A Report from the University of Vermont Transportation Research Center

Quantifying Biodiesel Fuel Effects on Light-Duty Diesel Engine Particle Composition by GCMS

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University of Vermont Transportation Research Center

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1. Introduction

1.0 Introduction & Project Objective

This report addresses a knowledge gap in the literature on the organic chemical composition of particulate matter (PM) emitted by light-duty diesel engines operating on biodiesel fuel. Specifically, this work summarizes the development of sampling and analytical protocols to quantify a series of target analytes in PM collected from laboratory engine dynamometer experiments. The target analytes include polycyclic aromatic hydrocarbons (PAHs), normal alkanes, fatty acid methyl esters (FAMES) and 26 polar organic compounds (POCs) that include carbonyl, aldehyde and quinone chemical classes. The target analytes were selected based on the availability of authentic chemical standards and prior research on petroleum diesel exhaust composition. Preliminary results are presented for analyses of a limited number of raw fuel and exhaust particulate matter samples collected during steady-state engine operation. The analytical method is evaluated in terms of variability among replicate analyses, blank quantitation and individual target analyte recoveries and detection limits.

1.1 Particulate Matter

Particulate matter (PM), including that from diesel engines, has received attention in recent decades because of its association with adverse health effects (Dockery et al., 1993; Pope and Dockery 2006; Bell et al., 2008). The main health effects of PM are (i) excess mortality, mainly among the elderly and chronically ill; (ii) effects on elderly with preexisting cardiopulmonary diseases; (iii) exacerbation of symptoms among people with acute and chronic pulmonary disease; and (d) increased eye and respiratory system irritation, especially asthma attacks and respiratory infections (Franchini and Mannuci. 2007; Riedl. 2008; Valavanidis et al., 2008). The chemical composition of PM may predict health effects better than other PM characteristics such as mass and size (Stanek et al., 2011). Recent laboratory studies have shown a relationship between PM compositional variability and PM-related toxicity, while epidemiologic studies have shown a regional heterogeneity in PM-related health effects (Bell et al., 2008; Zanobetti and Schwartz 2009). The majority of previous diesel engine exhaust studied focused on petroleum diesel fuel, but since the mid-2000s there has been an increase in biodiesel fuel use worldwide. Biodiesel still represents a minor volume of the total diesel fuel used worldwide, but its use is anticipated to increase in the future in response to energy security and global climate concerns. Therefore, it is important to quantify the chemical composition of diesel and biodiesel exhaust particulate and gas-phase emissions in order to better understand the relationships between fuel composition and the health effects of both diesel and biodiesel exhaust emissions.

1.2 Biodiesel Fuel

Depleting fossil fuel reserves and rising petroleum prices have led to the widespread introduction of alternative biomass-based fuels worldwide. Since 2005, U.S. energy policy has mandated increases in the quantity of renewable fuels used for transportation, including “biomass-based diesel” or biodiesel [EISA 2007; EPA 2010]. Biodiesel, a renewable fuel derived from a variety of animal or vegetable feedstocks, is a preferred alternative to petroleum diesel because it: (i) offers air pollution benefits for some pollutants [EPA 2002]; (ii) can be blended into existing diesel fuel supplies with no engine modifications; (iii) is an important strategy for both domestic energy independence and sustainable agricultural production; (iv) reduces net greenhouse gas emissions, and (v) it is biodegradable. A variety of feedstocks can be used to

produce biodiesel fuel that meets federal standards for on-road use (e.g., ASTM D6751) and does not compete with food resources.

Biodiesel is a mixture of mono-alkyl methyl esters derived from oilseed crops (soybean, canola, sunflower, etc.) and waste grease (used vegetable oil or animal fats) that undergo a transesterification process to produce liquid transportation fuels. This process reacts the naturally occurring triacylglycerols (TAGs), found in plants and animals, with an alcohol (e.g. methanol), in the presence of a strong alkali catalyst (e.g. potassium hydroxide), to produce a mixture of fatty acid methyl esters (FAMEs) and glycerol (**Figure 1-1**). The TAGs found in plants and animals consist of three long-chain fatty acids (-O-C(O)-R_1, -R_2, R_3; **Figure 1-1**), bonded to a glycerol backbone. The transesterification reaction produces three moles of FAME per mole of TAG and the resultant biodiesel fuel has a similar fatty acid composition to the original oil feedstock.

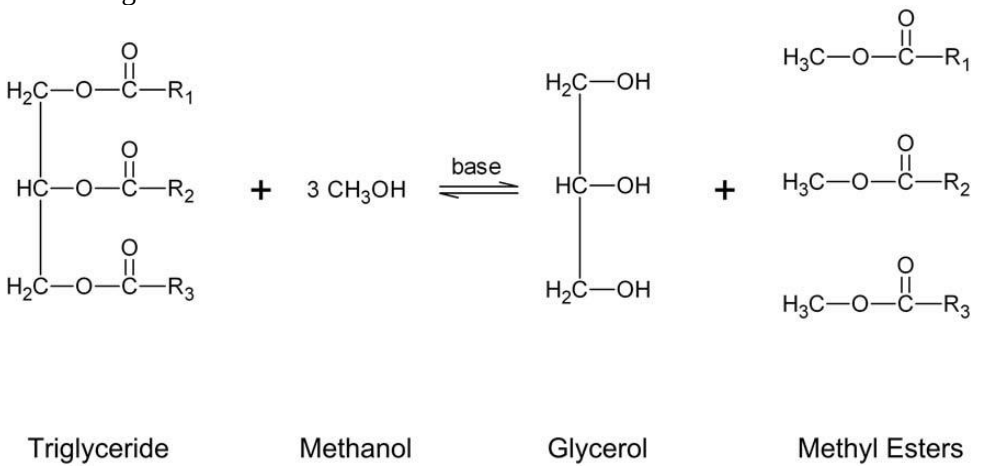


Figure 1-1. The transesterification process of triacylglycerols (TAGs or "triglycerides") to produce fatty acid methyl esters (FAMEs), the primary constituents of biodiesel and glycerol byproduct. (Clausen, 2008).

Biodiesel has advantages over petroleum diesel because it is renewable, biodegradable, can be domestically produced, and has a higher flash point, higher inherent lubricity, and no sulfur or aromatic compounds (Dunn. 2005, Bakeas et al., 2011). Biodiesel's chemical composition explains many of this renewable fuel's advantages and disadvantages over petroleum diesel (petrodiesel). In-engine advantages include: higher cetane number, increased lubricity, lower sulfur content, and decreased particulate matter (PM) mass emissions (Knothe, 2006; Moser, 2009). There are also inherent disadvantages to biodiesel: lower oxidative stability, decreased energy content by volume, an increase in NO_x emissions, and a higher gel point (Knothe, 2006; EPA, 2002). These characteristics are highly dependent on the specific chemical properties and proportions of the different FAMEs present in the biodiesel (**Figure 1-2**). The degree of saturation, for example, refers to the number of C=C double bonds and is an important indicator of melting point and other fuel properties. Notation to describe the FAME saturation state indicates the total number of carbons in the molecule as well as the number of double bonds. For example, "C16:0" for palmitic FAME. Saturated fatty acids that contain no carbon double bonds (e.g. palmitic and stearic acid) tend to have higher melting points and are typically solid or waxy at room temperature (Giakoumis, 2013). Mono-unsaturated (e.g. oleic acid; C18:1) and polyunsaturated (e.g. linoleic (C18:2), and linolenic acid (C18:3)) fatty acids have lower melting points and are liquids at room temperature. Studies have shown that biodiesel fuels produced from primarily unsaturated feedstocks (e.g. soy and canola) can also increase the total PM and NO_x emissions from combustion (Graboski, 2003). **Table 1-1** compares the properties of biodiesel and petroleum diesel fuels.

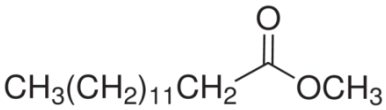
Table 1-1. Diesel and Biodiesel Fuel Properties

	Fuel Type	
	Petrodiesel (No. 2)	**Biodiesel (soybean)**
Chemical Structure	C_8-C_{25} Alkanes	Methyl esters of C_{14}-C_{20} fatty acids
Density (g/cm^3)[1]	0.85	0.88
Low Heating Value (Btu/gal)[2]	~128,450	~119,550
High Heating Value (Btu/gal)[2]	~137,380	~127,960
Cetane Number[1]	40-55	48-65
Flash Point (^oC)[1]	52-96	100-170

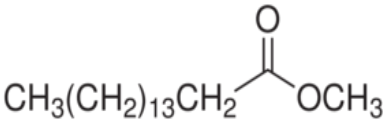
[1] McCormick R.L. 2009. Biodiesel handling and use guide: Fourth edition (revised). National Renewable Energy Laborator. Bolder, CO. NREL Report No. TP-540-43672; DOE/GO-102008-2658. Publisihed: 12-2009

[2] Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model, version 1.7. 2007. Input Fuel Specifications. Argonne National Laboratory. Chicago, IL.

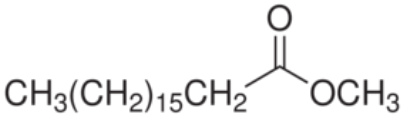
Biodiesel is less stable than petroleum diesel because it possesses fatty acids with double bonds that make biodiesel more susceptible to chemical oxidation, especially when stored over extended periods of time (Knothe. 2007). The location and orientation of the C=C double bond is an important determinant of the physical properties of the biodiesel fuel. *Cis*- and *trans*- isomers have different three-dimensional geometric orientations of the double bond(s) in any hydrocarbon chain. The *cis* isomer geometry has the two carbons adjacent to the double bond on the same side of the double bond, creating a "kink" in the hydrocarbon chain (i.e., linoleate, **Figure 1-2**). In the case of *trans*- isomers, the molecule is held in a straighter alignment, allowing it to be packed more densely, but also flow less freely. Melting points therefore tend to increase from *cis*- to *trans*- isomers. Double bond kinks in the *cis*- orientation act to increase the chance for steric interaction between molecules. This may increase the chemical reactivity of *cis*- isomers, and make them prone to oxidation. Biodiesel oxidation during fuel storage can introduce complications when the fuel is used due to the formation of precipitates, thus anti-oxidants are typically added to biodiesel to scavenge oxygen and inhibit oxidation during storage (Knothe, 2007). To date, no studies have examined effects of anti-oxidant composition on exhaust PM toxicity.



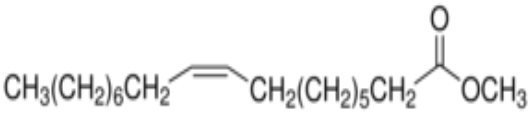
Methyl myristate
Tetradecanoic acid, methyl ester
C14:0



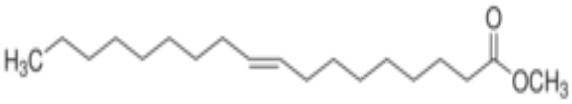
Methyl palmitate
Hexadecanoic acid, methyl ester
C16:0



Methyl stearate
Octadecanoic acid, methyl ester
C18:0

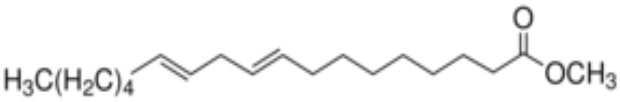


Methyl oleate
Cis-9-Octadecenoic acid, methyl ester
C18:1n9c

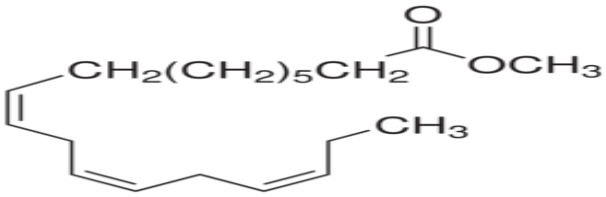


Methyl elaidate
Trans-9-Octadecenoic acid, methyl ester
C18:1n9t

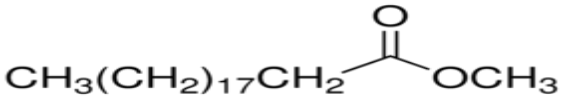
Methyl linoleate
Cis,cis-9,12-Octadecenoic acid, methyl ester
C18:2n6c



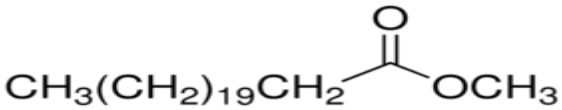
Methyl linolelaidate
Trans,trans-9,12-Octadecenoic acid, methyl ester
C18:2n6t



Methyl linolenate
Cis,cis,cis-9,12,15-Octadecenoic acid, methyl ester
C18:3



Methyl arachidate
Eicosanoic acid, methyl ester
C20:0



Methyl behenate
Docosanoic acid, methyl ester
C22:0

Figure 1-2. Fatty Acid Methyl Ester (FAME) structures for most important FAMES found in biodiesel fuel.

The location of the first C=C double bond in the fatty acid hydrocarbon chain also affects how the human body reacts to and metabolizes the compound. Omega-3 fatty acids have a double bond on the third carbon away from the ester group and are an essential nutrient for survival. Omega-6 fatty acids are also vital, but studies have shown that they can also be precursors for

cardiovascular disease, and prostate cancer when consumed in excess (Simopoulos, 2002). These studies however, were focused on ingestion of these compounds in foods, and the literature is lacking on the health effects of inhalation of these chemicals and their unregulated oxidation byproducts (Swanson, 2007).

1.3 Diesel Engine Emissions and Fuel Type

The EPA released a biodiesel exhaust emissions report in 2002 (EPA420-P-02-001) that showed a decrease in many regulated pollutants (e.g. carbon monoxide [CO], hydrocarbons [HC], and mass of particulate matter [PM]) with increasing biodiesel blend percentage (EPA, 2002). The report also included a list of mobile source air toxics (MSATs) from an on-road heavy-duty diesel engine that were statistically correlated to increasing volume percent biodiesel. The MSAT compounds (e.g. acetaldehyde, acrolein, benzene, 1,3-butadiene, ethylbenzene, formaldehyde, n-hexane, naphthalene, styrene, toluene, and xylene) are mostly unregulated under the Clean Air Act (CAA), but are comprised of chemicals "known or suspected to cause cancer or other serious health and environmental effects" (EPA 2013 – www.epa.gov/otaq/toxics.html, accessed 8/6/13). Diesel exhaust particulate matter and polycyclic aromatic hydrocarbons (PAHs) are examples of MSATs.

More recent research has shown that, with the exception of NO_x, most regulated emissions such as HC, CO, and PM, are significantly reduced with biodiesel (McCormick et al., 2001; EPA. 2002; Krahl et al., 2005; Knothe et al., 2006; Bakeas et al., 2011). Furthermore, most studies have found that the unregulated carcinogenic and mutagenic polycyclic aromatic hydrocarbons (PAHs) emissions decrease with biodiesel (Lin et al., 2006; Chien et al., 2009; Karavalakis et al., 2011). Various studies, however, have also shown that emissions of polar oxygenated compounds (POCs) such as carbonyls (also unregulated) increase with increasing biodiesel proportion in the fuel (Turrio-Baldassarri et al., 2004; Bikas and Zervas, 2007; Correa and Arbilla, 2008). Carbonyls have been previously linked to adverse health effects such as oxidative stress (Mauderly 1997), and they also play an important role in atmospheric chemistry because of their potential to form secondary organic aerosol via atmospheric reactions (Blando et al., 2000; Lim et al., 2005; Loeffler et al., 2006).

The PAHs and carbonyls can be emitted from the diesel engine in both the gas and particle phases. Some studies have measured the gas and particle emissions of PAHs, carbonlys, soot, and hydrocarbons from diesel and different biodiesel feedstocks (e.g Correa and Arbillia 2008; Payri et al., 2009; Bakeas et al., 2011; Karavalakis et al., 2011). Most of these studies, however, have concentrated on a single class of compounds (PAHs, hydrocarbons, or carbonyls). In other words, very limited studies have been conducted to comprehensively measure and compare emissions of a variety of organic compound classes using the same biodiesel feedstock, engine, and engine operating conditions. Measurement of various organic compound classes using the same engine and engine operating conditions can lead to a better comparison of PM emissions from diesel and biodiesel, which can ultimately lead to a better understanding of the causes of the differences in the health effects of diesel and biodiesel exhaust PM.

1.4 Project Objectives and Approach

No previous studies have compared the particle-phase carbonyl emissions in biodiesel exhaust PM to conventional diesel PM. However, studies like Schauer et al., 1999, Jakober et al., 2006 and Jakober et al., 2008 measured particle-phase concentrations of carbonyls in conventional diesel exhaust. There is a need to measure and quantify the particle-phase carbonyl emissions from biodiesel as well. Because many previous studies found gas-phase emissions of carbonyls in biodiesel exhaust significantly higher than those for conventional diesel exhaust, **one objective of**

the current study is to test the hypothesis that particle-phase concentrations of carbonyls in biodiesel exhaust are also greater than those for conventional diesel.

Here, the organic chemical composition of the total (both gas- and particle-phase) emissions from a light-duty diesel engine fueled with 20% soybean biodiesel (B20) was studied in comparison to petroleum diesel (B0). The emission rates for PAHs, carbonyls, alkanes, and fatty acid methyl esters (FAMEs) in exhaust filter samples were quantified by thermal desorption (TD)-gas chromatography/mass spectrometry (GC/MS) to gain quantitative understanding of the relationship between fuel biodiesel composition and exhaust emissions. In one test, the gas-phase emissions were separated from the particle-phase emissions during exhaust sampling by use of a denuder. Focus was put on quantifying 16 EPA PAHs, 26 POCs (carbonyls and quinones), 16 alkanes, and 10 FAMEs commonly found in soybean biodiesel; compounds associated with health effects, photochemistry and environmental degradation, and that had authentic standards available commercially. FAMEs were chosen mainly because of their abundance in soybean biodiesel, in spite of the fact that their health effects are not well documented. The mass concentrations of the chosen organic compound classes from diesel and biodiesel exhaust PM were obtained after PM extraction, sample concentration and GC/MS analysis. Carbonyls were quantified after sample derivatization to enable analysis by GC.

The sample preparation and TD-GCMS analytical procedures are described in detail in Section 2 and preliminary results for duplicate analyses of engine blank, B0 and B20 filter samples are described in Section 3. Quantitative evaluation of the analytical method is also described in Section 3. Recommendations for future work are summarized in Section 4.

2. Research Methodology

2.1. Gas Chromatography/Mass Spectrometry (GC/MS) Method Development

Chemicals and Standards. High purity organic solvents such as dichloromethane (DCM, OmniSolv. HR-GC Grade), acetone (OmniSolv. HR-GC Grade), n-hexanes (OmniSolv. HR-GC Grade), methanol (MeOH, B&J Brand for Purge and Trap GC Analysis), acetonitrile (ACN, Carbonyl-free B&J Brand) were all purchased from VWR International (West Chester, PA). The individual carbonyls, 14 n-alkane mix (C_{12} – C_{34}), and 10-FAME standard compounds were purchased from Sigma-Aldrich (Allentown, PA), while the 16 EPA PAH and deuterated PAHs were purchased from Ultra Scientific (North Kingstown, RI). Details on chemical standard composition (manufacturer, catalog #, compound list and concentration) are found in Appendix I.

Extraction of Target Analytes from Filters. Generally, the nonpolar analytes in the PM were extracted from the PM filters (Pall Gelman borosilicate quartz fiber filters (QFFs) – Part #: 7194 or FiberFilm (FF) – Part #: 7212) using a solvent mixture of dichloromethane (DCM)/Hexanes (1:1, v/v), while the polar compounds were extracted using methanol and subsequently derivatized with O-(2,3,4,5,6- pentafluorobenzyl) hydroxylamine to enable gas chromatography analysis. All extractions were performed three times in series and replicate extracts were combined for subsequent processing and analysis by thermal desorption GC/MS (TD-GCMS).

The quartz fiber filters analyzed in this study include; filters #72 and 73 (engine blanks), filters #112 and 114 (B00 filters), and filters #126 and 128 (B20 filters). **Table 2-1** summarizes the sampling conditions, PM mass, and PM mass concentration for each filter. The gravimetric PM mass reported in **Table 2-1** is based on pre- and post-run triplicate weighings of the filter using a Cahn microbalance with 1 µg sensitivity after filter conditioning for 24 hours at 30-40% relative humidity (conditions maintained in a Coy Chamber that houses the Cahn balance).

Table 2-1. Filter Sample Information for Filters Analyzed in this Study

Filter #	Test Date MM/DD/YY	Fuel	Filter Type	Sample Location	PM Mass (mg)	Flow rate (L/min)	Sample Time (min)	Total Flow (L)	PM Conc (µg/m³)	DR
72	8/23/11	Blank	QFF	DS	-1.302	N/A	N/A	N/A	N/A	N/A
73	8/31/11	Blank	QFF	DS	0.057	N/A	N/A	N/A	N/A	N/A
112	9/21/11	B00	QFF	DL-E	0.274	20	88	1760	155.68	21
114	9/22/11	B00	QFF	DL-E	0.233	20	84	1680	138.89	27
126	10/11/11	B20	FF	DL-C	0.148	10.4	75	780	189.74	30
128	10/12/11	B20	FF	DL-C	0.126	9.47	88	833.36	151.20	24

DR = exhaust volumetric dilution ratio during emissions testing.

Filter Extraction. Particle composition was determined by extracting ¼-inch diameter punches of the filters three times in series using hexane/dichloromethane (1:1, by volume) followed by concentration under N_2 gas to 50 microliter final volume. After addition of a deuterated PAH internal standard, 1 microliter of the concentrated extract was injected into a thermal desorption (TD) borosilicate glass vial and subsequently analyzed by GCMS. The GC-MS instrument conditions are in the **Table 2-2.**

Different extraction times and filter punch configurations were evaluated. The optimized extraction procedure is described here and results for extraction method development are described in **Section 3 (Results)**. A pair of 1/4-inch punches was cut from one side of each QFF using a punch bore. Using tweezers, both filter punches were placed in a 180 µL glass thermal desorption vial (glass TD-vial) to which 2 µL of a 4.4 ppm standard of tetracosane-d50 (recovery standard for nonpolar compounds) and 1 µL of a 6.6 ppm standard of 2-fluoro-9-fluorenone (recovery standard for polar compounds) were added. Next, 140 µL of a DCM/Hexane (1:1, v/v) solvent mixture was added to the vial in order to extract the nonpolar compounds by ultrasonication for 5 minutes. The punch pair was extracted two more times, and all the three extracts combined in a separate 180 µL glass TD-vial. After combining the three DCM/Hexane extracts, 2 µL of a 5 µg/mL standard of anthracene-d10 was added in order to estimate evaporative losses during sample concentration via nitrogen blowdown.

Table 2-2. Thermal Desorption-GC/MS Method Conditions for PM Extract Analysis

Conditions	
GC/MS	HP 5890/Agilent 5972
Column:	Restek RXI-XLB Fused Silica Capillary Column
Dimensions:	30m x 0.25mm x 0.25µm
Oven Program:	65 ^{o}C (12 min); 10 ^{o}C/min to 186 ^{o}C (3min) ; 2.5 ^{o}C/min to 300 ^{o}C (15 min)
TD Injector:	295 ^{o}C
Detector:	290 ^{o}C
Carrier Gas:	99.999% He @ 1mL/min
Injection:	Splitless

For polar compound analysis, the punch pair was also extracted three times with 140 µL of methanol by ultrasonication for 5 minutes each time. The three methanol extracts were combined in a separate 180 µL glass TD-vial. Both the polar and nonpolar extracts were then gently concentrated with N_2 gas to about 60 µL each. The two extracts (polar and nonpolar) were then combined in a 180 µL glass TD-vial because it was determined that some of the target analytes were extracted in both the methanol and DCM/Hexane subfractions. The combined extract was blown down to 100 µL, after which it was divided into two 50 µL fractions. One fraction was derivatized for the analysis of POCs (carbonyls and quinones in this study), while the other fraction was directly analyzed for nonpolar target analytes (PAHs, alkanes, and FAMEs). The nonpolar fraction was further concentrated to about 20 µL with N_2 gas and the solvent volatilized by gentle heating at 60 ^{o}C. Other methods of solvent evaporation that were evaluated included letting the sample sit in the fume hood at room temperature until all the solvent volatilized, and blowing down with N_2 gas until all the solvent volatilized**.** After all the solvent volatilized, the TD-vial containing the sample was spiked with 1 µL of a 2 ppm solution of phenanthrene-d10 and perylene-d12 then inserted into the TD-GCMS for analysis

The polar extract fraction was concentrated to 7 µL then 1 µL of a 2.42 ppm solution of 6-fluoro-4-chromanone (6F4C) quantitation standard was added to the extract, followed by 1.5 µL of a 25 mg/mL pentafluorobenzylhydroxylamine (PFBHA derivatizing agent in methanol) solution. Acetonitrile(ACN)/DCM solvent mixture (9:1, v/v) was then added to the vial to target a final volume of 30 µL and a PFBHA concentration of 5 mM. The sample derivatization reaction proceeded at room temperature for 24 hours, then excess PFBHA was quenched by adding 11 µL of acetone, waiting for at least 1 hour at room temperature for the oxime to form. The sample was then blown down to dryness in the fume hood at room temperature to evaporate remaining

PFBHA-acetone oxime. The sample was analyzed on the TD-GCMS using 1 μL of a 2 ppm solution of phenanthrene- d10 and perylene-d12 internal standards.

