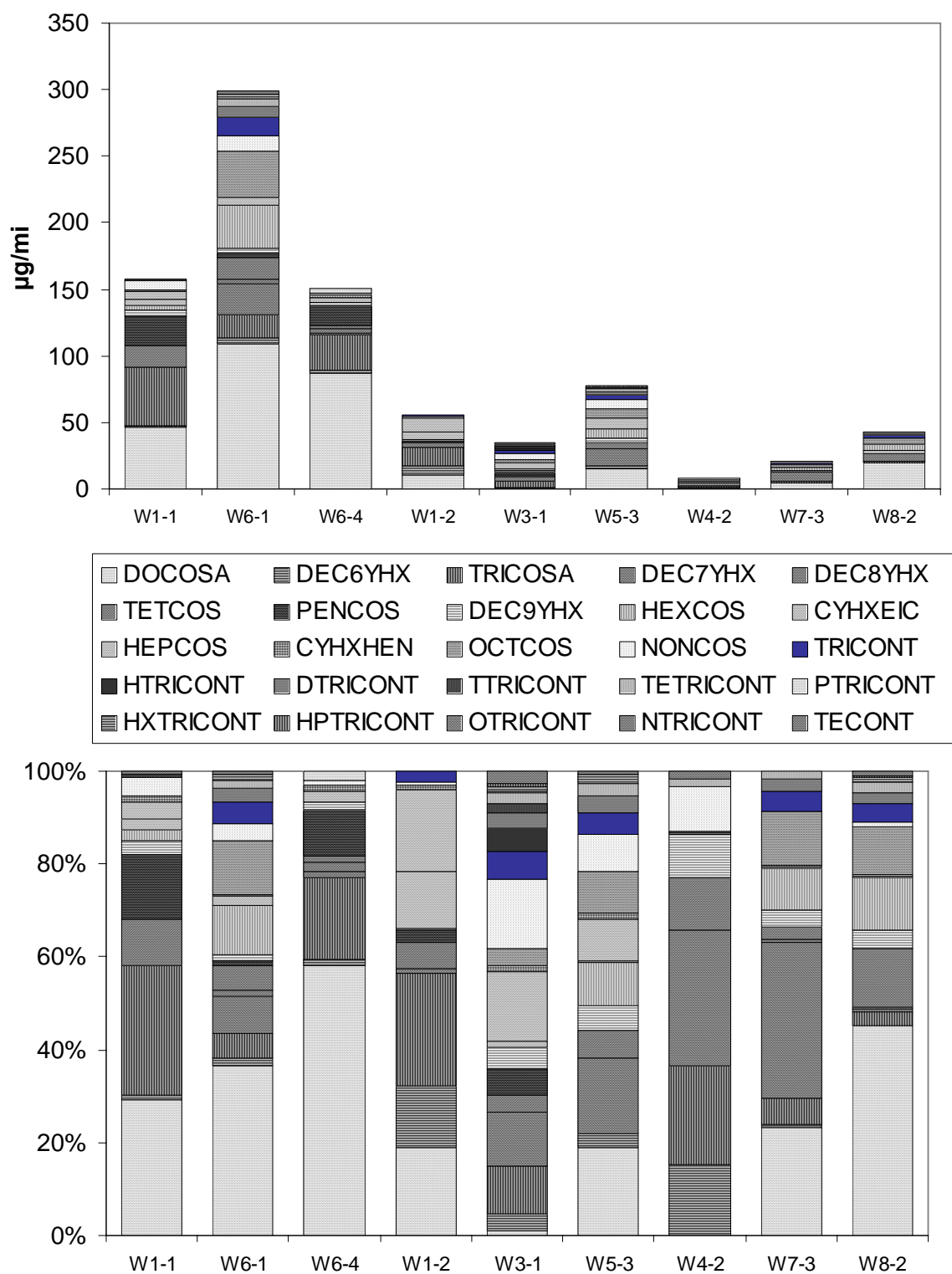
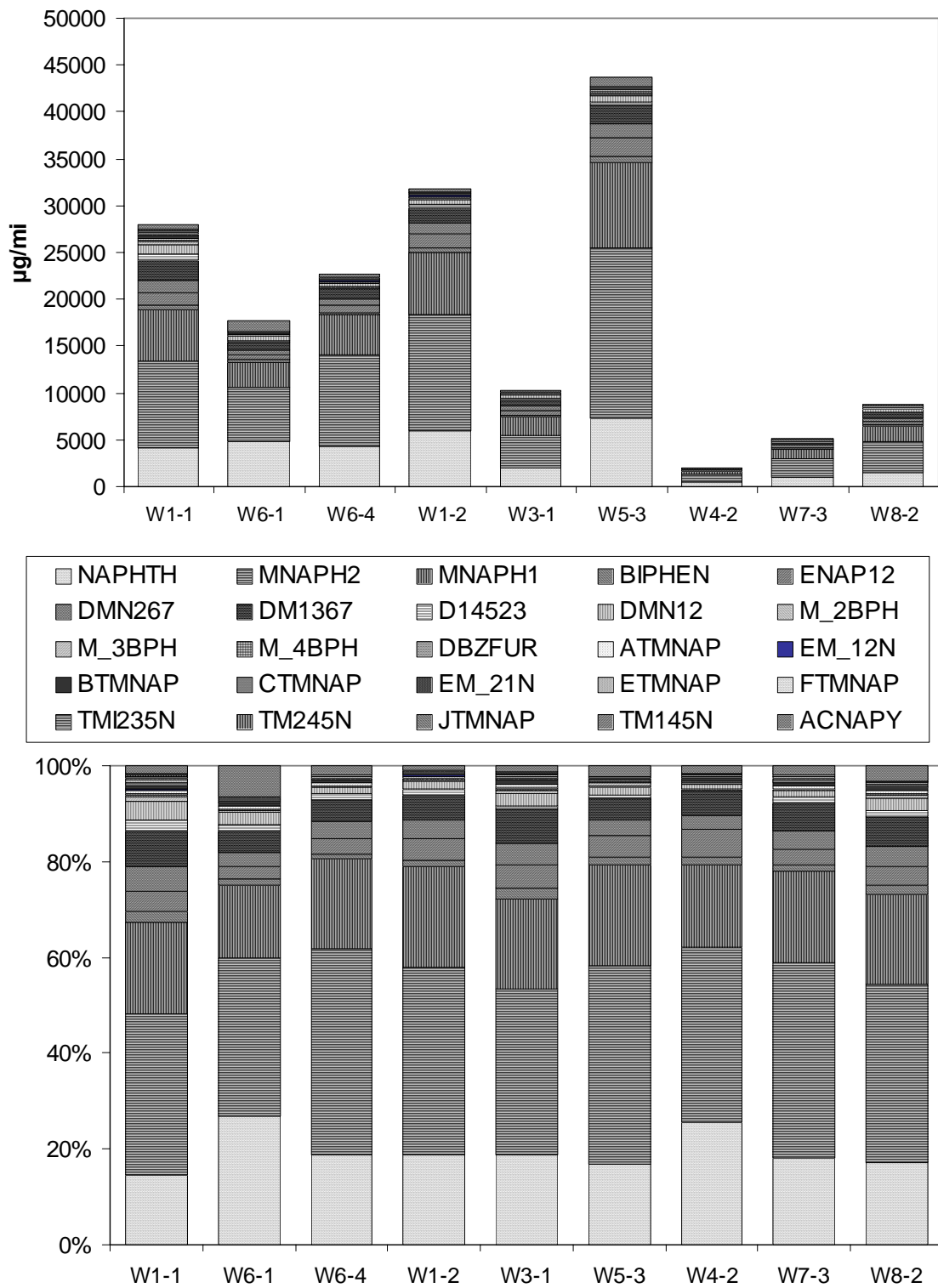Figure 3e. Abundances of >C21 alkanes in exhaust emissions in µg/mi and percent.

