Oxygenated Organics in Fine Particle Emissions from Gasoline and Diesel Vehicles for Source Apportionment

Report to the California Air Resources Board
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Disclaimer

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Abstract

Gaseous and particulate emissions from light-duty gasoline (LDV) and heavy-duty diesel (HDV) vehicles were collected using a denuder-filter-polyurethane foam sampling train. The particulate emissions were analyzed for carbonyls, organic acids and polycyclic aromatic hydrocarbons using gas chromatography-ion trap mass spectrometry in conjunction with multiple derivatization techniques. Over eighty compounds were observed with emission rate ranges for carbonyls (0.005 to 490 $\mu g\ km^{-1}$, 0.04 to 2100 $\mu g\ L^{-1}$), organic acids (0.02 to 580 $\mu g\ km^{-1}$, 0.7 to 19000 $\mu g\ L^{-1}$) and PAHs (0.008 to 150 $\mu g\ km^{-1}$, 0.028 to 73 $\mu g\ L^{-1}$) determined in this study. The total emissions of oxygenated organics accounted for 5-25% of the particulate organic carbon and 2-12% of the total PM mass emissions for the vehicles investigated. Emission rates for benzoquinone from both low-emission (190 $ng\ km^{-1}$, 1.7 $\mu g\ L^{-1}$) and three-way catalyst (1500 $ng\ km^{-1}$, 16 $\mu g\ L^{-1}$) LDV were determined. Coronene, a proposed LDV source apportionment tracer, was measured in the HDV Idle/creep emissions at nearly twice the emission rate per liter of fuel consumed versus the LDVs. This study succeeded in measuring new particulate oxygenated organic and relevant polycyclic aromatic compound emission rates from both LDVs and HDVs.

Executive Summary

Combustion emissions from light-duty gasoline vehicles (LDV) and heavy-duty diesel vehicles (HDV) were collected for the purpose of chemical speciation of the oxygenated organic components. The semi-volatile nature of many of the targeted analytes necessitated the removal of the gas-phase emissions to prevent sampling artifacts in the particulate matter (PM) emissions. Using an annular denuder-filter-polyurethane foam (PUF) sampling train the gaseous and particulate emissions were collected separately. This method of sample collection allows for the examination of the particulate matter emission with minimal concern for gas-phase emission artifacts. Vehicle exhaust was subjected to two turbulent dilutions with particle-free air and allowed to cool to near ambient temperature prior to sample collection. The successful dilution of the vehicle emissions was accomplished using a stack dilution tunnel and residence time chamber.

LDV emissions were collected during the summer of 2002 at the California Air Resources Board Haagen-Smit Laboratory. The LDV vehicle classes examined include low-emission vehicles (LEVs) and three-way catalyst equipped vehicles (TWCs). Emission samples were collected on a single set of substrates as a composite from several different vehicles within the LDV category. LDV emissions were collected for vehicles operated under the Federal Test Procedure. The methods of exhaust collection and dilution are consistent with previous dynamometer emissions measurements.

HDV emissions were collected during the summer of 2003 at the Ralph's grocery store distribution center in Riverside, CA. The HDVs were operated on a mobile heavy-duty dynamometer maintained by West Virginia University. Methods for vehicle exhaust capture and dilution are similar to those employed for the LDV emissions collection. The HDV emissions were collected using either a 5-mode transient driving cycle or repeated idle and creep test modes. Simulated vehicle load weights, 56,000 or 66,000 pounds, were applied using a combination of mechanical flywheels and electrical motor resistance.

Vehicle emission samples were sequentially extracted with 1:1 (v/v) hexane:dichloromethane and methanol solvents. Solvent extracts were split to facilitate the analysis of multiple classes of organic compounds. Carbonyl species were derivatized to oximes using *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride. Organic acids and phenols were derivatized to esters and ethers respectively with 2,3,4,5,6-pentafluorobenzyl bromide. Hydroxy-PAHs were converted to trimethyl silyl ethers by derivatization with N,O-*bis*-(trimethylsilyl)-trifluoroacetamide. Chemical analyses were performed using gas chromatography-ion trap mass spectrometry (GC-ITMS). GC-ITMS analysis utilized electron ionization and methane chemical ionization. In addition to the derivatization methods employed tandem mass spectrometry (MS-MS) was utilized to enhance instrument sensitivity for certain analytes. Internal standardization was employed with fluorinated or isotopically-labeled compounds to accurately quantify the emissions constituents.

The validity and accuracy of the analytical methods was verified using model compound recovery experiments. Additional quality assurance measures included the analysis of certified reference materials. The accuracy and precision of the chemical analysis methods were typically compound dependent and in general followed trends related to the volatility of the particular analyte. Extraction efficiency was monitored via recovery of representative spiked internal standards, and results were adjusted accordingly.

Results of the chemical speciation performed in this study include the identification and quantification of more than 80 components of motor vehicle exhaust. These 80 compounds were comprised of 43 carbonyls, 17 organic acids, 17 polycyclic aromatic hydrocarbons (PAHs), 3 hydroxy-PAHs and 1 phenol. The particulate emission rates for numerous carbonyl species are presented here for the first time.

The abundance of the oxygenated organic compounds in the LDV and HDV emissions was considerable. Contributions of the oxygenated organics to the PM emissions are displayed in Table ES-1. The oxygenated organics account for a much larger percentage of the PM and organic carbon emissions from the LDVs. The HDV Idle/creep emissions contain significantly more oxygenated organic compounds in relation to the HDV five-mode sample.

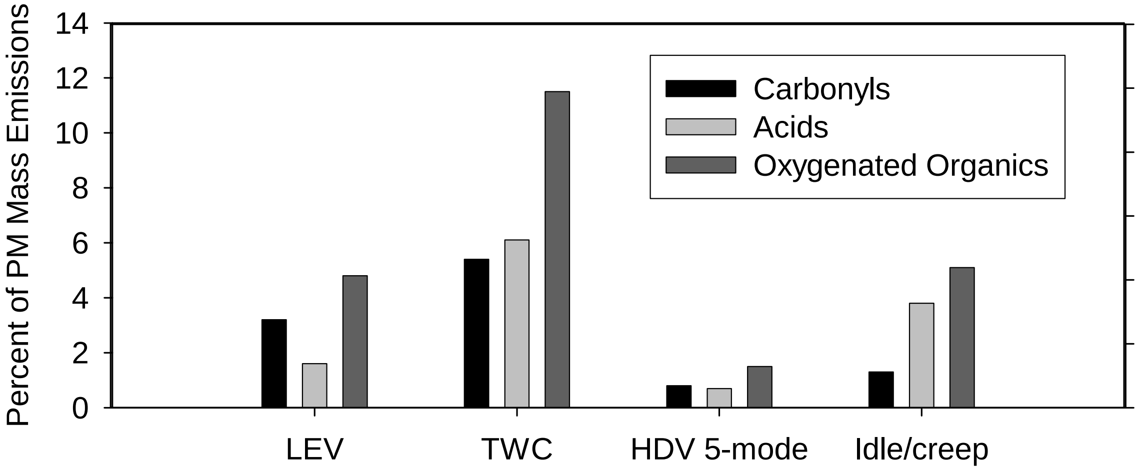


Table ES I: Oxygenated Organic Compound Contribution to Motor Vehicle PM Emissions

We measured the particulate emission rate ranges (mass per distance traveled, mass per fuel consumption) for carbonyls (0.005 to 490 μg km^{-1}, 0.04 to 2100 μg L^{-1}), organic acids (0.02 to 580 μg km^{-1}, 0.7 to 19000 μg L^{-1}) and PAHs (0.008 to 150 μg km^{-1}, 0.028 to 73 μg L^{-1}) in this study. For the majority of the compounds measured the LEV emissions were the lowest, with the HDV Idle/creep emissions the highest. Differences in the emission rates between the LEVs and the HDV Idle/creep sample were typically more than 10-fold.

Compounds unique to a particular vehicle class were minimally observed in this study. Benzoquinone was observed in both LDV samples but not in either HDV sample. Numerous aromatic species were observed in the HDV emissions that were not present in the LDV emissions. These species include perinaphthenone, anthraquinone, xanthone, naphthalic anhydride and 9-hydroxyfluorenone. Coronene, a proposed LDV source apportionment tracer, was observed in the LDV and the HDV Idle/creep emissions. Based on the results of this study we were not able to identify a unique component of either the LDV or HDV emissions that would serve as a suitable source apportionment tracer. We did however measure a proposed LDV tracer in HDV emissions. This result in conjunction with emission rates for benzoquinone and the oxygenated organic mass apportionment constitute significant achievements for the chemical speciation knowledge of motor vehicle emissions.

Abbreviations

Ac	Acetyl
BSTFA	N,O-*bis*-(trimethylsilyl)-trifluoroacetamide
CAS	Chemical Abstracts Service
CO_2	Carbon dioxide
CVS	Constant volume sampler
DCM	Dichloromethne
DFB	2,2'-difluorobiphenyl
Et	Ethyl
GC	Gas chromatography
HDV	Heavy-duty diesel vehicle
HSL	Haagen-Smit Laboratory
Ipr	Isopropyl
IS	Internal standard
ITMS	Ion trap mass spectrometry
IUPAC	International Union of Pure and Applied Chemistry
LDV	Light-duty gasoline vehicle
Lpm	Liter per minute
Me	Methyl
MeOH	Methanol
mL	Milliliter
mm	Millimeter
MS	Mass spectrometry
NA	Not available
ND	Not detected
ng	Nanogram
NIST	National Institute of Standards and Technology
OH	Hydroxyl
PAH	Polycyclic aromatic hydrocarbon
PFB	Pentafluorobenzyl
PFBBr	2,3,4,5,6-pentafluorobenzyl bromide
PFBHA	*O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride
pg	Picogram
Ph	Phenyl
PM	Particulate matter
$PM_{2.5}$	Particulate matter (aerodynamic diameter < 2.5 μm)
PTFE	Polytetrafluoroethylene
PUF	Polyurethane foam
RSD	Relative standard deviation
RTC	Residence time chamber
SDT	Stack dilution tunnel
SRM	Standard Reference Material
STD	Standard deviation
TMCS	Trimethylchlorosilane
TMS	Trimethylsilyl

URG	University Research Glassware
µg	Microgram
µL	Microliter
µm	Micrometer

1. Introduction

Our understanding of air quality, and thus our quality of life, generally depends on knowledge of the atmospheric pathways and ultimate fate of a large number of atmospheric pollutants that may prove detrimental to humans and the environment.[1] The impact of even low levels of airborne particulate matter (PM) on human health has been established.[2] More recent epidemiological evidence indicates a correlation of motor vehicle exhaust PM with both total and cardiovascular/respiratory-related daily deaths at sites in New Jersey.[3] The epidemiological results direct our attention to the necessity of determining the sources of atmospheric PM, specifically the contributions of motor vehicle emissions. Although not perfect, source apportionment modeling is by far the best tool for inferring the sources of airborne PM.[4]

According to Gertler et al. many areas in the United States have mobile sources, particularly motor vehicles, as dominant inputs of $PM_{2.5}$ to the atmosphere.[5] This is evident as common PM sources determined in the model results are the inputs from motor vehicle exhaust. The results of Schauer et al. identified diesel vehicles as the primary source of fine particulate matter to the Los Angeles air basin in the 1980s.[6] Watson et al. determined motor vehicle emissions accounted for 55% of the $PM_{2.5}$ mass in the Denver area during the Northern Front Range Air Quality Study, with light-duty gasoline vehicles contributing 60% of the $PM_{2.5}$ organic carbon approximately 2.5-3 times higher than for diesel motor vehicles.[7] Schauer et al. found that motor vehicle exhaust was the largest single contributor to fine particulate organic carbon in the South Coast Air Basin during a photochemical smog event in 1993.[8] Fraser et al. identified motor vehicle exhaust as the largest contributor to fine PM in the Houston area, with diesel vehicles being the predominant source independent of the season.[9] These previous source apportionment results for a variety of locales within the United States provide the motivation to more thoroughly evaluate the chemical contributions of motor vehicle emissions to atmospheric fine PM burdens.

Due to the substantial inputs of motor vehicles to atmospheric fine PM it is essential to accurately assess the impact of gasoline and diesel motor vehicles so that proper emissions controls can be applied for attainment of ambient $PM_{2.5}$ standards. Currently the two different motor vehicle classes are distinguished in PM source profiles using three main chemical species as described in Schauer et al.: 1) petroleum biomarkers (hopanes and steranes), 2) elemental carbon, and 3) certain polycyclic aromatic hydrocarbons (PAHs).[6] The basis for the application of these chemical species arises from source profile measurements conducted on heavy-duty diesel vehicles [10-12], medium-duty diesel vehicles [13], and gasoline vehicles (catalyst and non-catalyst equipped) [10, 11, 14]. Although these chemical species are currently utilized with acceptable separation of the two motor vehicle classes, there exist some potential pitfalls associated with their application, specifically PAHs, as unique tracers for motor vehicle combustion sources.

Based on the potential for existing organic tracer species to introduce uncertainty into source apportionment calculations of the contributions of gasoline and diesel motor vehicles to atmospheric $PM_{2.5}$, it appears necessary to investigate new source emissions samples for tracer species. Motor vehicle source profiles generated by Schauer et al. for both gasoline and diesel vehicles contain significant fractions, ~40% and ~85% respectively, of the emitted PM mass that remains unidentified.[13, 14] We hypothesize that further molecular speciation of certain organic compounds (aldehydes, ketones, quinones, multifunctional carbonyls, PAHs, hydroxy-PAHs, oxy-PAHs, carboxylic acids, hydroxy species and phenols) present in the emissions of gasoline and diesel motor vehicles will yield new compounds unique to each respective emissions source. This molecular speciation will utilize gas chromatography (GC) coupled with ion trap mass spectrometry (ITMS). To complement the GC-ITMS instrumentation our analysis protocols will utilize multiple derivatization techniques for compounds containing carbonyl, hydroxyl, and carboxylic functional groups. These derivatization reactions help facilitate the analysis of the chemical components of motor vehicle emissions that may be either too polar or non-volatile for GC analysis. Through the application of these tools we expect to observe chemical species not previously reported in motor vehicle PM emissions. These new compounds will likely have application for the mass apportionment of motor vehicle emission PM, possible application as unique source apportionment tracers and implications on the potent human health effects posed by the emissions. This proposed research falls in line the views of Zheng et al. in that more detailed understanding of composition and sources of fine PM are needed to identify the relative importance of source emission contributions in a way that will illuminate all of the major possibilities for PM control.[15] Advancing the known composition of the organic fraction of motor vehicle PM will help to increase the accuracy of source apportionment results as the primary emission organic fraction, which is the least well-characterized, may have the greatest impact on organic particle creation.[16]

2. Materials and Methods

2.1 Chemicals and Supplies

2.1.1 Analytical Standards

The chemicals used for identification and quantification of the organic constituents in motor vehicle emissions were obtained from multiple vendors. Due to the large number of compounds examined in this study they are not presented here but are provided in Appendix A. This source table identifies the compounds by their International Union of Pure and Applied Chemistry (IUPAC) name and also provides their CAS (Chemical Abstract Service) number (where available), molecular weight and a common name if appropriate.

Analytical standard mixtures of the oxygenated organic species were prepared as follows. Each individual standard was dissolved into organic solvent, acetonitrile for most carbonyls and acetone for most organic acids, with a target concentration of 1000 ng μL^{-1}. Once in solution mixtures of similar chemicals were prepared via dilution into acetonitrile or acetone where appropriate. A stock carbonyl calibration curve mixture was prepared by combining 2.5 mL of each of the compound mixtures presented in Appendix B in a 10 mL volume of acetonitrile yielding a targeted concentration of 2500 pg μL^{-1}. A similar procedure was followed for the organic acids targeting a 5000 pg μL^{-1} concentration in 10 mL volume of acetone, with the volumes and concentrations of the mixture solutions presented in Appendix C. Calibration curve solutions were then prepared via serial dilution of the calibration curve stock solutions to targeted concentrations ranging from 25 to 2500 pg μL^{-1} with the stock calibration curve solution serving as the highest point in the calibration range for the carbonyls. Further detail regarding the calibration procedure is provided in Section 2.3.3.3.

Stock solutions and calibration curves mixtures for the hydroxylated polycyclic aromatic hydrocarbons were prepared in a similar manner to the acid and carbonyl compounds. Each individual compound was dissolved into acetone with a target concentration of 100 ng μL^{-1}. A stock calibration curve mixture was prepared by combining 500 μL of each of the analyte solutions into a 10 mL volume of acetone yielding a concentration of 5 ng μL^{-1}, volumes and concentrations of the mixture solutions are presented in Appendix D. Calibration curve solutions were then prepared via serial dilution of the calibration curve stock solution into hexane to a targeted concentration of 2.5 to 1000 pg μL^{-1}.

Polycyclic aromatic hydrocarbon analytical standard mixtures were prepared using the following procedure. Most of the authentic standards were purchased in commercially prepared mixtures dissolved in hexane and/or toluene, and were used for standard preparation without any modifications. Pure standards of triphenylene and coronene were dissolved into hexane or toluene. A stock calibration curve mixture was prepared by combining these mixtures targeting a concentration range of 0.5 to 1.5 ng μL^{-1}, volumes and concentrations of the mixture solutions are presented in Appendix E. Calibration curve solutions were prepared via serial dilution of the calibration curve stock solutions to targeted concentrations ranging from 5 to 1500 pg μL^{-1}.

2.1.2 Organic Solvents

Since many of the analytes targeted in this project are present at extremely low levels in the PM emissions the highest purity organic solvents were utilized where necessary. Due to the numerous solvents employed a summary is provided, see Table I, which lists the solvent, purity, manufacturer, vendor and application. When necessary certain solvents were further purified using glass distillation through 6-chamber Snyder columns.

Table I: Organic Solvents Utilized with the Application and Vendor Information

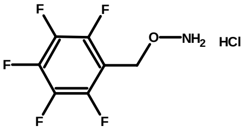
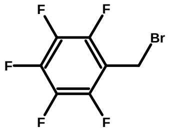
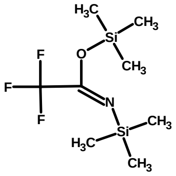
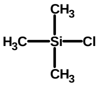
Solvent	Purity	Manufacturer	Vendor	Application
Acetone	trace analysis (glass-distilled)	Burdick and Jackson [1]	VWR [2]	standard preparation, chemical analysis
Acetone	HPLC grade	Omnisolve (VWR)	VWR [2]	cleaning glassware, glassware silanization
Acetonitrile	carbonyl-free	Burdick and Jackson [1]	VWR [2]	standard preparation, chemical analysis
Dichloromethane	trace-analysis	Burdick and Jackson [1]	VWR [2]	sample extraction, equipment cleaning, ionization source cleaning
Hexane	trace-analysis	Burdick and Jackson [1]	VWR [2]	standard preparation, sample extraction, equipment cleaning
Methanol	purge & trap	Fisher	Fisher [3]	sample extraction, equipment cleaning
Methanol	HPLC grade	J.T. Baker [4], Burdick and Jackson [1]	VWR [2]	glassware silanization
MTBE	HPLC grade	Fisher	Fisher [3]	glassware silanization
Toluene	HPLC grade (glass-distilled)	Burdick and Jackson [1]	VWR [2]	glassware silanization, standard preparation

[1] Burdick and Jackson, Honeywell International, Inc., Muskegon, MI, [2] VWR International, West Chester, PA, [3] Fisher Scientific, Fairlawn, NJ, [4] J.T. Baker, Phillipsburg, NJ

2.1.3 Derivatization Reagents

Due to the polar functional groups present on the targeted analytes multiple derivatization reagents were employed to facilitate chemical analysis by GC-MS. Carbonyl derivatization to generate oximes was performed using *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA). Species containing hydroxyl groups were derivatized to trimethyl silyl ethers using N,O-*bis*-(trimethylsilyl)-trifluoroacetamide (BSTFA), with catalysis by trimethylchlorosilane (TMCS). Organic acid derivatization to generate esters was performed using 2,3,4,5,6-pentafluorobenzyl bromide (PFBBr). These reagents are presented in Table II, with their molecular weights, CAS numbers, chemical structures, manufacturers, and vendors.

Table II: Derivatization Reagents and Their Structure and Vendor Information

Compound	CAS Number	Molecular Weight	Structure	Vendor
PFBHA	57981-02-9	249.57		Sigma-Aldrich [1]
PFBBr	1765-40-8	260.98		Sigma-Aldrich [1]
BSTFA	25561-30-2	257.40		Supelco [2] via Sigma-Aldrich [1]
TMCS	75-77-4	108.64		Sigma-Aldrich [1]

[1] Sigma-Aldrich Chemical Co., Inc., Milwaukee, WI, [2] Supelco, Bellfonte, PA

2.1.4 Equipment and Consumables

Emissions samples were collected for this project using an annular denuder-filter-polyurethane foam (PUF) sampling train. A schematic diagram of the sampler configuration is presented in Figure I, and an actual picture from the HDV collection event is provided in Figure II. As depicted in the figures, the aerosol enters the sampling train from the bottom and is drawn through the apparatus vertically with the flow rate controlled by electronic mass flow controllers.

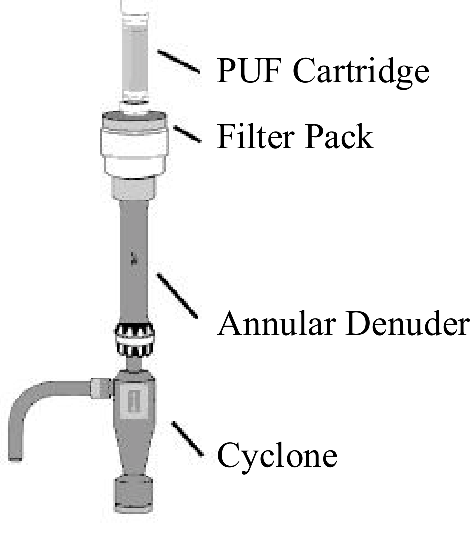


Figure I: Schematic Diagram of Sampling Train

Figure II: Photo of Sampling Train During HDV Collection Event in Riverside June, 2003

The majority of the sampling train hardware was obtained from University Research Glassware (URG), Chapel Hill, NC. These items included, listed in their configuration order, $PM_{2.5}$ Teflon-coated cyclone inlets, Teflon-coated annular denuder unions, eight-channel glass annular denuders, Teflon three-stage filter packs, and glass PUF holders. The annular denuders employed for the sample collection events are displayed in Figure III. Denuders were coated with XAD-4 polystyrene resin (Sigma-Aldrich) as described by Gundel et al. and Gundel and Lane.[17, 18] The exact coating procedure utilized for these sampling events will be described in further detail in Section 2.2.1.1.

Figure III: Profile and Top View of URG Annular Denuder

The collection media employed in this study were designed to separate the gas- and particle-phase chemical species from one another. Cyclone inlets were operated at 16.7 Lpm, per URG operating instructions, for a $PM_{2.5}$ size cut of the diluted vehicle exhaust. The initial gas-phase analytes were removed via the XAD-coated denuders. Particle-phase emission components were collected downstream of the denuders on 47 mm quartz fiber filters obtained from Pall (Ann Arbor, MI). Gas-phase species that may have adsorbed to the particulate surfaces and were desorbed during sample collection were trapped with two PUF plugs, obtained from URG, located in series downstream of the quartz filters. The flow rates through the two sampling legs were monitored with electronic mass flow controllers obtained from Hastings Instruments (Hampton, VA) . A further description of sampling media preparation protocols and cleaning procedures for the sampling hardware is provided in the following Section 2.2.1.

2.2 Sample Collection Preparation

2.2.1 Procedures for Sampling Media Preparation

Due to the trace levels of analytes targeted in this project it was essential to ensure that the working spaces were the cleanest available. To facilitate an organic contaminant free work surface procedures were conducted on aluminum foil. The foil is first baked in a muffle furnace at 550 ^{o}C for a period of twelve hours, to remove any organic species, and is hereafter referred to as baked foil.

2.2.1.1 Glassware Silanization Procedure

Due to the polar nature of the analytes targeted in this project all glassware utilized for the sample collection, storage and chemical analysis undergoes a silanization procedure to deactivate silanol groups on the glassware surface inhibiting sorption of our targeted chemical species. The glassware is initially soaked in a 15% solution of dichlorodimethylsilane (Sigma-Aldrich) in toluene for a period of no less than 24-hours. After soaking in the silanization solution the glassware is subjected to a three-stage solvent rinse procedure. The glassware is rinsed twice with toluene, twice with acetone and finally twice with methanol. Following the solvent rinse each piece of glassware is dried in an oven at 150 ^{o}C for no less than 15 minutes. Once dry the glassware is covered with baked foil for storage.

2.2.1.2 Coating Annular Denuders with XAD-4 Resin

The XAD-4 polystyrene resin obtained from Sigma-Aldrich was initially powderized to a particle diameter of approximately 1 μm using a rotary ball mill for a period of one week. Processing the resin into a powder form facilitates its application as a coating to the interior surfaces of the URG annular denuders. Once in powder form the resin is stored in the original shipping container until needed.

Prior to the start of the coating procedure the XAD-4 resin powder is first cleaned to remove any organic contaminants. Approximately 2.5 grams of material are added to an Erlenmeyer flask. To the flask 50 mL of DCM (Burdick and Jackson, trace analysis grade) and 50 mL of methanol (Fisher, purge and trap grade) is added. The flask is covered with baked foil and suspended in an ultrasonic cleaning bath. The bath is operated at maximum power for a period of five minutes, hereafter referred to as sonication. Upon completion of sonication the contents of the flask are passed through a 0.5 μm Teflon filter while under vacuum. The filter containing the resin is transferred onto a piece of baked foil and placed into an oven at 150 ^{o}F for a period of 30 minutes. Once the cleaned resin is dry it is used for the denuder coating.

The annular denuders are coated with the cleaned resin as follows. One gram of the cleaned resin is added to an Erlenmeyer flask along with 150 mL of hexane (Burdick and Jackson, trace analysis grade). The mixture is then sonicated for 10 minutes to create a suspension. One of the Teflon caps of the annular denuder is removed and the slurry is poured into the denuder. The denuder is capped and inverted 10 times. The cap is removed and the slurry poured back into the flask. Drying the denuder is accomplished using a stream of nitrogen, first passed through a hydrocarbon trap. The inversion/drying steps are repeated 9 times. After the tenth time a volume of 150 mL of pure hexane is used to rinsed the denuder and finally the denuder is dried with nitrogen. Once dried the denuder is capped, wrapped with bubble wrap and placed into its original shipping box for storage until the sample collection events. Note that each denuder is used for ten sample collections prior to repeating the resin-coating procedure.

2.2.1.3 Cleaning Filter Substrates

After receipt of the 47 mm quartz fiber filters they were preconditioned to minimize any residual organic material that may have been present. Individual filters were removed from their plastic container using solvent-rinsed forceps and placed as a single layer on baked foil. A second piece of baked foil was placed on top of the filter layer, which was followed by the addition of a second layer of quartz substrates. This was repeated until there were enough layers of foil and filters to complete collection of the necessary number of emissions samples. The layers of foil and filters were placed in a Lindberg/Blue muffle furnace (Ashville, NC) and baked at 550 ^{o}C for 12 hours. Under these temperature conditions any organic compound residues that were present on the filters are converted to carbon dioxide (CO_2) via pyrolysis.

Solvent-rinsed glass petri dishes were baked simultaneously with the foil and filters. Once free of organic residues these petri dishes served as storage containers for the filter substrates. A single clean filter was placed into a single clean petri dish bottom using a solvent-rinsed forceps. The dish was then covered with a piece of baked foil and capped with a plastic petri dish top labeled with the necessary filter identification information and finally wrapped with one inch Teflon tape, see Figure IV.

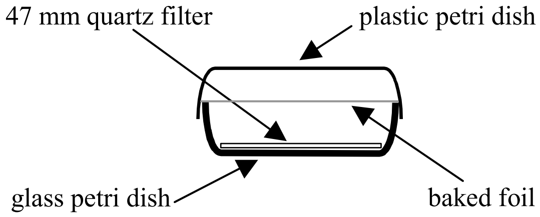


Figure IV: Filter Storage Container

The filters were then stored in a glass desiccator, under organic-free nitrogen and placed in a –20 ^{o}C freezer until the sampling event.

2.2.1.4 Cleaning PUF Substrates

The PUF substrates used for this project were obtained from URG. Prior to their application for emissions collection the substrates were subjected to a 24 hour Soxhlet extraction with a 1:1 (v/v) mixture of hexane:diethyl ether. A photo of the Soxhlet extraction setup is presented in Figure V. After the extraction the substrates are initially placed on baked foil in a fume hood to allow solvent evaporation for 30 minutes. The substrates are transferred into a muffle furnace at a temperature of 50 ^{o}C under grade 5 purity nitrogen gas for a period of 30 minutes. Once dried each substrate is transferred into a silanized 40 mL low-actinic glass bottle and sealed with a Teflon-lined cap. The bottles are wrapped with ½ inch Teflon tape and transferred to a –20 ^{o}C freezer for storage until the sample collection event.

Figure V: PUF Substrate Soxhlet Cleaning Setup

2.2.2 Procedures for Sampling Hardware Preparation

All of the sample collection hardware pieces were thoroughly cleaned prior to each emissions sampling event. Initially a bath is prepared with hot tap water and Alconox soap. All of the pieces are soaked for 1 hour without any scrubbing, to prevent the removal of the Teflon coatings. Each piece is then rinsed three times with warm tap water, followed by three rinses with deionized water. Upon completing the aqueous rinses the pieces are allowed to dry on laboratory bench soaker paper while covered with baked foil.

Once the individual pieces are dry they are subjected to a series of solvent rinses to remove any residual organic materials that remained after the aqueous cleaning steps. The items are placed on baked foil in a fume hood. Using the same solvents employed for sample extractions each piece is first rinsed with methanol and then the 1:1 (v/v) Hexane:DCM mixture. After completion of the organic solvent rinses each piece is allowed to dry in a fume hood for 15 minutes prior to complete drying using fluorocarbon-based canned air. Once completely dry the items are individually wrapped with baked foil and placed into new Ziplock® bags, wrapped with bubble-wrap and placed into cardboard boxes for storage and transport to the sample collection events.

2.3 Chemical Analysis Methodologies

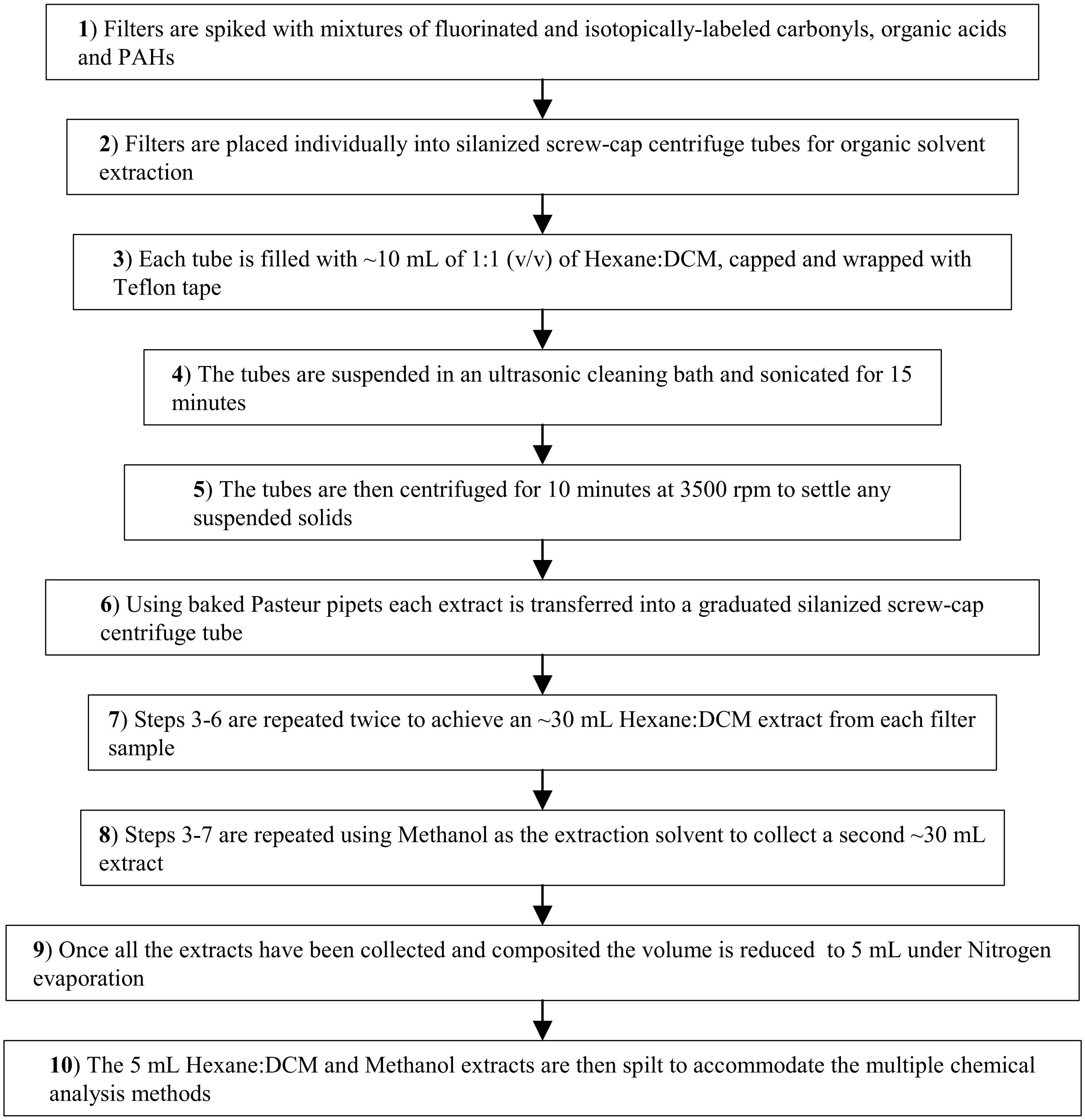
2.3.1 Chemical Extraction Procedures

2.3.1.1 Filter Substrate Extraction

The extraction procedure for PM filter samples is outlined in Figure VI. Concentrations of the spiked recovery species are provided in Table III for the oxygenated organics and in Table IV for the PAHs, additionally the chemical structures for internal standards employed in this project are provided in Appendix F. Data displaying the validity of the extraction and derivatization methods are provided in Section 2.3.4.1 for filters spiked with representative compounds. For each batch of samples extracted a method blank was also collected and NIST SRMs 1649 and 1650 were also extracted to provide further confidence in the methods being employed. Once the extracts had been reduced to a 5 mL volume they were distributed for the various derivatization and chemical analysis pathways for the organic speciation efforts. The manner in which the extracts were divided is provided in Figure VII.

