CHARACTERIZATION OF BIOFUELS BLENDS: EMISSIONS, PERMEATION AND APPORTIONMENT OF VOLATILE ORGANIC COMPOUNDS

by

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Dedication

To my family

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Chapter 1

Introduction

1.1 Background

The United States Environmental Protection Agency (EPA) establishes standards to help protect public health and the environment from harmful emissions associate with fuels, motor vehicles and engines based on the Clean Air Act. Therefore, strict regulations for fuel formulation and vehicle emissions are enforced. EPA has also established a renewable fuel standard (RFS) program for the transportation sector with the primary goal of increasing energy independence and secondarily to improve air quality under the Energy Policy Act of 2005. Since this Act was signed, use of renewable fuels has significantly increased as has the construction of new or expanded biofuel facilities. New motor fuels (petroleum fuels and biofuel blends) are now used widely in the U.S, and because their compositions differ from previous fuels, exposures and risks associated with these fuels may also differ. Information regarding the new motor fuels (e.g., gasoline containing ethanol, ultra-low sulfur diesel, and biodiesel) is very limited in the literature, especially for air toxics, which are known or suspected to cause adverse effects on public health.

Vehicle- and fuel-related sources are two key emission sources of volatile organic compounds (VOCs), responsible for 38% and 13% of these compounds, respectively.[1] Many VOCs are ozone (O_3) precursors,[2] mobile-source air toxics (MSATs),[3] and hazardous air pollutants (HAPs).[4] Changes in fuel composition can affect VOC emissions throughout the fuel cycle, known as "wells-to-wheels" for petroleum fuels, and "feedstocks-to-wheels" for biofuels.

In order to understand impacts of the new fuels, it is important to understand compositions of the new fuels, their vapors and vehicle exhaust. Fuel-related workers are directly exposed to these new fuels, therefore, it is important to understand their exposures. However, worker exposures are not representative of the general public. Thus, air pollutant levels monitored in ambient settings, including near-road settings, are needed to portray environmental exposures. The chemical composition of the sources just described, known as source profiles, are important for apportioning emission sources, estimating emissions, estimating exposures and for other purposes in air quality management.

This dissertation focuses on VOC emissions. It evaluates the composition of new petroleum fuels and biofuel blends, permeation of these fuels through personal protective equipment (PPE) materials, exhaust emissions from diesel engine using biodiesel blends, and identifies emission sources affecting a near-road site. Therefore, the following literature review focuses on the formulation of fuels, elastomer properties related to permeation, VOC emissions from vehicles, and receptor-based methods for source identification and apportionment.

The production and use of biofuels also raise many potentially important economic and social issues, e.g., increased use of land, water, pesticide and fertilizer, as well as secondary impacts affecting the food supply, among others. These issues are beyond the scope of this study.

1.1.1 Fuel formulation trends and properties

1.1.1.1 Fuel formula trends

Fuels are mixtures containing hundreds of hydrocarbon compounds. In addition, many fuel additives may use for improving combustion efficiency and reducing emissions including metals (e.g., lead), ethers (e.g., methyl tert-butyl ether, MTBE), alcohols (e.g., ethanol or methanol), and other chemicals (e.g., detergents and anti-oxidants). The formulation of transportation fuels has large impacts on the environment and human health. For example, leaded gasoline caused serious air pollution impacts that elevated blood lead levels in human, and thus was gradually phased out starting in 1973 in the U.S. MTBE replaced tetraethyl lead as a major oxygenate, however, this additive also was phased out starting in 1999 due to ground water contamination issues from leaking underground storage tanks.[5] Currently, ethanol is blended in many gasoline fuels as an oxygenate, usually less than 10% by volume, but the percentage can reach 15% for model year 2001 and newer vehicles. As discussed elsewhere, the impacts of ethanol in these fuels have not been fully investigated.

Starting in 2011, the annual average benzene content in gasoline has been limited to a maximum of 0.62% by volume. Biodiesel (methyl ethers) is blended in many diesel fuels as lubricity additive (up to 5%). Low biodiesel blends (up to 20%) are also used in many states without engine modification.

Sulfur content is also regulated by EPA. Sulfur in gasoline is limited to 30 ppm, and in diesel to 15 ppm. The lower sulfur levels would help to reduce emissions and also support emission control technology. However, the levels of benzene, other aromatics, aldehydes, and other components of fuels and their combustion products remain concerns for human health.

1.1.1.2 Properties of biofuel blends

As noted, biofuel blends including bioethanol-blends and biodiesel-blends have potential to reduce tailpipe emissions. However, the nature and production of biofuels have several characteristics that differ from conventional fuels, and these may affect the exposure of the general public as well as workers. First, low bioethanol blends (<20%) have higher vapor pressure that may increase evaporative emissions. Second, biofuels have lower energy content that may increase the consumption of fuels than conventional gasoline and diesel.[6] Third, biofuels can degrade some elastomers and metals used in vehicle fuel systems. For example, ethanol can degrade natural rubber, polyurethane, polymers and materials made of cork, and it is not compatible with soft metals such as zinc, brass, copper, lead and aluminum. These effects can increase the corrosion of steel used in underground storage tanks, piping and fittings, thus increasing risks of leakage to surrounding soils and groundwater environment.[7] Fourth, there is relatively little information regarding the composition of bioethanol and biodiesel blends, as well as vapor compositions of high ethanol blends.[8, 9] The composition of these fuels is hard to estimate from theoretical calculation because ethanol may exhibit non-ideal behavior in solution with non-polar gasoline hydrocarbons,[10, 11] and variation from feedstock (biomass source) may be considerable. The composition will alter permeation, volatilization and combustion emissions throughout the fuel cycle.

1.1.2 Permeation tests

Bioethanol can increase permeation and thus evaporative emissions from elastomers used in vehicles.[12-14] Most of the available studies tested whole vehicles using the sealed housing emissions determination (SHED) method,[15] thus effects of specific types of elastomers cannot be isolated. Other studies have used a simpler weighing method and obtained the mass loss rate of fuel,[16, 17] however, little information was provided regarding the composition of biofuels and their permeants.

The American Society for Testing and Materials (ASTM) provides a method for measuring the permeation resistance of chemical protective clothing, and a similar method is used for measuring fuel permeation through the sheet form of some polymeric materials.[18, 19] The breakthrough time (BT) and steady-state permeation rate (SSPR) are commonly used parameters describing the permeation resistance of elastomers and the suitability of a particular material for particular chemical. BT is defined as the time that the challenge chemical is first detected at the inner surface of the test sample. SSPR is defined as the permeation rate which has reached a dynamic equilibrium and does not change over time.

Permeation behavior can vary as a function of time. Typically, there are three stages. First, before breakthrough, the chemical has not permeated through the material. Second, after BT, the permeation rate will increase to reach steady-state. Last, the permeation rate maintains a steady-state rate. Such classical behavior does not apply to swelling or degrading elastomers.

Most permeation tests have been conducted using a single material and a single permeant,[20, 21] and information regarding mixtures, biofuels, and the composition of permeants is limited. Moreover, permeability is strongly dependent on elastomer properties. Different elastomers markedly differ in their mechanical and chemical properties. Chemicals resistance, tensile strength, hardness and elongation are additional factors affecting the selection of elastomers for vehicle fuel systems as well as personal protective equipment (PPE) for workers.

1.1.3 Elastomer properties

Natural rubber is an inexpensive material with good properties at low temperatures, mild pressures, and with a variety of chemicals. However, it is not recommended for contact with organic chemicals. Neoprene (the DuPont trade name) is a family of synthetic rubbers that are produced from polymerization of chloroprene. Due to their chemical inertness and insulative properties, these materials have been used widely as gaskets, hoses, corrosion-resistant coatings, wetsuits, electrical insulation, and personal protection clothing. Neoprene has been used in several fuel system components. Acrylonitrile butadiene rubber (NBR) is also commonly used in automotive systems, particularly in hoses and seals in pre-enhanced evaporative control systems. NBR (also called nitrile rubber or buna-N) is a synthetic rubber copolymer of acrylonitrile (ACN) and butadiene that is resistant to oil, fuel and other chemicals with low swelling, however, it has inferior strength and flexibility.

The California Air Resources Board (CARB) and the US EPA gradually imposed more stringent vehicle emission regulations that required higher performance and more exotic materials in fuel systems.[22] Newer vehicles incorporate components comprised of fluorinated elastomers (FKM) and high density polyethylene (HDPE). Viton (the DuPont trade name) is a type of FKM used in fuel systems for seals and gaskets, O-rings and other extruded applications. FKM has great resistance to many solvents, and the permeability of fuels tested on FKM decreased as the fluorine content increased.[16] However, FKM tested using CE-10 (10% ethanol, 45% toluene, and 45% isooctane), showed higher permeation rates than using pure fuel C (50% toluene, 50% isooctane), a reference fuel used by the Society of Automotive Engineers (SAE)[23]. FKM may allow greater ethanol permeation than high-density polyethylene (HDPE)[18] , described next.

High-density polyethylene (HDPE) is a polyethylene thermoplastic made from petroleum. It has good resistance to many solvents and a wide variety of applications, e.g., fuel tanks, chemical-resistant piping systems, and corrosion protection for steel pipelines. HDPE is an excellent barrier material for neat alcohols, but HDPE performance deteriorated when hydrocarbon mixtures.[18] Many other materials used in existing vehicle fuel systems may not be suitable for such fuels. For example, ethylene vinyl alcohol (EVOH), a material used in the middle layer of fuel tanks, is not a good barrier for ethanol or methanol fuel blends since both can act as plasticizers for EVOH.[18]

As noted, many commercial gasoline fuels now contain ethanol as an oxygenate. FKM may still have better performance than the other materials mentioned above. Overall, ethanol has the potential to alter permeation characteristics and the composition of VOC emissions, although speciation data is unavailable.

1.1.4 VOC emissions from vehicles

Exposure to high level of ambient air pollutants has been associated with many adverse health effects, including increased hospital visits due to respiratory, cardiovascular and other diseases.[24-31] In urban area, vehicles emit about 21% of air toxics, a result of both evaporative and exhaust emission.[32] Evaporative emissions result from canister breakthrough, permeation through gaskets, hoses, joints, fuel cap and fuel tanks, and leakage from fuel cap and fuel system. Exhaust emissions are associated with fuels, vehicle combustion condition and pollutant control technology. Both emissions are regulated by EPA. In part as a result of the more stringent tailpipe emission standards (e.g, the Tier 2 program phased in 2004 for light-duty vehicles), evaporative emissions have become the dominant vehicular source of VOCs. Other contributing factors to this switch include material degradation in fuel system components and inappropriate maintenance.

The sealed housing emissions determination (SHED) method is a standardized approach for estimating evaporative emissions for a whole vehicle under the federal test procedures (FTP).[15] These emissions can vary significantly due to vehicle's brand, model year, pollution control equipment, fuel type, mileage, maintenance and driving condition, and the materials used in the fuel system. The Society of Automotive Engineers (SAE) has recommended methods to estimate the fuel permeation of fuel system components, specifically gravimetric methods and mini-SHED testing, to understand their impacts on full vehicle SHED performance.[16, 33-35] However, test conditions and material components have not been well investigated.

Table 1.1 and Table 1.2 list vehicle emission measurements in the literature. Karlsson et al. (2006) investigated exhaust emissions from four popular Euro 4 conventional vehicles using the new European test cycle (NETC), Swedish commercial gasoline (≤5% ethanol), and two higher ethanol blends E17 (17% ethanol) and E43 (43%

ethanol). No significant changes in exhaust emissions were seen using ethanol blends.[36] Emissions from three flexible fuel vehicles (FFV) using the NETC were tested using three different percentage ethanol gasoline blends (E5, E10, E70, and E85), and higher acetaldehyde, methane and CO emissions were observed for the E70 and the E85 fuels compared to E5 and E10.[37] These studies suggest that emissions of FFV are not necessarily better than those of conventional vehicles. If should also be noted that the FFV vehicles had higher fuel consumption, and that no long-term tests were conducted.[36, 37]

In the U.S, FFV emissions have been tested using federal test procedure (FTP), reformulated gasoline (RFG), compressed natural gas (CNG), M85 (85% methanol, 15% gasoline) and E85 (85% ethanol, 15% gasoline). Most studies have focused on regulated pollutants, and thus information regarding the composition of evaporative and exhaust emissions is limited. Higher benzene emissions were observed for RFG compared to E85 for the same FFV and test procedure; higher acetaldehyde and formaldehyde emissions were observed for E85 compared to RFG; and higher formaldehyde emissions for M85 compared to RFG.[13, 38-40] Emissions from diesel vehicles using biodiesel blends are reviewed and detailed in Chapter 4. Of these studies, more detailed composition information on both evaporative and exhaust emission are needed to understand the impact of biofuels.

1.1.5 Source identification and apportionment methods

In air quality management, it is important to determine the significance of various pollutant sources. There are several approaches for identifying and apportioning sources. The source-oriented or dispersion modeling approach utilizes emission inventories, dispersion and transformation models, and meteorological and other data to follow emissions at the source to predict the pollutant concentration under various ambient conditions at specific spatial locations (called receptors). The more empirical receptor-oriented approach uses pollutant composition and other physical-chemical characteristics and statistical techniques such as regression and factor analysis to identify and apportion emission sources by matching known emission characteristics with those measured at a source. Source and receptor approaches are complementary, and these methods can be compared and sometimes reconciled. For many pollutants, however, emission inventories are unavailable or highly uncertain. Also, environmental conditions, including terrain, source characteristics, and meteorology, are very complex. In such cases, the source-oriented approach performs poorly and receptor methods of apportionment may be advantageous.

Receptor modeling is based on the assumption of mass conservation. The concentration of pollutant *i* at the sampling site (receptor) is assumed to be a linear combination of contributions from various sources (j=1…m).

$$C_i = \sum_{j=1}^{m} X_j S_{ij} \alpha_{ij} \qquad (1)$$

where C_i = the concentration of pollutant (i) at the receptor (µg/m^3), X_j = the total concentration of source (j) at the receptor (µg/m^3), S_{ij} = the mass fraction of pollutant (i) in the total emissions from source (j=1…m) (unit less),and α_{ij} = the adjustment factor for representing any gain or loss of pollutant (i) from source to the receptor.[41]

Eq. 1 may be solved using several approaches. Most solutions use either the chemical mass balance (CMB) or multivariate approaches,[42] as described below.

1.1.5.1 Chemical mass balance (CMB) methods

The CMB approach uses chemical and physical characteristic of VOCs and particles measured at a receptor to identify and quantify source contributions to measured pollutant levels. CMB typically uses a least squares solution to the set of linear equations represented by eq. (1) (one equation per compound i). The equation may be solved when compositions among the different sources are sufficiently different, source profiles are known, and the number of compounds used exceeds the number of source types to be estimated. In general, the modeling process consists of five steps: (1) identification of VOC sources; (2) selection of specific VOCs; (3) determination of source profiles (fraction of the selected VOCs in each type of source); (4) estimation of the uncertainty in receptor concentrations and source profiles; and (5) solution of the CMB equations. CMB models have been most widely used for particulate matter, though the literature has now includes a number of apportionments for VOCs.[43, 44] Source profiles can be obtained using measurements or taken from the literature. However, it is difficult and costly to obtain all profiles, e.g., fugitive emission of particulate matter from roadways, stack emissions, vehicle emissions. Moreover, emission characteristics can vary considerably over time and between specific sources, e.g., vehicles. For these reasons, receptor methods other than CMB have been used, described next.

1.1.5.2 Multivariate methods

Multivariate methods relax the constraint that the source profiles are known. Multivariate models applied to air quality studies include principal component analysis (PCA), factor analysis (FA), positive matrix factorization (PMF), and Unmix. These methods reduce the data into a smaller number of composite variables that ideally represent source categories as measured at a receptor site. FA and PCA do not need the emission sources characteristics, thus, these methods can be used to confirm known sources or explore unknown sources.[42] In PMF, users define the number of factors and add error estimates to the factors depending on the data. It is useful to weight the data due to sampling errors, detection limit issues, missing data or outliers. Details of algorithms can be found in Paatero and Tapper (1994).[45] UNMIX is a PCA-based method developed by US EPA that uses a new transformation method based on the self-modeling curve resolution (SMCR) technique in order to resolve sources,[46, 47] Multivariate methods are helpful for identifying unknown sources, but small contributors (<5%) can be difficult to identify by PCA, PMF and UNMIX models.[48, 49]

1.2 Research objectives

The objectives of this study are to improve the understanding of VOC exposure, permeation and emission for the use of biofuel-blends and differentiate emission contributions from gasoline and diesel vehicles using source apportionment analysis in a field study. The research has four specific objectives. The first three objectives are related to VOC exposure, permeation and emission for the use of biofuel-blends. The last objective related to VOC source apportionment analysis in a near road ambient site.

Objective 1: **Characterize the VOC composition of liquid and vapor fractions of current commercial motor vehicle fuels, including gasoline (<10% bioethanol), E85 (85% bioethanol), ultra-low sulfur diesel (ULSD) and B20 (20% biodiesel and 80% ULSD), and evaluate the collinearity of the profiles for receptor modeling.**

This information will help to describe the composition of spillage, leaks and emissions from fuel- and vehicle-related sources (e.g., storage tanks, vehicle refueling, running and evaporative losses) that may occur using current commercial motor vehicle fuels, and provides a set of liquid fuel and fuel vapor profiles for use in receptor modeling.

Objective 2: Evaluate the permeation behavior of biofuels through personal protective equipment (PPE) materials to understand the potential for dermal exposure of workers.

This information is essential for understanding the permeability of gasoline (<10% bioethanol), E85, ULSD and B20 fuels, worker exposures, suitability of different PPE materials, and also providing recommendations of PPE for handing these fuels.

Objective 3: Characterize exhaust emissions from diesel engines at various loads and speeds using B20 and ULSD fuels.

Emissions of regulated and unregulated pollutants from diesel engines are a strong function of fuel and without exhaust treatment systems. The experiments for this objective are designed to develop an understanding of the changes in the composition of exhaust emissions when using biodiesel blends and exhaust treatment systems. Such information is particularly needed for the toxic compounds associated with health risks. Moreover, emission measurements also facilitate the development of profiles for exhaust, which are useful for both emission inventories and receptor modeling.

Objective 4: Monitor and apportion levels and sources of VOCs at a near road site in Detroit, Michigan

This objective is aimed at characterizing the VOC concentrations, including their temporal variation, and identifying potential VOC sources at a near-road site in Detroit, Michigan using source apportionment analysis. Results are useful for exposure-response relationships, ozone formation potential, source apportionment and air quality management.

1.3 Organization of this dissertation

This dissertation is organized into six chapters. Chapter 1 (this chapter) has summarized literature findings, objectives of this research and importance of each objective. Chapters 2 to 5 pertain to each research objective described in Section 1.2. Chapter 6 integrates the major findings of the individual chapters, highlights strengths and limitation of this dissertation, and provides suggestions for further study.

Table 1.1 Exhaust and evaporative emissions from gasolilne vehicles using various fuels

Study	Karlsson (2006)									Serves (2005)				Ohio state, U.S.(1998)		Kelly et al. (1996)		
Brand-vehicle type	Saab-Gasoline			Volvo-Gasoline		Peugeot-Gasoline		Opel-Gasoline		Ford Focus-FFV				Ford Taurus - FFV		Chevrolet Lumina-FFV		
Test Procedure	NEDC			NEDC		NEDC		NEDC		NEDC				FTP		FTP		
Fuel	CG	E17	E43	CG	E43	CG	E43	CG	E43	E5	E10	E70	E85	RFG	E85	RFG	E50	E85
Exhaust emissions (mg/mile)																		
Acetaldehyde	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.68	0.77	5.43	8.28	0.30	13.02	0.84	11.10	17.21
Benzne	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	8.90	5.00	1.83
Formaldehyde	NA	NA	NA	NA	NA	NA	NA	NA	NA	1.12	1.01	1.22	1.28	0.99	2.26	2.79	3.38	3.36
1,3-butadiene	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.87	0.43	0.17
Hydrocarbons	43	62	43	31	19	25	25	25	31	34	32	33	64	117	189	188	161	145
Methane	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.7	3.4	6.4	10.7	21	46	39	52	63
Carbon monoxide	373	497	435	62	62	373	435	186	62	128	122	329	553	1,010	1,330	2,804	2,659	2,293
Carbon dioxide	158,760	146,457	145,339	145,587	140,927	112,530	113,090	96,375	102,278	99,626	100,248	96,520	94,656	412,100	389,800	465,852	448,435	435,092
Nitrogen oxides	12	12	25	12	19	12	81	25	211	269	423	161	300	NA	NA	220	163	160
Non-methane hydrocarbons	37.28	55.92	37.28	31.07	18.64	24.85	18.64	24.85	24.85	NA	NA	NA	NA	101	149	156	116	87
Nonmethane organic gases	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	150	158	165
Particular matter	NA	NA	NA	NA	NA	NA	NA	NA	NA	1.11	0.72	0.64	1.14	NA	NA	NA	NA	NA
Total volatile organic compounds	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	185	205	226
Ozone forming potential (mgO_3/mile)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	555	490	416
Evaporative emissions																		
Hydrocarbons (mg/test)	NA	NA	NA	NA	NA	NA	NA	NA	NA	3,400	3,633	NA	NA	NA	NA	382	506	378
Benzne (mg/mile)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Nonmethane organic gases(mg/mile)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ozone forming potential (mgO_3/mile)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

FFV, Flex fuel vehicle. NEDC, New European Test Cycle. FTP, Federal Test Procedure. RFG, reformulated gasoline. NA, Not available.

Table 1.2 Exhaust and evaporative emissions from gasoline vehicles using various fuels (Continued)

Study	Kelly et al. (1999)										Black et al. (1998)							
Brand-vehicle type	Ford Taurus-FFV		FFV		FFV		Dodge Spirit-FFV		B250-	Caravan-	FFV		FFV		FFV		CNG	
Test Procedure	FTP		FTP		FTP		FTP		FTP	FTP	FTP		FTP		FTP		FTP	
Fuel	RFG	E85	RFG	E85	RFG	M85	RFG	M85	CNG	CNG	RFG	M85	RFG	M85	RFG	E85	RFG	CNG
Exhaust emissions (mg/mile)																		
Acetaldehyde	0.28	9.85	NA	NA	0.49	0.20	0.48	0.27	0.35	NA	0.90	0.20	0.40	0.20	0.50	18.80	0.90	0.00
Benzne	2.86	1.01	NA	NA	3.96	0.92	5.33	1.42	0.34	NA	3.70	1.80	5.90	1.50	4.80	2.40	5.00	0.10
Formaldehyde	1.30	2.22	NA	NA	2.00	15.65	1.60	11.57	4.50	NA	2.50	14.90	1.80	14.50	2.50	4.00	2.90	0.70
1,3-butadiene	0.54	0.18	NA	NA	0.81	0.11	0.91	0.14	0.08	NA	0.40	0.00	0.40	0.00	0.10	0.10	0.50	0.00
Hydrocarbons	64	82	85	90	93	107	97	49	443	166	NA	NA	NA	NA	NA	NA	NA	NA
Methane	636	689	219,981	223,978	536	554	937	860	1,367	142	NA	NA	NA	NA	NA	NA	NA	NA
Carbon monoxide	212,666	201,402	437,235	222,292	220,628	201,676	185,010	171,169	262,275	364	1,440	2,480	3,360	5,140	1,970	3,190	1,700	540
Carbon dioxide	212,038	200,730	NA	97	220,107	201,139	184,089	170,322	261,295	389,541	NA	NA	NA	NA	NA	NA	NA	NA
Nitrogen oxides	154	150	307	196	NA	125	220	177	654	187	176	243	153	173	270	177	294	19
Non-methane hydrocarbons	134	125	218	144	236	217	194	147	381	22	NA	NA	NA	NA	NA	NA	NA	NA
Nonmethane organic gases	92	172	NA	NA	140	258	190	221	87	NA	116	304	151	284	140	244	154	6
Particular matter	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Total volatile organic compounds	104	199	NA	NA	168	275	218	237	1,218	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ozone forming potential (mgO$_3$/mile)	318	378	NA	NA	482	319	591	303	162	NA	458	521	537	611	562	761	660	46
Evaporative emissions																		
Hydrocarbons (mg/test)	319	390	245	191	NA	NA	779	767	454	311	NA	NA	NA	NA	NA	NA	NA	NA
Benzne (mg/mile)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	7.00	2.50	2.90	1.70	3.00	0.60	1.80	0
Nonmethane organic gases(mg/mile)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	613	355	161	190	182	126	117	NA
Ozone forming potential (mgO$_3$/mile)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1275	631	489	332	439	191	306	0

FFV, Flex fuel vehicle. NEDC, New European Test Cycle. FTP, Federal Test Procedure. RFG, reformulated gasoline. CNG, Compressed natural gas. NA, Not available.

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Chapter 2

Composition of current motor vehicle fuels and vapors and collinearity analysis for receptor modeling

2.1 Abstract

The formulation of motor vehicle fuels can alter the magnitude and composition of evaporative and exhaust emissions occurring throughout the fuel cycle. Information regarding the speciation of volatile organic compounds (VOCs) of motor fuels other than gasoline is very limited in the literature, especially for biofuel blends containing bioethanol and biodiesel. This study examined the liquid and headspace composition of four contemporary fuels: conventional gasoline (<10% of ethanol), E85 (85% ethanol and 15% gasoline), ultra-low sulfur diesel (ULSD), and B20 (20% soy bean biodiesel blend with 80% ULSD). Both liquid and headspace samples were collected and analyzed using similar methods. The composition of conventional gasoline (<10% of ethanol) and E85, including both neat fuel and headspace vapor, was dominated by aromatics and n-heptane, and despite its low gasoline content, E85 vapor contained higher concentrations of several target VOCs (n-octane, ethyl benzene, p-, m-,o-xylene, n-nonane) at 5 ^{o}C and 15 VOCs at 40 ^{o}C than those in gasoline vapor, which may due to adjustments in the formulation of E85. B20 and ULSD fuels were dominated by C_9 to C_{16} n-alkanes, followed by lower levels of aromatics (naphthalene, 1,2,3-trimethyl benzene). Partial pressures of 17 target VOCs in E85 showed a greater dependency on temperature than gasoline, resulting in compositional shifts. Headspace vapors of B20 and ULSD had similar VOC compositions and concentrations, and the most prevalent compounds were methylcyclohexane and cyclohexane. Headspace compositions predicted using the fuel's composition, vapor-liquid equilibrium theory, and activity coefficients (when available) correlated closely to measurements (r from 0.73-0.94). For E85, systematic underprediction of headspace vapor concentrations suggests that activity coefficients in the range of 1.5 to 2.0 are needed. Collinearity among profiles was evaluated using singular value variance-decomposition (SVD) analyses, which showed strong correlation among B20 and ULSD fuels and headspace vapors, but distinct profiles for gasoline and diesel fuels and their vapors. These results can be used to help estimate fuel related emissions and exposures, particularly as profiles in receptor models that are used to identify and apportion emission sources, and the collinearity analysis suggests that gasoline- and diesel-related emissions can be distinguished.

2.2 Keywords

Biofuels, collinearity, diesel, evaporative emission, gasoline, VOCs

2.3 Introduction

A range of motor vehicle fuels is available in the U.S. and other countries. Recent changes to gasoline-like fuels include ethanol additions to gasoline as an oxygenate, replacing methyl tert-butyl ether (MTBE), and the increased availability of E85, an 85% ethanol/15% gasoline blend. Gasoline (<10% of ethanol) and E85 use "bioethanol" produced from agricultural feedstock such as corn, which provides an at least partly renewable fuel. Recent changes for diesel fuels include lower sulfur content, now 15 ppm, forming ultra-low sulfur diesel (ULSD); and additions of methyl ethers derived from soybeans to form biodiesel blends B5, B10 and B20 containing 5, 10 and 20% fractions, respectively, of biodiesel in ULSD for use in unmodified diesel engines.

Fuel formulations alter the magnitude and composition of evaporative and exhaust emissions occurring throughout the fuel cycle.[1-3] In the U.S., reformulated gasoline, in which the Reid vapor pressure, aromatics, olefins and other reactive VOCs are controlled to limit emissions of precursors of ozone, is required in cities with the worst ozone problems.[4] Biofuels can reduce tailpipe emissions, however, ethanol-containing fuels have higher vapor pressures, which can increase evaporative emissions of volatile organic compounds (VOCs).[5] Some biofuels can degrade some elastomers and metals used in vehicle fuel systems, which can also increase permeation rates and evaporative emissions.[6, 7] Fuel formulation also alters emissions from inadvertent spills in which all fuel components fully evaporate, as well as situations in which the more volatile and permeable components are preferentially emitted, e.g., losses from storage tanks, refueling, and fuel system components.[7]

Fuel compositions vary widely, and an up-to-date understanding of fuel and vapor compositions is needed to estimate fuel-related emissions, as well as exposures and health risks. A typical composition of gasoline circa 1989 was 25-40% isoalkanes, 20-50% total aromatics (including 0.5-2.5% benzene), 4-8% alkanes, 3-7% cycloalkanes, 2-5% alkenes and l-4% cycloalkenes (all % volume).[8] Gasoline composition rapidly changed in California between 1995 and 1996 when both aromatics and alkenes were reduced.[9] Nowadays, gasoline contains mostly (55-77%) saturated hydrocarbons, 9-36%

aromatics, some unsaturated hydrocarbons and less than 10% of ethanol.[10] Information regarding the composition of both fuel and vapor for the new bioethanol and biodiesel blends is very limited.

Knowledge of source profiles is critical for receptor models, which apportion observed pollutant levels to different of emission sources.[11, 12] For apportioning VOC sources, these models are particularly valuable given the large uncertainties in VOC emission inventories.[13] To distinguish among source types using such models, each source profile must have a unique composition. Collinearity among profiles, a common problem, can degrade receptor model results by causing errors, inflating variances among predicted apportionments, decreasing goodness of fit, and diminishing the robustness of results.

This study investigates fuel and vapor compositions of current fuels, including two conventional petroleum-based diesel and gasoline (<10% of ethanol) fuels, and two biofuel blends. Vapor measurements are compared to predictions based on the fuel's composition and vapor-liquid equilibrium theory. The collinearity among fuel and vapor profiles is evaluated using variance decomposition analyses, and a set of profiles for receptor modeling is suggested.

2.4 Materials and Methods

2.4.1 Fuel and headspace sampling

Four commercial fuels were tested: "regular" conventional gasoline (containing < 10% of ethanol); E85; conventional ULSD; and B20. 1 L of each fuel was purchased from a Michigan fuel station in December 2007 and stored in a glass bottle placed in a laboratory safety cabinet. These samples represent a snapshot of the fuels since fuel composition can vary by brand, season and location.

Fuel composition was measured by diluting each fuel in pentane to 50 and 100 µl/ml, and then injecting 2 µL into an adsorbent-packed thermal desorption tube (TDT) for analysis. These dilution levels were established in pilot tests that responses fell within calibration curves. Two samples at each dilution level were collected and analyzed. The TDTs Scientific Instrument Services, Inc., Ringoes, NJ, USA) were packed with 160 mg Tenax GR and 70 mg Carbosieve SIII, and loaded using a stainless-steel loader (Scientific Instrument Services, Inc., Ringoes, NJ, USA) in a 35 ml/min flow of ultra-high purity grade helium. Cleaning, storage, shipping and analysis protocols for these TDTs have been described elsewhere.[14]

Headspace vapors were sampled and measured at 5, 20 and 40 ºC using TDTs, thus allowing full comparability between liquid and vapor measurements. 10 ml of each fuel was placed into a 60 ml amber glass vial that was then sealed with a screw cap and Teflon-lined septum. Vials of each fuel were maintained at the desired temperature (within 0.1 ºC) in a water bath for at least 30 min. The sampling sequence went from low to high temperature. A gas-tight syringe was used to sample and transfer 50 to 1000 µl of vapor, depending on fuel and temperature and established in pilot tests, into a TDT for analysis using the loader described earlier. Three to seven samples were taken for each fuel and temperature.