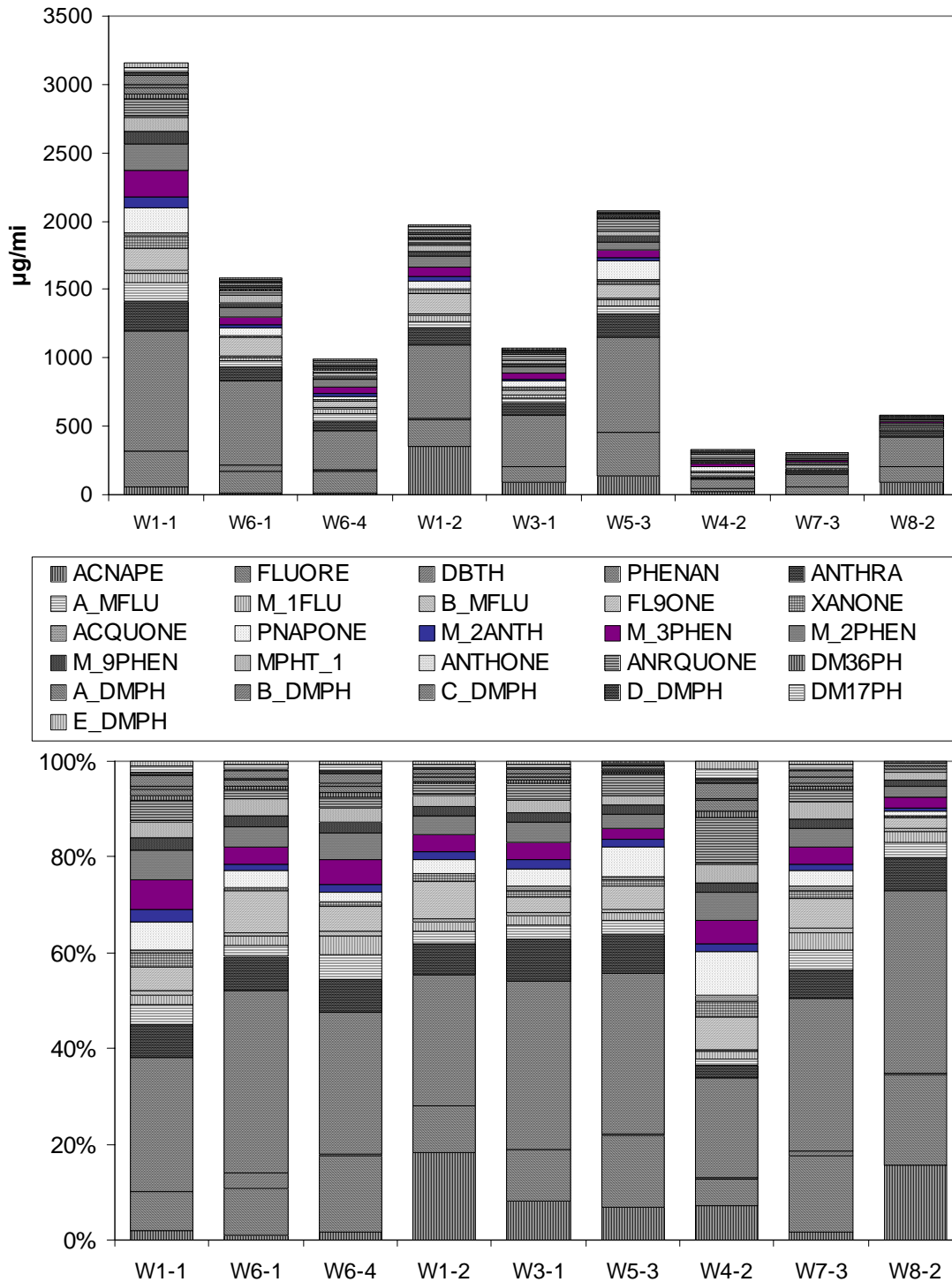Figure 3f. Abundances of naphthalenes in exhaust emissions in µg/mi and percent.