Table III: Oxygenated Organic Recovery Internal Standards

Compound	MW	Mixture Conc.	5 mL Extract Conc.	Targeted Analysis Conc.
	(g mol^{-1})	(ng µL^{-1})	(pg µL^{-1})	(pg µL^{-1})
-Carbonyls				
2-F-benzaldehyde	124.11	5.1	102.8	1028
5-F-1-indanone	150.15	4.9	98.5	985
5'-F-2'-OH-acetophenone	154.14	5.0	99.9	999
8-F-1-benzosuberone	178.20	5.0	100.2	1002
4-F-benzophenone	200.21	5.0	100.9	1009
-Carboxylic Acids				
d_5 benzoic acid	127.13	4.9	98.0	980
d_{11} hexanoic acid	127.18	5.1	101.5	1015
2-F-5-Me-benzoic acid	154.14	5.2	103.6	1036
$^{13}C_1$ dodecanoic acid	215.33	5.0	99.3	993
d_{35} octadecanoic acid	319.55	5.1	102.1	1021



1) Filters are spiked with mixtures of fluorinated and isotopically-labeled carbonyls, organic acids and PAHs

2) Filters are placed individually into silanized screw-cap centrifuge tubes for organic solvent extraction

3) Each tube is filled with ~10 mL of 1:1 (v/v) of Hexane:DCM, capped and wrapped with Teflon tape

4) The tubes are suspended in an ultrasonic cleaning bath and sonicated for 15 minutes

5) The tubes are then centrifuged for 10 minutes at 3500 rpm to settle any suspended solids

6) Using baked Pasteur pipets each extract is transferred into a graduated silanized screw-cap centrifuge tube

7) Steps 3-6 are repeated twice to achieve an ~30 mL Hexane:DCM extract from each filter sample

8) Steps 3-7 are repeated using Methanol as the extraction solvent to collect a second ~30 mL extract

9) Once all the extracts have been collected and composited the volume is reduced to 5 mL under Nitrogen evaporation

10) The 5 mL Hexane:DCM and Methanol extracts are then spilt to accommodate the multiple chemical analysis methods

Figure VI: PM Filter Extraction Procedure

Table IV: PAH Recovery Internal Standards

Compound	MW	Mixture Conc.[1]	5mL Extract Conc.	Targeted Analysis Conc.
	(g mol^{-1})	(ng µL^{-1})	(pg µL^{-1})	(pg µL^{-1})
d_8 naphthalene	136.19	10.4	104	518
d_{10} acenaphthene	164.23	10.2	102	512
d_{10} fluorene	176.24	10.4	104	518
d_{10} phenanthrene	188.25	9.7	97	489
d_{10} fluoranthene	212.27	10.3	103	512
d_{12} chrysene	212.27	10.4	104	519
d_{12} benzo[k]fluoranthene	264.33	9.8	98	490
d_{12} benzo[ghi]perylene	288.36	11.3	113	515
$^{13}C_6$ 3-phenanthrol	200.16	1.0	40	200

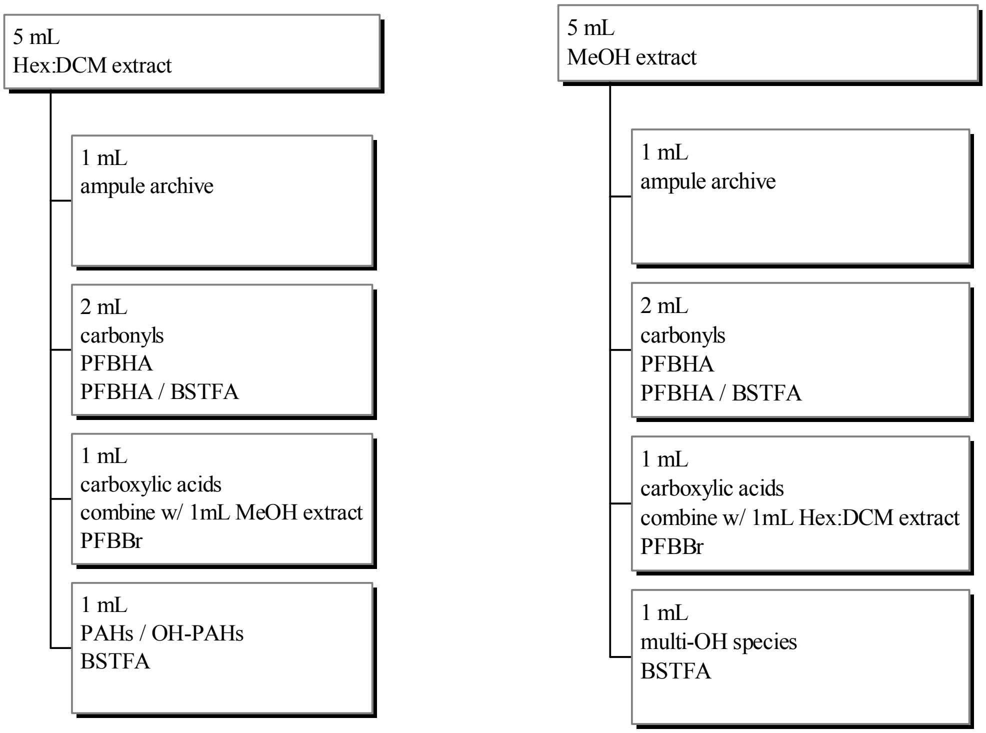
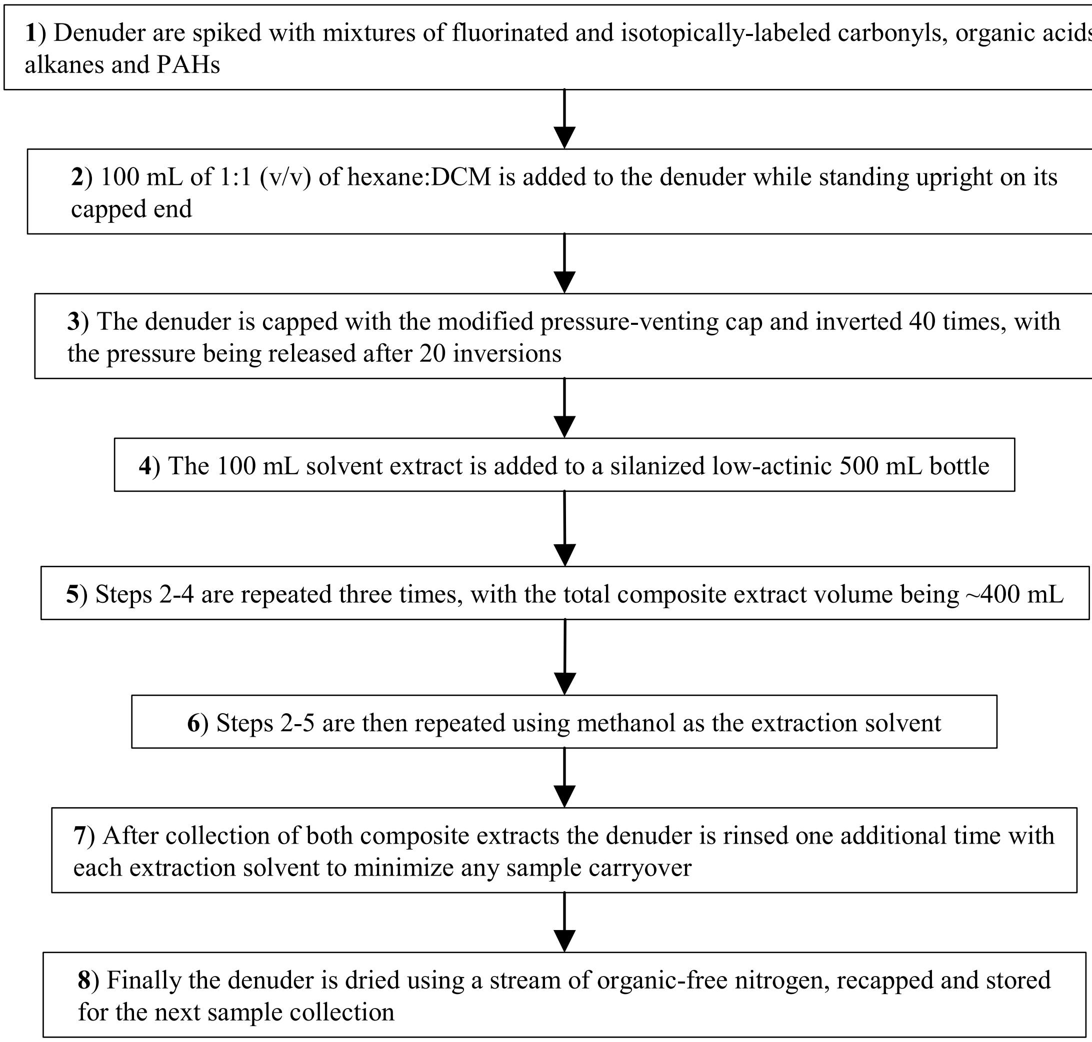


Figure VII: PM Extract Distribution Scheme

2.3.1.2 Annular Denuder Extraction Procedure

Although the results of any denuder analyses are not provided in this report the following description provides detail into the extraction procedures employed. Due to the necessity for using each denuder multiple times during the sample collection events the extractions were performed on-site (LDV collection) or at the University of CA, Riverside (HDV collection). All denuder samples were extracted within 24 hours of collection and stored over dry ice during any necessary transit or storage period prior to extraction.

The overall extraction procedure is outlined in Figure VIII. During each batch of denuder extractions similar volumes of the extraction solvents were retained to serve as method blanks during the chemical analysis of the denuder extracts. Although not available for the LDV sample collection a modified Teflon denuder cap was employed for the HDV sampling event that significantly decreased sample loss due to pressurization during extraction. Once collected the extracts were stored in low-actinic silanized bottles in a –20 °C freezer.



1) Denuder are spiked with mixtures of fluorinated and isotopically-labeled carbonyls, organic acids, alkanes and PAHs

2) 100 mL of 1:1 (v/v) of hexane:DCM is added to the denuder while standing upright on its capped end

3) The denuder is capped with the modified pressure-venting cap and inverted 40 times, with the pressure being released after 20 inversions

4) The 100 mL solvent extract is added to a silanized low-actinic 500 mL bottle

5) Steps 2-4 are repeated three times, with the total composite extract volume being ~400 mL

6) Steps 2-5 are then repeated using methanol as the extraction solvent

7) After collection of both composite extracts the denuder is rinsed one additional time with each extraction solvent to minimize any sample carryover

8) Finally the denuder is dried using a stream of organic-free nitrogen, recapped and stored for the next sample collection

Figure VIII: Annular Denuder Extraction Procedure

2.3.2 Derivatization Methods

2.3.2.1 Carbonyls

Sample extracts for carbonyl derivatization are first reduced in volume to <50 μL under organic-free nitrogen blow down. Once the extract volume has been reduced a 9:1 (v/v) mixture of carbonyl-free Acetonitrile:DCM is added to bring each sample to a volume of 500 μL. To each sample for derivatization is added a 50 mg mL^{-1} solution of PFBHA in methanol to a target PFBHA concentration of 5 mM. Each sample is capped, wrapped with Teflon tape, covered with baked foil and left at room temperature for a period of 24 hours. This procedure is a variation of methods previously utilized for carbonyl analysis in our laboratory.[19-23] The balanced chemical reaction for the conversion of carbonyls into their PFB oximes is provided in Figure IX.

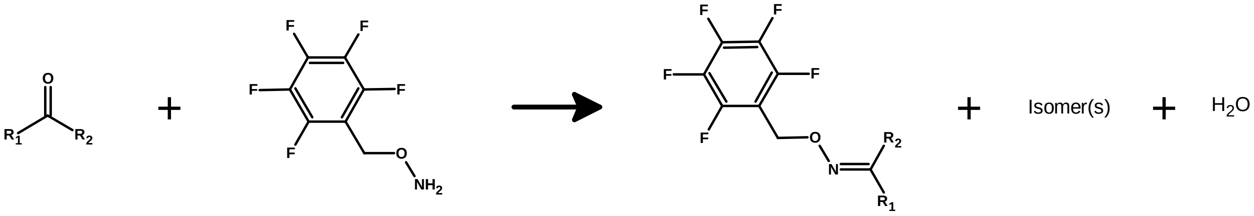


Figure IX: PFBHA Derivatization Reaction

2.3.2.2 Organic Acids

Sample extracts for organic acid/phenol derivatization are first taken to dryness under organic-free nitrogen blow down. Once the solvent has been evaporated acetone (Burdick and Jackson, trace analysis, glass-distilled) is added to bring each sample to a volume of 500 μL. To each sample for derivatization is added 20 μL of 10% PFBBr solution and 50 μL of 18-crown-6 ether solution (~4 mg mL^{-1}), both in acetone. Approximately 10 mg of potassium carbonate (Sigma-Aldrich) is added to each extract, the extracts are capped, wrapped with Teflon tape and sonicated for three hours. Upon completion of sonication the acetone is evaporated under nitrogen blow down, and the residue dissolved into hexane. This procedure is a variation of methods previously utilized for organic acid and phenol analysis.[24, 25] Balanced chemical reactions for the conversion of organic acids and phenols into their PFB esters and ether respectively is provided in Figure X.

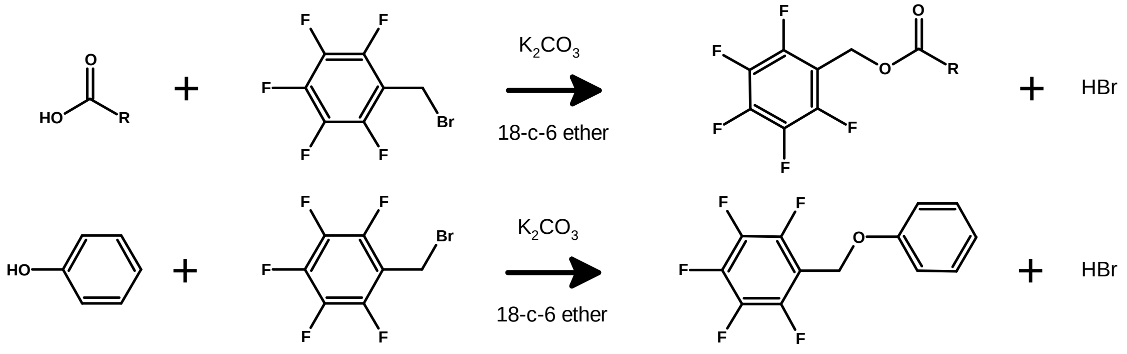


Figure X: PFBBr Derivatization Reaction

2.3.2.3 Hydroxy-PAHs

Sample extracts for analysis of hydroxylated polycyclic aromatic hydrocarbons are first reduced in volume to 200 μL under organic-free nitrogen blow down. To each sample 20 μL of a freshly prepared solution of 10% (v/v) TMCS in BSTFA is added. The samples are capped, wrapped with Teflon tape, and heated at 45°C for 24 hours to convert the targeted analytes to their trimethylsilyl derivatives. The balanced reaction for this conversion to trimethyl silyl (TMS) ethers is provided in Figure XI. Caution must be exercised to prevent any water from entering the samples as this will lead to hydrolysis of the BSTFA reagent and prevent any of the targeted analytes from undergoing derivatization. More detailed information on this procedure is available from Cahill et al.[26]

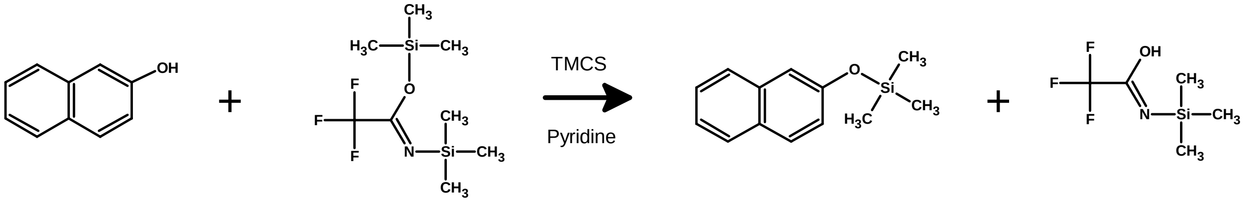


Figure XI: BSTFA Derivatization Reaction

2.3.3 GC-MS Data Acquisition Methods

2.3.3.1 Data Acquisition Parameters

The organic chemical speciation data collected for this project was obtained on a Varian 3400 gas chromatograph (GC) coupled with a Varian 2000 ion-trap mass spectrometer (ITMS). The instrument was operated in both electron ionization (EI) and methane chemical ionization (CH_4 CI) modes. This technique will be referred to as GC-ITMS from this point forward. Additionally, data files were processed using Varian Saturn GC-MS Workstation software version 5.51. with chromatographic peak integrations being performed manually. Note that for the oxygenated organic analyses the compound 2,2'-difluorobiphenyl (DFB) is added to each sample prior to injection to monitor instrument stability and ionization.

-Carbonyls:

The separation of the PFB oxime carbonyl derivatives is performed on an Agilent J&W DB-XLBMSD capillary GC column (30m x 0.25mm i.d. x 0.25 μm film thickness). The stationary phase for this particular column consists of a 5% phenyl/95% methyl substituted polysiloxane. Grade 5 helium is the carrier gas utilized for the analyses at a linear velocity of 37 cm s^{-1}. The gas was additionally purified using a VICI Helium purifier cartridge (Supelco, Bellfonte, PA)

Samples are injected using a cool-on-column technique rather than typical vapor injections. Samples volumes of 3-5 μL are introduced into the injection port containing a silanized liner with an approximately 1/8" plug of silanized glass wool. The injection port is initially at a temperature of 64 ^{o}C, roughly 5 ^{o}C below the solvent boiling temperature. The initial temperature is held for 30 seconds before the injection port temperature is ramped to 300 ^{o}C at a rate of 100 ^{o}C min^{-1}. The split vent remains off for the first five minutes of the injector temperature program. The introduction of samples in this manner allows us to use larger injection volumes than would be possible with a hot injector, which becomes limited by the solvent expansion volume in relation to the volume of the injection port liner.

The GC column oven is held at an initial temperature of 64 ^{o}C for the first five minutes of the analysis. This allows for cryo-focusing of the analytes on the head of the column as they vaporize out of the injection port. After five minutes the column oven is ramped to 330 ^{o}C at a rate of 5 ^{o}C min^{-1}. The column is held at this temperature for eight minutes, which leads to a total analysis time of 66.5 minutes per injection.

Operating conditions of the mass spectrometer are as follows: The ion trap oven, manifold and transfer line are held at 250, 80 and 270 ^{o}C respectively. EI analyses are performed with an emission current of 10 μA, a target ion count of 10000 and a maximum ionization time of 25000 μsec. The methane CI analyses are obtained with an emission current of 10 μA, a target total ion count of 5000, a maximum ionization time of 2000 μsec and a maximum reaction time of 60 μsec. These operating parameters are those recommended by the manufacturer with slight modification. The mass/charge range scanned in the EI and CI analyses are 50-650.

-Carboxylic Acids:

The analyses of the PFBBr acid derivatives are performed in an analogous manner as for the PFBHA carbonyl derivatives, with one exception. The methane CI analyses are conducted with the ion trap oven at a temperature of 150 ^{o}C. This arises from the ester bond being weaker than that of the oxime and thus more prone to extensive fragmentation at 250 ^{o}C trap oven temperatures. Thus the 150 ^{o}C temperature is used to help promote the retention of any pseudo-molecular ions formed during the chemical ionization process.

-Hydroxy-PAHs:

The hydroxy-PAH analysis is performed on a DB-XLBMSD capillary column (30m x 0.25mm i.d., 0.25 μm film thickness, 5% phenyl substituted polysiloxane) with grade 5 helium carrier gas at a linear velocity of 37 cm s^{-1}. Samples are introduced through a temperature programmable injection port that is held at the initial temperature of 64 °C for 30 seconds then ramped at a rate of 100 °C min^{-1} to a final temperature of 275 °C where it was held until the end of the column program. The column is held at an initial temperature of 64 °C for 5 minutes, to allow the analytes to pass through the injection port and become cryo-focused on the front-end of the analytical column. The column oven temperature is then increased at a rate of 5 °C min^{-1} to a final temperature of 330 °C followed by a 15-minute isothermal hold for a total run time of 73.2 minutes. The ion trap oven, manifold, and transfer line are operated at 220, 80, and 270 °C respectively. The mass/charge range monitored in the analyses is 50-650. Conditions for the electron impact (EI) ionization mass spectrometry/mass spectrometry (MS/MS) analysis of the hydroxy-PAHs were previously determined by Cahill et al. and are used in this study without any modifications.[26]

-PAHs:

Analysis of the PAHs is performed on a DB-5HT high temperature capillary column (30m x 0.25mm i.d., 0.1 μm film thickness, 5% phenyl substituted polysiloxane) with helium carrier gas at a linear velocity of 37 cm s^{-1}. Samples are introduced through a temperature programmable injection port that is held at the initial temperature of 64 °C for 1 minute, then ramped at a rate of 20 °C min^{-1} to a temperature of 120 °C, the rate of heating is then increased to 100 °C min^{-1} to a final injector temperature of 375 °C which is maintained the duration of the analysis. The column is initially at a temperature of 64°C for the first 7 minutes, to allow the analytes to pass through the injection port and become cryo-focused on the front-end of the analytical column. The column oven temperature is then increased at a rate of 5 °C min^{-1} to a final temperature of 400 °C followed by a 5-minute isothermal hold for a total run time of 79.2 minutes. The ion trap oven, manifold, and transfer line are operated at 220, 80, and 300 °C respectively. Electron impact (EI) ionization mass spectrometry/mass spectrometry (MS/MS) conditions for the analysis of the PAHs are given in Table V. The mass/charge range monitored in the analysis is 100-420.

Table V: Optimal Resonant Excitation Energies for PAHs

Segment	Elution Window	Targeted Compounds	Molecular Ion	Resonant Excitation Energy [a]	Quantification Ion [b]
	(min)		(m/z)	(V)	(m/z)
1	25.0 – 30.0	MW 178 isomers	178	2.6	152
2	30.0 – 36.0	MW 202 isomers	202	1.6	200
3	36.0 – 42.0	cyclopenta[cd]pyrene	226	1.8	224
		MW 228 isomers	228	2.0	226
4	42.0 – 48.0	MW 252 isomers	252	2.0	250
5	48.0 – 52.5	MW 276 isomers	276	2.8	274
		dibenz[a,h]anthracene	278	2.0	276
6	52.5 – 57	coronene	300	2.0	298

[a] The optimal energy was the excitation energy that gave the greatest intensity of a product ion,
[b] Most PAHs lose two hydrogen atoms to form the quantification ion, one exception are the MW 178 isomers which lose a $–C_2H_2-$ group to form the quantification ion

2.3.3.3 Instrument Calibration Procedures

Multiple point calibration curves, typically 5 or 6 points, are analyzed preceding and following each set of sample extracts. These calibration solutions range in concentration from 1 to 2500 pg uL^{-1} depending upon the analysis being performed. Calibration solutions are analyzed in order from the least to most concentrated solution to minimize any potential carryover between analyses. Following the last calibration point a solvent blank is injected to ensure no analyte carryover had occurred.

Calibration curves for the purpose of sample quantification are generated for analytes observed in the sample extracts using the instrument response for both the pre and post calibration curve. The formula utilized to generate the response curves is as follows:

$$(\text{Peak Area})_{\text{analyte}}/[\text{Conc.}]_{\text{analyte}} = \text{Response Factor x } (\text{Peak Area})_{\text{IS}}/[\text{Conc.}]_{\text{IS}}$$

This equation can be rearranged in multiple ways to generate appropriate calibration curves for accurate analyte quantification using the internal standardization method. Sample calibration curves used in this project are provided in Figure XII.

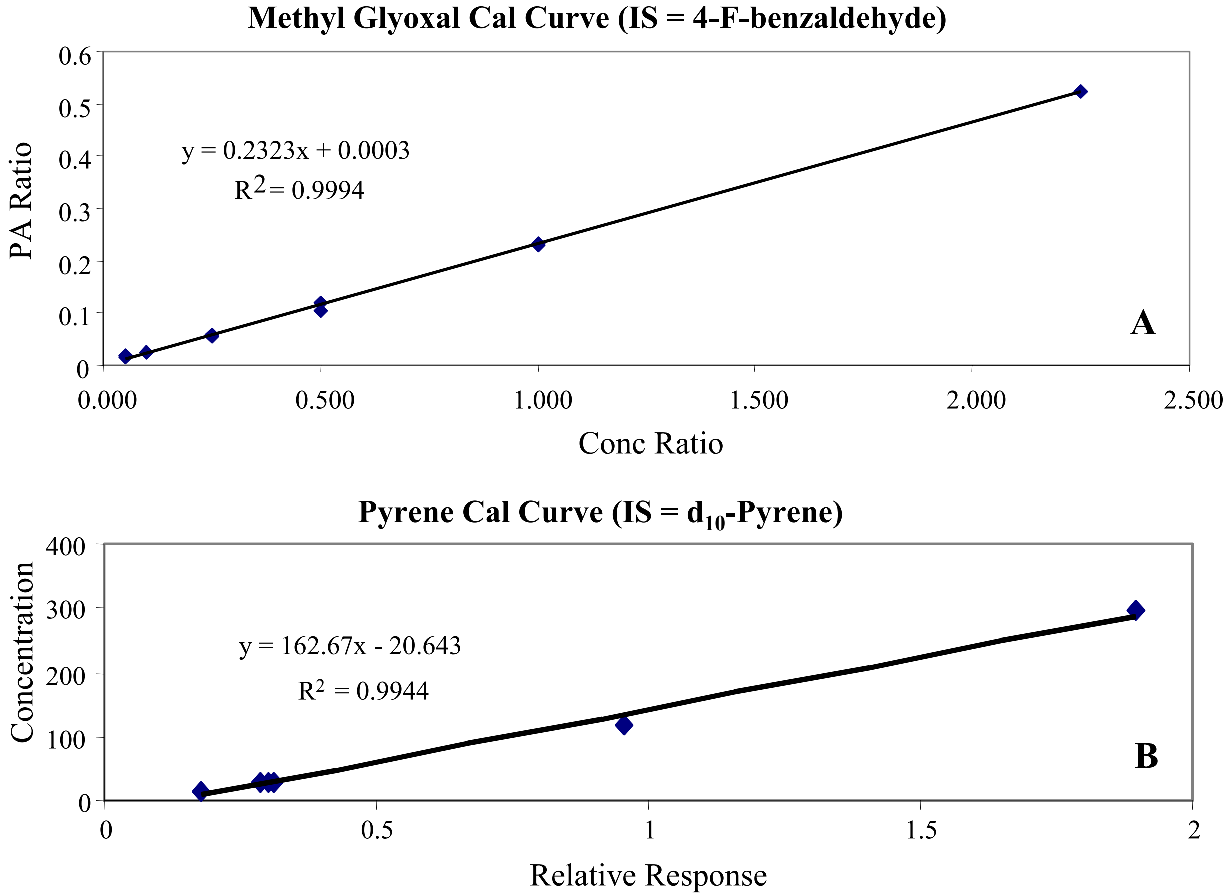


Figure XII: Sample Calibration Curves

A) Carbonyl as PFBHA Oxime in EI MS, B) PAH Pyrene Using MS/MS

2.3.3.3 Analyte Identification/Confirmation Procedures

The multiple derivatization procedures employed in this project give rise to useful mass spectra ions that can be utilized to identify chemical species in the motor vehicle PM samples. Representative spectra for several compounds from each of the analytical approaches are provided in Appendix G. General descriptions of the prominent ions for each derivatization method are listed in the following description:

- Carbonyls as PFBHA oximes: EI
    - Ion 181 corresponds to the PFB cation ($[C_7H_2F_5]^+$)
    - Ions arising from addition of a PFB cation yielding $[M+181]^+$
    - Occasionally molecular ($[M]^{\bullet+}$) or pseudo-molecular ($[M-H]^+$) ions are observed
    - Ions arising from fragmentation such as the loss of 15 mass units from methyl groups ($[M-CH_3]^+$) or the loss of 197 mass units which corresponds to ($[M-C_7H_2F_5O]^+$)
- Carbonyls as PFBHA oximes: CI
    - Ion 181 corresponds to the PFB cation ($[C_7H_2F_5]^+$)
    - Ions arising from addition of a PFB cation yielding $[M+181]^+$
    - Pseudo-molecular ions from proton addition reactions ($[M+H]^+$)
    - Fragment ions from the loss of 197 mass units ($[M-C_7H_2F_5O]^+$)

- Organic Acids as PFBBr esters: EI
    - Ion 181 corresponds to the PFB cation ($[C_7H_2F_5]^+$)
    - Aliphatic fragment ions with more than four carbon atoms
    - Fragment ions from the loss of 197 mass units ($[M-C_7H_2F_5O]^+$)
    - Fragment ions with the same number of carbon atoms as the underivatized analyte, likely a cyclic rearrangement with loss of $C_7H_2F_5O$ and H_2
    - Occasionally molecular ($[M]^{\bullet+}$) ions are observed
- Organic Acids as PFBBr esters: CI
    - Ion 181 corresponds to the PFB cation ($[C_7H_2F_5]^+$)
    - Ions arising from addition of a PFB cation yielding $[M+181]^+$
    - Aliphatic fragment ions with more than four carbon atoms
    - Fragment ions from the loss of 197 mass units ($[M-C_7H_2F_5O]^+$) or 181 mass units ($[M-C_7H_2F_5]^+$)
    - Fragment ions with the same number of carbon atoms as the underivatized analyte, likely a cyclic rearrangement with loss of $C_7H_2F_5O$ and H_2
    - Occasionally molecular ($[M]^{\bullet+}$) or pseudo-molecular ($[M-H]^+$ and $[M+H]^+$) ions are observed

- Hydroxy-PAHs as TMS ethers: EI MS
    - Ion 73 arising from the trimethylsilyl cation ($[C_3H_9Si]^+$
    - Ions arising from the loss of a TMS cation yielding ($[M-C_3H_9Si]^+$
    - Occasional pseudo-molecular ion $(M)^+$ is observed
    - Fragment ions from the loss of 15 mass units ($[M-CH_3)]^+$)
- Hydroxy-PAHs as TMS ethers: MS-MS
    - Ion 73 arising from the trimethylsilyl cation ($[C_3H_9Si]^+$)
    - Ions arising from the loss of a TMS cation yielding ($[M-C_3H_9Si]^+$)
    - Fragment ions from the loss of 15 mass units ($[M-CH_3)]^+$)

- PAHs: EI MS
    - Molecular ions are observed ($[M]^{\bullet+}$)
- PAHs: MS-MS
    - Fragment ion from the loss of 2 mass units ($[M-H_2]^{\bullet+}$)
    - Occasionally the loss of 26 mass units ($[M-C_2H_2]^{\bullet+}$) are observed

Chemical species were identified in this project in the stepwise manner that follows:

1. Comparison of the relative retention time of the analyte to authentic standards. The compounds used for retention time reference are the quantification internal standards and DFB.
2. Examination of the EI mass spectra for ions characteristic of the derivatization procedures (i.e. the 181 ion from the PFB cation in the PFBHA and PFBBr spectra, or the 73 ion from the TMS cation in the BSTFA spectra).
3. The EI mass spectra are then examined for a possible molecular ion or other characteristic derivatization fragments.
4. Where possible final confirmation is provided by the CI mass spectra containing a pseudo-molecular ion for the compound in question.
5. Confirmation is also obtained by the observation of the correct product ions in the MS-MS spectra for the PAH and Hydroxy-PAH analyses.

2.3.4 Method Validation

2.3.4.1 Recovery of Representative Compounds

To assess the accuracy and reliability of the extraction procedures and instrumental analysis methods an experiment was conducted using model compounds for each of the classes of compounds examined in this project. Mixtures of the model compounds were spiked onto clean filters, the solvent was allowed to evaporate and the filters were then treated in the exact same manner as one of the motor vehicle emissions PM samples. The concentrations examined, which targeted 100 pg μL^{-1} in the 5 mL extracts, attempted to emulate the trace levels anticipated in the PM samples. Data obtained from this experiment serve as the basis for the error in the emissions factors that are presented later in this report. A summary of the obtained results is presented in Tables VI, VII and VIII. Note that the results are presented with the compounds listed in order of decreasing volatility.

The mean carbonyl recovery plus/minus one standard deviation for the thirteen species examined is presented in Table VI. Eight of the thirteen compounds examined have good recoveries (80-120%). Compounds with recoveries below 80% include acrolein, 2,3-butanedione and t-2-hexenal. These species are three of the four most volatile analytes examined, thus their low recovery is not unexpected. Two compounds, glutaric dialdehyde and dodecanal, have recoveries in excess of 120%. The origin for the overestimation of these species is unknown. Examining the percent relative standard deviation for the model analytes yields good precision (%RSD < 20%) for all the compounds except benzaldehyde, 2-indanone and 2-pentanone. Considering that many of these analytes are semi-volatile with vapor pressures differing by more than 5 orders of magnitude the obtained recoveries are consistent with most of our expectations for the chemical analysis method.

These carbonyl recovery values are obtained using two quantification internal standards, 4-fluorobenzaldehyde and 6-fluoro-4-chromanone. Two internal standards are used due to differences in observed analyte recoveries during method development (data not presented). The 4-F-benzaldehyde internal standard has a greater vapor pressure than 6-F-4-chromanone, and provides more accurate quantification of the carbonyls with higher vapor pressures. The limitation of 4-F-benzaldehyde is that it does not accurately represent compounds with lower vapor pressures and tends to overestimate their recovery, as observed for 3,5-heptanedione (144%), nonanal (130%), t-4-decenal (161%) and dodecanal (184 %). The quantification of these same compounds using the less-volatile 6-F-4-chromaone internal standard yields better results for 3,5-heptanedione (108%), nonanal (101%), t-4-decenal (120%) and dodecanal (140%). The likely cause of overestimation for the less-volatile species using 4-F-benzaldehyde is evaporative loss during solvent reduction. Since 6-F-4-chromanone has a lower vapor pressure than 4-F-benzaldehyde it experiences less evaporative losses; leading to more accurate representation of the less-volatile carbonyl species. Using these recovery values as a guide the quantification of species containing one carbonyl moiety and fewer than eight carbon atoms will be performed using 4-F-benaldehyde, while species containing eight or more carbon atoms and multiple carbonyl moieties will be quantified using 6-F-4-chromanone.

Table VI: Extraction Recoveries of Model Carbonyls

Percent Recovery of Model Carbonyls from Filter Extractions Using Different Internal Standards

	4-F-benzaldehyde		6-F-4-chromanone	
Compound	Mean [1] ± STD	% RSD	Mean [1] ± STD	% RSD
acrolein	55 ± 10	19	37 ± 6	16
2,3-butanedione	30 ± 2	8	29 ± 2	5
2-pentanone	100 ± 41	41	77 ± 37	48
t-2-hexenal	51 ± 6	12	38 ± 6	16
3,5-heptanedione	144 ± 7	5	108 ± 8	8
glutaric dialdehyde	198 ± 28	14	150 ± 25	17
nonanal	130 ± 7	6	101 ± 8	7
t-4-decenal	161 ± 8	5	120 ± 8	6
2-decanone	109 ± 15	14	81 ± 5	6
benzaldehyde	127 ± 32	25	99 ± 31	31
2-indanone	89 ± 24	27	66 ± 15	22
dodecanal	184 ± 14	8	140 ± 19	13
2-tridecanone	112 ± 17	15	85 ± 6	7

[1] Mean is based on n=4 replicates

The recovery of model organic acids is presented in Table VII, in the same manner as for the carbonyls. Overall the recoveries for the acids are not as good as the values obtained for the carbonyls. The acid recovery values are typically lower than expected but absent of overestimation observed for the carbonyls. Good recovery (80-120%) is observed for only one species, decanoic acid. One possible explanation is that, unlike the carbonyls that are primarily in the hexane:DCM extract, the acids partition into both the hexane:DCM and methanol extracts. Although a composite sample from both of the extracts undergoes derivatization for chemical analysis there may be losses associated with such an approach.

Acid and phenol recovery values are presented using two quantification internal standards, 4-fluorobenzoic acid and $^{13}C_4$-octanoic acid. These two internal standards were evaluated to examine the differences between using an aromatic versus an aliphatic species for quantification. The recoveries for most species, decanoic acid being the exception, are very similar between the two internal standards. However the precision obtained, evaluated as %RSD, with 4-F-benozoic acid is much better than for $^{13}C_4$-octanoic acid. Based on this result the acid quantification in the PM extracts will be performed using 4-F-benzoic acid, with $^{13}C_4$-octanoic acid serving as a backup quantification internal standard.

Certain trends are observed for the phenols and acid subclasses. Similar recoveries are obtained for the two phenolic species examined (66 and 68%). The recovery of the aromatic acids is also consistent (53-60%). Alkanoic acid recovery does not increase with decreasing volatility and increasing carbon chain length as anticipated (pentanoic 32%, decanoic 107%, pentadecanoic 72 % and eicosanoic acid 54%). The alkanoic diacid species have the lowest recoveries of all the species examined. This is likely due to the inability of a monocarboxylic acid species to accurately represent the behavior of a diacid with respect to the derivatization procedure. Thus in the future an isotopically-labeled diacid internal standard will be employed.

Table VII: Extraction Recoveries of Model Organic Acids

Percent Recovery of Model Organic Acids and Phenols from Filter Extractions Using Different Internal Standards

Compound	4-F-benzoic acid		$^{13}C_4$-octanoic acid	
	Mean [1] ± STD	% RSD	Mean [1] ± STD	% RSD
phenol	66 ± 24	37	70 ± 34	48
pentanoic acid	32 ± 9	27	33 ± 13	39
3,5-dimethylphenol	68 ± 12	18	77 ± 22	28
2-indanol	37 ± 3	8	37 ± 8	22
benzoic acid	55 ± 4	7	54 ± 8	15
4-ethylbenzoic acid	53 ± 6	12	55 ± 14	25
1-naphthoic acid	60 ± 5	8	62 ± 9	15
decanoic acid	107 ± 20	19	29 ±10	35
7-oxo-octanoic acid	63 ± 5	8	62 ± 9	15
octanedioic acid	7 ± 2	25	11 ± 3	24
pentadecanoic acid	72 ± 11	15	73 ± 10	14
dodecanedioic acid	27 ± 16	58	29 ± 18	64
eicosanoic acid	54 ± 7	13	56 ± 10	19

[1] Mean is based on n=4 replicates

Values for the mean PAH and hydroxy-PAH recovery plus/minus one standard deviation for the model compounds examined are presented in Tables VIII and IX. Six of the thirteen PAHs examined have good recoveries (80-120%). Recoveries for the three most volatile PAHs, naphthalene, acenaphthylene, and acenaphthene are much lower than 80%; this was expected due to their volatility. Seven of the high molecular weight species, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene, have recoveries near 70% (70 – 73%). The origin for their underestimation was not determined. Isomers of a given molecular weight gave comparable recoveries, for example benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene all have mean recoveries of 70%, 73%, and 72% respectively. Examining the percent relative standard deviation for the model analytes yields good precision (%RSD < 20%) for all the compounds with the exception of naphthalene. Considering naphthalene is the most volatile PAH examined the poor precision is not surprising. Less precision in the recoveries of the more volatile compounds (acenaphthylene through pyrene) is observed compared with the larger, less volatile PAHs. Overall these results are consistent with our expectations for the behavior of these species.