2.4.2 VOC analysis

The TDTs were analyzed after spiking with 2 µL of an internal standard (1 ng/µL each of fluorobenzene and p-bromofluorobenzene) using an automated short-path thermal desorption system (Model 2000, Scientific Instrument Services, Ringoes, NJ, USA), on-column cryofocusing, gas chromatography and mass spectrometry (GC/MS, Model 6890/5973, Chemstation, G1701BA, Hewlett Packard, Palo Alto, CA, USA). The GC was equipped with a 60 m × 0.25 mm I.D. capillary column with 1.4 μm film thickness (DB-VRX, J&W Scientific, Agilent Technologies, Santa Clarita, CA, USA). The MS scanned for ions 29 - 270 amu with 3 scans/s and 0.1 amu step size. The method and its performance are detailed elsewhere.[14-16] The analysis included 95 target compounds; each calibrated using authentic standards, selected on the basis of their health significance and frequency of occurrence (Appendix Table A2.1). These target VOCs are a subset of VOCs contained in these fuels. Ethanol and methyl ethers were not included in the target VOCs, therefore, ethanol content in gasoline and E85 were not quantified as well as methyl ethers content in B20.

Quality assurance activities included blanks, spiked and duplicate samples for each test. All laboratory and field blanks were clean. A spiked standard (VOC standard mixture) was analyzed daily to check calibration, and all compounds were within 20% of the expected values. Replicate precisions were below 20%, thus replicates (n=3 to 7) were averaged. The total target VOC (TTVOC) concentration was calculated as the sum of target VOCs.

2.4.3 Prediction of headspace vapor composition

Headspace compositions of ideal mixtures can be predicted using the fuel's composition and Raoult’s law, which gives the partial pressure (p_i^{part}) as:

$$p_i^{part} = x_i \, p_{i,t}^{pure} \tag{1}$$

where x_i = mole fraction of compound *i* in liquid fuel (dimensionless), and $p_{i,t}^{pure}$ = vapor pressure of compound *i* in pure liquid (mm Hg) at temperature *t* (^{o}C). $p_{i,t}^{pure}$ is calculated at temperature t using the Antoine equation:[17]

$$log(p_{i,t}^{pure}) = a - b/(t + c) \tag{2}$$

where a, b and c = Antoine constants. This approach was used for ULSD and B20.

Ethanol exhibits non-ideal behavior in solution with non-polar hydrocarbons.[18-20] Activity coefficients γ_i are used to account for interactions:

$$p_i^{part} = \gamma_i \, x_i \, p_{i,t}^{pure} \tag{3}$$

Activity coefficients for several ethanol mixtures have been estimated. Using data from Bennett et al. (1993) who measured mole fractions and vapor pressures for a five-component mixture containing 9.65% (wt) ethanol , Harley et al. (2000) derived activity coefficients as γ_i = 2.8 for ethanol, 1.7 for 2,2,4-trimethylpentane, methylcyclohexane and toluene, and 1.6 for 1-heptene. Harley et al. (2000) also estimated activity coefficients using the Universal Functional-group Activity Coefficients (UNIFAC) model for a 24 component mixture that included 12 alkanes, 4 cycloalkanes, 1 alkene, 5 aromatics, ethanol and MTBE. For the 9.65% ethanol/gasoline blend, γ_i = 4.0 for ethanol, 1.3 for BTEX (benzene, toluene, ethylbenzene, p-,m-,o-xylenes), 1.2 for C_5+ alkanes, C_6+ cycloalkanes and C_9+ aromatics, and 1.1 for n-butane, cyclopentane, alkenes and MTBE. In the present study, the vapor composition of gasoline (with 10% ethanol) is predicted using these coefficients, the measured fuel composition, and eq. (3). Otherwise, eq. 1 was used since E85's ethanol fraction falls outside the limits where these activity coefficients are valid (6.5-18.5% mole fraction as stated by Harley et al. (2000).

2.4.4 Collinearity analysis

Pearson correlation coefficients and singular value variance-decomposition (SVD) analyses were used to investigate collinearity among the fuel and vapor profiles. The SVD procedure,[21, 22] obtains condition indexes (CIs) and variance-decomposition proportions from the decomposition of the source profiles as

$$\mathbf{X} = \mathbf{U}\,\mathbf{D}\,\mathbf{V}^{\mathrm{T}} \tag{4}$$

where $\mathbf{X}$ = n × p matrix containing the n VOC species and p source profiles; $\mathbf{U}^{\mathrm{T}}\mathbf{U} = \mathbf{V}^{\mathrm{T}}\mathbf{V} = \mathbf{I}_p$, where $\mathbf{I}_p$ = identity matrix; and $\mathbf{D}$ = diagonal matrix with nonnegative diagonal elements $\mu_1 \dots \mu_p$ called the singular values (SV) of $\mathbf{X}$. The CIs of $\mathbf{X}$ are the largest SV divided by the SV for each profile. The largest CI is the condition number of the matrix, which indicates the overall degree of dependencies or collinearity; if larger than 10 to 30, the matrix is ill-conditioned and potentially difficult to invert.[23] Variance-decomposition proportions $\pi_{j,k}$ combine $\mathbf{D}$ and $\mathbf{V}$:

$$\pi_{j,k} = \left(\frac{v_{kj}^2}{\mu_j^2}\right) / \sum_{j=1}^{p} \frac{v_{kj}^2}{\mu_j^2} \tag{5}$$

where $\pi_{j,k}$ = proportion of variance of the k^th profile associated with the j^th component of $\mathbf{X}$, and k = 1 ... p and j=1 … p. In a variance proportion table, adverse collinearity is detected by a high CI (greater than about 10 to 30) that is also associated with high variance-decomposition proportions for at least two regression coefficients, as shown by $\pi_{j,k}$ greater than about 0.5. This situation represents a "competing dependency". In contrast to correlation coefficients that show only pair-wise dependencies, the SVD procedure diagnoses dependencies involving multiple profiles.

2.5 Results and Discussion

2.5.1 Composition of neat gasoline

In neat gasoline, 29 target VOCs were detected, of which toluene, n-heptane, 1,2,4-trimethylbenzene, cyclohexane and p-,m-xylene were the five most prevalent compounds, accounting for 51% of the TTVOC concentration (Table 2.1). The 29 measured compounds accounted for 15% (wt) of gasoline since only certain VOC species in a limited range (C_6 to C_{16}) were quantified.

Appendix Table A2.2 summarizes gasoline compositions in recent literature that reported similar target species as those in the present study. Fuel compositions are reported in various units, e.g., mass fraction (e.g., ppm or percent), mole fraction, carbon fraction (ppbC), and fraction of quantified compounds. Harley and Kean (2004) provides one of the most complete analyses, including 315 species from C_2-C_{15}. The top five VOCs in 1990 Atlanta, GA, U.S. gasoline were toluene, 2-methylbutane, p-,m-xylene, 1,2,4-trimethylbenzene and n-butane, which accounted for 30% of the total nonmethane hydrocarbons (NMHC; ppbC basis).[24] In 2001 California gasoline, 2-methylbutane, toluene, p-,m-xylene, MTBE and 2,2,4-trimethylpentane were the top five compounds, accounting for 31% (wt).[9] In circa 1996 Vancouver gasoline, toluene, 2-methylbutane, p-,m-xylene, n-pentane and 2-methyl pentane were the top five compounds, accounting for 34% of NMHC.[25] In Washington gasoline from the same period, toluene, 2-methylbutane, p-,m-xylene, n-pentane and 2,2,4-trimethylpentane were the top five compounds, accounting for 33% of NMHC.[25] In a 2003 study, the top five compounds in South Korea gasoline were 2-methylbutane, toluene, 2-methylpentane, n-pentane and p-,m-xylene, accounting for 42% (wt).[26] In comparison, we found toluene, ethylbenzene, and p-m-xylene at levels 3 to 6 times lower; cyclohexane, methyl cyclohexane and n-heptane levels were similar to the Californian reformulated gasoline (which was relatively higher); and the naphthalene concentration was higher. The comparison fuels were relatively old (1989-2003), and the compositional differences likely reflect the lower levels of aromatics of aromatic compounds in newer reformulated gasoline. Still, this comparison shows composition can vary widely.

2.5.2 Composition of E85

In E85, 27 target VOCs were detected, and p-, m-xylene, toluene, n-heptane, 1,2,4-trimethylbenzene and o-xylene were the top compounds, accounting for 59% of the TTVOCs (Table 2.1). The TTVOC comprised 4.5% of the weight of E85, or 29.6% of the VOCs excluding. Given that E85 is an 85% bioethanol/15% gasoline blend, the VOC composition was expected to resemble that of gasoline, but with VOC concentrations (other than ethanol) approximately 85% lower. While both fuels contained the same compounds, VOC abundances differed considerably (Table 2.1). In E85, the TTVOC concentration was 31% of gasoline's (rather than the expected 15%); ethylbenzene, p-,m-xylene, o-xylene, n-octane and n-nonane had higher fractions (>50%); n-tetradecane, cyclohexane, and methyl cyclohexane had lower fractions (<10%); while benzene, naphthalene, n-decane, n-undecane, n-dodecane and n-tridecane had the "expected" fraction (15 ±5%).

Many factors affect fuel composition. First, refineries adjust the base gasoline properties to meet fuel vapor pressure requirements. Ethanol contents below about 40% show an increased vapor pressure (about 1 psi), which is compensated by lowering the volatility of the base gasoline; the opposite is seen for high ethanol blends like E85, where higher volatility gasoline is needed to increase vapor pressure.[6] This helps to explain the abundance of aromatics (other than benzene) in the Michigan E85, adjusted to maintain the fuel's vapor pressure. Other factors affecting composition include: seasonal changes to attain desired (and mandated) volatility limits; variation in the ethanol content of commercial E85; differences in blending, feedstocks and production method; and the use of additives, oxygenates, and small amounts of dye.[6, 27, 28] Composition can vary by both batch and brand, and since only a single winter sample of each fuel was tested, our results may not be representative. Thus, the fuel compositions in Table 2.1 do not portray the variation expected in commercial fuels.

2.5.3 Composition of neat ULSD and B20

28 VOCs were detected in neat ULSD and B20 (Table 2.1). C_9-C_{16} straight-chain alkanes were dominant, accounting for 90% of TTVOC. Among aromatic VOCs, naphthalene and 1,2,3-trimethyl benzene were the top species, accounting for 6% and 4% of the TTVOC for ULSD and B20, respectively. Target VOCs accounted for only a small fraction of components in the fuel, i.e., 10% (wt) of ULSD and 6% (wt) of B20.

As a 20% soy-based methyl esters/80% petroleum diesel blend, B20 would have 80% of the petroleum-derived VOCs of conventional ULSD if the base fuel was unaltered. The concentration of TTVOC in B20 was only 36% of that in ULSD, much lower than the 80% expected, and n-butylbenzene, naphthalene and cyclohexane had levels below 40%. In contrast, p-isopropyltoluene, 1,2,4-trimethylbenzene, n-heptane and n-pentadecane had the expected fraction (80±5%), while ethylbenzene, p-,m-xylene, o-xylene, isopropylbenzene, n-propylbenzene, sec-butylbenzene, and n-octane had higher than expected concentrations (>110%). Many VOCs in B20 had fractions around 60%

based on the VOCs in ULSD, e.g., C_9-C_{14} straight-chain alkanes and benzene. This evidence suggests that the composition of the ULSD used in B20 differed from conventional ULSD.

VOC compositions of diesel and biodiesel blends have been rarely reported. The top five VOCs in a 2006 study of diesel fuel in Taiwan were C_{13}-C_{16} and C_{18} straight-chain alkanes, accounting for 46.2% of the target compounds [29]. In comparison to the Taiwan diesel (Appendix Table A2.3), levels of n-decane and n-undecane were 2.5 and 1.4 times higher, n-dodecane and n-tridecane were similar, and n-tetradecane, n-pentadecane and n-hexadecane were 39 to 50% lower. VOC compositions in diesel fuels vary for the same reasons stated for gasoline and E85. Petroleum diesel also contains paraffins, cyclo-paraffins, and some aromatics.[30, 31] Pure soy biodiesel contains mainly linoleic acid methyl ester, oleic acid methyl ester, palmitic acid methyl ester and stearic acid methyl ester, which collectively accounted for 89% (wt) of the fuel.[29]

2.5.4 Vapor composition of gasoline

Concentrations of headspace vapors measured for the four fuels at 5, 20 and 40 ºC listed in Table 2.2. For gasoline, 17 target VOCs were detected at 5 ºC, and 20 VOCs at 40 ºC. Five VOCs accounted for nearly all (95-96%) of TTVOCs at each temperature: toluene (25-28%), benzene (19-20%), n-heptane (18-20%), cyclohexane (17-18%), and methyl cyclohexane (11-12%). The TTVOC concentration ranged from 16.1 at 5 ^{o}C to 63.9 g/m^3 at 40 ^{o}C. The headspace vapor was dominated by the higher volatility compounds, and the vapor fraction of several of the most prevalent VOCs in the liquid fuel (e.g., p-, m-xylene and 1,2,4-trimethylbenzene) was low.

Appendix Table A2.4 lists VOC compositions (as the fraction of TTVOC) of gasoline vapor measured in four studies reporting compounds similar to those measured here. Benzene, toluene, p-,m-xylene, cyclohexane and n-heptane were the top five VOCs (among our target VOCs) measured in Chicago,[32] Atlanta,[24] and South Korea,[26] while toluene, cyclohexane, methyl cyclohexane, n-heptane and benzene were the top VOCs in California reformulated gasoline vapor.[18] These studies show some similar patterns, although there are many differences: the Michigan gasoline had cyclohexane, methyl cyclohexane and n-heptane at similar fractions to the California reformulated gasoline vapor, but levels were 6-7 times higher than those in Chicago and Atlanta; benzene had similar fractions across the studies with the exception of California, which had levels less than half those elsewhere. As noted for the liquid fuels, results can vary by brand, season, location, formulation, year, etc. Vapor compositions are also affected by test conditions, e.g., temperature and measured compounds.

Gasoline vapor contains very volatile organic compounds (VVOCs) that were not measured in the present study, e.g., n-butane, isobutane, n-pentane and 2-methylbutane, which collectively accounted for 60-77% (wt) as measured in Chicago,[32] Atlanta (at 24 and 32 °C),[24] and South Korea (0 °C).[26] In California reformulated gasoline (with ethanol), 2-methylbutane, 2-methylpentane, ethanol, n-pentane and 2,2-dimethylbutane together accounted for 62% (wt) of the headspace vapor (at 38 °C).[18] These studies show significant variation in vapor concentrations.

2.5.5 Vapor composition of E85

The vapor composition of E85 was similar to that of gasoline, although concentrations of the more prevalent VOCs (e.g., cyclohexane, methylcyclohexane toluene) were several times lower (Table 2.2). For E85, the top five VOCs in headspace vapor were n-heptane (34-36%), cyclohexane (13-18%), toluene (13-14%), methylcyclohexane (8-10%) and benzene (8-9%), which collectively accounted for 77-85% of TTVOC in the headspace, depending on temperature. The TTVOC concentration in E85 vapor was 5.7 g/m^3 at 5 ^{o}C or 35% of that of gasoline vapor, and 33.0 g/m^3 at 40°C or 52% of gasoline vapor, both well above the 15% expected if the gasoline composition was unchanged. Several VOCs, including n-octane, ethyl benzene, p-, m-,o-xylene and n-nonane, accounted for most of this increase (their concentrations exceeded levels gasoline by a factor of 1.3 to 1.9 at 5 °C, and by 2.4 to 2.9 at 40 °C). Headspace concentrations of cyclohexane, methylcyclohexane and toluene were also higher than 15% expected (18-33% at 5 °C, 28-40% at 40 °C). Only the benzene concentration was close to 15% (15% at 5 °C, 20% at 40 °C). As seen for gasoline, several of the VOCs most prevalent in liquid E85 had low vapor concentrations, e.g., 1,2,4-trimethylbenzene and 4-ethyl toluene.

2.5.6 Vapor composition of ULSD and B20

B20 and ULSD had similar VOC compositions in headspace vapors (Table 2.2). The top five target VOCs were cycloalkanes (methylcyclohexane, cyclohexane) and alkanes (n-octane, n-nonane, n-heptane), which together accounted for 63-76% of TTVOC (depending on temperature). The most abundant aromatics were toluene (7% of TTVOC), p-,m-xylene (3-6%), and benzene (2-4%). ULSD had a slightly higher TTVOC headspace concentration (0.99 - 6.16 g/m^3 at temperatures of 5 and 40 ^{o}C, respectively) than ULSD (0.81-5.80 g/m^3). Concentrations of most VOCs in the two fuels were similar (within 20%) at each temperature, although B20 showed higher concentrations of n-octane, ethyl benzene, n-nonane, 4-ethyl toluene at 5 ^{o}C and n-tridecane and n-tetradecane at 40 ^{o}C, but lower concentrations of cyclohexane. As seen earlier, vapor and liquid compositions differed considerably, e.g., liquids were dominated by C_9-C_{16} straight-chain alkanes, and vapors by cyclo-alkanes and C_7-C_9 straight-chain alkanes.

The VOC composition of diesel and biodiesel fuels and vapors has been rarely reported. A 2006 study from Taiwan reporting on the top 20 VOCs in headspace vapors of conventional diesel and pure soy biodiesel at 25 °C identified the top five VOCs in conventional diesel vapor as n-octane, ethyl benzene, p-xylene, n-decane and toluene (together accounting for 39% of TTVOCs).[29] We had 13 VOCs in common with this study (Appendix Table A2.5). Concentrations of VOCs in the Michigan diesel vapor (measured at a slightly lower temperature of 20 °C) had much higher levels of 11 VOCs and little correlation with levels in the Taiwan diesel. As noted earlier, the Taiwan diesel fuel did not list methyl cyclohexane and other aromatics among the top 20 VOCs.

The top five VOCs in the Taiwan pure soy biodiesel vapor were linoleic acid methyl ester, oleic acid methyl ester, palmitic acid methyl ester, 1-penten-3-ol and capric acid methyl ester, which together accounted for 72% of TTVOCs.[29] The biodiesel vapor also contained small amounts of aromatics (6.4%) and alkanes (4.8%), which suggest that the “pure” soy biodiesel was actually a blend containing conventional petroleum diesel. More generally, much of the biodiesel vapor results from oxygenated compounds (23% of target compounds in the Taiwan diesel vapors),[29] excess alcohol produced during the transesterification process,[7] and oxidized soy biodiesel constituents; these compounds have higher volatility than methyl ethers.

2.5.7 Temperature dependence of vapor compositions

Vapor concentrations of target VOCs for E85 showed greater dependence on temperature than for gasoline. As examples: E85 had 6 VOCs at higher concentrations than in gasoline at 5 ^{o}C, and 15 VOCs at 40 ^{o}C; VOC concentrations in E85 vapor increased 4.4-15.4 times from 5 to 40 °C, compared to 3.8-5.8 times for gasoline (Figure 2.1); and while the TTVOC concentration in neat E85 was only 30% of gasoline's, E85's TTVOC vapor concentration was 50% of that of gasoline's at 40 °C. Partial pressure changes were especially large for the lower volatility VOCs in E85 due to low concentrations detected at 5 ^{o}C, e.g., 1,2,3-trimethyl benzene.

As mentioned, ULSD and B20 had similar vapor profiles (most VOCs showed low concentrations at 5 ^{o}C), and these fuels showed both similar and greater temperature dependencies than gasoline. Concentration increases (expressed as a ratio) from 5 to 40 °C were within 25% for most VOCs in ULSD and B20 vapors, although five VOCs (n-nonane, isopropylbenzene, n-propylbenzene, 4-ethylbenzene and sec-butylbenzene) showed greater temperature dependence for ULSD (13.4-17.1 times increase from 5 to 40 ^{o}C) than for B20 (8.4-11.1 times increase, Figure 2.1).

The contrasting results for gasoline and E85 fuels suggest interactions associated with ethanol that may depend on temperature. Harley et al. (2000) notes that activity coefficients increase with ethanol fraction. Bennett et al. (1993) showed only small differences for temperatures from 25 to 60 °C. Our results were reproducible, and no experimental errors or biases are known.

From the perspective of air quality and exposure, changes in VOC composition due to temperature represent variation and uncertainty in fuel-related evaporative emissions. For receptor modeling, such changes can adversely affect results, since profiles are usually assumed to be constant. As a practical matter, it may be sufficient to utilize seasonal analyses, which can account for some of the temperature effect. However, temperature-specific information pertaining to the vapor composition of motor vehicle fuels is scarce. Our results suggest the need to determine vapor profiles at several temperatures.

2.5.8 Estimated headspace composition

Predicted and measured target VOC concentrations in headspace vapors correlated closely for gasoline and E85 (r=0.88-0.94, depending on fuel and temperature), but the difference (or bias) between predicted and measured concentrations was sometimes large (Figure 2.2). For gasoline vapor, most VOCs were overpredicted by 24-200% compared to measured concentrations, although several major VOCs (benzene, n-heptane, methylcyclohexane and toluene) were underpredicted (8-66%). This pattern suggests errors in the activity coefficients used, which were approximate and derived for a different mixture. Predictions for E85 did not use activity coefficients, and all target VOC were underpredicted (by 55-100%), which suggests that appropriate activity factors are from 1.5 to 2.0, a range containing the estimate from Harley et al. (2000).

ULSD and B20 had lower correlation between predicted and observed vapor concentrations than gasoline (r=0.73-0.76 for ULSD; r=0.79-0.85 for B20, depending on temperature), and predicted versus observed concentrations showed more scatter (Figure 2.2). Most VOCs were underpredicted (by 10-80%); a few VOCs (e.g., n-nonane, 1,2,3-trimethyl benzene, naphthalene) were overpredicted (20-200%) compared to the measured concentrations. ULSD and B20 contain many other components (e.g., paraffins, cyclo-paraffins), and vapor concentrations may reflect interactions among mixture components. No activity coefficients were used in these predictions.

Differences between the predicted and measured concentrations can arise from many factors including: experimental errors; approximations in the Antoine equation; and missing or uncertain activity coefficients.[19, 33] Several studies have shown good agreement (r >0.9) between predicted and measured headspace compositions of gasoline.[20, 24, 26] No such studies have been identified for E85, ULSD and B20.

2.5.9 Collinearity analysis

Headspace compositions of each fuel at the three temperatures were highly correlated (r=0.92 to 1.00; Appendix Table A2.6), therefore compositions at the three temperatures were averaged to obtain a single headspace composition profile. Correlation coefficients among the other profiles ranged widely; ULSD and B20 fuels had negative correlation (not significant) with gasoline and E85 profiles.

The initial SVD analyses used eight profiles (four fuels and their headspace compositions), and CIs and variance decomposition proportions are shown in Table 2.3. CIs range up to 24.8, and the latter two CIs show possible collinearity problems, e.g., the 7th CI (16.2) shows competing dependencies between ULSD and B20 neat fuel profiles, and the 8th CI (24.8) shows dependencies between ULSD and B20 vapor profiles. Although the 6th CI (7.8) is less than 10, the variance-decomposition proportions suggest competing dependencies (described in Section 2.4.4) between gasoline fuel, E85 fuel and gasoline vapor. This set of eight profiles is too collinear to use simultaneously in a CMB receptor model.

The high correlation between ULSD and B20 fuel profiles (r=0.98) and vapors (r=0.92-0.99) suggest that it is appropriate to combine their profiles. Therefore, profiles for ULSD and B20 liquid fuels (expressed as percentage of TTVOC) were averaged. The ULSD and B20 headspace vapor profiles were similarly averaged. The SVD analysis using the resulting six profiles (Table 2.4) does not show degrading collinearity, e.g., CIs range to 7.1. This suggests that ULSD and B20 neat fuel, ULSD and B20 headspace, and E85 headspace can be distinguished. However, the 6th CI (7.1) still shows competing dependencies involving gasoline fuel, E85 fuel and gasoline headspace. Since little E85 is used currently relative to gasoline, the E85 profile might be omitted, at least in areas where this is true. Another approach to address collinearity issues might use additional VOCs, although this may require more laboratory work and statistical analyses to determine if this resolves the collinearity problems.

This analysis shows that receptor modeling should be able to distinguish diesel and gasoline fuels, and their vapors without the adverse effects from collinearity. Importantly, VOCs related to evaporative emissions from diesel fuel normally would be present at much lower concentrations, e.g., the TTVOC concentrations in neat diesel was 30% lower than in gasoline, and the TTVOC concentration in diesel headspace was about ten times lower. Collinearity is only one of several important sources of errors in receptor models, and other assumptions must be valid. In any case, however, profiles that minimize collinearity will provide more accurate and stable results.

2.6 Conclusion

Motor vehicle fuels contain hundreds of VOCs and differ widely in composition. In this study, four commercial fuels were characterized. Conventional gasoline showed liquid and vapor compositions generally comparable to earlier reports. For E85, ULSD and B20 fuels, however, the literature is very sparse. The dominant VOCs in gasoline and E85 included aromatic compounds (e.g., toluene, 1,2,4-trimethylbenzene, p-m-xylene) and alkanes (n-heptane, cyclohexane and methylcyclohexane). Headspace vapors were "enriched" in the fuel's more volatile components (e.g., benzene, cyclohexane, methylcyclohexane and n-heptane). In ULSD and B20, the dominant VOCs include alkanes and several aromatics (e.g., 1,2,3-trimethyl benzene and naphthalene). Vapors of these fuels contained toluene, p-,m-xylene and benzene at concentrations much lower than gasoline's. Depending on temperature, E85 vapor had higher concentrations of several or many VOCs than gasoline, and vapor pressures of the 17 measured VOCs in E85 increased considerably faster than gasoline. B20 and ULSD had similar VOC compositions in headspace vapors. Measured and predicted vapor concentrations correlated closely, although predictions for fuels other than gasoline showed large biases. While predictions are potentially simple and cost-efficient, measurements remain necessary given these limitations. The collinearity analysis showed that receptor models should be able to distinguish gasoline and diesel fuels using appropriately selected profiles; three combinations (ULSD and B20 neat fuel, ULSD and B20 vapor, and gasoline fuel, E85 fuel and gasoline vapor) are too collinear to separate.

The liquid and vapor compositions reported in this study can be used to help describe leaks and emissions from fuel- and vehicle-related sources (e.g., storage tanks, vehicle refueling, hot soaks, running and evaporative losses), define source profiles for receptor models aimed at apportioning emission sources, and to estimate exposures and risks related to fuels.

Because motor fuels continue to evolve, there will be a continuing need to update VOC speciation of liquid fuel and their vapors. In the U.S., for example, the allowable (but not required) content of ethanol in gasoline has just (2011) been increased to 15% (vol) from 10%.[34] The use of E15, along with the variation of VOCs demonstrated in commercial fuels, suggests a need to expand testing and reporting for speciated VOCs in vehicle fuels, specifically increasing the parameters reported beyond the benzene, (total) aromatics, (total) olefins, and other parameters currently required in the reformulated fuels program.[4]

Table 2.1 Composition of neat gasoline, E85, diesel and B20, and ratios comparing concentrations of gasoline and diesel fuels.

Fuel	Gasoline	E85	E85/Gasoline	Diesel	B20	B20/Diesel
Unit	(mg/L)	(mg/L)	(%)	(mg/L)	(mg/L)	(%)
Aromatics						
Benzene	6,144	862	14.0	67	37	55.2
Toluene	15,429	4,107	26.6	238	214	89.9
Ethylbenzene	3,075	1,994	64.8	124	186	149.6
p-Xylene,m-xylene	9,124	6,976	76.5	420	496	118.0
o-Xylene	4,614	2,789	60.4	185	212	114.8
Isopropylbenzene	351	156	44.5	44	70	160.3
n-Propylbenzene	2,107	665	31.6	115	167	145.7
p-Isopropyltoluene	88	29	33.1	112	83	74.7
4-Ethyl toluene	8,384	2,647	31.6	400	464	116.0
2-Ethyl toluene	3,462	928	26.8	194	264	136.0
1,3,5-Trimethylbenzene	4,060	1,030	25.4	202	150	74.2
1,2,4-Trimethylbenzene	10,613	3,267	30.8	720	575	79.9
1,2,3-Trimethyl benzene	3,945	975	24.7	2,118	961	45.4
sec-Butylbenzene	159	65	40.8	90	117	129.8
n-Butylbenzene	822	198	24.1	375	111	29.5
Styrene	14	4	32.0	<MDL	<MDL	NA
Naphthalene	2,240	378	16.9	3,000	1,220	40.7
Alkanes						
n-Heptane	12,776	3,331	26.1	174	138	79.2
n-Octane	2,872	1,551	54.0	481	612	127.3
n-Nonane	1,788	1,053	58.9	7,017	4,118	58.7
n-Decane	1,390	262	18.8	7,690	4,311	56.1
n-Undecane	1,118	121	10.8	7,729	4,562	59.0
n-Dodecane	822	85	10.4	8,369	5,002	59.8
n-Tridecane	644	80	12.4	13,437	7,625	56.7
n-Tetradecane	213	18	8.7	10,078	7,131	70.8
n-Pentadecane	62	<MDL	NA	9,028	7,581	84.0
n-Hexadecane	18	<MDL	NA	9,300	5,550	59.7
Cyclohexane	9,833	880	8.9	191	69	36.1
Methyl cyclohexane	8,282	778	9.4	426	270	63.4
Total target VOCs	113,687	34,925	30.7	80,722	51,645	64.0

<MDL: below method of detection limit. NA: Not available.

Table 2.2 Headspace vapor composition (mg/m^3) of gasoline, E85, ULSD and B20 at three temperatures.

Fuel	Gasoline			E85			ULSD			B20		
Temperature	5 ºC	20 ºC	40 ºC	5 ºC	20 ºC	40 ºC	5 ºC	20 ºC	40 ºC	5 ºC	20 ºC	40 ºC
Cyclohexane	3,122.8	6,005.6	11,845.7	1,021.0	1,613.5	4,543.3	266.8	477.0	904.9	146.5	213.0	807.6
Benzene	3,171.8	6,936.0	13,020.6	497.7	1,063.1	2,664.4	37.8	73.6	145.9	24.3	37.7	129.1
n-Heptane	3,021.1	6,837.1	12,846.3	2,049.0	4,336.0	11,269.2	101.1	220.7	525.6	81.0	139.7	473.4
Methyl cyclohexane	1,859.0	3,940.8	6,901.0	541.6	1,052.3	2,765.2	255.2	533.7	1,190.4	190.7	306.5	1,126.1
Toluene	4,284.1	9,910.0	15,892.2	756.1	1,805.2	4,372.6	67.6	158.0	401.7	58.2	108.3	378.4
n-Octane	105.9	275.1	490.6	198.0	537.1	1,424.8	69.6	179.7	588.3	89.9	179.7	600.4
Ethyl benzene	57.5	148.4	282.9	91.6	283.7	745.4	13.6	36.6	133.4	17.3	37.9	128.7
p,m-Xylene	181.6	466.0	924.5	312.2	1,002.4	2,645.2	36.6	102.3	350.0	37.0	84.0	321.1
o-Xylene	68.7	166.9	356.2	92.1	307.1	835.9	12.6	35.8	129.2	13.5	31.3	119.4
n-Nonane	9.3	16.4	66.4	16.4	33.2	189.2	54.7	167.5	677.8	70.6	176.2	667.3
Isopropylbenzene	2.1	2.9	11.8	2.3	3.9	25.8	2.0	5.8	27.1	3.2	7.9	27.0
n-Propylbenzene	15.1	32.1	86.0	9.2	36.5	115.0	3.4	10.2	47.2	4.7	12.0	45.2
4-Ethyl toluene	63.8	130.9	368.1	33.0	141.3	444.9	9.2	28.4	126.6	10.6	27.8	117.4
1,3,5-Trimethylbenzene	23.2	45.5	134.5	12.1	51.5	166.3	3.3	10.5	42.4	2.7	7.5	37.9
2-Ethyl toluene	20.0	40.5	116.5	9.3	41.4	132.7	3.8	11.7	60.8	5.8	15.1	58.5
1,2,4-Trimethylbenzene	66.4	130.0	392.2	29.9	135.4	445.6	10.0	30.6	132.6	8.4	22.9	117.5
n-Decane	<MDL	3.9	27.3	<MDL	2.5	24.8	25.3	76.8	362.8	24.1	65.7	346.1
sec-Butylbenzene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	1.2	3.5	20.4	1.9	5.0	20.3
1,2,3-trimethyl benzene	16.2	29.1	94.0	6.3	29.1	96.8	4.1	11.7	51.3	3.1	8.5	46.1
p-Isopropyltoluene	<MDL	<MDL	1.3	<MDL	<MDL	1.8	0.7	1.6	9.0	0.7	1.8	8.6
n-Butylbenzene	<MDL	1.6	11.7	<MDL	1.1	11.4	1.1	2.9	15.8	1.1	2.9	14.7
n-Undecane	<MDL	<MDL	8.3	<MDL	<MDL	8.3	10.8	28.8	161.6	9.8	23.9	151.3
Naphthalene	<MDL	1.7	13.8	<MDL	<MDL	20.8	<MDL	<MDL	0.9	<MDL	<MDL	0.7
n-Dodecane	<MDL	<MDL	1.7	<MDL	<MDL	4.8	3.2	6.2	39.4	3.5	6.1	40.7
n-Tridecane	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.9	1.4	12.3	1.1	1.9	15.4
n-Tetradecane	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.3	0.4	3.2	0.4	0.4	4.0
Total target VOCs	16,088.5	35,120.4	63,893.7	5,677.7	12,476.2	32,954.0	994.9	2,215.2	6,160.7	810.1	1,523.5	5,803.0

<MDL: below method of detection limit.