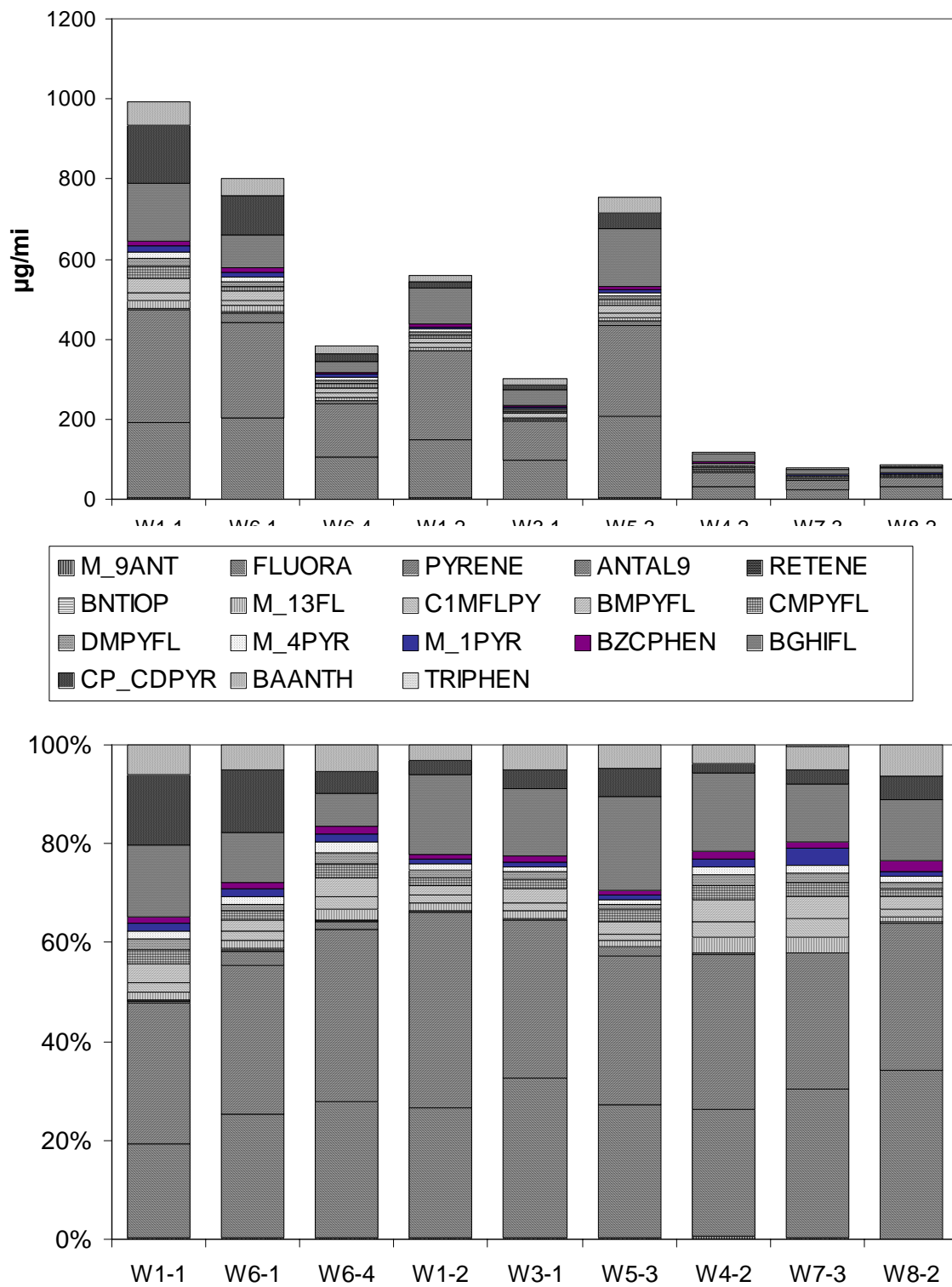Figure 3g. Abundances of other volatile PAHs in exhaust emissions in µg/mi and percent.