Table VIII: Extraction Recoveries of PAHs

Percent Recoveries of Polycyclic Aromatic Hydrocarbons

Compound	Mean[1] ± STD	% RSD
naphthalene	22 ± 12	55
acenaphthylene	47 ± 6	13
acenaphthene	63 ± 10	16
fluorene	107 ± 14	13
phenanthrene	99 ± 12	12
anthracene	95 ± 13	14
fluoranthene	96 ± 9	10
pyrene	92 ± 9	10
benz[a]anthracene	72 ± 5	7
chrysene	72 ± 5	8
benzo[b]fluoranthene	70 ± 6	8
benzo[k]fluoranthene	73 ± 7	9
benzo[a]pyrene	72 ± 6	9
indeno[1,2,3-cd]pyrene	72 ± 7	9
dibenz[a,h]anthracene	80 ± 3	4
benzo[ghi]perylene	72 ± 6	8

[1] Mean is based on n=4 replicates

Table IX: Extraction Recoveries of Hydroxy-PAHs

Percent Recoveries of Hydroxyl Polycyclic Aromatic Hydrocarbons

Compound	Mean[1] ± STD	% RSD
1-naphthol	33 ± 19	58
2-naphthol	119 ± 15	12
9-hydroxyfluorene	100 ± 12	12
9-hydroxyphenanthrene	12 ± 6	52
1-hydroxypyrene	6.5 ±1	22
1-hydroxyben[a]anthracene	43 ± 30	70
2-hydroxychrysene	84 ± 5	6
12-hydroxybenzo[a]pyrene	27 ± 4	14
11-hydroxybenzo[b]fluoranthene	75 ± 5	7
3-hydroxybenzo[e]pyrene	72 ± 4	6
11-hydroxybenzo[g]chrysene	30 ± 9	30

[1] Mean is based on n=4 replicates

The mean recoveries for model hydroxy-PAHs are presented in Table IX. The recoveries show highly variable results. Of the eleven compounds studied three species (2-naphthol, 9-hydroxyfluorene, and 2-hydroxychrysene) have good recoveries (80-120%). Recoveries for 11-hydroxybenzo[b]fluoranthene, and 3-hydroxybenzo[e]pyrene are slightly less, 75% and 72% respectively, but much better than the other six species examined (6.5 – 43%). Six of the eleven compounds investigated exhibit acceptable precision with a percent relative standard deviation below 20%. The poorest precision is observed for the compounds with the lowest recoveries (1-naphthol, 9-hydroxyphenanthrene, 1-hydroxypyrene, 1-hydroxybenz[a]anthracene, 12-hydroxybenzo[a]pyrene, and 11-hydroxybenzo[g]chrysene). Sources for the underestimation of these species were not identified, but could possibly be due the analytes degrading during the extraction process or sorption losses to the quartz filters. In contrast to the PAHs, the recovery and precision was highly variable between isomers notably the large difference between naphthol isomers. The lack of consistency in the model species agrees with the poor recoveries and precision for the sonication extraction of hydroxy-PAHs from quartz filters as reported by Cahill et.al..[26]

2.3.4.2 Analysis of NIST SRMs

National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) are used to monitor the accuracy of the chemical analysis methods during the extraction of PM emission samples for this project. NIST SRM 1650 Diesel PM and 1649 Urban Dust were the selected samples. Five and two milligrams were extracted for the 1649 and 1650 SRMs respectively. The following presents the results for the PAHs and a quality assurance comparison against the certified and published values. Also presented are the oxygenated organic species observed although no quality assurance comparison is made due to the lack of certified values for the species reported.

SRM IS Recovery:

Percent recovery of the spiked IS for the NIST SRM analyses are provided in Table X. These values are used to correct relevant compounds for the extraction efficiency of the chemical analysis methods. Internal standard recoveries for PAHs are much better for SRM 1649 urban dust than for SRM 1650 diesel particulate matter. Good recoveries, 80-120%, are obtained for all species examined in SRM 1649. The internal standard recoveries for SRM 1650 are highly dependent on the molecular weight of the analyte. Lighter molecular weight PAHs, $MW < d_{12}$ chrysene, are all recovered above 90%. The heavier species are significantly less at 76% for d_{12} benzo[k]fluoranthene and 64% for d_{12} benzo[ghi]perylene. Difficulties in extracting heavy PAHs from SRM 1650 have been widely reported and are believed to be related to the large amount of elemental carbon present in the sample.[27-29]

Recovery of the carbonyl IS from the SRMs are better by roughly 20% for 1649 versus 1650. SRM 1649 had better than 62% recovery for all three species, with 1650 recoveries exceeding 45%. The observed recoveries of the derivatized internal standards (2-F-benzaldehyde and 8-F-1-benzosuberone) are lower for the more volatile analyte by ~30%. This agrees well with the data obtained for model carbonyl analytes. Recovery of 8-F-1-benzosuberone, which best approximates non-volatile carbonyls, was acceptable for both 1649 (101%) and 1650 (79%). The origin of the recovery discrepancies between the 1649 and 1650 SRMs is not immediately obvious.

Table X: Internal Standard Recovery in NIST SRM Extractions

Percent Recovery of Spiked IS in NIST SRM Extracts

	SRM Sample	
Compound	1649	1650
PAHs [a]		
d_{10} acenaphthene	109	109
d_{10} fluorene	99	95
d_{10} phenanthrene	99	93
d_{12} chrysene	92	90
d_{12} benzo[k]fluoranthene	89	76
d_{12} benzo[ghi]perylene	97	63
carbonyls		
2-F-benzaldehyde [b]	71	49
8-F-1-benzosuberone [c]	101	79
4-F-benzophenone [d]	62	45
organic acids [e]		
d_{11}-hexanoic acid	15	2
$^{13}C_1$ dodecanoic acid	79	127
d_{35}-octadecanoic acid	110	158
d_5-benzoic acid	46	37
2-F-5-Me-benzoic acid	63	89

[a] Compounds were quantified using d_{10}-pyrene as the internal standard, [b] Compound was quantified as a PFBHA oxime using 4-F-Benzaldehyde as the internal standard, [c] Compound was quantified as a PFBHA oxime using 6-F-4-Chromanone as the internal standard, [d] Compound was quantified in its underivatized form using 2,2'-F-biphenyl as the internal standard, [e] Compounds were quantified as PFBBr esters using 4-F-benzoic acid as the internal standard

Variable results are obtained for the acid internal standard recoveries from SRMs 1649 and 1650. As expected the recovery of the most-volatile acid IS (d_{11}-hexanoic acid) is low for both 1649 (15%) and 1650 (2%). The alkanoic acid IS recoveries increase with increasing carbon number for the C_{12} and C_{18} acids in both SRM 1649 (79 and 110% respectively) and 1650 (127 and 158% respectively). The high recovery of d_{35}-octadecanoic acid in SRM 1650 is unexpected. Aromatic acid IS recovery was lower for the more-volatile IS (d_5-benzoic acid) in both SRM 1649 and 1650. The source of the dramatic increase in the recovery of the less-volatile aromatic acid IS (2-F-5-Me-benzoic acid) in SRM 1650, versus 1649, is not immediately obvious. Overall the acid IS recoveries exhibit variability similar to that observed in the recovery of model organic acids.

SRM Results:

The concentrations measured in NIST SRM 1649 are presented in Table XI. The results of the analysis agree quite well with the values reported by NIST as can be seen in the comparison plot shown in Figure XIII-A. More than half of the twelve PAHs identified fall within the certified value error ranges. Anthracene is being overestimated by a factor of three versus the NIST certified value. The source of this discrepancy was not able to be determined. Additional compounds that do not fall within the error bounds (fluoranthene, MW 228 isomers, dibenz[a,h]anthracene, and benzo[ghi]perylene) have an average percent error of 24 ± 9 percent. It should be noted that NIST recommends extracting 1 g to obtain the certified values, while we extracted only 5 mg to accurately represent the small amount of material present in our emission samples.

Table XI: PAHs in NIST SRM 1649

Polycyclic Aromatic Hydrocarbons in SRM 1649 Urban Dust

	Concentration (mg/kg) [a]		Notes: [c-f]
Compound	Experimental	NIST Certified	
phenanthrene	4.3 ± 0.5	4.14 ± 0.37	c
anthracene	1.7 ± 0.2	0.43 ± 0.08	c
fluoranthene	5.5 ± 0.5	6.45 ± 0.18	d
pyrene	5.3± 0.5	5.29 ± 0.25	d
MW 228 isomers [a]	4.9 ± 0.3	6.61 ± 0.19	d
benzofluoranthene isomers [b]	8.4 ± 0.6	8.36 ± 0.95	e
benzo[e]pyrene	2.7 ± 0.2	3.09 ± 0.19	e
benzo[a]pyrene	2.9 ± 0.3	2.51 ± 0.09	e
perylene	0.74 ± 0.01	0.65 ± 0.08	f
indeno[1,2,3-cd]pyrene	2.4 ± 0.2	3.18 ± 0.72	f
dibenz[a,h]anthracene	0.34 ± 0.01	0.29 ± 0.02	f
benzo[ghi]perylene	2.5 ± 0.2	4.01 ± 0.91	f
coronene	2.5 ± 0.2		f

[a] The MW 228 isomers are the sum of chrysene, triphenylene and benz[a]anthracene, [b] The isomers are the sum of benzo[b]fluoranthene and benzo[k]fluoranthene, [c] Corrected for recovery of d_{10} phenanthrene, [d] Corrected for recovery of d_{12} chrysene, [e] Corrected for recovery of d_{12} benzo[k]fluoranthene, [f] Corrected for recovery of d_{12} benzo[ghi]perylene

Concentrations of polycyclic aromatic hydrocarbons measured in SRM 1650 are provided in Table XII. Comparison of the NIST certified values with the values obtained in this study is presented in Figure XIII B. The experimental values, while somewhat lower, agree well with those reported by NIST. Values obtained for anthracene and pyrene fall within the given error limits. Concentrations determined for the other PAHs are slightly below the values reported by NIST with an average relative percent error of 34 ± 15 percent. Results of a four laboratory comparison study reported by Gratz et al. for analysis of fluoranthene, pyrene, benzo[a]pyrene, and benzo[ghi]perylene in SRM 1650 strongly agree with the values obtained in this study with all values falling within the given error limits.[30] Comparison of the results in this study with those of Gratz et al. is presented in Figure XIII-C. It should be noted that NIST recommends extracting 100 mg of the SRM to obtain their values while we extracted only 2 mg to emulate the small amount of material in our PM emission samples

Table XII: PAHs in NIST SRM 1650

Polycyclic Aromatic Hydrocarbons in SRM 1650 Diesel Particulate Matter

Compound	Concentration (mg/kg) [a]			Notes: [c-f]
	Experimental	NIST Certified	Gratz et al.	
phenanthrene	51 ± 6	68.40 ± 8.50		c
anthracene	1.0 ± 0.1	1.50 ± 0.60		c
fluoranthene	43 ± 4	49.90 ± 2.70	57.4 ± 13.8	d
pyrene	42 ± 4	47.50 ± 2.70	42.7 ± 4.09	d
MW 228 isomers [a]	20 ± 1	32.33 ± 3.17		d
benzofluoranthene isomers [b]	7.7 ± 0.6	11.45 ± 0.91		e
benzo[e]pyrene	4.3 ± 0.4	7.44 ± 0.53		e
benzo[a]pyrene	0.84 ± 0.08	1.33 ± 0.35	1.51 ± 0.95	e
indeno[1,2,3-cd]pyrene	3.4 ± 0.3	5.62 ± 0.53		f
dibenz[a,h]anthracene	0.45 ± 0.02	0.90 ± 0.20		f
benzo[ghi]perylene	2.3 ± 0.2	6.50 ± 0.94	3.38 ± 1.67	f
coronene	1.5 ± 0.1	2.00 ± 0.10		f

[a] The MW 228 isomers are the sum of chrysene, triphenylene and benz[a]anthracene, [b] The isomers are the sum of benzo[b]fluoranthene and benzo[k]fluoranthene, [c] Corrected for recovery of d_{10} phenanthrene, [d] Corrected for recovery of d_{12} chrysene, [e] Corrected for recovery of d_{12} benzo[k]fluoranthene, [f] Corrected for recovery of d_{12} benzo[ghi]perylene

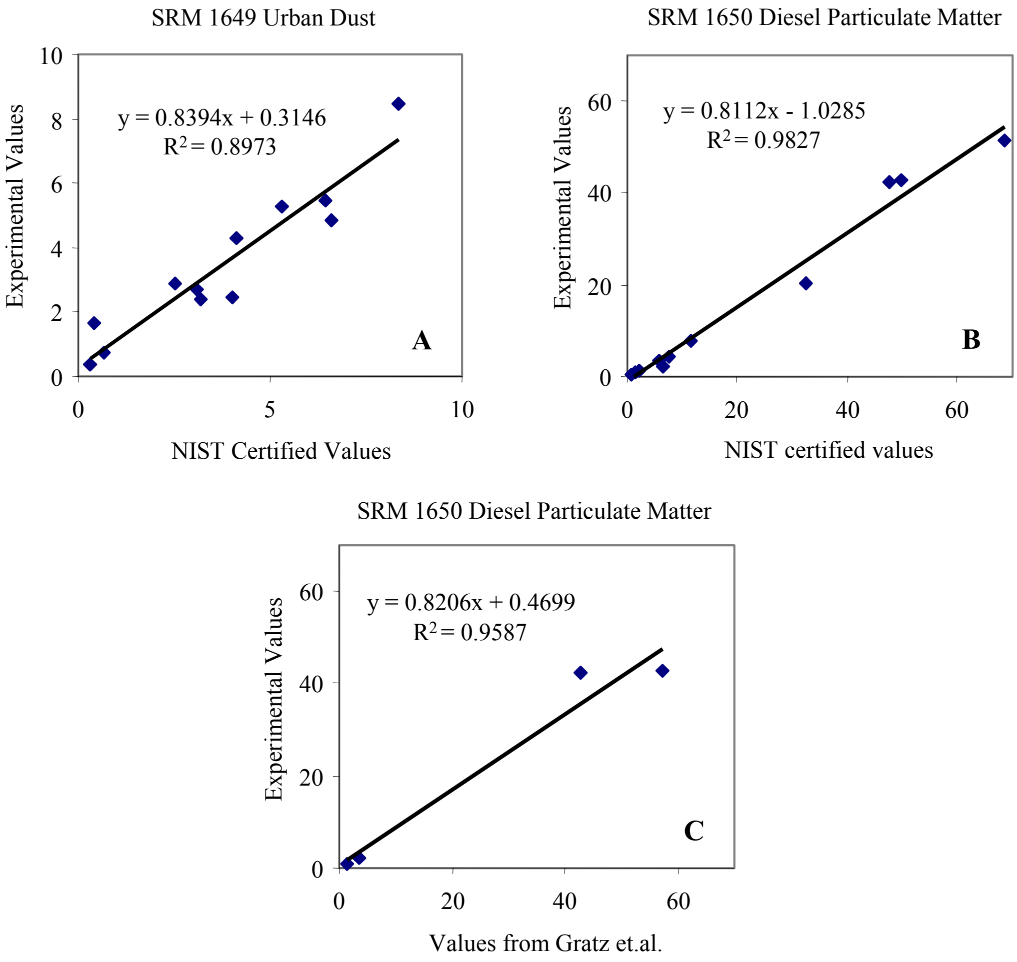


Figure XIII: PAH Comparison Plots to Certified and Published Values

A) Comparison to NIST SRM 1649 Certified Values, B) Comparison to NIST SRM 1650 Certified Values, C) Comparison to Gratz et al. Values for SRM 1650

The analysis of NIST SRMs 1649 and 1650 for carbonyl species yielded numerous species. Appendix H contains a qualitative comparison of chemical species observed in this study with the few available species in published literature from Oda et al.[31] It should be noted however that the Oda et al. study extracted gram quantities of the SRMs, while our values were obtained from approximately 5 mg of 1649 and 2 mg of 1650. Concentrations of the carbonyls observed in SRMs 1649 and 1650 are provided in Table XIII, in units of ppmm. There are more species detected and quantified in SRM 1650 versus 1649. All of the species observed are present at elevated levels in SRM 1650 versus 1649, which is expected. A breakdown of the species observed is provided in the following paragraphs.

Aliphatic aldehydes are observed in both SRM 1650 (C_3-C_{10}) and 1649 (C_3-C_9) at concentration ranges of 35-1360 and 9-190 ng mg^{-1} respectively, with butanal and hexanal being the most abundant. Aliphatic ketones (C_4-C_6) are observed in both 1650 and 1649. Concentrations of the C_4 and C_6 aliphatic aldehydes in relation to their ketone counterparts are approximately 6-8 times higher for SRM 1650 and 3-4 times higher in 1649. Unsaturated aliphatic carbonyls (C_3-C_6) are observed in both SRM 1650 and 1649, with concentrations in

1650 4-5 times higher than in 1649. Overall the total aliphatic carbonyl concentrations observed for SRM 1650 are 7-fold higher than for SRM 1649.

There are fewer aromatic carbonyls observed in the 1649 and 1659 SRMs relative to the aliphatic species. Benzaldehyde and the tolualdehyde isomers are the only aromatic aldehydes observed in SRM 1650, with only benzaldehyde present in 1649. Aromatic ketones (C_8-C_{13}) are present in both SRM 1650 and 1649, with many of the species being detected as underivatized analytes. These ketones ranged in concentration from 5-440 ng mg^{-1} in SRM 1650 while minimal abundance in SRM 1649 prevented quantification.

Dicarbonyls, both aliphatic and aromatic, are present in both SRM 1650 and 1649. The aliphatic species (C_2-C_6) concentrations are ~6-fold higher in the 1650 SRM versus 1649 for species observed in both SRMs. Methyl glyoxal is the compound observed at the highest level in both 1650 (2900 ng mg^{-1}) and 1649 (450 ng mg^{-1}). Pentanedione isomers are observed in SRM 1650, but not in 1649. Aromatic dicarbonyls are only observed in SRM 1650. The aromatic dicarbonyls were anthraquinone and naphthalic anhydride, with naphthalic anhydride being the fourth most abundant carbonyl in SRM 1650.

The carbonyl speciation completed in this project is more thorough than anything previously available in published literature. For SRM 1650 there were 22 aliphatic carbonyls, 10 aromatic carbonyls and 9 dicarbonyls identified. These carbonyls total 9.3 µg mg^{-1} for SRM 1650, approximately 1% of the SRM mass. The carbonyls identified in SRM 1649 included 20 aliphatic carbonyls, 5 aromatic carbonyls, and 4 dicarbonyls. These compounds total 1.2 µg mg^{-1}, which is approximately 0.1% of SRM 1649 mass.

Table XIII: Carbonyls Observed in NIST SRM 1649 and 1650

Compound	Concentration (ng/mg) [a] 1649 Urban Dust	 1650 Diesel PM
aliphatic aldehydes		
propanal	57	350
isobutanal	17	110
butanal	90	1400
pentanal	81	350
hexanal	190	1100
heptanal	15	75
octanal	9	35
nonanal	31	130
decanal		58
aliphatic ketones		
2-butanone	34	170
3-pentanone	2	13
2-pentanone	4	det
2-hexanone	53	190
unsaturated aliphatics		
acrolein	24	130
methacrolein	2	8
methyl vinyl ketone	10	47

crotonaldehyde	25	120
t-2-methyl-2-butenal	1	6
3-methyl-2-butenal	9	39
4-hexen-3-one	5	21
cyclic unsaturated aliphatics		
2-methyl-2-cyclopentenone	2	9
3-methyl-2-cyclopentenone		det
2-cyclohexenone		det
aromatic aldehydes		
benzaldehyde	10	63
o- & m-tolualdehyde		7
p-tolualdehyde		8
aromatic ketones		
acetophenone	det	5
perinaphthenone [b]		440
9-fluorenone	det	74
benzanthrone [b]	det	47
anthrone		det
benzophenone [b]	det	det
xanthone [b]		det
aliphatic dicarbonyls		
glyoxal	56	300
methyl glyoxal	450	2900
2,3-butanedione		15
2,3-hexanedione		36
2,5-hexanedione	42	310
2,3-pentanedione		det
2,4-pentanedione		det
aromatic dicarbonyls		
anthraquinone [b]		50
1,8-naphthalic anhydride [b]	28	740

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Compound was quantified in its underivatized form

Organic Acids / Phenols:

Chemical analysis of SRM 1650 and 1649 for organic acids and phenols yielded only 19 species. These species include alkanoic, alkenoic, aromatic and alkanedioic acids plus phenol. Due to the absence of published acid speciation values for SRMs 1650 and 1649 no qualitative comparisons are possible. A quantitative description of the organic acids and phenols is provided in Table XIV, in units of ppmm. There are more species detected and quantified in SRM 1649 versus 1650. This result is expected as organic acid formation occurs in the ambient atmosphere. A breakdown of the species observed is provided in the following paragraphs.

Table XIV: Organic Acids Observed in NIST SRM 1649 and 1650

Particulate Organic Acids in NIST SRMs

	Concentration (ng/mg) [a]	
Compound	1649 Urban Dust	1650 Diesel PM
alkanoic acids		
propanoic acid	2100	38000
butanoic acid	det	
pentanoic acid	det	42000
hexanoic acid	64	200
heptanoic acid	32	260
octanoic acid	11	6.5
nonanoic acid	15	22
decanoic acid	11	15
dodecanoic acid	50	77
tetradecanoic acid	34	
hexadecanoic acid	700	94
octadecanoic acid	370	77
unsaturated alkanoic acids		
oleic acid	170	det
aromatic acids		
benzoic acid	14	48
1-naphthoic acid		66
hydroxybenzoic acid	5	26
alkanedioic acids		
butanedioic acid	75	49
nonanedioic acid	58	
phenols		
phenol	3.4	4.8

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det)

Both the 1649 and 1650 SRMs contain many alkanoic acids (C_3-C_{18}). The small acids (C_3-C_7) were the most abundant species observed in SRM 1650. However correcting for the low recovery of d_{11}-hexanoic acid in the 1650 analysis may be skewing these numbers. Propanoic, hexadecanoic and octadecanoic acid are the most abundant acids in SRM 1649. Elevated levels of the C_{16} and C_{18} acids in SRM 1649 is consistent with previous ambient measurements.[4, 32] Other aliphatic acid differences include the presence of tetradecanoic acid in SRM 1649 and its absence in 1650, and quantifiable oleic acid in 1649 but not in 1650.

Aromatic species benzoic and hydroxybenzoic acid are observed in both SRMs. The concentrations of both species are higher in SRM 1650 versus 1649. Naphthoic acid is also observed in SRM 1650,at levels higher than benzoic acid, but is not observed in 1649. The only other aromatic species quantified in the PFBBr analyses is phenol. Phenol is present at slightly higher levels in SRM 1650 relative to 1649.

The only other acid species observed in the PFBBr analysis of the 1650 and 1649 SRMs are the alkanedioic acids. We measured butanedioic acid in both SRMs. The concentration of butanedioic acid was higher in SRM 1649 versus 1650. Nonanedioic acid is also observed in

SRM 1649. The higher levels and additional species present in SRM 1649 are expected as the alkanedioic acids are typically generated by secondary processes once emissions have been released into the troposphere. Previous ambient aerosol speciation by Rogge et al. observed butanedioic and nonanedioic as the two most abundant diacids in urban aerosols, which is consistent with our result for SRM 1649.[32]

3. Emissions from Light-duty Gasoline Vehicles

3.1 LDV Emissions Collection Conditions

Vehicle emission samples were collected at the Haagen-Smit Laboratory (HSL) in El Monte, CA during August and September of 2002. This sample collection was conducted in conjunction with the Ultrafine Particulate Matter Source Profile Measurement for Light-Duty Gasoline Vehicles in California. The emissions sampling conducted in this study utilized an analogous setup to that described by Schauer et al.[14] Briefly, vehicle test cycles were conducted on a Clayton AC-48 twin-roller hydraulic dynamometer, with the driving cycles being executed by the HSL staff. Exhaust emissions were captured at the end of the tailpipe and passed through three inch flexible stainless steel pipe to a Horiba CVS-4X/R CFV remote mixing tee, where a primary turbulent dilution was made with air passed through a HEPA filter and activated charcoal. The mixing tee was followed by a Horiba CVS-20B constant volume sampler (Horiba, Ann Arbor, MI). Using a heated 1/2 inch stainless steel line a sample of the Horiba CVS-20B exhaust was then drawn through a heated cyclone manifold and critical flow venturi. The sample then passed into an aluminum stack dilution tunnel (SDT), described in detail by Hildemann et al., and undergoes a second turbulent dilution with air passed through a HEPA filter and activated charcoal.[33] Sample from the SDT was drawn into a residence time chamber (RTC) to allow the diluted emissions to cool to approximately 25 ^{o}C prior to their removal at the bottom of the RTC. The overall dilution of the emissions samples was 127 for the LEV and 125 for the TWC. A diagram of the SDT and associated sampling equipment is provided in Figure XIV taken from Robert et al.[34]

A fraction of the diluted and cooled emissions were drawn from the bottom of the RTC through one-half inch stainless steel line to the inlet of two PM2.5 cyclones (URG, Chapel Hill, NC). Diluted vehicle emissions from the cyclone outlets were passed through a sampling train similar to that described by Schauer et al., with slight modifications.[14] The exact configuration of our sampling train has been described in Section 2.1.4. Briefly, XAD-coated eight-channel URG annular denuders in-series followed the cyclones. Downstream of the denuders were 47mm quartz fiber filters contained in URG Teflon filter packs. Filter blow off was collected on two URG PUF plugs, in-series prior to PTFE tubing connecting the sampling train to the Hastings electronic mass flow controllers that regulated the flow from a ¾ horsepower Gast vacuum pump (Benton Harbor, MI).

Upon completion of the sample collection the sampling media were stored as follows. Annular denuders were stored capped and on dry ice until extraction was completed, typically within 24 hours of sample collection. Denuder extracts were then stored within silanized amber vials at –20 ^{o}C. The filter samples were stored in glass petri dishes that were covered with baked foil and wrapped with PTFE tape, see Figure IV, prior to placement in a desiccator purged with 99.999% nitrogen. Each PUF plug was stored individually within a silanized amber glass jar with a PTFE-lined cap and wrapped with Teflon tape. Both the filter and PUF samples were stored at –20 ^{o}C.

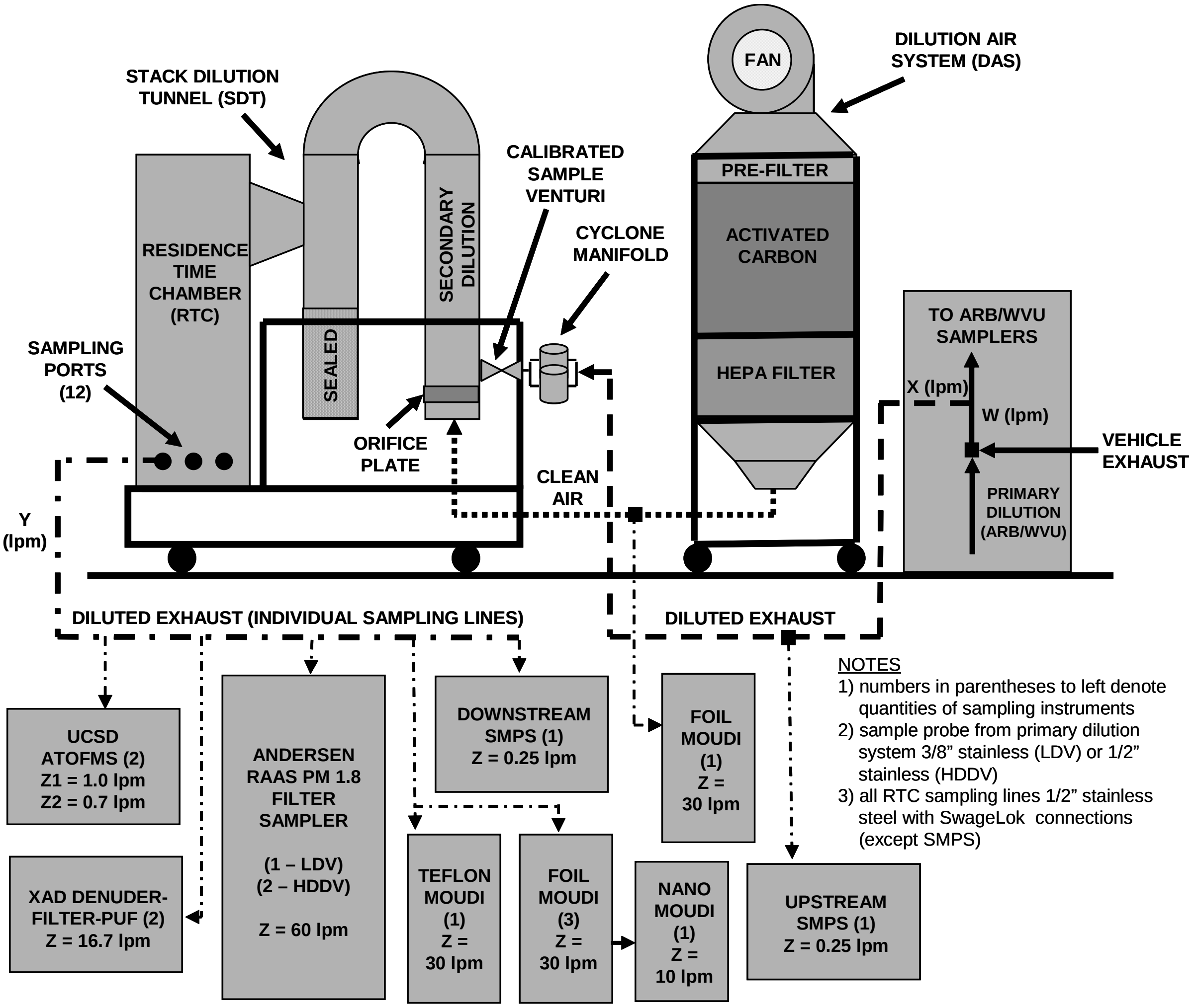


Figure XIV: Diagram of Sample Collection Dilution Configuration, Robert et al.

The CARB staff and University of California, Davis researchers selected the light-duty gasoline powered motor vehicles and driving cycles examined in this study. Passenger cars (PC), light-duty trucks (LDT) and sport utility vehicles (SUV) were included in the vehicle matrix. Various classes of emissions technologies were targeted in this selection. The vehicle classes described in this research include low-emission vehicles (LEVs) and three-way catalyst equipped vehicles (TWCs). LEVs are defined as vehicles in compliance with the certification guidelines set forth in the California Code of Regulations Title 13. Production years covered by the evaluated vehicles classes are 1988 through 2003. Further description of the specific vehicles examined within each class is provided in Table XV. The emission samples described in this report were collected using the Federal Test Procedure (FTP) driving cycle. The FTP cycle contains a cold start and multiple transient sections with a top speed of 56 miles hour^{-1} (mph). The FTP cycle also contains a ten-minute hot soak (engine off) prior to the last transient section.

Table XV: LDV Vehicle Matrix

Category [a]	Make	Model	Production Year	Number of Cylinders	Fuel Delivery [b]	Mileage
LEV PC	Chevrolet	Monte Carlo	2002	6	FI	20,230
LEV PC	Toyota	Camry	1999	6	SFI	43,160
LEV PC	Nissan	Sentra	1999	4	SFI	52,630
LEV PC	Honda	Accord	1998	4	SFI	97,811
LEV PC	Honda	Civic	1996	4	SFI	77,703
LEV LDT/SUV	Chevrolet	Silverado	2003	8	SFI	1,264
LEV LDT/SUV	Nissan	Pathfinder	2002	6	SFI	8,169
LEV LDT/SUV	Toyota	Tacoma	2000	6	SFI	51,554
LEV LDT/SUV	Jeep	Grand Cherokee	2000	6	SFI	31,751
LEV LDT/SUV	Ford	Explorer	1998	8	SFI	82,513
TWC PC	Cadillac	Sedan de Ville	1999	8	FI	35,320
TWC PC	Ford	Mustang	1998	6	SFI	10,697
TWC PC	Honda	Acura	1994	4	SFI	104,441
TWC PC	Ford	Taurus	1991	6	MPFI	136,983
TWC PC	Toyota	Camry	1991	4	MPFI	95, 532
TWC PC	Chrysler	Plymouth	1988	4	EPFI	32, 097

[a] PC=passenger car, LDT=light-duty truck, SUV = sports-utility vehicle [b] FI=fuel injection, SFI=sequential fuel injection, MPFI = multi-port fuel injection, EPFI=electronic port fuel injection

3.2 LDV Emission Factors

In order to express the chemical speciation data obtained in this project in terms of emitted mass numerous steps were completed following the chemical analyses. The exact procedure followed is outlined in Figure XV. Briefly each compound is quantified in the analyzed extract. This value undergoes a direct method blank subtraction. The method blank subtracted values are then converted to collected mass per filter, and corrected for IS recovery. Internal standards are matched to individual compounds based on structure and vapor pressure similarities. The IS recovery corrected mass is converted to a sampled concentration. The sampled concentration then undergoes a dilution ratio weighted blank subtraction with the pre-sampling blank. This approach assumes that the majority of contamination arises from the primary dilution system. Once the final blank subtraction is completed the corrected sampling concentration is converted to the corrected sampling mass. This sampled mass is converted to emitted mass using a formula that accounts for the volume fractions of the primary and secondary dilution flow rates comprising the collected sample. Once the emitted mass has been generated emission factors are then calculated based on distance traveled or fuel consumed, using averaged CO_2 emissions from the engine. LDV fuel consumption is calculated assuming 2.28 kg of gaseous CO_2 emissions per liter of gasoline consumed.[35]

Compounds are quantified in the extracts in units of pg / uL

↓

Extract concentrations undergo unadjusted method blank subtraction

↓

Extract concentration is converted to mass per filter and corrected for IS recovery as follows:

$$\left[\begin{array}{c}\text{IS Recovery}\\ \text{Corrected Mass}\\ \text{(pg)}\end{array}\right] = \left[\begin{array}{c}\text{Filter}\\ \text{Mass}\\ \text{(pg)}\end{array}\right] \times \frac{100}{\left[\begin{array}{c}\text{IS}\\ \text{Percent}\\ \text{Recovery}\end{array}\right]}$$

Filter mass is converted to sampled concentration in units of pg / m^3

↓

Sampled concentrations undergo pre-sampling blank subtraction using the following formula:

$$\left[\begin{array}{c}\text{Sampling}\\ \text{Blank-subtracted}\\ \text{Concentration}\\ (\text{pg / m}^3)\end{array}\right] = \frac{\left[\left[\begin{array}{c}\text{Sample}\\ \text{Concentration}\\ (\text{pg / m}^3)\end{array}\right] \times \left[\begin{array}{c}\text{Sample}\\ \text{Overall}\\ \text{Dilution Ratio}\end{array}\right]\right] - \left[\left[\begin{array}{c}\text{Pre-blank Sample}\\ \text{Concentration}\\ (\text{pg / m}^3)\end{array}\right] \times \left[\begin{array}{c}\text{Pre-blank}\\ \text{Overall}\\ \text{Dilution Ratio}\end{array}\right]\right]}{\left[\begin{array}{c}\text{Sample}\\ \text{Overall}\\ \text{Dilution Ratio}\end{array}\right]}$$

Sampling blank-subtracted concentrations are converted to collected mass in units of pg

↓

Blank-subtracted collected mass was converted to emission mass with the following formula:

$$\left[\begin{array}{c}\text{Emission}\\ \text{Mass}\\ \text{(pg)}\end{array}\right] = \left[\begin{array}{c}\text{Corrected}\\ \text{Sampled}\\ \text{Mass}\\ \text{(pg)}\end{array}\right] \times \frac{\left[\begin{array}{c}\text{Primary}\\ \text{Dilution}\\ \text{Flow Rate}\\ \text{(Lpm)}\end{array}\right]}{\left[\begin{array}{c}\text{SDT}\\ \text{Venturi}\\ \text{Flow Rate}\\ \text{(Lpm)}\end{array}\right]} \times \frac{\left[\begin{array}{c}\text{Diluted}\\ \text{RTC}\\ \text{Flow Rate}\\ \text{(Lpm)}\end{array}\right]}{\left[\begin{array}{c}\text{Sampling}\\ \text{Instrument}\\ \text{Flow Rate}\\ \text{(Lpm)}\end{array}\right]}$$

Emission mass is then used for calculation of emission factors

Figure XV: Diagram of the Generation of Emission Mass

Table XVI provides the percent recovery of the internal standards spiked onto the PM filters prior to solvent extraction. These IS are used for correction factors as outlined in Figure XV. The obtained IS recoveries are consistent with our expectations based on observed recovery of model compounds described in Section 2.3.4.1 and on the recovery of these same IS in the NIST SRM analyses.

Table XVI: Recovery of Spiked Internal Standards from LDV Samples

Percent Recovery of Spiked Internal Standards on LDV PM Emission Samples

	LDV Sample			
Compound	Pre-blank	LEV	TWC	Post-blank
carbonyls				
2-F-benzaldehyde [a]	82	79	67	78
8-F-1-benzosuberone [b]	114	104	120	88
4-F-benzophenone [c]	40	51	48	69
organic acids [d]				
d_{11}-hexanoic acid	20	20	21	29
$^{13}C_1$ dodecanoic acid	52	58	55	61
d_{35}-octadecanoic acid	53	65	63	70
d_5-benzoic acid	42	37	41	43
2-F-5-Me-benzoic acid	47	38	43	42
PAHs [e]				
d_{10} acenaphthene	37	49	21	64
d_{10} fluorene	35	49	26	61
d_{10} phenanthrene	54	67	22	82
d_{12} chrysene	131	93	82	96
d_{12} benzo[k]fluoranthene	122	87	86	56
d_{12} benzo[ghi]perylene	150	96	102	99

[a] Compound was quantified as a PFBHA oxime using 4-F-Benzaldehyde as the internal standard, [b] Compound was quantified as a PFBHA oxime using 6-F-4-Chromanone as the internal standard, [c] Compound was quantified in its underivatized form using 2,2'-F-biphenyl as the internal standard, [d] Compounds were quantified as PFBBr esters using 4-F-benzoic acid as the internal standard, [e] Compounds were quantified using d_{10}-pyrene as the internal standard

3.2.1 Carbonyls

A total of 35 carbonyl species are observed in the LDV particulate emissions. Emission factors on a distance traveled basis are presented in Table XVII and on a fuel consumption basis in Table XVIII. The description that follows addresses the distance traveled emission factors. A comparison between the LDV and HDV vehicles in Section 5 will address the fuel consumption emission factors. The ions used for quantification of each of the carbonyl species identified are presented in Appendix I, and instrumental detection limits are presented in Appendix J. The error range on each emission factors is based on the recovery %RSD of a similar compound obtained in the model analyte recovery experiment (see Section 2.3.4.1).