Recovery of Target Compounds. During method development, standards of some compounds of interest (PAHs and POCs) were spiked on clean QFFs and extracted. This was done in order to assess the validity and reliability of the extraction and analysis procedure. The same procedure employed during the extraction and analysis of the real-world diesel/biodiesel exhaust PM samples was used to extract the PAHs and POCs from clean (baked at 550 °C overnight) filters spiked with 13.26 ng of the 16 PAHs standard and 12 ng of a POCs standard containing 26 POCs.

2.1.1 GC/MS Instrument Conditions, Data Analysis and Target Analyte Quantitation

TD-GC/MS Instrument Conditions. Extracts from the filters were analyzed using a Hewlett-Packard gas chromatograph/mass spectrometer (5890GC/5972MSD, Agilent Technologies, Wilmington, DE) equipped with a thermal desorption (TD) syringeless injector (Lavigne Laboratories, Storrs Mansfield, CT). The system used 99.999% helium carrier gas flowing at 1 mL/min, and the nonpolar column used was an Rxi-XLB, 30 m length, 0.25 mm ID, and 0.25 μm film thickness. The TD injector temperature was 295 °C, while the detector temperature was 290 °C. The oven program used for analysis of all extracts was: 65 °C initial temperature held for 12 min to allow analyte thermal desorption (10 min at 295 °C), 10 °C/min ramp to 186 °C and held for 3 min, 2.5 °C/min ramp to 300 °C and held for 15 min. The analytes were ionized using electron impact ionization, and the mass spectra were obtained using scan mode for ions with m/z ranging from 50 to 650 amu.

Quantification of individual compound mass was based on target ion peak areas normalized to the phenanthrene-d10 internal standard, assuming unit response factors. PAHs were quantified based on extraction ion peak areas. Compound identifications were based on the NIST 2008 Library and authentic standards for n-alkanes, 16 PAHs, 26 carbonyls and 10 FAMES.

Data Analysis and Quantitation of Analytes. During TD-GCMS data analysis of the nonpolar compounds (16 PAHs and 13 even numbered alkanes (dodecane to hexatriacontane)), the phenanthrene-d10 internal standard peak area was used to quantify all the nonpolar compounds of interest and the 10 FAMEs, while 6-fluoro-4-chromanone was used to quantify the 26 POCs. Phenanthrene-d10 was the only internal standard used to quantify the unknown nonpolar compounds because its peak areas were more reproducible than those for perylene-d12 irrespective of sample type (standard, derivatized, or underivatized sample).
Three separate quantitation databases for quantifying (i) PAHs, (ii) Alkanes and FAMEs, and (iii) POCs were set up in ChemStation (Agilent Technologies, G1701BA Version B.01.00. These quantitation databases were set up by analyzing 5 standards of different concentrations (0.5, 1, 2.5, 5, and 10 ppm) for the PAHs, alkanes, and FAMEs, and the calibration curves for each individual compound obtained in ChemStation. Note that ChemStation calibration curves were not used for the POCs because most of the POC-oximes elute as multiple peaks (isomers from derivatization). Because ChemStation cannot sum up the isomers of each individual compound, the calibration curves of the POCs were made manually by exporting the calibration standard peak area data from ChemStation to MS Excel, where the peak areas of each compound's isomers were summed up and the corresponding calibration curves plotted. See Appendix II for the concentrations of the calibration standards and Appendix III for sample calibration curves.
To quantify the compounds of interest in the filter sample extracts, the chromatogram for that sample was loaded into Chemstation's Data Analysis program along with the data analysis file containing the Calibration Standards quantitation data. The file was then quantitated, and

ChemStation produced a report containing all the information (compound name, peak area, mass/concentration, qualifier ions, and retention time) for all the compounds in the quantitation database together with the information regarding the quantitated file (file name, sample name, operator name, date of quantitation, etc). If nonpolar compounds were quantified, ChemStation would give the mass/concentration of each compound in the database, but if POCs were quantified, peak areas for the compounds were produced by ChemStation. Therefore, for the POCs, the peak areas data was exported to MS Excel where further processing was performed to calculate the mass/concentration of each POC. **Table 2-3** shows the list of all target compounds used in this study.

Table 2-3. Target compounds quantified by TD-GC/MS analysis of PM Filter Punch Extracts

Compounds	Compound ID	CAS Number
PAHs		
Naphthalene	NAP	91-20-3
Acenaphthylene	ACY	208-96-8
Acenaphthene	ACE	83-32-9
Fluorene	FLU	86-73-7
Phenanthrene	PHEN	85-01-8
Anthracene	ANTH	120-12-7
Fluoranthene	FLUOR	206-44-0
Pyrene	PYR	129-00-0
Benzo[a]anthracene	BAA	56-55-3
Chrysene	CHRY	218-01-9
Benzo[b]fluoranthene	BBF	205-99-2
Benzo[k]fluoranthene	BBK	207-08-9
Benzo[a]pyrene	BAP	50-32-8
Indeno[1,2,3-cd]pyrene	IDP	193-39-5
Benzo[ghi]perylene	BGP	191-24-2
Dibenz[a,h]anthracene	DAA	53-70-3
POCs		
2-Pentanone	2PNN	107-87-9
3-Pentanone	3PNN	96-22-0
n-Hexanal	HXNL	66-25-1
n-Heptanal	HPTL	111-71-7
n-Octanal	OCTL	124-13-0
2-Nonanone	2NNE	821-55-6
n-Nonanal	NNNL	124-19-6
n-Decanal	DECL	112-31-2
Undecanal	UDCL	112-44-7
2-Hexanone	2HXN	591-78-6
2-Heptanone	2HPN	110-43-0
2-Octanone	2OCT	111-13-7
Dodecanal	DDCL	112-54-9
Benzaldehyde	BZDE	100-52-7
m-Tolualdehyde	mTOL	620-23-5
o-Tolualdehyde	oTOL	529-20-4
p-Tolualdehyde	pTOL	104-87-0
Acetophenone	ACNE	98-86-2
1-Indanone	1IND	83-33-0
9-Fluorenone	9FLN	486-25-9
Perinaphthenone	PNNN	548-39-0
Benzophenone	BZP	119-61-9

1,4-Benzoquinone	BQN	106-51-4
1,4-Naphthoquinone	NQN	130-15-4
Acenaphthoquinone	ACNQ	82-86-0
Anthraquinone	ATQ	84-65-1
Alkanes		
Dodecane	DDCN	112-40-3
Tetradecane	TDCN	629-59-4
Hexadecane	HDCN	544-76-3
Octadecane	ODCN	593-45-3
Eicosane	ECSN	112-95-8
Docosane	DCSN	629-97-0
Tetracosane	TCSN	646-31-1
Hexacosane	HCSN	630-01-3
Octacosane	OCSN	630-02-4
Triacontane	TCTN	638-68-6
Dotriacontane	DCTN	544-85-4
Tetratriacontane	TECTN	14167-59-0
Hexatriacontane	HCTN	630-06-8
FAMEs		
Myristic Acid Methyl Ester	MAME	124-10-7
Palmitic Acid Methyl Ester	PAME	112-39-0
Stearic Acid Methyl Ester	SAME	112-61-8
Oleic Acid Methyl Ester	OAME	112-62-9
Elaidic Acid Methyl Ester	EAME	1937-62-8
Linoleic Acid Methyl Ester	LIEC	112-63-0
Linolelaidic Acid Methyl Ester	LDIC	2566-97-4
Linolenic Acid Methyl Ester	LNIC	301-00-8
Arachidic Acid Methyl Ester	AAME	1120-28-1
Behenic Acid Methyl Ester	BAME	929-77-1

Estimation of Concentrations. Because the mass of PM collected on each filter varied by run due to slight changes in dilution ratio and sample flows, the measured mass of each target analyte was normalized to the total gravimetric mass of PM using **Equation 2.**

$$A = B \times \frac{C}{D} \qquad (2)$$

where,

A = Total Mass of Analyte on Filter (ng)
B = Measured mass of Analyte in extract (ng)
C = Number of Punches in Filter (C = 44)
D = Number of Punches per Extract (D = 2)

Note that it was assumed that the available diameter for the deposition of PM on a filter was 42 mm because the o-ring in the filter holder covered about 5 mm at the edge of the filter (each filter has a diameter of 47 mm). It was further assumed that the PM was uniformly deposited on the filter. Therefore, from those assumptions, the total number of 1/4 inch punches that could be cut out from the 42 mm diameter of the filter available for PM deposition was 44.
The concentrations (Mass of Analyte per Volume of Air Sampled, ng/m^3) of the analytes were obtained by dividing the mass of analyte (ng) on filter (A in Equation 2 above) by the volume of air (m^3) sampled during that particular run, and then multiplying by the dilution ratio of that run. The concentrations for a given fuel type (Engine Blank, B00, or B20) were determined by obtaining the average concentrations for the filters used during sampling of a particular fuel type.

For example, the concentrations for the engine blank were determined by averaging the concentrations for Filters #72 and #73, the B00 concentrations were obtained by averaging the concentrations for Filters #112 and #114, while the B20 concentrations were determined by averaging the concentrations for Filters #126 and #128.
The total concentration of a group of analytes of the same family (alkanes, PAHS, POCs, or FAMEs) was obtained by summing the concentrations of the individual compounds/analytes in that family.

2.1.2 Filter Punch Sequential Extractions and Analyte Percent Recoveries

Determination of the number of times a punch needed to be extracted for the complete removal of the compounds of interest was performed using a 16 PAHs standard. The extraction procedure differed slightly from the final procedure described above in that one 1/4- inch QFF punch was spiked with 1 µL of a 5 ppm standard containing the 16 EPA PAHs and then inserted in a 180 µL glass TD-vial. The punch was sequentially extracted by sonicating 3 times with 70 µL of extraction solvent (DCM:Hex, 1:1, v/v) for 3 minutes each time. The 3 extracts were put in separate TD-vials and each extract blown down to about 10 µL. The 3 TD-vial containing the sequential extracts were then each placed in a closed 30 mL vial and the solvent was allowed to volatilize at room temperature until the final solution volume in the TD-vial was about 1 to 2 µL. The sequential extracts from the punch were analyzed separately on the TD-GCMS using 1 µL of a 2 ppm internal standard solution of phenanthrene-d10 and perylene-d12 for quantitation. This experiment was performed in triplicate (QFF Punch #1, QFF punch #2, and QFF punch #3).

In addition to analyzing the extracts, the PAHs residual left on the filter punches was analyzed by inserting the extracted filter punches inside the TD-injector vial. The amount of PAHs left in the punch after extraction was then determined. This also made it possible to perform a mass balance on each of the PAHs in the standard.

2.1.3 Number of Filter Punches for Quantitative Filter Sample Analysis

Before the extraction of the real-world diesel/biodiesel filters could begin, the number of ¼-inch punches that needed to be extracted in order to obtain detectable concentrations of the compounds of interest (alkanes, PAHs, FAMEs, and POCs) was determined. This test was performed by extracting both a single punch and two punches ("punch pair") for filters (Filters #228 and 229) that were used to sample diluted exhaust from petrodiesel (B00). These two filters sampled exhaust at different ports of the sampling train during the same engine test. Also, Filter #228 was behind a 4-channel glass annular denuder (URG Corp., Chapel Hill, NC) coated with XAD adsorbent (Gundel et al., 1995, Gundel and Lane, 1999), while Filter #229 did not have a denuder upstream. The punch extracts for these two filters were analyzed for PAHs and POCs.

2.1.4 Target Analyte Quality Assurance and Detection Limits

After quantifying the compounds of interest, the integrated peak area for each compound was checked in ChemStation to make sure that (a) the correct peak was integrated (by examining the mass spectrum of each compound), and (b) the peak was correctly integrated by ChemStation software (i.e. the choice of baseline is correct). Usually, there are slight shifts in GC retention times, and sometimes, ChemStation misidentifies peaks for compounds with similar qualifier ions (after the retention times shifted). These errors lead to incorrect molecular assignments especially

for compounds that elute very close to each other. In such cases, the retention times for the misidentified peaks were adjusted such that ChemStation integrated the correct peak/peaks. Furthermore, the peak area for phenanthrene-d10 internal standard for each run was recorded and compared with the peak areas for phenanthrene-d10 in the runs immediately before and after the sample being analyzed. If the peak area for phenanthrene-d10 for a particular run was 2 times less than those for either the before or after runs, then that run was said to have had a bad injection, and the results for that run were not used in the subsequent analyses. Once the injection was flagged as bad, that sample was reanalyzed (if the sample was a standard, a fresh sample of the standard was re-injected in the TD-GCMS, but if it was a filter extract, a new pair of filter punches was extracted and the entire extraction and analysis process repeated).

Solvent blanks and filter blanks were also analyzed on the TD-GCMS to ensure that there was no interference of the target analytes from the solvents and filters. The solvent and filter blanks were treated the same way as the diesel and biodiesel PM filters (i.e. they were exposed to the same glassware, extracted and analyzed the same way as the diesel and biodiesel QFFs).

A check standard containing phenantherene-d10 and perylene-d12 (9 ppm in DCM) was analyzed every day before any samples (standards and filter extracts) were analyzed on the TD-GCMS. This was done in order to ascertain that the instrument performance was good before any samples could be analyzed. If peak areas for phenanthrene-d10 and perylene-d12 were less than 50% of those from the previous day (or the last time the check standard was analyzed), the check standard was reanalyzed. If the peak areas were again less than 50% of those from the previous day, then the TD-GCMS was checked for maintenance needs such as autotune and front end maintenance.

2.2 SAMPLING AND ANALYSIS OF DIESEL AND BIODIESEL FUELS

2.2.1 Fuel Sample Collection and Dilution for GC-MS analysis

The raw petro- and biodiesel fuel samples were taken from the top, middle and bottom of the fuel tank before and after each engine run. The density of each fuel sample was measured by the IROX-Diesel instrument (Grabner Instruments, Oklahoma) and the IROX-D average biodiesel blend percentage value was used to prepare diluted fuel samples. The measured fuel densities for each biofuel blend were 0.88, 0.849, 0.83, and 0.817 g/mL for B100, B50, B20 and B0, respectively. All fuel samples were stored in the freezer in 10mL amber glass vials until they were ready to be diluted for GC/MS analysis. The fuel samples were brought to room temperature and diluted to 25ppm (ug/g) in n-hexane using a two-step procedure. The first step pre-diluted the samples by injecting exactly 3uL of fuel using a Hamilton 10uL syringe into 1.5 mL of n-hexane. This brought the concentration to approximately 2500ppm (depending on fuel density). The volume of pre-diluted solution needed to further dilute the sample down to 25ppm in 1.5mL of hexane was then calculated using **Equation 3** and the calculated volume of fuel (approximately 9uL) was added using a Hamilton 25uL syringe. Three internal standards (i.e. phenanthrene-d10, tetracosane-d50, and methyl heneicosanoate) were also added to each sample at a concentration of 2ppm. These internal standards were chosen to represent a subset of the three primary functional group categories found in diesel and biodiesel fuel: PAHs, Alkanes, and FAMEs.

$$Vol,inj = 1.5mL \times 1000\frac{uL}{mL} \times \frac{25\,ppm}{Conc,solution} \quad (3)$$

where,

Vol,inj = Calculated volume of solution needed to dilute the sample to 25ppm
Conc,solution = Concentration of pre-diluted solution (ppm)

2.2.2 Fuel Sample GC-MS Instrument Conditions

The raw fuel samples were analyzed on an Agilent 6890 gas chromatograph equipped with an Agilent 5973N mass spectrometer detector, and an Agilent 7683 automated liquid sampler (ALS) injection. The software packages used were Chemstation revision E.02 and NIST08 mass spectral library. In order to resolve key analytes, the fuel samples were analyzed on both a Restek Rxi-XLB non-polar column and a Supelco SLB-IL100 polar column. The Rxi-XLB column was chosen to resolve the non-polar analytes such as alkanes and PAHs, while the SLB-IL100 column was used only to resolve the FAMEs and their isomers. The conditions and temperature programs for the GC methods used are detailed in **Table 2-4.** Before sampling on the GC/MS, diluted samples were removed from the freezer and allowed to equilibrate at room temperate for a period of time (>1 hour). The samples were then placed on the autosampler tray while a run sequence was programmed into Chemstation. A run sequence usually consisted of a total of seven runs, including four sample runs of varying biodiesel blend percentages, a check standard run containing three internal standards at 2ppm, and a hexane blank run at the beginning and end of the sequence.

Table 2-4. GC/MS Method Conditions for Fuel Analysis

Conditions	
Column:	Supelco SLB-IL100 Fused Silica Capillary Column
Dimensions:	30m x 0.25mm x 0.25 um
Oven:	50^0 C, 3^0 C/min to 200^0 C (60min)
Injector:	240^0 C
Detector:	240^0 C
Carrier Gas:	99.999% He @ 1mL/min
Injection:	1uL splitless
Column:	Restek Rxi-XLB Fused Silica Capillary Column
Dimensions:	30m x 0.25mm x 0.25um
Oven:	60^0 C, 3^0 C/min to 288^0 C (86min)
Injector:	250^0 C
Detector:	250^0 C
Carrier Gas:	99.999% He @ 1mL/min
Injection:	1uL splitless

2.2.3 Biodiesel Fuel FAMES Quantitation with Polar GC Column

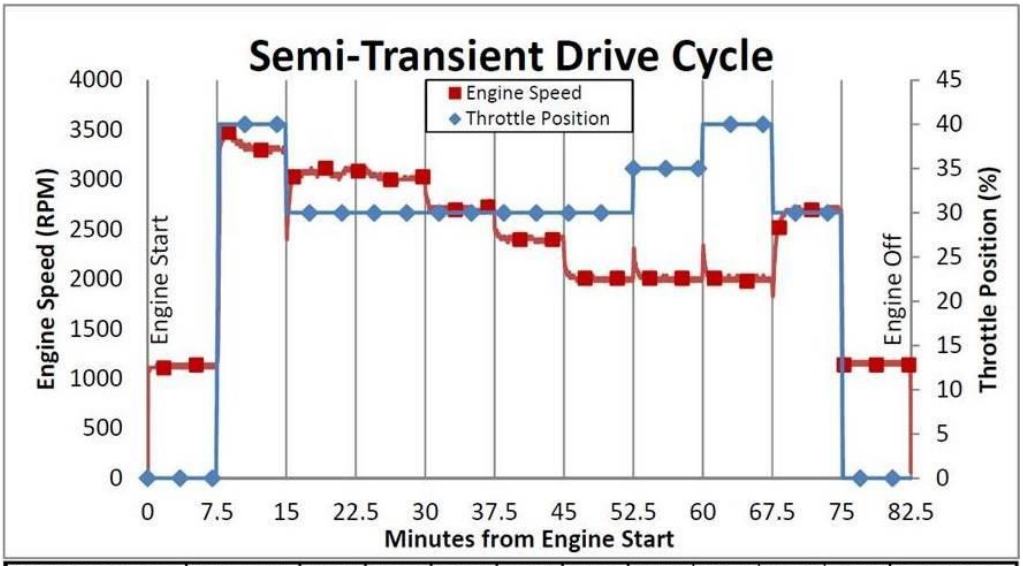
A quantitation database of compound retention times, qualifier ions, and calibrations curves was programmed into Chemstation for each set of analytes and for each column. The Restek Rxi-XLB column [30m x 0.25 mm i.d. x 0.25 µm film thickness] data analysis method consisted of 16 regulated EPA PAHs and 13 even-number n-alkanes from Dodecane (C12H26) to Hexatriacontane (C36H74). A five-point calibration for the 16 PAHs was performed using a 100 µm/mL (conc) chemical standard mixture purchased from Sigma-Aldrich (catalogue # PM-611) at individual concentration of 0.5, 1, 2.5, 5, and 10ppm in dichloromethane ([DCM] Omni-Solv HR-GC grade). Alkanes were calibrated using a chemical standard mixture of C10-C40 n-alkanes (50mg/L each) purchased from Sigma-Aldrich (catalogue # 68281-2ML-F) using six data points at individual concentrations of 0.5, 1, 2, 2.3 5, and 10ppm in HR-GC grade dichloromethane (DCM). The SUPELCO SLB-IL100 (30m x 0.25mm i.d. x 0.25 µm film thickness) polar column was used for the quantitation of FAMEs and a separate database was developed. The FAMEs

analysis database was programmed and calibrated using the 37-component FAME mix purchased from Supelco (catalogue # 47885-U) prepared from a 10mg/mL (concentration in DCM) ampule. A six-point calibration for these compounds was performed at a total concentration of 0.5, 1, 2.5, 5, 20, and 30ppm in DCM. Individual concentrations of FAMEs in the Supelco 37-component FAME mix varied from 2% to 6% (by weight), which made it necessary to adjust calibrations for the varying compound concentrations. Individual compound concentrations varied from 0.01 to 1.8ppm. For more detailed information on calibration curves and data, refer to Appendices I and III.

2.3 ENGINE SAMPLING AND TEST CONDITIONS

A 1.9 Liter, 4-cylinder, naturally aspirated Volkswagen light-duty diesel engine (nominal 44 kW @3600 rpm) with 60 kW, 145 N-m Klam K40 retarder (Armfield Ltd, model CM-12) that enables reproducible operating cycles was programmed to operate an 85-minute "aggressive" cycle comprised of different throttle and load settings (**Figure 2.1**). Particles from the engine's exhaust were collected simultaneously by multiple techniques to permit a variety of analyses: real-time monitoring of total particle number distribution (TSI, Inc. Engine Exhaust Particle Sizer, EEPS); Teflon-coated glass fiber ("FIberFilm", Pall Gelman T60A20) and/or quartz fiber filters ("QFF", Pall Tissuquartz 2500QAO-UP) for PM gravimetric mass and chemical analysis. This study examines the composition of PM collected on filter samples after single-stage exhaust dilution with dry (silica gel), hydrocarbon-free (activated charcoal) and HEPA-filtered room air. The engine was run in a laboratory at ambient temperature and humidity. The dilution ratio was monitored using orifice meters to measure the 1Hz flowrates at the dilution air inlet and the diluted exhaust outlet of a Dekati Diluter. Average dilution ratios over the entire test period are reported for each engine run (**Table 2.1 above**). After post-weighing, all filter samples were stored at -80^{o}C until chemical analysis by thermal desorption-GCMS (TD-GCMS). QA/QC procedures included blank, duplicate and calibration standard measurements as well as pre- and post-sampling verification of the real-time analyzers using laboratory calibration standard particles and gases. An "engine blank" run was performed identically without starting the diesel engine.

Engine emissions sampling was performed using two fuel compositions, ultralow sulfur diesel (Trono Fuels, Burlington, Vermont; petrodiesel or B0) and certified soybean-based biodiesel (Burke Oil, Chelsea, MA) blended at 20 % by volume (B20) with the Trono petrodiesel. The selection of B20 was based on current real-world use and soybean as the most commonly available feedstock in the U.S. today for commercially available American Society for Testing and Materials (ASTM) grade biodiesel fuel. The B20 was blended in the laboratory 24-hours prior to experiments and the blend volume percent and presence of any impurities were verified via the FTIR spectral analysis (Grabner Instruments IROX-D). Additional raw fuel samples at blend ratios of B50 and B100 were analyzed to evaluate trends in biodiesel fuel FAMES composition. Neat petrodiesel (B0) and neat biodiesel (B100) were used directly without modification.