Figure 3h. Abundances of semi-volatile PAHs in exhaust emissions in µg/mi and percent.
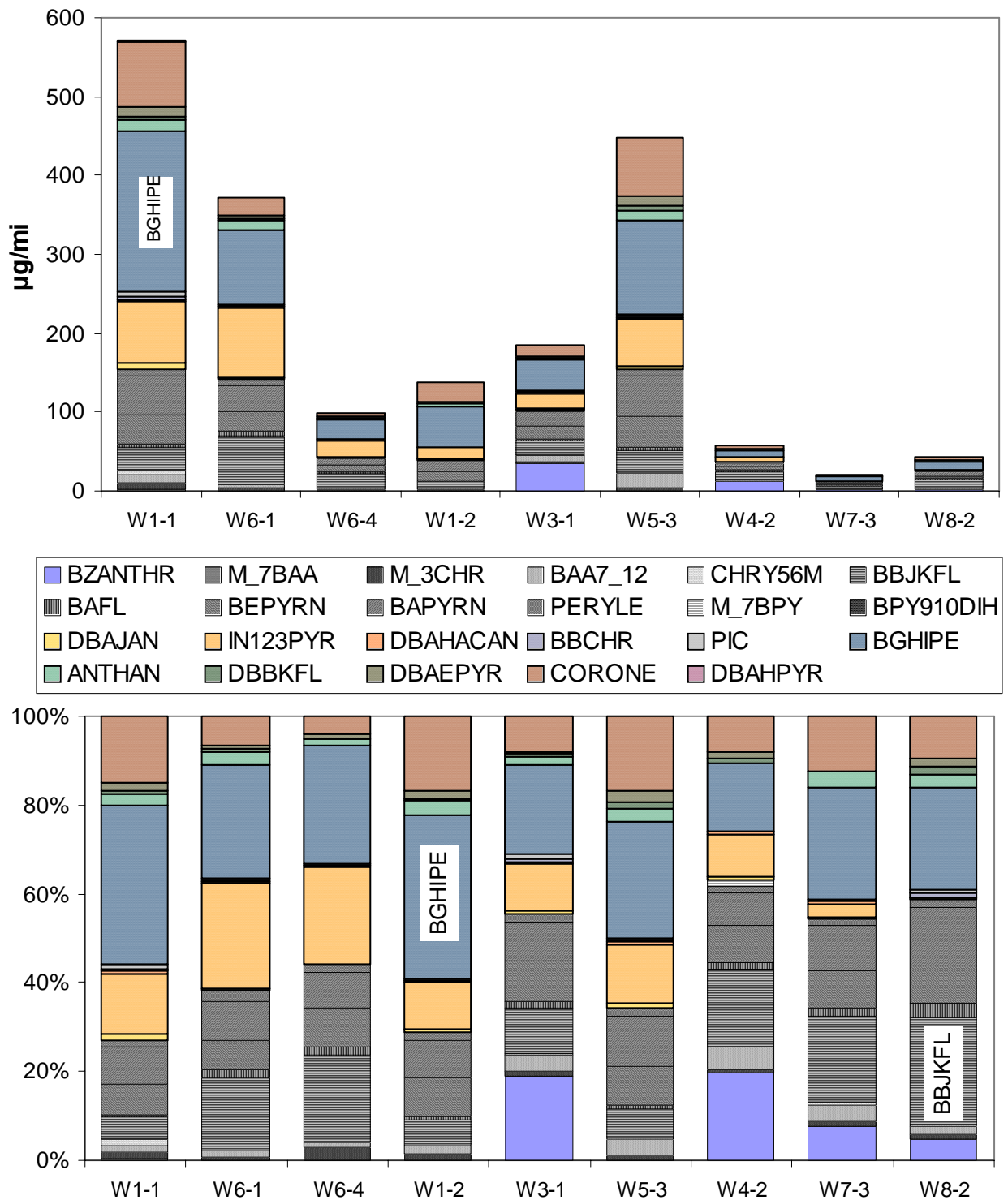
Figure 3i. Abundances of particle phase PAHs in exhaust emissions in µg/mi and percent.

Figure 4a. Correlation of exhaust emission rates of steranes and hopanes with concentrations in the corresponding lubrication oils.

Each data point is the mean of all composite samples for one compound.

Figure 4b. Correlation of exhaust emission rates of XRF elements and high MW alkanes with concentrations in the corresponding lubrication oils.