Twenty straight chain and three cyclic aliphatic carbonyls were measured in the LDV particulate emissions. Most of these species are present at higher levels in the TWC vehicle particulate emissions versus the LEV. Aliphatic aldehydes (C_3-C_{10}) are observed with the smaller aldehydes (C_3-C_7) higher in the TWC emissions while the larger aldehydes (C_8-C_{10}) are present in higher levels in the LEV particulate emissions. Butanal has largest aldehyde emission factor for both the LEV and TWC samples, and is the second most abundant species observed in both LDV samples. Three aliphatic ketones (C_4-C_6) are present in both LDV samples with concentrations lower than their aldehyde counterparts, similar to the results obtained for the NIST SRMs. Unsaturated aliphatic carbonyls (C_3-C_6) are observed in the LDV PM emissions with five compounds in the LEV emissions and eight species in the TWC emissions. Emissions of the unsaturated carbonyls are 3-20 times greater in the TWC emission relative to the LEV. The total aliphatic carbonyl particulate emissions are five-fold higher in the TWC sample versus the LEV.

Both aromatic aldehydes and ketones are present in the LDV particulate samples. Benzaldehyde and the o-and m-tolualdehyde isomers are components of the TWC emissions, while only the o- and m-tolualdehyde isomers are present in the LEV sample. In the TWC sample the tolualdehyde isomer concentration is ~40% of the levels of benzaldehyde. Three aromatic ketones (acetophenone, fluorenone, and benzophenone) are observed in both the LEV and TWC particulate emissions. Similar to the aliphatic carbonyls the aromatic carbonyls are measured at higher emission rates in the TWC particulate emissions than for the LEV.

Seven dicarbonyls were measured in the LDV particulate emissions, six aliphatic and one aromatic species. Aliphatic dicarbonyls (C_2-C_6) are observed in both the TWC and LEV samples. High levels of methyl glyoxal, glyoxal and 2,5-hexanedione were determined with methyl glyoxal being the most abundant carbonyl observed in both the TWC and LEV particulate emissions. Similar to most of the other carbonyl species the aliphatic dicarbonyls are emitted at elevated levels in the TWC emissions relative to the LEV. One aromatic dicarbonyl, benzoquinone, is observed in both LDV samples. Benzoquinone is the tenth most abundant carbonyl in the TWC particulate emissions and the thirteenth most abundant in the LEV sample. To our knowledge this is the first time that emission factors for benzoquinone are being reported. This result has significant impacts on the human health effects posed by these LDV emissions.

Using bulk data obtained from Robert et al. the carbonyls account for a significant portion of the PM and organic carbon emissions for LDVs. These particulate-bound carbonyls comprise 3.2 and 5.4% of the PM emission mass for the LEV and TWC vehicles respectively. When considering only the organic carbon emissions the carbonyls identified and quantified account for 7.7 and 12% of the LEV and TWC emissions respectively. Note that methyl glyoxal by itself accounts for 32% of the LEV carbonyls and 23% of the TWC emissions, making it a very significant species with regard to LDV particulate emissions.

Table XVII: LDV Carbonyl Emission Factors: Mass per Distance Traveled

LDV Particulate Carbonyl Emission Factors: Mass per Distance Traveled

	Emission Rate (ng km^{-1}) [a]		
Compound	LEV	TWC	Notes: [b-e]
aliphatic aldehydes			
propanal	300 ± 70	2500 ± 600	b
butanal	2800 ± 680	8900 ± 2100	b
isobutanal	190 ± 40	570 ± 140	b
pentanal	810 ± 190	3300 ± 800	b

hexanal		6700 ± 1600	b
heptanal	200 ± 15	280 ± 21	b
octanal	130 ± 10	54 ± 4	c
nonanal	430 ± 33	130 ± 10	c
decanal	240 ± 18		c
aliphatic ketones			
2-butanone	480 ± 200	1900 ± 780	b
3-pentanone	16 ± 7	130 ± 52	b
2-hexanone	390 ± 160	2800 ± 1100	b
unsaturated aliphatics			
acrolein	48 ± 9	950 ± 180	b
methacrolein		69 ± 13	b
methyl vinyl ketone		720 ± 130	b
crotonaldehyde	160 ± 30	900 ± 170	b
t-2-Me-2-butenal	5 ± 0.6	42 ± 5	b
3-Me-2-butenal	49 ± 6	140 ± 17	b
t-2-hexenal		71 ± 9	b
4-hexen-3-one	32 ± 4	200 ± 25	b
cyclic aliphatics			
2-Me-2-cyclopentenone	9 ± 1	25 ± 3	b
3-Me-2-cyclopentenone		120 ± 14	b
2-cyclohexenone	det	det	b
aliphatic dicarbonyls			
glyoxal	850 ± 66	1900 ± 150	b
methyl glyoxal	3800 ± 290	11000 ± 870	b
2,3-pentanedione	det	det	b
2,4-pentanedione	det	det	b
2,3-hexanedione	91 ± 4	59 ± 3	b
2,5-hexanedione	440 ± 21	1800 ± 87	b
aromatic aldehydes			
benzaldehyde		190 ± 48	b
o- & m-tolualdehyde	19 ± 5	69 ± 17	b
aromatic ketones			
acetophenone	21 ± 5	94 ± 21	b
9-fluorenone	28 ± 6	det	c
benzophenone	69 ± 16	220 ± 50	d
aromatic dicarbonyls			
benzoquinone	190 ± 9	1500 ± 70	d

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of 2-F-benzaldehyde, [c] Corrected for recovery of 8-F-1-benzosuberone, [d] Corrected for recovery of 4-F-benzophenone, [e] Compound was quantified in its underivatized form

Table XVIII: LDV Carbonyl Emission Factors: Mass per Fuel Consumed

LDV Particulate Carbonyl Emission Factors: Mass per Fuel Consumed

	Emission Rate (µg L^{-1} fuel burned) [a]		
Compound	LEV	TWC	Notes: [b-e]
aliphatic aldehydes			
propanal	2.8 ± 0.7	26 ± 6	b
butanal	26 ± 6	92 ± 22	b
isobutanal	1.7 ± 0.4	5.9 ± 1.4	b
pentanal	7.6 ± 1.8	34 ± 8	b
hexanal		69 ± 17	b
heptanal	1.9 ± 0.1	2.9 ± 0.2	b
octanal	1.2 ± 0.1	0.56 ± 0.04	c
nonanal	4.0 ± 0.3	1.3 ± 0.1	c
decanal	2.3 ± 0.2		c
aliphatic ketones			
2-butanone	4.5 ± 1.9	20 ± 8	b
3-pentanone	0.15 ± 0.06	1.3 ± 0.5	b
2-pentanone			b
2-hexanone	3.7 ± 1.5	29 ± 12	b
unsaturated aliphatics			
acrolein	0.44 ± 0.08	9.8 ± 1.8	b
methacrolein		0.72 ± 0.13	b
methyl vinyl ketone		7.4 ± 1.4	b
crotonaldehyde	1.5 ± 0.3	9.4 ± 1.7	b
t-2-Me-2-butenal	0.04 ± 0.01	0.43 ± 0.5	b
3-Me-2-butenal	0.46 ± 0.06	1.4 ± 0.2	b
t-2-hexenal		0.73 ± 0.09	b
4-hexen-3-one	0.29 ± 0.04	2.1 ± 0.3	b
cyclic aliphatics			
2-Me-2-cyclopentenone	0.09 ± 0.01	0.26 ± 0.03	b
3-Me-2-cyclopentenone		1.3 ± 0.2	b
2-cyclohexenone	det	det	b
aliphatic dicarbonyls			
glyoxal	7.9 ± 0.6	20 ± 2	b
methyl glyoxal	35 ± 3	120 ± 9	b
2,3-pentanedione	det	det	
2,4-pentanedione	det	det	b
2,3-hexanedione	0.85 ± 0.04	0.61 ± 0.03	b
2,5-hexanedione	4.1 ± 0.2	19 ± 1	b
aromatic aldehydes			
benzaldehyde		2.0 ± 0.5	b
o- & m-tolualdehyde	0.18 ± 0.04	0.71 ± 0.18	b
aromatic ketones			
acetophenone	0.19 ± 0.04	0.97 ± 0.22	b
9-fluorenone	0.26 ± 0.06	det	c

benzophenone	0.65 ± 0.14	2.3 ± 0.5	d
aromatic dicarbonyls			
benzoquinone	1.7 ± 0.1	16 ± 1	d

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of 2-F-benzaldehyde, [c] Corrected for recovery of 8-F-1-benzosuberone, [d] Corrected for recovery of 4-F-benzophenone, [e] Compound was quantified in its underivatized form

3.2.2 Organic Acids

Fourteen organic acids species were measured in the LDV particulate emissions. Emission factors on a distance traveled basis are presented in Table XIX and on a fuel consumption basis in Table XX. The description that follows addresses the distance traveled emission factors. A comparison between the LDV and HDV vehicles in Section 5 will address the fuel consumption emission factors. The ions used for quantification of each of the acid species identified are presented in Appendix K, and instrumental detection limits are presented in Appendix L. The error range on each emission factors is based on the recovery %RSD of a similar compound obtained in the model analyte recovery experiment (see Section 2.3.4.1).

Twelve of the 14 organic acids identified are aliphatic species. The eleven alkanoic acids (C_4-C_{18}) included the homologous series from butanoic to decanoic. Propanoic acid is observed in the LDV samples however high background levels prevented an accurate quantification thus this species is not reported. For these acids the emissions of the TWC vehicles are approximately 3-4 times greater than for the LEV emissions. Above ten carbon atoms the alkanoic acids are only observed for the even carbon atom isomers (C_{12}, C_{14}, C_{16} and C_{18}). These even carbon number alkanoic acids are the most abundant acids observed and emitted at higher rates for the TWC. Dodecanoic acid is approximately 3.5-fold higher from the TWC than the LEVs, while tetradecanoic, hexadecanoic and octadecanoic acids are 25, 15 and 100-fold higher respectively. Comparison to values observed by Rogge et al. for the C_{16}, C_{18} and C_{12} alkanoic acids show our values are significantly smaller by at least 40 percent or more (25 vs. 69 ug /km for hexadecanoic, 13 vs. 18 for octadecanoic and 4.3 vs. 41.4 for dodecanoic).[10] Comparison of the TWC emission factor for octadecanoic acid versus results obtained by Schauer et al. show our value is roughly three times greater (13 vs. 4.3 $\mu g\ km^{-1}$).[14] Oleic acid was observed at approximately six-fold higher emission rates in the TWC versus the LEV. Our value for oleic acid in the TWC sample is 50% greater than observed by Rogge et al. Differences in the vehicles, fuel and sample collection conditions likely explain most of the variability between our results and those of Rogge et al. In general the aliphatic acids observed and their concentrations fall in line with previous data for the TWC emissions, which adds confidence to the values obtained for the LEV.

Only two aromatic species, benzoic acid and phenol, are observed in the TWC and LEV emissions. Benzoic acid is found at ~13-fold higher emissions rate in the TWC particulate emissions relative to the LEV. However our emission factor of benzoic acid for TWC vehicles is 13-fold lower than that reported by Rogge et al.[10] This large difference is likely due to differences in fuel formulations between the two samples. Phenol is also observed in both LDV samples, with twice as much present in the TWC emissions versus the LEV. The lack of aromatic acids and phenols is expected as few previous studies have identified more than a handful of compounds.

When considering the sum of the quantified acids against bulk data taken from Robert et al. they comprise a few percent of the particulate emissions. For the LEV emissions the acids account for 1.6% of the emitted PM mass and 3.7% of the emitted particulate organic carbon. The TWC sample contained 6% of the PM mass as organic acids with the fraction of organic carbon totaling 13%. It should be noted that a majority of the acid mass is made up of species with an even number of carbon atom acids, exceeding ten carbon atoms total.

Table XIX: LDV Organic Acid Emission Factors: Mass per Distance Traveled

Organic Acid Emission Factors for LDV PM: Mass per Distance

	Emission Rate (ng km^{-1}) [a]		Notes: [b-e]
Compound	LEV	TWC	
alkanoic			
butanoic acid	490 ± 130	1200 ± 320	b
pentanoic acid		960 ± 260	b
hexanoic acid	560 ± 150	1300 ± 350	b
heptanoic acid	110 ± 30	370 ± 100	b
octanoic acid		160 ± 30	c
nonanoic acid	100 ± 20	550 ± 100	c
decanoic acid	110 ± 20	370 ± 70	c
dodecanoic acid	1200 ± 230	4300 ± 800	c
tetradecanoic acid	70 ± 10	1700 ± 250	c
hexadecanoic acid	1700 ± 250	25000 ± 3700	d
octadecanoic acid	130 ± 20	13000 ± 1700	d
alkenoic			
oleic acid	1200 ± 150	7500 ± 980	d
aromatic			
benzoic acid	20 ± 1	260 ± 20	e
phenols			
phenol	100 ± 40	200 ± 70	e

[a] Analytes that were observed with a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of d_{11} hexanoic acid, [c] Corrected for recovery of $^{13}C_1$ dodecanoic acid, [d] Corrected for recovery of d_{35} octadecanoic acid, [e] Corrected for recovery of d_5 benzoic acid

Table XX: LDV Organic Acid Emission Factors: Mass per Fuel Consumed

Organic Acid Emission Factors for LDV PM: Mass per Fuel Consumption

	Emission Rate (µg L^{-1} fuel burned) [a]		Notes: [b-e]
Compound	LEV	TWC	
alkanoic			
butanoic acid	4.6 ± 1.2	12 ± 3	b
pentanoic acid			b
hexanoic acid	5.2 ± 1.4	14 ± 4	b
heptanoic acid	1.0 ± 0.3	3.8 ± 1.0	b
octanoic acid		1.6 ± 0.3	c

nonanoic acid	0.9 ± 0.2	5.7 ± 1.1	c
decanoic acid	1.0 ± 0.2	3.8 ± 0.7	c
dodecanoic acid	11 ± 2	44 ± 8	c
tetradecanoic acid	0.7 ± 0.1	17 ± 3	c
hexadecanoic acid	16 ± 2	260 ± 40	d
octadecanoic acid	1.2 ± 0.2	130 ± 17	d
alkenoic			
oleic acid	11 ± 1	77 ± 10	d
aromatic			
benzoic acid	0.20 ± 0.01	2.7 ± 0.2	e
phenols			
phenol	1.0 ± 0.3	2.1 ± 0.8	e

[a] Analytes that were observed with a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of d_{11} hexanoic acid, [c] Corrected for recovery of $^{13}C_1$ dodecanoic acid, [d] Corrected for recovery of d_{35} octadecanoic acid, [e] Corrected for recovery of d_5 benzoic acid

3.2.3 PAHs

The PAH emission rates from the LDV samples are provided in Table XXI for distance traveled and in Table XXII for fuel consumption. The ions used for quantification of each of the PAH compounds identified are presented in Table V with instrumental detection limits provided in Appendix M. The same PAHs are observed in both LDV samples with the exception of anthracene, only observed in the LEVs, and the MW 228 isomers, only observed in the TWCs. All of the heavy PAHs, those of molecular weight 252 amu or higher, detected were observed in both samples. Heavy PAHs made up 58% of the total PAH emissions for the LEV sample while heavy PAHs were 75% of the PAHs quantified in the TWC sample. Emission rates of the light PAHs phenanthrene, fluoranthene, pyrene, and cyclopenta[cd]pyrene are two times higher in the TWC sample than the LEV sample. Most heavy PAHs were emitted at a rate five to seven times higher in the TWC vehicles than the LEV vehicles. The only hydroxy-PAHs observed in the LDV were the naphthol isomers, at 10x higher emission rates in the LEVs versus the TWCs. The naphthol isomers are some of the highest emitted aromatic hydrocarbons from the LEVs

Table XXI: LDV PAH Emission Factors: Mass per Distance Traveled

PAH Emission Factors for LDV PM: Mass per Distance

	Emission Rate (ng km^{-1}) [a]		Notes: [d-g]
Compound	LEV	TWC	
phenanthrene	120 ± 14	220 ± 25	d
anthracene	14 ± 2		d
fluoranthene	42 ± 4	74 ± 7	e
pyrene	83 ± 9	150 ± 15	e
cyclopenta[cd]pyrene	14 ± 2	33 ± 4	e
MW 228 isomers [b]		310 ± 24	e
benzofluoranthene isomers [c]	64 ± 6	640 ± 59	e

benzo[e]pyrene	32 ± 3	170 ± 16	f
benzo[a]pyrene	110 ± 10	540 ± 50	f
perylene	4.0 ± 0.5	19 ± 2	f
indeno[1,2,3-cd]pyrene	53 ± 5	290 ± 27	f
dibenz[a,h]anthracene	3.0 ± 0.1	17 ± 1	g
benzo[ghi]perylene	66 ± 5	430 ± 35	g
coronene	35 ± 3	240 ± 19	g
1-naphthol	90 ± 50	8.6 ± 5.1	
2-naphthol	120 ± 14	11 ± 1	

[a] Analytes that were observed with a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] The MW 228 isomers are the sum of chrysene, triphenylene and benz[a]anthracene, [c] The isomers are the sum of benzo[b]fluoranthene and benzo[k]fluoranthene, [d] Corrected for recovery of d_{10} phenanthrene, [e] Corrected for recovery of d_{12} chrysene, [f] Corrected for recovery of d_{12} benzo[k]fluoranthene, [g] Corrected for recovery of d_{12} benzo[ghi]perylene,

Table XXII: LDV PAH Emission Factors: Mass per Fuel Consumed

PAH Emission Factors for LDV PM: Mass per Fuel Consumption

	Emission Rate (µg / L fuel burned) [a]		Notes: [d-g]
Compound	LEV	TWC	
phenanthrene	1.1 ± 0.10	2.2 ± 0.3	d
anthracene	0.13 ± 0.02		d
fluoranthene	0.40 ± 0.04	0.76 ± 0.07	e
pyrene	0.78 ± 0.08	1.5 ± 0.2	e
cyclopenta[cd]pyrene	0.13 ± 0.02	0.35 ± 0.04	e
MW 228 isomers [b]		3.2 ± 0.2	e
benzofluoranthene isomers [c]	0.60 ± 0.06	6.6± 0.6	e
benzo[e]pyrene	0.30 ± 0.03	1.8 ± 0.2	f
benzo[a]pyrene	1.0 ± 0.1	5.6 ± 0.5	f
perylene	0.035 ± 0.003	0.20 ± 0.02	f
indeno[1,2,3-cd]pyrene	0.45 ± 0.05	3.0 ± 0.3	f
dibenz[a,h]anthracene	0.028 ± 0.001	0.18 ± 0.01	g
benzo[ghi]perylene	0.62 ± 0.05	4.4 ± 0.4	g
coronene	0.33 ± 0.03	2.4 ± 0.2	g
1-naphthol	0.8 ± 0.5	0.09 ± 0.05	
2-naphthol	1.1 ± 0.1	0.11 ± 0.01	

[a] Analytes that were observed with a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] The MW 228 isomers are the sum of chrysene, triphenylene and benz[a]anthracene, [c] The isomers are the sum of benzo[b]fluoranthene and benzo[k]fluoranthene, [d] Corrected for recovery of d_{10} phenanthrene, [e] Corrected for recovery of d_{12} chrysene, [f] Corrected for recovery of d_{12} benzo[k]fluoranthene, [g] Corrected for recovery of d_{12} benzo[ghi]perylene,

When individual PAH isomer group emission rates are presented as a percentage of the total PAH emission rate, as shown in Table XXII, an interesting trend is observed. Light PAHs (species with MW < 252) are observed as significantly different in their contribution to the total PAH emissions for the LEV and TWC. The TWC emissions are enriched in MW 178 isomers relative to the LEV and vice versa for the MW 202 isomers. However the contribution of the heavier species (MW of 252 and above) in the LEVs parallels the values for the TWCs. The similarities of the heavy PAH ratios implies a common source for these compounds in the LDV emissions. Concentrations of high molecular weight PAHs in gasoline motor vehicle emission samples have been correlated to the concentration of PAHs in the fuel itself.[36] Our results did not indicate a similar trend in the PAH percentages of total PAH emissions for the HDV samples;, which agrees with Marr et.al.[36]

Table XXIII: Ratio of PAH Isomers to Total PAHs in LDV Emissions

	(PAH isomers)/(total PAHs) Ratio [a]	
Compound	LEV	TWC
MW 178 isomers	16.5	30.0
MW 202 isomers	15.8	4.8
cyclopenta[cd]pyrene	1.8	0.7
MW 252 isomers	26.4	29.2
indeno[1,2,3-cd]pyrene	6.7	6.1
dibenz[a,h]anthracene	0.4	0.4
benzo[ghi]perylene	8.3	9.1
coronene	4.4	5.0

[a] Only compounds observed in both the LEV and TWC vehicle are listed

The availability of previous TWC dynamometer measurements allows for cross comparison in the PAHs measured. Figure XVI is a comparison of the particulate phase PAH emission rates of TWC vehicles with those reported by Schauer et.al..[14] A strong agreement is observed between the two data sets for the following compounds: fluoranthene, pyrene, cyclopenta[cd]pyrene, MW 228 isomers, benzo[e]pyrene, perylene, and indeno[1,2,3-cd]pyrene. One value was excluded from the comparison, benzo[a]pyrene. The value obtained for benzo[a]pyrene in this study (540 ng/km) is much higher than that found by Schauer et al. (20 ng/km).

Our results for the TWC vehicles also agree quite well with those of Cadle et al. for four of the five high molecular weight PAHs reported in their study.[37] Cadle et al. collected emissions samples during both the summer and winter months, however a comparison was only made to the summer collection to best represent our summertime collection period. A comparison is not made for the lighter, semi-volatile PAHs due to the differences in sampling techniques between the two studies. Figure XVI shows the comparison plot for the high molecular weight PAHs, only benzo[e]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[ghi]perylene were used to determine the linear fit on the comparison plot. Emission rate for the benzofluoranthene isomers are much higher in this study (640 ng/km) versus the value determined by Cadle et al. of 43 ng/km. Based on the few available comparisons we feel as though our data successfully represents the chemical composition of the TWC and LEV particulate emissions for PAHs, carbonyls and organic acids.

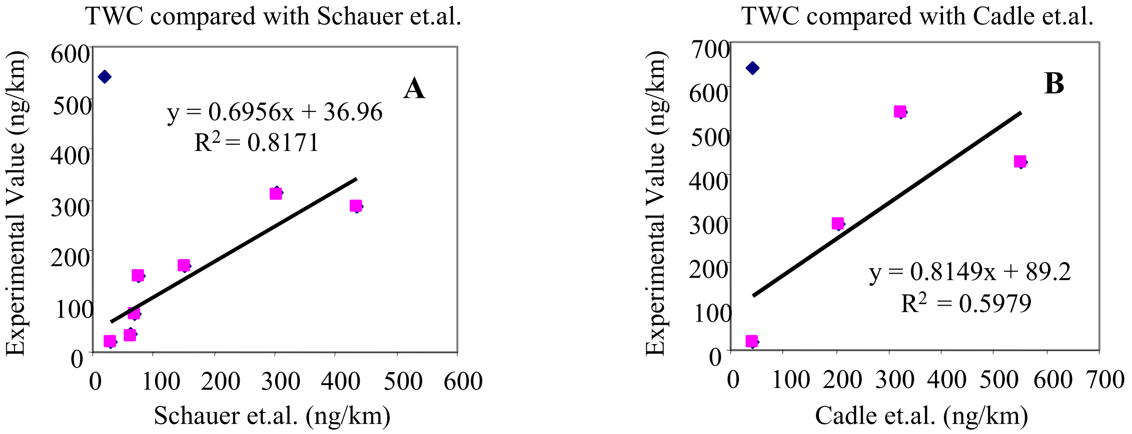


Figure XVI: Comparison of TWC PAH Values:

A) Schauer et al., B) Cadle et al.

4. Emissions from Heavy-duty Diesel Vehicles

4.1 HDV Emissions Collection Conditions

Heavy-duty diesel vehicle emissions were collected in Riverside, CA during June 2003. The collection procedure was similar to that described in Section 3.1 for the LDV samples. Briefly, heavy-duty diesel vehicles were driven on a mobile chassis dynamometer operated by West Virginia University (WVU). Simulation of vehicle load was accomplished using drive shafts connecting the hubs of the vehicle to flywheel weight sets. The test vehicle was subjected to a five-stage drive test cycle (HHDDT) consisting of a 30 minute idle, a 17 minute creep, an 11 minute transient stage and two cruise stages of 34 and 31 minutes, with a top speed of 65 miles per hour for the second cruise stage. The entire test cycle required approximately 3 hours for completion.

The vehicle exhaust was captured at the end of the stack mufflers and passed through heated three inch stainless steel tubing to a mixing box were the emissions were subjected to a primary dilution with HEPA-filtered air. The diluted emissions passed through a dilution tunnel controlled by a critical flow venturi. Using a heated ½-inch stainless steel line a sample of the WVU dilution tunnel exhaust was then drawn through a heated cyclone manifold and critical flow venturi. The sample then passed into the SDT and underwent a second turbulent dilution with air passed through a HEPA filter and activated charcoal. Sample from the SDT was drawn into the RTC to allow the diluted emissions to cool to approximately ambient temperatures prior to their removal at the bottom of the RTC. The cooled, diluted emissions were then collected as described in Section 3.1.

Results from the HDV PM samples provided in this report were taken from a 1999 Freightliner tractor. This vehicle contained a 1998 Detroit Diesel Series 60 engine that had 138,553 miles driven at the time of sample collection. The engine has six cylinders with a displacement of 12.7 L and 500 base horsepower. This vehicle was sampled under a 56,000 pound simulated load. The emission samples described in this report represent one test using the HHDDT driving cycle and one test using only the idle and creep modes of the HHDDT cycle that were repeated six times in succession. These separate tests will be identified as the 56K and Idle/Creep respectively.

4.2 HDV Emission Factors

The HDV emission factors are generated using the procedure described in Section 3.2. The only difference between the calculation of the LDV and HDV emission factors was the conversion factor for fuel consumption from CO_2 emissions. HDV fuel consumption is calculated using 2.77 kg of gaseous CO_2 emissions per liter of diesel fuel consumed.[35]

Table XXIV provides the percent recovery of the internal standards spiked onto the PM filters prior to solvent extraction. These IS are used for correction factors as outlined in Figure XV. The obtained IS recoveries are consistent with our expectations based on observed recovery of model compounds described in Section 2.3.4.1 and on the recovery of these same IS in the NIST SRM analyses.

Table XXIV: Recovery of Spiked Internal Standards from HDV Samples

Percent Recovery of Spiked Internal Standards Used for HDV Extraction Efficiency Correction

	HDV Sample		
Compound	Pre-blank	Idle / Creep	'99 Frtlnr 56K
carbonyls			
2-F-benzaldehyde [a]	67	64	75
8-F-1-benzosuberone [b]	55	111	110
4-F-benzophenone [c]	66	43	42
organic acids [d]			
d_{11}-hexanoic acid	13	5	10
$^{13}C_1$ dodecanoic acid	88	102	61
d_{35}-octadecanoic acid	97	121	63
d_5-benzoic acid	36	37	33
2-F-5-Me-benzoic acid	55	81	65
PAHs [e]			
d_{10} acenaphthene	11	15	14
d_{10} fluorene	20	22	14
d_{10} phenanthrene	50	62	42
d_{12} chrysene	117	107	82
d_{12} benzo[k]fluoranthene	99	94	64
d_{12} benzo[ghi]perylene	107	100	38

[a] Compound was quantified as a PFBHA oxime using 4-F-Benzaldehyde as the internal standard, [b] Compound was quantified as a PFBHA oxime using 6-F-4-Chromanone as the internal standard, [c] Compound was quantified in its underivatized form using 2,2'-F-biphenyl as the internal standard, [ad] Compounds were quantified as PFBBr esters using 4-F-benzoic acid as the internal standard, [e] Compounds were quantified using d_{10}-pyrene as the internal standard

4.2.1 Carbonyls

Thirty-seven carbonyl species were observed in the HDV particulate emissions. Emission factors per distance traveled are presented in Table XXV and on a fuel consumption basis in Table XXVI. Due to the small number of miles driven in the idle/creep sample (3.2 miles) emission factors are not presented on per distance traveled, but are provided for fuel consumption. The description that follows addresses the distance traveled emission factors for the 56K sample. The ions used for quantification of each of the carbonyl species identified are presented in Appendix I, and instrumental detection limits are presented in Appendix J. The error range on each emission factors is based on the recovery %RSD of a similar compound obtained in the model analyte recovery experiment (see Section 2.3.4.1).

A total of 22 aliphatic carbonyls are observed in the 56K HDV PM emissions. These 22 aliphatic carbonyls are comprised of ten aldehydes, three ketones, seven unsaturated species and two cyclic aliphatic compounds. In general the species observed are similar to those present in the LDV emissions. Aliphatic aldehydes (C_3-C_{11}) are abundant in the HDV 56K emissions, with hexanal and butanal being the second and third most abundant carbonyls observed. Three aliphatic ketones (C_5-C_6) are observed with 2-hexanone being emitted at an order of magnitude or more above the two pentanone isomers. The unsaturated aliphatic carbonyls observed (C_3-C_6) are in general all at low levels, with acrolein being the most abundant followed by crotonaldehyde and methyl vinyl ketone. The two cyclic carbonyls observed are C_6 isomers, both present at low levels, with one species containing a five-member ring and the other having a six-member ring. Overall the aliphatic carbonyls account for 55% of the total carbonyls quantified in the 56K HDV emissions.

Nine aromatic carbonyls are measured in the 56K HDV sample. The four aromatic aldehydes and five aromatic ketones are all emitted at low levels (<20 μg km^{-1}). Of the aromatic aldehydes observed benzaldehyde is measured at more than 10-fold higher emission rates than the tolualdehyde isomers. The five aromatic ketones observed are acetophenone, fluorenone, benzophenone, perinaphthenone, and xanthone. Perinaphthenone is the most abundant oxygenated-PAH observed (19 μg km^{-1}) which is consistent with the SRM 1650 analysis. Manchester- Nesvig et al. observed perinaphthenone as a component of ambient PM in southern California.[4] As a whole the aromatic carbonyls account for less than 4% of the total carbonyl emissions.

Both aromatic and aliphatic dicarbonyls are observed in the 56K HDV emissions. The two aromatic species observed are naphthalic anhydride and anthraquinone. Similar to the observation in the SRM 1650 analysis naphthalic anhydride was measured at higher levels than for anthraquinone. The aliphatic dicarbonyls (C_2-C_6) are dominated by methyl glyoxal. Methyl glyoxal is the most abundant carbonyl observed, and was measured at ~7-times higher emission rates than for glyoxal. This ratio (7) between methyl glyoxal and glyoxal is similar to that observed for SRM 1650 (10). The dicarbonyls, both aliphatic and aromatic, comprise 41% of the particulate carbonyl emissions in the 56K HDV sample.

In general the carbonyls account for a smaller percentage of the PM emissions for the HDV than is observed for the LDV. Using bulk data from Robert et al. the particulate carbonyls comprise 0.8% of the 56K HDV PM mass. When considering particulate organic carbon the carbonyls are 2.3% of the emitted mass. These values are roughly one-half the values observed for the LEV and one-fifth of the TWC values.

Table XXV: HDV Carbonyl Emission Factors: Mass per Distance Traveled

HDV Particulate Carbonyl Emission Factors: Mass per Distance Traveled

Compound	Emission Rate (μg km^{-1}) [a] ’99 Frtlnr 56K	Notes: [b-e]
aliphatic aldehydes		
propanal	91 ± 22	b
butanal	220 ± 50	b
isobutanal	9.2 ± 2.2	b
pentanal	77 ± 18	b
hexanal	240 ± 60	b
heptanal	15 ± 1	b
octanal	16 ± 1	c
nonanal	55 ± 4	c
decanal	35 ± 3	c
undecanal	det	
aliphatic ketones		
3-pentanone	2.8 ± 1.1	b
2-pentanone	5.0 ± 2.0	b

2-hexanone	51 ± 21	b
unsaturated aliphatics		
acrolein	29 ± 5	b
methacrolein	0.2 ± 0.04	b
methyl vinyl ketone	15 ± 3	b
crotonaldehyde	18 ± 3	b
3-Me-2-butenal	5.3 ± 0.6	b
t-2-hexenal	1.6 ± 0.2	b
4-hexen-3-one	2.5 ± 0.3	b
cyclic aliphatics		
3-Me-2-cyclopentenone	4.3 ± 0.5	b
2-cyclohexenone	1.4 ± 0.2	b
aliphatic dicarbonyls		
glyoxal	73 ± 6	b
methyl glyoxal	490 ± 40	b
2,4-pentanedione	0.9 ± 0.007	b
2,3-hexanedione	3.9 ± 0.2	b
2,5-hexanedione	48 ± 2	b
aromatic aldehydes		
benzaldehyde	17 ± 4	b
o- & m-tolualdehyde	0.9 ± 0.2	b
p-tolualdehyde	1.2 ± 0.3	b
aromatic ketones		
acetophenone	0.8 ± 0.2	b
9-fluorenone	11 ± 2	c
benzophenone	9.0 ± 2.0	d,e
perinaphthenone	19 ± 4	d,e
xanthone	2.2 ± 0.5	d,e
aromatic dicarbonyls		
anthraquinone	10 ± 0.4	d,e
1,8-naphthalic anhydride	59 ± 3	d,e

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of 2-F-benzaldehyde, [c] Corrected for recovery of 8-F-1-benzosuberone, [d] Corrected for recovery of 4-F-benzophenone, [e] Compound was quantified in its underivatized form

As indicated previously the emission factors for the idle/creep sample are not generated on distance-traveled basis due to the small number of miles driven. Therefore in order to compare the idle/creep sample to the 56K sample emission factors are generated on a fuel consumption basis. The fuel consumption emission factors are presented in Table XXVI. A brief discussion follows comparing the HDV emission samples, with a more thorough comparison provided in Section 5.

In general the same aliphatic carbonyls are observed in the idle/creep emissions as in the HDV 56K sample. However there are significantly more aromatic species observed and quantified in the 56K sample in relation to the idle/creep emissions. This result does not agree with those of Fraser et al. that observed fluorenone and xanthone in similar amounts for HDV vehicles operated under transient and idle conditions.[12] The source of this discrepancy is not immediately obvious.

For carbonyls that are measured in both HDV samples the emissions of most species are typically 4-fold higher in the idle/creep emissions versus the 56K sample. However methyl glyoxal, which is the most abundant carbonyl in the 56K HDV sample, is emitted in the idle/creep emissions at less than twice the rate as the transient cycle emissions on the basis of emissions per unit of fuel consumed. The three most abundant carbonyl species (butanal, hexanal and methyl glyoxal) are consistent between the two HDV samples with the only difference being the order of abundance.

Table XXVI: HDV Carbonyl Emission Factors: Mass per Fuel Consumed

HDV Particulate Carbonyl Emission Factors: Mass per Fuel Consumed

	Emission Rate (μg L^{-1} fuel burned) [a]		
Compound	Idle/Creep	'99 Frtlnr 56K	Notes: [b-e]
aliphatic aldehydes			
propanal	550 ± 130	210 ± 50	b
isobutanal	120 ± 30	21 ± 5	b
butanal	2100 ± 500	500 ± 120	b
pentanal	560 ± 130	170 ± 40	b
hexanal	1400 ± 340	540 ± 130	b
heptanal	120 ± 7	33 ± 2	b
octanal	110 ± 8	35 ± 3	c
nonanal	200 ± 15	120 ± 9	c
decanal	140 ±10	80 ± 6	c
undecanal		det	
aliphatic ketones			
2-butanone	410 ± 170		b
3-pentanone	19 ± 8	6.3 ± 2.6	b
2-pentanone		11 ± 5	b
2-hexanone	400 ± 160	110 ± 50	b
unsaturated aliphatics			
acrolein	230 ± 40	65 ± 12	b
methacrolein	14 ± 3	0.5 ± 0.1	b
methyl vinyl ketone	120 ± 20	33 ± 6	b
crotonaldehyde	170 ± 30	41 ± 8	b
t-2-Me-2-butenal	5.9 ± 0.7		b
3-Me-2-butenal	54 ± 7	12 ± 1	b
t-2-hexenal		3.6 ± 0.4	b
4-hexen-3-one	30 ± 4	5.7 ± 0.7	b
cyclic aliphatics			
2-Me-2-cyclopentenone	2.1 ± 0.3		b
3-Me-2-cyclopentenone	35 ± 4	9.7 ± 1.2	b
2-cyclohexenone	det	3.3 ± 0.4	b

aliphatic dicarbonyls			
glyoxal	410 ± 30	170 ± 10	b
methyl glyoxal	1900 ± 150	1100 ± 90	b
2,4-pentanedione		2.1 ± 0.2	b
2,3-hexanedione	det	8.7 ± 0.4	b
2,5-hexanedione	430 ± 20	110 ± 5	b
aromatic aldehydes			
benzaldehyde	88 ± 22	38 ± 10	b
o- & m-tolualdehyde		1.9 ± 0.5	b
p-tolualdehyde		2.8 ± 0.7	b
aromatic ketones			
acetophenone	23 ± 5	1.8 ± 0.4	b
9-fluorenone		24 ± 5	c
benzophenone	det	20 ± 5	d,e
perinaphthenone		43 ± 10	d,e
xanthone		5.1 ± 1.1	d,e
aromatic dicarbonyls			
anthraquinone		21 ± 1	d,e
1,8-naphthalic anhydride		133 ± 6	d,e

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of 2-F-benzaldehyde, [c] Corrected for recovery of 8-F-1-benzosuberone, [d] Corrected for recovery of 4-F-benzophenone, [e] Compound was quantified in its underivatized form

4.2.2 Organic Acids

A total of 17 organic acids species are observed in the HDV particulate emissions. Emission factors on a distance-traveled basis are presented in Table XXVII and for fuel consumption in Table XXVIII. Due to the small number of miles driven in the idle/creep sample (3.2 miles) emission factors are not presented on a distance-traveled basis, but are provided for fuel consumption. The description that follows addresses the distance traveled emission factors. The ions used for quantification of each of the acid species identified are presented in Appendix K, and instrumental detection limits are presented in Appendix L. The error range on each emission factors is based on the recovery %RSD of a similar compound obtained in the model analyte recovery experiment (see Section 2.3.4.1).