Drive Cycle Parameter	Warm Up Idle	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5	Mode 6	Mode 7	Mode 8	Mode 9	Cool Down Idle
Throttle Position (%)	0	40	30	30	30	30	30	35	40	30	0
Engine Speed (RPM)	No Load	3300	3100	3000	2700	2400	2000	2000	2000	2700	No Load

Figure 2.1. Engine drive cycle used for diesel and biodiesel PM generation.

3. Results

3.1 GC/MS Extraction and Method Development Results

The results for filter sample extraction method development show a high percent recovery (~75%) of the PAH standards in the first extraction. In order to achieve at least a 95% recovery of the standards, three sequential 3-minute sonication extractions were necessary. For the extraction of real-world diesel and biodiesel filters, sonication for 5 minutes was necessary to dislodge analytes from the PM. Low recoveries were observed for the more volatile PAHs (e.g. naphthalene, acenaphthylene), as well for the low molecular weight POCs (e.g. 2-hexanone, 2-heptanone, undecanal), which suggests loss during blowdown. Overall, the reproducibility of the extraction procedure indicated good precision with RSD values less than 20% for the majority (>90%) of the target analytes. The number of ¼-inch punches needed in order to obtain adequate resolution on the GC/MS was determined by analysis of both single and punch-pair extractions. The mass detected by the GC/MS in punch-pair extracts was greater, ranging from a factor of two to a factor of four, than the mass detected in single-punch extracts, which indicates a better signal to noise ratio for quantitation in punch-pair extracts.

The method development for analysis of diesel/biodiesel samples shows that the non-polar analytes (e.g. alkanes, PAHs) are easily resolved and quantified on a nonpolar GC column, such as the Restek Rxi-XLB used in these experiments. However, it was found that FAMEs were being double counted on the nonpolar column due to coelution of target analytes such as palmitic acid, methyl ester and cis-9-hexadecanoic acid, methyl ester; therefore, a polar column, such as the Supelco SLB-IL100 polar column, should be used for quantitation of FAMEs.

Filter punch analysis for the diesel/biodiesel exhaust PM indicated an increase in nearly all target analyte classes (Alkanes, PAHs, FAMEs, and POCs) for B20 biodiesel exhaust. Target analytes were chosen based on their toxicological and environmental degradation effects, and computed in terms of emission rates per volume of exhaust (ng/m^3) as well as PM concentration per mass of PM in the exhaust ($ng/\mu g_{PM}$). Over all the samples analyzed, compared to B0 petrodiesel, the emission rates for B20 biodiesel increased by a factor of 4 for alkanes, 1.5 for PAHs, 20 for FAMEs, and 2 for POCs.

For biodiesel samples, saturated FAMEs made up 81% of the FAMEs detected in the exhaust PM, while they made up only 13% of the total FAMEs in the raw fuel. In addition, long-chain fatty acids (e.g. arachidic acid, methyl ester [C20:0] and behenic acid, methyl ester [C22:0]) were not detected in the raw fuel, but were abundant in the exhaust PM. Ester-bound aldehydes, also known as core aldehydes (e.g. 9-oxo-nonanoic acid, methyl ester), were also identified in the exhaust PM. The mechanism for the formation of these long-chain fatty acids and core aldehydes will be the subject of future investigations.

Appendices VI and VII contain the analytical results for individual target analyte concentrations in exhaust PM (normalized by exhaust sample volume and by PM mass), cumulative organic compound emissions in each functional group class and fuel composition.

Instrument Detection Limits. Method detection limit (MDL) is defined as the amount of analyte that can be identified, measured, and reported with 99% confidence that the amount of analyte in a sample is greater than zero (Method 556, US EPA 1998).

The method detection limits were estimated according to Method 556 (US EPA 1998) using Equation 1.

$$Method\ Detection\ Limit\ (MDL) = St_{(n-1,\ \ 1-alpha\ =\ 99)} \qquad (1)$$

where S = standard deviation of n runs for a sample whose concentration of the analyte is about 5 times the noise level, n = number of replicate, and $t_{(n-1,\ 1-alpha=99)}$ is the Student's t-value for the 99% confidence level with n-1 degrees of freedom.

MDL for the PAHs were determined by analyzing a 0.125 ppm PAHs standard (number of runs, $n = 7$) on the TD-GCMS, while the detection limits for the alkanes were determined using a 0.7 ppm standard ($n=7$), and the detection limits for the PFBHA-oximes for the POCs were estimated using 2 µL of a 2 ppm standard ($n=8$). The MDLs for the FAMEs were determined by analyzing a 40 ppm standard of the 10 FAMEs mix four times ($n=4$) on the TD-GCMS. **Table 3-1** below shows the MDLs of the alkanes, PAHs, PFBHA-oximes for the POCs, and FAMEs.

Table 3-1. Method detection limits of the alkanes, PAHs, FAMEs, and PFBHA-oximes for the POCs. n = number of replicate runs.

Alkanes *(n=7)*	**MDL (ng)**	**POC-oximes *(n=8)***	**MDL (ng)**
Dodecane	0.62	2-Pentanone	10.67
Tetradecane	0.45	3-Pentanone	13.71
Hexadecane	0.31	n-Hexanal	3.23
Octadecane	0.19	n-Heptanal	2.41
Eicosane	0.24	n-Octanal	2.93
Docosane	0.20	2-Nonanone	2.48
Tetracosane	0.21	n-Nonanal	2.04
Hexacosane	0.21	n-Decanal	1.67
Octacosane	0.23	Undecanal	1.00
Triacontane	0.28	2-Hexanone	5.66
Dotriacontane	0.30	2-Heptanone	4.11
Tetratriacontane	0.21	2-Octanone	3.44
Hexatriacontane	0.62	Dodecanal	1.08
PAHs *(n=7)*	**MDL (ng)**	Benzaldehyde	2.72
Naphthalene	0.11	m-Tolualdehyde	2.40
Acenaphthylene	0.12	o-Tolualdehyde	3.42
Acenaphthene	0.17	p-Tolualdehyde	2.18
Fluorene	0.09	Acetophenone	2.72
Phenanthrene	0.13	1-Indanone	1.05
Anthracene	0.10	9-Fluorenone	1.30
Fluoranthene	0.13	Perinaphthenone	0.65
Pyrene	0.14	Benzophenone	0.92
Benzo[a]anthracene	0.16	1,4-Benzoquinone	2.60
Chrysene	0.12	1,4-Naphthoquinone	1.48
Benzo[b]fluoranthene	0.15	Acenaphthoquinone	1.69
Benzo[k]fluoranthene	0.23	Anthraquinone	0.55
Benzo[a]pyrene	0.21	**FAMEs (*n=4*)**	**MDL (ng)**
Indeno[1,2,3-cd]pyrene	0.25	Myristic Acid Methyl Ester	0.71
Benzo[ghi]perylene	0.23	Palmitic Acid Methyl Ester	1.29
Dibenz[a,h]anthracene	0.19	Oleic Acid Methyl Ester	2.67
		Elaidic Acid Methyl Ester	0.98
		Stearic Acid Methyl Ester	0.83
		Linolenic Acid Methyl Ester	0.52
		Linoleic Acid Methyl Ester	11.69

		Linolelaidic Acid Methyl Ester	0.17
		Arachidic Acid Methyl Ester	0.24
		Behenic Acid Methyl Ester	0.67

The detection limits for the alkanes and PAHs looked quite reasonable, while the detection limits for some of the POCs did not look so reasonable. For example, the PFBHA-oximes for 2-pentanone, 3-pentanone, and 2-hexanone had quite high detection limits (>5 ng for all the above mentioned compounds) which seems very unrealistic. Other compounds such as n-hexanal, n-heptanone, 2-octanone, and o-tolualdehyde had MDLs greater than 3 ng. Because these compounds could barely be detected by the TD-GCMS for the concentration used to determine the detection limits, their peak areas were quite variable, which later led to very high standard deviations. The high standard deviations obtained led to high values of detection limits for the above mentioned compounds (see Equation 1). The rest of the compounds had reasonable detection limits as seen in Table 1. However, the detection limits for the PFBHA-oximes of the POCs were generally seen to be greater than those for the alkanes and PAHs. Most of the FAMEs had plausible detection limits with the exception of linoleic acid methyl ester which had detection limits over 10 ng. The peak areas for palmitic acid, oleic acid, and linoleic acid methyl esters were quite variable, which led to high standard deviation values, and hence high detection limits as seen in Equation 1.

Sequential Extractions. From sequential extractions of the filter punches, on average about 75% of the mass of the PAHs spiked on the punch was extracted in the first extraction, additional mass was extracted during the second extract (about 20%), and less than 5% of the mass was extracted in the third extract **(Figure 3-1 (a), (b), and (c)).** Thus, three sequential extractions were determined to be sufficient to extract all the PAH compounds from the filter punches. Analysis of the residual in the filter punches showed that very little PAH mass was left behind on the filter; the measured residual mass accounted for less than 4% of the spiked amount for all PAHs and all three QFF replicate punches (**Figure 3-1(d)).**

The total %recoveries for all the three filter punches were quite high, ranging from 68 to 130%. However, there was some inconsistency for the more volatile PAHs (naphthalene, acenaphthylene, acenaphthene, and fluorene) which had recoveries that were not so reproducible. The high volatility of these PAHs could explain the variability observed among the three extracts. The rest of the PAHs had relatively reproducible recoveries that ranged from 70 to 113% with RSD values less than 20%.

It was also established that the three sequential, 3-minute sonication extractions removed at least 95% of the target PAH compounds. During the extraction of the real-world diesel/biodiesel filters, however, 5 minutes of sonication were employed during each extraction. This was done because it was believed that dislodging analytes from particulate matter needs more time than that required to remove the compounds from a blank filter punch.

From the sequential extraction results, it was established that three 3-minute sequential extractions by sonication were sufficient to remove/extract at least 95% of the compounds of interest. During the extraction of the real-world diesel/biodiesel filters, however, 5 minutes of sonication were employed during each extraction. This was done because it was believed that dislodging compounds/analytes from particulate matter needs more time than that required to remove the compounds from a blank filter punch.

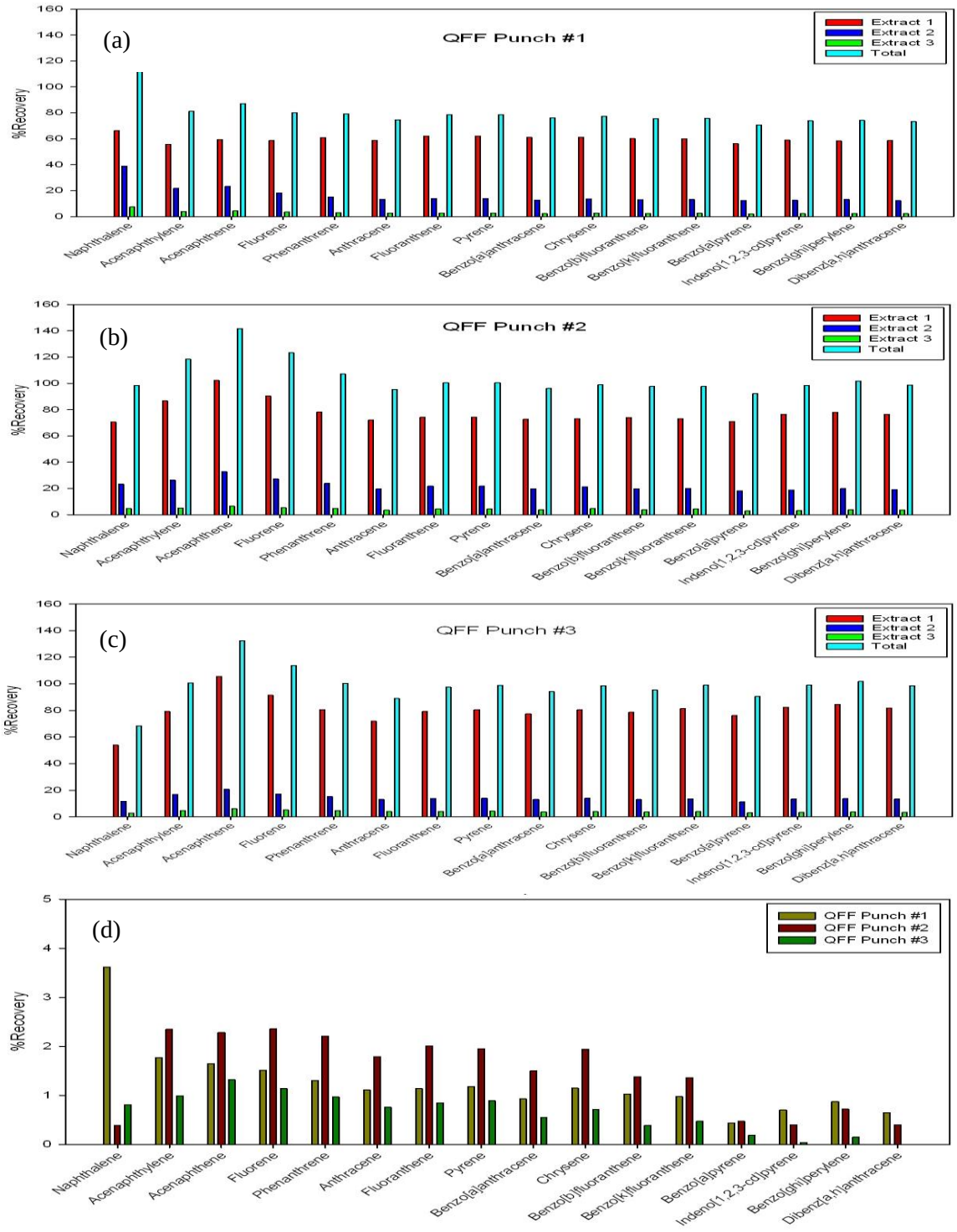


Figure 3-1. Percent Recoveries of the PAHs obtained after 3 sequential extractions of three different 1/4 inch QFF punches spiked with 1 µL of a 5 ppm 16 PAHs standard. (a) QFF Punch #1, (b) QFF Punch #2, (c) QFF Punch #3, (d) Residual PAHs in the QFF punches.

Extract Recovery of Target Analytes. Percent recoveries for the PAHs spiked to clean QFFs with the PAH and POC standards are shown in Table 3-2. The %Recoveries for all PAHs were good and ranged from 72-112% with the exception of naphthalene (1.6%). The very low recovery for naphthalene was not surprising given its high vapor pressure, which suggests loss during the blowdown/ sample concentration step. Acenaphthylene also had a lower recovery (72%) compared to the rest of the PAHs, and this can also be attributed to its higher volatility compared to the other PAHs. The RSD values for all the PAHs were quite low (<20%), suggesting good precision of the procedure.

Table 3-2. Average percent recoveries of the PAHs spiked on 1/4 inch QFF punches. Number of replicates n=4.

PAH	Mean	Std Dev	%RSD
Naphthalene	1.6	0.1	5.3
Acenaphthylene	71.8	9.4	13.1
Acenaphthene	82.2	8.8	10.7
Fluorene	112.7	7.6	6.7
Phenanthrene	105.3	9.4	8.9
Anthracene	100.9	10.4	10.3
Fluoranthene	105.2	9.1	8.6
Pyrene	105.6	8.7	8.2
Benzo[a]anthracene	106.0	8.7	8.2
Chrysene	106.3	9.1	8.6
Benzo[b]fluoranthene	104.3	7.4	7.1
Benzo[k]fluoranthene	105.1	7.2	6.8
Benzo[a]pyrene	101.1	6.7	6.6
Indeno[1,2,3-cd]pyrene	106.4	6.7	6.3
Benzo[ghi]perylene	107.8	6.5	6.0
Dibenz[a,h]anthracene	109.5	6.5	6.0

Average percent recoveries for the POCs (**Table 3-3)** were typically much lower than those for the PAHs. Recoveries for most of the POCs were greater than 60%, but for 2-hexanone, 2-heptanone, undecanal, dodecanal, m-tolualdehyde, 9-fluorenone, and benzoquinone %Recoveries were between 50-60%. Only 2-pentanone, 3-pentanone, 1-indanone, and acenaphthoquinone had recoveries less than 50%. The low recoveries of 2-pentanone and 3-pentanone were expected because of their high vapor pressures, which means that these compounds were possibly lost during the concentration/blowdown step. The reason for the low recoveries of 1-indanone and acenaphthoquinone is not known. Very high recoveries were obtained for perinaphthenone and anthraquinone, 131% and 203%, respectively. The precision for the extractions was quite good as most of the POCs registered RSD values less than 20%. Only 2-pentanone, 3-pentanone, and acenapthoquinone had RSD values greater than 20%. The high variability for 2-pentanone and 3-pentanone was expected because of their high volatility, but the reason for the high variability of acenaphthoquinone is not known.

The results for the extraction of QFF punches spiked with the PAHs and POCs standards indicated that the analytes in the diesel and biodiesel exhaust PM could be extracted and analyzed with good reproducibility (<20% RSD), but that POC extraction and analysis was not as effective as that for PAHs.

Table 3-3. Average percent recoveries of the POCs spiked on ¼-inch QFF punches. Number of replicates n=4.

Compounds	Mean	Std Dev	%RSD
2-Pentanone	32.2	6.9	21.5
3-Pentanone	24.1	7.9	32.8
2-Hexanone	53.0	11.4	21.5
n-Hexanal	74.1	7.8	10.5
2-Heptanone	56.7	10.4	18.3
n-Heptanal	84.9	15.7	18.5
2-Octanone	81.5	13.7	16.8
n-Octanal	91.0	4.6	5.1
2-Nonanone	67.8	13.5	19.9
n-Nonanal	80.4	6.6	8.3
n-Decanal	60.2	6.0	10.1
Undecanal	56.8	6.3	11.0
Dodecanal	55.8	5.4	9.7
Benzaldehyde	70.0	9.0	12.8
1,4-Benzoquinone	51.7	9.4	18.2
Acetophenone	66.1	7.6	11.5
m-Tolualdehyde	59.1	7.5	12.7
o-Tolualdehyde	65.5	12.0	18.2
p-Tolualdehyde	61.9	7.1	11.5
1-Indanone	48.8	3.8	7.8
1,4-Naphthoquinone	75.0	8.9	11.9
9-Fluorenone	59.6	4.3	7.3
Perinaphthenone[a]	131.9	11.9	9.0
Benzophenone	71.3	10.5	14.7
Acenaphthoquinone	30.1	12.3	40.8
Anthraquinone[a]	203.3	11.4	5.6

[a] the analyte was quantitated in its un-derivatized form.

3.2 Quantitation and Recovery Standards

The four compounds added to the filter punch extracts during processing were intended to be useful for evaluating samples experiencing analytical losses due to (a) poor nonpolar compound extraction (tetracosane-d50); (b) excessive blowdown and evaporative loss (anthracene-d10); (c)poor or incomplete derivatization reaction yield (6-Fluoro-4-Chromanone); and (d) poor polar fraction extraction (2-Fluoro-9_Fluorenone). **Table 3-4** shows the average recoveries of these quantitation and recovery standards that were used during the extraction of the QFF punches spiked with PAHs and POCs. For polar analytes, 6-fluoro-4-chromanone was used as the quantitation standard for the derivatized POCs, and it had an average %recovery of 95%, with an RSD value of 8.6%. This means that the derivatization process was both successfully and reproducibly performed. The %recovery for the POCs recovery standard (2-fluoro-9-fluorenone) was low (only 46.5%), but it was quite reproducible with a %RSD value of 12% for four replicate standards. The extraction and analysis of the nonpolar compound recovery standards (anthracene-d10 and tetracosane-d50) were

quite good with percent recoveries of 82.9% and 77.5%, respectively. The %RSD values for anthracene-d10 and tetracosane-d50 were also good (15.4% and 12.5% for anthracene-d10 and tetracosane-d50, respectively). These results for the quantitation and recovery standards confirm that these compounds could be used with confidence for the quantitation of the recoveries of the extracted analytes in the real-world diesel and biodiesel filter samples.

Table 3-4. Average percent recoveries for the quantitation and recovery standards used during the extraction of the 1/4 inch QFF punches spiked with PAHs and POCs. Number of replicates n=4.

Compound	Mean	Std Dev	%RSD
6-Fluoro-4-Chromanone	95.5	8.2	8.6
2-Fluoro-9-Fluorenone	46.5	5.6	12.1
Anthracene-d10	82.9	12.7	15.4
Tetracosane-d50	77.5	9.6	12.5

Determination of Number of 1/4 inch Punches to be Extracted. The mass of PAHs and POCs in the single punch and the punch-pair extracts from the denuded (Filter #228) and undenuded (Filter #229) filters are shown in **Tables 3-5 and 3-6, re**spectively. No PAH were detected in the single or punch-pair extracts for Filter #228 (**Table 3-4**) possibly because all the PAHs were deposited in the XAD-coated denuder upstream of Filter #228. For Filter #229, four PAHs (acenaphtylene, acenaphtene, phenantherene, and pyrene) were detected in the one punch extract, while 7 PAHs were detected in the punch-pair extract. Acenaphthylene and acenaphthene were detected in the single punch extract for Filter #229, but they were not seen in the punch-pair extract for the same filter. The reason for this discrepancy could be loss of these two PAHs during the extraction and analysis of the punch-pair extract for Filter #229 because of their higher volatility and also due to the fact that the concentrations of these PAHs detected in the single punch extract were near the detection limits. The total mass of PAHs detected in the single punch extract for Filter #229 was 2.44 ng, while that detected in the punch-pair extract of the same filter was 6.98 ng, more than two times the single punch mass. The higher mass in the extract of two punches suggests the possibility of better analytical accuracy when concentrations are higher. Also, this result indicates that in order to achieve improved detectability of the PAHs in the real-world diesel/biodiesel exhaust PM samples, two punches need to be combined into a single extract.

Ten POCs were detected in the single punch extract for Filter #228, while 16 POCs were detected in the punch-pair extract for the same filter (**Table 3-6**). The total mass of POCs in the single punch extract for Filter #228 was 4.48 ng, and that in the punch-pair extract was 27.62 ng, again more than a factor of two increase when a second punch is extracted. For the undenuded Filter #229, more POCs were detected in the punch-pair extract than in the single punch extract (20 POCs punch-pair versus 16 POCs single punch). The total mass of POCs in the single punch extract for Filter #229 was 3.10 ng, while that in the punch-pair extract was 11.99 ng, a factor of four difference. The POCs extraction results also confirmed that extraction of a pair of punches in a single extraction led to better detectability of the analytes of interest than extraction of a single punch.

Table 3-5. PAHs detected in single punch and punch-pair extracts of Filters #228 and 229*

	Filter #228 1 Punch	Filter #228 2 Punches	Filter #229 1 Punch	Filter #229 2 Punches
Compound	**Mass of PAH (ng)**	**Mass of PAH (ng)**	**Mass of PAH (ng)**	**Mass of PAH (ng)**

Naphthalene	ND	ND	ND	ND
Acenaphthylene	ND	ND	Bel Cal	ND
Acenaphthene	ND	ND	1.32	ND
Fluorene	ND	ND	ND	1.22
Phenanthrene	ND	ND	0.6	0.6
Anthracene	ND	ND	ND	ND
Fluoranthene	ND	ND	ND	0.62
Pyrene	ND	ND	0.52	0.54
Benzo[a]anthracene	ND	ND	ND	2.48
Chrysene	ND	ND	ND	1.78
Benzo[b]fluoranthene	ND	ND	ND	0.28
Benzo[k]fluoranthene	ND	ND	ND	ND
Benzo[a]pyrene	ND	ND	ND	ND
Indeno[1,2,3-cd]pyrene	ND	ND	ND	ND
Benzo[ghi]perylene	ND	ND	ND	ND
Dibenz[a,h]anthracene	ND	ND	ND	ND
Total	**-**	**-**	**2.44**	**6.98**

Both Filters #228 and 229 were used for sampling during a B00 run. Filter #228 was downstream of a denuder, while Filter #229 did not have a denuder in front of it. ND means that the analyte was not detected; Bel Cal means that the compound was detected but its concentration was so small that the ChemStation software gave a negative value ("Below Calibration").