Each data point is the mean of all composite samples for one compound.

Particulate PAH

y = 2.41x + 1.69
R^2 = 0.69

exhaust emission rate (ug/mi)

concentration in lube oil (ppm)

naphthalenes

y = 8.97x - 307.37
R^2 = 0.92

exhaust emission rate (ug/mi)

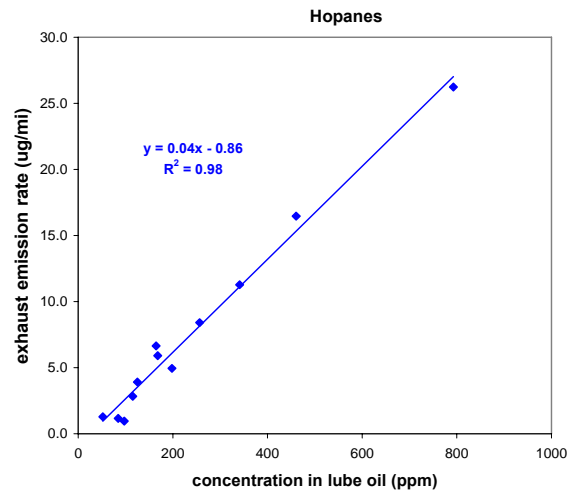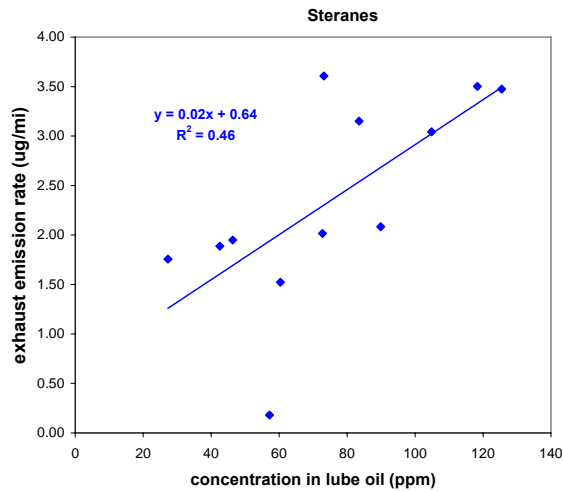concentration in lube oil (ppm)
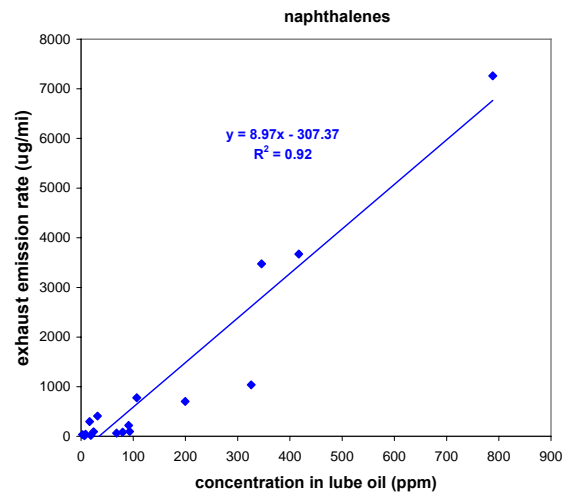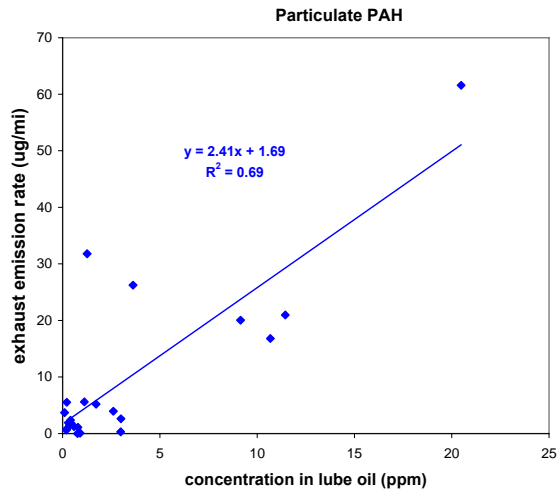
Figure 4c. Correlation of exhaust emission rates of particle phase and volatile PAH with concentrations in the corresponding lubrication oils.