Thirteen of the 17 organic acids observed are n-alkanoic acids. The species observed span butanoic (C_4) to octadecanoic (C_{18}). As discussed earlier propanoic acid is observed but is not reported due to the high background levels that prevented accurate quantification. The acids show a decreasing abundance from hexanoic to nonanoic. For species with more than ten carbon atoms the even species are enriched in relation to the odd species, a result that was previously observed by Rogge et al.[10] The most abundant acid observed is dodecanoic followed by hexanoic, heptanoic, hexadecanoic and octadecanoic, which differ from those reported by Rogge et al. for HDV vehicles. The source of the discrepancy may lie in the differences in engine technology, fuel formulation, vehicle driving cycles or application of vehicle load weights in the current study.

The four species that are not n-alkanoic acids included oleic acid, benzoic acid, 4-methylbenzoic acid and phenol. Oleic acid and phenol are not present at quantifiable concentrations in the 56K HDV emissions. Benzoic acid and its 4-methyl substituted isomer are measured at similar concentrations, which is surprising. Usually the methyl-substituted species would be expected to exist at a level below that of the non-substituted parent, as observed for benzaldehyde and the tolualdehyde isomers. The emission rate at which benzoic acid is observed is approximately one-third of that reported by Rogge et al., while our value for 4-methylbenzoic acid is roughly four times higher. One possible explanation for the different observed emission rates is differences in the fuel formulations.

Using data for the bulk PM emissions, taken from Robert et al., the acids quantified for the 56K HDV emissions accounted for 0.7% of the total PM mass or 2.3% of the organic carbon mass. Thus these species are small contributors to the organic carbon and PM emissions for the HDV transient emissions sample evaluated.

Table XXVII: HDV Organic Acid Emission Factors: Mass per Distance Traveled

Organic Acid Emission Factors for HDV PM: Mass per Distance Traveled

	Emission Rate (ug km^{-1}) [a]	
Compound	’99 Frtlnr 56K	Notes: [b-e]
alkanoic		
butanoic acid	det	b
pentanoic acid	det	b
hexanoic acid	470 ± 130	b
heptanoic acid	120 ± 30	b
octanoic acid	25 ± 5	c
nonanoic acid	1.4 ± 0.3	c
decanoic acid	3.4 ± 0.6	c
dodecanoic acid	580 ± 110	c
tridecanoic acid	6.8 ± 1.0	c
tetradecanoic acid	70 ± 10	c
pentadecanoic acid	18 ± 3	d
hexadecanoic acid	120 ± 20	d
octadecanoic acid	95 ± 13	d
alkenoic		
oleic acid	det	d
aromatic		
benzoic acid	59 ± 4	e
4-methylbenzoic acid	56 ± 4	e
phenols		
phenol	det	e

[a] Analytes that were observed with a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of d_{11} hexanoic acid, [c] Corrected for recovery of $^{13}C_1$ dodecanoic acid, [d] Corrected for recovery of d_{35} octadecanoic acid, [e] Corrected for recovery of d_5 benzoic acid

As indicated previously the emission factors for the idle/creep sample are not generated on distance-traveled basis due to the small number of miles driven. Therefore in order to compare the idle/creep sample to the 56K sample emission factors are generated for fuel consumption. The fuel consumption emission factors are presented in Table XXVIII. A brief discussion follows comparing the HDV emission samples with respect to the organic acids and phenols observed, with a more thorough comparison provided in Section 5 between both LDV and HDV vehicles.

Table XXVIII: HDV Organic Acid Emission Factors: Mass per Fuel Consumed

Organic Acid Emission Factors for HDV PM: Mass per Fuel Consumption

	Emission Rate (μg L^{-1} fuel burned) [a]		Notes: [b-e]
Compound	Idle / Creep	'99 Frtlnr 56K	
alkanoic			
butanoic acid	det	det	b
pentanoic acid	19000 ± 5100	det	b
hexanoic acid	1200 ± 320	1100 ± 290	b
heptanoic acid	210 ± 57	270 ± 74	b
octanoic acid	10 ± 2	55 ± 11	c
nonanoic acid	det	3.2 ± 0.6	c
decanoic acid	det	7.7 ± 1.4	c
dodecanoic acid	440 ± 83	1300 ± 250	c
tridecanoic acid		15 ± 2	c
tetradecanoic acid	380 ± 56	160 ± 23	c
pentadecanoic acid		40 ± 6	d
hexadecanoic acid	3700 ± 550	270 ± 40	d
octadecanoic acid	2700 ± 350	220 ± 30	d
alkenoic			
oleic acid	1200 ± 160	det	d
aromatic			
benzoic acid	55 ± 4	130 ± 10	e
4-methylbenzoic acid		130 ± 10	e
phenols			
phenol	11 ± 4	det	e

[a] Analytes that were observed with a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of d_{11} hexanoic acid, [c] Corrected for recovery of $^{13}C_1$ dodecanoic acid, [d] Corrected for recovery of d_{35} octadecanoic acid, [e] Corrected for recovery of d_5 benzoic acid

Many of the same organic acids observed in the 56K HDV emissions are also present in the idle/creep emissions. Eleven of the fourteen species in the idle/creep emissions are n-alkanoic acids. The biggest difference between the idle/creep emissions and the 56K emissions is the large amount of pentanoic acid observed for the idle/creep sample. This species was by far the most abundant organic acid in the idle/creep emissions. Other differences between the idle/creep sample versus the 56K sample are the enrichment of the C_{14}, C_{16} and C_{18} acids.

Specifically hexadecanoic and octadecanoic are measured at emission rates more than an order of magnitude greater than for the 56K sample. It is possible that these species were present in the ambient air during the emissions testing and drawn into the engine where they were less efficiently destroyed during combustion at the lower engine temperatures of the idle/creep sample. Additional differences included the absence of the tridecanoic and pentadecanoic acid species in the idle/creep emissions. The source of this discrepancy is unknown.

The three species that are not n-alkanoic acids are oleic acid, benzoic acid and phenol. There are dramatic differences in the idle/creep emissions for both oleic acid and phenol in relation to the 56K emissions. Both oleic acid and phenol are observed below the limits of quantification in the 56K emissions, however both species are quantified in the idle/creep emissions with significant amounts of oleic acid. This observation may add further evidence to our hypothesis regarding the source of the elevated C_{16} and C_{18} alkanoic acid abundance in the idle/creep emissions. Benzoic acid in the idle/creep sample is measured at roughly one-half the emission rate observed for the 56K emissions.

A comparison to Rogge et al. is provided in Figure XVII for the HDV alkanoic acids. The comparison is shown for both linear and logarithmic axis scales. The correlation between the two data sets is poor. Even though the correlation is less than ideal there are similarities between the two data sets for certain alkanoic acid species. The likely source for this discrepancy once again is the differences in the vehicles, fuel formulations, driving cycles and vehicle load that were used in the different studies.

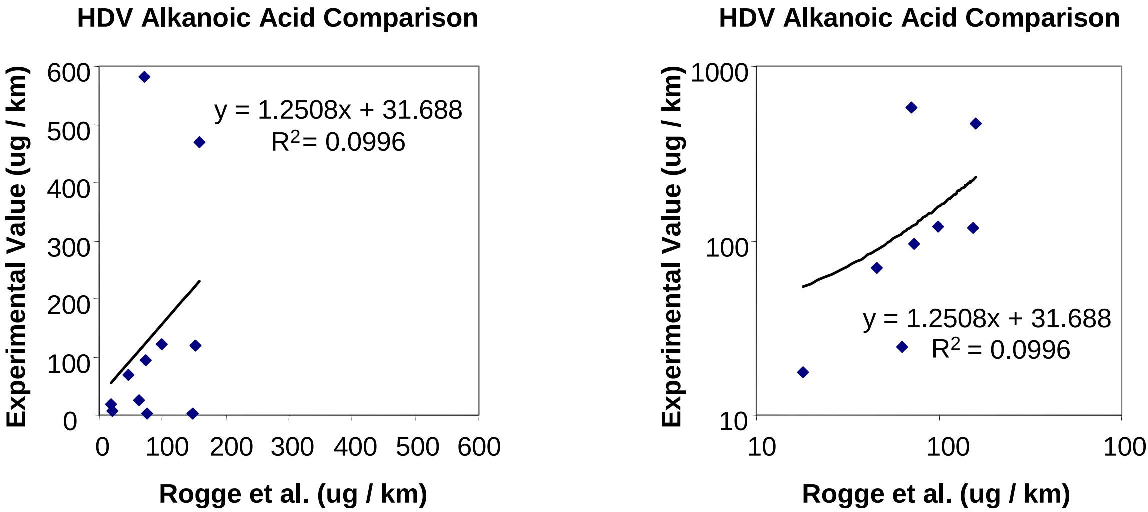


Figure XVII: Comparison of HDV Alkanoic Acids to Rogge et al.

4.2.3 PAHs

Polycyclic aromatic hydrocarbon results for the analysis of the HDV samples are given in terms of mass per distance in Table XXIX and in terms of mass of compound per liter of fuel in Table XXX. The following discussion is based on the mass per liter of fuel data. The same PAH species are observed in both samples with the exception of the MW 228 isomers, which are only observed in the 56K sample, and the two heavy PAHs benzo[ghi]perylene and coronene, which are only observed in the Idle/creep sample. Heavy PAHs made up 41% of the total PAH emissions for the Idle/creep sample while only 8% of the PAHs quantified in the 56K sample. Light PAHs with higher emission rates for the 56K sample than in the Idle/creep sample include phenanthrene, fluoranthene, and pyrene. The ratios of 56K emissions to Idle/creep emissions for these species are two, eight and five respectively. Benzo[e]pyrene is emitted at almost exactly the same rate for both HDV samples. The only other PAHs detected in both samples, benzo[a]pyrene and indeno[1,2,3-cd] pyrene, are observed in the HDV idle/creep sample at twice the emission rate of the 56K sample. Significantly different PAH profiles are obtained for the different operating conditions. Higher molecular weight PAHs, specifically benzo[ghi]perylene and coronene, are observed in the HDV idle/creep sample and not in the HDV 56K sample. Notably coronene is 5% of the total amount of PAHs quantified in the HDV idle/creep sample, this compound has been proposed as a tracer of LDV motor vehicle exhaust.[6, 38]

Table XXIX: HDV PAH Emission Factors: Mass per Distance Traveled

PAH Emission Factors for HDV PM: Mass per Distance

Compound	Emission Rate (μg km^{-1}) [a] '99 Ftrlnr 56K	Notes: [d-g]
phenanthrene	32 ± 4	d
anthracene		d
fluoranthene	17 ± 2	e
pyrene	25 ± 3	e
cyclopenta[cd]pyrene		e
MW 228 isomers [b]	21 ± 2	e
benzofluoranthene isomers [c]	det	e
benzo[e]pyrene	2.1 ± 0.2	f
benzo[a]pyrene	3.9 ± 0.4	f
perylene		f
indeno[1,2,3-cd]pyrene	1.70 ± 0.2	f
dibenz[a,h]anthracene		g
benzo[ghi]perylene	det	g
coronene		g
1-naphthol	0.54 ± 0.32	
2-naphthol	3.0 ± 0.4	
9-hydroxyfluorene	2.1 ± 0.3	

[a] Analytes that were observed with a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] The MW 228 isomers are the sum of chrysene, triphenylene and benz[a]anthracene, [c] The isomers are the sum of benzo[b]fluoranthene and benzo[k]fluoranthene, [d] Corrected for recovery of d_{10} phenanthrene, [e] Corrected for recovery of d_{12} chrysene, [f] Corrected for recovery of d_{12} benzo[k]fluoranthene, [g] Corrected for recovery of d_{12} benzo[ghi]perylene

Table XXX: HDV PAH Emission Factors: Mass per Fuel Consumed

PAH Emission Factors for HDV PM: Mass per Fuel Consumption

	Emission Rate (µg / L fuel burned) [a]		
Compound	Idle / Creep	'99 Frtlnr 56K	Notes: [d-g]
phenanthrene	30 ± 4	73 ± 9	d
anthracene			d
fluoranthene	4.6 ± 0.4	39 ± 4	e
pyrene	12 ± 1	56 ± 6	e
cyclopenta[cd]pyrene			e
MW 228 isomers [b]	det	47 ± 4	e
benzofluoranthene isomers [c]	1.1 ± 0.1	det	e
benzo[e]pyrene	4.6 ± 0.4	4.7 ± 0.4	f
benzo[a]pyrene	16 ± 1	8.8 ± 0.8	f
perylene			f
indeno[1,2,3-cd]pyrene	6.4 ± 0.6	3.9 ± 0.4	f
dibenz[a,h]anthracene			g
benzo[ghi]perylene	1.2 ± 0.1	det	g
coronene	4.0 ± 0.3		g
1-naphthol	1.5 ± 0.9	1.2 ± 0.7	
2-naphthol	2.6 ± 0.3	6.7 ± 0.8	
9-hydroxyfluorene		4.8 ± 0.6	

[a] Analytes that were observed with a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] The MW 228 isomers are the sum of chrysene, triphenylene and benz[a]anthracene, [c] The isomers are the sum of benzo[b]fluoranthene and benzo[k]fluoranthene, [d] Corrected for recovery of d_{10} phenanthrene, [e] Corrected for recovery of d_{12} chrysene, [f] Corrected for recovery of d_{12} benzo[k]fluoranthene, [g] Corrected for recovery of d_{12} benzo[ghi]perylene

Three hydroxy-PAHs are observed in the HDV emissions. The compounds observed are 1-naphthol, 2-naphthol and 9-hydroxyfluorene. These species are observed at lower emission rates than a majority of the PAHs measured. 2-Naphthol has higher emission rates versus 1-naphthol in both the Idle/creep and 56K HDV samples. 9-Hydroxyfluorene is observed in only the 56K sample. The emissions 2-naphthol are higher for the 56K sample versus the Idle/creep, while the emission rate for 1-naphthol is similar for the two samples.

A comparison of the particulate phase PAH emission rates of the HDV 56K sample with those reported by Rogge et al. is shown in Figure XVIII.[10] Good agreement is shown between the results of the two studies despite the fact, that of all classes of chemicals examine by Fraser et al. in HDV emissions, the greatest variability was observed in the emission rates of the PAHs.[12] The following compounds were evaluated in the comparison plot: phenanthrene, fluoranthene, pyrene, MW 228 isomers, benzo[a]pyrene, and benzo[e]pyrene.

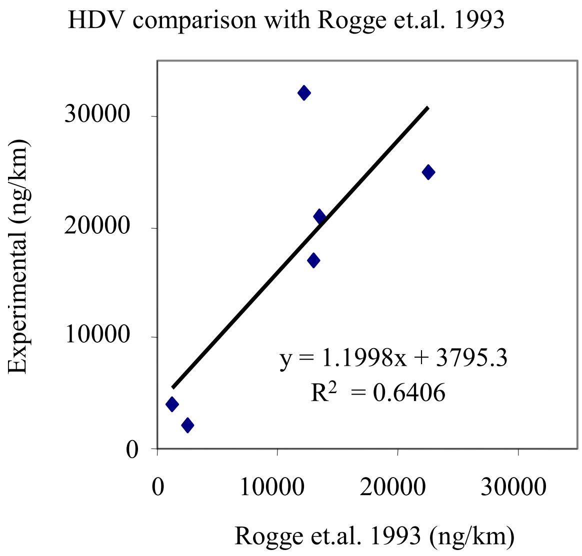


Figure XVIII: HDV PAH Comparison to Rogge et al.

5. Comparison Between Vehicle Types

5.1 Carbonyl Comparisons

Emission rates for the measured carbonyl species are calculated based on the compound emission mass divided by the amount of fuel consumed by the test vehicles during the entire test. These emission factors are presented in Table XXXI. A general trend is observed for the carbonyls on a fuel consumption basis. The carbonyl emissions are highest for the HDV idle/creep followed by the HDV 56K, TWC and finally the LEV. Emissions for the HDV samples are much greater in relation to the LDV samples. The HDV Idle/creep emissions are typically more than 10x greater than the LDV and ~4x greater than the HDV 56K. Many species have emission rates in the HDV idle/creep sample that are more than 100x greater than measured in the LEV emissions. No carbonyl species are observed with similar emission rates between the Idle/creep sample and 56K samples.

When examining the individual carbonyl species the ten highest emitted carbonyls, on a fuel consumption basis, are methyl glyoxal (35-1900 µg L^{-1}), butanal (26-2100 µg L^{-1}), hexanal (69-1400 µg L^{-1}), propanal (2.8-550 µg L^{-1}), pentanal (7.6-560 µg L^{-1}), glyoxal (7.9-410 µg L^{-1}), 2,5-hexanedione (4.1-430 µg L^{-1}), 2-hexanone (3.5-400 µg L^{-1}) 2-butanone (4.5-410 µg L^{-1}) and nonanal (1.3-200 µg L^{-1}). These are consistent between the LDV and HDV emissions with isolated exceptions. Slight differences are observed between the LEV and TWC emissions. LEV vehicles have higher octanal, nonanal, and decanal particulate emission rates than was measured for the TWC. Other speciation differences observed are more aromatic species in the HDV emissions versus the LDV. Examples include perinaphthenone, xanthone, anthraquinone and naphthalic anhydride, which are only observed in the HDV emissions. However benzoquinone is measured in the LDV emissions, but not in the HDV. Benzoquinone is the tenth most abundant carbonyl in the TWC PM emissions (16 µg L^{-1}) and the twelfth for the LEV (1.7 µg L^{-1}). Thus in general the major speciation differences are the greater abundance of aromatic species in the HDV emissions and the presence of benzoquinone in the LDV emissions.

Table XXXI: Carbonyl Emission Factor Comparison: Mass per Fuel

Particulate Carbonyl Emission Factors: Compound Mass Per Liter Fuel Consumed

	Emission Rate (µg / L fuel burned) [a]				
	LDV		HDV		
Compound	LEV	TWC	'99 Frtlnr 56K	Idle/creep	Notes: [b-e]
aliphatic aldehydes					
propanal	2.8 ± 0.7	26 ± 6	210 ± 50	550 ± 130	b
isobutanal	26 ± 6	92 ± 22	21 ± 5	120 ± 30	b
butanal	1.7 ± 0.4	5.9 ± 1.4	500 ± 120	2100 ± 500	b
pentanal	7.6 ± 1.8	34 ± 8	170 ± 40	560 ± 130	b
hexanal		69 ± 17	540 ± 130	1400 ± 340	b
heptanal	1.9 ± 0.1	2.9 ± 0.2	33 ± 2	120 ± 7	b
octanal	1.2 ± 0.1	0.56 ± 0.04	35 ± 3	110 ± 8	c
nonanal	4.0 ± 0.3	1.3 ± 0.1	120 ± 9	200 ± 15	c

decanal	2.3 ± 0.2		80 ± 6	140 ±10	c
undecanal			det		
aliphatic ketones					
2-butanone	4.5 ± 1.9	20 ± 8		410 ± 170	b
3-pentanone	0.15 ± 0.06	1.3 ± 0.5	6.3 ± 2.6	19 ± 8	b
2-pentanone			11 ± 5		b
2-hexanone	3.5 ± 1.5	29 ± 12	110 ± 50	400 ± 160	b
unsaturated aliphatics					
acrolein	0.44 ± 0.08	9.8 ± 1.8	65 ± 12	230 ± 40	b
methacrolein		0.72 ± 0.13	0.5 ± 0.1	14 ± 3	b
methyl vinyl ketone		7.4 ± 1.4	33 ± 6	120 ± 20	b
crotonaldehyde	1.5 ± 0.3	9.4 ± 1.7	41 ± 8	170 ± 30	b
t-2-Me-2-butenal	0.04 ± 0.01	0.43 ± 0.5		5.9 ± 0.7	b
3-Me-2-butenal	0.40 ± 0.05	1.3 ± 0.2	12 ± 1	54 ± 7	b
t-2-hexenal		0.73 ± 0.9	3.6 ± 0.4		b
4-hexen-3-one	0.29 ± 0.04	2.1 ± 0.3	5.7 ± 0.7	30 ± 4	b
cyclic aliphatics					
2-Me-2-cyclopentenone	0.09 ± 0.01	0.26 ± 0.03		2.1 ± 0.3	b
3-Me-2-cyclopentenone		1.2 ± 0.2	9.7 ± 1.2	35 ± 4	b
2-cyclohexenone	det	det	3.3 ± 0.4	det	b
aliphatic dicarbonyls					
glyoxal	7.9 ± 0.6	20 ± 2	170 ± 10	410 ± 30	b
methyl glyoxal	35 ± 3	120 ± 9	1100 ± 90	1900 ± 150	b
2,3-pentanedione	det	det			
2,4-pentanedione	det	det	2.1 ± 0.2		b
2,3-hexanedione	0.85 ± 0.04	0.61 ± 0.03	8.7 ± 0.4	det	b
2,5-hexanedione	4.1 ± 0.2	19 ± 1	110 ± 5	430 ± 20	b
aromatic aldehydes					
benzaldehyde		2.0 ± 0.5	38 ± 10	88 ± 22	b
o- & m-tolualdehyde	0.18 ± 0.04	0.71 ± 0.18	1.9 ± 0.5		b
p-tolualdehyde			2.8 ± 0.7		b
aromatic ketones					
acetophenone	0.19 ± 0.04	0.97 ± 0.22	1.8 ± 0.4	23 ± 5	b
9-fluorenone	0.26 ± 0.06	det	24 ± 5		c
benzophenone	0.65 ± 0.14	2.3 ± 0.5	20 ± 5	det	d,e
perinaphthenone			43 ± 10		d,e
xanthone			5.1 ± 1.1		d,e
aromatic dicarbonyls					
benzoquinone	1.7 ± 0.1	16 ± 1			b
anthraquinone			21 ± 1		d,e
1,8-naphthalic anhydride			133 ± 6		d,e

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of 2-F-benzaldehyde, [c] Corrected for recovery of 8-F-1-benzosuberone, [d] Corrected for recovery of 4-F-benzophenone, [e] Compound was quantified in its underivatized form

To provide another method of comparison carbonyl emission rates are calculated using the bulk PM emissions taken from Robert et al. The emission rates on a PM mass basis are displayed in Table XXXII. The general trend observed for the carbonyl emissions on the PM emission basis is that the TWC are greater than the LEV, HDV idle/creep and finally the HDV 56K. This general trend is observed for a majority of the measured carbonyls. Species that do not follow the general trend include nonanal, decanal, heptanal and acrolein. Note the elevated emission rates of octanal and nonanal in the LEV, versus the TWC, are also observed for emission rates based on fuel consumption. Based on these emission rates carbonyls are emitted as the largest percentage of the TWC emissions followed by the LEV, HDV idle/creep and HDV 56K.

The highest emission rates for individual carbonyls are observed in the same order as for the fuel consumption based emission factors. Methyl glyoxal was the most abundant carbonyl followed by butanal, hexanal, propanal, glyoxal and 2,5-hexanedione. Although more aromatic species are observed in the HDV emissions the compounds that were observed in both the LDV and HDV emissions were emitted at higher rates from the LDV due to the higher PM emissions of the HDV. The one aromatic species measured in only the LDV emissions, benzoquinone, is emitted at 1700 ppmm from the TWC and 500 ppmm from the LEV. The observed benzoquinone emission rates are much higher than the lone quinone species measured in the HDV emissions, anthraquinone at 42 ppmm in the HDV 56K emissions.

Table XXXII: Carbonyl Emission Factor Comparison: Mass per PM Mass

Carbonyl Emission Factors: Compound Mass Per PM Mass

	Emission Rate (pg µg^{-1} PM) [a]				
	LDV		HDV		
Compound	TWC	LEV	Idle/Creep	'99 Frtlnr 56K	Notes: [b-e]
aliphatic aldehydes					
propanal	2700 ± 650	800 ± 190	720 ± 170	410 ± 99	b
isobutanal	630 ± 150	500 ± 120	160 ± 39	42 ± 10	b
butanal	9800 ± 2300	7600 ± 1800	2800 ± 660	1000 ± 240	b
pentanal	3700 ± 870	2200 ± 530	740 ± 180	350 ± 83	b
hexanal	7300 ± 1800		1800 ± 430	1100 ± 260	b
heptanal	310 ± 23	540 ± 41	150 ± 12	67 ± 5	b
octanal	60 ± 4	350 ± 26	140 ± 11	71 ± 5	c
nonanal	140 ± 11	1200 ± 87	260 ± 20	250 ± 19	c
decanal		650 ± 49	180 ± 14	160 ± 12	c
undecanal				det	
aliphatic ketones					
2-butanone	2100 ± 850	1300 ± 540	540 ± 220		b
3-pentanone	140 ± 57	44 ± 18	24 ± 10	13 ± 5	b
2-pentanone				23 ± 9	b
2-hexanone	3100 ± 1300	1000 ± 420	530 ± 220	230 ± 94	b
unsaturated aliphatics					
acrolein	1000 ± 190	130 ± 24	300 ± 56	130 ± 24	b
methacrolein	76 + 14		19 ± 4	1 ± 0.2	b

methyl vinyl ketone	790 ± 150		160 ± 30	66 ± 12	b
crotonaldehyde	1000 ± 190	430 ± 81	220 ± 41	83 ± 16	b
t-2-Me-2-butenal	46 ± 6	13 ± 2	8 ± 1	24 ± 3	b
3-Me-2-butenal	140 ± 17	120 ± 14	71 ± 9	7 ± 1	b
t-2-hexenal	78 ± 9				b
4-hexen-3-one	220 ± 27	85 ± 10	40 ± 5	11 ± 1	b
cyclic aliphatics					
2-Me-2-cyclopentenone	27 ± 3	25 ± 3	3 ± 0.3		b
3-Me-2-cyclopentenone	130 ± 15		47 ± 6	19 ± 2	b
2-cyclohexenone	det	det	det	7 ± 1	b
aliphatic dicarbonyls					
glyoxal	2100 ± 170	2300 ± 180	540 ± 41	330 ± 26	b
methyl glyoxal	12000 ± 960	10000 ± 790	2500 ± 200	2200 ± 170	b
2,3-pentanedione	det	det			
2,4-pentanedione	det	det		4 ± 0.3	b
2,3-hexanedione	65 ± 3	250 ± 11	det	18 ± 1	b
2,5-hexanedione	2000 ± 95	1200 ± 56	560 ± 27	220 ± 10	b
aromatic aldehydes					
benzaldehyde	210 ± 53		120 ± 29	76 ± 19	b
o- & m-tolualdehyde	75 ± 19	52 ± 13		4 ± 1	b
p-tolualdehyde				6 ± 1	b
aromatic ketones					
acetophenone	100 ± 23	56 ± 13	31 ± 7	4 ± 1	b
9-fluorenone	det	75 ± 17		49 ± 11	c
benzophenone	240 ± 54	190 ± 42	det	41 ± 9	d,e
perinaphthenone				86 ± 19	d,e
xanthone				10 ± 2	d,e
aromatic dicarbonyls					
benzoquinone	1700 ± 79	500 ± 24			b
anthraquinone				42 ± 2	d,e
1,8-naphthalic anhydride				270 ± 13	d,e

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of 2-F-benzaldehyde, [c] Corrected for recovery of 8-F-1-benzosuberone, [d] Corrected for recovery of 4-F-benzophenone, [e] Compound was quantified in its underivatized form

Using the PM emission based carbonyl emission rates a comparison was made using the speciation data from the HDV 56K sample versus the results obtained from the analysis of NIST SRM 1650. The data for this comparison are provided in Table XXXIII. Many of the same species are observed in both samples at similar concentrations. It is rather surprising how little the carbonyl speciation differs between the two emission samples that were collected by different dilution techniques using different fuel formulations over 20 years apart.

Table XXXIII: Diesel Particulate Carbonyl Comparison: HDV 56K vs. NIST SRM 1650

HDV Particulate Carbonyls Comparison

	Concentration (ppmm) [a]	
Compound	HDV 56 K	NIST 1650
aliphatics	(pg μg^{-1} PM)	(ng mg^{-1})
propanal	410 ± 99	350
isobutanal	42 ± 10	110
butanal	1000 ± 240	1360
pentanal	350 ± 83	350
hexanal	1100 ± 260	1130
heptanal	67 ± 5	75
octanal	71 ± 5	35
nonanal	250 ± 19	130
decanal	160 ± 12	58
2-butanone		170
3-pentanone	13 ± 5	13
2-pentanone	23 ± 9	
2-hexanone	230 ± 94	190
acrolein	130 ± 24	130
methacrolein	1 ± 0.2	8
methyl vinyl ketone	66 ± 12	47
crotonaldehyde	83 ± 16	120
t-2-methyl-2-butenal	24 ± 3	6
3-methyl-2-butenal	7 ± 1	39
4-hexen-3-one	11 ± 1	21
cyclics / aromatics		
2-methyl-2-cyclopentenone		9
3-methyl-2-cyclopentenone	19 ± 2	det
2-cyclohexenone	7 ± 1	det
benzaldehyde	76 ± 19	63
o- & m-tolualdehyde	4 ± 1	7
p-tolualdehyde	6 ± 1	8
acetophenone	4 ± 1	5
perinaphthenone [b]	86 ± 19	440
9-fluorenone	49 ± 11	74
benzanthrone [b]		47
anthrone		det
benzophenone [b]	41 ± 9	det
xanthone [b]	10 ± 2	det
dicarbonyls		
glyoxal	330 ± 26	300
methyl glyoxal	2200 ± 170	2900
2,3-butanedione		15
2,3-hexanedione	18 ± 1	36

2,5-hexanedione	220 ± 10	310
2,3-pentanedione		det
2,4-pentanedione	4 ± 0.3	det
anthraquinone [b]	42 ± 2	50
1,8-naphthalic anhydride [b]	270 ± 13	740

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Compound was quantified in its underivatized form

Emission rates for carbonyls on a distance-traveled basis are presented in Table XXXIV. As indicated earlier the HDV idle/creep emissions are not calculated due to the small distance traveled during sample collection. As expected the HDV carbonyl emission rates are larger than the TWC and LEV samples. These HDV emission rates are typically more than 10x larger than the TWC emissions and ~100x greater than the LEV. Based on these emission rates one can generalize that one HDV operating under normal driving conditions emits as many carbonyls as at least 10 TWC vehicles and 100 LEV for equivalent distance traveled. This result indicates the efficiency with which the LEV and TWC operate in relation to the HDV, although it is understood that these vehicles serve different purposes in the modern transportation system.

Table XXXIV: Carbonyl Emission Factor Comparison: Mass per Distance

Particulate Carbonyl Emission Factors: Mass Per Distance Traveled

	Emission Rate [a]			
	LDV (ng km^{-1})		HDV (µg km^{-1})	
Compound	LEV	TWC	’99 Frtlnr 56K	Notes: [b-e]
aliphatic aldehydes				
propanal	300 ± 70	2500 ± 600	91 ± 22	b
butanal	2800 ± 680	8900 ± 2100	220 ± 50	b
isobutanal	190 ± 40	570 ± 140	9.2 ± 2.2	b
pentanal	810 ± 190	3300 ± 800	77 ± 18	b
hexanal		6700 ± 1600	240 ± 60	b
heptanal	200 ± 15	280 ± 21	15 ± 1	b
octanal	130 ± 10	54 ± 4	16 ± 1	c
nonanal	430 ± 33	130 ± 10	55 ± 4	c
decanal	240 ± 18		35 ± 3	c
undecanal			det	
aliphatic ketones				
2-butanone	480 ± 200	1900 ± 780		b
3-pentanone	17 ± 7	130 ± 52	2.8 ± 1.1	b
2-pentanone			5.0 ± 2.0	b
2-hexanone	380 ± 160	2800 ± 1100	51 ± 21	b
unsaturated aliphatics				
acrolein	48 ± 9	950 ± 180	29 ± 5	b
methacrolein		69 ± 13	0.2 ± 0.04	b
methyl vinyl ketone		720 ± 130	15 ± 3	b

crotonaldehyde	160 ± 30	900 ± 170	18 ± 3	b
t-2-Me-2-butenal	5 ± 0.6	42 ± 5		b
3-Me-2-butenal	43 ± 5	130 ± 16	5.3 ± 0.6	b
t-2-hexenal		71 ± 9	1.6 ± 0.2	b
4-hexen-3-one	32 ± 4	200 ± 25	2.5 ± 0.3	b
cyclic aliphatics				
2-Me-2-cyclopentenone	9 ± 1	25 ± 3		b
3-Me-2-cyclopentenone		120 ± 14	4.3 ± 0.5	b
2-cyclohexenone	det	det	1.4 ± 0.2	b
aliphatic dicarbonyls				
glyoxal	850 ± 66	1900 ± 150	73 ± 6	b
methyl glyoxal	3800 ± 290	11000 ± 870	490 ± 40	b
2,3-pentanedione	det	det		
2,4-pentanedione	det	det	0.9 ± 0.007	b
2,3-hexanedione	91 ± 4	59 ± 3	3.9 ± 0.2	b
2,5-hexanedione	440 ± 21	1800 ± 87	48 ± 2	b
aromatic aldehydes				
benzaldehyde		190 ± 48	17 ± 4	b
o- & m-tolualdehyde	19 ± 5	69 ± 17	0.9 ± 0.2	b
p-tolualdehyde			1.2 ± 0.3	b
aromatic ketones				
acetophenone	21 ± 5	94 ± 21	0.8 ± 0.2	b
9-fluorenone	28 ± 6	det	11 ± 2	c
benzophenone	69 ± 16	220 ± 50	9.0 ± 2.0	d,e
perinaphthenone			19 ± 4	d,e
xanthone			2.2 ± 0.5	d,e
aromatic dicarbonyls				
benzoquinone	190 ± 9	1500 ± 70		b
anthraquinone			10 ± 0.4	d,e
1,8-naphthalic anhydride			59 ± 3	d,e

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of 2-F-benzaldehyde, [c] Corrected for recovery of 8-F-1-benzosuberone, [d] Corrected for recovery of 4-F-benzophenone, [e] Compound was quantified in its underivatized form

5.2 Organic Acid Comparisons

As was done for the carbonyls emission rates are calculated based on the compound emission mass divided by the amount of fuel consumed by the test vehicles during the entire test. These emission factors are presented in Table XXXV. A general trend is observed with the acid emissions highest for the HDV idle/creep followed by the HDV 56K, TWC and finally the LEV. Exceptions to the general trend include octanoic acid (higher in HDV 56K versus idle/creep), nonanoic (higher in TWC versus HDV 56K), decanoic (lowest in HDV idle/creep), dodecanoic (much greater in HDV 56K versus idle/creep) and benzoic (HDV 56K double the idle/creep). Another general trend observed is the alkanoic acids with even carbon atoms are typically observed at higher levels than species containing an odd number of carbon atoms. This result has been previously reported for TWC and HDV emissions.[14, 32]

Few speciation differences are observed between the LDV and HDV emission. 4-Methylbenzoic acid is one compound only observed in the HDV 56K emissions. Pentanoic acid is only observed in the HDV samples and only quantified in the idle/creep emissions, where it was the most abundant acid measured. Both the LDV and HDV emissions are enriched in hexadecanoic and octadecanoic acid, consistent with previous studies. The odd carbon number acids above decanoic acid (tridecanoic and pentadecanoic) are only observed in the HDV 56K emissions. Oleic acid and phenol are observed in all the emission samples but were surprisingly measured at the lowest amounts in the HDV 56K emissions. Comparing the emission rates of nonanoic and decanoic acids in the LDV versus their aldehyde counterparts, nonanal and decanal, reveals that TWC emit higher levels of the acids while the LEV emit higher levels of the aldehydes. The origin of this difference is unknown. We did not observe the alkanedioic acids, C_4-C_{14}, in any of these emissions samples. This is not surprising as these species tend to be formed during secondary atmospheric processes.