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Table 3-6. POCs detected in single punch vs. punch-pair extracts of Filters #228 and 229*

	Filter #228 1 Punch	Filter #228 2 Punches	Filter #229 1 Punch	Filter #229 2 Punches
Compound	**Mass of POC (ng)**	**Mass of POC (ng)**	**Mass of POC (ng)**	**Mass of POC (ng)**
2-Pentanone	ND	ND	ND	ND
3-Pentanone	ND	ND	ND	ND
n-Hexanal	0.02	0.22	0.02	0.06
n-Heptanal	ND	ND	ND	ND
n-Octanal	ND	ND	ND	ND
2-Nonanone	ND	ND	ND	ND
n-Nonanal	0.07	0.76	0.20	0.50
n-Decanal	0.17	0.92	0.06	0.48
Undecanal	0.06	0.20	0.09	0.17
2-Hexanone	ND	1.47	0.06	0.06
2-Heptanone	0.40	0.56	0.20	1.56
2-Octanone	0.15	0.89	0.99	5.08
Dodecanal	0.13	0.31	0.15	0.27
Benzaldehyde	ND	0.18	0.03	0.21
m-Tolualdehyde	ND	0.02	0.01	0.04
o-Tolualdehyde	ND	ND	ND	ND
p-Tolualdehyde	ND	ND	ND	0.01
Acetophenone	ND	0.08	0.03	0.10
1-Indanone	ND	ND	ND	0.01
9-Fluorenone	ND	0.02	ND	0.03
Perinaphthenone	ND	ND	0.72	2.08
Benzophenone	0.31	0.39	0.40	0.46

1,4-Benzoquinone	ND	ND	0.01	0.09
1,4-Naphthoquinone	ND	0.02	0.04	0.08
Acenaphthoquinone	ND	ND	ND	ND
Anthraquinone	0.03	0.06	0.09	0.12
Total Mass (ng)	**1.49**	**6.10**	**3.10**	**11.20**

*** Both Filters #228 and 229 were used for sampling during a B00 run. Filter #228 was downstream of a denuder, while Filter #229 did not have a denuder in front of it. ND means that the analyte was not detected.**

3.3 Quantitation and Speciation of Exhaust PM Filter Samples

PM Filter Gravimetric Mass. The B00 filters had mpre gravimetric mass than the B20 filters as seen in Table 3-7. As expected, the filetrs used for the blank runs had very little PM mass sampled although filter #72 had a negative PM measurement of -1.302. The negative mass for filter #72 could be due to measurement errors or due to the moisture absorbed by the QFF used for that particular run. Note that QFFs are hygroscopic, and therefore, are capable of giving inaccurate gravimetric mass measurements especially for very small mass measurements. In general, the PM concentrations (µg/m3) were unexpectedly found to be higher in B20 than in B00. Such an observation was surprising given that previous research has shown that the PM concentrations decrease with increasing biodiesel concentration (e.g. McComick et al., 2001; Knothe et al., 2006).

Table 3-7. PM mass (mg) and concentration (µg/m³) for the filters analyzed in this study.

Filter ID #	Test Date MM/DD/YY	Fuel	Filter Type	PM Mass (mg)	Flow rate (L/min)	Sample Time (min)	Total Flow (L)	PM Con (µg/m³)	DR
72	8/23/11	Blank	QFF	-1.302	N/A	N/A	N/A	N/A	19
73	8/31/11	Blank	QFF	0.057	N/A	N/A	N/A	N/A	21
112	9/21/11	B00	QFF	0.274	20	88	1760	155.68	21
114	9/22/11	B00	QFF	0.233	20	84	1680	138.89	27
126	10/11/11	B20	FF	0.148	10.4	75	780	189.74	30
128	10/12/11	B20	FF	0.126	9.47	88	833.36	151.20	24

3.2.1 Alkanes

The concentrations of even n-alkane (C_{12} – C_{34}) target analytes measured in engine blanks (filters #72 and #73), B00 (filters #112 and #114), and B20 (filters #126 and #128) filters (**Table 3-8**) show the alkanes detected in the engine blank filters were not identified with certainty mainly because their spectra did not match those for the authentic standards (their Q-values were less than 50%). For the B00 filters, with the exception of dodecane, tetradecane, hexadecane, dotriacontane, and tetratriacontane the rest of the alkanes were above their detection limits, and were also detected with Q-values greater than 50%. In the B20 filters, dodecane, tetradecane, hexadecane, octadecane, triacontane, and dotriacontane were detected with Q-values less than 50%. The rest of the alkanes in the B20 filters were above their detection limits, and their Q-values were greater than 50%. The concentrations of alkanes emitted generally increased with increasing molecular weight (size) of the alkanes especially for B20. More variability was seen in the concentrations of alkanes in the B20 filters as seen in Table 1 (RSD values for most of the alkanes in B20 were greater than 20%, while most of those for B00 were

less than 20%). The average total alkanes concentrations were found to be about 3.2 times higher in B20 than in B00. This kind of trend was not expected because petrodiesel has more hydrocarbons than biodiesel, therefore, petrodiesel is expected to have more hydrocarbon emissions than biodiesel. Additionally, previous research has shown that the concentrations of hydrocarbons decrease with increasing biodiesel. For example, Payri et al., 2009 found that the total hydrocarbons decreased by 34%, 54%, and 64% with used frying oil biodiesel blends of B30, B50, and B100, respectively in a single cylinder DI diesel engine equipped with a Bosch common rail injection system. Sharp (1998) found that the hydrocarbons emissions decreased by almost 20% and 100% with B20 and B100 biodiesel fuel blends run in a 1997 Cummins N14 engine and a 1997 Cummins B5.9 engine. The discrepancy of our results from the published literature could be mainly due to the inconstant dilution ratios that were used during sampling. But it should be noted that the GCMS speciation of normal alkanes does not account for the large number of branched alkanes present in exhaust that would be detected by conventional spectroscopic exhaust analyzers.

Table 3-8. Concentrations (ng/m³) of the alkanes in petrodiesel (B00) and soybean biodiesel (B20) exhaust PM.

Concentrations (ng/m³)						
Fuel Type	**Blank**		**B00**		**B20**	
Filter ID	**#72**	**#73**	**#112**	**#114**	**#126**	**#128**
Air (L)	1240.0	1302.0	1760.0	1680.0	780.0	833.4
Dodecane	420.4[a]	80.2[a]	1078.4[a]	1642.5[a]	3451.1[a]	2703.8
Tetradecane	44.7[a]	90.3[a]	725.9[a]	900.4[a]	7558.7[a]	3762.7[a]
Hexadecane	109.4[a]	35.8[a]	639.8[a]	492.4[a]	1355.2	825.6[a]
Octadecane	21.7	21.5	454.4	629.6	1026.9	535.7[a]
Eicosane	23.6[a]	20.3[a]	295.1	629.6	5765.8	1670.2
Docosane	25.9[a]	23.7[a]	5172.9	2870.0	18627.3	2981.1
Tetracosane	42.4	40.7	3642.7	2550.0	28963.6[c]	4103.0
Hexacosane	58.4[a]	54.6	1558.9	1357.6	3560.5	2098.8
Octacosane	107.1[a]	105.6	1825.3	2377.6	8602.4	4323.6
Triacontane	132.4[a]	129.4[a]	2250.9	2694.2	9208.4	5187.0[a]
Dotriacontane	154.1[a]	148.6	2339.7[a]	3056.4[a]	9393.6	5666.0[a]
Tetratriacontane	172.3[a]	164.2[a]	2546.0[a]	3408.2[a]	8434.0	6094.6

N.D. means that the compound was not detected during TD-GCMS analysis. [a] Mass spectrum did not match with that routinely seen for the known authentic chemical standards (Q-value less than 50). [b] Compound concentration was below the limit of detection and was therefore substituted with the limit of detection. [c] Compound concentration was outside calibration range. [d] Compound did not pass visual inspection.

3.2.2 PAHs

Almost all of the PAHs identified in both the B00 and B20 filters; (a) did not match the spectra for the authentic standards (b) had concentrations below the detection limits and (c) did not pass the visual inspection criterion (**Table 3-9**). Therefore, this means that the concentrations of PAHs

obtained were quite uncertain. The concentrations of PAHs generally increased with increasing molecular weight (increasing number of rings) for both fuel types. The volatile PAHs such as naphthalene, acenaphthylene, acenaphthene, and fluorene were surprisingly detected in all filters for both fuel types including the engine blanks in spite of their high volatility. With the exception of acenaphthene, the rest of the PAHs were detected in both B00 filters (filter #112 and #114). Anthracene and benzo[k]fluoranthene were not detected in any of the B20 filter samples. High variability was further seen in most of the PAHs detected in B20 especially fluorene, fluoranthene, pyrene, benzo[a]anthracene, and chrysene that were detected in filter #126 but not in filter #128. The total PAHs concentrations were found to be 1.9 times higher in B20 than in B00. The reason for this observation could also be due to the inconstant dilution ratios used. Although many previous studies reported reductions in PAHs emissions with increasing biodiesel, some studies reported increases in PAHs emissions with increasing biodiesel. For example, Karavalakis et al., 2011 reported both reductions and increases in PAHs emissions for the variety of biodiesel fuels and driving cycles they used in their study. The authors found that the used frying oil methyl esters (UFOME) biodiesel blends resulted in 11, 27, 21, and 19% increases in total PAHs emissions for the New European Driving Cycle (NEDC), Artemis Urban, Road, and Motorway driving cycles, respectively. Although our results corroborate results from some of the previous studies, it is important to note that most PAHs were not detected with a lot of certainty given that their concentrations were near the detection limits. Future work will aim at extracting bigger punches in order to increase the mass of PAHs extracted, and thus injected onto the GC column for analysis.

Table 3-9. Concentrations (ng/m³) of the PAHs in petrodiesel (B00) and soybean biodiesel (B20) exhaust PM.

Concentrations (ng/m³)						
Fuel Type	**Blank**		**B00**		**B20**	
Filter ID	**#72**	**#73**	**#112**	**#114**	**#126**	**#128**
Air (L)	1240.0	1302.0	1760.0	1680.0	780.0	833.4
PAHs						
Naphthalene	3.8[b,d]	3.7[a,b,d]	56.7[b,d]	76.4[b,d]	182.9[b,d]	137.0[b,d]
Acenaphthylene	4.3[a,b,d]	N.D.	63.3[a,b,d]	168.8[a,b]	204.2[b,d]	152.9 [a,b,d]
Acenaphthene	6.0[a,b,d]	5.7[a,b,d]	N.D.	119.0[a,b,d]	284.7[a,b,d]	213.2 [a,b,d]
Fluorene	3.4[a,d]	N.D.	49.6[a]	63.3[b]	168.3[a,b,d]	N.D.
Phenanthrene	4.6[a,b,d]	4.3[b,d]	67.5[a,b]	90.9[b]	217.5[b]	162.9[b]
Anthracene	N.D.	N.D.	50.9[a,b,d]	68.6[b,d]	N.D.	N.D.
Fluoranthene	N.D.	N.D.	66.1[a,b,d]	89.1[a,b,d]	213.2[a,b,d]	N.D.
Pyrene	N.D.	N.D.	72.1[a,b,d]	97.1[b,d]	232.4[b]	N.D.
Benzo[a]anthracene	N.D.	N.D.	81.0[b,d]	109.1[a,b,d]	261.0[b,d]	N.D.
Chrysene	N.D.	N.D.	63.2[a,b,d]	85.1[a,b,d]	203.6[a,b,d]	N.D.
Benzo[b]fluoranthene	N.D.	N.D.	79.8[a,b]	107.4[b]	257.1[b]	192.5[a,b]
Benzo[k]fluoranthene	N.D.	N.D.	119.7[a,b]	161.2[a,b]	N.D.	N.D.
Benzo[a]pyrene	N.D.	N.D.	109.2[b,d]	147.1[a,b,d]	352.1[a,b,d]	263.6 [a,b,d]
Indeno[1,2,3-cd]pyrene	N.D.	N.D.	130.1[b,d]	175.2[b]	419.3[a,b,d]	314.0 [a,b,d]

Benzo[ghi]perylene	N.D.	N.D.	119.0[b]	160.3[a,b]	383.6 [a,b,d]	287.3 [a,b,d]
Dibenz[a,h]anthracene	N.D.	N.D.	101.4[a,b,d]	136.5[a,b]	326.8 [a,b,d]	244.7 [a,b,d]

N.D. means that the compound was not detected during TD-GCMS analysis. [a] Mass spectrum did not match with that routinely seen for the known authentic chemical standards (Q-value less than 50). [b] Compound concentration was below the limit of detection and was therefore substituted with the limit of detection. [c] Compound concentration was outside calibration range. [d] Compound did not pass visual inspection.

3.2.3 FAMEs

All FAMEs were detected in both B00 and B20 filters. In general, the individual FAMEs concentrations were greater in the B20 PM filters than in the B00 PM filters (**Table 3-10**), as expected. It is important to note that the FAMEs detected in the B00 filters (#112 and 114) did not match the spectra for the authentic standards (Q-values less than 50%), with the exception of palmitic acid methyl ester, elaidic acid methyl ester, and stearic acid methyl ester. Because petrodiesel does not contain FAMEs, it was not surprising that most of the FAMEs detected in the B00 filters had such uncertainties in their identification. Most of the FAMEs detected in the B20 filters were detected with high confidence. Only linolenic acid, linoleic acid, and linolelaidic acid methyl esters were either detected with concentrations below the detection limits, or with a Q-value less that 50% for filter #126. Myristic acid, linolenic acid, linoleic acid, and linolelaidic acid methyl esters were the only FAMEs that were either detected with concentrations below the detection limits, or with a Q-value less that 50% for filter #128.

The saturated FAMEs (myristic acid ME, palmitic acid ME, stearic acid ME, arachidic acid ME, and behenic acid ME) made up most of the FAMEs mass detected in the B20 PM filters. The saturated FAMEs contributed to 65% of the total FAMEs concentration for filter #126, and 75% of the FAMEs concentration for filter #128. This was expected given that the saturated FAMEs are less reactive to oxidation than the unsaturated FAMEs. Therefore, during the combustion of the FAMEs in the engine, the unsaturated FAMEs are more susceptible to oxidation because of the presence of the double bonds, while the saturated FAMEs do not easily provide reactive sites for oxidation. In spite of the fact that biodiesel is majorly made up of unsaturated FAMEs, it is evident from these results that the biodiesel exhaust PM is mostly composed of saturated FAMEs as seen in Table 3. More variability was seen in the palmitic acid methyl ester and stearic acid methyl ester concentrations with RSD values greater than 100% for both methyl esters.

It is also important to note that arachidic acid methyl ester and behenic acid methyl ester were not detected in the raw biodiesel fuel samples. Other methyl esters that are not shown in Table 5 such as heneicosanoic acid methyl ester were detected in the B20 filter samples. It was quite surprising to see FAMEs that were not detected in the raw fuel samples. This, therefore, implies that these FAMEs were probably produced during the combustion of the biodiesel fuel/FAMEs, most likely the unsaturated FAMEs in the engine. Note that odd-numbered FAMEs do not occur in nature, which implies that the observed odd-numbered FAMEs in this study were formed during the combustion of biodiesel in the engine. More studies need to be conducted in order to better understand the mechanism by which the extra FAMEs are produced during the combustion of the FAMEs in the engine.

The average total concentrations per fuel type were also obtained and it was found that the blank filters (filters #72 and #73) had an average total concentration of 11 ng/m^3, while the B00 filters (filters #112 and #114) had an average total concentration of 16990 ng/m^3, and the B20 filters had an average total concentration of 188981 ng/m^3. A lot of variability was seen in the FAMEs concentrations for B20, where most of the FAMEs had %RSD values greater than 50%. The average total FAMEs concentration of B20 was found to be 11 times higher than that

of B00. Because B00 is a pure petrodiesel fuel, it was not expected to see any FAMEs in the B00 PM filter samples. Therefore, the FAMEs detected in the engine blank and B00 filters were potentially due to carryover in the engine.

Table 3-10. Concentrations (ng/m³) for the FAMEs in petrodiesel (B00) and soybean biodiesel (B20) exhaust PM.

Concentrations (ng/m³)						
Fuel Type	**Blank**		**B00**		**B20**	
Filter ID	**#72**	**#73**	**#112**	**#114**	**#126**	**#128**
Air (L)	1240.0	1302.0	1760.0	1680.0	780.0	833.4
FAMEs						
Myristic Acid ME	44.0[b]	32.8	7355.9[a,c]	9313.5[a,c]	4587.4	914.7[b]
Palmitic Acid ME	438.9[c]	232.1[c]	4324.2[c]	4579.4	122983.8[c]	4840.4
Oleic Acid ME	159.9	89.7[b,c]	1393.2[a,b,c]	1876.6[a,b,c]	15765.4	3362.7[c]
Elaidic Acid ME	34.6[a,b,c]	32.9[a,b,c]	786.0	826.5[c]	37035.7[c]	1404.9[c]
Stearic Acid ME	125.3[b]	48.4[b]	1101.9[b]	1480.7[b]	113245.1[c]	8987.5[b]
Linolenic Acid ME	19.8[a,b,c]	20.0[a]	284.6[a,c]	368.1[a,b,c]	3467.9[a]	695.4 [a,b,c]
Linoleic Acid ME	412.5[b,c]	392.8[a,b,c]	6102.6[a,b,c]	8219.9[a,b,c]	19671.4[b]	14729.5 [a,b,c]
Linolelaidic Acid ME	13.9	10.1	151.5[a]	204.0[a]	488.2[a]	359.2[a]
Arachidic Acid ME	8.6[a,b,c]	8.2[b,c]	127.4[a,b,c]	171.6[a,b,c]	16034.8[c]	3277.4[c]
Behenic Acid ME	23.8[b]	22.7[b,c]	352.1[a,b,c]	474.3[a,b]	22364.5[c]	5035.8[c]

N.D. means that the compound was not detected during TD-GCMS analysis. [a] Mass spectrum did not match with that routinely seen for the known authentic chemical standards (Q-value less than 50). [b] Compound concentration was below the limit of detection and was therefore substituted with the limit of detection. [c] Compound concentration was outside calibration range. [d] Compound did not pass visual inspection.

3.2.4 Carbonyls

In general, the individual carbonyls concentrations were greater in the B20 filter samples than in the B00 filter samples with the exception of perinaphthenone (**Table 3-11**). 2-Hexanone, 2-octanone, and nonanal showed somewhat higher variability in the B20 PM than the rest of the carbonyls. 1,4-Benzoquinone and acenaphthoquinone were not detected in any of the filters for both fuel types. Furthermore, octanal and 2-nonanone were only detected in filter #126 (B20). 2-Pentanone and 3-pentanone had concentrations below the detection limits in both B00 and B20 filters. With the exception of filter #72, the concentrations of 2-heptanone in the rest of the filters were below the detection limit. The low and medium molecular weight carbonyls (mostly aliphatic carbonyls with MW<160) such as hexanal, heptanal, nonanal, decanal, 2-hexanone, and 2-octanone appeared to contribute the most to the observed concentrations in both B00 and B20. Previous studies such as (Jakober et al., 2008; Guarieiro et al., 2008; Karavalakis et al., 2011 etc.) have shown that the carbonyls emissions in diesel engines fueled with both diesel and biodiesel

are dominated by the low molecular weight carbonyls. The aliphatic carbonyls contributed 70% to the total concentration in B00, while they contributed 71% to the total concentration for B20. The aliphatic carbonyls concentration was 2.3 times higher in B20 than in B00, while the aromatic carbonyls concentration was 2.2 times higher in B20 than in B00.

The high concentrations of the carbonyls in the engine blank runs could probably be due to background contamination. The average total concentration for B20 was 2.3 times higher than that for B00. Based on previous literature, this result was expected. For example, Cahill and Okamoto (2012) found that the total gas and particle-phase aldehyde emission rates were about 1 to 2 times higher when soybean B50 and B100 fuels were used for the two drive cycles they used in their study. It is also important to note that most of the previous studies (e.g. Guarieiro et al., 2008; Correa and Arbilla. 2008; Karavalakis et al., 2011) have mostly concentrated on gas-phase carbonyl emissions only, and they found that there were considerable increases in carbonyl emissions with increasing biodiesel percentage.

The increase in carbonyl emissions with biodiesel can be attributed to the presence of oxygen atoms in the ester molecule of biodiesel fuel (Correa and Arbilla. 2008). Additionally, the ester group could be responsible for the higher carbonyl emissions in biodiesel because the decomposition of the ester group can lead to formation of carbonyl and olefin products by bimolecular hydrogen abstraction (Schwartz et al., 2006).

Table 3-11. Concentrations (ng/m³) for the carbonyls in petrodiesel (B00) and soybean biodiesel (B20) exhaust PM..

Concentrations (ng/m³)						
Fuel Type	**Blank**		**B00**		**B20**	
Filter ID	**#72**	**#73**	**#112**	**#114**	**#126**	**#128**
Air (L)	1240.0	1302.0	1760.0	1680.0	780.0	833.4
POCs						
2-Pentanone	N.D.	53.1[b]	1128.6[b]	1800.8[b]	4593.0[b]	3887.7[b]
3-Pentanone	28.6[b,c]	32.1[b,c]	581.7[b]	829.2[b]	1966.0[b]	1560.1[b]
n-Hexanal	93.9	94.2	1953.5	2579.8	10709.4[c]	5793.6
n-Heptanal	174.7	103.8	3803.4[c]	5363.3[c]	8734.3[c]	3281.4
n-Octanal	N.D.	N.D.	N.D.	N.D.	5564.4	N.D.
2-Nonanone	N.D.	N.D.	N.D.	N.D.	4904.8	N.D.
n-Nonanal	157.6	186.6[c]	2691.6[c]	4194.1[c]	20592.4[c]	8626.2[c]
n-Decanal	74.3	114.4	1389.0	2002.2	6040.2	2975.2
Undecanal	50.3	58.4	863.9	1175.7	3015.8	1900.5
2-Hexanone	168.9	149.0	5707.1[c]	8607.1[c]	10424.3[c]	21558.2[c]
2-Heptanone	50.5[b]	219.1[c]	945.0[b]	1186.9[b]	2198.9[b]	4596.9[b]
2-Octanone	185.9[c]	172.8[c]	3912.5[c]	6488.3[c]	2716.5[b]	10788.4[b]
Dodecanal	46.7	61.1	831.1	1141.9	2951.8	1763.9
Benzaldehyde	86.8	84.6	1321.4	1761.9	4282.3	3228.0
m-Tolualdehyde	56.0	53.6	861.9	1119.4	2731.9	2046.1
o-Tolualdehyde	72.0	89.7	746.9[b]	1829.1	6067.4	4619.3

p-Tolualdehyde	54.3	52.0	819.6	1097.2	2586.3	1944.8
Acetophenone	59.7	57.5	902.7	1217.0	2931.3	2168.5
1-Indanone	23.0[c]	22.6[c]	348.5[c]	468.9[c]	1102.3[c]	N.D.
9-Fluorenone	47.6	44.9	751.2	N.D.	2296.9	1700.9
Perinaphthenone	N.D.	N.D.	1272.1	1216.4	N.D.	676.6[c]
Benzophenone	173.7	217.5[c]	3342.8[c]	4589.7[c]	10663.5[c]	8723.6[c]
1,4-Benzoquinone	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1,4-Naphthoquinone	N.D.	N.D.	347.0[b,c]	N.D.	1090.9[b,c]	833.9[b,c]
Acenaphthoquinone	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Anthraquinone	18.0[c]	18.1[c]	392.2[c]	517.9[c]	1289.9[c]	682.8[c]

N.D. means that the compound was not detected during TD-GCMS analysis. [a] Mass spectrum did not match with that routinely seen for the known authentic chemical standards (Q-value less than 50). [b] Compound concentration was below the limit of detection and was therefore substituted with the limit of detection. [c] Compound concentration was outside calibration range. [d] Compound did not pass visual inspection.