Table 2.3 Singular value variance-decomposition proportions of 8 compositional profiles.

Variable	Singular Value							
Rank order	1	2	3	4	5	6	7	8
Eigenvalue	4.38	1.69	0.98	0.64	0.21	0.07	0.02	0.01
Condition Index	1.00	1.61	2.11	2.63	4.54	7.80	16.22	24.79
Variance Decomposition Proportions								
Gasoline	0.004	0.000	0.012	0.001	0.090	**<u>0.76</u>**	0.004	0.128
E85	0.004	0.005	0.055	0.123	0.007	**<u>0.58</u>**	0.009	0.217
ULSD	0.001	0.008	0.004	0.000	0.000	0.002	**<u>0.96</u>**	0.023
B20	0.001	0.008	0.005	0.000	0.000	0.000	**<u>0.97</u>**	0.019
HS-Gasoline	0.006	0.003	0.006	0.103	0.189	**<u>0.69</u>**	0.003	0.000
HS-E85	0.010	0.004	0.020	0.058	**<u>0.81</u>**	0.095	0.000	0.005
HS-ULSD	0.000	0.001	0.002	0.001	0.000	0.000	0.003	**<u>0.99</u>**
HS-B20	0.000	0.001	0.003	0.002	0.000	0.003	0.002	**<u>0.99</u>**

HS = headspace using average of profiles measured at 5, 20, and 40 °C. Bold and underlined proportions show possibility of degrading collinearity.

Table 2.4 Singular value variance-decomposition proportions of 6 profiles.

Variable	Singular Value					
Rank order	1	2	3	4	5	6
Eigenvalue	3.56	0.99	0.66	0.50	0.21	0.07
Condition Index	1.00	1.90	2.32	2.66	4.10	7.09
Variance Decomposition Proportions						
Gasoline	0.008	0.002	0.008	0.000	0.101	**<u>0.88</u>**
E85	0.010	0.070	0.114	0.043	0.008	**<u>0.76</u>**
ULSD+B20	0.017	0.269	**<u>0.67</u>**	0.007	0.023	0.012
HS-Gasoline	0.011	0.022	0.002	0.090	0.198	**<u>0.68</u>**
HS-E85	0.017	0.016	0.004	0.060	**<u>0.81</u>**	0.094
HS-ULSD+B20	0.022	0.132	0.075	**<u>0.71</u>**	0.001	0.063

HS = headspace using average of profiles measured at 5, 20, and 40 °C. ULSD+B20 = average of ULSD and B20 profiles. Bold and underlined proportions show possibility of degrading collinearity.

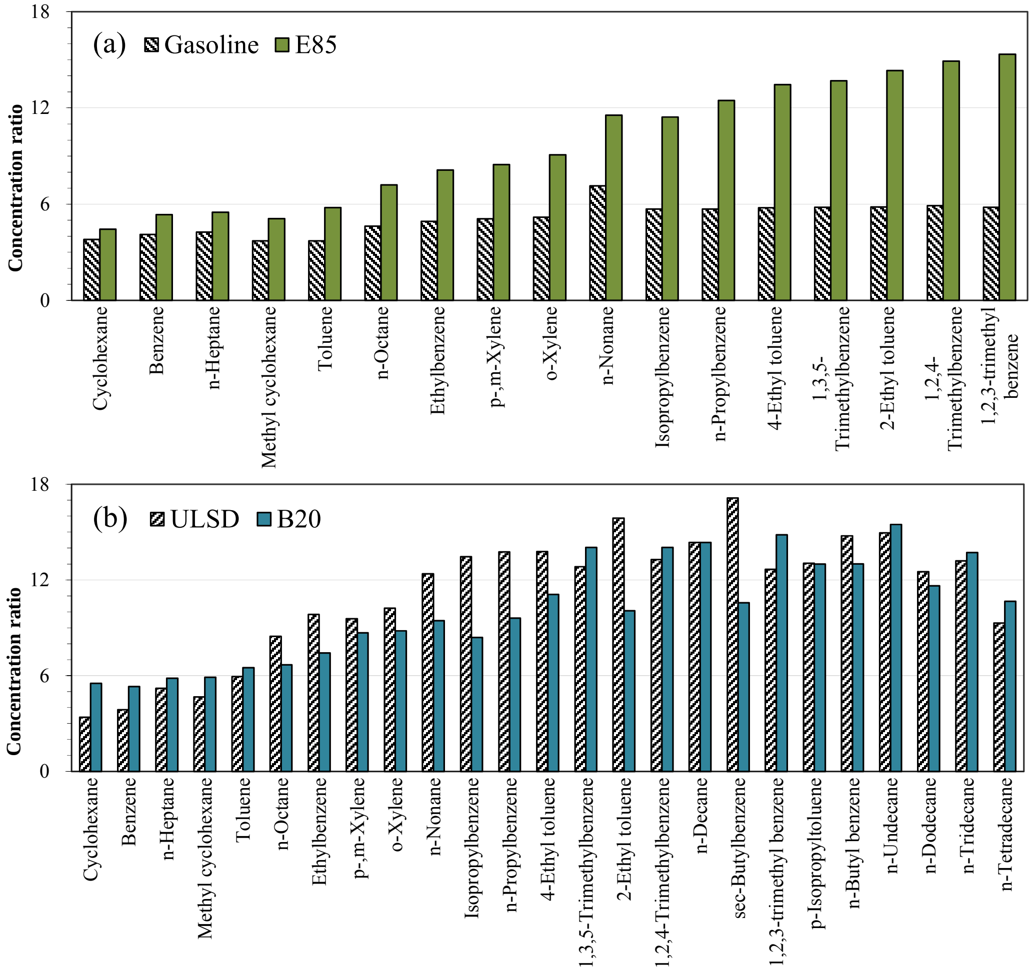

Figure 2.1 Ratio of vapor concentrations at 40 and 5 ^{o}C for the four fuels.

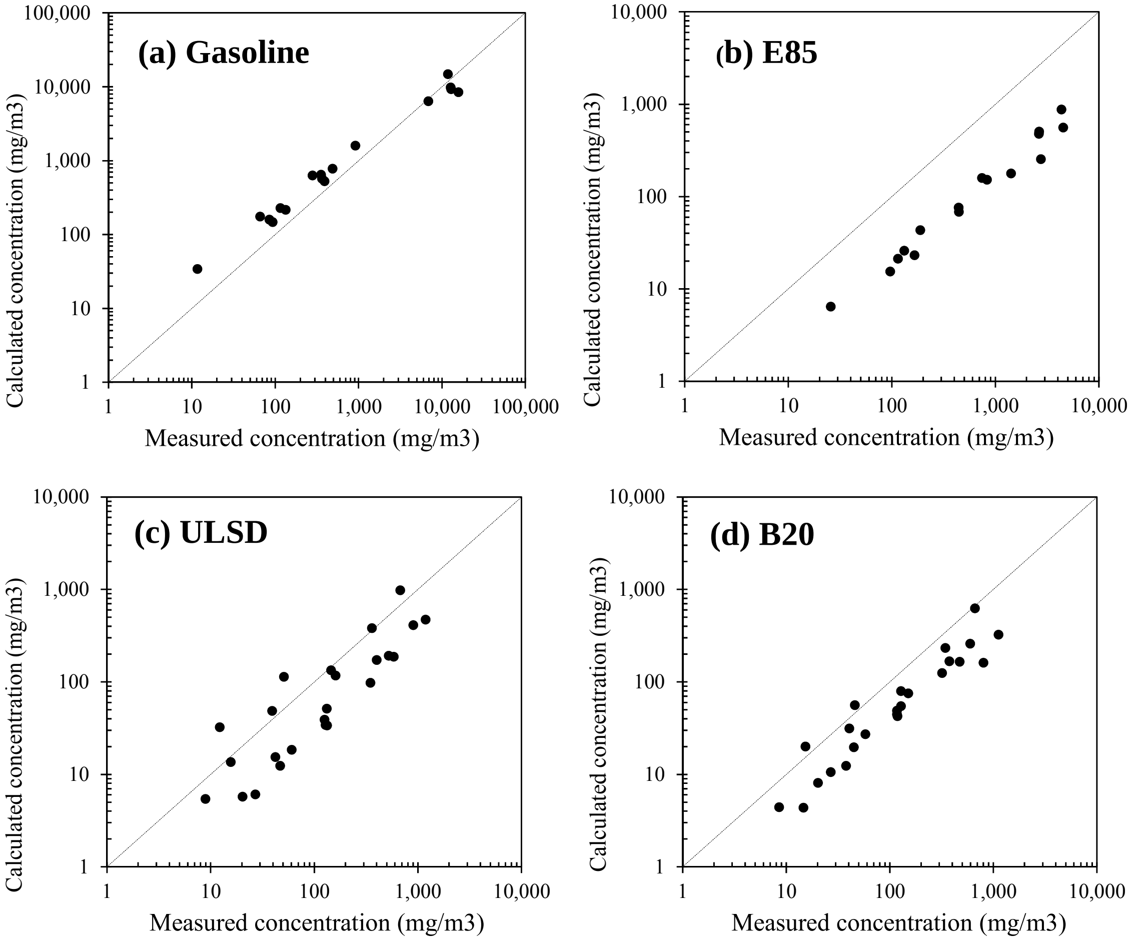

Figure 2.2 Predicted versus measured headspace vapor compositions at 40 °C for the four fuels.

2.7 Appendix

Table A2.1 Target compounds and analytical performance.

No.	Name	CAS No.	RT(min)	Slope	Intercept	LOD(ng)	Target ion	Qualifier ion
1	**Fluorobenzene**	462-06-6	17.41	1.000	0.000	0.244	96	70
2	1,3-Butadiene	106-99-0	5.07	0.127	0.000	1.123	54	39,37
3	Methanol	67-56-1	4.00	0.000	0.000	0.000	31	32
4	Carbon disulfide	75-15-0	9.63	0.000	0.000	0.000	76	44
5	Methylene chloride	75-09-2	9.02	0.239	0.000	0.000	84	49
6	1,2-Dichloroethylene (trans,E)	156-60-5	8.60	0.271	0.000	0.168	61	96
7	Methyl t-butyl ether	1634-04-4	11.53	0.401	0.000	0.5 - 1.0	73	57
8	1,1-Dichloroethane	75-34-3	11.86	0.221	0.000	0.977	63	83
9	Propanenitrile	107-12-0	11.95	0.296	0.000	0.5 - 1.0	54	55
10	Hexane	110-54-3	12.16	0.271	0.000	0.000	57	86
11	Methacrylonitrile	126-98-7	13.42	0.148	0.000	1.0 - 3.0	41	67
12	1,2-Dichloroethylene (Cis, Z)	156-59-2	13.47	0.270	0.000	0.151	61	96
13	2-Butanone	78-93-3	13.11	0.360	0.434	0.000	43	72, 57
14	2,2-Dichloropropane	594-20-7	14.24	0.280	0.000	0.149	77	97, 41
15	Bromochloromethane	74-97-5	13.89	0.175	0.000	0.074	130	130
16	Chloroform	67-66-3	14.04	0.361	0.000	0.080	83	47
17	Methyl acrylate	96-33-3	14.29	0.410	0.000	1.087	55	85,27
18	Ethyl acetate	141-78-6	14.19	0.224	0.000	1.0 - 3.0	43	45
19	Tetrahydrofuran	109-99-9	14.89	0.257	0.000	1.0 - 3.0	42	72
20	1,1,1-Trichloroethane	71-55-6	15.92	0.336	0.000	0.093	97	61, 117
21	Cyclohexane	110-82-7	16.58	0.250	0.000	0.283	56	84
22	1,2-Dichloroethane	107-06-2	15.69	0.254	0.000	0.055	62	49, 98
23	Butyl chloride	109-69-3	15.94	0.425	0.000	0.167	56	41,27
24	1,1-Dichloropropene	563-58-6	16.39	0.331	0.000	0.082	75	110
25	Benzene	71-43-2	16.89	1.008	0.000	0.053	78	50
26	Carbontetrachloride	56-23-5	16.78	0.157	0.000	0.230	117	82
27	Chloroacetonitrile	107-14-2	16.57	0.278	0.000	1.0 - 3.0	75	48
28	1,2-Dichloropropane	78-87-5	18.26	0.239	0.000	0.199	63	76, 41
29	Trichloroethylene	79-01-6	18.36	0.315	0.000	0.111	130	95
30	n-Heptane	142-82-5	18.22	0.289	0.000	0.291	43	71
31	Dibromomethane	74-95-3	18.15	0.218	0.000	0.134	174	93
32	2-Nitropropane	79-46-9	18.41	0.134	0.000	0.5 - 1.0	43	41,27
33	Bromodichloromethane	75-27-4	18.45	0.283	0.000	0.105	83	129
34	2,5-Dimethyl furan	625-86-5	18.75	0.343	0.000	0.155	96	43
35	Methyl cyclohexane	108-87-2	19.46	0.410	0.000	0.085	83	55
36	Methyl methacrylate	80-62-6	18.90	0.313	0.000	0.5 - 1.0	41	69, 100
37	1,1-Dichloro-2-propanone	513-88-2	19.84	0.174	0.087	0.028	43	83
38	1,3-Dichloropropene (Cis, Z)	10061-01-5	19.87	0.388	0.000	0.192	75	110
39	Methyl isobutyl ketone	108-10-1	22.13	0.344	0.118	0.000	43	58, 85, 100
40	Toluene	108-88-3	21.47	1.205	0.000	0.065	91	92
41	1,3-Dichloropropene (trans, E)	10061-02-6	20.78	0.354	0.000	0.146	75	110, 49
42	1,1,2-Trichloroethane	79-00-5	21.08	0.258	0.000	0.159	97	83, 61
43	1,3-Dichloropropane	142-28-9	21.57	0.424	0.000	0.081	76	41
44	**p-Bromofluorobenzene**	460-00-4	27.67	1.000	0.000	0.031	174	95
45	Dibromochloromethane	124-48-1	22.07	0.661	0.000	0.074	129	127
46	Ethyl methacrylate	97-63-2	21.70	0.944	0.000	0.157	69	41, 99, 114
47	2-Hexanone	591-78-6	20.16	0.429	0.951	0.020	43	58, 71,
48	n-Octane	111-65-9	22.13	0.909	0.000	0.123	43	85
49	1,2-Dibromoethane	106-93-4	22.57	0.705	0.000	0.146	107	109, 27
50	Terachloroethene	127-18-4	22.95	0.973	0.000	0.105	166	129
51	Chlorobenzene	108-90-7	24.46	2.093	0.000	0.070	112	77
52	1,1,1,2-Tetrachloroethane	630-20-6	24.27	0.698	0.000	0.116	131	117, 95
53	Ethylbenzene	100-41-4	24.95	3.417	0.000	0.038	91	106
54	p-Xylene,m-Xylene	106-42-3	25.44	2.663	0.000	0.060	91	106
55	Bromoform	75-25-2	25.66	0.612	0.000	0.293	173	252
56	Styrene	100-42-5	26.30	2.410	0.000	0.042	104	78
57	o-Xylene	95-47-6	26.50	2.784	0.000	0.043	91	106
58	n-Nonane	111-84-2	25.83	0.672	0.000	0.236	43	41
59	1,1,2,2-Tetrachloroethane	79-34-5	26.46	1.118	0.000	0.087	83	131, 168
60	1,2,3-Trichloropropane	96-18-4	26.87	0.975	0.000	0.119	75	110
61	Isopropylbenzene (cumene)	98-82-8	27.58	3.712	0.000	0.036	105	120
62	Bromobenzene	108-86-1	28.30	1.274	0.000	0.060	77	156
63	1,4-Dichlor-2-butene (trans, E)	110-57-6	26.97	0.421	0.000	0.004	75	89, 124
64	a-Pinene (1R)-(+)	7785-70-8	28.08	1.410	0.000	0.053	93	77, 105
65	2-Chlorotoluene	95-49-8	29.34	2.431	0.000	0.039	91	126
66	n-Propylbenzene	103-65-1	29.05	4.258	0.000	0.071	91	120
67	4-Chlorotoluene	106-43-4	29.63	2.538	0.000	0.101	91	126
68	4-ethyl toluene	622-96-8	29.68	3.093	0.000	0.093	105	120
69	1,3,5-Trimethylbenzene	108-67-8	30.21	3.127	0.000	0.061	105	120
70	Pentachloroethane	76-01-7	30.30	0.603	0.000	0.186	167	117
71	2-ethyl toluene	611-14-3	30.70	2.939	0.000	0.099	105	120
72	Phenol	108-95-2	29.04	0.991	0.000	3.0 - 10.0	94	66
73	tert-Butylbenzene	98-06-6	31.29	3.259	0.000	0.066	119	91, 134
74	1,2,4-Trimethylbenzene	95-63-6	31.82	3.191	0.000	0.056	105	120
75	n-Decane	124-18-5	30.55	1.019	0.000	0.070	57	43
76	1,3-Dichlorobenzene	106-46-7	32.40	2.027	0.000	0.024	146	111, 75
77	1,4-Dichlorobenzene	541-73-1	32.63	2.047	0.000	0.041	146	111, 75
78	sec-Butylbenzene	135-98-8	32.23	4.161	0.000	0.064	105	134
79	1,2,3-trimethyl benzene	526-73-8	33.24	2.427	0.000	0.068	105	120
80	p-Isopropyltoluene	99-87-6	32.88	3.900	0.000	0.070	119	134
81	Limonene (R)-(+)	5989-27-5	32.93	0.927	0.000	0.076	68	93, 136
82	**1,2-Dichlorobenzene-d4**	2199-69-1	33.54	1.000	0.000	0.000	150	115
83	1,2-Dichlorobenzene	95-50-1	33.60	1.974	0.000	0.098	146	111,75
84	n-Butylbenzene	104-51-8	33.93	3.360	0.000	0.102	91	134
85	o-Cresol	95-48-7	33.21	0.887	0.000	0.000	108	79,90
86	Hexachloroethane	67-72-1	34.74	0.406	0.000	0.145	166	201, 117
87	p-Cresol,m-Cresol	106-44-5	33.81	0.689	0.000	0.000	107	77
88	1,2-Dibromo-3-chloropropane	96-12-8	34.62	0.728	0.000	0.163	157	75
89	Nitrobenzene	98-95-3	35.07	0.524	0.000	0.000	123	77,51
90	n-Undecane	1120-21-4	34.57	1.264	0.000	0.088	57	43
91	1,2,4-Trichlorobenzene	120-82-1	37.32	1.777	0.000	0.052	180	145, 109
92	Naphthalene	91-20-3	37.81	5.609	0.000	0.105	128	102
93	n-Dodecane	112-40-3	36.86	1.328	0.000	0.071	57	43
94	1,2,3-Trichlorobenzene	87-61-6	38.21	1.758	0.000	0.055	180	145
95	Hexachlorobutadiene	87-68-3	37.96	0.963	0.000	0.044	225	260, 190
96	n-Tridecane	629-50-5	39.00	1.097	0.000	0.063	57	43
97	n-Tetradecane	629-59-4	41.25	1.112	0.000	0.051	57	43
98	n-Pentadecane	629-62-9	43.89	1.056	0.000	0.043	57	43
99	n-Hexadecane	544-76-3	47.20	1.064	0.000	0.060	57	43
100	n-Heptadecane	629-78-7	0.00	1.010	0.000	0.057	57	43

Bold font means internal standard

Table A2.2 VOC composition of neat gasoline in this study and five literature studies.

References	This study	1	2	2	3	4	4	5
Fuel type	Gasoline	Gasoline	Gasoline	Gasoline	Reformulated gasoline	Reformulated gasoline		Gasoline
Season and year	Winter 2007	Summer 1990	Before 1996	Before 1997	Spring 1999	Summer 2001	Summer 2001	Winter before 2003
Location	Michigan, U.S	Atlanta, U.S	Vancouver, Canada	Washington, U.S	San Francisco, California, U.S	Berkeley, California, U.S	Sacramento , California, U.S	South Korea
unit	(wt %)	(ppbC% of NMOC[1])	(% NMHC[2])	(% NMHC[2])	(wt %)	(wt %)	(wt %)	(wt %)
Benzene	0.82	1.53	2.11	2.37	0.56	0.54	0.54	2.92
Toluene	2.06	8.11	9.91	9.99	7.63	8.26	7.84	12.86
Ethylbenzene	0.41	1.80	1.64	1.86	1.24	1.49	1.52	1.53
p-Xylene,m-Xylene	1.22	6.30	7.21	7.55	6.83	6.25	6.48	5.20
Styrene	0.00	0.19	-	-	-	-	-	-
o-Xylene	0.62	2.60	2.78	2.85	2.30	2.26	2.36	2.20
4-Ethyl toluene	1.12	2.59	0.82	0.87	-	-	-	-
2-Ethyl toluene	0.46	0.95	0.72	0.75	-	-	-	-
1,3,5-Trimethylbenzene	0.54	1.42	1.07	1.07	1.04	0.80	0.85	1.33
1,2,4-Trimethylbenzene	1.42	4.18	-	-	2.81	2.63	2.80	4.75
1,2,3-trimethyl benzene	0.53	1.01	0.75	0.73	0.46	0.53	0.56	-
Isopropylbenzene	0.05	-	-	-	-	0.09	0.11	-
n-Propylbenzene	0.28	0.71	0.54	0.58	0.32	0.46	0.51	-
sec-Butylbenzene	0.02	-	-	-	0.04	0.04	0.06	-
p-Isopropyltoluene	0.01	-	-	-	-	0.02	0.03	-
n-Butyl benzene	0.11	1.29	-	-	0.06	0.05	0.09	-
Naphthalene	0.30	-	-	-	0.18	0.14	0.13	-
Cyclohexane	1.31	0.25	0.35	0.55	1.31	1.67	1.61	0.48
Methyl cyclohexane	1.10	0.57	0.60	0.13	1.89	1.44	1.78	1.13
n-Heptane	1.70	0.85	1.03	0.90	2.03	1.46	1.61	2.81
n-Octane	0.38	0.45	0.45	0.37	0.40	0.47	0.65	1.05
n-Nonane	0.24	0.22	0.12	0.15	0.10	0.19	0.28	0.27
n-Decane	0.19	0.20	-	-	0.03	0.08	0.12	-
n-Undecane	0.15	0.20	-	-	0.01	0.05	0.05	-
n-Dodecane	0.11	0.30	-	-	0.00	0.01	0.02	-
n-Tridecane	0.09	0.08	-	-	0.00	-	-	-
n-Tetradecane	0.03	0.01	-	-	-	-	-	-
n-Pentadecane	0.01	-	-	-	-	-	-	-
n-Hexadecane	0.00	-	-	-	-	-	-	-

— : Not reported

1: Conner et al. (1995) define nonmethane organic compounds (NMOC) as the sum of all GC peaks eluting from the columns, C2-C14, 85 compounds.

2: McLaren et al. (1996) define nonmethane hydrocabons (NMHC) as the sum of all GC peaks eluting from the column, C2-C10, 105 compounds.

3: Harley et al. (2000) 4: Harley et al. (2004) 5: Na et al. (2004)

Table A2.3 Selected VOC concentrations (mg/L) in neat diesel in this study and the literature study.

Reference	This study	Peng et al. (2006)
Fuel type	ULSD	Diesel
Season and year	Winter 2007	Before 2005
Location	Michigan, U.S	Taiwan
n-Decane	7,690	3,000
n-Undecane	7,729	5,450
n-Dodecane	8,369	8,750
n-Tridecane	13,437	13,200
n-Tetradecane	10,078	16,450
n-Pentadecane	9,028	18,100
n-Hexadecane	9,300	16,500

Table A2.4 Target VOC fractions (% of TTVOC) of gasoline vapor in this study and four literature studies.

References	This study			1	2		3	4
Fuel	Gasoline			Gasoline	Gasoline		Reformulated gasoline	Gasoline
Season and year	Winter 2007			Summer 1989	Summer 1990		Spring 1999	Winter before 2003
Vapor temperature	5 °C	20 °C	40 °C	NA	24 °C	32 °C	38 °C	0 °C
Location	Michigan, U.S			Chicago, U.S	Atlanta, U.S		California, U.S	South Korea
Benzene	19.71	19.75	20.38	23.99	24.47	18.93	7.68	32.57
Toluene	26.63	28.22	24.87	31.78	36.01	37.69	34.83	35.43
Ethylbenzene	0.36	0.42	0.44	4.05	3.00	3.83	1.87	1.14
p-,m-Xylene	1.13	1.33	1.45	11.53	9.23	12.02	8.80	3.43
Styrene	<MDL	<MDL	<MDL	-	0.39	0.32	-	-
o-Xylene	0.43	0.48	0.56	3.74	3.34	4.36	2.62	1.14
4-Ethyl toluene	0.40	0.37	0.58	0.62	2.26	2.55	-	-
2-Ethyl toluene	0.12	0.12	0.18	0.31	0.80	0.91	-	-
1,3,5-Trimethylbenzen	0.14	0.13	0.21	0.62	1.09	1.24	0.56	-
1,2,4-Trimethylbenzen	0.41	0.37	0.61	1.56	3.06	3.44	1.12	0.57
1,2,3-trimethyl benzen	0.10	0.08	0.15	0.16	0.68	0.74	-	-
Isopropylbenzene	0.01	0.01	0.02	-	-	-	-	-
n-Propylbenzene	0.09	0.09	0.13	0.31	0.60	0.75	-	-
sec-Butylbenzene	<MDL	<MDL	<MDL	-	-	-	-	-
p-Isopropyltoluene	<MDL	<MDL	0.00	-	-	-	-	-
n-Butyl benzene	<MDL	0.00	0.02	-	0.76	0.76	-	-
Naphthalene	<MDL	0.00	0.02	-	-	-	-	-
Cyclohexane	19.41	17.10	18.54	7.79	3.49	2.49	17.23	5.71
Methyl cyclohexane	11.55	11.22	10.80	3.43	3.32	2.47	12.17	5.71
n-Heptane	18.78	19.47	20.11	8.10	5.95	5.44	12.55	13.14
n-Octane	0.66	0.78	0.77	1.87	0.96	1.26	0.56	1.14
n-Nonane	0.06	0.05	0.10	-	0.22	0.32	-	-
n-Decane	<MDL	0.01	0.04	0.16	0.12	0.17	-	-
n-Undecane	<MDL	<MDL	0.01	-	0.08	0.11	-	-
n-Dodecane	<MDL	<MDL	0.00	-	0.12	0.15	-	-
n-Tridecane	<MDL	<MDL	<MDL	-	0.03	0.05	-	-
n-Tetradecane	<MDL	<MDL	<MDL	-	0.02	0.00	-	-
TTVOC	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

<MDL: below method of detection limit. — : Not reported.

1: Doskey et al. (1992) 2: Conner et al. (1995) 3: Harley et al. (2000) 4: Na et al. (2004)

Table A2.5 Selected VOC concentrations (mg/m3) in diesel vapor composition in this study and literature.

Reference	This study	Peng et al. (2006)
Fuel type	ULSD	Diesel
Vapor temperature	20 °C	25 °C
Season and year	Winter 2007	Before 2005
Location	Michigan, U.S	Taiwan
n-Heptane	220.7	24.6
Methyl cyclohexane	533.7	4.5
Toluene	158.0	25.2
n-Octane	179.7	31.0
Ethyl benzene	36.6	29.6
p-,m-Xylene*	102.3	29.3
o-Xylene	35.8	20.1
n-Nonane	167.5	22.5
n-Propylbenzene	10.2	9.0
n-Decane	76.8	26.0
n-Undecane	28.8	19.7
n-Dodecane	6.2	10.1
n-Tridecane	1.4	5.3

* Peng et al. (2006) measured p-xylene only.

Table A2.6 Pearson correlation coefficients for the four fuels and headspace compositions at each temperature.

	Gasoline	G-5	G-20	G-40	E85	E85-5	E85-20	E85-40	ULSD	ULSD-5	ULSD-20	ULSD-40	B20	B20-5	B20-20	B20-40
Gasoline	1.00	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
G-5	**0.72**	1.00	-	-	-	-	-	-	-	-	-	-	-	-	-	-
G-20	**0.74**	**1.00**	1.00	-	-	-	-	-	-	-	-	-	-	-	-	-
G-40	**0.74**	**1.00**	**1.00**	1.00	-	-	-	-	-	-	-	-	-	-	-	-
E85	**0.76**	0.11	0.22	0.26	1.00	-	-	-	-	-	-	-	-	-	-	-
E85-5	**0.67**	**0.77**	**0.77**	**0.80**	0.24	1.00	-	-	-	-	-	-	-	-	-	-
E85-20	**0.71**	**0.75**	**0.77**	**0.79**	0.39	**0.99**	1.00	-	-	-	-	-	-	-	-	-
E85-40	**0.73**	**0.74**	**0.76**	**0.79**	0.44	**0.99**	**1.00**	1.00	-	-	-	-	-	-	-	-
ULSD	-0.50	-0.22	-0.27	-0.30	-0.43	-0.21	-0.25	-0.30	1.00	-	-	-	-	-	-	-
ULSD-5	**0.51**	**0.58**	**0.55**	**0.60**	0.09	**0.56**	**0.49**	**0.54**	-0.21	1.00	-	-	-	-	-	-
ULSD-20	**0.52**	**0.56**	**0.53**	**0.58**	0.14	**0.56**	**0.50**	**0.54**	-0.20	**0.99**	1.00	-	-	-	-	-
ULSD-40	**0.49**	0.46	0.45	0.49	0.21	0.49	0.44	**0.50**	-0.14	**0.92**	**0.96**	1.00	-	-	-	-
B20	-0.49	-0.26	-0.28	-0.30	-0.41	-0.23	-0.25	-0.29	**0.98**	-0.22	-0.21	-0.14	1.00	-	-	-
B20-5	**0.50**	**0.51**	**0.50**	**0.54**	0.15	**0.53**	**0.49**	**0.53**	-0.20	**0.96**	**0.99**	**0.98**	-0.21	1.00	-	-
B20-20	0.48	0.44	0.43	0.48	0.21	0.48	0.45	**0.50**	-0.17	**0.90**	**0.95**	**0.99**	-0.17	**0.98**	1.00	-
B20-40	0.47	0.43	0.42	0.46	0.20	0.46	0.42	0.47	-0.13	**0.90**	**0.95**	**1.00**	-0.13	**0.97**	**0.99**	1.00

2.8 References

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Chapter 3

Evaluation of the permeation behavior of biofuels through personal protective equipment (PPE) materials and the potential for dermal exposure of workers.

3.1 Abstract

Biofuels and conventional fuels differ in terms of their evaporation rates, permeation rates and exhaust emissions, which can alter exposures of workers, especially those in the fuel refining and distribution industries. This study investigates the permeation of biofuel blends including E85 (bioethanol 85% and 15% gasoline), B20 (biodiesel 20% and 80% diesel), and conventional petroleum fuels (gasoline and ultra-low sulfur diesel) through glove materials used in occupational settings (neoprene, nitrile and Viton) and laboratories (latex, nitrile and vinyl), as well as a standard reference material (neoprene sheet). Permeation tests followed the American Society for Testing and Materials (ASTM) F739-99 method. Permeation rates (PRs) and breakthrough times (BT) were measured using photoionization detectors (PIDs), and fuel and permeant compositions were measured using gas chromatography/mass spectrometry (GC/MS) which identified 100 target volatile organic compounds (VOCs). Additionally, we estimate exposures for three occupational scenarios, and recommend personal protective equipment (PPE) suitable for use with these fuels.