Each data point is the mean of all composite samples for one compound.
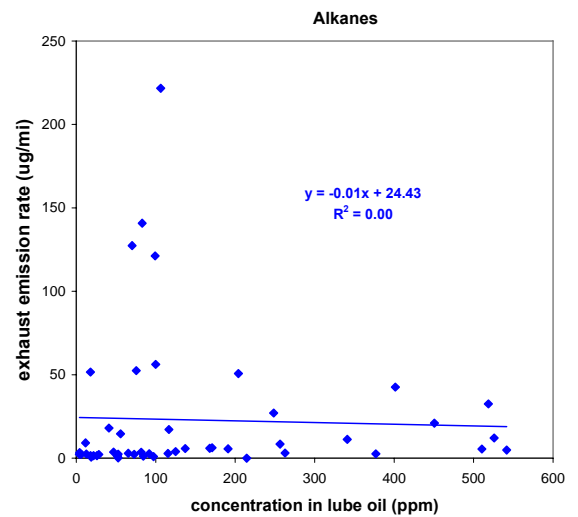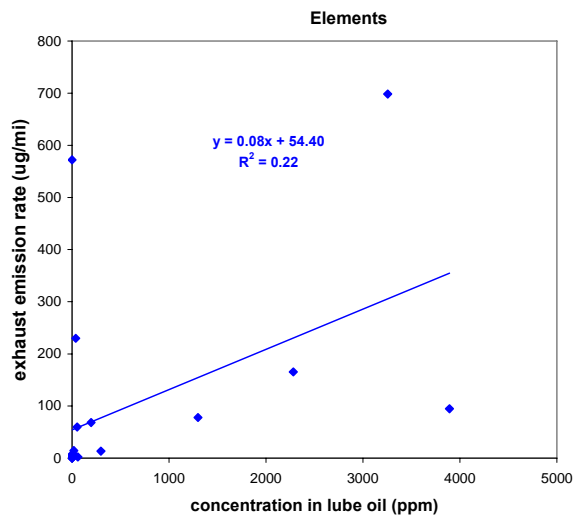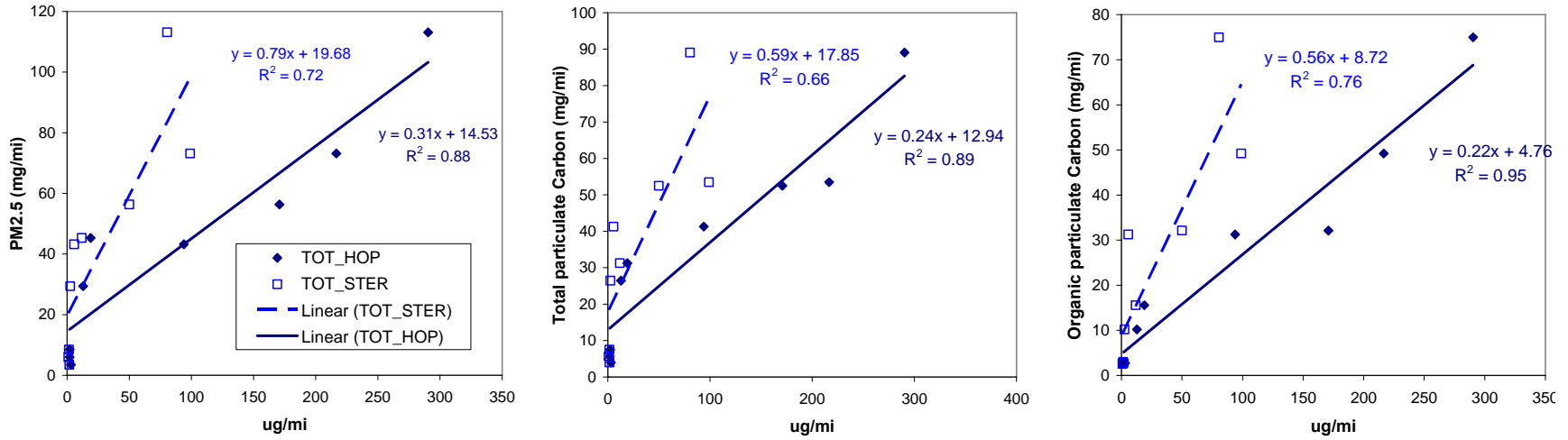
Figure 5a. Exhaust emission rates of sum of hopanes and steranes vs PM, TC, and OC.

Data points are the 9 vehicle exhaust composites.

Figure 5b. Exhaust emission rates of sum of particle phase PAHs vs PM, TC, and OC.

Figure 5c. Exhaust emission rates of individual gasoline marker PAHs vs PM, TC, and OC.

Figure 6. Exhaust emission rates sum of hopanes and individual gasoline marker PAHs versus EC.

Data points are the 52 vehicle exhaust composites in both Rounds 1 and 2.

Table 4. Percent contributions of lubricating oil to exhaust emissions estimated from ratios of sum of hopanes in exhaust and corresponding lubricating oil.