3.3 Fuel Composition as a Function of Biodiesel Blend Percentage

The FAMEs, PAHs, and Alkanes were quantitated in the raw fuel samples prepared with Burke soy biodiesel and Shell petrodiesel. Each compound was then grouped according to its functional group and the aggregate mass for each group is shown below in **Figure 3-2**. Values represent an average of 45 raw fuel samples, consisting of 8 B0 samples, 10 B20 samples, 12 B50 samples, and 15 B100 samples. Error bars represent one standard deviation from the mean. FAMEs were shown to increase linearly with increasing biodiesel blend percentage, while alkanes and PAHs decreased. The alkanes did not show a linear relationship, and also showed little change from B0 to B50 blends and a steep drop after B50. This may be due to the fact that odd number alkanes were not quantitated by GCMS, therefore accounting for only a fraction of the alkanes present in the petrodiesel. None of the 16 EPA PAHs were seen in any of the raw fuels. There were, however, various tetramethyl naphthalene compounds that were observed in the raw petrodiesel. These compounds were quantified based on the calibration curves for naphthalene, and are represented in **Figure 3-2**.

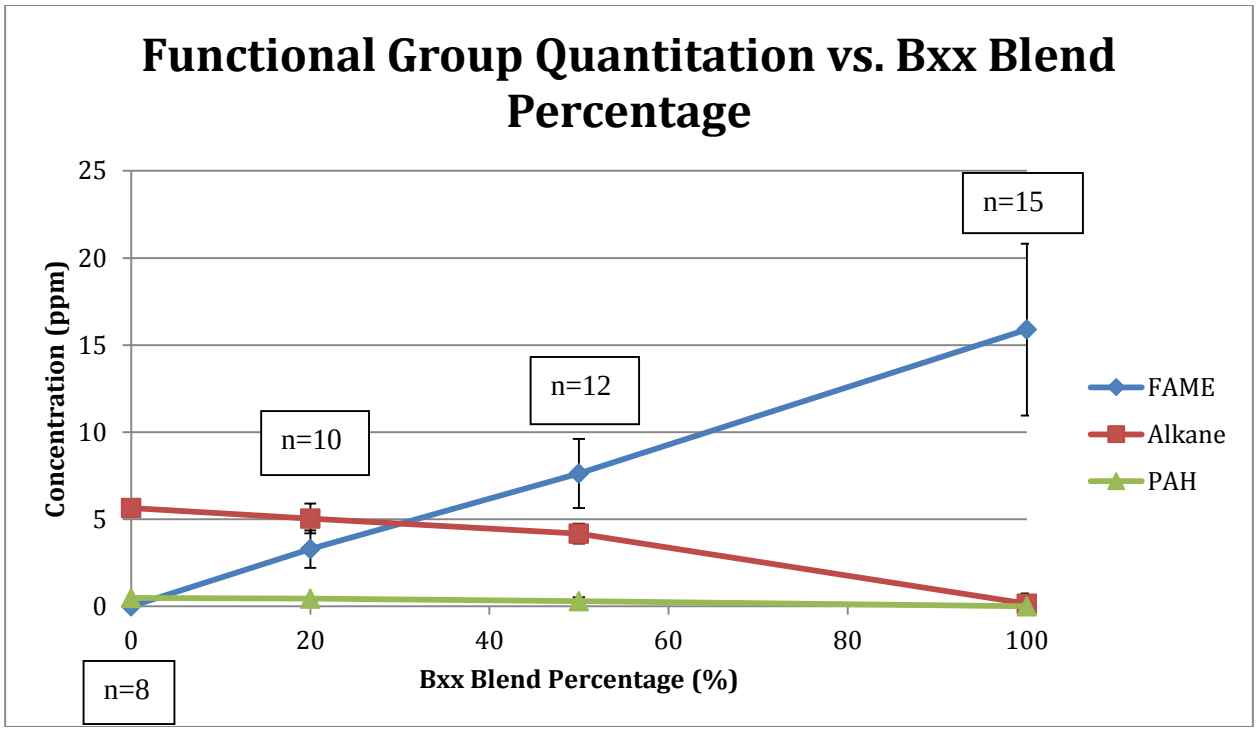


Figure 3-2. Distribution of each primary functional group as a function of biodiesel blend percentage. FAMEs were seen to increase linearly with increasing biodiesel percentage while alkanes and PAHs decrease.

3.3.1 Biodiesel Fuel Composition by Feedstock

The proportions of the FAMEs present in biodiesel can also vary from feedstock to feedstock. Three different biodiesel samples were taken from different feedstocks and analyzed for their relative proportion of FAMEs. These values were then compared to literature values for soybean biodiesel (Moser,2009). The results are summarized in **Table 3-12**.

Table 3-12. The proportion of FAMEs found in biodiesel relative to the total FAMEs found in each sample.

Proportions of FAMEs by Feedstock

	Feedstock			
Fatty acid	Burke	UConn	WVO	Moser 2009
C14:0	0	0	0	0
C16:0	10	9	10	11
C18:0	3	2	3	4
C18:1	40	22	26	23
C18:2	43	62	56	54
C18:3	4	5	5	8
C20:0	0	0	0	0
C22:0	0	0	0	0

The UConn soybean biodiesel and the waste vegetable oil had similar proportions of FAMEs to the values for soybean biodiesel reported by Moser. The Burke soy biodiesel had much higher relative concentrations of methyl oleate (C18:1) than the other two samples. This indicates that

the feedstocks from which these biodiesels were produced varied slightly. This could also impact the chemical composition and quantity of exhaust PM that would be expected from the combustion of each type of biodiesel.

3.3.2 FAMES Chemical Composition of Exhaust PM

A pair of duplicate runs was completed in October 2012 with a B20 blend of Burke soy biodiesel and Shell petrodiesel. The PM from these runs was diluted through the exhaust dilution system and collected on fiber film filters #126 and 128. Filter #126 had a 189.74 µg/m^3 of PM while filter #128 had 151.20 µg/m^3. The $^1/_4$ inch punches from these filters were collected in pairs and analyzed by GCMS to determine the chemical composition. The FAMEs were quantitated in both the raw fuels and the exhaust PM to develop a better understanding of how biodiesel reacts in a diesel engine. The results for the raw fuel are shown below in **Figure 3-3**.

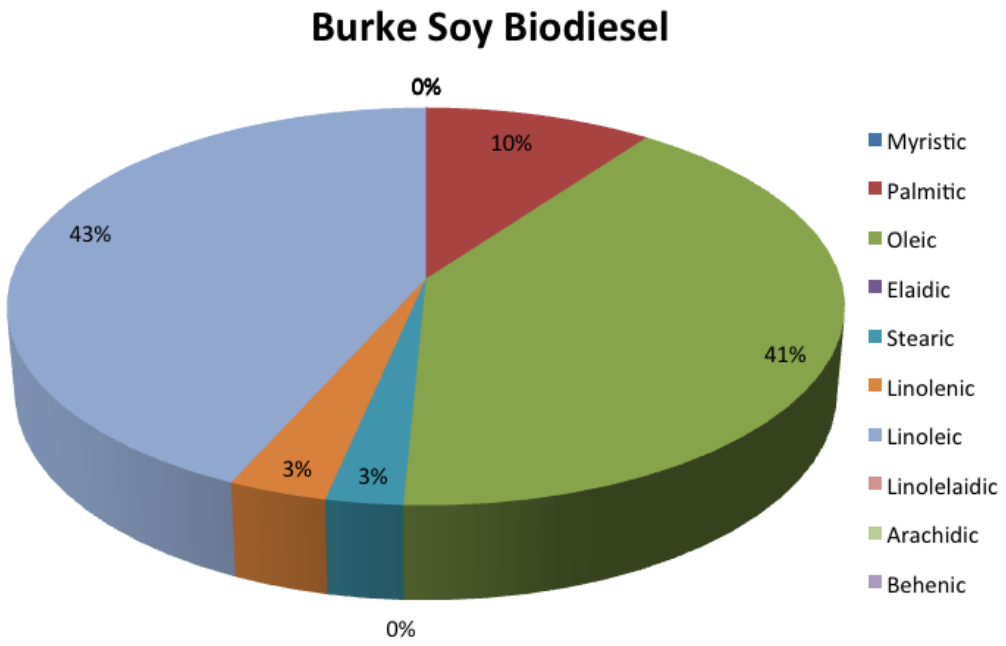


Figure 3-3. Proportions of FAMEs found in the raw Burke soy biodiesel used for engine runs on October 2011. The values represent an average of five runs taken over three days from different locations in the gas tank before and after engine runs.

The raw Burke soybean biodiesel was primarily composed of unsaturated FAMEs (e.g. oleic and linoleic acid). Only 11% of the FAMEs found in these samples were fully saturated. Unsaturated FAMEs have higher energy content by volume, so it would be assumed that a biodiesel with a higher proportion of saturated FAMEs would be desirable, however, **Figure 3-4** shows that the FAMEs found in the exhaust PM are primarily saturated. This implies that saturated FAMEs are inherently less reactive than unsaturated FAMEs, and saturated FAMEs pass through the combustion cylinders in the diesel engine relatively unscathed.

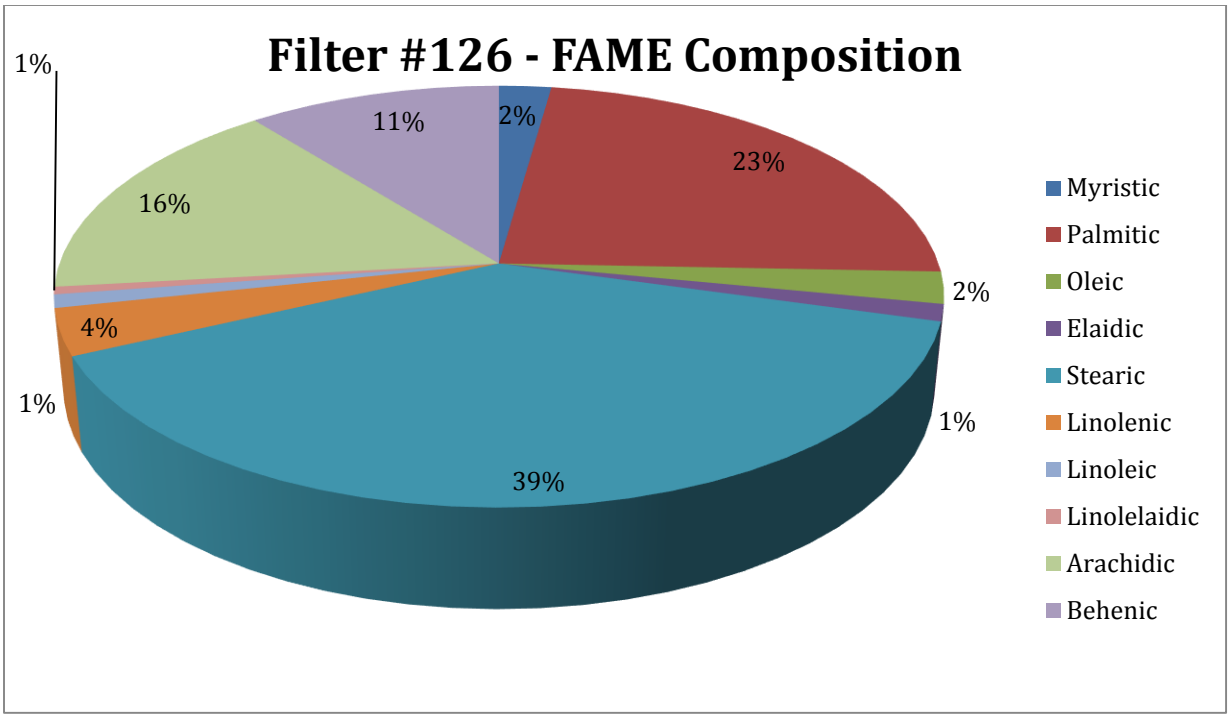


Figure 3-4. The proportions of FAMEs found in the exhaust PM for fiber film filter #126 run on October 11, 2011. The values shown represent an average of two runs taken from different 1/4 inch punch pairs that were analyzed by TD-GCMS.

The unsaturated FAMEs found in filter #126 made up 89% of the total FAMEs found in the exhaust PM. The larger FAMEs (i.e. arachidic and behenic acid) were not detected in the raw fuel, but had distinct, gaussian peaks in the exhaust. The origin of these FAMEs could have been pyrosynthesis during combustion. This is substantiated by the fact that odd-numbered FAMEs were also identified, but could not have been present in the original fuel due to the fact that they do not occur naturally. The proportions of the unsaturated FAMEs (e.g. oleic and linoleic acid) decreased by 38% and 41%, respectively, indicating that it is primarily the unsaturated FAMEs that contribute to combustion. The relative standard deviations (RSD) for these measurements were less than 20% for all compounds except linolelaidic acid and behenic acid, which had RSD values higher than 90%. The source of variability for these compounds is not known, but could likely be caused by coelution of FAMEs in the nonpolar column. It is not advised to use a nonpolar column for quantitation of FAMEs, but due to the high complexity of real world exhaust samples, it was deemed necessary.

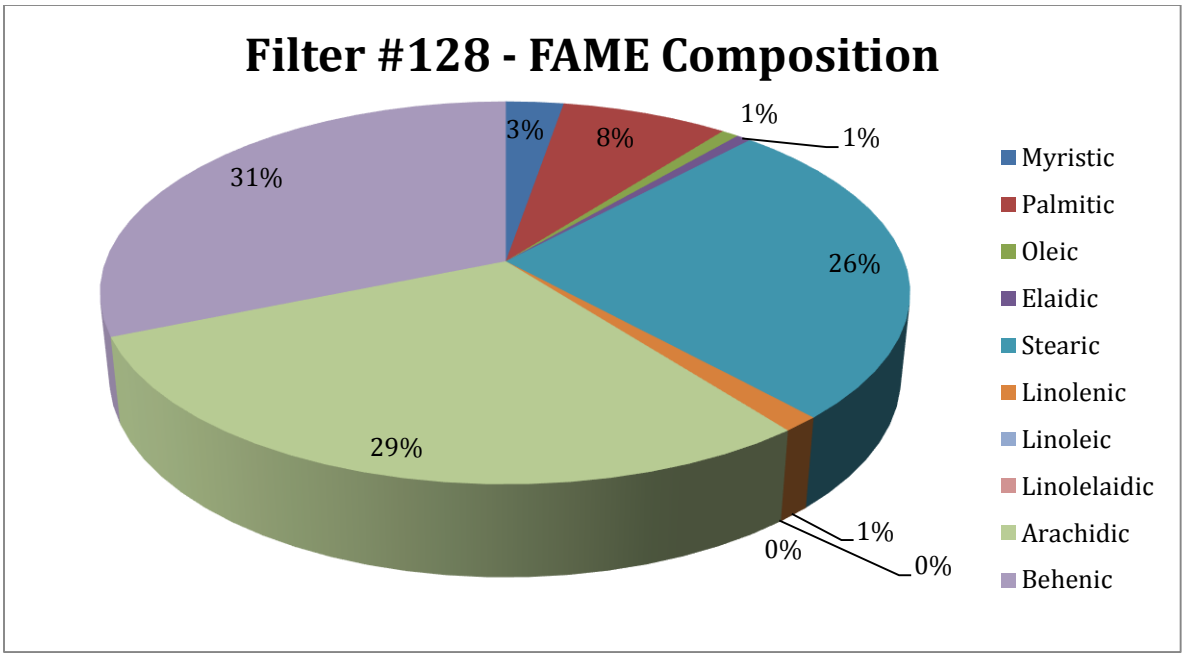


Figure 3-5. The proportions of FAMEs found in the exhaust PM for fiber film filter #128 run on October 21, 2011. The values shown represent an average of two runs taken from different 1/4 inch punch pairs that were analyzed by TD-GCMS.

3.4 "Fingerprint" Composition by GCMS Extracted Ion Pattern

Identification of compounds via GC/MS involves verifying retention time through the use of chemical standards, analyzing the mass spectral "fingerprint", and calculating qualifier ion ratios. Qualifier ions refer to secondary peaks in a compound's mass spectrum. These mass spectral peaks should elute with the same retention time and have a similar peak shape to the most abundant ion in the spectrum (i.e. target ion). This is typically checked in Chemstation by overlaying extracted ion chromatograms (EIC) at m/z values corresponding to the target and qualifier ions of the compound of interest.

MATLAB has the capability to display the EIC in a 3D plot, allowing the user to view a variety of EIC chromatograms for many different compounds over a much wider retention time range. This has several advantages over Chemstation, such as; the ability to deconvolute real-world exhaust samples with large unresolved complex mixtures (UCM), the ability to align peaks based on their retention time, and the ability to normalize the z-axis to the response of the internal standard over a series of runs. Figures 3-6 and 3-7 show three-dimensional color-coded plots of functional group classes for a B0 and B20 PM filter sample, respectively, based on code written in MATLAB to import the GC/MS data files and classify GC peaks based on individual ion ratios.

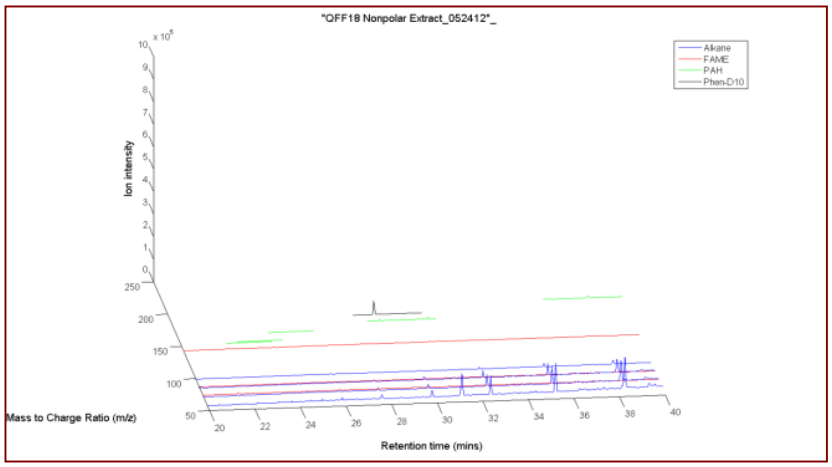


Figure 3-6. 3D EIC from 20 to 40 minutes for B0 Fiber Film filter #18 run on the Armfield engine on 11/4/2010.

In **Figure 3-6**, the petrodiesel three-dimensional extracted ion chromatogram is shown with color-codings by functional group. Blue lines are plotted at m/z values of 57, 71, 85 and 99 which correspond to the target and qualifier ions for straight chain alkanes. Red lines are plotted at m/z values of 74, 85, and 174 which correspond to target ions for FAMEs. Green lines are plotted at specific retention times and m/z values corresponding to the 16 EPA PAHs, and the black line is plotted at m/z 188 and corresponds to the internal standard, Phenathrene-D10.

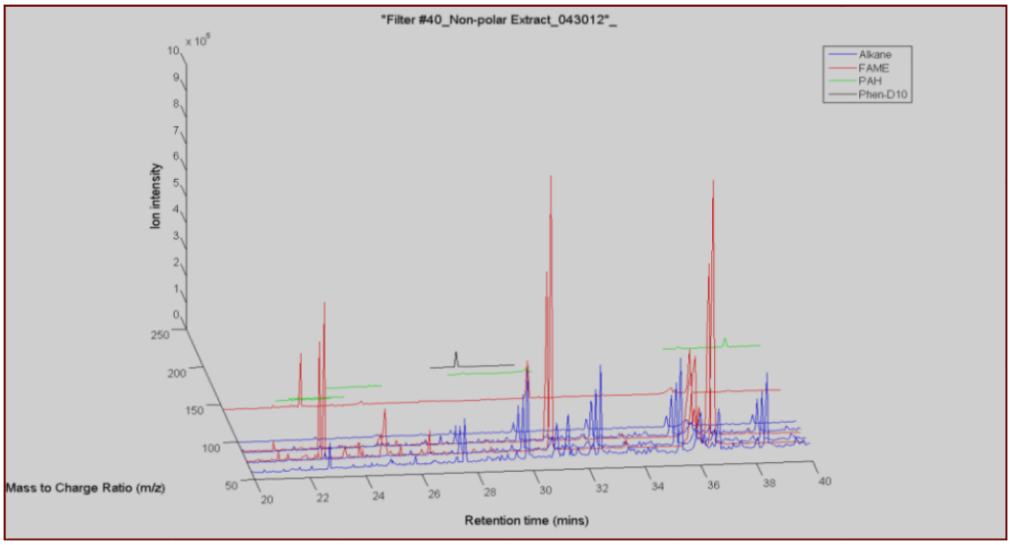


Figure 3-7. The 3D EIC from 20 to 40 minutes for B20 Teflon filter #40 run on 11/9/2010.

In **Figure 3-7**, the three large clusters of red peaks from left to right correspond to 9-oxononanoic acid, methyl ester (an oxidation byproduct of oleic acid, methyl ester), palmitic acid, methyl ester, and stearic acid, methyl ester. These FAMEs are reproducibly seen in all biodiesel exhaust samples. Ester-bound aldehydes, also known as core aldehydes, were identified in the exhaust PM for biodiesel fuels. One such example of a core aldehyde, 9-oxononanoic acid, methyl ester (RT = 22.5mins), may induce hepatic lipid peroxidation and may also affect hepatic metabolism (Minamoto *et al*, 1988). Studies have shown that these compounds are a product of thermoxidation of both oleic acid and linoleic acid, the primary constituents of soy-based biodiesel (Berdeaux *et al*, 2002).

4. Conclusions

In the present study, we examined the differences in emissions from a light-duty diesel engine fueled with petrodiesel (B0) and at 20% blend of biodiesel (B20). We focused on the emissions of alkanes, PAHs, carbonyls, and FAMEs. These organic compound families were chosen mainly because of their known health effects and their impact on environmental degradation. The emissions were computed based on the volume of air sampled (ng/m^3) during the run.

The concentrations for the individual alkanes were generally seen to increase with increasing molecular weight for both petrodiesel and biodiesel. The total alkanes concentrations in biodiesel were surprisingly found to be about 3 times higher than those in petrodiesel. The individual PAHs concentrations also increased with increasing molecular weight (number of rings) for both fuel types, while the total PAHs concentrations in biodiesel were found to be about 1.5 times higher than those in petrodiesel.

There was no concentration dependence on molecular weight for the individual FAMEs. However, it was observed that the saturated FAMEs dominated the FAMEs detected in the biodiesel exhaust PM. The saturated FAMEs made up 70% of the total FAMEs detected in the biodiesel exhaust PM, while they made up only 13% of the total FAMEs in the raw biodiesel fuel. The mechanism of the formation of the longer chain saturated FAMEs (such as arachidic acid and behenic acid methyl esters) that were not found in the raw biodiesel fuel, but found in the biodiesel exhaust PM warrants future investigation. The study results indicate that most of the *un*saturated FAMEs in biodiesel fuel are combusted in the engine, while the saturated FAMEs make it through the engine as unburned fuel. The concentrations measured for the FAMEs in biodiesel were 11 times higher than the petrodiesel concentrations and emission rates.

The low molecular weight carbonyls dominated the carbonyls emissions in both petrodiesel and biodiesel. On average, 70% of the carbonyls emissions in petrodiesel were due to the aliphatic carbonyls, while 71% of the carbonyls emissions in biodiesel were due to the aliphatic carbonyls. The total carbonyls concentrations in biodiesel were 2 times higher than the petrodiesel concentrations and emission rates.

The preliminary results of this study show that use of biodiesel leads to an increase in the concentrations of most of the compounds studied (alkanes, PAHs, and carbonyls). More replicate engine runs, however, need to be conducted in order to make more accurate conclusions about the effect of biodiesel on the emission of alkanes, PAHs, and carbonyls. We are currently conducting a sampling campaign that involves measurement of emissions from different biodiesel blends (B00, B10, B20, B50, and B100) for both soybean and waste grease biodiesel feedstocks. Three replicate engine runs will be completed for each biodiesel blend. Raw exhaust PM filter samples, not the diluted exhaust samples extracted in this report, are collected for chemical analysis to achieve higher measured mass in punch extracts to make more reliable conclusions on the effect of biodiesel on the emission of alkanes, PAHs, carbonyls, and FAMEs.

References Cited

Bakeas, E., G. Karavalakis, et al. (2011). "Biodiesel emissions profile in modern diesel vehicles. Part 1: Effect of biodiesel origin on the criteria emissions." Sci Total Environ 409(9): 1670-1676.

Bell, M. L., K. Ebisu, et al. (2008). "Seasonal and regional short-term effects of fine particles on hospital admissions in 202 US counties, 1999-2005." Am J Epidemiol 168(11): 1301-1310.