PR and BT depended on the fuel-glove combination. Gasoline had the highest PR among the four fuels based on the PID measurements and the total target VOC concentration. E85 fuel had BTs that were two to three times longer than gasoline through neoprene, nitrile Sol-Vex, and the standard reference materials. BT values for B20 fuel were slightly shorter than for diesel for the latex, vinyl, nitrile examination and the standard neoprene materials. The composition of permeants differed from neat fuels, e.g., permeants were significantly enriched in the lighter aromatics including benzene. Viton was the least permeable glove material among the tested materials for the four fuels tested. Among the scenarios, fuel truck drivers had the highest uptake via inhalation based on the personal measurements available in the literature, and gasoline station attendants had highest uptake via dermal exposure if gloves were not worn. Appropriate selection and use of gloves can protect workers from dermal exposures, however, the current recommendations from the National Institute for Occupational Safety and Health (NIOSH) should be revised to account for contemporary fuel formulations.

3.2 Keywords

B20, biofuels, dermal exposure, E85, glove, permeation, PPE, VOC

3.3 Introduction

Bioethanol and biodiesel fuels have the potential to reduce tailpipe emissions, reduce net carbon emissions and improve energy security, and they have emerged as leading alternative fuels to supplement or replace fossil fuels in the transportation sector. Although pure biofuels are less toxic, they are usually blended with conventional fuels that contain many toxic compounds, for instance, benzene, which is classified as a known human carcinogen.[1] In addition, biofuels can hasten the degradation of certain elastomers and can significantly increase permeation and evaporation rates,[2-4] which in turn can increase inhalation and dermal exposures, respectively, for both workers and the public.[5] These effects depend on the specific elastomer-fuel combination. At present, information regarding permeation rates and permeant compositions for biofuels through different elastomers and personal protective equipment (PPE) is very limited.

The permeation resistance of PPE materials is generally measured using the ASTM F739-99a method.[6] Key outcomes of this test include breakthrough time (BT)[7], defined as the time a challenge chemical is detected at specific permeation rate (e.g., 0.1 μg/cm^2-min used in this study) at the inner surface of the test material, and the steady-state permeation rate (SSPR), reached when the forces affecting permeation have achieved a dynamic equilibrium and the permeation rate does not change with time.[6] In the U.S, manufacturers are not required to conduct specific performance tests on PPE, but several do publish results of permeation tests for specific chemicals. While information regarding BTs and SSPRs for single chemicals exists for a variety of materials,[8] information for biofuels and most other mixtures is very limited. Thus, permeation tests using these new fuels are needed. In addition, complex mixtures such as biofuels require chemical-specific analyses to quantify SSPRs, exposures and risks for individual toxic components. Such information is also very limited.

This study investigates permeation of biofuel blends and conventional petroleum fuels, including gasoline and diesel, through common PPE materials. We characterize BTs, 8 hr PRs and permeant compositions, present exposure estimates for several occupational exposure scenarios, and make recommendations regarding PPE materials suitable for use with motor fuels.

3.4 Methods and Materials

3.4.1 Fuels and personal protective equipment (PPE)

Four commercial fuels were tested including E85 (85% bioethanol and 15% gasoline), B20 (20% biodiesel and 80% diesel), conventional gasoline and petroleum diesel. All fuels were purchased from a commercial gas station (Marathon Oil) in winter in Ann Arbor, Michigan, USA. Gasoline sold in Michigan contains ethanol (about 10%), and fuel formulations vary seasonally. The test fuels were winter blends which contain a higher fraction of aromatics (including benzene) than summer blends, which helps vehicles start more easily in cold weather. About one liter of each fuel was collected and stored in an amber glass bottle with a plastic screw cap and Teflon lined septum.

Six different personal protective equipment (PPE) materials were tested, including gloves made of neoprene (Ansell 29-865 unsupported glove with embossed grip and light cotton flock lined, Ansell Healthcare LLC, NJ, USA); nitrile (Ansell 37-165 green Sol-Vex® unlined glove with embossed grip, Ansell Healthcare LLC, NJ, USA); and Viton® (North Safety Products., Cranston, RI, USA). These gloves ranged in thickness (0.34 to 0.68 mm, specific thickness listed in Table 3.1), price (neoprene costs about $3, nitrile Sol-Vex about $6 and Viton about $50), stiffness, and other characteristics. We also tested three types of inexpensive disposable gloves commonly used in laboratory and medical settings (not for chemical protection): natural latex rubber (natural latex rubber, Fisherbrand™ powder-free exam gloves, Fisher Scientific, Pittsburgh, PA , USA); nitrile (nitrile butadiene rubber, Fisherbrand™ powder-free exam gloves, Fisher Scientific, Pittsburgh, PA, USA); and vinyl (Tru-Touch™ powdered polyvinyl chloride exam gloves, Fisher Scientific, Pittsburgh, PA , USA). These thin (0.11 to 0.15 mm) and flexible gloves are designed for infection and sterility control, e.g., in medical examinations, rather than applications in which chemical resistance is required, although they are also used (but not recommended) for many other purposes. We also tested a standard neoprene sheet (0.43 mm thick, NS-5550, Pesce Lab Sales, Kennett Square, PA, USA) as a reference recommended in the ASTM method.[6]

For each glove, two or more 80 mm diameter disks were cut from the back or palm of the gloves, conditioned for 24 h at 25 ºC and 35% relative humidity, weight to 1 mg resolution, and thickness measured at five random locations using a micrometer to 0.03 mm resolution. Duplicates were obtained from different pairs or packages of gloves to help account for any manufacturing variation.

3.4.2 Permeation Tests

Samples were tested in open-loop permeation tests following the ASTM F739-99a method.[6] Three 8-hr tests were run simultaneously using the setup shown in Figure 3.1, and each PPE material-fuel pair was tested in duplicate (different pair or box of gloves). Samples were mounted in 51 mm diameter glass permeation cells (PTC-200, Pesce Lab Sales, Kennett Square, PA, USA) immersed in a water bath maintained at 25±0.3 °C, a typical working temperature, as monitored using a thermocouple and data logger (Logic Beach Inc., La Mesa, CA, USA). Laboratory air was used at a nominal flow rate of 0.13 L min^{-1}, within the ASTM method's recommended range (0.05 to 0.15 L min^{-1}), served as the collection medium.

Each permeation cell was monitored by a separate photo ionization detector (PID) using a 10.6 eV lamp (RAE System, Inc., Sunnyvale, CA, USA) that was interfaced to a data logger. Breakthrough time (BT) was determined as the time when the permeation rate reach 0.1 μg/cm^2-min (toluene equivalents) as measured by the PID. Permeation rates (PRs) in this study were measured at 8 hours and not normalized by the thickness of glove. The PID manufacturer provides correction factors (CFs) in isobutylene equivalents for adjusting PID responses from the calibration standard to individual chemicals (Technical Note TN-106, RAE System, Inc., Sunnyvale, CA, USA). In this study, toluene was used as a calibration standard at concentrations ranging from 0 to 750 ppm. The CF for each fuel, expressed as toluene equivalents, was calculated as the CF in isobutylene equivalents divided by the CF for toluene. CFs for the tested fuels in isobutylene equivalents were obtained from the PID's manufacturer. CFs in toluene equivalents were 1.80 for gasoline and1.40 for ULSD.

The correction factor for a mixture (e.g., E85 and B20) is calculated from the sum of the mole fractions X_i of each component i, divided by the respective CF_i:

$$CF_{mix} = 1 / (X_1/CF_1 + ... + X_i/CF_i) \qquad (1)$$

E85 has high CF due to the PID's low response for ethanol. For E85, a CFs of 11.60 was calculated using equation 1, assuming a mixture of 85% ethanol and 15% gasoline. For B20, the calculated CF was 1.59, assuming 80% ULSD and 20% methyl ethers. These calculations assume that the CFs for individual elements of the mixture are representative.

3.4.3 Volatile organic compound compositions

The VOC composition of the permeant was measured at 2, 4 and 8 hrs into each test. A gas-tight syringe was used to transfer a 0.5 mL sample of the air exiting the permeation cell into a thermal desorption tube (TDT, stainless steel, 10 cm x 4 mm; Scientific Instrument Services, Inc., Ringoes, NJ, USA) packed with 160 mg of Tenax

GR (Scientific Instrument Services, Inc., Ringoes, NJ, USA) and 70 mg of Carbosieve SIII (Supelco, Bellefonte, PA, USA). Duplicate VOC samples were collected at the 8 hr point. Blank samples were collected before each test to test the cleanliness of the system. A total of 280 TDT tubes were collected and analyzed (4 fuels, 6 glove materials, one reference material, 3 points for the first run (2, 4 and 8 hr), 1 point for the second run (8 hr), duplicates of each fuel-glove combination, and VOC duplicates and blanks). Analysis of the TDT samples followed protocols described elsewhere.[9-11] In brief, each TDT was spiked with 2 μL of an internal standard (1 ng μL^{-1} each of fluorobenzene and p-bromofluorobenzene), and then analyzed using a short-path thermal desorption/cryofocusing system (Scientific Instrument Services, Inc., Ringoes, NJ, USA) and gas chromatography/mass spectrometry (6890/5973, Agilent, Palo Alto, CA, USA). VOC standards included an EPA 502/524 standard VOC Mix A, EPA 524 Rev 4 Update Mix (Supelco Inc., Bellefonte, PA, USA) plus 26 other compounds, representing a total of 101 target VOCs that included alkanes, aromatic, halogenated and phenolic compounds. These target VOCs are a subset of VOCs contained in these fuels. Ethanol and methyl ethers (biodiesel) were not included in the target VOCs; therefore, ethanol content in gasoline and E85 was not quantified. Similarly, the methyl ether content in B20 was not quantified. The PRs of target VOCs were measured at an exposure time of 8 hours.

Fuel composition was measured by spiking 2 μl of diluted fuel (50 and 100 μl mL^{-1} in pentane) into TDTs, which were then analyzed by the TD-GC-MS method described above. These tests were performed in triplicate.

3.4.4 Quality Assurance and Quality Control (QA/QC)

The QA/QC program included laboratory and field blanks, spiked and duplicate samples for each test. All laboratory and field blanks were clean. A spiked standard (101 VOCs standard mixture) was analyzed daily to check the calibration of GC/MS, and all compounds were within 20% of the expected values. Detection limits established using seven low concentrations spiked samples and TD-GC-MS method were 0.06 to 2.0 ng, depending on the compound. Based on a 0.5 mL sample volume, 130 mL/min flow rate and 19.3 cm^2 permeation area, the parameters used in the tests, method detection limits (MDLs) for the permeation tests ranged from 0.0002 to 0.0074 μg/cm^2-min, depending on the compound. Duplicate samples were sampled at each test point, and replicate precision for most compounds was below 20%.

3.4.5 Data Analysis

The permeation rate was determined by averaging the PID measurements over two duplicate tests. The composition of neat fuels and permeants was determined by averaging TD-GC-MS analyses over four replicates.

The suitability of a glove for each fuel was evaluated using BTs and considering a material as “not recommended” if the BT was less than 30 min; “poor,” “fair,” “good,” and “excellent” ratings were assigned for BTs between 30-120, 120-240, 240-480, and greater than 480 min, respectively.

The potential for worker exposure was evaluated for several scenarios (described below). In each, the average daily dose due to inhalation (ADD_I; μg kg^{-1} day^{-1}) was calculated as:[12]

$$ADD_I = \frac{C \times IR \times D \times RT}{BW \times AT} \qquad (1)$$

where C = concentration in inhaled air (μg m^{-3}); IR= inhalation rate (m^3 day^{-1}), D = duration (day); BW = body weight (kg); AT = averaging time (day); and RT =retention factor.

With dermal protection, the average daily dose due to dermal uptake ($ADD_{D,GLOVES}$, μg kg^{-1} day^{-1}) was:

$$ADD_{\mathrm{D,GLOVES}} = \frac{PR \times SA \times D \times EF}{BW \times AT} \tag{2}$$

where PR = permeation rate through glove or skin (μg cm^{-2} min^{-1}); SA = skin surface area contacted (cm^2); and EF = event frequency (event day^{-1}). In cases where gloves were not worn, the dermal ADD (ADD_D, μg kg^{-1} day^{-1}) was calculated as:

$$ADD_D = \frac{V \times EF \times \rho \times C_i}{BW} \tag{3}$$

where V = volume of fuel contacting the skin in each exposure scenario per event (mL $event^{-1}$); ρ = fuel density (g mL^{-1}); and C_i= concentration of component *i* in fuel (μg g^{-1}). C_i was based on measured values: 8,204, 1,097, 79 and 43 μg g^{-1} for benzene in gasoline, E85, diesel and B20, respectively, and 1,000,000 μg g^{-1} for total hydrocarbons. We assumed complete retention and absorption (no evaporation) in the case of eq. (3), and negligible ingestion and ocular exposures. These assumptions are approximate but reasonable "worst case" scenarios for screening level exposure estimates of a worker handling exclusively E85.

ADD predictions were compared to threshold limit values (TLVs) and recommended exposure limits (REL).[13, 14] The TLV is defined as the concentration of a substance to which most workers can be exposed without adverse effects. The REL is an 8 or 10 h time-weighted-average (TWA) exposure and/or ceiling. For gasoline, the TLV is 300 ppm, which is equivalent to an ADD of 97,714 μg kg^{-1} d^{-1}. For benzene, the TLV is 0.5 ppm, equivalent to an ADD of 116 μg kg^{-1} d^{-1}, and the REL is 0.1 ppm, equivalent to an ADD of 23.2 μg kg^{-1} d^{-1}. Permissible exposure limits (PEL) were not utilized given the lack of information for gasoline. The PEL for benzene is 1 ppm (TWA), which is 10 times higher than the REL. The risk-specific concentration of benzene is 0.13 to 0.45 μg m^{-3} (0.04-0.14 ppb), a concentration that represents a one-in-a-million excess cancer risk for lifetime (70 year) exposure.[1, 12]

3.4.6 Scenario Descriptions

Simplified exposure scenarios for a fuel truck driver, a service station attendant, and a laboratory worker were analyzed. These scenarios, which utilized worst case assumptions with respect to complete retention and absorption of the chemicals, were primarily aimed at determining the relative performance of specific PPE materials, and they do not necessary represent the actual exposure of workers.

The following parameters were assumed in each scenario: 8 hr workday; 70 kg male worker; inhalation rate of 15.2 m^3 per day, hand surface area of 840 cm^2;[12] and negligible ingestion and ocular exposures. Airborne THC and benzene concentrations were taken from the literature (described below), and the dermal dose was calculated using the measured permeation rates at 8 hour. The duration of dermal exposures was set as the total contact time minus the breakthrough time. Inhalation and dermal exposures were calculated for both conventional and biofuels using eqs. (1-3). Dermal uptake without the use of PPE also was estimated, in which case we assumed 100% absorption with a assumed quantify of fuel, assigned subjectively. We recognize that these are simplified exposure scenarios, and that other exposure pathways sometimes can be significant, e.g., ingestion.[15] The older studies in the literature of truck drivers and service station workers tend not to reflect current VOC exposures, which have been lowered due to changes in fuel formulations and fuel handling technologies. Thus, we limited our analysis to the more recent studies (mostly conducted in the 1990s) and to those which clearly used personal sampling measurements. The majority of the samples was taken using passive sampling method (charcoal tubes, silica gel tubes, Chromosorb 106 tubes, Tenax tubes or passive dosimeters), and most studies used gas chromatography analyses. Different methods for instrument calibration for THC determinations were employed, and the ethanol content was not included in the THC measurements. Specific information is available in individual papers.[16]

The fuel delivery scenario represents an individual who loads, drives and delivers fuel to retail gasoline stations. For conventional fuels, literature values of full-shift personal THC concentrations averaged 14.2 ppm (range: 8 to 60 ppm), based on 392 personal samples from three studies.[16] For benzene, the full-shift personal inhalation benzene concentration averaged 0.25 ppm (range: n.d. to 45 ppm), based on 3,472 personal measurement from nine studies conducted in the 1980s and 1990s.[16] These values fall well below the current TLVs for gasoline vapor (300 ppm) and benzene (0.5 ppm). Monitoring data for individuals handling E85 are very limited and inadequate to estimate inhalation exposures. For THC, we assumed that E85 would cause the same inhalation exposures as conventional gasoline since the total vapor pressure of the fuel is likely to be similar due to engine requirements (although the composition of the vapor will change) and comparable spillage rates. For benzene, we reduced the concentration by 85%, commensurate to the reduction of conventional fuel (the source of the benzene), giving 0.0375 ppm. These estimates are approximate but reasonable for screening level exposure estimates of a worker handling exclusively E85. They exclude the ethanol exposure.

We assumed that the worker wore new nitrile Sol-Vex gloves during loading/unloading events, which lasted 2 hours per day, and that fuel contacted about 25% of the hand's surface area during these events, a result of contact with wet or leaky hoses, valves, depth gauges, fuel splashes, etc. For comparison, we estimated exposures if the worker did not wear gloves and absorbed 5 mL of fuel daily. No respiratory PPE was used.

In the scenario for the gasoline service station attendant, the full-shift personal inhalation THC concentration averaged 10.5 ppm based on 73 personal samples ranging 0.46 to 114 ppm, and 0.14 ppm for benzene, based on 938 personal measurement ranging n.d. to 2.08 ppm as measured in eight studies conducted in the 1980s and 1990s.[16] For E85, we assumed the same inhalation exposures for THC, but again reduced the benzene exposure by 85%, giving 0.021 ppm. Dermal exposure was estimated assuming that the worker wore neoprene gloves during vehicle refueling events. We assumed that the attendant fueled 50 vehicles daily, for 5 min each, and that fuel contacted about 6% of the hand's surface area (half of the area of one palm). Dermal exposure may occur during refueling events due to contact with wet or leaky fuel caps, nozzles, fuel splashes, etc. For comparison, dermal uptake without any PPE was calculated by assuming that a small amount of fuel (0.2 mL) contacted and was absorbed through the attendant's hand during each of the 50 fueling events.

In the third scenario, a full-time technician analyzes fuel properties in the laboratory. Negligible inhalation exposure was assumed since a fume hood is utilized. Dermal exposure was estimated assuming that the technician wore nitrile examination gloves to handle fuel samples for 3 hr each day. About 2.5% of the total hand's surface area (several fingers) was assumed to have contact with the fuel. As a comparison case, we assumed that the technician handled fuel samples without wearing gloves, and that 1 mL of fuel contacted and was absorbed by the skin.

3.5 Results

3.5.1 Permeation Behavior

The laboratory tests showed four permeation behaviors, as classified by Nelson et al.[17] and depicted in Figure 3.2:

- Figure 3.2 (a) shows a logistic trend consisting of three stages: a period before BT where no permeation was observed, followed by a rapid rise in BT, and then a gradual leveling-off to a constant value. This behavior was shown by neoprene challenged by E85, latex challenged by diesel and B20, and SRM challenged by diesel and B20.
- Figure 3.2 (b) shows a high PR near the beginning of exposure, which then decreases and eventually levels off. This behavior indicates a moderate to high degree of swelling.[17] Latex challenged by E85, and vinyl challenged by regular gasoline and E85 showed this pattern.
- Figure 3.2 (c) is similar to (b) but after the high peak, the PR continues to gradually decrease and does not become constant. This behavior may result from structural

modifications of the material. Nitrile-exam and neoprene SRM challenged by E85 suggested this behavior.

- Figure 3.2 (d) has a two-stage increase in permeation rates which then stabilize, caused by a high degree of swelling. Vinyl challenged by diesel and B20 evidenced this trend.

These behaviors illustrate the complexity of the mechanisms underlying permeation and their specificity to the PPE material-solvent combination. Chemicals may dissolve in, react with, and diffuse through PPE materials. Exposure may also degrade materials and alter properties, leaving the materials soft, hard, brittle or swollen.[13, 17-19] While permeation mechanisms are not the focus of this work, it should be noted that in several cases (e.g., Figure 3.2), the permeation rate did not approach a steady-state condition and results at 8 hr may underestimate earlier exposures.

3.5.2 Breakthrough Time

BT test results are summarized in Table 3.1. For E85 and gasoline, Viton had the greatest resistance and BTs exceeded 8 hr (the test duration). For E85 through nitrile Sol-Vex, neoprene, and the neoprene SRM, BTs were 2 to 5 times longer than those for gasoline. BTs for the laboratory and examination gloves (latex, nitrile and vinyl) were very short (< 5 min). These materials are much thinner than the industrial gloves (neoprene, nitrile Sol-Vex and Viton), and results reflect both the thickness and chemical resistance of the materials. Note that BTs for E85 might be underestimated since the PID has low sensitivity for ethanol. For diesel and B20, nitrile Sol-Vex and Viton showed the best resistance and BTs exceeded 8 hr; neoprene’s BT was 386 ± 26 min; and nitrile and the SRM showed relatively rapid BT (40 to 90 min). Again, the latex and vinyl gloves had very rapid BT (<5 min). In all cases except neoprene, B20 had slightly (but not statistically significantly) shorter BTs than diesel. The presence of biodiesel may accelerate the BTs in these PPE materials, with the effect depending on the quantity of biodiesel blends (i.e., B5, B10, B20 or B50). It should also be noted that higher blends of biodiesel are not compatible with certain types of rubber compounds, metals and plastics.[20]

The literature regarding BT times of fuels through PPE materials is limited. One glove manufacturer reported a BT of >360 min for gasoline through the nitrile Sol-Vex glove,[21] longer but comparable to our results for the same glove (208 min). Although the same protocol was used, differences can arise from variability in the PPE materials, fuels and test conditions.[8] For same material, the BT and the time to reach the steady-state permeation rate generally increases with material thickness. Results in Table 3.2 and Table 3.3 do not account for thickness as our purpose was to measure permeation rates from commonly used commercial gloves. For a fuel-material combination where Fick's laws of diffusion apply, BT and PR will be inversely related to the square of material's thickness based.

To be protective, BTs of PPE should exceed the possible exposure time, and generally shorter BT indicates poorer chemical resistance.[6] However, BT is only one of several factors considered in selecting PPE materials. Other factors include mechanical properties (e.g., tensile strength), durability, the chemical’s toxicity, and cost.

3.5.3 Permeation Rates

After 8 hr of exposure to gasoline, PRs for the different glove types had the following ranking: latex > neoprene SRM ≈ neoprene ≈ nitrile > nitrile Sol-Vex > vinyl

> Viton (Table 3.1). The latex gloves ruptured when challenged by gasoline, thus no PR is given for this fuel. The PID's linear range (0~2000 ppm toluene equivalent) was exceeded for nitrile, neoprene and neoprene SRM, thus, PRs are approximate for these materials. As noted previously, the 8 hr PR for vinyl challenged by gasoline showed an early BT and a declining PR, and this value may not be suitable to estimate cumulative exposure.

For E85, the PR rankings of the materials changed slightly: nitrile > latex > neoprene ≈ neoprene SRM> vinyl > nitrile Sol-Vex > Viton. Because permeation rates declined through the test, the PR of latex and vinyl challenged by E85 may not be suitable to estimate exposure.

Diesel and B20 fuels had similar PRs for the same PPE material. PRs ranged between zero (i.e., not detected) to 36 $\mu g\ cm^{-2}\ min^{-1}$ among the six PPE materials, and the ranking was latex > vinyl > neoprene SRM> neoprene ≈ nitrile > nitrile Sol-Vex ≈ Viton.

For all materials except vinyl, gasoline had the highest PR among the four fuels, e.g., PRs with the neoprene SRM were 72, 45, 17 and 19 $\mu g\ cm^{2}\ min^{-1}$ for gasoline, E85, diesel and B20, respectively. Given the rapid breakthrough, vinyl would not be recommended as a PPE for any of these fuels.

As mentioned, PR information for fuels is limited. One report for gasoline and nitrile Sol-Vex gloves indicated a PR of $<0.9 \mu g\ cm^{-2}\ min^{-1}$, considerably lower than our results (23.4 $\mu g\ cm^{-2}\ min^{-1}$).[21] As noted for BTs, PRs depend on the chemical-material combination,[22] and differences may be caused by the test conditions and measurement approaches, including differences in the fuel. Motor fuels are mixtures containing hundreds of chemicals, e.g., gasoline contains components such as benzene, toluene, ethylbenzene and xylenes (BTEX) that are aggressive to rubber compounds and that can increase permeation rates. Our base gasoline contained approximately 10% ethanol,[23] which may account for the higher PR. Several reports have shown that nitrile gloves have lower PRs for the BTEX compounds than neoprene gloves.[8, 24] Our results are consistent with this, and show that this applies across the four fuels.

3.5.4 Permeant Compositions

Permeation rates of individual VOCs for all PPE–fuel combinations were estimated (and are shown in the supplemental materials as Table 3.2and Table 3.3) with the exception of tests in which BTs exceeded 8 hr (Viton with all four fuels, and B20 and diesel with nitrile Sol-Vex), and tests in which the PPE failed (latex with gasoline). Permeant compositions depended strongly on the glove-fuel combination and, in many cases, permeants were "enriched" in the abundance of the lighter aromatic VOCs, and "depleted" in the heavier alkanes, relative to the composition of the neat fuel. Figure 3.3 shows "enrichment factors," defined as the ratio of permeant composition to the neat fuel composition, for selected VOCs and the four fuels through nitrile and neoprene materials. Since not all compounds were quantified, this analysis is restricted to the target compounds measured above MDLs, and compositions are calculated as the concentration of a specific (target) VOC divided by the sum of target VOCs. Despite this limitation, the enrichment factors show dramatic differences between the compositions of the permeants and the neat fuels, e.g., individual VOCs can be enriched or depleted by up to one to two orders of magnitude.

Neat gasoline showed 29 of the target VOCs, and the composition was dominated by the BTEX compounds, n-heptane, 1,2,4-trimethylbenzene and cyclohexane. Most of the compounds in the neat fuel (17 to 22) were detected as permeants, and most of the tested materials had high PRs (and enrichment factors) of toluene and benzene relative to the other target VOCs. While the degree of enrichment or depletion for specific VOCs depended on the PPE, the general patterns across the tested PPEs were similar, e.g., toluene and benzene were enriched in both nitrile and neoprene gloves (Figure 3.3).

Other than ethanol, the major VOCs in E85 were xylenes, toluene, n-heptane, 1,2,4-trimethyl benzene and 4-ethyl toluene. If gasoline was blended with ethanol on a volumetric basis and fuel formulations were unchanged, then concentrations of VOCs in E85 would be expected to be 85% lower than those in gasoline. Benzene's reduction of was 86%, in the expected range, however, xylene's level was only 30% lower, and toluene, n-heptane, and 1,2,4-trimethylbenene were only 70% lower.

The permeants of most of the tested PPE materials showed similar patterns for E85 and gasoline, e.g., modest enrichment of benzene and toluene, and significant depletion of other aromatics and longer alkanes, e.g., n-nonane and trimethyl benzene (Figure 3.3). For the nitrile glove and compared to gasoline, PRs for E85 were reduced by 85%, the "expected" amount for toluene, 92% for benzene and 85% for toluene, but only 25% for xylenes. For the neoprene glove, PRs were reduced by 96 to 98% for toluene, benzene and n-heptane, and by 80% for xylene. These reductions reflect changes in the fuel composition as well as VOC-PPE interactions.

Diesel and B20 fuels were dominated by C_9-C_{16} alkanes, and the BTEX fraction was small, about 0.1% of neat fuel. With volumetric blending of fuels and unchanged formulations, VOCs in B20 would be reduced by only 20% from that in conventional diesel. However, we found that concentrations of most aromatics in B20 slightly increased compared to conventional diesel, e.g., xylenes levels increased by 17% higher, while alkane levels generally decreased, e.g., C_9-C_{16} alkanes were 16 to 44% lower.

Among the PPE materials, diesel and B20 permeants were dominated by the BTEX compounds, n-heptane, 1,2,4-trimethylbenzene and cyclohexane. Permeants of these fuels had generally similar enrichment factors (Figure 3.3). Both nitrile and neoprene gloves enriched most aromatics and cyclohexanes, e.g., BTEX permeants were enriched by 13 to 40 times for diesel and 11 to 34 times for B20, while long alkanes were depleted, e.g., n-dodecane. These results demonstrate substantially higher PRs for several of the toxic compounds in these fuels, as compared to the bulk of the fuel's constituents.

The laboratory results show significant variation in the composition of permeants through different fuel-PPE combinations, critical information for occupational exposure assessment. For complex chemical mixtures such as motor fuels, permeant compositions strongly depend on the chemical and PPE material; differences among fuels and PPEs can be very large; and toxic permeants like benzene can be enriched far above the fraction found in the fuel. These differences are important for estimating dermal exposures and evaluating the suitability of a material for a given application.

3.5.5 Exposure Scenarios

Results of the three scenarios are summarized in Table 3.4. For the fuel delivery worker handling gasoline, the THC inhalation dose (4,600 $\mu g\ kg^{-1}\ d^{-1}$) was well below the estimated gasoline TLV (97,700 $\mu g\ kg^{-1}\ d^{-1}$), and the THC dermal dose using nitrile Sol-Vex gloves was also lower (8,424 $\mu g\ kg^{-1}\ d^{-1}$) than the TLV. However, the benzene inhalation exposure (57 $\mu g\ kg^{-1}\ d^{-1}$) exceeded the REL (23 $\mu g\ kg^{-1}\ d^{-1}$). The dermal dose of benzene (381 μg kg^{-1} d^{-1}) was much higher than the inhalation exposure. For E85, the THC inhalation dose was the same as gasoline's and the inhalation dose of benzene was 85% lower, following the assumed fraction, and the THC and benzene dermal doses were very low. Based on our permeation results, the nitrile Sol-Vex gloves would largely prevent dermal exposure from B20 and diesel fuels (BT > 8 h). In contrast, a worker who is bare-handed or wearing cotton or other non-chemically resistant gloves could experience significant dermal exposure, e.g., absorption of 5 mL of fuel during the day would increase the THC dose to 53,494 and 56,113 μg kg^{-1} d^{-1}, and the benzene dose would increase to 439 and 62 μg kg^{-1} d^{-1} for handling gasoline and E85, respectively.

For the service station attendant, the THC inhalation dose (3,420 μg kg^{-1} d^{-1}) was below the TLV, but again, the benzene inhalation dose (32 μg kg^{-1} d^{-1}) exceeded the REL. Dermal doses of gasoline and E85 were higher than inhalation doses if neoprene gloves were worn and remained intact. For THC, the dermal doses from gasoline and E85 were >11,198 and 6,180 μg kg^{-1} d^{-1}, respectively (the former was not determined specifically as the PID's calibration range was exceeded), and benzene dermal doses were 1,779 and 25 μg kg^{-1} d^{-1} for gasoline and E85, respectively. Based on the measured breakthrough times, neoprene gloves would prevent dermal exposure from B20 and diesel fuels for 6 hours. However, if PPE was not worn, dermal doses were very high: 106,998 and 112,226 μg kg^{-1} d^{-1} for THC, and 878 and 123 μg kg^{-1} d^{-1} for benzene, for gasoline and E85, respectively, depending on the fuel and assuming absorption of 10 mL of fuel. Given better control of air emissions, expected in areas using vapor recovery systems and lower volatility fuels, the inhalation dose would be significantly reduced, which would increase the relative importance of the dermal dose.

In the third scenario, the laboratory technician had dermal THC doses that fell below the TLV, but the dermal benzene dose for gasoline exceeded the REL when nitrile examination gloves were worn. (Inhalation exposure was assumed to be negligible in this scenario.) However, because BTs for gasoline and E85 for the nitrile examination glove were very short (<5 min), the use of these gloves in this application is not acceptable. They may be (marginally) acceptable for very short term use (<1 hr) with diesel fuels. If PPE was not used and dermal contact with 1 mL of fuel occurred, then the dermal THC dose was 10,700 to 12,200 $\mu g\ kg^{-1}\ d^{-1}$, and the benzene doses were range greatly 0.5, 1, 12, 88 $\mu g\ kg^{-1}\ d^{-1}$ for B20, diesel, E85 and gasoline, respectively.

In each of the scenarios, the duration of inhalation exposure was assumed to be 8 hr, while the duration of the dermal exposure depended on the difference between the assumed contact time and the BT time. In some regards, the results present the best case, i.e., use of new gloves. BTs will be reduced and permeation resistance will be weaker with gloves that have been previously exposed, thus, exposures would increase if workers did not wear new gloves each day. We used PRs measured after 8 hr of exposure, which might underestimate exposure with vinyl gloves due to their permeation behavior (as shown in Figure 3.2 (b) and (d)). Other factors that would tend to increase exposures include glove wear and tear, exposure to multiple fuels, temperature extremes, and possibly other environmental conditions.