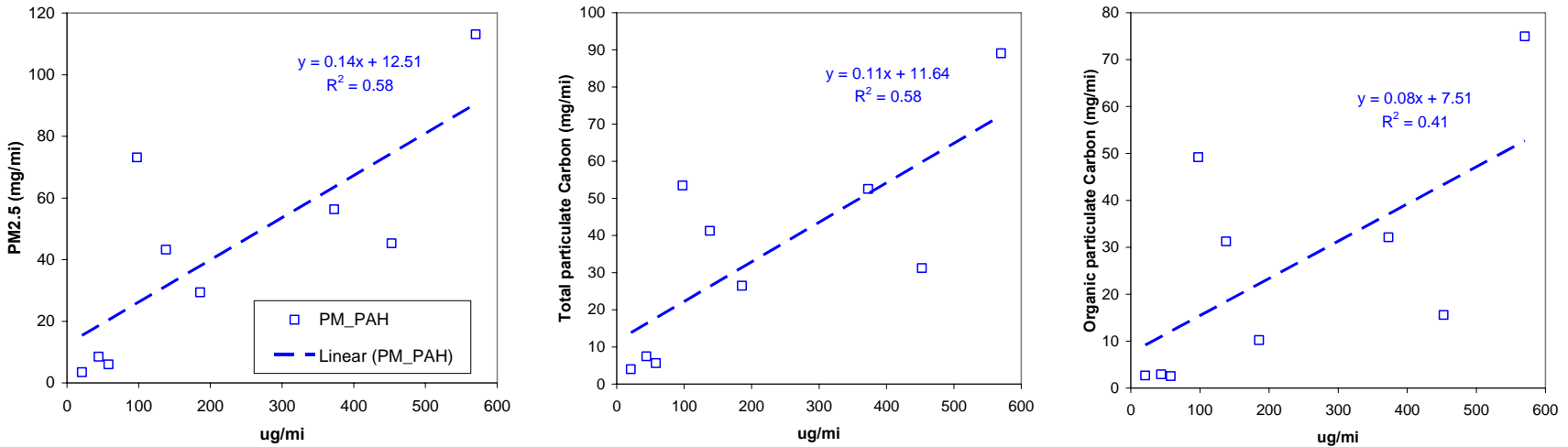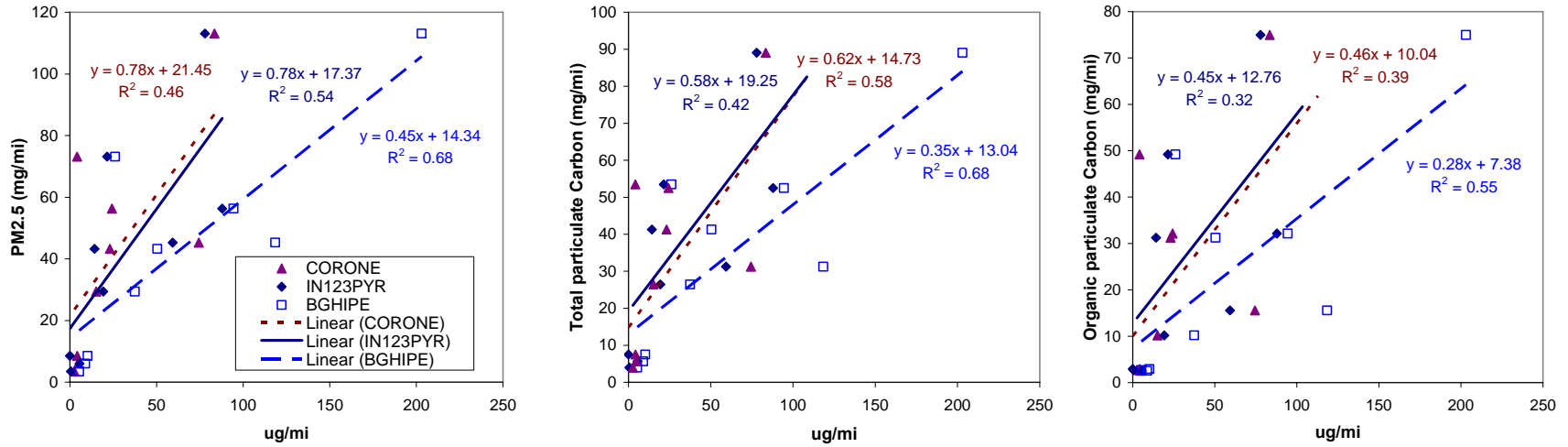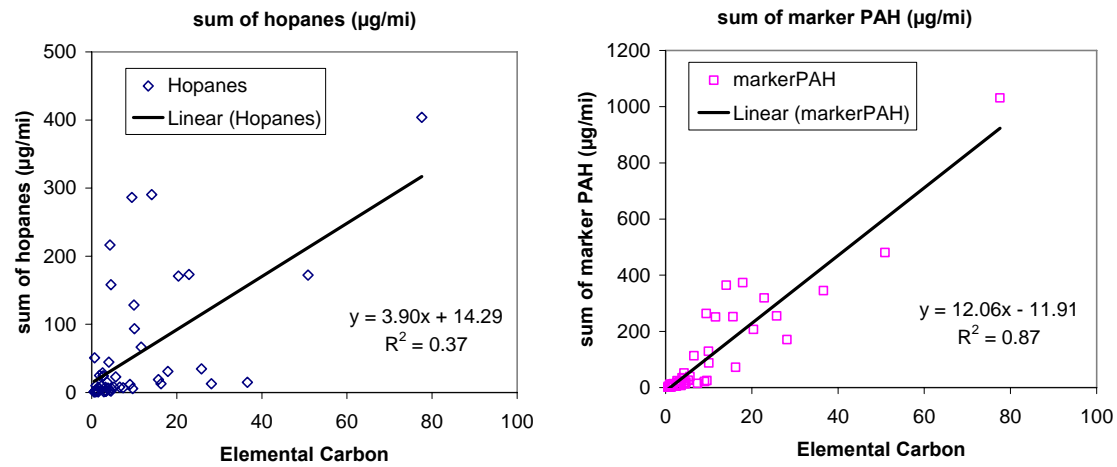| Parameter		High W1-1	High W6-1	High W6-4	Med W1-2	Med W3-1	Med W5-3	Low W4-2	Low W7-3	Low W8-2	mean	Stdev
P	Phosphorus	167.3	86.3	144.6	389.3	122.2	12.3	51.9	21.9	25.9	113.5	117.7
Zn	Zinc	112.3	19.3	44.8	269.8	32.5	18.7	15.1	11.0	9.5	59.2	85.2
Ca	Calcium	64.6	19.0	36.1	134.8	31.5	9.6	14.7	3.8	7.6	35.8	41.7
S	Sulfur	11.7	50.1	78.9	29.8	46.6	0.8	3.6	4.7	3.4	25.5	27.7
Fe	Iron	0.7	0.2	0.2	0.5	0.6	0.2	0.2	0.3	0.0	0.3	0.2
Si	Silicon	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pb	Lead	11.2	4.1	8.5	9.4	1.5	1.7	0.5	2.0	0.0	4.3	4.2
HOP17	17a(H),21ß(H)-30-Norhopane	106.2	90.8	94.8	84.9	85.8	80.3	94.8	93.5	82.8	90.4	8.0
HOP19	17a(H),21ß(H)-Hopane	87.0	92.9	92.7	92.2	76.2	61.3	78.6	63.0	67.1	79.0	12.9
HOP21	22S-17a(H),21ß(H)-30-Homohopane	88.5	122.2	103.7	69.2	87.0	82.8	61.4	54.3	89.0	84.2	20.9
HEXAD	Hexadecane	10.7	3.9	10.3	6.1	16.3	0.4	0.9	0.7	0.5	5.5	5.8
OCTAD	Octadecane	29.1	5.4	23.6	20.8	57.9	1.7	9.7	1.8	0.4	16.7	18.7
EICOSA	Eicosane	62.4	10.3	40.2	120.4	0.0	10.6	0.0	3.2	1.1	35.4	43.7
TRICOSA	Tricosane	76.9	71.0	115.9	180.1	0.0	0.0	71.3	33.4	138.7	98.2	49.6
NAPHTH	Naphthalene	0.7	0.2	0.3	0.3	0.7	0.0	0.1	0.0	0.0	0.3	0.3
MNAPH2	2-methylnaphthalene	0.6	0.4	0.3	0.4	0.8	0.0	0.2	0.0	0.0	0.3	0.3
MNAPH1	1-methylnaphthalene	0.6	0.5	0.3	0.4	0.8	0.0	0.2	0.0	0.0	0.3	0.3
FLUORE	Fluorene	0.9	0.6	0.5	0.2	0.7	0.0	0.2	0.0	0.0	0.4	0.3
PHENAN	Phenanthrene	1.1	0.3	0.8	0.3	0.8	0.0	0.2	0.1	0.1	0.4	0.4
ANTHRA	Anthracene	0.7	0.6	1.0	0.3	1.1	0.0	0.4	0.1	0.1	0.5	0.4
FLUORA	Fluoranthene	1.5	0.3	0.5	0.3	0.9	0.0	0.2	0.1	0.2	0.5	0.5
PYRENE	Pyrene	2.8	0.5	1.0	0.4	2.2	0.1	0.4	0.2	0.6	0.9	0.9
IN123PYR	Indeno[123-cd]pyrene	0.0	0.0	0.1	0.1	0.0	0.0	0.2	0.1	0.0	0.1	0.1