Berdeaux, Oliver. 2002. Evolution of short-chain glycerol-bound compounds during thermoxidation of FAME and monoacid TAG. Journal of the American Oil Chemists' Society 2002, Volume 79, Issue 3, pp 279-285

Bikas, G. Z., E (2007). "Non-regulated pollutants emitted from Euro 3 diesel vehicles as a function of their mileage." Energy & Fuels 21(5): 2731–2736.

Blando, J. D. and B. J. Turpin (2000). "Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility." Atmospheric Environment 34(10): 1623-1632.

Cahill, MT., Okamoto. AR., 2012. Emissions of acrolein and other aldehydes from biodiesel-fueled heavy-duty vehicles. Environ. Sci. Technol. 2012, 46, 8382-8388.

Chien, S.-M. H. Y.-J. C., S-C.; Yang, H-H (2009). "Effects of biodiesel blending on barticulate and polycyclic aromatic hydrocarbon emissions in nano/ultrafine/fine/coarse ranges from diesel engine." Aerosol and Air Quality Research 9(1): 18-31.

Clausen, E. C., M. Popp, et al. (2008). "Yield Characteristics of Biodiesel Produced from Chicken Fat-Tall Oil Blended Feedstocks." Department of Transportation Research and Special Programs Administration: 76.

Correa, S. M. and G. Arbilla (2008). "Carbonyl emissions in diesel and biodiesel exhaust." Atmospheric Environment 42(4): 769-775.

Dockery, D., C. I. Pope, et al. (1993). "An association between air pollution and mortality in six U.S. cities." N Engl J Med 329(24): 1753-1759.

Dunn, R. O. (2005). "Effect of antioxidants on the oxidative stability of methyl soyate (biodiesel)." Fuel Processing Technology 86(10): 1071-1085.

EPA, U. S. (2002). A comprehensive analysis of biodiesel impacts on exhaust emissions. Draft Technical Report 420-P-02-001. Cincinnati, OH, National Service Center for Environmental Publications.

EPA, U. S. (2013) Mobile Source Air Toxics- Basic Information.

Franchini, M. and P. Mannuci (2007). "Short-term effects of air pollution on cardiovascular diseases: outcome and mechanisms." Journal of Thrombosis and Haemostatics 5: 2169-2174.

Giakoumis, E. G. (2013). "A statistical investigation of biodiesel physical and chemical properties, and their correlation with the degree of saturation." Renewable Energy 50: 858-878.

Graboski, M. S., R. L. McCormick, et al. (2003). The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine. National Renewable Energy Laboratory. Golden, Colorado, Colorado School of Mines.

Gundel, L.A., Lee,V.C., Mahanama,R.K., Stevens, R.K., Daisey, J.M., 1995. Direct determination of the phase distributions of semi-volatile polycyclic aromatic hydrocarbons using annular denuders. Atmos. Environ. 29 (14), 1719–1733.
Gundel, L.A., and D.A. Lane. 1999. Sorbent-coated diffusion denuders for direct measurement of gas/particle partitioning by semi-volatile organic compounds. In Gas and Particle Partition Measurements of Atmospheric Semivolatile Organic Compounds. Lawrence Berkeley National Lab., CA

Jakober, A. C., Charles, M.J., Kleeman, J.M., Green, G.P. (2006). "LC-MS analysis of carbonyl compounds and their occurrence in diesel emissions." Anal Chem 78(14): 5086-5093.

Jakober, C. A., M. A. Robert, et al. (2008). "Carbonyl emissions from gasoline and diesel motor vehicles." Environ Sci Technol 42(13): 4697-4703.

Knothe, G. (2007). "Some aspects of biodiesel oxidative stability." Fuel Processing Technology 88(7): 669-677.

Knothe, G., C. A. Sharp, et al. (2006). "Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine." Energy & Fuels 20(1): 403-408.

Krahl, J., Munack, A., Schroder, O., Stein, H., Bunger, J. (2005). Influence of biodiesel and different petrodiesel fuels on exhaust emissions and health effects. The Biodiesel Handbook. G. Knothe, Van Gerpen, J., Krahl, J., Eds. Champaign, IL, AOCS Press: 175-182.

Lim, H. J., A. G. Carlton, et al. (2005). "Isoprene forms secondary organic aerosol through cloud processing: Model simulations." Environ Sci Technol 39(12): 4441-4446.

Lin, Y. C., W. J. Lee, et al. (2006). "PAH emissions and energy efficiency of palm-biodiesel blends fueled on diesel generator." Atmospheric Environment 40(21): 3930-3940.

Lindsay, W., Sacks, JD., Dutton, SJ., Dubois, J-JB (2011). "Attributing health effects to apportioned components and sources of particulate matter: An evaluation of collective results." Atmospheric Environment 45(32): 5655-5663.

Loeffler, K. W., C. A. Koehler, et al. (2006). "Oligomer formation in evaporating aqueous glyoxal and methyl glyoxal solutions." Environ Sci Technol 40(20): 6318-6323.

Mauderly, J. (1997). Health issues concerning inhalation of petroleum diesel and biodiesel exhaust. Plant Oils as Fuels: Present State of Science and Future Developments. N. S. Martini, J. Berlin, Springer: 92-103.

McCormick, R. L., Alleman, T. L. (2005). Effect of biodiesel fuel on pollutant emissions from diesel engines. The Biodiesel Handbook. G. Knothe, Van Gerpen, J., Krahl, . Champaign, IL, AOCS Press: 165-174.

Minamoto S, Kanazawa K, Ashida H, Natake M. 1988. Effect of orally administered 9-oxononanoic acid on lipogenesis in rat liver. Biochim Biophys Acta. 1988 Feb 4;958(2):199-204.

Moser, B. R. (2009). "Biodiesel production, properties, and feedstocks." In Vitro Cellular & Developmental Biology-Plant 45(3): 229-266.

Payri F., Bermudez RV., Tormos B., Linares GW., 2009. Hydrocarbon emissions speciation in diesel and biodiesel exhausts. Atmos. Environ. 43 (6), 1273-1279.

Pope, C. I., Dockery, DW. (2006). "Health effects of fine particulate air pollution: lines that connect." J Air Waste Manag Assoc 56: 709-742.

Riedl, M. A. (2008). "The effect of air pollution on asthma and allergy." Curr Allergy Asthma Rep 8(2): 139-146.

Schauer, J., Kleeman, MJ., Cass, GR., Simoneit, BRT (1999). "Measurement of emissions from air pollution sources. 2. C1 through C30 organic compounds from medium duty diesel trucks." Environ. Sci. Technol 33(10): 1578-1587.

Schwartz WR, McEnally CS, Pfefferle LD. Decomposition and hydrocarbon growth processes for esters in non-premixed flames. J Phys Chem 2006: 110:6643-8.

Sharp, AC., 1998. Exhaust emissions and performance of diesel engines with biodiesel fuels, In: Biodiesel Environmental Workshop, Southwest Research Institute, Washington DC.

Simopoulos, A. P. (2002). "The importance of the ratio of omega-6/omega-3 essential fatty acids." Biomed Pharmacother 56(8): 365-379.

Swanson, K. J., M. C. Madden, et al. (2008). "Biodiesel Exhaust: The Need for Health Effects Research." Environmental Health Perspectives 115(4): 496-499.

Tong, D. M., C. W. Hu, et al. (2011). "Cetane Number Prediction of Biodiesel from the Composition of the Fatty Acid Methyl Esters." Journal of the American Oil Chemists Society 88(3): 415-423.

Turrio-Baldassarri, L., C. L. Battistelli, et al. (2004). "Emission comparison of urban bus engine fueled with diesel oil and 'biodiesel' blend." Sci Total Environ 327(1-3): 147-162.

US EPA, Method 556, 1998. Determination of carbonyl compounds in drinking water by pentafluorobenzylhydroxylamine derivatization and capillary gas chromatography with electron capture detection. National Exposure Research Laboratory, Office of Research and Development, US Environmental Protection Agency, Cincinnati, OH.

Valavanidis, A., K. Fiotakis, et al. (2008). "Airborne particulate matter and human health: toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms." J Environ Sci Health C Environ Carcinog Ecotoxicol Rev 26(4): 339-362.

Zanobetti, A. and J. Schwartz (2009). "The effect of fine and coarse particulate air pollution on mortality: a national analysis." Environ Health Perspect 117(6): 898-903.

Appendices

Tables of QA/QC data and raw experimental results are provided in the following 7 appendices.

Appendix I. Chemical Standard Mixture Compositions

Table I-A. Commercially available standard compound mixture compositions

Compounds	Compound ID	CAS Number	Conc	Supplier	Cat #
PAHs Mix (100 µg/mL each in DCM)					
				Ultra Scientific	PM-611
Naphthalene	NAP	91-20-3	100		
Acenaphthylene	ACY	208-96-8	100		
Acenaphthene	ACE	83-32-9	100		
Fluorene	FLU	86-73-7	100		
Phenanthrene	PHEN	85-01-8	100		
Anthracene	ANTH	120-12-7	100		
Fluoranthene	FLUOR	206-44-0	100		
Pyrene	PYR	129-00-0	100		
Benzo[a]anthracene	BAA	56-55-3	100		
Chrysene	CHRY	218-01-9	100		
Benzo[b]fluoranthene	BBF	205-99-2	100		
Benzo[k]fluoranthene	BBK	207-08-9	100		
Benzo[a]pyrene	BAP	50-32-8	100		
Indeno[1,2,3-cd]pyrene	IDP	193-39-5	100		
Benzo[ghi]perylene	BGP	191-24-2	100		
Dibenz[a,h]anthracene	DAA	53-70-3	100		
POCs					
2-Pentanone	2PNN	107-87-9	Pure	Sigma Aldrich	68950-100ML
3-Pentanone	3PNN	96-22-0	Pure	Sigma Aldrich	127604-100ML
2-Hexanone	2HXN	591-78-6	Pure	Sigma Aldrich	02473-5ML
2-Heptanone	2HPN	110-43-0	Pure	Sigma Aldrich	02476-1ML
2-Octanone	2OCT	111-13-7	Pure	Sigma Aldrich	02479-1ML
2-Nonanone	2NNE	821-55-6	Pure	Sigma Aldrich	108731-5G
n-Hexanal	HXNL	66-25-1	Pure	Sigma Aldrich	115606-2ML
n-Heptanal	HPTL	111-71-7	Pure	Sigma Aldrich	W254002
n-Octanal	OCTL	124-13-0	Pure	Sigma Aldrich	O5608-25ML
n-Nonanal	NNNL	124-19-6	Pure	Sigma Aldrich	442719
n-Decanal	DECL	112-31-2	Pure	Sigma Aldrich	D7384-25G
Undecanal	UDCL	112-44-7	Pure	Sigma Aldrich	U2202-25G
Dodecanal	DDCL	112-54-9	Pure	Sigma Aldrich	W261505
Benzaldehyde	BZDE	100-52-7	Pure	Sigma Aldrich	B1334-2G
m-Tolualdehyde	mTOL	620-23-5	Pure	Sigma Aldrich	T35505-5G
o-Tolualdehyde	oTOL	529-20-4	Pure	Sigma Aldrich	117552-25G
p-Tolualdehyde	pTOL	104-87-0	Pure	Sigma Aldrich	T35602-100G
Acetophenone	ACNE	98-86-2	Pure	Sigma Aldrich	42163-1ML-F
1-Indanone	1IND	83-33-0	Pure	Sigma Aldrich	I2304-10G
9-Fluorenone	9FLN	486-25-9	Pure	Sigma Aldrich	F1506-5G-A
Perinaphthenone	PNNN	548-39-0	Pure	Sigma Aldrich	P10801-1G
Benzophenone	BZP	119-61-9	Pure	Sigma Aldrich	239852-50G
1,4-Benzoquinone	BQN	106-51-4	Pure	Sigma Aldrich	PHR1028-1G
1,4-Naphthoquinone	NQN	130-15-4	Pure	Sigma Aldrich	70372-50G
Acenaphthoquinone	ACNQ	82-86-0	Pure	Sigma Aldrich	A201-25G-A
Anthraquinone	ATQ	84-65-1	Pure	Sigma Aldrich	31466-250MG
Alkanes Mix (50 mg/L each in n-heptane)					
				Sigma Aldrich	68281-2ML-F
Dodecane	DDCN	112-40-3	50		

Tetradecane	TDCN	629-59-4	50		
Hexadecane	HDCN	544-76-3	50		
Octadecane	ODCN	593-45-3	50		
Eicosane	ECSN	112-95-8	50		
Docosane	DCSN	629-97-0	50		
Tetracosane	TCSN	646-31-1	50		
Hexacosane	HCSN	630-01-3	50		
Octacosane	OCSN	630-02-4	50		
Triacontane	TCTN	638-68-6	50		
Dotriacontane	DCTN	544-85-4	50		
Tetratriacontane	TECTN	14167-59-0	50		
Hexatriacontane	HCTN	630-06-8	50		
FAMEs Mix, 100 mg Neat					
			(% of each FAME in Mix)	Sigma Aldrich	18917-1AMP
Myristic Acid Methyl Ester	MAME	124-10-7	4		
Palmitic Acid Methyl Ester	PAME	112-39-0	10		
Stearic Acid Methyl Ester	SAME	112-61-8	6		
Oleic Acid Methyl Ester	OAME	112-62-9	25		
Elaidic Acid Methyl Ester	EAME	1937-62-8	10		
Linoleic Acid Methyl Ester	LIEC	112-63-0	34		
Linolelaidic Acid Methyl Ester	LDIC	2566-97-4	2		
Linolenic Acid Methyl Ester	LNIC	301-00-8	5		
Arachidic Acid Methyl Ester	AAME	1120-28-1	2		
Behenic Acid Methyl Ester	BAME	929-77-1	2		
Internal, Quantitation and Recovery Standards					
Phenanthrene-d10	Phen-d10	1517-22-2	1000 µg/mL in DCM	Ultra Scientific	IST-230
Perylene-d12	Pery-d12	1520-96-3	2000 µg/mL in DCM	Ultra Scientific	ATS-150-1
Anthracene-d10	Anth-d10	1719-06-8	1000 µg/mL in DCM	Ultra Scientific	IST-110
Tetracosane-d50	TECSN-d50	16416-32-3	Pure	Sigma Aldrich	451770-100MG
6-Fluoro-4-chromanone	6F4C	66892-34-0	Pure	Sigma Aldrich	364991-1G
2-Fluoro-9-fluorenone	2F9F	343-01-1	Pure	Sigma Aldrich	F9000-1G
Other Chemicals					
Pentafluorobenzylhydroxylamine	PFBHA	57981-02-9	Pure	Sigma Aldrich	76735-1G

Appendix II. GC/MS Calibration Standards

Table II-A. Calibration standards used for preparation of calibration curves

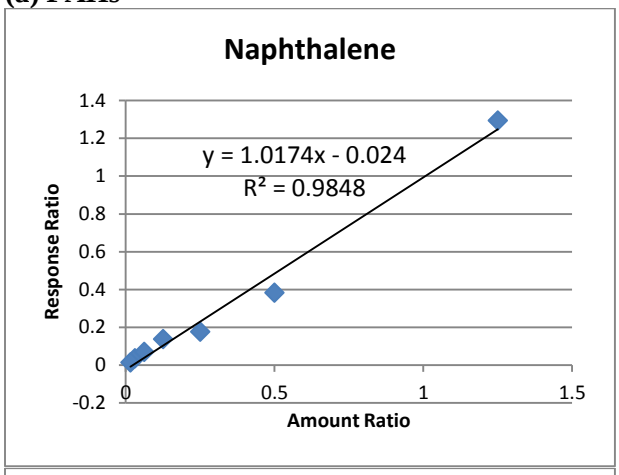
	Standard 1 (ng/µL)	Standard 2 (ng/µL)	Standard 3 (ng/µL)	Standard 4 (ng/µL)	Standard 5 (ng/µL)
PAHs	0.6	1.3	2.7	6.6	13.3
Alkanes	0.6	1.3	2.7	6.6	13.3
Carbonyls	2	4	6	8	10
FAMEs					
Myristic Acid ME (C14:0)	0.5	1.1	1.6	2.1	2.7
Palmitic Acid ME (C16:0)	1.3	2.7	4.0	5.3	6.6
Oleic Acid ME (C18:1)	3.3	6.6	10.0	13.3	16.6
Elaidic Acid ME (C18:1)	1.3	2.7	4.0	5.3	6.6
Stearic Acid ME (C18:0)	0.8	1.6	2.4	3.2	4.0
Linolenic Acid ME (C18:3)	0.7	1.3	2.0	2.7	3.3
Linoleic Acid ME (C18:2)	4.5	9.0	13.5	18.0	22.5
Linolelaidic Acid ME (C18:2)	0.3	0.5	0.8	1.1	1.3
Arachidic Acid ME (C20:0)	0.3	0.5	0.8	1.1	1.3
Behenic Acid ME (C22:0)	0.3	0.5	0.8	1.1	1.3

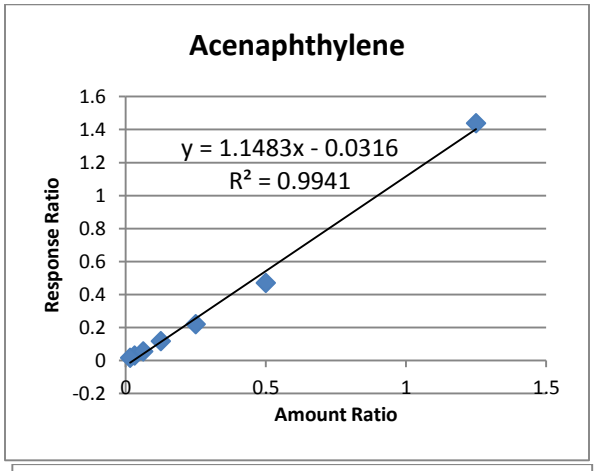
All PAHs, alkanes, and carbonyls were at equal concentrations in their respective standards. The FAMEs in the mix were at different concentrations, i.e. myristic acid ME (4%), palmitic acid ME (10%), oleic acid ME (25%), elaidic acid ME (10%), stearic acid ME (6%), linolenic acid ME (5%), linoleic acid ME (34%), linolelaidic acid ME (2%), arachidic acid ME (2%), and behenic acid ME (2%).

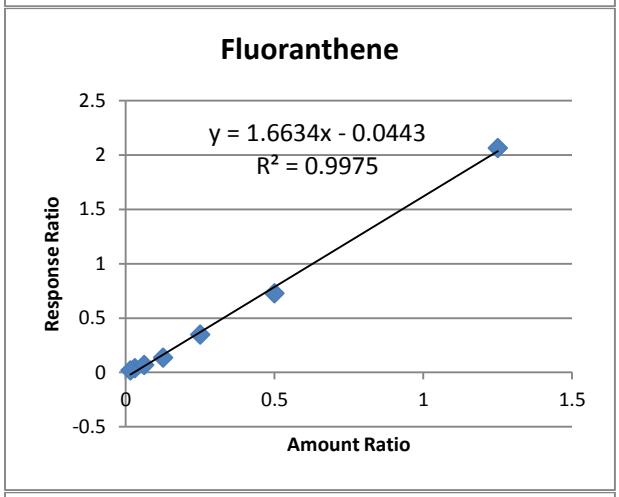
Appendix III. GC/MS Calibration Curves

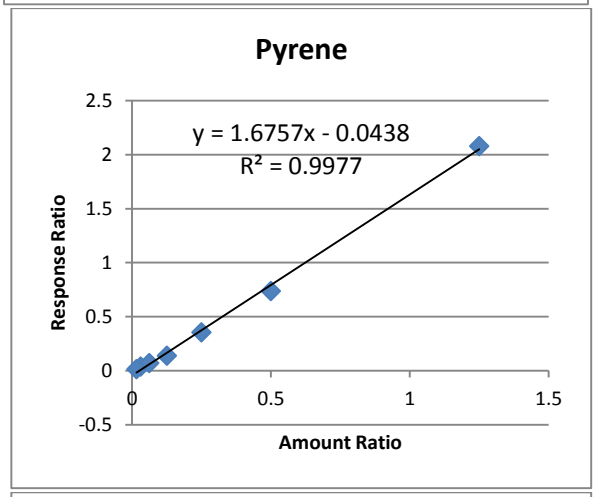
Figure III-A. Example Calibration Curves for Target Analytes