While we have focused on dermal exposures, inhalation doses in the first two scenarios were significant. In the first two scenarios, we assumed that the inhalation exposure of benzene for the worker handling E85 was reduced by 85% compared to handling gasoline. In most cases, however, workers may service multiple fuels, each with a different composition, which can significantly alter airborne concentrations and exposures. Reported concentrations of exposures and concentrations during refueling vary greatly. Airborne concentrations measured at service stations range from 2,070 to 3,303,000 μg m^{-3} for THC (reported, as 0.46 to 734 ppm), and from <32 to 9,200 μg m^{-3} for benzene (reported as <0.01 to 2.88 ppm).[16] For benzene, 1,300 μg m^{-3} was reported in personal breathing zone air sampled during refueling in Alaska in 1995;[25] 40 μg m^{-3} in personal breathing zone air of several fuel station attendants in South Korea;[26] but only 3 μg m^{-3} at a fuel station in North Carolina in 1998-1999.[27] As noted, inhalation and sometimes ingestion exposures must be considered, in addition to dermal exposures, to estimate the total burden.[15]

3.6 Discussion

In the United States, PPE materials typically are selected based on laboratory permeation testing that follow the ASTM F 739 protocol. Test results can vary significantly among studies, and higher collection flow rates in the ASTM F739 protocol have been shown to increase the apparent permeation rates.[8, 24] We found modest variation between most replicates (typically under 20%), and moderate variation (< 50%) between batches (different pair or box of gloves). BTs and PRs were determined by the PID using toluene equivalents, and were not chemical-specific. BTs and PRs for E85 might be underestimate given that the PID has low sensitivity for ethanol, although its response was adjusted using correction factors. Not all compounds in the fuels could be identified and quantified, including the ethanol in gasoline and E85, and the methyl ethers in B20. Only a subset of the many types of PPE materials and fuels available could be tested. In addition, the laboratory tests and standard protocols do not consider the chemical's toxicity and other properties, physical stress and wear of the glove, repeated uses of the glove, and elevated temperatures and other environmental factors, all of which are expected to affect permeation resistance. Our tests and exposure scenarios dealt with gasoline, E85, diesel and B20 fuels separately. In practice, these fuels are often handled together, and exposures will occur to a mixture of these (and possibly other) fuels.

We made many assumptions in the exposure scenarios. We noted that inhalation doses in the first two scenarios depend on many factors, including the airborne concentrations (which in turn depend on meteorology, traffic, fuel composition, the effectiveness of the vapor recovery system, the frequency of operations and other factors), as well as breathing rates, and activity durations. While we based our assumptions on published references, several of the studies were old, e.g., conducted in the 1980s, and concentrations of airborne VOCs in many areas are now expected to be lower. Still, airborne concentrations of benzene and THC used in the service station and fuel delivery scenarios fell well below current TLVs. At present, service stations and most fuel delivery trucks distribute both conventional and biofuels, thus the higher exposures from any of the fuels handled will tend to dominate exposure. Rather than evaluating exposures for such mixtures, however, we assumed that workers handled only one type of fuel (conventional fuels or biofuels). While facilitating comparisons, this may underestimate exposures. We previously noted the lack of monitoring data for airborne THC, ethanol and benzene at facilities handling biofuels. Lastly, our scenarios assumed complete retention and absorption, negligible ingestion and ocular exposures.

Ingestion exposures can be important if workers siphon fuel by mouth or do not wash their hands.[15]

In the U.S., methyl tertiary-butyl ether's (MTBE) use as an gasoline oxygenate additive has been phased out,[23] and many regions, including much of the Midwest, California and New York, now routinely mix ethanol into all grades of gasoline.[28] Ethanol's use has grown very rapidly, e.g., U.S. production increased from 1.63 billion gallons in 2000 to 9.0 billion gallons in 2008.[29] As mandated by the Energy Policy Act 2005, the use of renewable fuels has significantly increased, as has the construction of new or expanded biofuel facilities, including gasoline blenders. (Ethanol needs to be blended into gasoline at the last step of fuel distribution to avoid moisture absorption). Workers at all of these facilities may be exposed to ethanol-gasoline blends.

Because ethanol and biodiesel (methyl ethers) are less toxic than conventional fuels, the overall exposure to toxic compounds should be reduced. However, true exposures depend on many factors and can be difficult to predict. First, biofuel blends are neither pure biofuels nor ideal mixtures, thus exposures estimates based on simple calculations (like those used here) are subject to considerable uncertainty. Second, the presence of ethanol can increase permeation rates due to the degradation of certain materials and elastomers in hoses, pipes, gaskets, fuel tank caps, etc., although the use of equipment and materials designed for biofuels should keep permeation acceptably low. Third, we show that benzene permeation rates through many glove materials is fast relative to many other compounds, thus dermal doses will not be reduced proportionally to the reduction of benzene (and other compounds) in the fuel.

The last update of the NIOSH permeation guidance occurred in 1999,[30] before the widespread use of ethanol as an oxygenate additive in gasoline. The NIOSH information, as well as the manufacturers' laboratory-generated data on chemical permeation, are key inputs for selecting glove and other PPE materials. Based on this study and the widespread use of ethanol containing fuels, we recommend that the NIOSH guidance for gasoline fuels should be updated, and that it should consider the more toxic components (like benzene) that tend to permeate through PPE. This updated information should be used to select appropriate PPE.

3.7 Conclusions

Both conventional and alternative fuels contain benzene and other toxic compounds, and require controls to limit inhalation and dermal exposures. Permeation tests were conducted for four fuels (conventional gasoline, ethanol-gasoline or E85, diesel, biodiesel or B20) through three types of gloves commonly used as PPE, three gloves used in laboratory settings (not for chemical protection), and a reference material. Results show the dependence of (toluene equivalent) breakthrough time (BT) and permeation rate (PR) on the fuel-PPE material combinations. Among the four fuels, gasoline tended to have the highest PRs, and only the Viton glove gave excellent protection (BT > 8 hr). Diesel and B20 had low PRs, and both Viton and nitrile Sol-Vex materials gave good protection; neoprene also could give acceptable protection. The existing NIOSH PPE recommendations for fuels do not account for contemporary gasoline formulations that now contain ethanol that can affect permeation characteristics. We recommend that these recommendations be revisited following tests of both conventional and biofuels.

Motor fuels are complex mixtures of hydrocarbons that include toxic compounds such as benzene. This study is unique in quantifying the composition of permeants through the glove materials. We show that many of the toxic VOCs are not reduced by the expected percentage for the blend, e.g., 85% for E85 compared to gasoline, and 20% for B20 compared to diesel. More significantly, permeants through the tested PPE materials were enriched in certain compounds, including several aromatics and alkanes, especially for the diesel and B20 fuels. This means that individuals protected by PPE but who experience repeated dermal exposures will have much larger exposures of toxics than would be expected based on the total PR and the fuel composition. This has significant implications for exposure assessment, especially for retrospective or historical assessments.

Inhalation and dermal exposures estimated for fuel delivery workers, service station attendants and laboratory workers can exceed guidelines (TLVs or RELs). Although simplified and representing only a subset of occupational settings where PPE is worn, the scenarios demonstrate the importance of selecting and wearing appropriate PPE.

3.8 Recommendations

Table 3.5 summarizes experimental BT results and classifies the suitability of gloves for each fuel combination. Viton gloves showed the highest chemical resistance among the tested materials, and it is the only suitable choice for handling gasoline. Nitrile Sol-Vex gloves can be used for E85, diesel and B20. Neoprene gloves are suitable for only short exposures to diesel and B20 fuels. The laboratory and examination gloves fared poorly in the fuel applications. The nitrile exam glove might be suitable for very brief exposures to diesel and B20. Latex and vinyl gloves are not recommended for any application involving fuels. The qualitative ratings in Table 3.5 provide simple, but useful guidance to users. Such ratings also can help account for variation in performance that is expected under actual use, as discussed before.

E85, diesel and B20 are not in the current NIOSH database or any identified PPE product guide. Gasoline is the only fuel listed in the NIOSH PPE database, and the recommended PPE include nitrile, Viton™ and Barricade™ coated suits (Viton and Barricade are trademarks of the DuPont company) for 8 hr exposure, or polyvinyl alcohol (PVA) , polyethylene/ethylene-vinyl alcohol gloves (PE/EVAL) and Responder™ suits (Responder is a trademark of the Life-Guard company) for 4 hr exposure.[30] The NIOSH guidelines date back to 1999, before the widespread use of ethanol in gasoline. The Ansell chemical resistance guide (2008), indicates that for nitrile Sol-Vex gloves with gasoline (unleaded, Shell Premium winter blend, ethanol content not available), the BT exceeds 480 min.[31] However, our results indicate that the use of nitrile Sol-Vex gloves with gasoline (containing 10% ethanol) should not exceed 200 min.

As noted, PPE recommendations from NIOSH and PPE manufacturers are key inputs in glove selection. Our results show a need to update the NIOSH PPE guidelines for gasoline. We also recommend that PR and BT tests conducted by NIOSH and manufacturers include both conventional and biofuels, and that the worst case result among the motor fuels should be used in general recommendations for PPE materials for motor fuels since most workers are likely to encounter several fuel types, and since biofuels and conventional fuels often cannot be distinguished. PPE decisions should maintain a protective posture that accounts for experimental variation in BT and PR results, which itself is likely to be dwarfed by the variation in occupational settings. Most users would be protected using a margin of error or confidence level approach. Thus, we recommend that PPE users request and glove manufacturers supply data for specific fuel formulations and other chemicals, including mixtures were appropriate and that test procedures display both a mean value and a 95th percentile value designed to account for variability and uncertainty. Lastly, many of the sturdier and more expensive gloves are worn repeatedly, and a month's use is not uncommon. Methods to ensure that PPE materials perform satisfactorily with such repeated use patterns, which represent prolonged though intermittent exposure, should be considered.

Wearing PPE is one of the primary methods for preventing dermal exposure in the workplace. When used, PPE generally masks the sensation of chemical exposure, and most gloves do not show any physical evidence of breakthrough. The use of BT and sometimes PR results from laboratory tests of new PPE materials as selection criteria may not reflect performance under workplace conditions where elevated temperatures, flexing, abrasion, pressure, and product variation are encountered. Ideally, the goal of zero tolerance should be sought, thus BT is a more protective criterion. Of course, material selection should also consider abrasion resistance, strength, temperature range, flexibility, puncture resistance, and cost. It is important to achieve user acceptance, allowing the worker to perform the task. While Viton gloves had the best performance in terms of BT and PR, they are also the most expensive. Laboratory gloves are not recommended for general workplace settings; however, they are worn by the general public and in many occupational settings (especially in developing countries). Our results indicate that such gloves provide little protection against exposure to fuels.

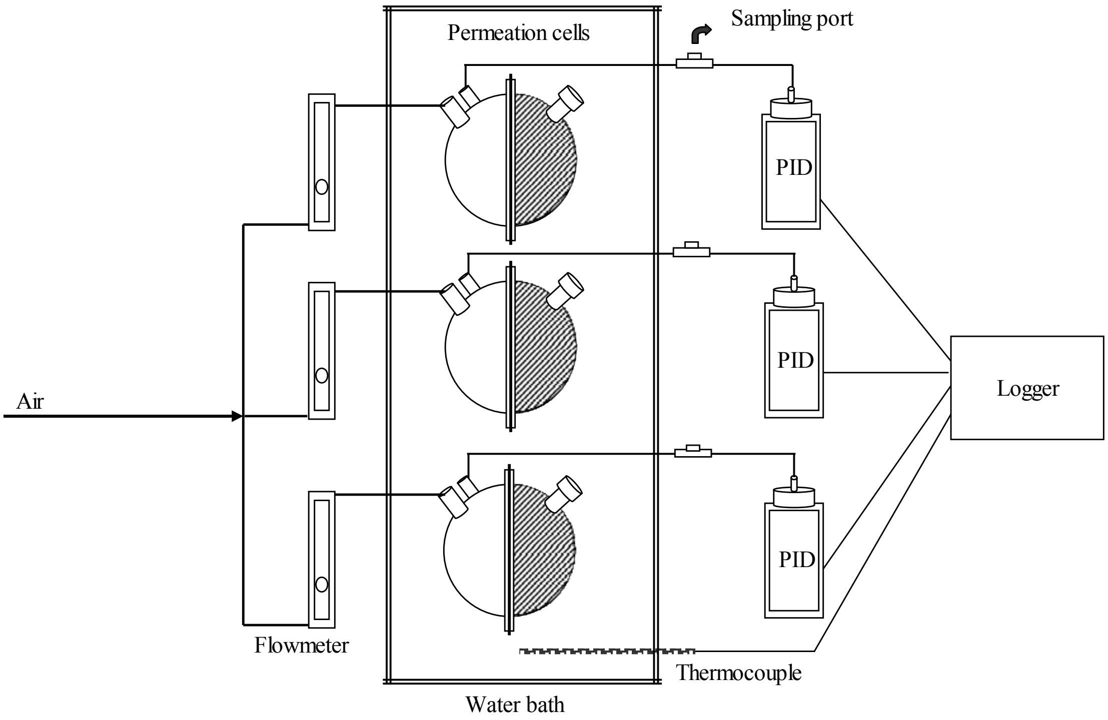
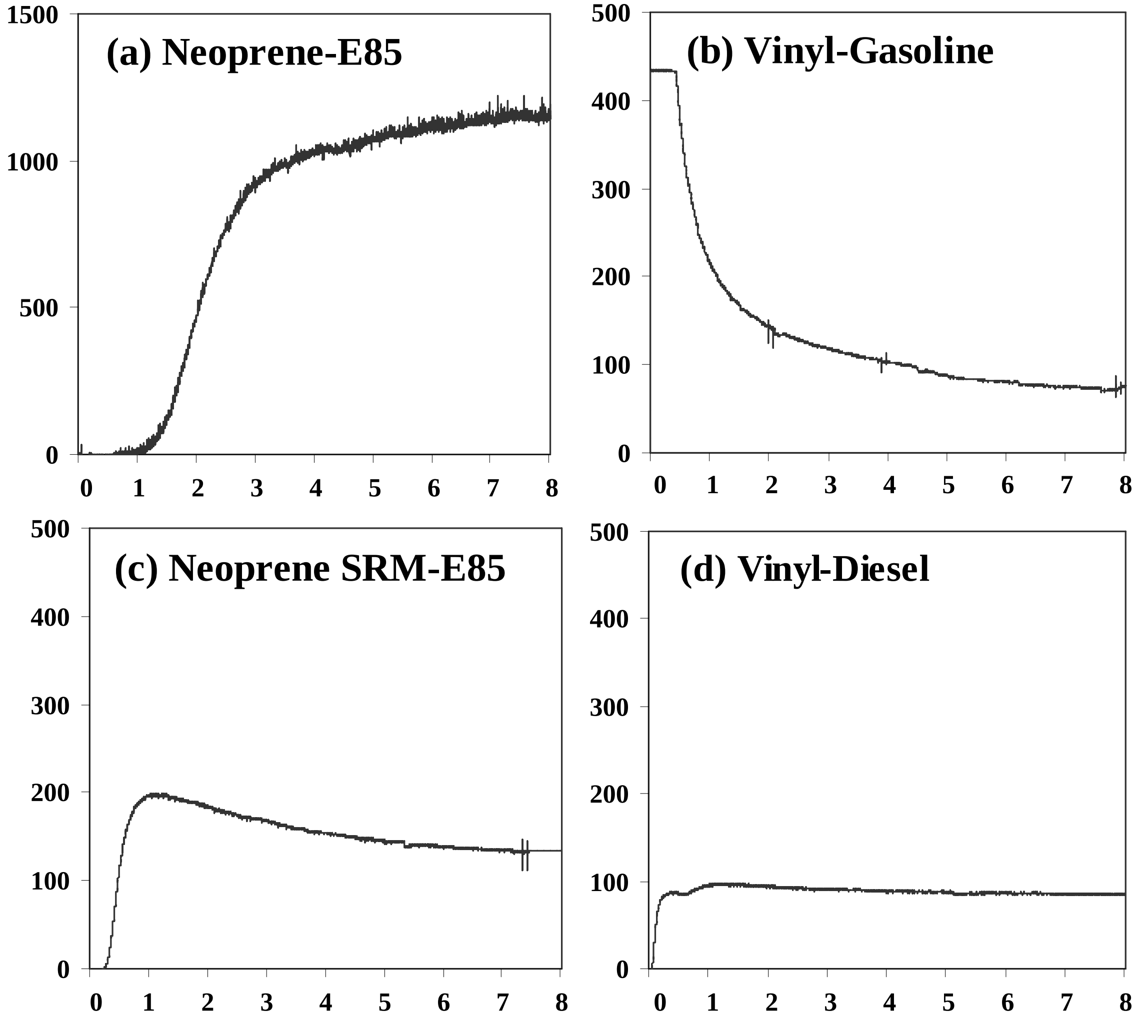


Figure 3.1 Permeation test layout.
The right (shaded) side of the permeation cell is filled with fuel. The water bath is maintained at 25 ^{o}C.


(a) Neoprene-E85

(b) Vinyl-Gasoline

(c) Neoprene SRM-E85

(d) Vinyl-Diesel

Figure 3.2 Breakthrough curves showing different permeation behaviors for indicated PPE-fuel combinations.

(a) Neoprene-E85, (b) Vinyl-Gasoline, (c) Neoprene SRM-E85, (d) Vinyl-Diesel. The x-axis is time (0 to 8 hr). The y-axis is the concentration in toluene equivalents (ppm).

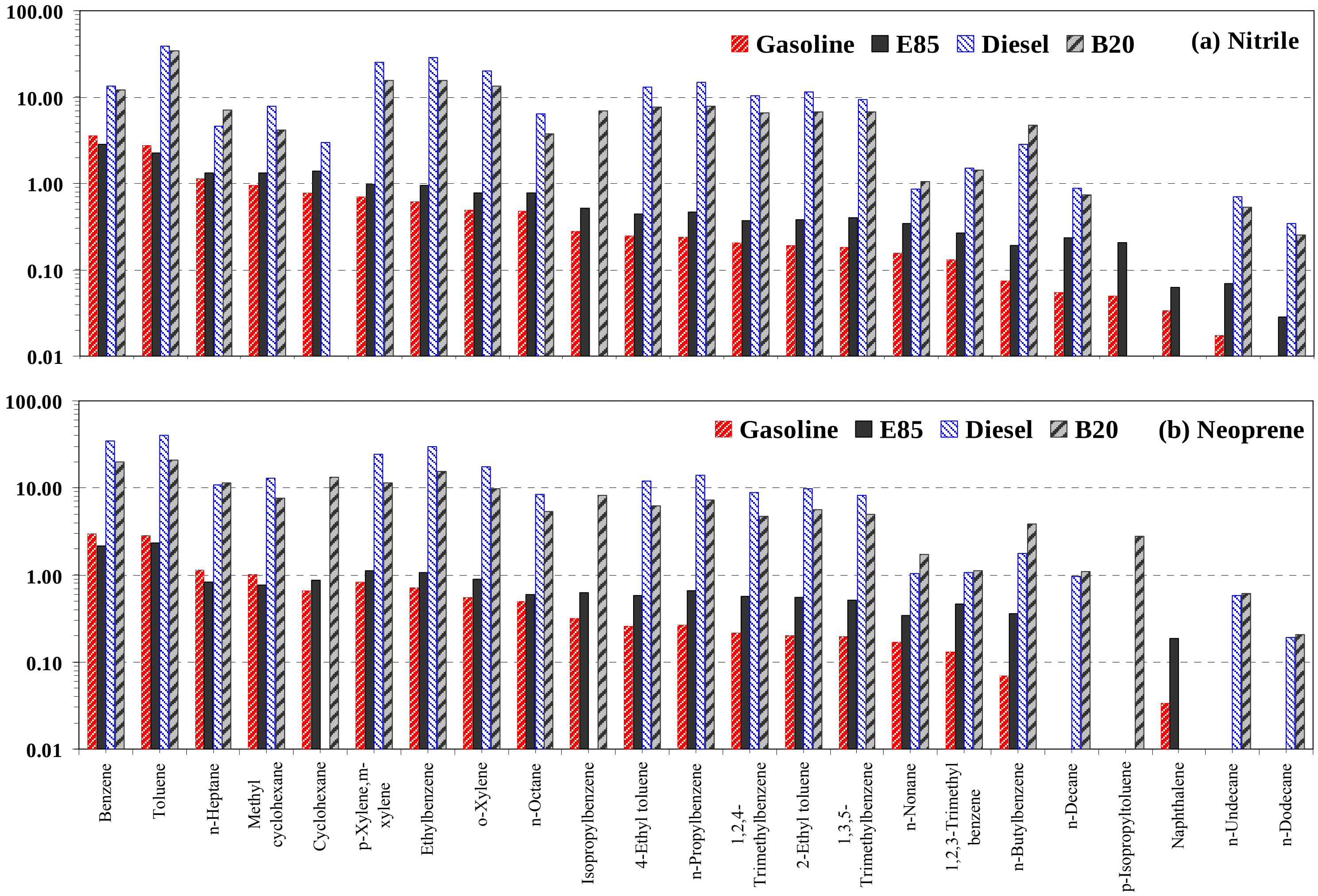


Figure 3.3Enrichment factors for selected VOCs in permeants relative to neat fuels.
(a) EF for E85, B20, gasoline and diesel through nitrile gloves; (b) enrichment factors for same fuels though neoprene gloves.

Table 3.1 Summary of thickness, breakthrough times and 8 hr permeation rates for each glove-fuel combination.

Fuel	Glove type	Thickness (mm)		Breakthrough time (min)		Permeation rate (µg cm^{-2} min^{-1})	
		Ave	Stdev	Ave	Stdev	Ave	Stdev
Gasoline	Latex	0.14	0.00	NA[A]	NA[A]	NA[A]	NA[A]
	Nitrile	0.11	0.00	2.1	NA[B]	>63.3[EC]	NA[B]
	Vinyl	0.14	0.01	0.9	0.6	12.2	0.5
	Nitrile-Sol-Vex	0.59	0.02	208.1	NA[B]	23.4	NA[B]
	Neoprene	0.51	0.00	22.4	NA[B]	>65.6[EC]	NA[B]
	Viton	0.43	0.01	ND	ND	ND	ND
	SRM	0.39	0.01	4.9	2.7	>71.5[EC]	0.06[EC]
E85	Latex	0.14	0.00	0.8	NA[B]	58.3	NA[B]
	Nitrile	0.10	0.00	3.2	NA[B]	94.1	NA[B]
	Vinyl	0.14	0.00	1.1	0.1	32.3	15.6
	Nitrile-Sol-Vex	0.61	0.01	433.5	NA[B]	1.5	NA[B]
	Neoprene	0.50	0.01	66.0	NA[B]	44.8	NA[B]
	Viton	0.41	0.00	ND	ND	ND	ND
	SRM	0.38	0.00	14.2	0.7	44.7	11.5
Diesel	Latex	0.14	0.01	3.4	NA[B]	36.4	NA[B]
	Nitrile	0.11	0.01	92.6	NA[B]	3.1	NA[B]
	Vinyl	0.14	0.00	3.0	0.4	24.4	3.2
	Nitrile-Sol-Vex	0.67	0.02	ND	NA[B]	ND	NA[B]
	Neoprene	0.49	0.01	363.6	NA[B]	2.2	NA[B]
	Viton	0.42	0.01	ND	ND	ND	ND
	SRM	0.38	0.00	47.2	1.2	17.3	2.1
B20	Latex	0.15	0.00	1.3	NA[B]	31.1	NA[B]
	Nitrile	0.11	0.00	88.3	NA[B]	3.8	NA[B]
	Vinyl	0.14	0.00	1.7	0.3	25.3	0.1
	Nitrile-Sol-Vex	0.63	0.04	ND	NA[B]	ND	NA[B]
	Neoprene	0.50	0.01	399.7	NA[B]	5.6	NA[B]
	Viton	0.37	0.05	ND	ND	ND	ND
	SRM	0.39	0.01	42.4	1.1	19.3	3.7

SRM= standard reference material (neoprene sheet)

A: Not captured by PID because of material broken during testing.

B: Only one measurement available

EC: Exceeded the linear range of PID calibration

ND= Not detected by PID

Table 3.2 Compositions of neat fuels, and 8 hr permeation rates through six glove materials for gasoline and E85 fuels.

	Gasoline						E85						
	Neat Fuel	Nitrile	Nitrile-Sol-Vex	Neoprene	Vinyl	SRM	Neat Fuel	Latex	Nitrile	Nitrile-Sol-Vex	Neoprene	Vinyl	SRM
	Conc (mg/L)	PR (μg/cm^2-min)					Conc (mg/L)	PR (μg/cm2-min)					
Aromatics													
Benzene	6144	10.846	1.060	9.965	0.333	8.205	862	1.635	0.863	0.019	0.195	0.115	0.212
Toluene	15429	21.387	1.487	23.948	1.027	22.402	4107	5.383	3.313	0.025	1.020	0.655	1.082
Ethylbenzene	3075	0.950	0.208	1.185	0.038	0.978	1994	1.155	0.676	0.017	0.221	0.098	0.327
p,m-Xylene	9124	3.152	0.750	4.022	0.137	3.320	6976	4.129	2.431	0.062	0.820	0.363	1.244
o-Xylene	4614	1.120	0.252	1.371	0.042	1.166	2789	1.303	0.775	0.016	0.264	0.115	0.441
Isopropylbenzene	351	0.049	0.010	0.061	<MDL	0.053	156	0.048	0.028	<MDL	0.010	0.004	0.019
n-Propylbenzene	2107	0.253	0.071	0.300	0.011	0.265	665	0.172	0.110	0.002	0.046	0.019	0.080
p-Isopropyltoluene	88	0.002	<MDL	<MDL	<MDL	0.002	29	0.003	0.002	<MDL	<MDL	<MDL	0.002
4-Ethyl toluene	8384	1.018	0.289	1.176	0.044	1.085	2647	0.661	0.410	0.010	0.164	0.068	0.322
2-Ethyl toluene	3462	0.332	0.091	0.371	0.013	0.359	928	0.191	0.125	0.002	0.054	0.022	0.111
1,3,5-Trimethylbenzene	4060	0.372	0.098	0.431	0.011	0.408	1030	0.241	0.144	0.002	0.056	0.023	0.133
1,2,4-Trimethylbenzene	10613	1.097	0.355	1.244	0.054	1.199	3267	0.625	0.428	0.010	0.197	0.083	0.393
1,2,3-Trimethyl benzen	3945	0.255	0.082	0.280	0.012	0.282	975	0.127	0.093	0.001	0.048	0.020	0.097
sec-Butylbenzene	159	0.005	<MDL	<MDL	<MDL	<MDL	65	0.010	0.004	<MDL	<MDL	<MDL	<MDL
n-Butylbenzene	822	0.031	0.012	0.031	0.002	0.034	198	0.018	0.013	<MDL	0.008	0.003	0.015
Styrene	14	0.002	<MDL	<MDL	<MDL	<MDL	4	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Naphthalene	2240	0.038	0.027	0.040	0.008	0.042	378	0.010	0.008	<MDL	0.007	0.003	0.013
Alkanes													
n-Heptane	12776	7.218	0.422	7.834	0.130	7.760	3331	7.237	1.554	0.015	0.291	0.223	0.360
n-Octane	2872	0.675	0.051	0.781	0.011	0.740	1551	1.512	0.429	0.004	0.097	0.061	0.162
n-Nonane	1788	0.139	<MDL	0.163	<MDL	0.152	1053	0.351	0.130	<MDL	0.038	<MDL	0.068
n-Decane	1390	0.038	<MDL	<MDL	<MDL	0.038	262	0.045	0.022	<MDL	<MDL	<MDL	0.010
n-Undecane	1118	0.010	<MDL	<MDL	<MDL	0.012	121	0.009	0.003	<MDL	<MDL	<MDL	0.006
n-Dodecane	822	0.002	<MDL	<MDL	<MDL	<MDL	85	0.003	0.001	<MDL	<MDL	<MDL	<MDL
n-Tridecane	644	<MDL	<MDL	<MDL	<MDL	<MDL	80	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
n-Tetradecane	213	<MDL	<MDL	<MDL	<MDL	<MDL	18	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
n-Pentadecane	62	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
n-Hexadecane	18	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Cyclohexane	9833	3.749	0.228	3.531	0.116	4.214	880	1.744	0.437	0.002	0.080	0.063	0.132
Methyl cyclohexane	8282	3.876	0.210	4.523	0.068	4.853	778	1.801	0.361	0.002	0.064	0.063	0.149

This table excludes E85 and gasoline through Viton gloves since BT exceeded 8 hr and target VOCs were not detected. This table excludes the gasoline - latex combination due to this material's failure. <MDL indicates measurement below method detection limit. SRM refers to a standard reference material (neoprene sheet) recommended by ASTM 739-99a method.

Table 3.3 Compositions of neat fuels and 8-hr permeation rates through six glove materials for diesel and B20 fuels.

	Diesel						Biodiesel (B20)					
	Neat Fuel	Latex	Nitrile	Neoprene	Vinyl	SRM	Neat Fuel	Latex	Nitrile	Neoprene	Vinyl	SRM
	Conc (mg/L)	PR (μg/cm^2-min)					Conc (mg/L)	PR (μg/cm^2-min)				
Aromatics												
Benzene	67	0.131	0.002	0.009	0.064	0.040	37	0.056	0.003	0.009	0.033	0.026
Toluene	238	0.498	0.023	0.038	0.314	0.190	214	0.334	0.053	0.053	0.231	0.180
Ethylbenzene	124	0.131	0.009	0.015	0.085	0.056	186	0.144	0.021	0.034	0.117	0.091
p-Xylene,m-xylene	420	0.357	0.027	0.040	0.238	0.158	496	0.296	0.056	0.067	0.224	0.193
o-Xylene	185	0.123	0.009	0.013	0.084	0.055	212	0.113	0.021	0.025	0.086	0.075
Isopropylbenzene	44	0.021	<MDL	<MDL	0.015	0.010	70	0.030	0.003	0.007	0.024	0.021
n-Propylbenzene	115	0.040	0.004	0.006	0.030	0.022	167	0.049	0.009	0.014	0.039	0.037
p-Isopropyltoluene	112	0.007	<MDL	<MDL	0.006	0.005	83	0.008	<MDL	0.003	0.007	0.007
4-Ethyl toluene	400	0.115	0.013	0.019	0.091	0.068	464	0.115	0.026	0.034	0.092	0.090
2-Ethyl toluene	194	0.048	0.006	0.008	0.039	0.029	264	0.062	0.013	0.018	0.049	0.050
1,3,5-Trimethylbenzene	202	0.044	0.005	0.007	0.036	0.027	150	0.032	0.007	0.009	0.025	0.026
1,2,4-Trimethylbenzene	720	0.133	0.019	0.025	0.113	0.088	575	0.098	0.027	0.032	0.078	0.083
1,2,3-Trimethyl benzen	2118	0.051	0.008	0.009	0.045	0.035	961	0.038	0.010	0.013	0.032	0.034
sec-Butylbenzene	90	0.014	<MDL	<MDL	<MDL	<MDL	117	0.021	<MDL	0.005	0.017	0.017
n-Butylbenzene	375	0.013	0.003	0.003	0.011	0.009	111	0.013	0.004	0.005	0.010	0.012
Styrene	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Naphthalene	3000	<MDL	<MDL	<MDL	<MDL	<MDL	1220	<MDL	<MDL	<MDL	0.000	<MDL
Alkanes												
n-Heptane	174	0.509	0.002	0.007	0.280	0.124	138	0.269	0.007	0.018	0.167	0.100
n-Octane	481	0.519	0.008	0.016	0.291	0.145	612	0.506	0.016	0.039	0.343	0.234
n-Nonane	7017	0.530	0.016	0.028	0.342	0.210	4118	0.597	0.031	0.084	0.454	0.369
n-Decane	7690	0.273	0.017	0.029	0.214	0.155	4311	0.252	0.023	0.056	0.197	0.199
n-Undecane	7729	0.110	0.014	0.018	0.096	0.079	4562	0.108	0.017	0.033	0.086	0.102
n-Dodecane	8369	0.030	0.007	0.006	0.023	0.021	5002	0.032	0.009	0.012	0.021	0.032
n-Tridecane	13437	0.010	0.002	<MDL	0.007	<MDL	7625	0.010	0.004	0.005	0.005	0.009
n-Tetradecane	10078	0.002	<MDL	<MDL	<MDL	<MDL	7131	0.002	<MDL	<MDL	<MDL	<MDL
n-Pentadecane	9028	<MDL	<MDL	<MDL	<MDL	<MDL	7581	<MDL	<MDL	<MDL	<MDL	<MDL
n-Hexadecane	9300	<MDL	<MDL	<MDL	<MDL	<MDL	5550	<MDL	<MDL	<MDL	<MDL	<MDL
Cyclohexane	191	0.860	0.001	<MDL	0.369	0.150	69	0.311	<MDL	0.011	0.173	0.079
Methyl cyclohexane	426	1.388	0.008	0.022	0.754	0.318	270	0.744	0.008	0.024	0.436	0.246

This table excluded B20 and diesel through Viton and nitrile Sol-Vex gloves since BT exceeded 8 hr and target VOCs were not detected. <MDL indicates measurement below method detection limit. SRM refers to a standard reference material (neoprene sheet) recommended by ASTM 739-99a method.