Table XXXV: Acid Emission Factor Comparison: Mass per Fuel

Particulate Organic Acid Emission Factors: Compound Mass Per Liter Fuel Consumed

	Emission Rate (µg / L fuel burned) [a]				
Compound	LEV	TWC	HDV 56K	HDV Idle/Creep	Notes: [b-e]
alkanoic					
butanoic acid	4.6 ± 1.2	12 ± 3	det	det	b
pentanoic acid			det	19000 ± 5100	b
hexanoic acid	5.2 ± 1.4	14 ± 4	1100 ± 290	1200 ± 320	b
heptanoic acid	1.0 ± 0.3	3.8 ± 1.0	270 ± 74	210 ± 57	b
octanoic acid		1.6 ± 0.3	55 ± 11	10 ± 2	c
nonanoic acid	0.9 ± 0.2	5.7 ± 1.1	3.2 ± 0.6	det	c
decanoic acid	1.0 ± 0.2	3.8 ± 0.7	7.7 ± 1.4	det	c
dodecanoic acid	11 ± 2	44 ± 8	1300 ± 250	440 ± 83	c
tridecanoic acid			15 ± 2		c
tetradecanoic acid	0.7 ± 0.1	17 ± 3	160 ± 23	380 ± 56	c
pentadecanoic acid			40 ± 6		
hexadecanoic acid	16 ± 2	260 ± 40	270 ± 40	3700 ± 550	d
octadecanoic acid	1.2 ± 0.2	130 ± 17	220 ± 30	2700 ± 350	d
alkenoic					
oleic acid	11 ± 1	77 ± 10	det	1200 ± 160	d
aromatic					
benzoic acid	0.20 ± 0.01	2.7 ± 0.2	130 ± 10	55 ± 4	e
4-Me-benzoic acid			130 ± 10		
phenols					
phenol	1.0 ± 0.3	2.1 ± 0.8	det	11 ± 4	e

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of d_{11} hexanoic acid, [c] Corrected for recovery of $^{13}C_1$ dodecanoic acid, [d] Corrected for recovery of d_{35} octadecanoic acid, [e] Corrected for recovery of d_5 benzoic acid

Table XXXVI: Acid Emission Factor Comparison: Mass per PM Mass

Particulate Organic Acid Emission Factors: Compound Mass per Mass of PM

	Emission Rate (pg / µg PM) [a]				
Compound	TWC	LEV	HDV Idle/Creep	HDV 56K	Notes: [b-e]
alkanoic					
butanoic acid	1300 ± 350	1300 ± 360	det	det	b
pentanoic acid			25000 ± 6700	det	b
hexanoic acid	1400 ± 390	1500 ± 410	1600 ± 440	2100 ± 570	b
heptanoic acid	400 ± 110	290 ± 79	270 ± 74	550 ± 150	b
octanoic acid	170 ± 33		13 ± 3	110 ± 21	c
nonanoic acid	600 ± 110	260 ± 48	det	6 ± 1	c
decanoic acid	410 ± 77	290 ± 55	det	15 ± 3	c
dodecanoic acid	4700 ± 880	3300 ± 620	580 ± 110	2600 ± 500	c
tridecanoic acid				31 ± 5	c
tetradecanoic acid	1800 ± 270	200 ± 29	500 ± 74	320 ± 46	c
pentadecanoic acid				80 ± 12	
hexadecanoic acid	27000 ± 4000	4600 ± 680	4900 ± 730	540 ± 79	d
octadecanoic acid	14000 ± 1800	340 ± 44	3600 ± 470	430 ± 57	d
alkenoic					
oleic acid	8200 ± 1100	3200 ± 420	1600 ± 210	det	d
aromatic					
benzoic acid	290 ± 21	52 ± 4	72 ± 5	270 ± 20	e
4-Me-benzoic acid				260 ± 19	
phenols					
phenol	220 ± 80	280 ± 100	15 ± 5	det	e

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of d_{11} hexanoic acid, [c] Corrected for recovery of $^{13}C_1$ dodecanoic acid, [d] Corrected for recovery of d_{35} octadecanoic acid, [e] Corrected for recovery of d_5 benzoic acid

In order to provide another method of comparison organic acid emission rates are calculated using the bulk PM emissions from Robert et al. The emission rates on a PM mass basis are displayed in Table XXXVI. No general trend is observed for the acid emissions on the PM emission basis. Similar emission rates between the LDV and HDV were observed for hexanoic and heptanoic acid. Nonanoic, decanoic and dodecanoic acids are emitted in the greatest amounts from TWC followed by LEV, HDV 56K and the Idle/creep when based on PM emission rates. Tetradecanoic acid emissions rates are the largest from TWC and least from LEV. Hexadecanoic and octadecanoic acids are emitted at the highest rates from the TWC by a factor of five above any of the other emissions. Octadecanoic acid is emitted at approximately 50-60% of the hexadecanoic acid emissions for all samples except the LEV. This result is even more puzzling when considering that the emission rate of oleic acid for the LEV is nearly 10x greater than octadecanoic acid. This reduced octadecanoic acid concentration could not be explained. Benzoic acid is emitted at the highest rate from the TWC and HDV 56K emissions, approximately 4-5 fold higher than for the LEV and HDV Idle/creep emissions. This result becomes rather puzzling when considering that phenol is observed at similar levels to benzoic acid in the TWC emissions but is only detected in the HDV 56K sample. In conclusion the PM based emission rates do not yield consistent trends for the organic acids.

Using the PM emission based organic acid emission rate a comparison is made using the speciation data from the HDV 56K sample versus the results obtained from the analysis of NIST SRM 1650. The data for this comparison are provided in Table XXXVII. Many of the same species were observed in both samples. These data do not agree nearly as well as for the carbonyl comparison. One area of agreement is the relative abundance of octadecanoic acid versus hexadecanoic acid (~80% for both samples). Again it should be noted that the small alkanoic acids in the NIST SRM 1650 sample may be skewed due to the extraction efficiency correction for the low recovery of d_{11}-hexanoic acid.

Table XXXVII: Diesel Particulate Organic Acid Comparison:

HDV 56K vs. NIST SRM 1650

	Concentration (ppmm) [a]	
Compound	HDV 56K	NIST SRM 1650
aliphatics	(pg μg^{-1} PM)	(ng mg^{-1})
propanoic acid	det	38000
butanoic acid	det	
pentanoic acid	det	42000
hexanoic acid	2100 ± 570	200
heptanoic acid	550 ± 150	260
octanoic acid	110 ± 21	6.5
nonanoic acid	6 ± 1	22
decanoic acid	15 ± 3	15
dodecanoic acid	2600 ± 500	77
tridecanoic acid	31 ± 5	
tetradecanoic acid	320 ± 46	
pentadecanoic acid	80 ± 12	
hexadecanoic acid	540 ± 79	94
octadecanoic acid	430 ± 57	77
oleic acid	det	det
aromatics		
benzoic acid	270 ± 20	48
4-methylbenzoic acid	260 ± 19	
1-naphthoic acid		66
OH benzoic acid		26
phenol	det	4.8

[a] Analytes that were observed at a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det)

Emission rates for organic acids on a distance-traveled basis are presented in Table XXXVIII. As indicated earlier the HDV idle/creep emissions are not calculated due to the small distance traveled during sample collection. As expected the HDV acid emission rates are larger than for the TWC and LEV samples. These HDV emission rates are typically more than 10x larger than the TWC emissions and ~100x greater than the LEV. The elevated emission of the C_{14}, C_{16} and C_{18} alkanoic acids in the TWC versus the LEV is an interesting result.

Table XXXVIII: Acid Emission Factor Comparison: Mass per Distance

Particulate Organic Acid Emission Factors: Compound Mass Per Distance Traveled

	Emission Rate [a]			
	LDV (ng km^{-1})		HDDV (ug km^{-1})	
Compound	TWC	LEV	'99 Frtlnr 56K	Notes: [b-e]
alkanoic				
butanoic acid	1200 ± 320	490 ± 130	det	b
pentanoic acid			det	b
hexanoic acid	1300 ± 350	560 ± 150	470 ± 130	b
heptanoic acid	370 ± 100	110 ± 30	120 ± 30	b
octanoic acid	160 ± 30		25 ± 5	c
nonanoic acid	550 ± 100	100 ± 20	1.4 ± 0.3	c
decanoic acid	370 ± 70	110 ± 20	3.4 ± 0.6	c
dodecanoic acid	4300 ± 800	1200 ± 230	580 ± 110	c
tridecanoic acid			6.8 ± 1.0	c
tetradecanoic acid	1700 ± 250	70 ± 10	70 ± 10	c
pentadecanoic acid			18 ± 3	c
hexadecanoic acid	25000 ± 3700	1700 ± 250	120 ± 20	d
octadecanoic acid	13000 ± 1700	130 ± 20	95 ± 13	d
alkenoic				
oleic acid	7500 ± 980	1200 ± 150	det	d
aromatic				
benzoic acid	260 ± 20	20 ± 1	59 ± 4	e
4-Me-benzoic acid			56 ± 4	e
phenols				
phenol	200 ± 70	100 ± 40	det	e

[a] Analytes that were observed with a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] Corrected for recovery of d_{11} hexanoic acid, [c] Corrected for recovery of $^{13}C_1$ dodecanoic acid, [d] Corrected for recovery of d_{35} octadecanoic acid, [e] Corrected for recovery of d_5 benzoic acid

5.3 PAH Comparisons

Emission rates of the PAHs in LDV and HDV are calculated for fuel consumption in Table XXXIX. Observed speciation differences between the LDV and HDV include the measurement of cyclopenta[cd]pyrene, perylene and dibenz[a,h]anthracene in the LDV samples but not in the HDV emissions. For the light PAHs (MW = 228 or less) a general trend is observed where the emission rates are greatest for the HDV 56K sample and typically followed by the Idle/creep, TWC and finally LEV samples. The heavier PAH (MW > 228) show a different trend were the greatest emission rates are observed in the HDV Idle/creep sample and typically followed by the 56K, TWC and finally LEV emission rates. For PAH species that were observed in both LDV and HDV samples only the emission rates of the benzofluoranthene isomers and benzo[ghi]perylene in the TWC exceeds the rate for either HDV sample. It should be noted that the emission rate for coronene, a proposed LDV source apportionment tracer, was measured highest in the HDV Idle/creep emissions at nearly double the emission of the TWC and more than an order of magnitude larger than the LEV. This result casts a shadow of doubt as to the validity of source apportionment studies employing coronene as a unique LDV emission species.

Table XXXIX: PAH Emission Factor Comparison: Mass per Fuel

Particulate PAH Emission Factors: Mass per Fuel Consumed

	Emission Rate (µg / L fuel burned) [a]				
Compound	LEV	TWC	HDV Idle/Creep	HDV 56K	Notes: [d-g]
phenanthrene	1.1 ± 0.10	2.2 ± 0.3	30± 4	73 ± 9	d
anthracene	0.13 ± 0.02				d
fluoranthene	0.40 ± 0.04	0.76 ± 0.07	4.6 ± 0.4	39 ± 4	e
pyrene	0.78 ± 0.08	1.5 ± 0.2	12 ± 1	56 ± 6	e
cyclopenta[cd]pyrene	0.13 ± 0.02	0.35 ± 0.04			e
MW 228 isomers [b]		3.2 ± 0.2	det	47 ± 4	e
benzofluoranthene isomers [c]	0.60 ± 0.06	6.6± 0.6	1.1 ± 0.1	det	e
benzo[e]pyrene	0.30 ± 0.03	1.8 ± 0.2	4.6 ± 0.4	4.7 ± 0.4	f
benzo[a]pyrene	1.0 ± 0.1	5.6 ± 0.5	16 ± 1	8.8 ± 0.8	f
perylene	0.035 ± 0.003	0.20 ± 0.02			f
indeno[1,2,3-cd]pyrene	0.45 ± 0.05	3.0 ± 0.3	6.4 ± 0.6	3.9 ± 0.4	f
dibenz[a,h]anthracene	0.028 ± 0.001	0.18 ± 0.01			g
benzo[ghi]perylene	0.620 ± 0.05	4.4 ± 0.4	1.2 ± 0.1	det	g
coronene	0.33 ± 0.03	2.4 ± 0.2	4.0 ± 0.3		g
1-naphthol	0.8 ± 0.5	0.09 ± 0.05	1.5 ± 0.9	1.2 ± 0.7	
2-naphthol	1.1 ± 0.1	0.11 ± 0.01	2.6 ± 0.3	6.7 ± 0.8	
9-hydroxyfluorene				4.8 ± 0.6	

[a] Analytes that were observed with a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] The MW 228 isomers are the sum of chrysene, triphenylene and benz[a]anthracene, [c] The isomers are the sum of benzo[b]fluoranthene and benzo[k]fluoranthene, [d] Corrected for recovery of d_{10} phenanthrene, [e] Corrected for recovery of d_{12} chrysene, [f] Corrected for recovery of d_{12} benzo[k]fluoranthene, [g] Corrected for recovery of d_{12} benzo[ghi]perylene

Efforts to make alternative comparisons between the LDV and HDV emissions were made using emission rates expressed in terms of the total PM emissions for each sample. The PAH emission factors calculated as pg of PAH per µg of PM mass are presented in Table XL. Different trends are observed when the emission rates are expressed in this manner. The LEV emission rates of the light PAHs phenanthrene, fluoranthene, and pyrene are the largest followed by the TWC, HDV 56K and finally the Idle/creep. The emission rates for heavier PAHs (MW > 228) are typically the greatest for the TWC followed by the LEV, Idle/creep and finally the HDV 56K sample. The fact that the HDV emissions are lower is likely due to the much higher PM emission rates versus the LDV samples. In general the emission rates based on total PM emissions are much higher for the LDV in relation to the HDV.

Table XL: PAH Emission Factor Comparison: Mass per PM Mass

Particulate PAH Emission Factors: Compound Mass per PM Mass

	Emission Rate (pg / µg PM) [a]				
Compound	LEV	TWC	HDV Idle/Creep	HDV 56K	Notes: [d-g]
phenanthrene	320 ± 37	240 ± 28	40 ± 5	150 ± 17	d
anthracene	39 ± 5				d
fluoranthene	110 ± 11	81 ± 8	6 ± 0.6	78 ± 7	e
pyrene	230 ± 23	160 ± 17	15 ± 2	110 ± 11	e
cyclopenta[cd]pyrene	38 ± 4	37 ± 4			e
MW 228 isomers [b]		350 ± 26		95 ± 7	e
benzofluoranthene isomers [c]	170 ± 16	700 ± 65	1 ± 0.1		e
benzo[e]pyrene	87 ± 8	190 ± 17	6 ± 0.6	10 ± 1	f
benzo[a]pyrene	300 ± 27	600 ± 55	21 ± 2	18 ± 2	f
perylene	10 ± 1	21 ± 2			f
indeno[1,2,3-cd]pyrene	140 ± 13	320 ± 30	8 ± 1	8 ± 1	f
dibenz[a,h]anthracene	8 ± 0.3	20 ± 0.7			g
benzo[ghi]perylene	180 ± 15	470 ± 38	2 ± 0.1	det	g
coronene	94 ± 8	260 ± 21	5 ± 0.4		g
1-naphthol	230 ± 140	9.4 ± 5.6	1.9 ± 1.2	2.5 ± 1.5	
2-naphthol	320 ± 38	12 ± 2	3.4 ± 0.4	14 ± 2	
9-hydroxyfluorene				10 ± 1	

[a] Analytes that were observed with a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] The MW 228 isomers are the sum of chrysene, triphenylene and benz[a]anthracene, [c] The isomers are the sum of benzo[b]fluoranthene and benzo[k]fluoranthene, [d] Corrected for recovery of d_{10} phenanthrene, [e] Corrected for recovery of d_{12} chrysene, [f] Corrected for recovery of d_{12} benzo[k]fluoranthene, [g] Corrected for recovery of d_{12} benzo[ghi]perylene

The emission rate of the three measured hydroxy-PAHs have some interesting trends. When the emission factors are compared using fuel consumption the lowest emissions are measured for the TWC followed by the LEV, Idle/creep and finally 56K. This order changes when using the PM mass emission factors as the highest emissions are measured for the LEV followed by the 56K, TWC and the Idle/creep. These comparisons help illustrate the high emission rate of hydroxy-PAHs from the LEVs.

PAH emission rates based on distance traveled are presented in Table XLI. As indicated earlier Idle/creep emission rates are not determined due to the small number of miles driven during sample collection. The general trend for the PAH emission on a distance traveled basis are the largest being the HDV 56K followed by the TWC and LEV. These emission rates are typically more than 100x greater for the HDV 56K emissions versus the LEV for compounds observed in both samples. Also of note is that the difference in the emission rates between the TWC and LEV increases as the PAHs increase in molecular weight.

Table XLI: PAH Emission Factor Comparison: Mass per Distance

Particulate PAH Emission Factors: Compound Mass per Distance Traveled

	Emission Rate [a]			
	LDV (ng km^{-1})		HDV (μg km^{-1})	
Compound	LEV	TWC	'99 Frtlnr 56K	Notes: [d-g]
phenanthrene	120 ± 14	220 ± 25	32 ± 4	d
anthracene	14 ± 2			d
fluoranthene	42 ± 4	74 ± 7	17 ± 2	e
pyrene	83 ± 9	150 ± 15	25 ± 3	e
cyclopenta[cd]pyrene	14 ± 2	33 ± 4		e
MW 228 isomers [b]		310 ± 24	21 ± 2	e
benzofluoranthene isomers [c]	64 ± 6	640 ± 59	det	e
benzo[e]pyrene	32 ± 3	170 ± 16	2.1 ± 0.2	f
benzo[a]pyrene	110 ± 10	540 ± 50	3.9 ± 0.4	f
perylene	4.0 ± 0.5	19 ± 2		f
indeno[1,2,3-cd]pyrene	53 ± 5	290 ± 27	1.7 ± 0.2	f
dibenz[a,h]anthracene	3.0 ± 0.1	17 ± 1		g
benzo[ghi]perylene	66 ± 5	430 ± 35	det	g
coronene	35 ± 3	240 ± 19		g
1-naphthol	90 ± 50	8.6 ± 5.1	0.54 ± 0.32	
2-naphthol	120 ± 14	11 ± 1	3.0 ± 0.4	
9-hydroxyfluorene			2.1 ± 0.3	

[a] Analytes that were observed with a signal:noise ratio below 10:1 but above 3:1 are listed as detected (det), [b] The MW 228 isomers are the sum of chrysene, triphenylene and benz[a]anthracene, [c] The isomers are the sum of benzo[b]fluoranthene and benzo[k]fluoranthene, [d] Corrected for recovery of d_{10} phenanthrene, [e] Corrected for recovery of d_{12} chrysene, [f] Corrected for recovery of d_{12} benzo[k]fluoranthene, [g] Corrected for recovery of d_{12} benzo[ghi]perylene

6. Summary and Conclusions

Forty-three carbonyls were observed in the particulate emissions of LEV, TWC and HDV. Theses compounds were comprised of 10 aliphatic aldehydes (C_3-C_{11}), 6 unsaturated aliphatic aldehydes (C_3-C_6), 4 aliphatic ketones (C_4-C_6), 5 unsaturated aliphatic ketones (C_4-C_6), 4 aromatic aldehydes (C_7-C_8), 5 aromatic ketones (C_8-C_{13}), 6 aliphatic dicarbonyls (C_2-C_6) and 3 aromatic dicarbonyls (C_6-C_{14}). The thoroughness of this carbonyl speciation exceeds all previously reported particulate carbonyl emissions.

Emission factors were generated for the vehicle types evaluated in this study. Where possible emission rates were calculated using the vehicle distance traveled in addition to the emission rates determined for fuel consumption. In general the carbonyl emission rates were the lowest for the LEV (5-3800 ng km^{-1}, 0.04-35 µg L^{-1}) followed by the TWC (25-11000 ng km^{-1}, 0.26-120 µg L^{-1}), HDV 56K (0.2-490 µg km^{-1}, 0.5-1100 µg L^{-1}) and finally the HDV Idle/creep (2.1-2100 µg L^{-1}). The HDV Idle/creep emissions were typically more than 10x greater than the LDV and ~4x greater than 56K emissions. There are numerous species in the HDV Idle/creep emitted at more than 100x larger than observed for the LEV. No carbonyl species were observed with similar emission rates between the Idle/creep and 56K HDV samples.

In order to compare between all the emissions samples the emission factors based on fuel consumption were typically employed. Using these emission rates the following species are the typically the ten most abundant carbonyls observed, listed with the range of emission rates measured. Methyl glyoxal (35-1900 µg L^{-1}) is the most abundant carbonyl followed by butanal (26-2100 µg L^{-1}), hexanal (69-1400 µg L^{-1}), propanal (2.8-550 µg L^{-1}), pentanal (7.6-560 µg L^{-1}), glyoxal (7.9-410 µg L^{-1}), 2,5-hexanedione (4.1-430 µg L^{-1}), 2-hexanone (3.5-400 µg L^{-1}), 2-butanone (4.5-410 µg L^{-1}) and nonanal (1.3-200 µg L^{-1}). There are isolated instances where deviation is observed to this compound list.

Carbonyl speciation differences observed between the emission samples are as follows. LEV vehicles were found to emit octanal, nonanal, and decanal at higher rates in the particulate emissions than measured for the TWC. More aromatic species were observed in the HDV emissions versus the LDV. Specific examples include perinaphthenone (19 µg km^{-1}, 43 µg L^{-1}), xanthone (2.2 µg km^{-1}, 5.1 µg L^{-1}), anthraquinone (10 µg km^{-1}, 21 µg L^{-1}) and naphthalic anhydride (59 µg km^{-1}, 133 µg L^{-1}), which were only observed in the HDV 56K emissions. Benzoquinone was one aromatic carbonyl measured in the LDV emissions, but not in the HDV. Benzoquinone was the tenth most abundant carbonyl in the TWC emissions (1500 ng km^{-1}, 16 µg L^{-1}) and the twelfth for the LEV (190 ng km^{-1}, 1.7 µg L^{-1}). Thus in general the major speciation differences were the greater abundance of aromatic species in the HDV emissions and the presence of benzoquinone in the LDV emissions. Excellent agreement was observed for the carbonyl species and concentrations in the NIST 1650 SRM and the HDV 56K sample from this study, adding further confidence in our observed carbonyl speciation and emission rates.

The entire carbonyls were totaled for each of the emission samples for both distance and fuel emission rates. A comparison for the total carbonyl emission rates per distance traveled is presented in Figure XIX. Based on total carbonyls emitted per kilometer driven the TWC and HDV 56K emissions are roughly 4x and 140x greater than measured for the LEV. A similar comparison using the emission rates per fuel consumed is presented in Figure XX. This comparison yields emission rates for the TWC, HDV 56K and HDV Idle/creep samples that are approximately 5x, 35x and 90x times greater than measured for the LEV. These comparisons serve to display the broad range of carbonyl emission rates between the LDV and HDV.

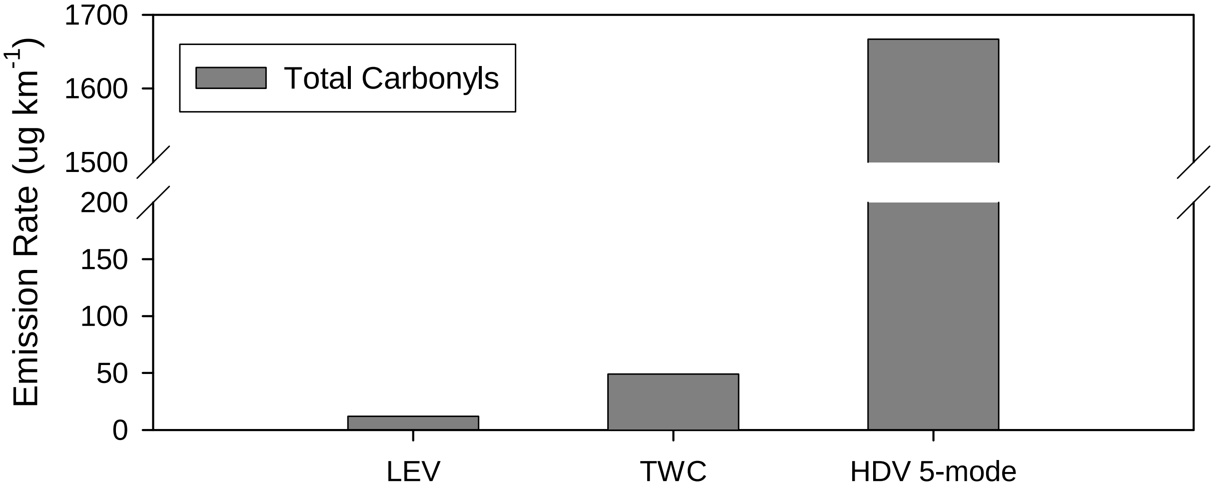


Figure XIX: Total Carbonyl Emission Rate Comparison: Mass per Distance

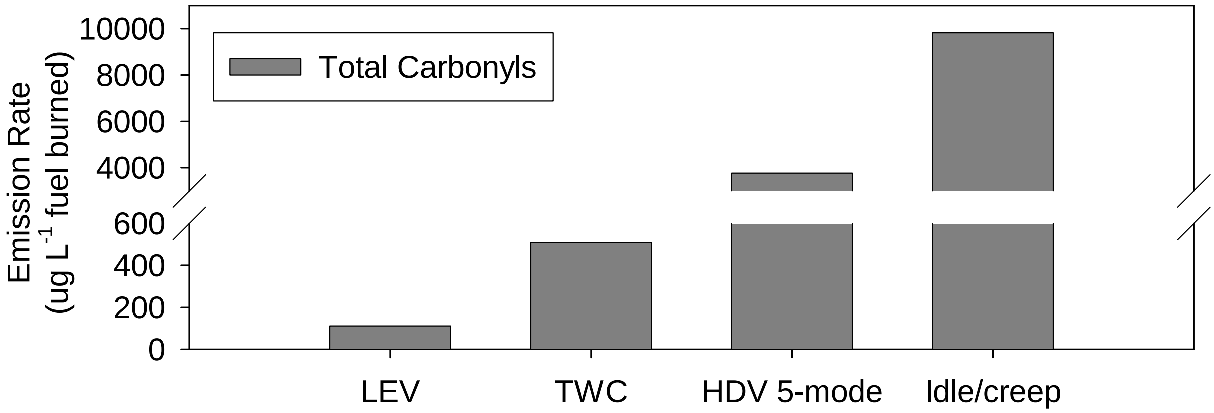


Figure XX: Total Carbonyl Emission Rate Comparison: Mass per Fuel

A total of 17 organic acids and phenol were observed in the PM emission samples. The acids consisted of 14 alkanoic acids (C_3-C_{18}), 1 alkenoic acid (C_{18}) and 2 aromatic acids (C_7-C_8). The acid speciation that was observed in this study is consistent with previously identified components of motor vehicle emission PM. The emission rates of the organic acids were typically lowest for the LEV (20-1700 ng km^{-1}, 0.7-16 µg L^{-1}) followed by the TWC (160-25000 ng km^{-1}, 1.6-260 µg L^{-1}), the HDV 56K (1.4-580 µg km^{-1}, 3.2-1300 µg L^{-1}) and finally the HDV Idle/creep (10-19000 µg L^{-1}).

Organic acid speciation differences were observed as follows. Alkanoic acids with an even number of carbon atoms were typically observed at higher emission rates than alkanoic acids containing an odd number of carbon atoms, with odd number acids above C_{10} only observed in the HDV 56K emissions. 4-Methylbenozoic acid was only observed in HDV 56K sample, at similar emission rates to benzoic acid. Similarly pentanoic acid was only measured in the HDV Idle/creep emissions, where it was the highest emitted species measured. Both LDV and HDV emissions were found enriched in hexadecanoic and octadecanoic acids, consistent with previous motor vehicle source measurements. One surprising result was the measurement of oleic acid and phenol at the lowest emission rates in the HDV 56K emission sample. Thus other than a few isolated differences the organic acid species observed were consistent between the LDV and HDV.

Organic acids and phenol were totaled for each of the emission samples for both distance and fuel emission rates. A comparison for the total acid emission rates per distance traveled is presented in Figure XXI. Based on the total acids/phenol emitted per kilometer driven the TWC and HDV 56K emissions are roughly 10x and 280x greater than measured for the LEV, which is nearly double the ratios observed for the total carbonyls. A similar comparison using the acid emission rates per fuel consumed is presented in Figure XXII. This comparison yields emission rates for the TWC, HDV 56K and HDV Idle/creep samples that are approximately 10x, 70x and 535x times greater than measured for the LEV. These comparisons serve to display the broad range of organic acid emission rates between the LDV and HDV, and the extreme differences in emission rates between the LEV and HDV Idle/creep.

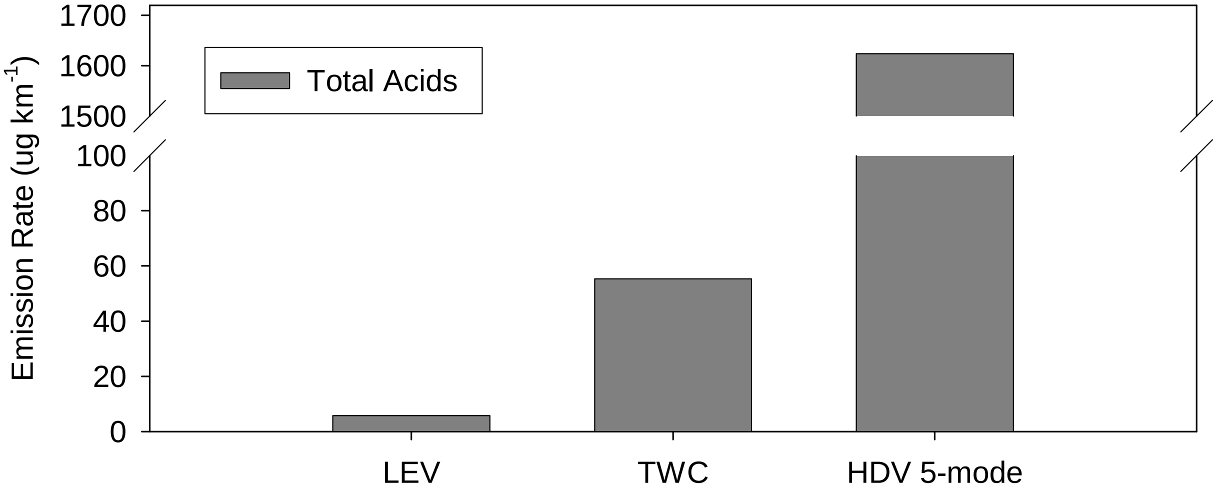


Figure XXI: Total Organic Acid Emission Rate Comparison: Mass per Distance

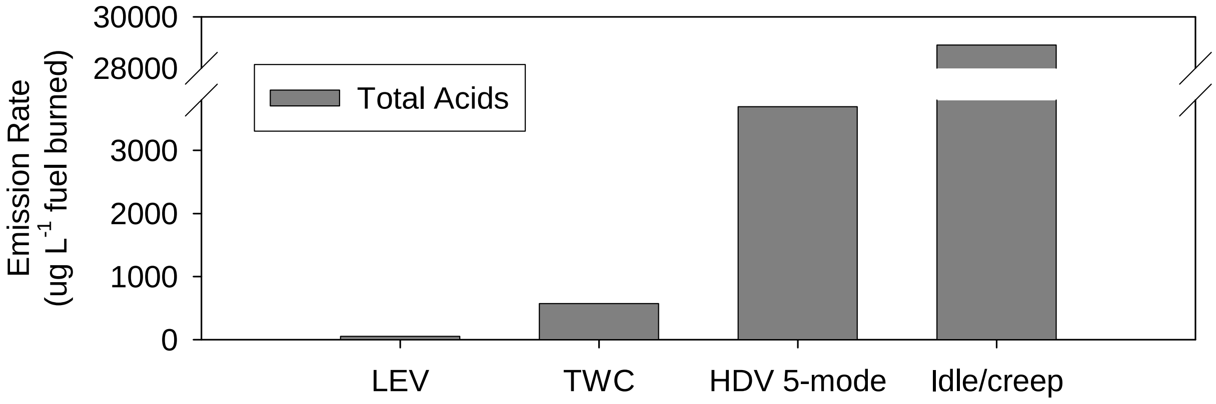


Figure XXII: Total Organic Acids Emission Rate Comparison: Mass per Fuel

The emission rates for all the oxygenated organics observed in this project were totaled. This total, as well as the totals for the carbonyls and acids, were then expressed in terms of the total PM mass and particulate organic carbon emissions for each test. These numbers are presented in Figure XXIII for the carbonyls, acids and total oxygenated organics. Interesting trends are observed for each of the PM emission samples.

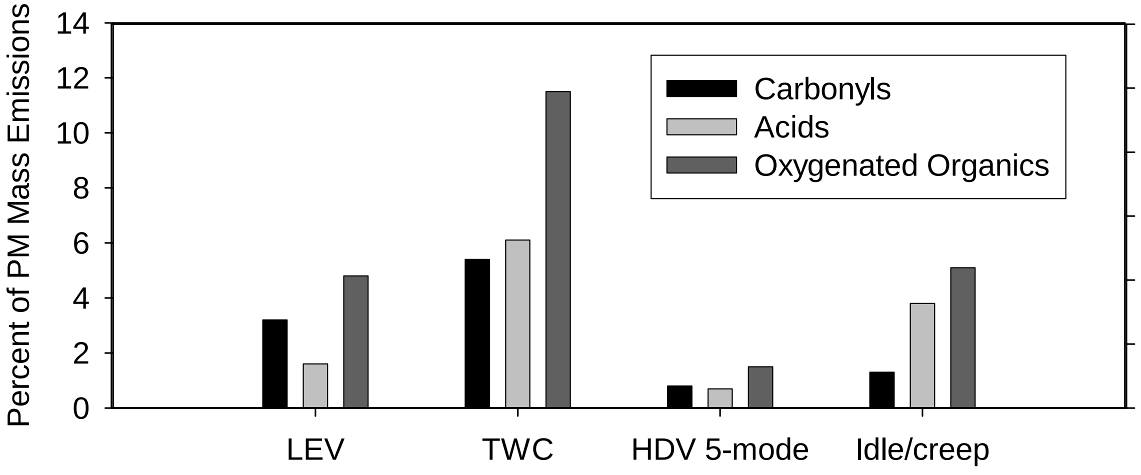


Figure XXIII: Oxygenated Organics as Percent of Particulate Emissions

The oxygenated organics contributed the greatest amount of mass to the TWC particulate emissions, followed by the LEV, HDV Idle/creep and finally HDV 56K. TWC vehicles emit carbonyls and organic acids at similar rates. Total TWC oxygenated organics comprise 12% of the PM mass and 25% of the particulate organic carbon. The LEVs were found to emit carbonyls at twice the rate of organic acid emissions. The total LEV oxygenated organics account for 5% of the PM mass and 11% of the particulate organic carbon. HDV Idle/creep emissions were observed enriched in organic acids relative to the carbonyls. Total Idle/creep oxygenated organic emissions account for 5% of PM and 10% of particulate organic carbon emissions. The HDV 56K emissions contained similar amounts of the carbonyls and organic acids. Oxygenated organics as a whole comprised only 2% of the PM and <5% of the particulate organic carbon emissions for the HDV 56K sample.

A total of 20 polycyclic aromatic compounds were measured in this study. These 20 species were composed of 17 PAHs (C_{14}-C_{24}) and 3 hydroxy-PAHs (C_{10}-C_{13}). The polycyclic aromatic compounds measured in this study are consistent with species reported in previous motor vehicle emissions characterizations. The measured emission rates of the polycyclic aromatic species were typically lower than those observed for the oxygenated organic compounds.

In general the fuel consumption emission rates for the polycyclic aromatics were lowest for the LEVs: (8-320 ng km^{-1}, 0.028-1.1 μg L^{-1}), followed by the TWCs: (20-1100 ng km^{-1}, 0.18-10 μg L^{-1}), HDV Idle/creep: (1.1-30 μg L^{-1}) and finally the HDV 56K: (8-150 μg km^{-1}, 3.9-73 μg L^{-1}). However, different trends were observed for different polycyclic aromatic species. The light PAHs were measured in the HDV 56K sample at more than 30x the emission rate of the LDV and ~2x greater than the Idle/creep. Typically the heavy PAHs emission rates were only slightly higher in the HDV emissions versus the LDVs. The five highest emitted PAHs were phenanthrene (1.1-73 μg L^{-1}), fluoranthene (0.40-56 μg L^{-1}), pyrene (0.78-56 μg L^{-1}), benzo[a]pyrene (1.0-16 μg L^{-1}), and indeno[1,2,3-cd]pyrene (0.45-6.4 μg L^{-1}). Note that the two naphthol isomers measured in this study are emitted from the LEVs at rates equivalent to the highest PAHs, but this not observed for the other PM emissions samples.

Differences in the chemical speciation measured include the following. Anthracene, cyclopenta[cd]pyrene, perylene and dibenz[a,h]anthracene were not observed in the HDV samples. More heavy PAHs were measured in the LDV versus the HDV emissions. 9-hydroxyfluorene was only detected in the HDV 56K emissions. Coronene was observed in the LDV and HDV Idle/creep emissions, but was not observed in the 56K sample. This result presents a problem, as coronene is a proposed LDV tracer for source apportionment modeling. The application of coronene as a unique LDV tracer may lead to overestimation of the contribution to ambient PM made by LDV emissions, and a corresponding underestimation of the contribution from HDV emissions.

The ability of the chemical analysis procedures described in this report to accurately measure carbonyls, organic acids and PAHs in motor vehicle emission samples was established. Through the application of multiple derivatization reactions in conjunction with GC-ITMS and MS-MS techniques it was possible to selectively examine each of our targeted compound classes. The sensitivity of our analysis methods facilitated the identification of more than 75 compounds in the PM emissions samples.

The results obtained in this project are viewed as successful. Numerous carbonyl species were identified in the particulate-phase for the first time. Of particular importance is the measurement of benzoquinone emission factors for both LEV and TWC vehicles. These emissions are of concern from the viewpoint of human health effects. Quinones have the ability to undergo redox cycling within the human body yielding numerous reactive oxygen species directly or indirectly. The risks posed by quinones to the human body should not be ignored.

The oxygenated organics identified in this project account for a significant portion of the PM emissions. This is most pronounced for the LDV where they accounted for 25 and 11%of the TWC and LEV particulate organic carbon emissions respectively. LEVs were found enriched in carbonyls in relation to organic acids, while the reverse was observed for the HDV

Idle/creep emissions. The TWC and HDV 56K samples had more equivalent emissions of carbonyls to organic acids.

A unique source apportionment tracer for either LDV or HDV emissions was not identified within the carbonyl, organic acid and PAH species measured in the current study. Furthermore, PAH species, i.e. coronene, were measured in HDV Idle/creep emissions that have been previously proposed as source tracers of LDV emissions. Benzoquinone was the only species identified that was unique to the gasoline combustion. However, benzoquinone can be formed via secondary atmospheric processes; excluding it from application as a source apportionment LDV tracer. Overall the project succeeded in identifying new particulate-phase carbonyls, advancing the mass apportionment of motor vehicle PM emissions and providing new data on proposed LDV source apportionment tracers.