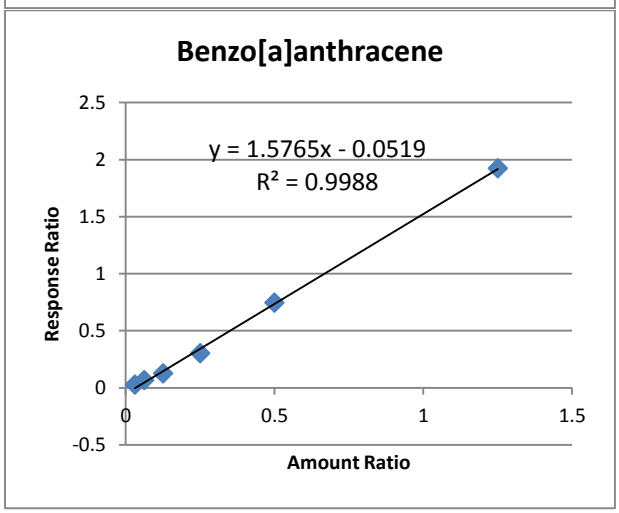
(a) PAHs

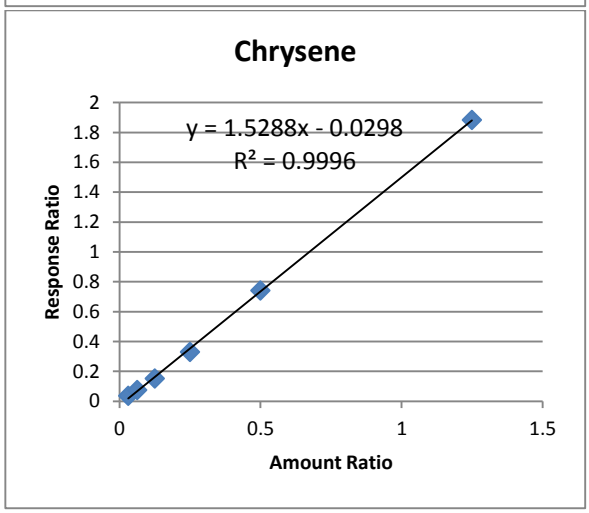


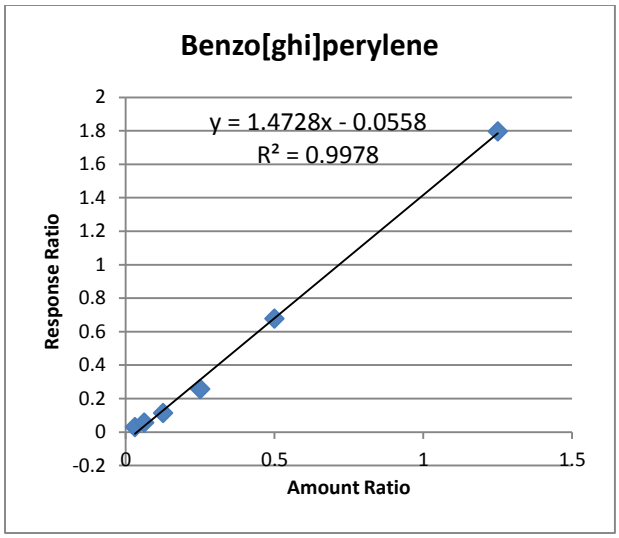


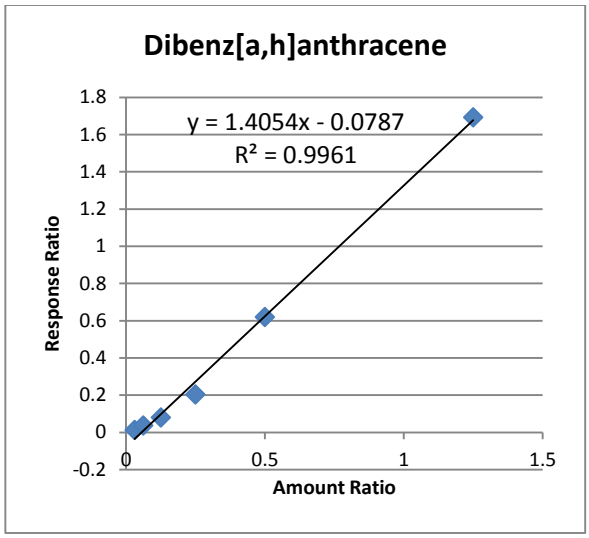




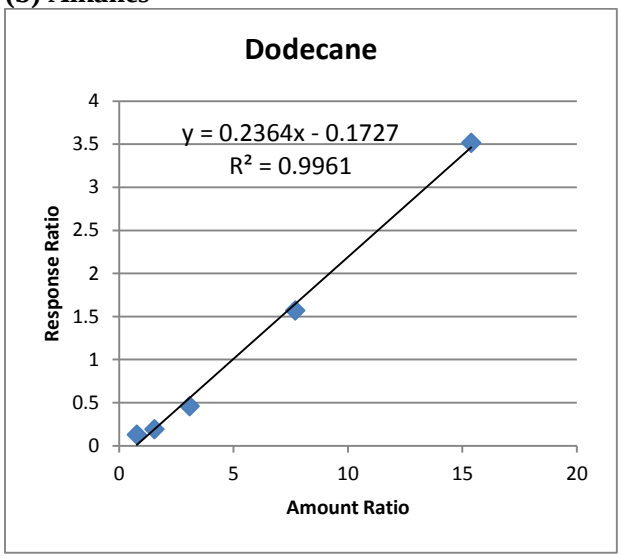


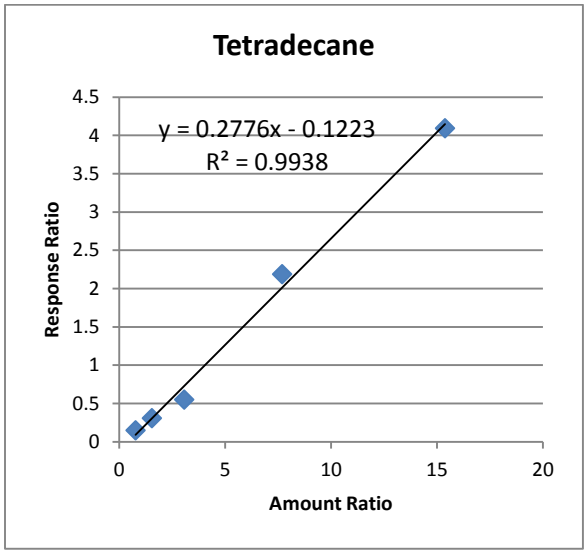


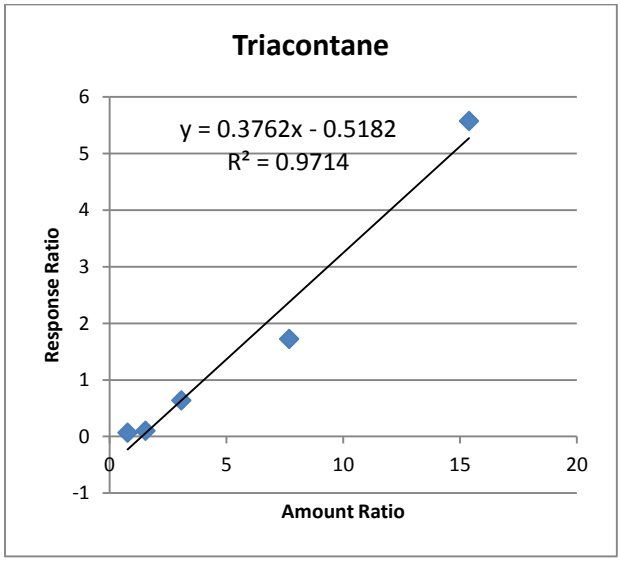

Benzo[ghi]perylene
y = 1.4728x - 0.0558
R² = 0.9978
Response Ratio
Amount Ratio

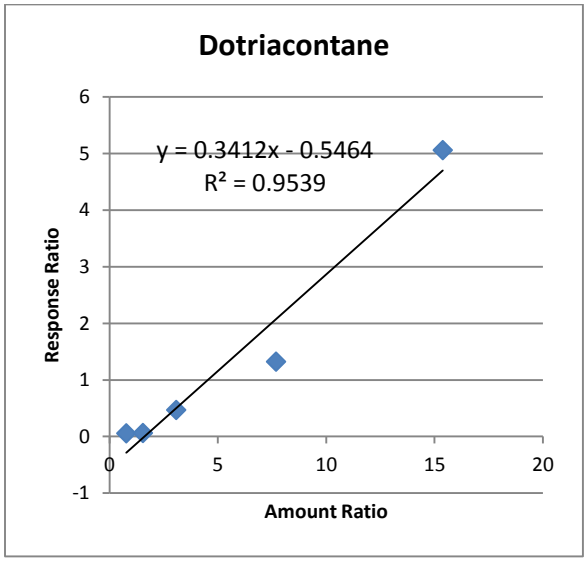

Dibenz[a,h]anthracene
y = 1.4054x - 0.0787
R² = 0.9961
Response Ratio
Amount Ratio

(b) Alkanes

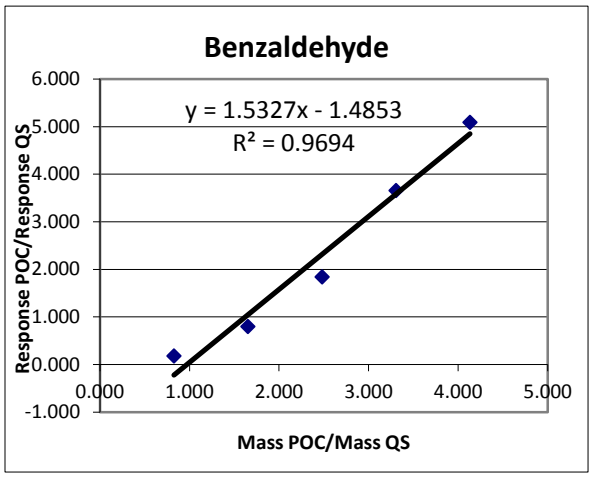

Dodecane
y = 0.2364x - 0.1727
R² = 0.9961
Response Ratio
Amount Ratio

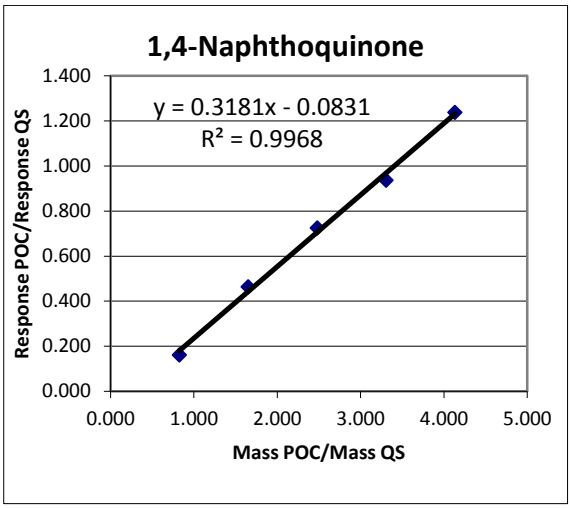

Tetradecane
y = 0.2776x - 0.1223
R² = 0.9938
Response Ratio
Amount Ratio

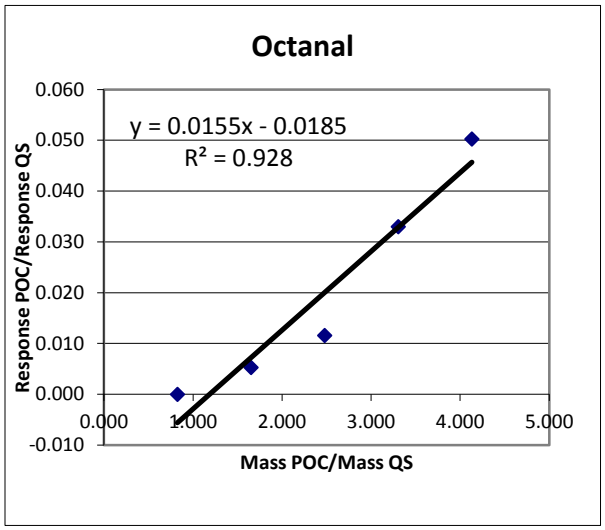

Triacontane
y = 0.3762x - 0.5182
R² = 0.9714
Response Ratio
Amount Ratio

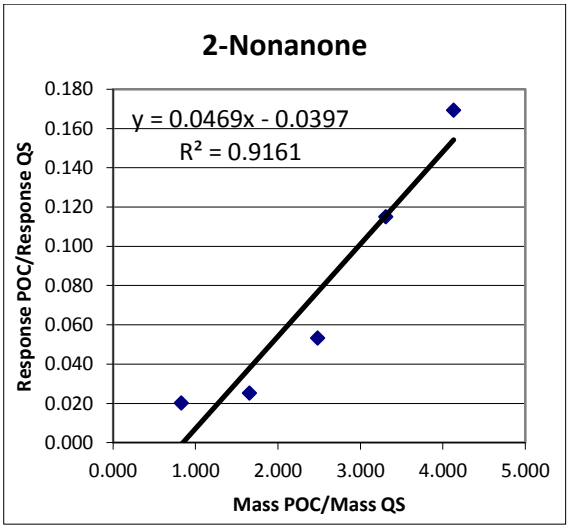

Dotriacontane
y = 0.3412x - 0.5464
R² = 0.9539
Response Ratio
Amount Ratio

(c) Carbonyls

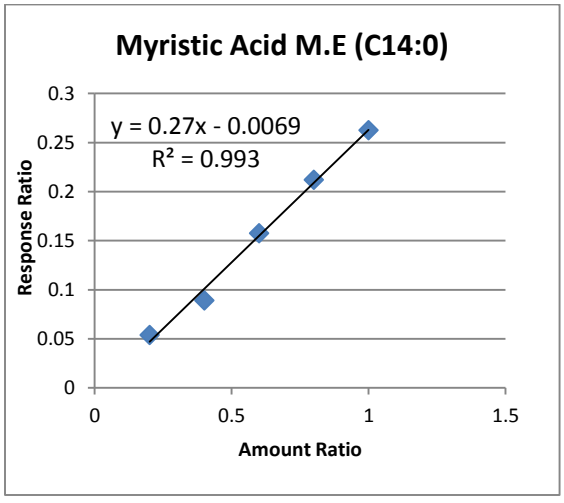


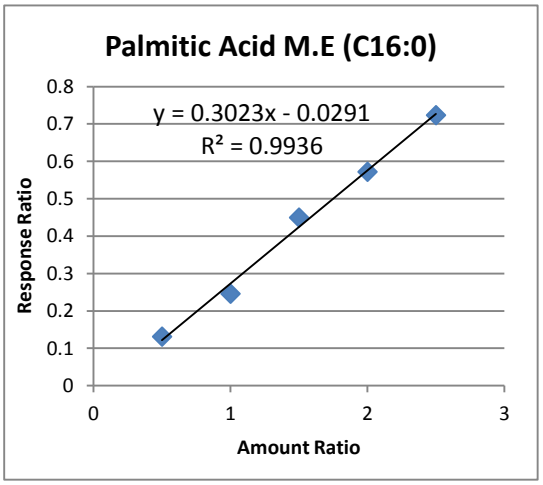


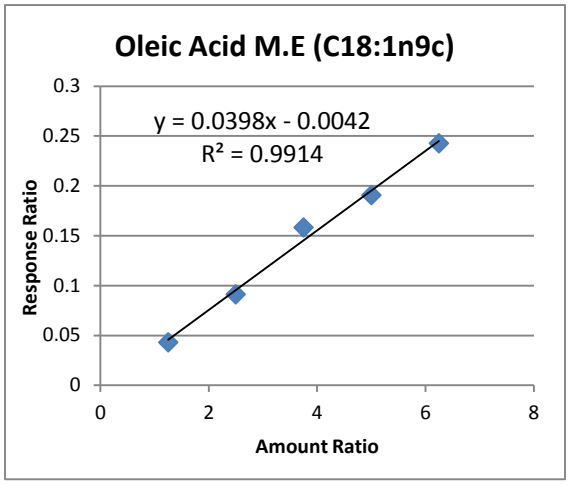


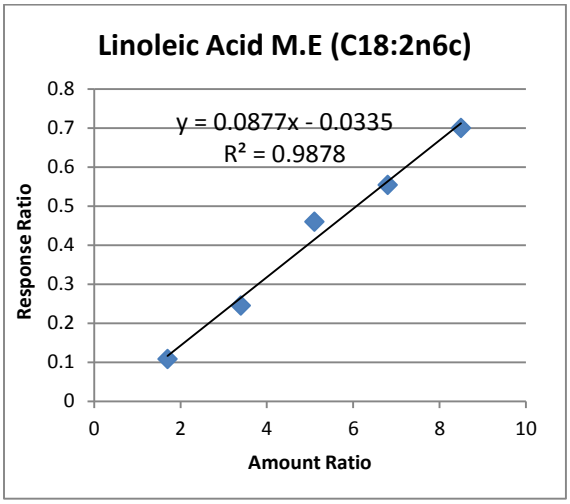


(d) FAMEs






Oleic Acid M.E (C18:1n9c)
y = 0.0398x - 0.0042
R² = 0.9914
Response Ratio
Amount Ratio
0
0.05
0.1
0.15
0.2
0.25
0.3
0
2
4
6
8


Linoleic Acid M.E (C18:2n6c)
y = 0.0877x - 0.0335
R² = 0.9878
Response Ratio
Amount Ratio
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
2
4
6
8
10

Appendix IV. Carbonyl Quantification Ions

Table IV-A. Mass Spectrometry Quantification Ions for Individual Carbonyls

Compound	MW_i	MW_f	Most Abundant Ions	RT
Aliphatic Carbonyls				
2-Pentanone	86	281	181, 195, 253, 264, 281	20.27, 20.39
3-Pentanone	86	281	181, 253, 281	20.16
2-Hexanone	100	295	181,195, 236, 253	21.62, 21.76
Hexanal	100	295	181, 239, 195	22.66, 22.71
2-Heptanone	114	309	181, 253, 72, 266	22.88, 23.07
Heptanal	114	309	181, 239, 252	24.00
2-Octanone	128	323	72, 181, 253, 323	24.09, 24.30
Octanal	128	323	181, 239, 323	25.34
2-Nonanone	142	337	181, 236, 253, 337	25.41, 25.70
Nonanal	142	337	181, 239, 252, 337	27.08
Decanal	156	351	181, 239, 252, 334	29.28
Undecanal	170	365	181, 239, 252	31.85
Dodecanal	184	379	181, 198, 239	34.71
Aromatic Carbonyls				
Benzaldehyde	106	301	181, 271, 301	25.95, 26.12
1,4-Benzoquinone	108	303	181, 195, 317, 498	48.75
Acetophenone	120	315	181, 298, 315	27.10
m-Tolualdehyde	120	315	181, 285, 315	28.13
o-Tolualdehyde	120	315	181, 300, 315	28.24
p-Tolualdehyde	120	315	181, 285, 315	28.50
1-Indanone	132	327	116, 181, 327	32.19, 32.66
1,4 Napthoquinone	158	353	181, 295, 353	41.73
9-Fluorenone	180	375	152, 180, 192 166, 181, 375	28.28, 48.49
Perinaphthenone	180	375	152, 180, 76	32.84
Benzophenone	182	572	182, 105, 77 165, 181, 196, 377	25.53, 38.33
Acenaphthoquinone	182	377	153, 181, 377 152, 181, 572	50.69, 68.80
Anthraquinone	208	403	152, 180, 208	34.79
2-Fluoro 9-Fluorenone	198	393	198, 170, 85 181, 393, 195, 363	27.57, 47.79, 47.96
6-Fluoro 4-Chromanone	166	361	181, 361, 149, 108	33.69, 34.73

MW_i = Molecular Weight of Carbonyl, MW_f = Molecular Weight of PFBHA-oxime of Carbonyl, RT = Retention Time.

Appendix V. Recovery and Quantitation Standard Results

Table V-A. Percent Recoveries for the Recovery and Quantitation Standards Obtained During Extraction of the Diesel and Biodiesel Filters.

Filter Punch Pair	Tetracosane-d50	Anthracene-d10	2-Fluoro-9-fluorenone	6-Fluoro-4-chromanone
Filter #72 Punch Pair 1	78.8	49.8	91.8	52.1
Filter #72 Punch Pair 2	103.0	50.4	78.5	76.5
Filter #73 Punch Pair 1	73.4	49.6	117.4	52.7
Filter #73 Punch Pair 2	75.2	51.0	74.1	75.2
Filter #112 Punch Pair 1	117.9	50.2	88.4	68.8
Filter #112 Punch Pair 2	139.2	77.4	102.1	52.8
Filter #114 Punch Pair 1	70.6	50.0	103.3	56.6
Filter #114 Punch Pair 2	78.2	49.8	94.7	72.1
Filter #126 Punch Pair 1	74.6	50.0	90.6	30.4
Filter #126 Punch Pair 2	199.0	109.4	88.3	75.8
Filter #128 Punch Pair 1	32.4	50.8	89.0	46.7
Filter #128 Punch Pair 2	96.5	51.6	80.4	69.0
Mean	**94.9**	**57.5**	**91.5**	**60.7**
STD	**42.3**	**18.1**	**11.9**	**14.4**
RSD	**44.6**	**31.5**	**13.0**	**23.7**

Appendix VI. Target Analyte Concentrations for Extracted PM Filters.

The following tables summarize the GC/MS analysis results for the blank, B0 and B20 PM filters collected and extracted in this study. The following flag key applies to all of these tables for the measured analyte mass, concentrations and emission rates.

Table VI-A. GC/MS Data Flag Descriptions

Flag	Description
a	mass spectrum didn't match with that routinely seen for the known authentic chemical standards (Q-value less than 50)
b	compound concentration was substituted with the limit of detection
c	compound concentration is outside calibration range
d	compound did not pass visual inspection

Table VI-B. Target Alkane and PAH Analyte Total Mass by Fuel Type

Total Mass on Filter (ng)						
Fuel Type	Blank		B0		B20	
Filter ID	#72	#73	#112	#114	#126	#128
ALKANES						
Dodecane	521.3 [a]	104.4 [a]	90.4 [a]	102.2 [a]	89.7 [a]	93.9
Tetradecane	55.4 [a]	117.5 [a]	60.8 [a]	56.0 [a]	196.5 [a]	130.7 [a]
Hexadecane	135.7 [a]	46.6 [a]	53.6 [a]	30.6 [a]	35.2	28.7 [a]
Octadecane	26.9	28.0	38.1	39.2	26.7	18.6 [a]
Eicosane	29.3 [a]	26.5 [a]	24.7	39.2	149.9	58.0
Docosane	32.2 [a]	30.9 [a]	433.5	178.6	484.3	103.5
Tetracosane	52.5	53.0	305.3	158.7	753.1 [c]	142.5
Hexacosane	72.4 [a]	71.1	130.7	84.5	92.6	72.9
Octacosane	132.8 [a]	137.4	153.0	147.9	223.7	150.1
Triacontane	164.1 [a]	168.5 [a]	188.6	167.6	239.4	180.1 [a]
Dotriacontane	191.1 [a]	193.5	196.1 [a]	190.2 [a]	244.2	196.7 [a]
Tetratriacontane	213.6 [a]	213.8 [a]	213.4 [a]	212.1 [a]	219.3	211.6
PAHs						
Naphthalene	4.8 [b,d]	4.8 [a,b,d]	4.8 [b,d]	4.8 [b,d]	4.8 [b,d]	4.8 [b,d]
Acenaphthylene	5.3 [a,b,d]	N.D.	5.3 [a,b,d]	10.5 [a,b]	5.3 [b,d]	5.3 [a,b,d]
Acenaphthene	7.4 [a,b,d]	7.4 [a,b,d]	N.D.	7.4 [a,b,d]	7.4 [a,b,d]	7.4 [a,b,d]
Fluorene	4.2 [a,d]	N.D.	4.2 [a]	3.9 [b]	4.4 [a,b,d]	N.D.
Phenanthrene	5.7 [a,b,d]	5.7 [b,d]	5.7 [a,b]	5.7 [b]	5.7 [b]	5.7 [b]
Anthracene	N.D.	N.D.	4.3 [a,b,d]	4.3 [b,d]	N.D.	N.D.
Fluoranthene	N.D.	N.D.	5.5 [a,b,d]	5.5 [a,b,d]	5.5 [a,b,d]	N.D.
Pyrene	N.D.	N.D.	6.0 [a,b,d]	6.0 [b,d]	6.0 [b]	N.D.
Benzo[a]anthracene	N.D.	N.D.	6.8 [b,d]	6.8 [a,b,d]	6.8 [b,d]	N.D.
Chrysene	N.D.	N.D.	5.3 [a,b,d]	5.3 [a,b,d]	5.3 [a,b,d]	N.D.
Benzo[b]fluoranthene	N.D.	N.D.	6.7 [a,b]	6.7 [b]	6.7 [b]	6.7 [a,b]
Benzo[k]fluoranthene	N.D.	N.D.	10.0 [a,b]	10.0 [a,b]	N.D.	N.D.
Benzo[a]pyrene	N.D.	N.D.	9.2 [b,d]	9.2 [a,b,d]	9.2 [a,b,d]	9.2 [a,b,d]
Indeno[1,2,3-cd]pyrene	N.D.	N.D.	10.9 [b,d]	10.9 [b]	10.9 [a,b,d]	10.9 [a,b,d]
Benzo[ghi]perylene	N.D.	N.D.	10.0 [b]	10.0 [a,b]	10.0 [a,b,d]	10.0 [a,b,d]
Dibenz[a,h]anthracene	N.D.	N.D.	8.5 [a,b,d]	8.5 [a,b]	8.5 [a,b,d]	8.5 [a,b,d]

Table VI-C. Target FAME and POC Analyte Total Mass by Fuel Type

Total Mass on Filter (ng)						
Fuel Type	Blank		B0		B20	
Filter ID	#72	#73	#112	#114	#126	#128
FAMEs						
Myristic Acid ME	54.5 [b]	42.7 [b]	616.5 [a,b,c]	579.5 [a,b,c]	119.3 [b]	31.8 [b]
Palmitic Acid ME	544.3 [b,c]	302.2 [b,c]	362.4 [b,c]	284.9 [b]	3197.6 [c]	168.1 [b]
Oleic Acid ME	198.2	116.8 [c]	116.8 [a,c]	116.8 [a,c]	409.9	116.8 [b,c]
Elaidic Acid ME	42.9 [a,b,c]	42.9 [a,b,c]	65.9	51.4 [b,c]	962.9 [c]	48.8 [b,c]
Stearic Acid ME	155.4 [b]	63.0 [b]	92.4 [b]	92.1 [b]	2944.4 [c]	312.1 [b]
Linolenic Acid ME	24.6 [a,c]	26.0 [a]	23.9 [a,c]	22.9 [a,c]	90.2 [a]	24.1 [a,c]
Linoleic Acid ME	511.5 [c]	511.5 [a,c]	511.5 [a,b,c]	511.5 [a,b,c]	511.5	511.5 [a,b,c]
Linolelaidic Acid ME	17.3	13.1	12.7 [a]	12.7 [a]	12.7 [a]	12.5 [a]
Arachidic Acid ME	10.7 [a,b,c]	10.7 [b,c]	10.7 [a,b,c]	10.7 [a,b,c]	416.9 [c]	113.8 [c]
Behenic Acid ME	29.5 [b]	29.5 [b,c]	29.5 [a,b,c]	29.5 [a,b]	581.5 [c]	174.9 [c]
POCs						
2-Pentanone	N.D.	69.1 [b]	94.1 [b]	111.8 [b]	120.6 [b]	135.2 [b]
3-Pentanone	35.5 [b,c]	41.8 [b,c]	48.5 [b]	51.5 [b]	51.6 [b]	54.2 [b]
n-Hexanal	116.5	122.6	162.8	160.2	281.2 [c]	201.4
n-Heptanal	216.6	135.2	317.0 [c]	333.1 [c]	229.3 [c]	114.1
n-Octanal	N.D.	N.D.	N.D.	N.D.	146.1	N.D.
2-Nonanone	N.D.	N.D.	N.D.	N.D.	128.8	N.D.
n-Nonanal	195.4	243.0 [c]	224.3 [c]	260.5 [c]	540.6 [c]	299.9 [c]
n-Decanal	92.1	148.9	115.7	124.4	158.6	103.4
Undecanal	62.4	76.1	72.0	73.0	79.2	66.1
2-Hexanone	209.4	194.0	475.6 [c]	534.6 [c]	273.7 [c]	749.5 [c]
2-Heptanone	62.7 [b]	285.3 [c]	78.7 [b]	73.7 [b]	57.7 [b]	159.8 [b]
2-Octanone	230.5 [c]	224.9 [c]	326.0 [c]	403.0 [c]	71.3 [b]	375.1 [b]
Dodecanal	57.9	79.6	69.3	70.9	77.5	61.3
Benzaldehyde	107.7	110.1	110.1	109.4	112.4	112.2
m-Tolualdehyde	69.4	69.8	71.8	69.5	71.7	71.1
o-Tolualdehyde	89.2	116.8	62.2 [b]	113.6	159.3	160.6
p-Tolualdehyde	67.4	67.7	68.3	68.1	67.9	67.6
Acetophenone	74.0	74.9	75.2	75.6	77.0	75.4
1-Indanone	28.6 [c]	29.4 [c]	29.0 [c]	29.1 [c]	28.9 [c]	N.D.
9-Fluorenone	59.0	58.5	62.6	N.D.	60.3	59.1
Perinaphthenone	N.D.	N.D.	106.0	75.5	N.D.	23.5 [c]
Benzophenone	215.4	283.2 [c]	278.6 [c]	285.1 [c]	280.0 [c]	303.3 [c]
1,4-Benzoquinone	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1,4-Naphthoquinone	N.D.	N.D.	28.9 [b,c]	N.D.	28.6 [b,c]	29.0 [b,c]
Acenaphthoquinone	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Anthraquinone	22.3 [c]	23.6 [c]	32.7 [c]	32.2 [c]	33.9 [c]	23.7 [c]