Table 3.4 Average daily dose of workers for three exposure scenarios.

	Unit	1. Fuel truck driver		2. Fuel attendant		3. Laboratory technician			
Inhalation parameters									
Concentration of THC in air	µg m^{-3}	63720	63720	47250	47250				
Concentration of benzene in air	µg m^{-3}	798	120	447	67				
Duration	hr	8	8	8	8				
Dermal exposure parameters									
Glove type		Nitrile Sol-Vex		Neoprene		Nitrile exam			
Fuel type		Gasoline	E85	Gasoline	E85	Gasoline	E85	Diesel	B20
Duration	hr	2.0	2.0	3.8	3.1	2.0	1.9	0.5	0.5
THC permeation rate	µg cm^{-2} min^{-1}	23.40	1.47	>65.60[A]	44.78	>63.30[A]	94.14	3.13	3.77
Benzene permeation rate	µg cm^{-2} min^{-1}	1.06	0.02	9.96	0.19	13.10	0.96	0.003	0.01
Dose									
THC inhalation exposure	µg kg^{-1} day^{-1}	4,612	4,612	3,420	3,420				
THC dermal exposure	µg kg^{-1} day^{-1}	8,424	528	>11198[A]	6,180	>2239[A]	3,301	26	36
Sum of THC exposure	µg kg^{-1} day^{-1}	13,036	5,141	>14618[A]	9,600	>2239[A]	3,301	26	36
Benzene inhalation exposure	µg kg^{-1} day^{-1}	57.72[B]	8.66[C]	32.33[B]	4.85[C]				
Benzene dermal exposure	µg kg^{-1} day^{-1}	381	7	6,804	27	463	34	0.02	0.06
Sum of benzene exposure	µg kg^{-1} day^{-1}	439	16	1,733	32	463	34	0.02	0.06

THC= total hydrocarbon. A : Exceeded the linear range of PID calibration.

B: Based on literature and may not reflect current exposures.

C: Assumed 15% of benzene inhalation exposure of gasoline and may not reflect current exposures.

Table 3.5 Ratings of selected PPE materials for gasoline, E85, diesel and B20 fuels based on BTs.

	Gasoline	E85	Diesel	B20
Latex	NR	NR	NR	NR
Vinyl	NR	NR	NR	NR
Nitrile	NR	NR	P	P
Neoprene	NR	P	G	G
Nitrile (Sol-Vex)	F	G	E	E
Viton	E	E	E	E

NR = Not recommended (BT ≤ 30 mins)
P = Poor (30< BT≤ 120 mins)
F = Fair (120< BT≤ 240 mins)
G = Good (240< BT≤ 480 mins)
E = Excellent (BT ≥ 480 mins)

Note: BT was defined as the time when PR reach 0.1 µg /cm^2 - min (toluene equivalent) measured by the PID and adjusted by correction factors for each fuel.

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Chapter 4

Characterization of exhaust emissions from diesel engines at various loads and speeds using B20 and ULSD fuels.

4.1 Abstract

Diesel exhaust contains numerous known toxic air pollutants and has been classified as a probable human carcinogen. A number of engine operation strategies, aftertreatment technologies and fuels have been developed to reduce exhaust emissions and meet increasingly stringent regulations. Limited information exists regarding emissions of many pollutants, such as benzene and other hydrocarbons, and the effect of using biodiesel fuels or blends on emissions is also unclear. This study investigates both regulated and unregulated chemicals emitted from two diesel engines using biodiesel blends (B20) and conventional ultra-low sulfur diesel (ULSD) fuels. The engines utilized a diesel oxidation catalyst (DOC), diesel particle filters (DPFs) and exhaust gas recirculation (EGR), and tests were performed at idle and several load conditions.

B20 and aftertreatment systems did not significantly affect engine performance (e.g., power and fuel consumption), therefore, emission comparisons for each test condition were valid across fuels and aftertreatments. Under load, B20 generally reduced emissions of particulate matter (PM), nonmethane hydrocarbons (NMHCs) and target volatile organic compounds (TVOCs), however, nitrogen oxides (NO_x) and formaldehyde

emissions increased at certain conditions. The DOC and catalyzed DPF converted a high fraction of carbon monoxide (CO), NMHC, formaldehyde, TVOC and PM (with DPF only) if exhaust temperature exceeded 250 °C. Importantly, for the DOC-equipped 2002 1.7 L engine, B20 gave lower DOC conversion efficiencies than ULSD, resulting in higher emissions of formaldehyde and several VOCs. This did not occur for the DPF-equipped 2007 6.4 L engine. Compared to ULSD, B20 increased emissions of PM_{10}, EC and formaldehyde from the 1.7 L engine (with and without the DOC) and from the 2004 6.4 L engine. B20 also increased TTVOC emissions from the DOC-equipped 1.7 L engine by 43-46%, which may due to lower DOC conversion efficiencies compared to ULSD.

Emissions depend strongly on fuel formulation, engine type, engine operating conditions, aftertreatment technologies, engine wear and maintenance, and many other factors. Idle emissions, which have not been well characterized, have attracted considerable attention at schools and other locations due to potentially high exposures. The emission profiles developed in this study demonstrate effects of the new fuels, engine calibrations, and emission control systems. They can also be used to update emission profiles used in modeling and inventory studies, including the toxic compounds associated with health risks.

4.2 Keywords

Biodiesel, diesel oxidation catalyst (DOC), diesel particle filter (DPF), emissions, volatile organic compounds.

4.3 Introduction

Due to environmental and health concerns, limits on diesel exhaust emissions have been imposed in many countries.[1-3] Diesel exhaust emissions depend on fuel formulation, engine type, emission control technology, engine age, maintenance and other factors. The use of alternative fuels, such as biodiesel, has rapidly grown in the transportation sector due to their potential to reduce emissions of conventional pollutants, e.g., particulate matter (PM), carbon monoxide (CO), nitrogen oxides (NO_x), and non-methane hydrocarbon (NMHC), as well as net carbon emissions, and also to improve energy security. In the U.S., ultra-low sulfur diesel fuel (ULSD, sulfur content less than 15 ppm) has been phased in since 2006 for on-road diesel vehicles,[4] and biodiesel blends also are widely available. Only a small fraction of U.S. light-duty vehicles (LDVs) are diesel, although most heavy-duty vehicles (HDVs) are diesel.[5] In Europe, diesel LDVs now predominate, and biodiesel fuels are also widely used, largely due to tax policies that have reduced the price of these fuels relative to gasoline, the historically high price of fuel, and the greater efficiency of diesel engines.[5, 6]

Increasingly stringent emission standards apply to the conventional or "regulated pollutants" in diesel exhaust.[7] A variety of control technologies are used to meet PM, CO, NO_x and NMHC emission standards. Exhaust gas recirculation (EGR) helps reduce NO_x emissions, which are primarily formed from the reaction of nitrogen and oxygen at high temperatures, by recirculating a portion of the exhaust gas, thus reducing the excess oxygen into the engine, and by reducing peak combustion temperatures. Diesel oxidation catalysts (DOC) oxidize CO, gas phase hydrocarbons, and some of the soluble organic fraction (SOF) of diesel particulate matter (DPM).[8] Diesel particle filters (DPFs), which require use of ULSD fuel, physically trap and remove PM from the exhaust stream, and achieve reductions of 90 percent or more.[9]

Effects of biodiesel fuels on diesel engine performance (and emissions) have been reviewed by Lapuerta et al. (2008)[10] and others.[11-13] Performance with biodiesel blends and conventional diesel fuels is usually similar, except that the brake-specific fuel consumption (BSFC) increases with the biodiesel fraction, reflecting the lower energy content of biodiesel.[10, 12, 13] For regulated pollutants, biodiesel fuels reduce smoke opacity, PM, CO and NMHC emissions, but increase NO_x emissions.[10, 11, 14-17]

Information regarding emissions of "unregulated" pollutants, which include individual species in both gaseous and particulate phases, e.g., volatile organic compounds (VOCs) like benzene and formaldehyde, and polycyclic aromatic hydrocarbons (PAHs) like benzo(a)pyrene, is less much complete than that for the regulated pollutants. Reduced emissions might be expected for biodiesel blends, given results observed for PM and NMHC, however, the literature is inconsistent and variable. In 2002, U.S. EPA identified 11 toxics in diesel exhaust (acetaldehyde, acrolein, benzene, 1,3-butadiene, ethyl benzene, formaldehyde, n-hexane, naphthalene, styrene, toluene and xylene), and stated that emissions would "increase or decrease when biodiesel is blended with diesel fuel, and of those <species> that decrease, the magnitude of that decrease will vary from one toxic to another".[18] More recent studies of carbonyl emissions, e.g., acetaldehyde and formaldehyde, show both increased[19-21] and decreased[22-24] emissions using biodiesel fuels. Information pertaining to unregulated emissions is particularly scarce for biodiesel fuels that meet current ULSD requirements, for modern engines with EGR and other after-treatment systems, and for various engine loads.

The use of biodiesel and other fuels, as well as exhaust controls such as DOC, are designed to reduce emissions and comply with emission limits. However, these strategies may change the composition and the toxicity of exhaust. While investigations of toxicity are beyond the scope of the present work, it is worth noting that some evidence exists for the increased toxicity of diesel exhaust from biofuels, some evidence exists for the reduced toxicity of diesel exhaust from biofuels and aftertreatment system. For example, Microtox tests examining the gaseous fraction of exhaust, show that B10 had higher acute toxicity and cytotoxicity than regular diesel for all test conditions, including idle.[19] In tests examining particle extracts from diesel exhaust using rape seed methyl ethers and rapeseed oil fuel blends, mutagenic effects increased compare to ULSD, although CO, PM and NMHC emissions were much lower than for ULSD (NO_x emissions increased up to 15%).[25] Using a Golf 1.9 L engine, a DOC and B100, PM oxidative potential was only reduced by 20% compared to diesel (sulfur <50 ppm) without a DOC (PM oxidative potential was determined by dithiothreitol (DTT) assay to evaluate the toxic activity from PM samples detailed in Cho et al. (2005).[26,27] Further investigation, which could use both laboratory and epidemiological approaches, is needed to explore these effects.

This objective of this study is to investigate both regulated and unregulated emissions from two diesel engines, and to compare emissions using conventional petroleum diesel (ULSD) to a biodiesel blend. Emissions are tested both with and without a DOC and a DPF, and at various loads.

4.4 Methods and Materials

The overall experimental design is shown in Table 4.1. It included tests conducted using two engines, two fuels, two to four speed/load conditions, and several engine-specific aftertreatments (described in Sections 4.4.1 and 4.4.2). A schematic of the sampling and analysis system is shown in Figure 4.1. Each type of measurement is described in turn (Sections 4.4.3 to 4.4.7).

4.4.1 Test engines, emission control systems and fuels

Two diesel engines were used (specifications are shown in Table 4.2). The first is a 2002 1.7 L displacement engine manufactured by General Motors (GM, Detroit, MI, USA), which is used in Honda and Opel vehicles. This engine is equipped with EGR and a platinum-based DOC, which was provided by GM and described elsewhere.[14] The second engine is a 2007 6.4 L "Power Stroke" engine manufactured by Ford (Detroit, MI, USA), which is used in small pick-up trucks, school buses, International trucks, and many other vehicles. This engine is equipped with an EGR system and designed to operate with a platinum/palladium catalyzed DPF and ULSD under 2007 emission calibration.

Two fuels were used: certificated ultra-low sulfur diesel fuel (ULSD, sulfur content <15 ppm); self-blended B20 containing 20% soy methyl ester (Peter Cremer North America, Cincinnati, OH, US) and 80% ULSD. Fuel properties are listed in Appendix Table A4.1, as analyzed by Paragon Laboratories (Livonia, MI, USA).

4.4.2 Test conditions

Test conditions are listed in Table 4.1. The 1.7 L engine was operated under 2002 emission calibration for all tests, including idle and three load conditions (200 kPa BMEP at 1500 rpm, 600 kPa BMEP at 1500 rpm, and 900 kPa BMEP at 2500 rpm), each with and without the DOC, and each with ULSD and B20 fuels. The 6.4 L engine was operated under calibrations for both 2004 and 2007 standards (Table 4.1). Under the

2004 calibration, the engine was operated under idle and two load conditions (600 kPa BMEP at 1500 rpm, and 900 kPa BMEP at 2500 rpm) without the DPF, each with ULSD and B20 fuels. Under the 2007 calibration, the engine was operated under idle and one load condition (900 kPa BMEP at 2500 rpm) with the DFP, each with ULSD and B20 fuels.

For both engines, the engine speed and brake mean effective pressure (BMEP) were the only two parameters adjusted; other parameters were controlled by the manufacturer's engine control unit (ECU), e.g., fuel amount, ignition timing, EGR percentage, etc. Measured power outputs and EGR percentages for each test are reported in Table 4.1. For the 1.7 L engine, the EGR was turned off manually for the 900 kPa BMEP tests due to an EGR cooler limitation, i.e., the EGR inlet temperature exceeded the 80 ^{o}C limit of the valve, which could damage it.

Each engine was fully warmed up before each test, including the idle test. To avoid contamination, the engine's lubricant oil (Mobil One 10W-30, Buffalo, NY, USA) was changed after switching fuels.

4.4.3 Emission measurements

After each engine operating condition stabilized, the sampling sequence was as follows: First, exhaust gases were sequentially measured by the combustion emission bench, smoke opacity and Fourier transform infrared (FTIR) spectrometer. Second, a partial flow dilution system collected PM_{10} on Teflon and quartz filters sequentially, and then exhaust gases on adsorbent-filled thermal desorption tubes (TDT) for speciated volatile organic compounds (VOCs). Finally, the emission bench, smoke opacity and FTIR spectrometer measurements were repeated.

4.4.4 Combustion emission bench and FTIR spectrometer

For the 1.7 L engine, CO, NO_x and NMHC were measured by a combustion emission bench (CEB II, AVL North America, Inc., Plymouth, MI, USA). Measured parameters are listed in Appendix Table A4.2.

Formaldehyde was measured using a Fourier transform infrared (FTIR) spectrometer (2030-HS high speed multi-gas analyzer, MKS Instruments, Inc., Andover, MA, USA). The FTIR also measured CO and NO_x, which closely matched measurements from the emission bench (within 10%). For the 6.4 L engine, the emission bench was not fully functional, thus NMHC measurements were unavailable; CO and NO_x measurements from the FTIR were used.

4.4.5 Smoke opacity

Smoke opacity was measured by a filter-paper-method smoke meter (AVL 415S, North America, Inc., Plymouth, MI, USA) using a reflectometer that compares the blackness of the filtered exhaust sample on a 0 to 10 filter smoke number (FSN) scale at 0.001 resolution. The black carbon (BC) concentration can be estimated through the following empirical equation:[28]

$$\text{BC (mg/m}^3) = 4.95\ K\ \text{FSN} \exp(0.38\ \text{FSN}) / 0.405 \tag{1}$$

where (unitless) $K = 1$ if $\text{FSN} \leq 8$, and $K = 1 + [(\text{FSN} - 8)/2]^{10}$ if $\text{FSN} > 8$. Based on the manufacturer's application notes[29] and empirical equations discussed by Northrop et al.,[25] FSN closely correlates to carbon concentrations, even at low soot conditions, therefore, BC concentrations can be calculated for comparison and discussion rather than FSN.

4.4.6 Filter particulate measurements

A partial flow dilution system (model BG-2, Sierra Emissions System, Inc., Dewitt, MI, USA) sampled particulate matter (PM_{10}). This unit, which meets the ISO 16183 method,[30] drew a partial flow (6-60 L/min) from the engine exhaust, which was then diluted with filtered house air (dilution ratio=1-10), passed through a cyclone to eliminate PM larger than 10 µm aerodynamic diameter prior, where it enters the sampling port. Depending on the test, sampling flow rates were 6-60 L/min, dilution ratios were 1-10, and sampling times were 2-40 min.

PM_{10} samples for gravimetric analysis were collected on Teflon filters (46.2 mm dia, PTFE membrane with support ring, Model 7592-104, Whatman Inc., Piscataway, NJ, USA). Both prior and following use, filters were conditioned at 25 ^{o}C and 33% relative humidity for at least 48 hr, and weighed to 1 µg accuracy using a microbalance (ME5, Sartorius, Edgewood, NY, USA).

PM_{10} for organic and elemental carbon (OC/EC) analyses was sampled on quartz filters (47 mm diameter, Type R-100, binder free, SKC Inc., Eighty Four, PA, USA). Prior to sampling, the filters were fired at 900 ºC for 3 hr, and stored in an air tight container at 5 ^{o}C. The filters were analyzed using a thermo/optical carbon analyzer (TOA, Sunset Laboratory Inc., Tigard, OR, USA) following the NIOSH method 5040 protocol,[31, 32] which entailed removing a 1.5 cm^2 rectangular punch from the filter, determining OC and EC mass, correcting for the filter's deposition area (11.94 cm^2), the exhaust flow rate, and dilution ratio. OC data was excluded due to absorption artifacts and sampling unit limitations. While the use of two sequential filters can help to compensate for artifacts,[33-35] the partial flow dilution system could only accommodate a single filter holder.

4.4.7 Speciated VOC measurements

The partial flow dilution system (descried earlier) was used to sample exhaust gases on adsorbent-filled thermal desorption tubes (TDT, stainless steel, 10 cm x 4 mm; Scientific Instrument Services, Inc., Ringoes, NJ, USA) containing 160 mg of Tenax GR and 70 mg of Carbosieve SIII. The dilution flow (~200 ml/min) was drawn by a personal sampling pump (224-PCXR8, SKC Inc., Eighty Four, PA, USA) for sampling times from 10 to 20 min, depending on tests. The flow rate was measured (Dry Cal DC-Lite, Bios International, Butler, NJ, USA) before and after sampling. A filter was placed upstream of the TDT to avoid particle accumulation. The TDTs were conditioned at 325ºC for 6 h before sampling. Duplicate VOC samples were collected sequentially, and a background (filtered air) sample was collected before running the engine.

VOC analysis protocols have been described elsewhere.[36-38] In brief, each TDT was spiked with 2 μL of the internal standard (containing 1 ng μL^{-1} each of fluorobenzene and p-bromofluorobenzene), then analyzed using a short-path thermal desorption/cryofocusing system (Scientific Instrument Services, Inc., Ringoes, NJ, USA) and gas chromatography/mass spectrometry (GC 5973/ MS 6890, Agilent, Palo Alto, CA, USA). VOC standards included a EPA 502/524 standard VOC Mix A, EPA 524 Rev 4 Update Mix (Supelco Inc., Bellefonte, PA, USA) and plus 26 other compounds, representing a total of 100 different target VOCs, e.g., alkanes, aromatics, halogenated, and phenols. The quality assurance and quality control (QA/QC) program included laboratory and field blanks, spiked and duplicate samples. All laboratory and field blanks were clean. Spiked (standard mixture) samples were analyzed to check the calibration of GC/MS. Method detection limits (MDLs), established using seven low concentration spiked samples, ranged from 0.04 to 2 μg m^{-3} depending on the VOC. Speciated VOC emissions were averaged from the two sequential samples for each condition and fuel, and the duplicate precision was usually less than 15%.

4.4.8 Data analysis

The brake mean effective pressure (BMEP) provides a means of normalizing power output across different engine displacements, thus allowing comparisons across different engines. This paper uses the BMEP values (in kPa) to describe test conditions (rather than speed or power). Brake specific emissions (g/kW-hr) were calculated and used for all conditions except idle, which has a brake specific power near 0 kW. For idling, emission rates were expressed as mass per time (g/hr or mg/hr).

Data analyses include calculation of means and standard deviations for each parameter, condition and fuel. Data from the emission bench, FTIR and smoke meter were averaged based on two to three measurements. The Student's T test (2 tails, at significance level $p = 0.05$) was used to examine the emission differences between ULSD and B20 fuels, and with and without aftertreatment, respectively. Statistical tests for some measurements may not be very useful when only a few samples were obtained, specifically, only one PM sample was collected for 1.7 L engine at all test conditions, and the 6.4 L engine at 2007 calibration; and only two samples were collected for target VOCs for all tests.

4.5 Results and Discussions

Results are first discussed for the 1.7 L engine in Section 4.5.1, and then for the 6.4 L engine in Section 4.5.2. Results from the two engines at the same conditions (i.e. idle and 900 kPa BMEP) are compared in Section 4.5.3. Section 4.5.4 discussed regulated emissions corresponding national emission standards. Section 4.5.5 discussed biodiesel and aftertreatment effects with respect to literature.

4.5.1 Results for 1.7 L diesel engine

4.5.1.1 Engine Performance Characteristics

Three performance characteristics, specifically, brake specific power (kW), brake specific fuel consumption (BSFC, gram fuel/kW-hr) and thermal efficiency (TE, %), were calculated and compared for B20 and ULSD fuels at three conditions (Figure 4.2). The DOC had no significant effect on performance; therefore, results were averaged by condition, regardless of the use of DOC. B20 and ULSD fuels yielded similar performance for same test condition, and no significant fuel effect on power, BSFC and TE. However, BSFC was slightly higher with B20 at 600 and 900 kPa BEMP (3.23 and 2.43%) than ULSD.

The performance results follow trends in the literature, e.g., using the BSFC empirical equation from U.S. EPA, BSFC increased by 1.02% with B20 fuel as compared to diesel fuel.[18] Other studies have shown similar power outputs, higher BSFC, and similar or slightly higher TE using biodiesel blends.[10, 13, 18] For example, Dobrucali et al. (2008) found that diesel and biodiesel blends yielded similar engine power (within 1.5%); BSFC generally increased with biodiesel content (maximum increase over diesel fuel was

16% using B100 at 75% load); and TE for biodiesel blends were similar or slightly higher than for diesel fuel (up to 7% using B100 at 25% load).[13]

4.5.1.2 CO, NOx, NMHC and PM_{10} emissions

Figure 4.3 displays emissions of the regulated pollutants for the 1.7 L engine, comparing results using ULSD and B20 fuels, with and without the DOC, and the four running conditions. Differences between ULSD and B20 fuels were not statistically significant for CO, NO_x and NMHC emissions. Differences with and without the DOC were statistically significant for CO and NMHC emissions at 600 and 900 kPa. Several trends are noted with respect to load. For CO, brake-specific emissions were highest at 200 kPa (both fuels), 6-12 times higher than seen at 600 and 900 kPa (Figure 4.3). The DOC eliminated 99.9% of CO at 600 and 900 kPa, but removals were negligible at 200 kPa due to the low exhaust temperature (160°C); the minimum temperature needed for effective removal is 250°C.

NO_x emissions increased at low loads, reaching about 6 g/kW-hr at 200 kPa (Figure 4.3). 600 and 900 kPa loads yielded comparable emissions (3.6-4.2 g/kW-hr). Several differences were seen between fuels: B20 yielded engine-out emissions about 10% higher at 200 kPa, 13% lower at 600 kPa, and 4% lower at 900 kPa than ULSD (at 600 and 900 kPa, the differences approached statistical significance, $p=0.07$). NMHC emissions reached a maximum at 200 kPa BMEP, and were about 4-5 times higher than at 900 kPa (Figure 4.3). B20 lowered engine-out emissions by 4-19% compared to ULSD (at 600 and 900 kPa, the changes that approached statistical significance, $p=0.06$). As seen with CO, DOC conversion rates at 200 kPa BEMP were minimal (18 and 26% for ULSD and B20, respectively). At higher loads, DOC reduced NMHC emissions statistically significant for both fuels, but interestingly, the DOC conversion rates were lower (45-76%) for B20 than for ULSD (74-92%).

For loaded conditions, PM_{10} emissions increased with BMEP (Figure 4.3), and differences between ULSD and B20 fuels were significant 600 and 900 kPa BMEP. B20 lowered emission rates by 14-24% compared to ULSD at 200, 600 and 900 kPa BMEP ($p=0.07$ including 200, 600 and 900 kPa BMEP; $p=0.03$ including 600 and 900 kPa BMEP only). The DOC did not significantly affect PM_{10} emissions at 600 and 900 kPa; however, at 200 kPa BMEP, PM_{10} emissions with the DOC were 42-56% lower than engine-out measurements for both fuels ($p=0.06$). Possibly, the DOC removed some vapor phase organics that partitioned to PM at 200 kPa BMEP (seen with NMHC, DOC conversion rates were 18-26%).

Idle emissions are also shown in Figure 4.3 in units of mass per time. B20 produced higher emissions of CO (by 12%, $p=0.03$), NMHC (11%, $p=0.01$) and PM_{10} (30%, $p=0.02$), but changes for NO_x where not significant (-2%, $p=0.46$), all compared to ULSD. Idle emissions were largely unaffected by the presence of the DOC. Overall, the idle emission trends for the two fuels were opposite of the three loaded conditions. (Idle emissions are further discussed in Section 4.5.3.)

A number of studies have shown that biodiesel fuels lower CO and NMHC emissions, but increase NO_x emissions compared to petroleum diesel.[10, 11, 14-16, 39-41] Similar trends were observed in this study, although most of the differences between the ULSD and B20 fuels used were not statistically significant. The low fraction of biodiesel used (20%), and the limited number of samples and tests might explain these results.

4.5.1.3 Black and elemental carbon

Emissions of BC (derived from filter smoke number <FSN> using eq. 1) and elemental carbon (EC, derived using thermal optical analysis <TOA> and a different filter) increased with engine load, like PM_{10} (Figure 4.4). BC and EC emissions using the two fuels were similar at idle and 200 kPa conditions. At 600 and 900 kPa BMEP, EC emissions using B20 were lower by 14-31% than using ULSD (p=0.05). The DOC did not affect BC and EC emissions.

The BC and EC measurements showed very high correlation (R^2 = 0.96-0.97) and slopes near 1 (0.99-1.04) across all conditions and fuels used (Figure 4.4b). TOA is applicable to low concentrations, and the EC measurements obtained are highly reproducible and often used in ambient air monitoring where it serves as a surrogate for diesel PM. Thus, EC measurements are especially valuable at low concentrations if high resolution measurements are needed. On the other hand, BC (FSN) is determined without exhaust dilution, therefore, this measure can be used to confirm the performance and calibration of the partial flow dilution system used for filter sampling.

4.5.1.4 Formaldehyde

Formaldehyde emissions are shown in Figure 4.5. While B20 produced somewhat higher emissions of formaldehyde (both with and without the DOC), differences between ULSD and B20 fuels were not statistically significant. The DOC significantly lowered formaldehyde emissions by 70-95% at 600 and 900 kPa for both fuels. Importantly, formaldehyde emissions at 200 kPa BMEP were considerably higher -- by 15 to 30 times -- than emissions at 600 and 900 kPa (p=0.01). The DOC further increased emissions by 17-20% at idle (p=0.01) and by 19-33% at 200 kPa BMEP (p=0.17) for both fuels. At idle and 200 kPa BMEP, the DOC was not expected to reduce formaldehyde emissions given the low exhaust temperatures, as seen for CO and NMHC emissions. However, increased emissions were unexpected. These results suggest a modest increase in formaldehyde emissions when the catalyst is cool.

4.5.1.5 Total target volatile organic compounds

Both fuel type and the presence of the DOC affected TTVOC emissions, following similar patterns as seen for NMHC (Section 4.5.1.2). Considering engine-out emissions, B20 lowered TTVOC emissions by 2, 22 and 25% at 200, 600 and 900 kPa BMEP, respectively, compared to ULSD. Differences at 600 and 900 kPa were statistically significant (p=0.01).

The DOC greatly reduced TTVOC emissions at higher loads for both fuels (p= 0.01-0.03), and DOC conversion rates were lower for B20 fuels (78-85%) than for ULSD (89-92%, p=0.04). DOC conversion rates at 200 kPa BEMP were only 19% for ULSD. (DOC-out tests for B20 at 200 kPa BMEP failed.) Given the low conversion rates for B20, DOC-out emissions with B20 exceeded ULSD at 600 and 900 kPa BMEP by 43-46% (p=0.04). At idle, B20 and ULSD yielded similar engine-out emission rates, and emissions were largely unaffected by the presence of the DOC.

TTVOC represented 7-22% of NMHCs, depending on the fuel, test condition and DOC status. Similar fractions (4-22%) have been reported in the literature using Tenax adsorbents for sampling diesel exhaust.[24, 42-44]

4.5.1.6 Target volatile organic compounds

18 aromatic and 9 n-alkanes compounds were detected in the exhaust (Table 4.3). Benzene, toluene, naphthalene and 1,2,3-trimethylbenzene were the top four aromatic compounds, and $C_{9\text{-}13}$ n-alkanes were abundant. Emissions of these VOCs followed

trends discussed earlier for TTVOC. Engine-out emissions for B20 fuel were generally lower than for ULSD, and reductions at 600 and 900 kPa were statistically significant for 15 VOCs, e.g., benzene was reduced by 2-25%, while toluene and p-,m-xylene were reduced by 22-32%. While changes were not statistically significant, B20 increased emissions of a few VOCs at 200 kPa BMEP, e.g., naphthalene emissions increased by 44% at 200 kPa BMEP (p=0.22), but decreased by 2-19% (p=0.19) at 600 and 900 kPa BMEP compared to ULSD, possibly due to particle/vapor partitioning. Emissions of C_{12-15} n-alkanes showed patterns similar to naphthalene.

The DOC significantly reduced emissions at 600 and 900 kPa BMEP of all detected VOCs with conversion rates for ULSD (72-99%) and B20 (48-98%). As seen for NMHC and TTVOC, DOC-out emissions of target VOCs at 600 and 900 kPa BMEP were higher for B20 than for ULSD due to low DOC conversion rates.

At idle (Table 4.4), B20 and ULSD had similar engine-out emission rates of VOCs, and the DOC made little difference. B20 had higher DOC-out emissions than ULSD, e.g., DOC-out benzene emissions for B20 was 55% higher than for ULSD), as seen for other conditions.

4.5.2 Results for 6.4 L diesel engine

This section discusses exhaust emissions from the 6.4 L engine for 2004 and 2007 calibrations, the latter using the catalyzed DPF (Table 4.5). NMHC measurements were unavailable due to equipment issues.

4.5.2.1 CO, NOx and PM_{10}

For the 2004 calibration, CO and NO_x emissions decreased with increasing BMEP, but PM_{10} emissions increased. These results applied to both ULSD and B20 fuels.

Differences between fuels were statistically significant at 600 and 900 kPa BMEP (except for CO emission at 600 kPa BMEP). B20 lowered emissions of CO (by 14%) and PM_{10} (by 24-28%), but increased emissions of NO_x (by 15-20%) emissions. At idle, B20 increased emissions of CO, PM_{10} and NO_x (21, 87 and 10% increases over ULSD, respectively), showing a different emission pattern than the load conditions.

For the 2007 calibration, differences in CO and NO_x emissions using ULSD and B20 fuel were statistically different at idle and 900 kPa BMEP. (PM emissions could not be tested due to the small sample size). At idle, B20 lowered emissions of CO (by 15%) and PM_{10} (82%), but increased NO_x (23%). However, at 900 kPa BMEP, B20 lowered CO (28%) emissions, but increased NO_x (15%) and PM_{10} (25%) emissions.