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Appendix A: Authentic Standards

Table A.1: Carbonyl standards utilized in this project along with their source information

Compound	CAS Number	MW (g mol^{-1})	Vendor	Common Name
aliphatic ketones				
2-butanone	78-93-3	72.11	SA[1]	
2-pentanone	107-87-9	86.13	SA[1]	
3-pentanone	96-22-0	86.13	SA[1]	
2-hexanone	591-78-6	100.16	SA[1]	
2-heptanone	110-43-0	114.19	SA[1]	
2-octanone	111-13-7	128.22	SA[1]	
3-nonanone	925-78-0	142.24	SA[1]	
2-decanone	693-54-9	156.27	SA[1]	
2-undecanone	112-12-9	170.30	SA[1]	
6-undecanone	927-49-1	170.30	SA[1]	
2-tridecanone	593-08-8	198.35	SA[1]	
aliphatic aldehydes				
propanal	123-38-6	58.08	SA[1]	propionaldehyde
butanal	123-72-8	72.11	SA[1]	butyraldehyde
isobutanal	78-84-2	72.11	SA[1]	isobutyraldehyde
pentanal	110-62-3	86.13	SA[1]	valeraldehyde
isopentanal	590-86-3	86.13	SA[1]	isovaleraldehyde
hexanal	66-25-1	100.16	SA[1]	
heptanal	111-71-7	114.19	SA[1]	
octanal	124-13-0	128.22	SA[1]	
nonanal	124-19-6	142.24	SA[1]	
decanal	112-31-2	156.27	SA[1]	
undecanal	112-44-7	170.30	SA[1]	
dodecanal	112-54-9	184.32	SA[1]	
tridecanal	10486-19-8	198.35	SA[1]	
tetradecanal	124-25-4	212.37	SA[1]	
aliphatic dicarbonyls	0	0.00		
ethanedial	107-22-2	58.04	SA[1]	glyoxal
2-ketopropanal	79-98-8	72.06	SA[1]	methyl glyoxal
2,3-butanedione	431-03-8	86.09	SA[1]	diacetyl
1,3-cyclopentanedione	3859-41-4	98.10	SA[1]	
2,3-pentanedione	600-14-6	100.12	SA[1]	
2,4-pentanedione	123-54-6	100.12	SA[1]	
pentanedial	111-30-8	100.12	SA[1]	glutaric dialdehyde
2,3-hexanedione	3848-24-6	114.14	SA[1]	
3,4-hexanedione	4437-51-8	114.14	SA[1]	
2,5-hexanedione	110-13-4	114.14	SA[1]	acetonyl acetone

Table A.1: Cont.

5-Me-1,3-cyclohexanedione	4341-24-6	126.16	SA [1]	
3,5-heptanedione	7424-54-6	128.17	SA [1]	
3-Et-2,4-pentanedione	1540-34-7	128.17	SA [1]	
1-Ph-1,2-propanedione	579-07-7	148.16	SA [1]	
5-Ipr-1,3-cyclohexanedione	18456-87-6	154.21	SA [1]	
unsaturated aliphatic carbonyls				
2-propenal	107-02-8	56.06	SA [1]	acrolein
2-Me-2-propenal	78-85-3	70.09	SA [1]	methacrolein
2-butenone	78-94-4	70.09	SA [1]	methyl vinyl ketone
trans 2-butenal	123-73-9	70.09	SA [1]	crotonaldehyde
3-Me-2-butenal	107-86-8	84.12	SA [1]	
trans-2-Me-2-butenal	497-03-0	84.12	SA [1]	
2,4-hexadienal	142-83-6	96.13	SA [1]	sorbic aldehyde
trans-2-hexenal	6728-26-3	98.14	SA [1]	leaf aldehyde
5-hexen-2-one	109-49-9	98.15	SA [1]	
4-hexen-3-one	2497-21-4	98.15	SA [1]	
trans-4-decenal	65405-70-1	154.25	SA [1]	
hydroxy aliphatic carbonyls				
1-OH-acetone	116-09-6	74.08	SA [1]	acetol
1-OH-2-butanone	5077-67-8	88.11	SA [1]	
3-OH-2-butanone	513-86-0	88.11	SA [1]	
3-OH-3-Me-2-butanone	115-22-0	102.13	SA [1]	
4-OH-3-Me-2-butanone	3393-64-4	102.13	SA [1]	
5-OH-2-pentanone	1071-73-4	102.13	SA [1]	3-Ac-1-propanol
4-OH-4-Me-2-pentanone	123-42-2	116.16	SA [1]	
cyclic aliphatic carbonyls				
2-Me-2-cyclopenten-1-one	930-68-7	96.13	SA [1]	
3-Me-2-cyclopenten-1-one	1123-09-7	96.13	SA [1]	
2-cyclohexen-1-one	83-72-7	96.13	SA [1]	
3,5-Me-2-cyclohexen-1-one	1073-13-8	124.18	SA [1]	
4,4-Me-2-cyclohexen-1-one	1120-73-6	124.18	SA [1]	
aromatic aldehydes				
benzaldehyde	100-52-7	106.12	Acros [2]	
2-Me-benzaldehyde	529-20-4	120.15	SA [1]	o-tolualdehyde
3-Me-benzaldehyde	620-23-5	120.15	SA [1]	m-tolualdehyde
4-Me-benzaldehyde	104-87-0	120.15	SA [1]	p-tolualdehyde
3-Ph-2-propen-1-al	14371-10-9	132.16	SA [1]	trans-cinnamaldehyde
4-Et-benzaldehyde	4748-78-1	134.18	SA [1]	
2-Et-benzaldehyde	22927-13-5	134.18	SA [1]	
3,4-Me-benzaldehyde	5973-71-7	134.18	SA [1]	
2,4,6-Me-benzaldehyde	487-68-3	148.21	SA [1]	mesitaldehyde
4-formylbiphenyl	3218-36-8	182.22	SA [1]	4-biphenylcarboxaldehyde
2-formylfluorene	30084-90-3	194.23	SA [1]	2-fluorenecarboxaldehyde

Table A.1: Cont.

1-formylpyrene	3029-19-4	230.27	SA[1]	1-pyrenecarboxaldehyde
7-formylbenz[a]anthracene	7505-62-6	256.30	MRI[3]	
aromatic ketones	0	0		
methyl phenyl ketone	90-44-8	120.15	SA[1]	acetophenone
1-indanone	83-33-0	132.16	SA[1]	
2-indanone	615-13-4	132.16	SA[1]	
1-formylnaphthalene	66-77-3	156.18	SA[1]	1-naphthaldehyde
2-formylnaphthalene	66-99-9	156.18	SA[1]	2-naphthaldehyde
2-Et-1-indanone	98-86-2	160.22	SA[1]	
9-fluorenone	57653-14-2	180.21	SA[1]	
1H-phenalen-1-one	486-25-9	180.21	SA[1]	perinaphthenone
diphenyl ketone	548-39-0	182.22	SA[1]	benzophenone
9,10-dihydro-9-oxoanthracene	127-17-3	194.23	SA[1]	anthrone
oxoxanthene	90-47-1	196.21	SA[1]	xanthone
phenyl 3-tolyl ketone	643-65-2	196.25	SA[1]	3-Me-benzophenone
1,1-Ph-ethanal	947-91-1	196.25	SA[1]	diphenyl acetaldehyde
7H-benz[de]anthracen-7-one	82-05-3	230.27	SA[1]	benzanthrone
phenyl 4-biphenyl ketone	2128-93-0	258.32	SA[1]	4-benzoylbiphenyl
9,10-dihydrobenzo[a]pyren-7(8H)-one	3331-46-2	270.33	SA[1]	
aromatic dicarbonyls				
1,4-benzoquinone	106-51-4	108.10	SA[1]	
Me-benzoquinone	553-97-9	122.12	SA[1]	toluquinone
1,3-indandione	606-23-5	146.15	SA[1]	
1,4-naphthoquinone	130-15-4	158.15	SA[1]	
1,2-naphthoquinone	524-42-5	158.15	SA[1]	
1,2-diacetylbenzene	704-00-7	162.19	SA[1]	
1,3-diacetylbenzene	6781-42-6	162.19	SA[1]	
1,4-diacetylbenzene	1009-61-6	162.19	SA[1]	
2-Me-1,4-naphthoquinone	58-27-5	172.18	SA[1]	menadione
1,2-acenaphthylenedione	82-86-0	182.18	SA[1]	acenaphthenequinone
1,8-naphthalic anhydride	81-84-5	198.17	SA[1]	
anthracene-9,10-dione	84-65-1	208.21	SA[1]	anthraquinone
phenanthrene-9,10-dione	84-11-7	208.21	SA[1]	phenanthrenequinone
1,2-aceanthrylenedione	6373-11-1	232.23	SA[1]	aceanthrenequinone
4,4'-diacetylbiphenyl	787-69-9	238.29	SA[1]	
naphthacene-5,12-dione	1090-13-7	258.27	SA[1]	5,12-naphthacenequinone
benz[a]anthracene-3,4-dione	74877-25-1	258.27	MRI[3]	
benz[a]anthracen-7,12-dione	2498-66-0	258.27	SA[1]	1,2-benzanthraquinone
chrysene-1,2-dione	NA	258.28	MRI[3]	1,2-chrysenequinone
chrysene-1,4-dione	100900-16-1	258.28	SA[1]	1,4-chrysenequinone
benzo[a]pyrene-7,10-dione	71241-25-3	282.29	MRI[3]	
benzo[e]pyrene-4,5-dione	66788-08-7	282.29	MRI[3]	
pentacene-6,13-dione	3029-32-1	308.33	SA[1]	6,13-pentacenequinone

Table A.1: Cont.

hydroxy aromatic carbonyls				
2-OH-benzaldehyde	90-02-8	122.12	SA [1]	salicylaldehyde
3-OH-benzaldehyde	100-83-4	122.12	SA [1]	
4-OH-benzaldehyde	123-08-0	122.12	SA [1]	
2,3-OH-benzaldehyde	24677-78-9	138.12	SA [1]	
2,3,4-OH-benzaldehyde	2144-08-3	154.12	SA [1]	pyrogallolaldehyde
2-OH-1,4-naphthoquinone	2758-18-1	174.15	SA [1]	natural orange
2-OH-9-fluorenone	6949-73-1	196.20	SA [1]	
nitro carbonyls				
5-NO_2-2-furaldehyde	698-63-5	141.09	SA [1]	
2-NO_2-benzaldehyde	552-89-6	151.12	SA [1]	
3-NO_2-benzaldehyde	99-61-6	151.12	SA [1]	
-Internal Standards				
carbonyls				
d_6-benzaldehyde	17901-93-8	112.13	CIL [4]	
2-F-benzaldehyde	446-52-6	124.11	SA [1]	
4-F-benzaldehyde	459-57-4	124.11	SA [1]	
5-F-1-indanone	700-84-5	150.15	SA [1]	
6-F-4-chromanone	66892-34-0	166.15	SA [1]	
8-F-1-benzosuberone	24484-21-7	178.20	SA [1]	
2-F-9-fluorenone	343-01-1	198.19	SA [1]	
4-F-benzophenone	345-83-5	200.21	SA [1]	
dicarbonyls				
d_4-benzoquinone	2237-14-1	112.10	SA [1]	
hydroxy carbonyls				
$^{13}C_6$ 4-OH-benzaldehyde	NA	128.06	CIL [4]	
5'-F-2'-OH-acetophenone	394-32-1	154.14	SA [1]	

[1] Sigma-Aldrich Chemical Co., Inc., Milwaukee, WI

[2] Acros Organics, Geel, Belgium

[3] Midwest Research Institute, Kansas City, MO

[4] Cambridge Isotope Laboratories, Andover, MA

Table A.2: Organic acid and hydroxy-aromatic standards utilized in this project along with their source information

Compound	CAS Number	MW	Vendor	Common Name
		(g mol^{-1})		
alkanoic acids				
ethanoic acid	64-19-7	60.05	Fisher [1]	acetic acid
propanoic acid	79-09-4	74.08	SA [2]	propionic acid
butanoic acid	107-92-6	88.11	SA [2]	butyric acid
pentanoic acid	109-52-4	102.13	SA [2]	valeric acid
hexanoic acid	142-62-1	116.16	SA [2]	caproic acid
heptanoic acid	111-14-8	130.18	SA [2]	
octanoic acid	124-07-2	144.21	SA [2]	caprylic acid
nonanoic acid	112-05-0	158.24	SA [2]	
decanoic acid	334-48-5	172.26	SA [2]	capric acid
undecanoic acid	112-37-8	186.29	SA [2]	
dodecanoic acid	143-07-7	200.32	SA [2]	lauric acid
tridecanoic acid	638-53-9	214.34	SA [2]	
tetradecanoic acid	544-63-8	228.27	SA [2]	myristic acid
pentadecanoic acid	1002-84-2	242.40	SA [2]	
hexadecanoic acid	57-10-3	256.42	SA [2]	palmitic acid
heptadecanoic acid	506-12-7	270.45	SA [2]	margaric acid
octadecanoic acid	57-11-4	284.48	SA [2]	stearic acid
nonadecanoic acid	646-30-0	298.50	SA [2]	
eicosanoic acid	506-30-9	312.53	SA [2]	arachidic acid
alkenoic acids				
2-propenoic acid	79-10-7	72.06	SA [2]	acrylic acid
2-Me-2-propenoic acid	79-41-4	86.09	SA [2]	methacrylic acid
trans-3-hexenoic acid	1577-18-0	114.14	SA [2]	
cis-9-octadecenoic acid	112-80-1	282.46	SA [2]	oleic acid
hydroxy alkanoic acids				
1-OH-ethanoic acid	79-14-1	76.05	SA [2]	glycolic acid
aromatic acids				
benzoic acid	65-85-0	122.12	SA [2]	
4-Me-benzoic acid	99-94-5	136.15	SA [2]	p-toluic acid
4-Et-benzoic acid	619-64-7	150.17	SA [2]	
1-naphthoic acid	86-55-5	172.18	SA [2]	
9-fluorenecarboxylic acid	1989-33-7	210.23	SA [2]	
alkanedioic acids	0	0.00		
ethanedioic acid	144-62-7	90.03	SA [2]	oxalic acid
propanedioic acid	141-82-2	104.06	SA [2]	malonic acid
butanedioic acid	110-15-6	118.09	SA [2]	succinic acid

Table A.2: Cont.

pentanedioic acid	110-94-1	132.11	SA [2]	glutaric acid
hexanedioic acid	124-04-9	146.14	SA [2]	adipic acid
heptanedioic acid	111-16-0	160.17	SA [2]	pimelic acid
octanedioic acid	505-48-6	174.19	SA [2]	suberic acid
nonanedioic acid	123-99-9	188.22	SA [2]	azelaic acid
decanedioic acid	111-20-6	202.25	SA [2]	sebacic acid
undecanedioic acid	1852-04-6	216.27	SA [2]	
dodecanedioic acid	693-23-2	230.30	SA [2]	
tridecanedioic acid	505-52-2	244.33	SA [2]	
tetradecanedioic acid	821-38-5	258.35	SA [2]	
alkenedioic acids	0	0.00		
trans-2-butenedioic acid	110-17-8	116.07	SA [2]	fumaric acid
cis-2-butenedioic acid	110-16-7	116.07	SA [2]	maleic acid
cis-2-Me-2-butenedioic acid	498-23-7	130.1	SA [2]	citraconic acid
aromatic diacids	0	0		
1,2-benzenedicarboxylic acid	88-99-3	166.13	SA [2]	phthalic acid
1,3-benzenedicarboxylic acid	121-91-5	166.13	SA [2]	isophthalic acid
1,4-benzenedicarboxylic acid	100-21-0	166.13	SA [2]	terephthalic acid
hydroxyaromatic acids	0	0		
2-OH-benzoic acid	69-72-7	138.12	SA [2]	salicylic acid
3-OH-benzoic acid	99-06-9	138.12	SA [2]	
4-OH-benzoic acid	99-96-7	138.12	SA [2]	
nitro acids	0	0		
3,5-NO2-benzoic acid	99-34-3	212.12	SA [2]	
oxo-acids				
2-ketopropanoic acid	119-61-9	88.06	SA [2]	pyruvic acid
2-ketobutyric acid	600-18-0	102.09	SA [2]	
succinic semialdehyde	692-29-5	102.09	SA [2]	4-oxobutanoate
2-ketopentanoic acid	1821-02-9	116.12	SA [2]	2-oxopentanoate
3-Me-2-ketopentanoic acid	1460-34-0	130.14	SA [2]	3-Me-2-oxo-valeric acid
4-acetyl-butyric acid	3128-06-1	130.14	SA [2]	5-oxohexanoate
6-oxo-heptanoic acid	3128-07-2	144.17	SA [2]	
2-ketopentanedioic acid	328-50-7	146.1	SA [2]	2-ketoglutaric acid
7-oxo-octanoic acid	14112-98-2	158.2	SA [2]	
4-ketopimelic acid	502-50-1	174.15	SA [2]	
hydroxy aromatics	0	0		
phenol	108-95-2	94.11	SA [2]	
3,5-Me-phenol	108-68-9	122.16	SA [2]	
2-indanol	4254-29-9	134.18	SA [2]	
1-OH-naphthalene	90-15-3	144.17	SA [2]	1-naphthol
2-OH-naphthalene	135-19-3	144.17	SA [2]	2-naphthol
9-OH-fluorene	1689-64-1	182.22	SA [2]	9-fluorenol

Table A.2: Cont.

9-OH-phenanthrene	484-17-3	194.23	SA[2]	9-phenanthrol
1-OH-pyrene	5315-79-7	218.25	SA[2]	1-pyrenol
1-OH-benz[a]anthracene	69847-26-3	244.29	MRI[3]	
2-OH-chrysene	65945-06-4	244.29	MRI[3]	
11-OH-benzo[b]fluoranthene	NA	268.31	MRI[3]	
12-OH-benzo[a]pyrene	56892-33-2	268.31	MRI[3]	
3-OH-benzo[e]pyrene	77508-02-2	268.31	MRI[3]	
11-OH-benzo[g]chrysene	115187-66-1	294.35	MRI[3]	
3-OH-dibenz[a,h]anthracene	1421-80-3	294.35	MRI[3]	
-Internal Standards				
acids				
d_5 benzoic acid	1079-02-3	127.13	CIL[4]	
d_{11} hexanoic acid	95348-44-0	127.18	CIL[4]	
4-F-benzoic acid	456-22-4	140.11	SA[2]	
2-F-5-Me-benzoic acid	321-12-0	154.14	SA[2]	
$^{13}C_4$ octanoic acid	124-07-2	148.17	CIL[4]	
diacids				
$^{13}C_2$ succinic acid	110-15-6	120.07	CIL[4]	
hydroxy aromatics				
d_5 phenol	108-95-2	99.12	CIL[4]	
$^{13}C_6$ 3-hydroxyphenanthrene	NA	200.16	CIL[4]	

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[1] Fisher Chemicals, Fairlawn, NJ

[2] Sigma-Aldrich Chemical Co., Inc., Milwaukee, WI

[3] Midwest Research Institute, Kansas City, MO

[4] Cambridge Isotope Laboratories, Andover, MA

Table A.3: Polycyclic Aromatic Hydrocarbons utilized in this project along with their source information

Compound	CAS Number	MW	Vendor
		(g mol^{-1})	
anthracene	120-12-7	178.23	NIST [1]
phenanthrene	85-01-8	178.23	NIST [1]
fluoranthene	206-44-0	202.25	NIST [1]
pyrene	129-00-0	202.25	NIST [1]
cyclopenta[cd]pyrene	27208-37-3	226.27	AC [2]
benz[a]anthracene	56-55-3	228.29	NIST [1]
chrysene	218-01-9	228.29	NIST [1]
triphenylene	217-59-4	228.29	SA [3]
benzo[a]pyrene	50-32-8	252.31	NIST [1]
benzo[e]pyrene	192-97-2	252.31	NIST [1]
benzo[b]fluoranthene	205-99-2	252.31	NIST [1]
benzo[k]fluoranthene	207-08-9	252.31	NIST [1]
perylene	198-55-0	252.31	NIST [1]
dibenz[a,h]anthracene	53-70-3	278.35	NIST [1]
benzo[ghi]perylene	191-24-2	276.33	NIST [1]
indeno[1,2,3-cd]pyrene	193-39-5	276.33	NIST [1]
coronene	191-07-1	300.35	SA [3]
-Internal Standards			
d_{10} phenanthrene	1517-22-2	188.29	CIL [4]
d_{10} fluoranthene	93951-69-0	212.31	CIL [4]
d_{10} pyrene	1718-52-1	212.31	CIL [4]
d_{12} chrysene	1719-03-5	240.35	CIL [4]
d_{12} benzo[k]fluoranthene	93952-01-3	264.37	CIL [4]
d_{12} perylene	1520-96-3	264.37	CIL [4]
d_{12} benzo[ghi]perylene	93951-66-7	288.39	CIL [4]

[1] NIST SRM 1491 – aromatic compounds in hexane/toluene

[2] Accustandard Inc., New Haven, CT

[3] Sigma-Aldrich Chemical Co., Inc., Milwaukee, WI

[4] Cambridge Isotope Laboratories, Andover, MA

Appendix B: Carbonyl Standard Mixtures

Table B.1: Preparation of the aromatic carbonyl mixture

Compound	Initial Conc.	Volume Added	Mixture Conc.
	(ng μL^{-1})	(μL)	(ng μL^{-1})
benzaldehyde	50.4	2000	10.1
o-tolualdehyde	50.4		10.1
m-tolualdehyde	50.4		10.1
p-tolualdehyde	50.4		10.1
trans-cinnamaldehyde	50.1		10.0
3,4-Me-benzaldehyde	50.6		10.1
4-Et-benzaldehyde	49.9		10.0
2-Et-benzaldehyde	50.0		10.0
5-NO_2-2-furaldehyde	49.9		10.0
mesitaldehyde	50.2		10.0
2-NO_2-benzaldehyde	49.8		10.0
3-NO_2-benzaldehyde	50.2		10.0
acetophenone	50.0	2000	10.0
1-indanone	50.1		10.0
2-indanone	50.2		10.0
1-naphthaldehyde	50.0		10.0
2-naphthaldehyde	49.9		10.0
2-Et-1-indanone	50.3		10.1
9-fluorenone	49.9		10.0
perinaphthenone	50.2		10.0
benzophenone	50.3		10.1
4-biphenylcarboxaldehyde	50.2		10.0
anthrone	49.7		9.94
2-fluorenecarboxaldehyde	50.4		10.1
xanthone	49.9		10.0
3-Me-benzophenone	49.9		10.0
diphenyl acetaldehyde	50.4		10.1
benzanthrone	50.5		10.1
1-pyrenecarboxaldehyde	50.5		10.1
4-benzoylbiphenyl	50.4		10.1
9,10-dihydrobenzo[a]pyren-7(8H)-one	50.1		10.0
7-formylbenz[a]anthracene	98.6	1010	10.0

Table B.2: Preparation of the aliphatic carbonyl mixture

Compound	Initial Conc.	Volume Added	Mixture Conc.
	(ng μL^{-1})	(μL)	(ng μL^{-1})
propionaldehyde	49.8	2000	10.0
butyraldehyde	50.5		10.1
isobutyraldehyde	50.1		10.0
valeraldehyde	50.1		10.0
isovaleraldehyde	50.2		10.0
hexanal	50.3		10.1
heptaldehyde	50.1		10.0
octyl aldehyde	50.0		10.0
nonyl aldehyde	50.1		10.0
decyl aldehyde	50.3		10.1
undecyl aldehyde	1200	85	10.2
dodecyl aldehyde	1188	85	10.1
tridecyl aldehyde	1301	75	9.76
tetradecyl aldehyde	1228	80	9.82
2-butanone	50.5	2000	10.1
2-pentanone	50.3		10.1
3-pentanone	49.7		9.93
2-hexanone	50.1		10.0
2-heptanone	50.6		10.1
2-octanone	50.6		10.1
3-nonanone	50.0		10.0
2-decanone	49.7		9.94
2-undecanone	50.2		10.0
6-undecanone	50.8		10.2
2-tridecanone	50.3		10.1
acrolein	100	1000	10.0
crotonaldehyde	100		10.0
methacrolein	101		10.1
methyl vinyl ketone	100		10.0
3-Me-2-butenal	100		10.0
trans-2-Me-2-butenal	100		10.0
2,4-hexadienal	101		10.1
trans-2-hexenal	99.5		9.95
5-hexen-2-one	101		10.1
4-hexen-3-one	101		10.1
trans-4-decenal	100		10.0
3-Me-2-cyclopenten-1-one	49.9	2000	10.0
2-cyclohexen-1-one	50.0		10.0
3,5-Me-2-cyclohexen-1-one	49.7		9.94
4,4-Me-2-cyclohexen-1-one	50.3		10.1

Table B.3: Table B.2: Preparation of the dicarbonyl mixture

Compound	Initial Conc.	Volume Added	Mixture Conc.
	(ng μL^{-1})	(μL)	(ng μL^{-1})
glyoxal	50.6	2000	10.1
methyl glyoxal	49.9		10.0
2,3-butanedione	50.4		10.1
1,3-cyclopentanedione	49.9		10.0
2,4-pentanedione	49.5		9.9
2,3-pentanedione	50.1		10.0
glutaric dialdehyde	49.8		10.0
acetonylacetone	50.0		10.0
2,3-hexanedione	50.4		10.1
3,4-hexanedione	49.5		9.90
5-Me-1,3-cyclohexanedione	50.3		10.1
3,5-heptanedione	49.6		9.91
3-Et-2,4-pentanedione	50.4		10.1
1-Ph-1,2-propanedione	50.1		10.0
5-Ipr-1,3-cyclohexanedione	49.9		10.0
1,2-diacetylbenzene	50.3		10.1
1,3-diacetylbenzene	50.4		10.1
1,4-diacetylbenzene	50.6		10.1
4,4'-diacetylbiphenyl	49.8		10.0
1,4-benzoquinone	50.3	2000	10.1
Me-benzoquinone	50.0		10.0
1,3-indandione	49.9		10.0
1,4-naphthoquinone	50.3		10.1
1,2-naphthoquinone	50.4		10.1
2-Me-1,4-naphthoquinone	50.3		10.1
acenaphthenequinone	50.4		10.1
1,8-naphthalic anhydride	49.7		9.93
anthraquinone	50.0		10.0
phenanthrenequinone	50.4		10.1
aceanthrenequinone	44.8		9.0
1,4-chrysenequinone	50.0		10.0
5,12-naphthacenequinone	49.8		10.0
benz[a]anthracen-7,12-dione	50		10.0
6,13-pentacenequinone	96.4	1040	10.0
chrysene-1,2-dione	103	970	10.0
benz[a]anthracene-3,4-dione	99.4	1010	10.0
benzo[a]pyrene-7,10-dione	98.2	1020	10.0
benzo[e]pyrene-4,5-dione	94.5	1060	10.0

Appendix C: Organic Acid Calibration Mixture

Table C: Preparation of the organic acid calibration stock mixture

Compound	Individual Conc. (ng μL^{-1})	Volume Added (μL)	Calibration. Mix. Conc. (ng μL^{-1})
formic acid	48.8	1050	5.1
acetic acid	47.2		5.0
propanoic acid	49.7		5.2
butanoic acid	48.2		5.1
pentanoic acid	47.0		4.9
hexanoic acid	46.4		4.9
heptanoic acid	45.9		4.8
octanoic acid	46.5		4.9
nonanoic acid	43.1		4.5
decanoic acid	50.5		5.3
undecanoic acid	50.0		5.3
dodecanoic acid	49.4		5.2
tridecanoic acid	47.0		4.9
tetradecanoic acid	47.8		5.0
pentadecanoic acid	49.5		5.2
hexadecanoic acid	47.1		4.9
heptadecanoic acid	50.5		5.3
octadecanoic acid	48.6		5.1
oleic acid	49.0		5.1
nonadecanoic acid	54.9		5.8
trans-3-hexenoic acid	934	55	5.1
eicosanoic acid	1018	50	5.1
oxalic acid	98.8	500	4.9
malonic acid	101		5.1
butanedioic acid	103		5.2
pentanedioic acid	95.2		4.8
hexanedioic acid	105		5.2
heptanedioic acid	106		5.3
octanedioic acid	100		5.0
nonanedioic acid	104		5.2
decanedioic acid	103		5.1
undecanedioic acid	977	50	4.9
dodecanedioic acid	1064	50	5.3
1,11-undecanedicarboxylic acid	983	50	4.9
1,12-dodecanedicarboxylic acid	1041	50	5.2
phenol	192	260	5.0
3,5-Me-phenol	209	240	5.0

Table C: Cont.

2-indanol	431	120	5.2
DL-malic acid	98.6	500	4.9
fumaric acid	97.8		4.9
maleic acid	100		5.0
glycolic acid	104		5.2
glyoxylic acid	100		5.0
L-tartaric acid	99.1		5.0
pyruvic acid	127		6.3
citraconic acid	100		5.0
acrylic acid	105		5.3
methacrylic acid	102		5.1
benzoic acid	50.1	1000	5.0
p-toluic acid	50.1		5.0
4-Et-benzoic acid	49.7		5.0
salicylic acid	50.0		5.0
3-OH-benzoic acid	50.2		5.0
4-OH-benzoic acid	50.6		5.1
3,5-NO$_2$-benzoic acid	50.7		5.1
1-naphthoic acid	49.9		5.0
9-fluorenecarboxylic acid	50.7		5.1
phthalic acid	49.6		5.0
isophthalic acid	50.5		5.1
terephthalic acid	50.0		5.0

Appendix D: Hydroxy-PAH Calibration Mixture

Table D: Preparation of the hydroxylated polycyclic aromatic hydrocarbon calibration mixture

Compound	Stock Mix. Conc.	Volume Added	Calibration. Mix. Conc.
	(ng μL^{-1})	(μL)	(ng μL^{-1})
1-naphthol	105	500	5.25
2-naphthol	111		5.55
9-hydroxyfluorene	99.6		4.98
9-hydroxyphenanthrene	102		5.1
1-hydroxypyrene	102		5.1
1-hydroxyben[a]anthracene	111		5.55
2-hydroxychrysene	105.4		5.27
12-hydroxybenzo[a]pyrene	109.8		5.49
11-hydroxybenzo[b]fluoranthene	111.0		5.55
3-hydroxybenzo[e]pyrene	99.0		4.95
11-hydroxybenzo[g]chrysene	106.8		5.34

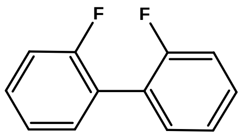
Appendix E: PAH Calibration Mixture

Table E: Preparation of the polycyclic aromatic hydrocarbon calibration stock mixture

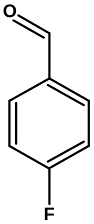
Compound	Individual Conc.	Volume Added	Calibration. Mix. Conc.
	(ng µL^{-1})	(µL)	(pg µL^{-1})
phenanthrene	7.01	400	1402
anthracene	7.82		1564
fluoranthene	5.91		1182
pyrene	5.89		1178
benz[a]anthracene	3.59		718
chrysene	7.03		1406
benzo[b]fluoranthene	5.25		1050
benzo[k]fluoranthene	5.57		1114
benzo[e]pyrene	5.62		1124
benzo[a]pyrene	6.79		1358
perylene	7.12		1424
indeno[1,2,3-cd]pyrene	6.29		1258
dibenz[a,h]anthracene	5.18		1036
benzo[ghi]perylene	5.29		1058
cyclopenta[c,d]pyrene	50	40	1000
triphenylene	10.18	200	1018
coronene	10.3	200	1030