BGHIPE	Benzo(ghi)perylene	1.1	0.4	2.2	0.5	1.9	0.1	1.1	0.5	0.6	0.9	0.7
CORONE	Coronene	0.6	0.2	1.3	0.0	0.7	0.0	0.3	0.3	0.3	0.4	0.4

4   CONCLUSIONS

Consumption of lubricating oils by worn engines can be a substantial contributor to PM emissions relative to fuel-related combustion particles. In contrast, properly maintained newer engines produce very little particulate matter from lubricating oil. The composition of PM emissions of new and worn engines can be very different chemically because their main source and formation processes are different. These compositional differences may have important implications with regard to health impacts. Compositional differences of PM emissions for motor vehicles are also important considerations in the application of source composition profiles for emission inventory development and source apportionment by receptor modeling.

We analyzed a subset of nine used oil samples and three unused oils. Correlations of emissions of hopanes and steranes with organic carbon and PM emissions indicated that PM emissions of high emitters were mainly associated with consumption of lubricating oils. The rates of oil consumption were estimated from the exhaust emissions of hopanes and abundances of hopanes in the corresponding lubricating oil. Based upon consumption rates and chemical composition of the oils, we determined that the contributions of PAHs that were absorbed in the lubricating oil to PAHs in exhaust emissions were small. This limited dataset indicate that fuel-combustion was the primary source of PAHs.

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APPENDICES

A – Chemical Composition of Lubricating Oil

B – Chemical Composition for Corresponding Exhaust Samples