As expected, CO and PM_{10} emissions for the 2007 calibration (using the catalyzed DPF) were lower than for the 2004 calibration (without DPF). These differences were statistically significant and applied to both fuels and all test conditions. At idle, NO_x emissions for the 2007 calibration were lower (66-70%, p=0.00) than those for the 2004 calibration. At 900 kPa BMEP, however, NO_x emissions for the 2007 calibration were about 2.5 times higher than for the 2004 calibration (p=0.01). While CO and PM_{10} emissions were reduced using the 2007 calibration, NO_x emissions at loads need further adjustment on this engine with the controls used.

4.5.2.2 Black and elemental carbon

For the 2004 calibration, BC and EC emissions were highly correlated across all test conditions, e.g., ULSD gave a slope of 0.94 and R^2= 0.98), and B20 gave a slope of 0.99 and R^2= 0.97. Emissions followed patterns shown for PM_{10} (Table 4.5). For the 2004 calibration and loaded conditions, B20 lowered BC and EC emissions by 34-46%

(p=0.00-0.02) compared to ULSD; at idle, B20 increased BC and EC emissions by 15-50% (p=0.03). Much of the difference between PM_{10} and EC is the organic matter (OM) fraction (Figure 4.6). At idle, EC comprised only a small fraction (3-4%) of PM_{10}, thus, the bulk of PM_{10} was organic matter (OM), e.g., unburned fuel and oil. At load (600 and 900 kPa BMEP), the OM fraction decreased significantly, probably a result of improved combustion. Comparing the two fuels, B20 increase the OM fraction compared to ULSD.

The 2007 calibration using the DPF significantly reduced BC and EC emissions. In fact, BC and EC levels fell below method detection limits.

4.5.2.3 Formaldehyde

Formaldehyde emission patterns were similar to those for CO (Table 4.5). These emissions were significantly affected by fuel in all tests except for the 2004 calibration at 600 kPa BMEP. For the 2004 calibration, B20 increased emissions at idle (by 29%), but lowered emissions at load (by 7-13%). For the 2007 calibration, B20 lowered emissions both at both idle (29%) and load (23%). As expected, the 2007 calibration had lower emissions than the 2004 calibration; these differences were statistically significant and applied to for both fuels and all test conditions.

4.5.2.4 Total target volatile organic compounds (TTVOC)

B20 fuel gave lower TTVOC emissions than ULSD (Table 4.5). For the 2004 calibration, B20 lowered emissions by 13 to 32% (statistically significant at 600 and 900 kPa BEMP, idle p=0.11). For the 2007 calibration at 900 kPa BMEP, B20 fuel lowered emissions by 76%, (p=0.08). As for formaldehyde, TTVOC emissions for the 2007 calibration were all significantly lower than those for the 2004 calibration, e.g.., 65% and

91% reductions were seen for ULSD and B20, respectively, at 900 kPa BMEP. (Formaldehyde emission measurements failed at idle.)

4.5.2.5 Target volatile organic compounds

19 aromatics and 10 alkanes were detected with compositions that depended on engine calibration and test condition (Table 4.5). For the 2004 calibration idle and 600 kPa BMEP tests, benzene and toluene were the top two aromatic VOCs, and n-nonane and n-decane were the top two aliphatic VOCs; at 900 kPa BMEP, the composition shifted to naphthalene, 2-methylnaphthalene, 1,2,4-trimethylbenzene, n-dodecane and n-tridecane.

B20 lowered emissions of most VOCs compared to ULSD, as shown earlier for TTVOC. For the 2004 calibration and idle and 600 kPa BMEP tests, B20 lowered VOC emissions by 14 to 58%, except for benzene using ULSD at idle (9% increase, p=0.01); at 900 kPa BMEP, VOC emissions for the two fuels were similar, although B20 increased benzene by 52% (p=0.17). For the 2007 calibration at 900 kPa BMEP, B20 lowered (13-88 %) emissions of most VOCs, but changes were small and not statistically significant.

As expected, the 2007 calibration (using the catalyzed DPF) significantly reduced VOC emissions at load (900 kPa, both fuels) compared to the 2004 calibration (without DPF). Reductions ranged from 83 to 99% for B20, and from 42 to 99% for ULSD, depending on the VOC.

4.5.3 Comparison of emissions from the two engines

The 1.7 and 6.4 L engines were both operated at idle and 900 kPa BMEP conditions. Emissions from the smaller engine using the 2002 emission calibration were expected to be higher than those for the larger engine, which were designed to meet newer (2004 and 2007) and more stringent emission standards.[45, 46] However, two cases have not been investigated thoroughly and thus are particularly interesting: emissions at idle, and effects of biodiesel blends.

4.5.3.1 Idle emissions and comparison to load conditions

For the 1.7 L engine at idle (without DOC), engine-out emissions of NMHC and formaldehyde were the highest among tests and 4-15 times higher than other three load conditions (based on emission expressed as mass/hour); CO emissions were higher than the 600 kPa BMEP test by 3-4 times; PM_{10} were higher than 200 kPa BMEP test by 1.5-2 times; while BC, EC, NO_x and TTVOC were all lower than loaded conditions. The DOC had little effect on emissions at idle.

For the 6.4 L engine at idle under the 2004 calibration (without the catalyzed DPF), emissions of CO, NO_x, PM_{10}, BC, EC and TTVOC were all lower than the loaded conditions. Emissions of formaldehyde were similar to the loaded conditions. Under the 2007 calibration with catalyzed DPF, emissions of NO_x, PM_{10} and formaldehyde were lower, but CO emissions were higher than the load condition (900 kPa BMEP). BC and EC measurements were below detection limits, and TTVOC measurements failed at idle under 2007 calibration.

B20 increased emissions of PM_{10}, EC and formaldehyde compared to ULSD for the 1.7 L engine, both with and without the DOC, and for the 6.4 L engine using the 2004 calibration (Figure 4.7). B20 increased TTVOC emissions for the 1.7 L engine with DOC.

4.5.3.2 Idle tests and comparison to the literature

Despite its much smaller displacement, at idle emissions from the 1.7 L engine of CO (77 g/hr), NO_x (13 g/hr), EC (31 g/hr), formaldehyde (3.8 g/hr) and TTVOC (625 mg/hr) were two or more times higher than the 6.4 L engine; however, PM_{10} emissions for B20 from the 1.7 L engine and the 6.4 L engine (2004 calibration) were similar (Figure 4.7, Appendix Table A4.3). Emissions of most VOCs from the 1.7 L engine were also higher than those for the 6.4 L diesel engine, e.g., naphthalene emissions were 25 and 30 times higher for ULSD and B20, respectively.

In the literature, emissions while idling span a wide range. Most of the relevant literature focused on heavy-duty diesel vehicles using conventional fuels (not ULSD or biodiesel blends) with limited emission control systems. Khan et al. (2000) examined 19 medium heavy-duty diesel vehicles (HDDVs) with model years from 1974 to 2001 and no EGR, DOC or DPF, finding average emission rates of 10 to 45 g/hr of CO, 34 to 161 g/hr of NO_x, 1 to 20 g/hr of NMHC, and 4 g/hr of PM_{10} emissions.[47] Several years later, the same group examined 75 HDDVs from 1969 to 2005, again without EGR, DOC or DPF, and emissions averaged 20 to 35 g/hr of CO, 48 to 86 g/hr of NO_x, 6 to 23 g/hr of NMHC, and 1-4 g/hr of PM_{10}.[48] Six school buses using Caterpillar engines equipped with DOC had idle emissions of 30 g/hr of CO, 65 g/hr of NO_x, 17 g/hr of NMHC, and 350 mg/hr of PM_{10}.[49]

Compared to the literature, the 1.7 L engine at higher idle emissions of CO and NMHC, but lower emissions of NO_x and PM_{10} emissions, while the 6.4 L engine had higher emissions of NO_x, while emissions of CO and PM_{10} were similar to findings of Kinsey et al. (2007).[49] These results suggest that the engine calibration and ULSD effectively lowers NO_x and PM_{10} emissions at idle, though effects on CO and NMHC are limited, probably due to incomplete combustion and conversion by the DOC.

Idle emissions have drawn considerable attention, including the development of management strategies, especially for school buses.[50] For example, California EPA established an idle emission reduction program in 2005 which required that 2008 and newer HDDVs have a (non-programmable) engine system that automatically shuts down the engine after five min of idling.[51]

4.5.3.3 900 kPa BMEP

Emissions of CO, EC, PM_{10} formaldehyde and TTVOC from the 1.7 L diesel engine (without the DOC) exceeded emissions from the 6.4 L engine (2004 calibration) by 1.7-5.6 times (Appendix Table A4.4). As described earlier (Sections 4.5.1 and 4.5.2), the DOC reduced CO, formaldehyde and TTVOC emissions for the 1.7 L engine, and the catalyzed DPF reduced EC, PM_{10}, CO, formaldehyde and TTVOC emissions for the 6.4 L engine. The 2007 calibration of the 6.4 L engine resulted in higher NO_x emissions than the 1.7 L engine, and also higher NO_x emissions of the 6.4 L engine with the 2004 calibration. Other than the high load case for NO_x, the lowest emissions of all pollutants were achieved by the 2007 calibration of the 6.4 L engine.

4.5.4 Comparison to regulated emission standards

In the U.S., emissions of light-duty diesel vehicles are regulated using federal test procedure 75 (FTP-75), which uses a simulated driving cycle and expresses emission limits as mass/distance (g/mile, g/km). The conditions used in the present study were primarily designed to evaluate effects of fuels and aftertreatments, and they are not directly comparable to results obtained using the FTP-75 procedure. However, to provide a rough comparison of the test results to the standards, the following was assumed: vehicle speeds of 35, 40 and 70 mile/hr for tests of 200 kPa BMEP at 1500 rpm, 600 kPa BMEP at 1500 rpm, and 600 kPa BMEP at 2500 rpm, respectively (Table 4.6).

Emissions from the 1.7 L diesel engine (model year 2002) were compared to Tier 1 standards (FTP-75), and also the supplemental FTP (SFTP) standards, which account for emissions during aggressive highway driving (US06) and while the vehicle's air conditioning system is operating (SC03).[45, 52] Tier 1 standards were defined for light-duty vehicles in the Clean Air Act in 1990, and were phased-in between 1994 and 1997; the Tier 1 SFTP were phased in between 2000 and 2004.[45] The 1.7 L diesel engine exceeded Tier 1 standards for several conditions and each pollutant (Table 4.6), e.g., NMHC emissions exceeded limits at 35 mile/hr using ULSD without the DOC; and NO_x exceeded limits at 40 mile/hr using ULSD without the DOC. At 70 mile/hr, emissions did not exceed Tier 1 SFTP standards for any fuel and aftertreatment, although NO_x exceeded limits for FTP-75 test.

Regulated emissions from heavy-duty diesel vehicles are measured in dynamometer tests and are expressed in g/kW-h units using a transient FTP cycle. Both 2004 and 2007 emission standards[53] were used to compare results obtained using the 6.4 L diesel engine (Table 4.7). CO and PM_{10} emissions attained standards, while NO_x emissions exceeded the 2004 standards by up to a factor of 2 and 2007 standards by nearly 50-fold.

Overall, emissions of 2002 1.7 engine under load conditions were acceptable with Tier 1 and SFTP standards, but it is clear that strategies for reducing NO_x emissions of the 6.4 engine were needed for both 2004 and 2007 calibrations. Since the tests in this study neither used the FTP-75 procedure (applicable to light-duty diesel vehicles) nor the transient FTP cycle test (applicable to heavy-duty diesel engines), the comparison to standards is approximate. Further, the assumptions used may be simplistic. However, the tests might represent certain driving conditions, e.g., the 6.4 L diesel engine at 2,500 rpm and 900 kPa BMEP can represent a school bus or large truck at highway speeds. This comparison helps to interpret test results in the context in which emission measurements are usually conducted.

4.5.5 Comparison to the literature

This section examines effects of biodiesel fuels and aftertreatment technologies, emphasizing tests in the literature. Studies have reported emissions obtained under transient FTP, new European driving cycle (NEDC) and steady-state conditions, and the engines and test conditions used do not exactly match those in this study. Thus, general trends are emphasized.

4.5.5.1 Effect of biodiesel fuels

In comparison to petroleum diesel, biodiesel fuels have been reported to lower emissions of CO, NMHC and PM_{10}, but to increase NOx emissions.[10, 11, 14-18] EPA established correlations for biodiesel on CO, NMHC, PM_{10} and NO_x using measurements of 43 unmodified heavy duty diesel engines presenting transient FTP. Using these correlations and assuming 20% biodiesel, emissions of CO, NMHC and PM_{10} are predicted to decrease by 12, 20 and 15%, respectively, and NO_x increase about 1.9%, as compared to diesel fuel with ~300 ppm sulfur.[18] Similar patterns were observed in the present study, for example, for the 6.4 L engine under the 2004 calibration at 900 kPa

BMEP, B20 lowered emissions of CO (by 14%) and PM_{10} (by 28%), but increased greater amount of NO_x (by 20%) emissions than transient FTP.

The effect of biodiesel on formaldehyde emissions remains uncertain. Formaldehyde emissions using biodiesel blends, as compared to petroleum diesel, have both decreased[18, 22, 24] and increased[19-21, 44] without clear patterns. In the present study, B20 increased formaldehyde emissions from the 1.7 L diesel engine under all tests without DOC (DOC results discussed in next section), but B20 reduced emissions from the 6.4 L diesel engine under load (600 and 900 kPa BMEP).

For most aromatic pollutants, biodiesel fuels generally have lowered emissions compared to conventional diesel, although emissions of benzene and several other VOCs sometimes increase.[10] EPA reported consistent reductions in ethylbenzene, naphthalene and xylene using biodiesel, however, EPA did not draw conclusions for benzene, toluene and styrene due to the variation in the literature.[18] The literature contains a number of engine studies tested using a variety of biodiesel blends. Using a six cylinder heavy-duty diesel engine without aftertreatment, B20 (20% biodiesel from castor oil, 80% Brazil commercial diesel) yielded a 21% reduction in the total of eight monoaromatic hydrocarbons (benzene, toluene, ethyl benzene, o-xylene, m,p-xylenes,1,2,4-trimethyl benzene and 1,3,5-trimethyl benzene) compared to Brazil commercial diesel.[54] Using a 0.4 L single cylinder engine, emissions of carbon number C_4, C_6 and C_8 VOCs increased using B30 (30% biodiesel from used fried oils, 70% European diesel fuel), compared to diesel fuels.[55] Using a 7.8 L 6-cylinder diesel engine without aftertreatment systems, B20 (20% rapeseed oil, 80% diesel fuel) increased benzene emissions, but decreased toluene and xylene emissions compared to diesel fuel (sulfur <300 ppm).[20] Using a 4.3 L 4-

cylinder diesel engine without aftertreatment systems, biodiesel (waste cooking oil) increased benzene emissions but decreased toluene and xylene emissions, compared to Chinese ULSD (sulfur <50 ppm).[24] Sharp et al. (2000) tested three heavy-duty diesel engines under transient FTP using B20 (20% soy methyl ether, sulfur =370 ppm) and diesel (sulfur =476 ppm), and found speciated $C_{1\text{-}12}$ VOC emissions varied depending on engine as followed: For a Cummins 14 L engine, B20 lowered 13% of total speciated $C_{1\text{-}12}$ VOC emissions, but increased benzene emission by 44% compared to diesel (sulfur =476 ppm); For a Detroit Diesel Corporation Series 50 engine, B20 had same levels of speciated $C_{1\text{-}12}$ VOC and benzene emissions compared to diesel; For a Cummins 5.9 L engine, B20 lowered 5% of total speciated $C_{1\text{-}12}$ VOC emission, but increased benzene emission by 3% compared to petroleum diesel.[56] Using a 5.9 L Cummins (Interact System B, ISB), B20 increased benzene emissions compared to ULSD, and B100 increased naphthalene emissions, compared to ULSD.[57] Of these studies, most found similar reduction trends as NMHC for total speciated VOCs, but benzene emissions sometimes observed increment with biodiesel blends. In this study, B20 generally reduced total speciated VOC emissions, although VOC emissions increased for 1.7 L diesel engine with DOC.

4.5.5.2 Effects of aftertreatment technology

DOC conversion efficiencies using biodiesel blends have been evaluated in several studies. Sharp et al. (2000) tested two heavy-duty diesel engines under transient FTP with and without DOC using B20 (20% soy methyl ether, sulfur =370 ppm) and diesel (sulfur =476 ppm), and found speciated $C_{1\text{-}12}$ VOC emissions varied depending on engine as followed: For a Detroit Diesel Corporation Series 50 engine, DOC had lower conversion rate for B20 (20%) than diesel (40%) based on total speciated C_{1-12} VOC emissions, therefore resulted in B20 with DOC had 33% higher total speciated C_{1-12} VOC emission than diesel with DOC (e.g., benzene emission for B20 with DOC were 5% higher than diesel with DOC); For a 5.9 L Cummins engine using B20, DOC conversion rates for total speciated C_{1-12} VOC emission was 23%, and for benzene emission was 27%. The comparison to diesel fuel with DOC was omitted because the DOC-out total speciated C_{1-12} VOCs emissions were 48% higher than engine-out emissions for diesel fuel, e.g. DOC-out benzene emission were 19% higher than engine-out emissions. Possibly, the variation of speciated VOC emission was large for that engine or DOC was not working properly.[56] Using the two engines described above, DOCs increased formaldehyde emissions regardless of fuels and engines.[56] Using Golf 1.9 L engine under NEDC, a DOC with B100 reduced PM emissions by 43%, but resulted in similar OC and water soluble organic carbon (WSOC) emissions compared to conventional diesel (sulfur <50 ppm) without a DOC.[27] Of these studies with DOC, speciated VOC emissions varied depending on engine and test condition, and difficult to make conclusion.

The joint use of DFP and ULSD on heavy-duty diesel engines significantly reduces emissions of CO, PM, NMHC, aromatics, alkenes, carbonyls, PAHs, hopanes and steranes, compared to base diesel fuels or baseline tests.[27, 35, 43, 58, 59] Catalyzed DPF effectively removed PM, PM-associated PAHs, and total nitro-PAHs, and also effectively converted gaseous hydrocarbons, however, catalyzed DPF-out formaldehyde emissions increased compared to engine-out emissions obtained using both ULSD and B20.[57]

In this study, the DOC lowered CO and NMHC emissions, but B20 obtained lower conversion rates for NMHC, formaldehyde and target VOCs compared to ULSD, thus emissions using B20 were higher than those using ULSD. With the catalyzed DPF, most emissions were significantly reduced, but NO_x emissions increased; this applied to both ULSD and B20 fuels.

The formation of benzene and aromatics is generally explained by reactions involving acetylene and light hydrocarbons, by cyclization reactions, and by the combination of propargyl radicals.[60] Benzene serves as a precursor to form polycyclic aromatic hydrocarbons (PAHs), and PAHs are precursors to soot.[61, 62] Due to the toxicity and health concerns of such compounds, it is important to evaluate emissions of unregulated compounds for modern engines and advanced aftertreatment technologies.

4.6 Conclusion

This study investigated two diesel engines equipped with various exhaust aftertreatment systems, and focused on comparing emissions using biodiesel and conventional (petroleum) fuels. In addition to the conventional pollutants, monitoring included non-regulated pollutants, including speciated VOCs and EC. Along with compositional changes, biodiesel fuels and blends affect fundamental fuel properties, e.g., viscosity, density, vapor pressure and heat value, all of which can affect emissions.

Tests conducted using the 1.7 L diesel engine equipped with EGR and a DOC included idle and three load conditions and both B20 and ULSD fuels. Engine power output, BSFC and thermal efficiencies were unaffected by fuels or the DOC. In general, B20 reduced PM and NMHC emissions, and did not significantly change CO and NO_x emissions. At high loads (600 and 900 kPa BMEP) when its operating temperature was reached, the DOC removed 45 to 100% of the CO and NMHC. However, the DOC conversion efficiency for NMHC using B20 fuels was significantly lower than for ULSD at high loads. Emissions of other pollutants depended on fuels, test conditions, and the presence of the DOC. Compared to ULSD, B20 reduced emissions of most VOCs, however, with the DOC and for certain conditions, emissions of several VOCs increased, including aromatic compounds.

The second engine had a displacement of 6.4 L and was operated under a 2004 calibration without a DPF, and also using a 2007 calibration with EGR and a DPF. For the 2004 calibration, B20 lowered CO and PM_{10} emissions compared to ULSD, however, NO_x emissions were about 20% higher. At idle, B20 produced higher emissions of CO, NO_x, PM_{10}, EC, formaldehyde and benzene emissions. For the 2007 calibration and at high load (900 kPa BMEP), emissions of CO, PM_{10}, EC, formaldehyde and TTVOC were all reduced compared to the 2004 calibration for both ULSD and B20. In comparison to the two engines, the 6.4 L engine had lower emissions of all measured pollutants than the 1.7 L engine except for NO_x emissions.

Unregulated emissions, which usually comprise a small fraction of gaseous and particulate emissions, can be important due to their known or potential toxicity and health impact. In particular, benzene and formaldehyde emissions depend strongly on fuels and exhaust gas treatments. Engine combustion, emission control strategies and other processes that form or affect these emissions are very complex.

This work demonstrates the dependence of the composition and emission rates of diesel exhaust, including both regulated and unregulated components, on fuel, engine calibration, and treatment technology. The results should facilitate the development of emission profiles that include toxic species, which are useful for both emission inventories and receptor modeling aimed at identifying and apportioning the sources of ambient air pollutants.

Table 4.1 Experimental design and test conditions.

Test	Engine	Fuel	Emission calibration	BMEP (kPa)	Speed (rpm)	After treatments	Power (kW)	EGR (%)
1	1.7 L Isuzu / General Motor	ULSD	2002	idle	800	EGR	NA	27
2				200	1500	EGR	4	20
3				600	1500	EGR	13	17
4				900	2500	None	32	NA
5				idle	800	DOC/EGR	NA	27
6				200	1500	DOC/EGR	4	20
7				600	1500	DOC/EGR	13	17
8				900	2500	DOC	32	NA
9		B20	2002	idle	800	EGR	NA	27
10				200	1500	EGR	4	20
11				600	1500	EGR	13	17
12				900	2500	None	32	NA
13				idle	800	DOC/EGR	NA	27
14				200	1500	DOC/EGR	4	20
15				600	1500	DOC/EGR	13	17
16				900	2500	DOC	32	NA
17	6.4 L Ford	ULSD	2004	idle	665	EGR	NA	2
18				600	1500	EGR	49	10
19				900	2500	EGR	120	19
20			2007	idle	665	DPF/EGR	NA	2
21				900	2500	DPF/EGR	120	15
22		B20	2004	idle	665	EGR	NA	2
23				600	1500	EGR	49	10
24				900	2500	EGR	120	19
25			2007	idle	665	DPF/EGR	NA	2
26				900	2500	DPF/EGR	120	15

NA: not applicable

Table 4.2 Engine specifications.

Designer/Manufacturer	Isuzu/General Motor	Navistar International/Ford
Model year	2002	2008
Number of cylinders	4	4
Displaced Volume (L)	1.7	6.4
Compression ratio	16:1	16.7:1
Bore (mm)	79	98
Stroke (mm)	86	105
Fuel system	Direct-Injection common rail	Direct-Injection, high pressure common rail, piezoelectric actuation
Exhaust Gas Recirculation (EGR)	Poppet-style control valve	Dual EGR coolers with EGR exhaust catalysts
Aspiration	Variable Geometry Turbocharger	Two compound turbochargers, smaller turbo uses variable geometry turbine
Horsepower	100 bhp @ 4400rpm	350 bhp @ 3000 rpm

Table 4.3 Target VOC emissions for the 1.7 L diesel engine.

BMEP (kPa)	200				600				900			
Fuel	ULSD	ULSD	B20	B20	ULSD	ULSD	B20	B20	ULSD	ULSD	B20	B20
Aftertreatment	None	DOC	None	DOC	None	DOC	None	DOC	None	DOC	None	DOC
Unit	(mg/kW-h)		(mg/kW-h)		(mg/kW-h)		(mg/kW-h)		(mg/kW-h)		(mg/kW-h)	
Sum of aromatics	**96.85**	**85.59**	**91.64**	**NA**	**20.64**	**1.71**	**16.31**	**2.13**	**42.43**	**4.45**	**35.12**	**6.58**
Benzene	41.74	34.27	37.90	NA	8.99	0.11	6.72	0.10	12.40	0.88	12.14	0.86
Toluene	16.84	16.51	13.15	NA	2.16	0.15	1.46	0.10	4.05	0.38	3.01	0.35
Ethylbenzene	1.64	1.70	1.35	NA	0.22	0.04	0.17	0.03	0.40	0.05	0.31	0.07
p-,m-xylene	3.35	4.21	2.63	NA	0.43	0.10	0.30	0.07	0.86	0.13	0.59	0.15
o-xylene	1.56	1.96	1.27	NA	0.20	0.04	0.15	0.03	0.40	0.06	0.28	0.06
4-ethyltoluene	1.56	1.81	1.38	NA	0.21	0.05	0.18	0.03	0.46	0.09	0.35	0.09
2-ethyltoluene	1.15	1.36	1.12	NA	0.15	0.03	0.15	0.02	0.35	0.07	0.29	0.06
1,2,3-trimethylbenzene	9.24	6.90	8.39	NA	2.50	0.23	1.87	0.21	5.19	0.68	3.46	0.75
1,2,4-trimethylbenzene	1.68	2.02	1.60	NA	0.29	0.07	0.26	0.05	0.61	0.13	0.48	0.13
1,3,5-trimethylbenzene	0.38	0.48	0.43	NA	0.08	0.02	0.08	0.01	0.14	0.03	0.13	0.03
Styrene	3.14	3.56	2.64	NA	0.61	0.04	0.45	0.03	1.25	0.16	0.99	0.15
Isopropylbenzene	0.16	0.19	0.14	NA	0.02	< MDL	0.02	< MDL	0.04	< MDL	0.03	< MDL
n-propylbenzene	0.55	0.63	0.55	NA	0.07	< MDL	0.07	0.01	0.18	0.03	0.15	0.04
p-Isopropyltoluene	0.30	0.26	0.28	NA	0.08	0.01	0.06	0.01	0.15	0.02	0.11	0.02
n-butylbenzene	1.87	1.26	1.77	NA	0.54	0.05	0.43	0.05	1.15	0.15	0.83	0.19
Naphthalene	11.30	7.98	16.24	NA	3.86	0.75	3.78	1.32	14.02	1.50	11.34	3.45
2-methylnaphthalene	0.30	0.33	0.55	NA	0.14	0.02	0.12	0.04	0.52	0.04	0.43	0.11
1-methylnaphthalene	0.12	0.15	0.26	NA	0.07	0.01	0.06	0.02	0.24	0.02	0.21	0.05
Sum of alkanes	**110.88**	**82.65**	**111.42**	**NA**	**42.29**	**3.34**	**33.07**	**5.07**	**86.98**	**9.85**	**61.64**	**14.31**
n-octane	0.71	0.86	0.66	NA	0.36	0.04	0.20	0.10	0.27	0.08	0.25	0.17
n-nonane	28.77	22.31	22.20	NA	8.36	0.38	5.96	0.43	11.54	1.51	7.71	1.36
n-decane	22.00	17.53	18.46	NA	6.90	0.38	5.15	0.34	9.97	1.37	6.81	1.09
n-undecane	17.68	14.97	16.01	NA	6.24	0.48	4.70	0.52	10.46	1.57	7.19	1.53
n-dodecane	16.18	11.94	17.50	NA	6.73	0.65	5.35	0.98	14.14	1.80	10.00	2.63
n-tridecane	20.93	12.98	27.81	NA	10.47	1.08	8.71	2.02	26.48	2.52	19.58	5.18
n-tetradecane	3.37	1.73	5.59	NA	2.12	0.19	1.75	0.39	7.03	0.50	5.09	1.18
n-pentadecane	0.86	0.27	1.82	NA	0.67	0.06	0.62	0.13	3.34	0.28	2.47	0.59
n-hexadecane	0.38	0.06	1.38	NA	0.44	0.08	0.62	0.15	3.75	0.23	2.54	0.60
TTVOCs	**207.73**	**168.24**	**203.06**	**NA**	**62.93**	**5.05**	**49.38**	**7.20**	**129.41**	**14.29**	**96.77**	**20.90**
TTVOCs / NMHC (%)	**6.57**	**6.46**	**8.09**	NA	**12.54**	**12.39**	**11.84**	**7.23**	**21.61**	**9.24**	**17.04**	**6.65**

CE %: DOC conversion efficiency. NA: data not available. < MDL: below method detection limit. TTVOC: sum of target VOCs.

Table 4.4 Idle emission measurements for the 1.7 L diesel engine.

Condition	Idle			
Fuel	ULSD	B20	ULSD	B20
Aftertreatment	None	None	DOC	DOC
unit	(mg/h)			
Benzene	110.79	128.93	79.75	123.96
Toluene	48.53	49.81	37.47	51.64
Ethylbenzene	5.59	6.18	4.09	6.55
p-,m-xylene	11.03	10.51	8.65	10.89
o-xylene	5.55	5.27	4.22	5.34
4-ethyltoluene	6.04	5.75	4.52	5.70
2-ethyltoluene	4.75	2.73	3.63	4.37
1,2,3-trimethylbenzene	36.45	33.64	21.89	31.99
1,2,4-trimethylbenzene	6.23	5.94	4.58	5.67
1,3,5-trimethylbenzene	1.34	1.28	1.05	1.16
Styrene	9.42	10.64	6.89	12.24
Isopropylbenzene	0.55	0.59	0.44	0.54
n-propylbenzene	1.99	2.20	1.50	2.27
p-Isopropyltoluene	1.11	1.05	0.71	0.99
n-butylbenzene	7.15	6.62	3.95	6.57
Naphthalene	62.20	62.92	29.85	51.67
2-methylnaphthalene	2.11	2.31	1.01	1.59
1-methylnaphthalene	0.84	0.97	0.40	0.57
n-heptane	< MDL	< MDL	< MDL	< MDL
n-octane	0.91	< MDL	0.68	< MDL
n-nonane	82.22	76.44	65.71	74.96
n-decane	65.59	59.80	43.83	57.64
n-undecane	57.68	52.74	32.86	48.71
n-dodecane	59.80	57.78	29.36	48.41
n-tridecane	95.38	95.22	43.38	72.35
n-tetradecane	19.81	19.54	7.30	12.87
n-pentadecane	5.85	5.60	1.37	2.66
n-hexadecane	3.10	3.60	0.52	0.83
TTVOC	**712.0**	**708.1**	**439.6**	**642.1**

< MDL: below method detection limit

Table 4.5 Emission measurements for the 6.4 L diesel engine.