Appendix F: Internal Standard Structures

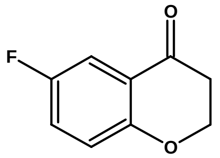
Carbonyl Quantification IS: Primary



2,2’-F-biphenyl

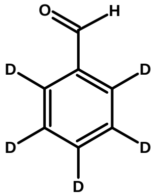


4-F-benzaldehyde

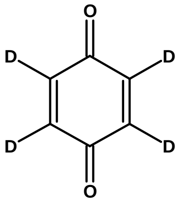


6-F-4-chromanone

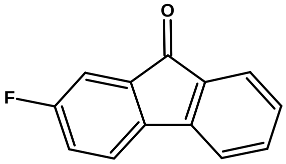
Carbonyl Quantification IS: Secondary



d_5-benzaldehyde

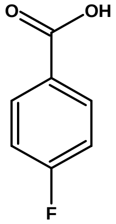


d_4-benzoquinone

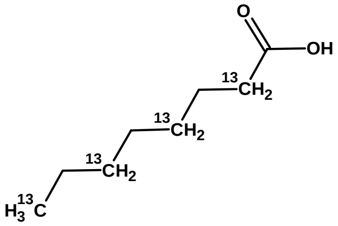


2-F-9-fluorenone

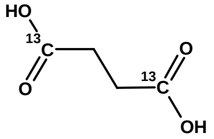
Organic Acid Quantification IS



4-F-benzoic acid

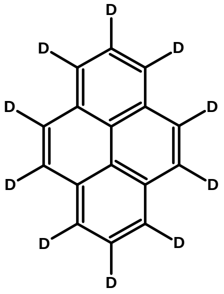


$^{13}C_4$-octanoic acid



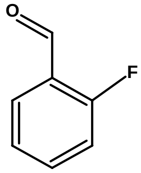
$^{13}C_2$-butanedioic acid

PAH Quantification IS

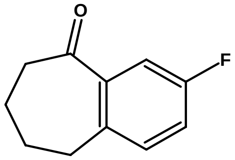


d_{10}-pyrene

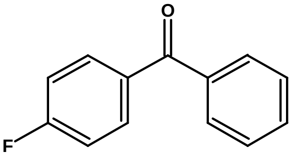
Carbonyl Recovery IS



2-F-benzaldehyde

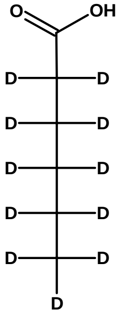


8-F-1-benzosuberone

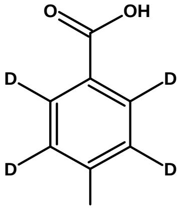


4-F-benzophenone

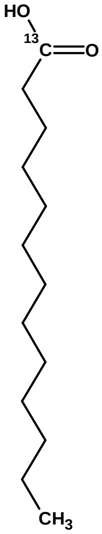
Organic Acid Recovery IS



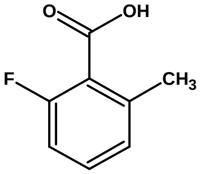
d_{11}-hexanoic acid



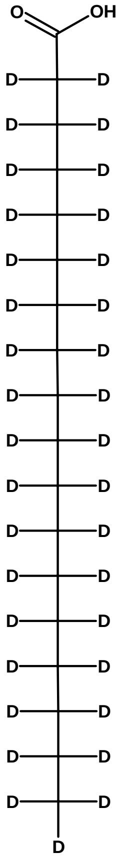
d_5-benzoic acid



$^{13}C_1$-dodecanoic acid

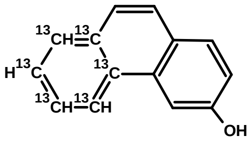


2-F-5-Me-benzoic acid

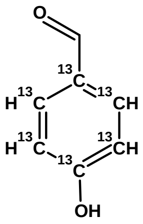


d_{35}-octadecanoic acid

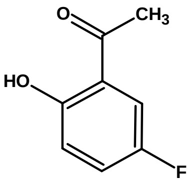
Hydroxy-PAH and Hydroxy-Carbonyl IS



$^{13}C_6$-3-OH-phenanthrene

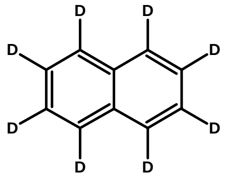


$^{13}C_6$-4-OH-benzaldehyde

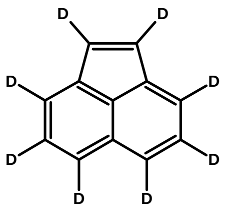


2-F-5-OH-acetophenone

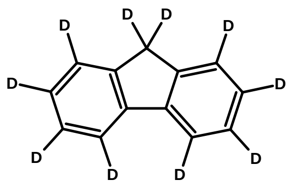
PAH Recovery IS



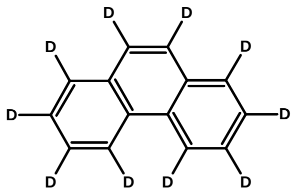
d$_8$-naphthalene



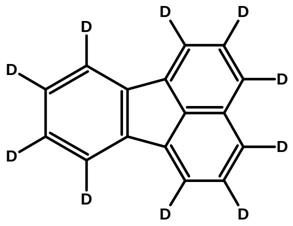
d$_{10}$-acenaphthene



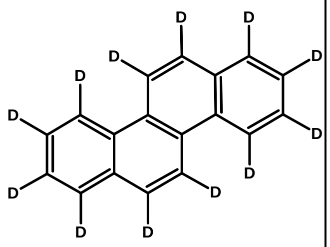
d$_{10}$-fluorene



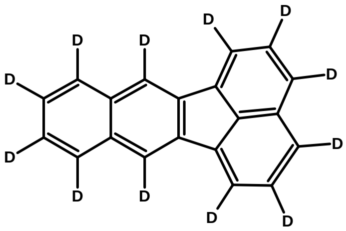
d$_{10}$-phenanthrene



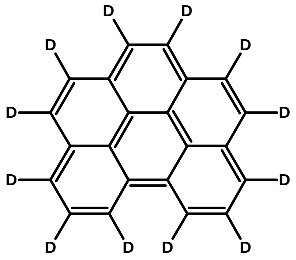
d$_{10}$-fluoranthene



d$_{12}$-chrysene



d$_{12}$-benzo[k]fluoranthene



d$_{12}$-benzo[ghi]perylene

Appendix G: Examples of Compound Mass Spectra

Figure G1: Mass Spectra of Methacrolein PFBHA Oxime

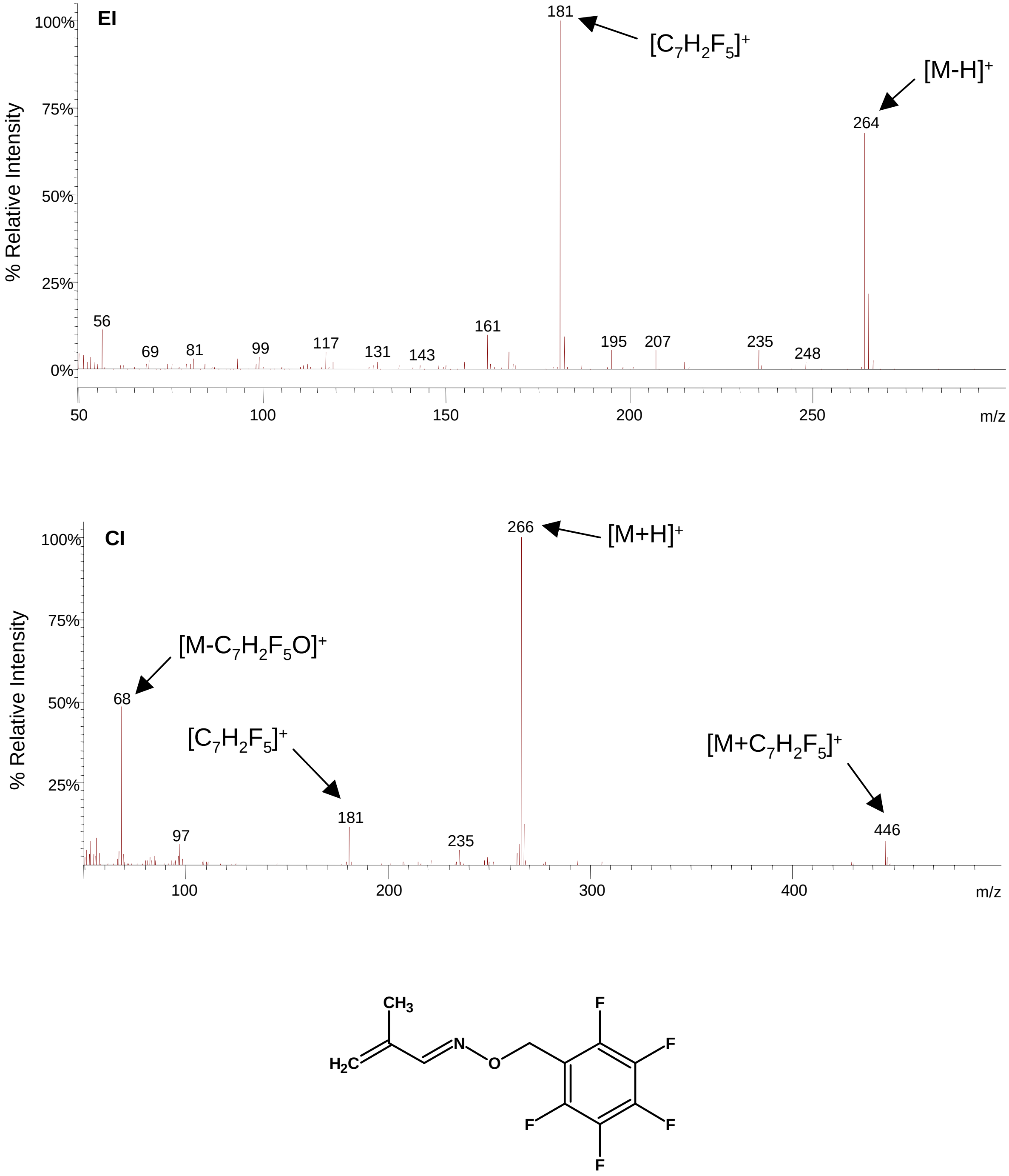


Figure G2: Mass Spectra of Acetophenone PFBHA Oxime

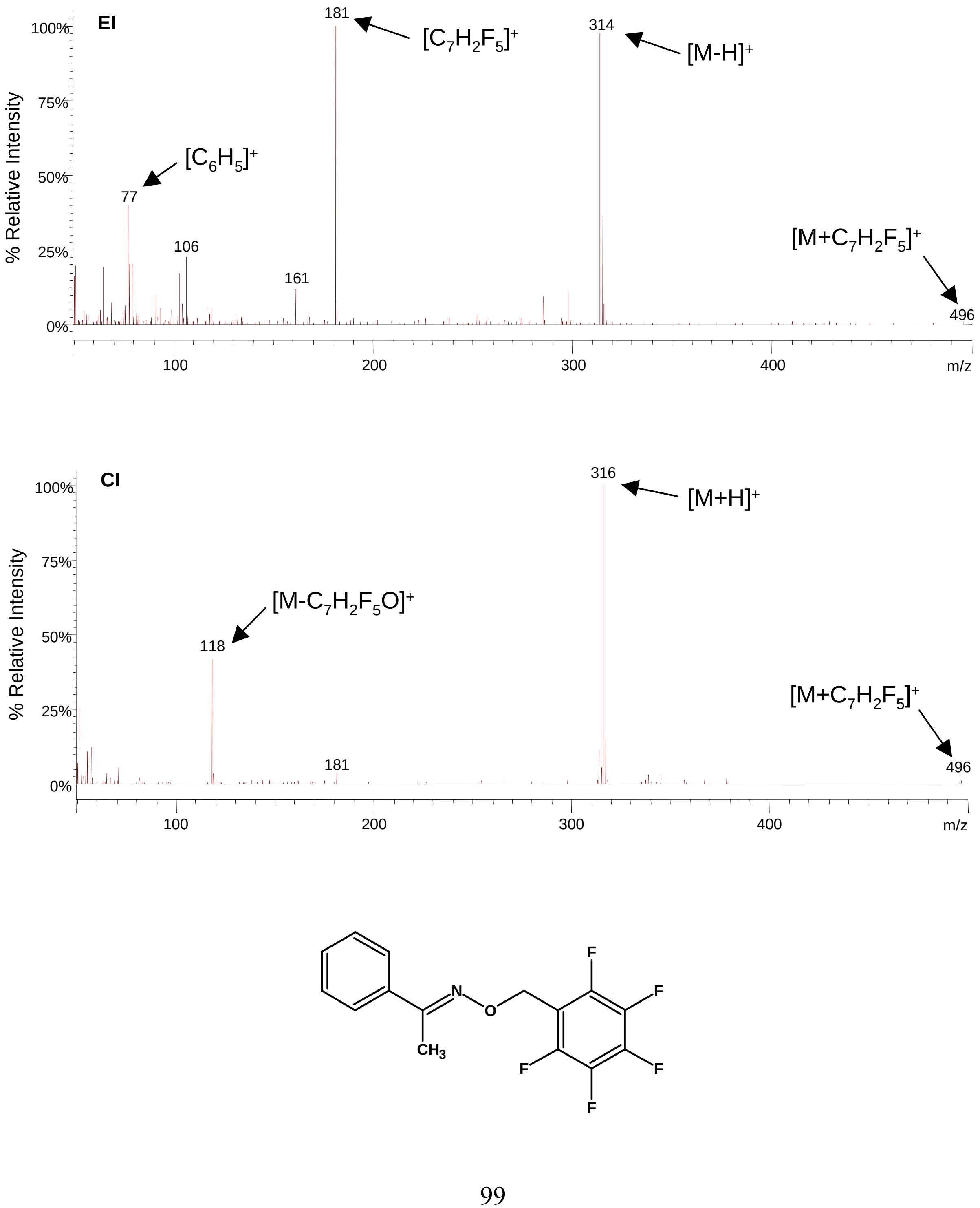
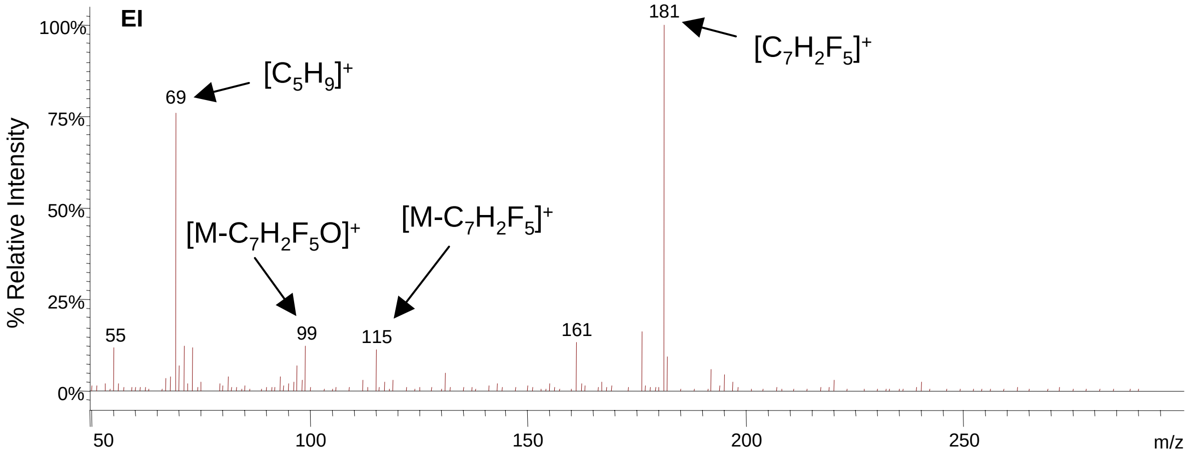
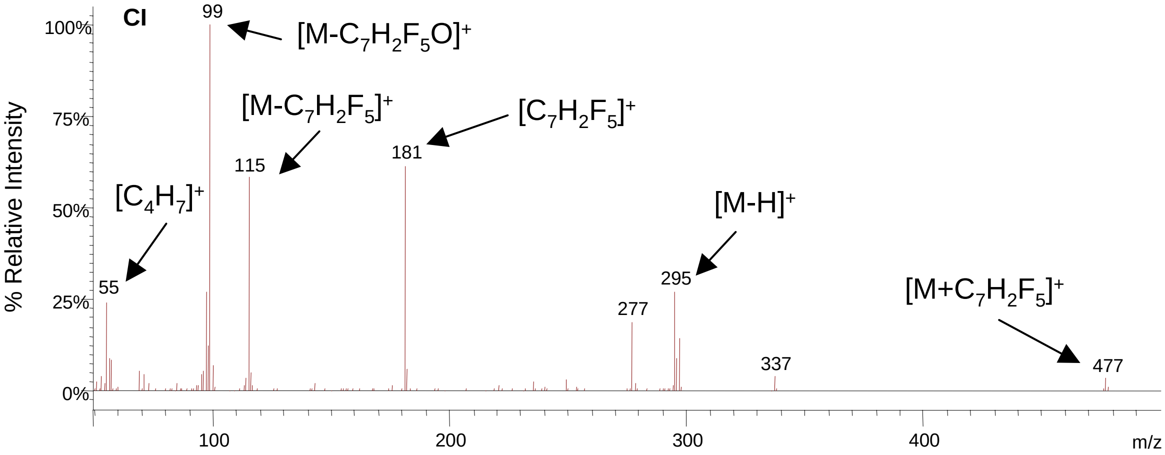


Figure G3: Mass Spectra of Hexanoic Acid PFBBr Ester





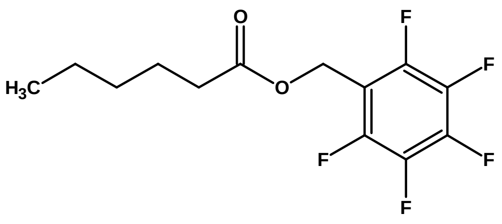


Figure G4: Mass Spectra of Hexadecanoic Acid PFBBr Ester

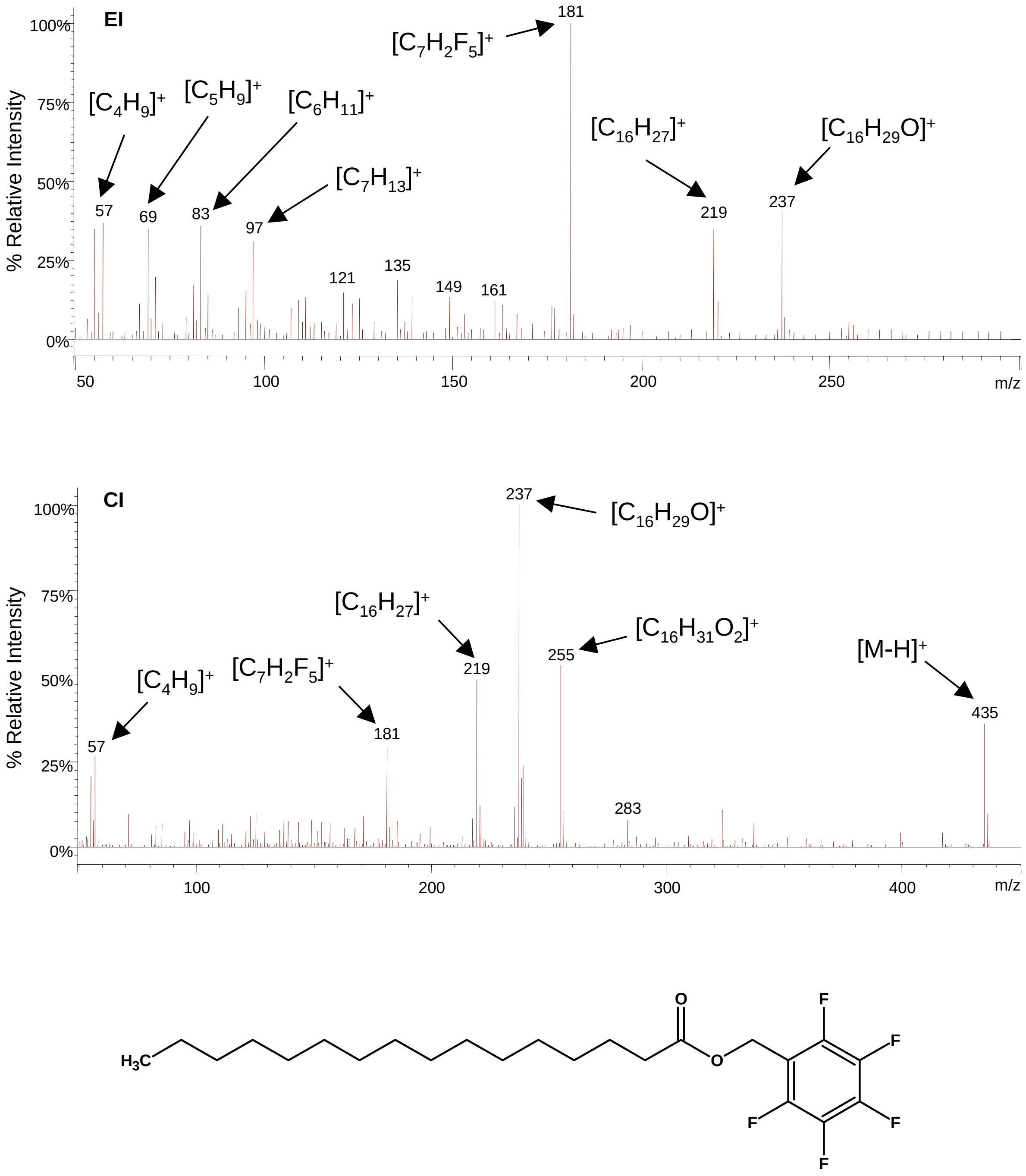


Figure G5: Mass Spectra of Benzoic Acid PFBBr Ester

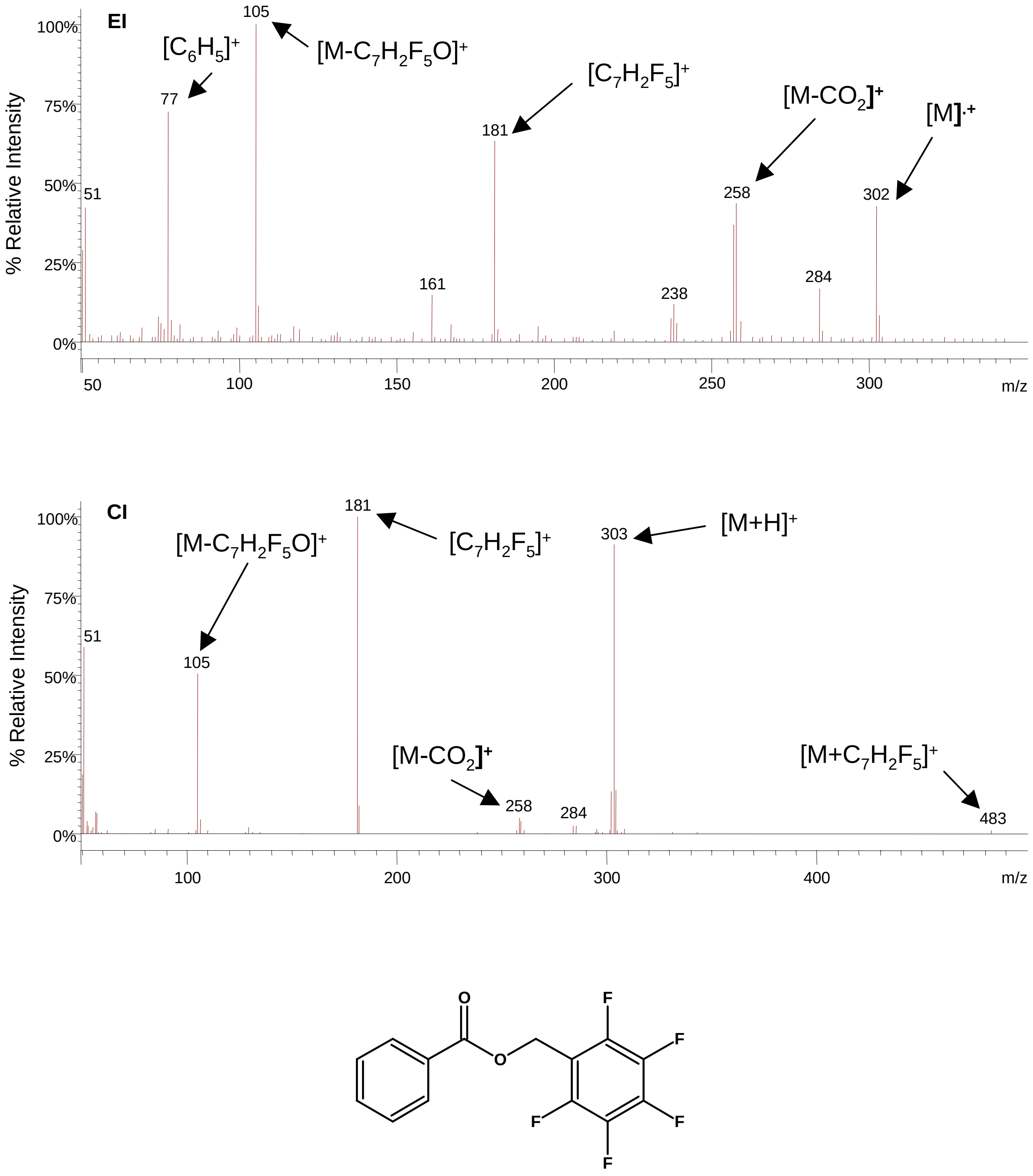
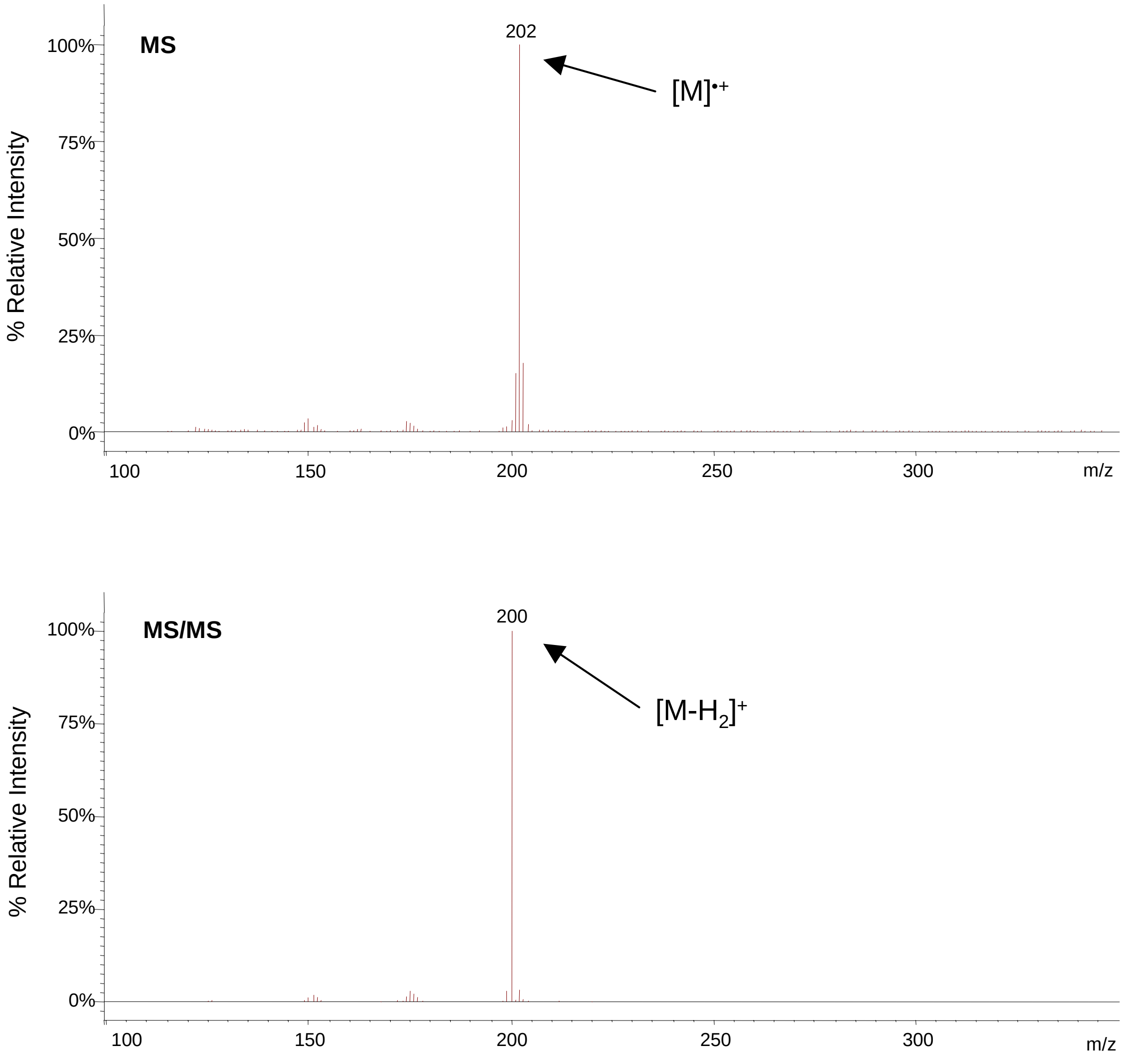
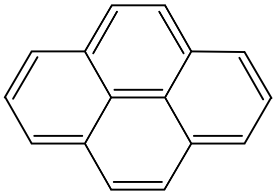


Figure G6: Mass Spectra of Pyrene





Appendix H: NIST SRM Carbonyl Qualitative Comparison

Table H: Qualitative Comparison of Particulate Carbonyls in NIST SRMs

	1649 Urban Dust		1650 Diesel PM	
Compound	Experimental	Oda et al.	Experimental	Oda et al.
aliphatics				
propanal	●		●	
butanal	●		●	
isobutanal	●		●	
pentanal	●		●	
hexanal	●		●	
heptanal	●		●	
octanal	●		●	
nonanal	●		●	
decanal			●	
2-butanone	●		●	
3-pentanone	●		●	
2-pentanone	●			
2-hexanone	●		●	
acrolein	●		●	
methacrolein	●		●	
methyl vinyl ketone	●		●	
crotonaldehyde	●		●	
t-2-methyl-2-butenal	●		●	
3-methyl-2-butenal	●		●	
4-hexen-3-one	●		●	
2-methyl-2-cyclopentenone	●		●	
3-methyl-2-cyclopentenone			●	
2-cyclohexenone			●	
glyoxal	●		●	
methyl glyoxal	●		●	
2,3-butanedione			●	
2,3-hexanedione			●	
2,5-hexanedione	●		●	
2,3-pentanedione			●	
2,4-pentanedione			●	
aromatics				
benzaldehyde	●		●	
o- & m-tolualdehyde			●	
p-tolualdehyde			●	

Table H: Qualitative Comparison of Particulate Carbonyls in NIST SRMs

	1649 Urban Dust		1650 Diesel PM	
Compound	Experimental	Oda et al.	Experimental	Oda et al.
acetophenone	●		●	
naphthaldehydes		●		●
perinaphthenone			●	
9-fluorenone	●	●	●	●
anthrone			●	
9-formylphenanthrene				●
benzophenone	●		●	
4-formylbiphenyl				●
xanthone			●	●
benzanthrone	●	●	●	●
1,4-naphthoquinone				●
acenaphthenequinone				●
anthraquinone		●	●	●
2-Me-anthraquinone		●		●
benz[a]anthracen-1,2-dione		●		●
5,12-naphthacenequinone		●		●
1,8-naphthalic anhydride	●		●	

Appendix I: Carbonyl Identification / Quantification Ions

Table I: Carbonyl Quantification Ion Identification [a]

Compound	PFBHA Oxime	RT	Analysis MW	Quantification Ion	
		(min)	(g mol^{-1})	(m/z)	ID
aliphatic aldehydes					
propanal	Y	15.15, 15.33	253.08	181	$[C_7H_2F_5]^+$
isobutanal	Y	16.27	267.11	181	$[C_7H_2F_5]^+$
butanal	Y	17.67, 17.78	267.11	181	$[C_7H_2F_5]^+$
pentanal	Y	20.44, 20.57	281.13	181	$[C_7H_2F_5]^+$
hexanal	Y	23.03, 23.13	295.16	239	$[C_9H_6F_5NO]^+$
heptanal	Y	25.48	309.19	181	$[C_7H_2F_5]^+$
octanal	Y	27.84	323.22	222	$[C_8HF_5NO]^+$
nonanal	Y	30.13	337.24	222	$[C_8HF_5NO]^+$
decanal	Y	32.29	351.27	222	$[C_8HF_5NO]^+$
undecanal	Y	34.41	365.3	222	$[C_8HF_5NO]^+$
aliphatic ketones					
2-butanone	Y	16.69, 16.78	267.11	181	$[C_7H_2F_5]^+$
2-pentanone	Y	18.79, 18.98	281.13	181	$[C_7H_2F_5]^+$
3-pentanone	Y	18.63	281.13	264	$[M-{}^{\bullet}OH]^+$
2-hexanone	Y	21.12	295.16	181	$[C_7H_2F_5]^+$
unsaturated aliphatics					
acrolein	Y	15.72	251.06	181	$[C_7H_2F_5]^+$
methacrolein	Y	17.33	265.09	181	$[C_7H_2F_5]^+$
methyl vinyl ketone	Y	17.56, 17.69	265.09	264	$[M-{}^{\bullet}H]^+$
crotonaldehyde	Y	19.68, 19.90	265.09	250	$[M-{}^{\bullet}CH_3]^+$
t-2-Me-2-butenal	Y	21.52, 21.89	279.12	264	$[M-{}^{\bullet}CH_3]^+$
3-Me-2-butenal	Y	22.76, 23.06	279.12	264	$[M-{}^{\bullet}CH_3]^+$
t-2-hexenal	Y	24.81, 24.91	293.14	250	$[C_{10}H_5F_5NO]^+$
4-hexen-3-one	Y		293.15	278	$[M-{}^{\bullet}CH_3]^+$
cyclic aliphatics					
2-Me-2-cyclopentenone	Y	24.95	291.13	291	$[M]^{\bullet+}$
3-Me-2-cyclopentenone	Y	26.73, 26.89	291.13	291	$[M]^{\bullet+}$
2-cyclohexenone	Y	26.24, 26.43	291.13	274	$[M-{}^{\bullet}OH]^+$
aliphatic dicarbonyls					
glyoxal	Y	34.78, 35.04	448.04	181	$[C_7H_2F_5]^+$
methyl glyoxal	Y	35.56	462.06	265	$[M-C_7H_2F_5O]^+$
2,3-pentanedione	Y	34.70, 36.16	490.12	293	$[M-C_7H_2F_5O]^+$
2,4-pentanedione	Y	35.95, 36.71	490.12	293	$[M-C_7H_2F_5O]^+$
2,3-hexanedione	Y	35.86, 37.11	504.14	307	$[M-C_7H_2F_5O]^+$
2,5-hexanedione	Y	38.22	504.14	292	
aromatic aldehydes					
benzaldehyde	Y	28.70, 28.90	301.12	271	$[M-{}^{\bullet}NO]^+$
o- & m-tolualdehyde	Y	29.72, 30.70, 31.18	315.15	300	$[M-{}^{\bullet}CH_3]^+$

p-tolualdehyde	Y	31.30, 31.53	315.15	315	$[M]^{\bullet+}$
aromatic ketones					
acetophenone	Y	30.1	315.15	314	$[M-{}^{\bullet}H]^{+}$
9-fluorenone	Y	44.69	375.21	375	$[M]^{\bullet+}$
benzophenone	N	27.89	182.22	105	$[M-C_6H_5]^{+}$
perinaphthenone	N	35.15	180.21	180	$[M]^{\bullet+}$
xanthone	N	33.89	196.21	196	$[M]^{\bullet+}$
aromatic dicarbonyls					
benzoquinone	Y	44.6	498.1	498	$[M]^{\bullet+}$
anthraquinone	N	36.6	208.21	208	$[M]^{\bullet+}$
1,8-naphthalic anhydride	N	38.54	198.17	154	$[M-CO_2]^{\bullet+}$

[a] Quantification specifics pertain to the EI analyses but identification was confirmed by the CI analyses

Appendix J: Carbonyl Instrumental Detection Limits

Table J: Instrumental Limits of Quantification and Detection for Carbonyls

Compound	LOQ [a] (pg/μL)	LOD [b] (pg/μL)
recovery IS		
2-F-benzaldehyde	17	5.2
5-F-1-indanone	5.0	1.5
8-F-1-benzosuberone	7.3	2.2
4-F-benzophenone	14	4.1
4-F-benzophenone [c]	6.4	1.9
aliphatic aldehdyes		
propanal	14	4.1
isobutanal	19	5.6
butanal	15	4.4
pentanal	14	4.1
hexanal	65	20
heptanal	6.0	1.8
octanal	21	6.3
nonanal	7.7	2.3
decanal	17	5.1
undecanal	15	4.4
aliphatic ketones		
2-butanone	2.5	0.8
3-pentanone	2.7	0.8
2-pentanone	6.3	1.9
2-hexanone	16	4.8
unsaturated aliphatics		
acrolein	15	4.5
methacrolein	13	4.0
methyl vinyl ketone	2.6	0.8
crotonaldehyde	4.5	1.3
t-2-Me-2-butenal	6.2	1.9
3-Me-2-butenal	10	2.9
4-hexen-3-one	2.6	0.8
t-2-hexenal	13	4.0
cyclic aliphatics		
2-Me-2-cyclopentenone	4.2	1.3
3-Me-2-cyclopentenone	3.2	1.0
2-cyclohexenone	4.9	1.5
aliphatic dicarbonyls		
glyoxal	34	10
methyl glyoxal	17	5.0
2,3-butanedione	7.8	2.3
2,3-pentanedione	3.8	1.1

2,4-pentanedione	7.1	2.1
2,3-hexanedione	4.4	1.3
2,5-hexanedione	1.8	0.6
aromatic aldehdyes		
benzaldehyde	4.5	1.4
o- & m-tolualdehyde	2.2	0.7
p-tolualdehyde	3.0	0.9
aromatic ketones		
acetophenone	1.4	0.4
fluorenone	12	3.6
perinaphthenone [c]	38	11
benzophenone [c]	7.0	2.1
xanthone [c]	7.5	2.3
benzanthrone [c]	25	7.5
aromatic dicarbonyls		
benzoquinone	52	16
anthraquinone [c]	14	4.2
1,8-naphthalic anhydride [c]	32	9.7

[a] Limit of quantification determined using a signal:noise ratio of 10:1,

[b] Limit of detection determined using a signal:noise ratio of 3:1,

[c] Compounds were analyzed in their underivatized form

Appendix K: Organic Acid and Phenol Identification/Quantification Ions

Table K: PFBBr Derivative Quantification Ion Identification [a]

Compound	RT (min)	PFB MW (g mol^{-1})	Quantification Ion (m/z)	Quantification Ion ID
alkanoic				
butanoic acid	17.98	268.11	181	$[C_7H_2F_5]^+$
pentanoic acid	20.64	282.13	181	$[C_7H_2F_5]^+$
hexanoic acid	23.18	296.16	181	$[C_7H_2F_5]^+$
heptanoic acid	25.62	310.18	83	$[C_6H_{11}]^+$
octanoic acid	27.96	324.21	125	$[C_8H_{13}O]^+$
nonanoic acid	30.22	338.24	69	$[C_5H_9]^+$
decanoic acid	32.38	352.26	181	$[C_7H_2F_5]^+$
dodecanoic acid	36.47	380.32	181	$[C_7H_2F_5]^+$
tridecanoic acid	38.31	394.34	195	$[C_{13}H_{23}O]$+
tetradecanoic acid	40.25	408.27	209	$[C_{14}H_{25}O]^+$
pentadecanoic acid	41.96	422.30	223	$[C_{15}H_{27}O]^+$
hexadecanoic acid	43.76	436.42	237	$[C_{16}H_{29}O]^+$
octadecanoic acid	47.02	464.48	265	$[C_{18}H_{33}O]^+$
alkenoic				
oleic acid	46.66	462.46	263	$[C_{18}H_{31}O]^+$
aromatic				
benzoic acid	28.56	302.12	105	$[M\text{-}C_7H_2F_5O]^+$
4-Me-benzoic acid	31.34	316.15	119	$[M\text{-}C_7H_2F_5O]^+$
1-naphthoic acid	40.17	352.18	155	$[M\text{-}C_7H_2F_5O]^+$
alkanedioic				
butanedioic acid	38.04	478.24	101	$[C_4H_5O_3]^+$
nonnanedioic acid	46.48	548.37	351	$[M\text{-}C_7H_2F_5O]^+$
hydroxy aromatics				
phenol	23.80	274.11	274	$[M]^{\bullet+}$

[a] Quantification specifics pertain to the EI analyses but identification was confirmed by the CI analyses

Appendix L: Organic Acid and Phenol Instrumental Limits of Detection

Table L: Instrumental Limits of Quantification and Detection for Organic Acids and Phenols

Compound	LOQ [a]	LOD [b]
	(pg/μL)	(pg/μL)
recovery IS		
d_{11} hexanoic acid	11	3.2
d_5 benzoic acid	6.9	2.1
2-F-5-Me-benzoic acid	7.4	2.2
$^{13}C_1$ dodecanoic acid r	15	4.6
d_{35} octadecanoic acid	45	13
alkanoic		
butanoic acid	16	4.9
pentanoic acid	2.6	0.8
hexanoic acid	7.8	2.3
heptanoic acid	15	4.4
octanoic acid	25	7.5
nonanoic acid	18	5.3
decanoic acid	10	3.1
dodecanoic acid	4.2	1.3
tridecanoic acid	21	6.3
tetradecanoic acid	40	12
pentadecanoic acid	56	17
hexadecanoic acid	30	8.9
octadecanoic acid	19	5.6
alkenoic		
oleic acid	50	15
aromatic		
benzoic acid	4.3	1.3
4-methylbenzoic acid	5.7	1.7
1-naphthoic acid	12	3.6
alkanedioic		
butanedioic acid	11	3.4
nonanedioic acid	32	9.7
hydroxy aromatics		
phenol	2.8	0.8

[a] Limit of quantification determined using a signal:noise ratio of 10:1,

[b] Limit of detection determined using a signal:noise ratio of 3:1

Appendix M: PAH Limits of Detection and Quantification Using MS/MS

Table M: Instrumental Limits of Quantification and Detection for PAHs

Compound	LOQ [a] (pg/μL)	LOD [b] (pg/μL)	Notes: [c-d]
phenanthrene	0.47	0.14	
anthracene	1.8	0.53	
fluoranthene	0.13	0.04	
pyrene	0.11	0.03	
cyclopenta[cd]pyrene	0.51	0.15	
MW 228 isomers	0.16	0.05	c
benzofluoranthene isomers	0.23	0.07	d
benzo[e]pyrene	0.22	0.06	
benzo[a]pyrene	0.60	0.18	
perylene	0.45	0.13	
indeno[1,2,3-cd]pyrene	0.31	0.09	
dibenz[a,h]anthracene	0.33	0.10	
benzo[ghi]perylene	0.38	0.11	
coronene	1.1	0.33	

[a] Limit of quantification determined using a signal:noise ratio of 10:1, [b] Limit of detection determined using a signal:noise ratio of 3:1, [c] The MW 228 isomers are the sum of chrysene, triphenylene and benz[a]anthracene, [d] The isomers are the sum of benzo[b]fluoranthene and benzo[k]fluoranthene