Table VI-D. Target Alkane and PAH Analyte Concentrations by Fuel Type

Concentrations (ng/m^3)						
Fuel Type	Blank		B0		B20	
Filter ID	#72	#73	#112	#114	#126	#128
Air (L)	1240.00	1302.00	1760.00	1680.00	780.00	833.36
ALKANES						
Dodecane	420.4 [a]	80.2 [a]	1078.4 [a]	1642.5 [a]	3451.1 [a]	2703.8
Tetradecane	44.7 [a]	90.3 [a]	725.9 [a]	900.4 [a]	7558.7 [a]	3762.7 [a]
Hexadecane	109.4 [a]	35.8 [a]	639.8 [a]	492.4 [a]	1355.2	825.6 [a]
Octadecane	21.7	21.5	454.4	629.6	1026.9	535.7 [a]
Eicosane	23.6 [a]	20.3 [a]	295.1	629.6	5765.8	1670.2
Docosane	25.9 [a]	23.7 [a]	5172.9	2870.0	18627.3	2981.1
Tetracosane	42.4	40.7	3642.7	2550.0	28963.6 [c]	4103.0
Hexacosane	58.4 [a]	54.6	1558.9	1357.6	3560.5	2098.8
Octacosane	107.1 [a]	105.6	1825.3	2377.6	8602.4	4323.6
Triacontane	132.4 [a]	129.4 [a]	2250.9	2694.2	9208.4	5187.0 [a]
Dotriacontane	154.1 [a]	148.6	2339.7 [a]	3056.4 [a]	9393.6	5666.0 [a]
Tetratriacontane	172.3 [a]	164.2 [a]	2546.0 [a]	3408.2 [a]	8434.0	6094.6
PAHs						
Naphthalene	3.8 [b,d]	3.7 [a,b,d]	56.7 [b,d]	76.4 [b,d]	182.9 [b,d]	137.0 [b,d]
Acenaphthylene	4.3 [a,b,d]	N.D.	63.3 [a,b,d]	168.8 [a,b]	204.2 [b,d]	152.9 [a,b,d]
Acenaphthene	6.0 [a,b,d]	5.7 [a,b,d]	N.D.	119.0 [a,b,d]	284.7 [a,b,d]	213.2 [a,b,d]
Fluorene	3.4 [a,d]	N.D.	49.6 [a]	63.3 [b]	168.3 [a,b,d]	N.D.
Phenanthrene	4.6 [a,b,d]	4.3 [b,d]	67.5 [a,b]	90.9 [b]	217.5 [b]	162.9 [b]
Anthracene	N.D.	N.D.	50.9 [a,b,d]	68.6 [b,d]	N.D.	N.D.
Fluoranthene	N.D.	N.D.	66.1 [a,b,d]	89.1 [a,b,d]	213.2 [a,b,d]	N.D.
Pyrene	N.D.	N.D.	72.1 [a,b,d]	97.1 [b,d]	232.4 [b]	N.D.
Benzo[a]anthracene	N.D.	N.D.	81.0 [b,d]	109.1 [a,b,d]	261.0 [b,d]	N.D.
Chrysene	N.D.	N.D.	63.2 [a,b,d]	85.1 [a,b,d]	203.6 [a,b,d]	N.D.
Benzo[b]fluoranthene	N.D.	N.D.	79.8 [a,b]	107.4 [b]	257.1 [b]	192.5 [a,b]
Benzo[k]fluoranthene	N.D.	N.D.	119.7 [a,b]	161.2 [a,b]	N.D.	N.D.
Benzo[a]pyrene	N.D.	N.D.	109.2 [b,d]	147.1 [a,b,d]	352.1 [a,b,d]	263.6 [a,b,d]
Indeno[1,2,3-cd]pyrene	N.D.	N.D.	130.1 [b,d]	175.2 [b]	419.3 [a,b,d]	314.0 [a,b,d]
Benzo[ghi]perylene	N.D.	N.D.	119.0 [b]	160.3 [a,b]	383.6 [a,b,d]	287.3 [a,b,d]
Dibenz[a,h]anthracene	N.D.	N.D.	101.4 [a,b,d]	136.5 [a,b]	326.8 [a,b,d]	244.7 [a,b,d]

Table VI-E. Target FAME and POC Analyte Concentrations by Fuel Type

Concentrations (ng/m^3)						
Fuel Type	Blank		B0		B20	
Filter ID	#72	#73	#112	#114	#126	#128
Air (L)	1240.00	1302.00	1760.00	1680.00	780.00	833.36
FAMEs						
Myristic Acid ME	44.0 [b]	32.8	7355.9 [a,c]	9313.5 [a,c]	4587.4	914.7 [b]
Palmitic Acid ME	438.9 [c]	232.1 [c]	4324.2 [c]	4579.4	###### [c]	4840.4
Oleic Acid ME	159.9	89.7 [b,c]	1393.2 [a,b,c]	1876.6 [a,b,c]	15765.4	3362.7 [c]
Elaidic Acid ME	34.6 [a,b,c]	32.9 [a,b,c]	786.0	826.5 [c]	37035.7 [c]	1404.9 [c]
Stearic Acid ME	125.3 [b]	48.4 [b]	1101.9 [b]	1480.7 [b]	###### [c]	8987.5 [b]
Linolenic Acid ME	19.8 [a,b,c]	20.0 [a]	284.6 [a,c]	368.1 [a,b,c]	3467.9 [a]	695.4 [a,b,c]
Linoleic Acid ME	412.5 [b,c]	392.8 [a,b,c]	6102.6 [a,b,c]	8219.9 [a,b,c]	19671.4 [b]	14729.5 [a,b,c]
Linolelaidic Acid ME	13.9	10.1	151.5 [a]	204.0 [a]	488.2 [a]	359.2 [a]
Arachidic Acid ME	8.6 [a,b,c]	8.2 [b,c]	127.4 [a,b,c]	171.6 [a,b,c]	16034.8 [c]	3277.4 [c]
Behenic Acid ME	23.8 [b]	22.7 [b,c]	352.1 [a,b,c]	474.3 [a,b]	22364.5 [c]	5035.8 [c]
POCs						
2-Pentanone	N.D.	53.1 [b]	1128.6 [b]	1800.8 [b]	4593.0 [b]	3887.7 [b]
3-Pentanone	28.6 [b,c]	32.1 [b,c]	581.7 [b]	829.2 [b]	1966.0 [b]	1560.1 [b]
n-Hexanal	93.9	94.2	1953.5	2579.8	10709.4 [c]	5793.6
n-Heptanal	174.7	103.8	3803.4 [c]	5363.3 [c]	8734.3 [c]	3281.4
n-Octanal	N.D.	N.D.	N.D.	N.D.	5564.4	N.D.
2-Nonanone	N.D.	N.D.	N.D.	N.D.	4904.8	N.D.
n-Nonanal	157.6	186.6 [c]	2691.6 [c]	4194.1 [c]	20592.4 [c]	8626.2 [c]
n-Decanal	74.3	114.4	1389.0	2002.2	6040.2	2975.2
Undecanal	50.3	58.4	863.9	1175.7	3015.8	1900.5
2-Hexanone	168.9	149.0	5707.1 [c]	8607.1 [c]	10424.3 [c]	21558.2 [c]
2-Heptanone	50.5 [b]	219.1 [c]	945.0 [b]	1186.9 [b]	2198.9 [b]	4596.9 [b]
2-Octanone	185.9 [c]	172.8 [c]	3912.5 [c]	6488.3 [c]	2716.5 [b]	10788.4 [b]
Dodecanal	46.7	61.1	831.1	1141.9	2951.8	1763.9
Benzaldehyde	86.8	84.6	1321.4	1761.9	4282.3	3228.0
m-Tolualdehyde	56.0	53.6	861.9	1119.4	2731.9	2046.1
o-Tolualdehyde	72.0	89.7	746.9 [b]	1829.1	6067.4	4619.3
p-Tolualdehyde	54.3	52.0	819.6	1097.2	2586.3	1944.8
Acetophenone	59.7	57.5	902.7	1217.0	2931.3	2168.5
1-Indanone	23.0 [c]	22.6 [c]	348.5 [c]	468.9 [c]	1102.3 [c]	N.D.
9-Fluorenone	47.6	44.9	751.2	N.D.	2296.9	1700.9
Perinaphthenone	N.D.	N.D.	1272.1	1216.4	N.D.	676.6 [c]
Benzophenone	173.7	217.5 [c]	3342.8 [c]	4589.7 [c]	10663.5 [c]	8723.6 [c]
1,4-Benzoquinone	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1,4-Naphthoquinone	N.D.	N.D.	347.0 [b,c]	N.D.	1090.9 [b,c]	833.9 [b,c]
Acenaphthoquinone	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Anthraquinone	18.0 [c]	18.1 [c]	392.2 [c]	517.9 [c]	1289.9 [c]	682.8 [c]

Table VI-F. Target Alkane and PAH Analyte Emission Rates by Fuel Type

Emission Rates (ng$_x$/ug$_{PM}$)						
Fuel Type	Blank		B0		B20	
Filter ID	#72	#73	#112	#114	#126	#128
PM (ug)	-1.302	0.06	0.26	0.18	0.15	0.13
ALKANES						
Dodecane	-400.4 [a]	1842.2 [a]	329.9 [a]	438.0 [a]	606.3 [a]	745.1
Tetradecane	-42.5 [a]	2073.9 [a]	222.0 [a]	240.1 [a]	1327.9 [a]	1036.9 [a]
Hexadecane	-104.2 [a]	822.6 [a]	195.7 [a]	131.3 [a]	238.1	227.5 [a]
Octadecane	-20.7	494.3	139.0	167.9	180.4	147.6 [a]
Eicosane	-22.5 [a]	467.3 [a]	90.3	167.9	1012.9	460.3
Docosane	-24.7 [a]	544.5 [a]	1582.3	765.3	3272.4	821.5
Tetracosane	-40.3	934.6	1114.2	680.0	5088.2 [c]	1130.7
Hexacosane	-55.6 [a]	1255.2	476.8	362.0	625.5	578.4
Octacosane	-102.0 [a]	2425.3	558.3	634.0	1511.2	1191.5
Triacontane	-126.1 [a]	2973.7 [a]	688.5	718.4	1617.7	1429.5 [a]
Dotriacontane	-146.7 [a]	3414.0	715.6 [a]	815.1 [a]	1650.2	1561.5 [a]
Tetratriacontane	-164.1 [a]	3773.2 [a]	778.7 [a]	908.8 [a]	1481.7	1679.6
PAHs						
Naphthalene	-3.7 [b,d]	83.9 [a,b,d]	17.4 [b,d]	20.4 [b,d]	32.1 [b,d]	37.7 [b,d]
Acenaphthylene	-4.1 [a,b,d]	N.D.	19.4 [a,b,d]	45.0 [a,b]	35.9 [b,d]	42.1 [a,b,d]
Acenaphthene	-5.7 [a,b,d]	130.6 [a,b,d]	N.D.	31.7 [a,b,d]	50.0 [a,b,d]	58.7 [a,b,d]
Fluorene	-3.2 [a,d]	N.D.	15.2 [a]	16.9 [b]	29.6 [a,b,d]	N.D.
Phenanthrene	-4.3 [a,b,d]	99.8 [b,d]	20.6 [a,b]	24.2 [b]	38.2 [b]	44.9 [b]
Anthracene	N.D.	N.D.	15.6 [a,b,d]	18.3 [b,d]	N.D.	N.D.
Fluoranthene	N.D.	N.D.	20.2 [a,b,d]	23.8 [a,b,d]	37.5 [a,b,d]	N.D.
Pyrene	N.D.	N.D.	22.0 [a,b,d]	25.9 [b,d]	40.8 [b]	N.D.
Benzo[a]anthracene	N.D.	N.D.	24.8 [b,d]	29.1 [a,b,d]	45.9 [b,d]	N.D.
Chrysene	N.D.	N.D.	19.3 [a,b,d]	22.7 [a,b,d]	35.8 [a,b,d]	N.D.
Benzo[b]fluoranthene	N.D.	N.D.	24.4 [a,b]	28.7 [b]	45.2 [b]	53.1 [a,b]
Benzo[k]fluoranthene	N.D.	N.D.	36.6 [a,b]	43.0 [a,b]	N.D.	N.D.
Benzo[a]pyrene	N.D.	N.D.	33.4 [b,d]	39.2 [a,b,d]	61.9 [a,b,d]	72.7 [a,b,d]
Indeno[1,2,3-cd]pyrene	N.D.	N.D.	39.8 [b,d]	46.7 [b]	73.7 [a,b,d]	86.5 [a,b,d]
Benzo[ghi]perylene	N.D.	N.D.	36.4 [b]	42.7 [a,b]	67.4 [a,b,d]	79.2 [a,b,d]
Dibenz[a,h]anthracene	N.D.	N.D.	31.0 [a,b,d]	36.4 [a,b]	57.4 [a,b,d]	67.4 [a,b,d]

Table VI-G. Target FAME and POC Analyte Emission Rates by Fuel Type

Emission Rates (ng$_x$/ug$_{PM}$)						
Fuel Type	Blank		B0		B20	
Filter ID	#72	#73	#112	#114	#126	#128
PM (ug)	-1.302	0.06	0.26	0.18	0.15	0.13
FAMEs						
Myristic Acid ME	-41.9 [b]	753.1	2250.0 [a,c]	2483.6 [a,c]	805.9	252.1 [b]
Palmitic Acid ME	-418.0 [c]	5333.4 [c]	1322.7 [c]	1221.2	21605.3 [c]	1333.9
Oleic Acid ME	-152.2	2060.5 [b,c]	426.1 [a,b,c]	500.4 [a,b,c]	2769.6	926.7 [c]
Elaidic Acid ME	-32.9 [a,b,c]	756.2 [a,b,c]	240.4	220.4 [c]	6506.3 [c]	387.2 [c]
Stearic Acid ME	-119.3 [b]	1112.3 [b]	337.1 [b]	394.9 [b]	19894.4 [c]	2476.8 [b]
Linolenic Acid ME	-18.9 [a,b,c]	459.6 [a]	87.1 [a,c]	98.2 [a,b,c]	609.2 [a]	191.6 [a,b,c]
Linoleic Acid ME	-392.8 [b,c]	9025.7 [a,b,c]	1866.6 [a,b,c]	2192.0 [a,b,c]	3455.8 [b]	4059.2 [a,b,c]
Linolelaidic Acid ME	-13.3	231.7	46.3 [a]	54.4 [a]	85.8 [a]	99.0 [a]
Arachidic Acid ME	-8.2 [a,b,c]	188.4 [b,c]	39.0 [a,b,c]	45.8 [a,b,c]	2816.9 [c]	903.2 [c]
Behenic Acid ME	-22.7 [b]	520.8 [b,c]	107.7 [a,b,c]	126.5 [a,b]	3928.9 [c]	1387.8 [c]
POCs						
2-Pentanone	N.D.	1219.6 [b]	343.3 [b]	479.3 [b]	814.7 [b]	1072.7 [b]
3-Pentanone	-27.24 [b,c]	737.1 [b,c]	176.9 [b]	220.7 [b]	348.8 [b]	430.5 [b]
n-Hexanal	-89.46	2164.0	594.1	686.7	1899.7 [c]	1598.6
n-Heptanal	-166.37	2385.9	1156.8 [c]	1427.6 [c]	1549.4 [c]	905.4
n-Octanal	N.D.	N.D.	N.D.	N.D.	987.1	N.D.
2-Nonanone	N.D.	N.D.	N.D.	N.D.	870.1	N.D.
n-Nonanal	-150.07	4288.4 [c]	818.6 [c]	1116.4 [c]	3652.9 [c]	2380.2 [c]
n-Decanal	-70.76	2627.8	422.4	532.9	1071.5	820.9
Undecanal	-47.94	1342.2	262.7	313.0	535.0	524.4
2-Hexanone	-160.87	3422.8	1735.7 [c]	2291.0 [c]	1849.2 [c]	5948.5 [c]
2-Heptanone	-48.14 [b]	5034.1 [c]	287.4 [b]	315.9 [b]	390.1 [b]	1268.4 [b]
2-Octanone	-177.01 [c]	3969.4 [c]	1189.9 [c]	1727.0 [c]	481.9 [b]	2976.8 [b]
Dodecanal	-44.45	1404.6	252.8	303.9	523.6	486.7
Benzaldehyde	-82.70	1943.5	401.9	469.0	759.6	890.7
m-Tolualdehyde	-53.34	1231.8	262.1	298.0	484.6	564.6
o-Tolualdehyde	-68.54	2061.7	227.2 [b]	486.9	1076.3	1274.6
p-Tolualdehyde	-51.74	1194.9	249.3	292.0	458.8	536.6
Acetophenone	-56.87	1322.2	274.5	323.9	520.0	598.3
1-Indanone	-21.94 [c]	518.4 [c]	106.0 [c]	124.8 [c]	195.5 [c]	N.D.
9-Fluorenone	-45.31	1032.4	228.5	N.D.	407.5	469.3
Perinaphthenone	N.D.	N.D.	386.9	323.8	N.D.	186.7 [c]
Benzophenone	-165.44	4998.4 [c]	1016.7 [c]	1221.7 [c]	1891.6 [c]	2407.1 [c]
1,4-Benzoquinone	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1,4-Naphthoquinone	N.D.	N.D.	105.5 [b,c]	N.D.	193.5 [b,c]	230.1 [b,c]
Acenaphthoquinone	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Anthraquinone	-17.15 [c]	416.1 [c]	119.3 [c]	137.8 [c]	228.8 [c]	188.4 [c]

Table VI-H. Cumulative Results and Statistics by Fuel Type

	Mean, Standard Deviation, and RSD of Primary Functional Groups by Fuel Type								
Fuel Type	**Blank**			**B0**			**B20**		
Total Mass on Filter (ng)	$\bar{x}$	St. Dev.	RSD	$\bar{x}$	St. Dev.	RSD	$\bar{x}$	St. Dev.	RSD
Alkanes	1409.27	308.41	21.88	1647.48	340.45	20.66	2070.95	966.87	46.69
PAHs	14.12	6.34	44.95	71.02	7.27	10.24	54.16	16.87	31.14
FAMEs	850.88	363.35	42.70	1223.25	93.62	7.65	5030.75	5794.56	115.18
POCs	2233.27	312.91	14.01	2982.17	102.80	3.45	3190.92	77.48	2.43

Concentrations (ng/m3)	$\bar{x}$	St. Dev.	RSD	$\bar{x}$	St. Dev.	RSD	$\bar{x}$	St. Dev.	RSD
Alkanes	1113.63	281.07	25.24	22569.17	55.62	0.25	72949.79	46665.64	63.97
PAHs	11.20	5.38	48.02	1004.98	309.71	30.82	1879.20	937.34	49.88
FAMEs	674.79	309.15	45.81	16990.43	2269.75	13.36	188981.15	229244.80	121.31
POCs	20884.95	31721.19	151.89	11855.40	1749.17	14.75	23474.84	3231.15	13.76

Emission Rates (ng/ug_{PM})	$\bar{x}$	St. Dev.	RSD	$\bar{x}$	St. Dev.	RSD	$\bar{x}$	St. Dev.	RSD
Alkanes	9885.53	15747.85	159.30	6460.11	609.78	9.44	14811.24	5375.62	36.29
PAHs	77.82	130.26	167.39	283.40	60.80	21.45	390.89	78.74	20.14
FAMEs	4815.33	8013.18	166.41	4832.39	178.72	3.70	34542.16	38373.77	111.09
POCs	1753.89	185.70	10.59	1753.89	185.70	10.59	106405.52	18453.92	17.34

Appendix VII. Biodiesel Blend Fuel Composition.

Table VII -A. Polar vs. Nonpolar GC Column FAMES Quantitation of Biodiesel Fuel Blends

Restek Rxi-XLB Non-Polar Column

	B20 Samples			B50 Samples			B100 Samples		
FAMES	Mean Conc. (ppm)	St. Dev (ppm)	RSD (%)	Mean Conc. (ppm)	St. Dev (ppm)	RSD (%)	Mean Conc. (ppm)	St. Dev (ppm)	RSD (%)
C14:0	0.000	0.000	0	0.000	0.000	0	0.000	0.000	0
C16:0	0.568	0.146	26	1.936	0.624	32	3.735	0.713	19
C18:0	0.243	0.129	53	0.698	0.181	26	1.361	0.197	14
C18:1n9t	0.000	0.000	0	0.068	0.127	188	0.361	0.413	115
C18:1n9c	0.917	0.309	34	4.876	1.524	31	13.471	3.087	23
C18:2n6t	0.141	0.073	52	0.393	0.199	51	1.121	0.296	26
C18:2n6c	1.583	0.239	15	5.748	1.824	32	16.455	4.625	28
C18:3	0.000	0.000	0	0.000	0.000	0	0.000	0.000	0
C20:0	0.043	0.136	316	0.122	0.220	181	0.095	0.197	208
C22:0	0.000	0.000	0	0.000	0.000	0	0.000	0.000	0
SUM	3.495	0.886	25	13.840	4.334	31	36.599	7.752	21

Supelco SLB-IL100 Polar Column

	B20 Samples			B50 Samples			B100 Samples		
FAMES	Mean Conc. (ppm)	St. Dev (ppm)	RSD (%)	Mean Conc. (ppm)	St. Dev (ppm)	RSD (%)	Mean Conc. (ppm)	St. Dev (ppm)	RSD (%)
C14:0	0.000	0.000	0	0.000	0.000	0	0.000	0.000	0
C16:0	0.357	0.240	67	0.741	0.191	26	1.425	0.314	22
C16:1	0.015	0.017	114	0.024	0.014	60	0.049	0.036	73
C18:0	0.105	0.098	93	0.237	0.070	29	0.492	0.130	26
C18:1n9t	0.166	0.573	346	0.188	0.624	332	0.000	0.000	0
C18:1n9c	1.228	0.847	69	2.333	0.940	40	5.420	1.888	35
C18:2n6t	0.000	0.000	0	0.000	0.000	0	0.000	0.000	0
C18:2n6c	1.492	0.894	60	2.805	0.656	23	6.487	2.413	37
C18:3	0.123	0.106	87	0.271	0.058	21	0.899	0.550	61
C20:0	0.000	0.000	0	0.000	0.000	0	0.020	0.014	71
C20:1	0.001	0.002	424	0.000	0.000	0	0.034	0.032	94
C22:0	0.000	0.000	0	0.000	0.000	0	0.000	0.000	0
SUM	3.280	1.081	33	7.625	1.985	26	15.887	4.939	31