Calibration	2004		2007		2004				2007	
Condition	Idle	Idle	Idle	Idle	600 kPa (1500 rpm)	600 kPa (1500 rpm)	900 kPa (2500 rpm)	900 kPa (2500 rpm)	900 kPa (2500 rpm)	900 kPa (2500 rpm)
Fuel	ULSD	B20	ULSD	B20	ULSD	B20	ULSD	B20	ULSD	B20
Aftertreatment	None	None	DPF	DPF	None	None	None	None	DPF	DPF
Emission										
unit	(g/h)		(g/h)		(g/kW-h)				(g/kW-h)	
CO	28.82	34.83	21.96	18.66	1.46	1.49	1.01	0.87	0.03	0.02
NOx	9.50	10.43	2.90	3.55	4.88	5.59	3.50	4.23	8.58	9.87
NMHC	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Formaldehyde	1.288	1.662	0.868	0.616	0.027	0.024	0.020	0.018	0.010	0.008
unit	(mg/h)		(mg/h)		(mg/kW-h)				(mg/kW-h)	
PM10	310.87	580.94	22.51	4.09	56.73	43.35	108.50	78.44	0.60	0.75
BC	23.74	27.21	<MDL	<MDL	31.73	16.49	79.90	52.56	<MDL	<MDL
EC	11.88	17.85	<MDL	<MDL	31.31	16.91	77.18	50.71	<MDL	<MDL
Benzene	35.39	38.53	NA	NA	0.75	0.64	0.72	1.10	0.02	0.01
Toluene	21.10	18.22	NA	NA	0.45	0.32	0.80	0.78	0.11	0.03
Ethylbenzene	4.31	3.56	NA	NA	0.10	0.07	0.19	0.18	0.05	0.01
p-,m-xylene	11.83	7.98	NA	NA	0.33	0.20	0.61	0.52	0.16	0.03
o-xylene	4.85	3.37	NA	NA	0.14	0.09	0.24	0.21	0.08	0.01
4-ethyltoluene	6.08	4.12	NA	NA	0.20	0.12	0.43	0.35	0.18	0.02
2-ethyltoluene	3.30	2.25	NA	NA	0.11	0.07	0.25	0.20	0.11	0.01
1,2,3-trimethylbenzene	4.59	3.07	NA	NA	0.21	0.15	0.50	0.43	0.27	0.03
1,2,4-trimethylbenzene	8.32	5.54	NA	NA	0.35	0.24	0.81	0.69	0.39	0.05
1,3,5-trimethylbenzene	2.82	1.80	NA	NA	0.11	0.07	0.23	0.19	0.10	0.01
Styrene	2.49	1.04	NA	NA	0.13	0.11	0.24	0.25	0.00	0.00
Isopropylbenzene	1.26	0.85	NA	NA	0.03	0.02	0.06	0.05	0.02	0.00
n-propylbenzene	2.27	1.62	NA	NA	0.07	0.05	0.15	0.14	0.06	0.01
p-isopropyltoluene	0.91	0.60	NA	NA	0.04	0.02	0.11	0.08	0.04	0.01
n-butylbenzene	1.25	0.94	NA	NA	0.06	0.05	0.15	0.13	0.09	0.01
Naphthalene	2.52	2.13	NA	NA	0.25	0.22	0.89	0.85	0.49	0.12
2-methylnaphthalene	2.07	1.75	NA	NA	0.17	0.15	0.80	0.86	0.36	0.13
1-methylnaphthalene	1.25	1.00	NA	NA	0.10	0.09	0.48	0.51	0.22	0.08
n-heptane	2.42	1.76	NA	NA	0.09	0.06	0.16	0.13	0.02	0.02
n-octane	3.58	1.67	NA	NA	0.19	0.09	0.33	0.22	0.03	0.03
n-nonane	18.68	10.26	NA	NA	0.95	0.48	1.72	1.34	0.25	0.08
n-decane	17.61	10.73	NA	NA	1.03	0.63	2.04	1.64	0.58	0.09
n-undecane	9.46	6.37	NA	NA	0.74	0.51	1.99	1.67	0.82	0.14
n-dodecane	5.02	3.38	NA	NA	0.66	0.43	2.86	1.89	0.84	0.21
n-tridecane	4.64	3.36	NA	NA	0.51	0.40	2.22	2.11	1.08	0.37
n-tetradecane	3.29	2.40	NA	NA	0.36	0.24	1.60	1.33	0.61	0.18
n-pentadecane	2.82	1.99	NA	NA	0.33	0.22	1.34	1.07	0.53	0.12
n-hexadecane	1.54	1.09	NA	NA	0.27	0.18	0.95	0.89	0.49	0.07
TTVOC	**186.5**	**142.1**	**NA**	**NA**	**8.7**	**6.0**	**22.9**	**19.9**	**8.0**	**1.9**

NA: data not available. < MDL: below method detection limit

Table 4.6 Comparisons of regulated emission standards for the 1.7 L diesel engine.

Fuel	Emission calibration	BMEP (kPa)	Speed (rpm)	After treatments	Assumed vehicle speed (mile/hr)	CO (g/mile)	PM$_{10}$ (g/mile)	NOx (g/mile)	NMHC (g/mile)	NMHC+NOx (g/mile)
ULSD	2002	200	1500	EGR	35	2.34	0.01	0.68	**0.36**	1.04
		600	1500	EGR	40	0.58	0.04	**1.36**	0.16	1.53
		900	2500	None	70	1.38	0.09	**1.73**	0.27	2.01
		200	1500	DOC/EGR	35	2.26	0.01	0.76	0.29	1.04
		600	1500	DOC/EGR	40	0.51	0.03	1.19	0.14	1.32
		900	2500	DOC	70	1.46	0.07	**1.66**	0.26	1.92
B20	2002	200	1500	EGR	35	2.53	0.00	0.59	0.30	0.89
		600	1500	EGR	40	0.00	0.04	1.03	0.01	1.04
		900	2500	None	70	0.00	0.08	**1.59**	0.07	1.66
		200	1500	DOC/EGR	35	2.27	0.00	0.64	0.21	0.85
		600	1500	DOC/EGR	40	0.00	0.03	1.05	0.03	1.08
		900	2500	DOC	70	0.00	0.07	**1.71**	0.14	1.86
EPA Tier 1 Emission Standards										
Federal Test Procedure (FTP-75)						4.20	0.10	1.25	0.31	-
Tier 1 Supplemental Federal Test Procedure (SFTP)						4.20	-	-	-	2.07
Aggressive highway driving (US06)						11.10	-	-	-	-
Air conditioning system operating (SC03)						3.70	-	-	-	-

Bold values were excessed the emission standards.

Table 4.7 Comparisons of regulated emission standards for the 6.4 L diesel engine.

Fuel	Emission calibration	BMEP (kPa)	Speed (rpm)	After treatments	CO (g/Kw-h)	NOx (g/Kw-h)	PM$_{10}$ (g/Kw-h)
ULSD	2004	600	1500	EGR	1.46	**4.88**	0.06
	2004	900	2500	EGR	1.01	**3.50**	0.11
	2007	900	2500	DPF/EGR	0.03	**8.58**	0.00
B20	2004	600	1500	EGR	1.49	**5.59**	0.04
	2004	900	2500	EGR	0.87	**4.23**	0.08
	2007	900	2500	DPF/EGR	0.02	**9.87**	0.00
EPA emission standards for model year 2004 and later					20.78	3.22	0.13
EPA emission standards for model year 2007 and later					20.78	0.20	0.01

Bold values were excessed the emission standards.

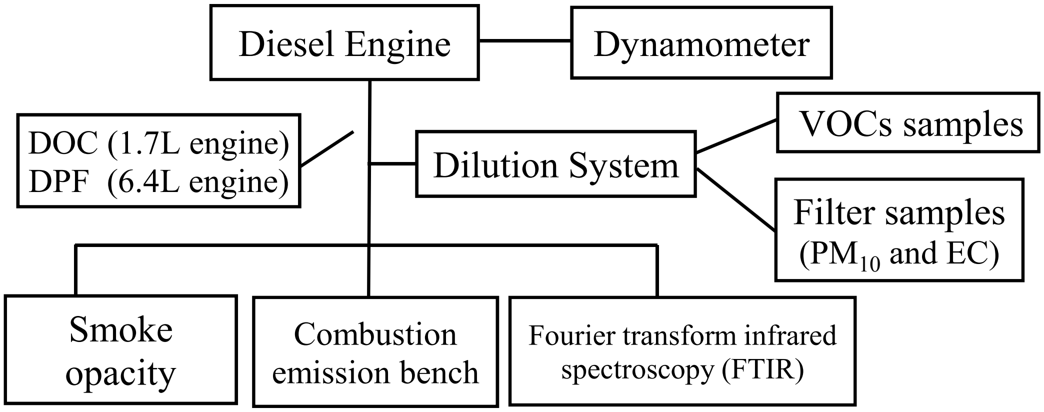

Figure 4.1 Schematic of sampling and analysis system.

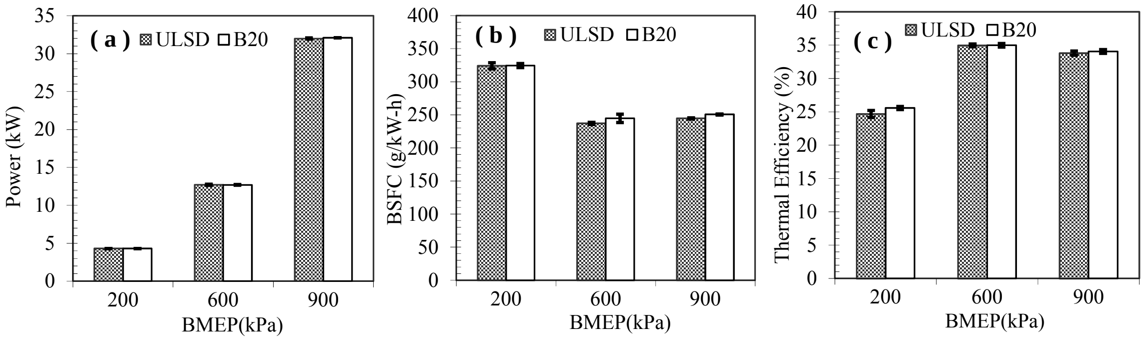

Figure 4.2 Performance of the 1.7 L diesel engine comparing two fuels. (a) Brake specific power (kW); (b) brake specific fuel consumption (BSFC, g fuel/kW-hr); and (c) thermal efficiency (%).

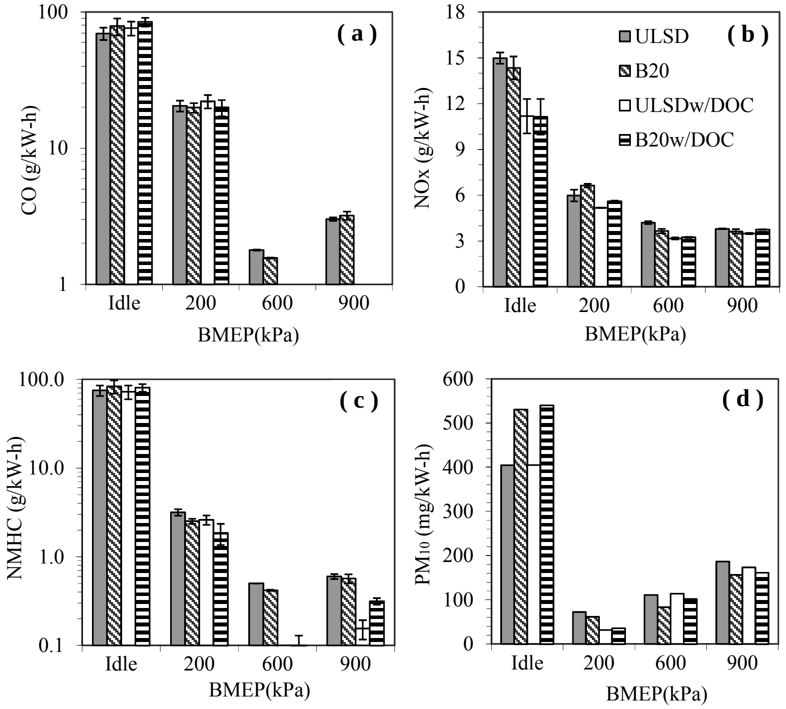

Figure 4.3 Brake specific emissions for the 1.7 L engine using ULSD and B20 fuels at idle and other three conditions: (a) carbon monoxide (CO); (b) nitrogen oxides (NOx); (c) non-methane hydrocarbons (NMHC); and (d) PM_{10}. Idle condition emissions in g/hr for CO, NOx and NMHC, and mg/hr for PM_{10}.

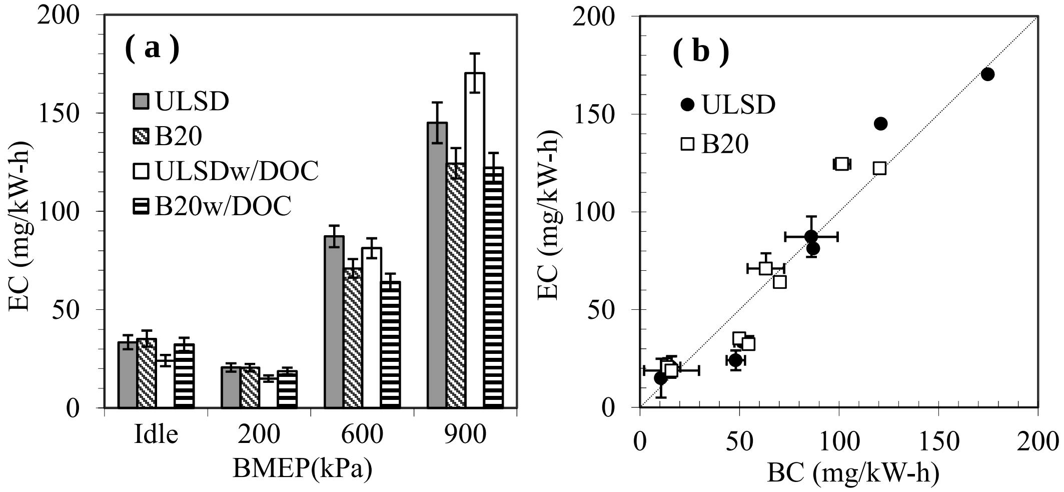

Figure 4.4 Brake specific emissions of (a) element carbon (EC), idle emissions in mg/hr; and (b) regression line between BC and EC from the 1.7 L diesel engine using ULSD and B20 fuels at idle and other three conditions.

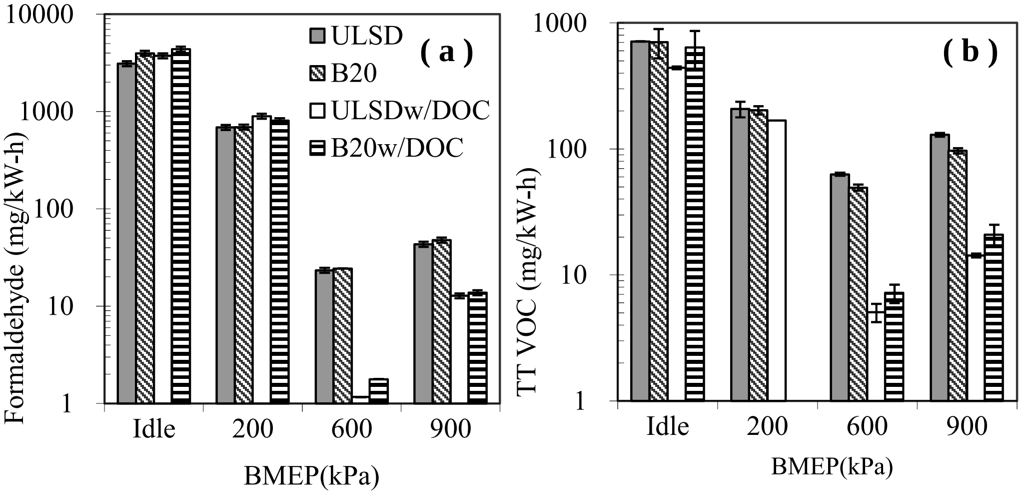

Figure 4.5 Brake specific emissions of (a) formaldehyde and (b) total target volatile organic compounds (TTVOCs) from a 1.7 L diesel engine using ULSD and B20 for four conditions. Idle emissions in mg/hr.

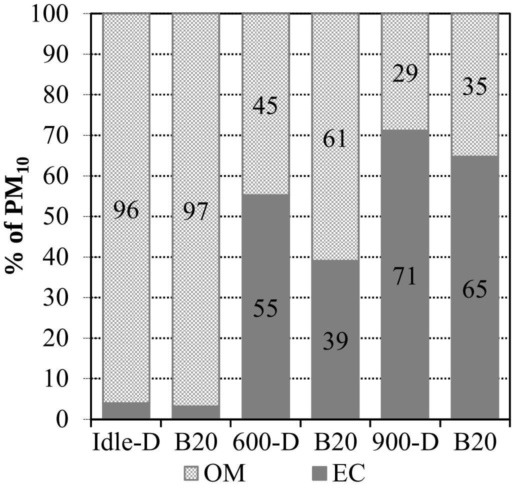

Figure 4.6 Organic matter (OM) and elemental carbon (EC) fractions of PM_{10} from the 6.4 L diesel engine for ULSD and B20 fuels and three conditions (2004 calibration).

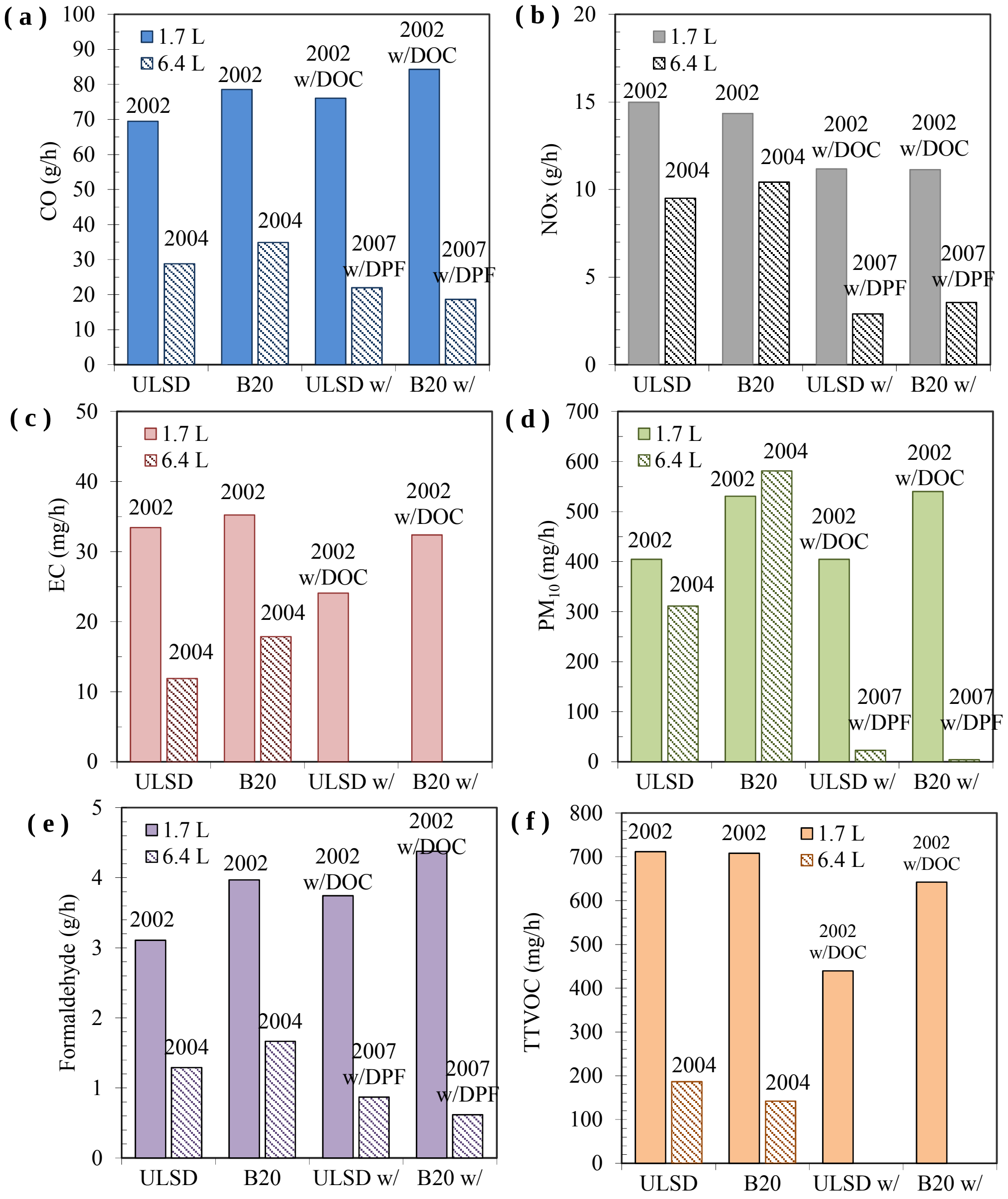

Figure 4.7 Comparison of emissions from 1.7 and 6.4 L engines at idle using ULSD and B20 fuels for (a) carbon monoxide (CO), (b) nitrogen oxides (NOx), (c) elemental carbon (EC), (d) PM_{10}, (e) formaldehyde, and (f) TTVOC.

4.7 Appendix

Table A4.1 Properties of pure biodiesel and ULSD fuels.

Fuel parameters	B100	ULSD	Resolution	Method
Kinematic Viscosity (mm^2/s)	3.92	2.347	0.001	ASTM D445
Gross Heating Value (BTU/lb)	17135	19699	175	ASTM D240
Net Heating Value (BTU/lb)	16057	18472	475	ASTM D240
Cetane Number	46.7	45.7		ASTM D613
Carbon (wt%)	77.27	86.55	0.05	ASTM D5291
Hydrogen (wt%)	11.82	13.45	0.05	ASTM D5291
Oxygen (wt%)	10.91	<0.05	0.05	ASTM D5622

Table A4.2 Summary of parameters measured on combustion emission bench.

Species	Methods (Gas analyzer)	Range	Range (ppm)	Error (ppm)
CO	Nondispersive infrared (ABB Uras 14 EGA)	1	1200	17
		2	11000	154
		3	70000	980
CO_2	Nondispersive infrared (ABB Uras 14 EGA)	1	80000	1120
		2	200000	2800
O_2	Paramagnetic (ABD Magnos 16 EGA)	1	60000	840
		2	250000	3500
CO_2 (EGR)	Nondispersive infrared (ABB Uras 14 EGA)	1	40000	560
		2	80000	1120
NOx	Chemiluminescence (CLD 700 AL)	1	65	1
		2	450	8
HC	Flame ionization detector (ABB Multi-FID 14 EGA)	1	500	7
		2	2600	36
CH_4	Flame ionization detector (ABB Multi-FID 14 EGA)	1	200	3

Table A4.3 Idle emissions from 1.7 Land 6.4 L diesel engines.

Engine and calibration	1.7 L, 2002 calibration				6.4 L, 2004 calibration		6.4 L, 2007 calibration	
Fuel	ULSD	B20	ULSD	B20	ULSD	B20	ULSD	B20
Aftertreatment	None	None	DOC	DOC	None	None	DPF	DPF
unit	(g/h)				(g/h)		(g/h)	
CO	69.46	78.57	76.08	84.30	28.82	34.83	21.96	18.66
NOx	14.98	14.34	11.18	11.14	9.50	10.43	2.90	3.55
NMHC	75.06	83.11	72.38	80.63	NA	NA	NA	NA
Formaldehyde	3.11	3.97	3.74	4.38	1.29	1.66	0.87	0.62
unit	(mg/h)				(mg/h)		(mg/h)	
PM10	404.70	530.71	404.83	540.21	310.87	580.94	22.51	4.09
BC	51.57	49.99	48.15	54.65	23.74	27.21	<MDL	<MDL
(FSN)	(0.13)	(0.12)	(0.12)	(0.13)	(0.04)	(0.05)	<MDL	<MDL
EC	33.43	35.21	24.08	32.37	11.88	17.85	<MDL	<MDL
Benzene	110.79	128.93	79.75	123.96	35.39	38.53	NA	NA
Toluene	48.53	49.81	37.47	51.64	21.10	18.22	NA	NA
Ethylbenzene	5.59	6.18	4.09	6.55	4.31	3.56	NA	NA
p-,m-xylene	11.03	10.51	8.65	10.89	11.83	7.98	NA	NA
o-xylene	5.55	5.27	4.22	5.34	4.85	3.37	NA	NA
4-ethyltoluene	6.04	5.75	4.52	5.70	6.08	4.12	NA	NA
2-ethyltoluene	4.75	2.73	3.63	4.37	3.30	2.25	NA	NA
1,2,3-trimethylbenzene	36.45	33.64	21.89	31.99	4.59	3.07	NA	NA
1,2,4-trimethylbenzene	6.23	5.94	4.58	5.67	8.32	5.54	NA	NA
1,3,5-trimethylbenzene	1.34	1.28	1.05	1.16	2.82	1.80	NA	NA
Styrene	9.42	10.64	6.89	12.24	2.49	1.04	NA	NA
Isopropylbenzene	0.55	0.59	0.44	0.54	1.26	0.85	NA	NA
n-propylbenzene	1.99	2.20	1.50	2.27	2.27	1.62	NA	NA
p-Isopropyltoluene	1.11	1.05	0.71	0.99	0.91	0.60	NA	NA
n-butylbenzene	7.15	6.62	3.95	6.57	1.25	0.94	NA	NA
Naphthalene	62.20	62.92	29.85	51.67	2.52	2.13	NA	NA
2-methylnaphthalene	2.11	2.31	1.01	1.59	2.07	1.75	NA	NA
1-methylnaphthalene	0.84	0.97	0.40	0.57	1.25	1.00	NA	NA
n-heptane	< MDL	< MDL	< MDL	< MDL	2.42	1.76	NA	NA
n-octane	0.91	< MDL	0.68	< MDL	3.58	1.67	NA	NA
n-nonane	82.22	76.44	65.71	74.96	18.68	10.26	NA	NA
n-decane	65.59	59.80	43.83	57.64	17.61	10.73	NA	NA
n-undecane	57.68	52.74	32.86	48.71	9.46	6.37	NA	NA
n-dodecane	59.80	57.78	29.36	48.41	5.02	3.38	NA	NA
n-tridecane	95.38	95.22	43.38	72.35	4.64	3.36	NA	NA
n-tetradecane	19.81	19.54	7.30	12.87	3.29	2.40	NA	NA
n-pentadecane	5.85	5.60	1.37	2.66	2.82	1.99	NA	NA
n-hexadecane	3.10	3.60	0.52	0.83	1.54	1.09	NA	NA
TTVOC	**712.00**	**708.06**	**439.60**	**642.11**	**186.48**	**142.10**	**NA**	**NA**

NA: data not available. < MDL: below method detection limit

Table A4.4 Emissions rates from 1.7 Land 6.4 L diesel engines at 900 kPa BMEP.

Engine and calibration	1.7 L, 2002 calibration				6.4 L, 2004 calibration		6.4 L, 2007 calibration	
Fuel	ULSD	B20	ULSD	B20	ULSD	B20	ULSD	B20
Aftertreatment	None	None	DOC	DOC	None	None	DPF	DPF
unit	(g/kW-h)				(g/kW-h)		(g/kW-h)	
CO	3.01	3.19	0.00	0.00	1.01	0.87	0.03	0.02
NOx	3.79	3.63	3.49	3.75	3.50	4.23	8.58	9.87
NMHC	0.60	0.57	0.15	0.31	NA	NA	NA	NA
Formaldehyde	0.043	0.048	0.013	0.014	0.020	0.018	0.010	0.008
unit	(mg/kW-h)				(mg/kW-h)		(mg/kW-h)	
$PM_{2.5}$	186.52	156.75	173.06	161.49	108.50	78.44	0.60	0.75
BC	120.99	101.54	174.72	120.54	79.90	52.56	<MDL	<MDL
(FSN)	(0.92)	(0.82)	(1.18)	(0.94)	(0.84)	(0.58)	<MDL	<MDL
EC	145.00	124.37	170.28	122.24	77.18	50.71	<MDL	<MDL
Benzene	12.40	12.14	0.88	0.86	0.72	1.10	0.020	0.014
Toluene	4.05	3.01	0.38	0.35	0.80	0.78	0.105	0.034
Ethylbenzene	0.40	0.31	0.05	0.07	0.19	0.18	0.050	0.010
p-,m-xylene	0.86	0.59	0.13	0.15	0.61	0.52	0.161	0.026
o-xylene	0.40	0.28	0.06	0.06	0.24	0.21	0.077	0.011
4-ethyltoluene	0.46	0.35	0.09	0.09	0.43	0.35	0.176	0.022
2-ethyltoluene	0.35	0.29	0.07	0.06	0.25	0.20	0.110	0.014
1,2,3-trimethylbenze	5.19	3.46	0.68	0.75	0.50	0.43	0.271	0.032
1,2,4-trimethylbenze	0.61	0.48	0.13	0.13	0.81	0.69	0.391	0.048
1,3,5-trimethylbenze	0.14	0.13	0.03	0.03	0.23	0.19	0.096	0.012
Styrene	1.25	0.99	0.16	0.15	0.24	0.25	0.003	0.001
Isopropylbenzene	0.04	0.03	< MDL	< MDL	0.06	0.05	0.020	0.002
n-propylbenzene	0.18	0.15	0.03	0.04	0.15	0.14	0.059	0.008
p-Isopropyltoluene	0.15	0.11	0.02	0.02	0.11	0.08	0.041	0.006
n-butylbenzene	1.15	0.83	0.15	0.19	0.15	0.13	0.085	0.010
Naphthalene	14.02	11.34	1.50	3.45	0.89	0.85	0.488	0.122
2-methylnaphthalene	0.52	0.43	0.04	0.11	0.80	0.86	0.360	0.127
1-methylnaphthalene	0.24	0.21	0.02	0.05	0.48	0.51	0.219	0.079
n-heptane	< MDL	< MDL	< MDL	< MDL	0.16	0.13	0.016	0.018
n-octane	0.27	0.25	0.08	0.17	0.33	0.22	0.033	0.028
n-nonane	11.54	7.71	1.51	1.36	1.72	1.34	0.245	0.079
n-decane	9.97	6.81	1.37	1.09	2.04	1.64	0.578	0.088
n-undecane	10.46	7.19	1.57	1.53	1.99	1.67	0.819	0.143
n-dodecane	14.14	10.00	1.80	2.63	2.86	1.89	0.835	0.210
n-tridecane	26.48	19.58	2.52	5.18	2.22	2.11	1.080	0.367
n-tetradecane	7.03	5.09	0.50	1.18	1.60	1.33	0.611	0.179
n-pentadecane	3.34	2.47	0.28	0.59	1.34	1.07	0.532	0.124
n-hexadecane	3.75	2.54	0.23	0.60	0.95	0.89	0.490	0.066
TTVOC	**129.41**	**96.77**	**14.29**	**20.90**	**22.91**	**19.86**	**7.97**	**1.88**

NA: data not available. < MDL: below method detection limit

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Chapter 5

Characterization and apportionment of volatile organic compounds at a near road site in Detroit, Michigan.

5.1 Abstract

Exposure to traffic pollutants can alter lung function, trigger asthma attacks, and adversely affect health, especially for susceptible populations that live near major roads. Air toxics associated with traffic emissions, including volatile organic compounds (VOCs) such as benzene, are complex mixtures that vary spatially and temporally. In this study, VOCs were measured daily near a major highway in Detroit from September 1, 2009 to August 16, 2010, and concentrations were apportioned to different sources using positive matrix factorization (PMF), a multivariate receptor model.

A total of 41 VOCs were detected (ranging from methylene chloride to n-hexadecane) with an annual average total target VOC concentration of 13.9 ±8.8 µg/m^3. Seasonal variation was significant, and concentrations of most VOCs were highest in fall and lowest in summer, however, benzene concentrations peaked (0.99 ±0.40 µg/m^3) in winter. Weekday and weekend variation was also significant. The seasonal apportionment identified 6-8 source types, the most important being vehicle exhaust (explaining 21-29% of the variation depending on season), diesel exhaust (6-15%), fuel evaporation (17-22%), solvent-based industrial emissions (15-30%), biomass burning (0-17%), and biogenic emissions (2-5%). The study results can aid air quality management,

including identifying sources of ozone precursors, apportioning emission sources, and estimating exposure.

5.2 Keywords

Near roadway emissions, PMF, volatile organic compounds, source apportionment.

5.3 Introduction

Traffic-related air pollutants have gathered considerable attention recently[1, 2] due to a number of studies that link exposures of traffic-related air pollutants to elevate risks of morbidity and mortality.[3-7] As examples, children living near major highways in Nottingham in UK, Netherlands and San Francisco were shown to have elevated risks for the development of asthma and reduced lung function;[2] exposure to particulate matter (PM) was associated with cardiac and pulmonary mortality in children adults based on 29 peer-reviewed studies;[1] and exposure to diesel exhaust emissions was associated with increased rates of symptoms and hospitalizations for asthma in children in Netherlands.[8]

Traffic-related pollutants are complex mixtures comprised of primary exhaust emissions, which include particulate matter (PM), carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (VOCs), and semi-volatile organic compounds (SVOCs) including polycyclic aromatic hydrocarbons (PAHs). In addition, secondary pollutants are formed from primary pollutants via photochemical or chemical reactions, e.g., ozone (O_3) is formed from NO_x and VOC precursors by photochemical reactions.[9] Additional traffic-related pollutants include unburned or partially burned fuel and oils, resuspended road dust, particles generated from tires, brakes, bearings and other vehicle components.[10] Diesel-powered vehicles can have especially high PM emissions, and contain elemental carbon (EC), PAHs, and other components.[11]

Most air pollution epidemiology studies examining traffic pollution have focused on PM and O_3. However, VOCs are also important traffic-related pollutants since many are O_3 precursors,[12] mobile-source air toxics (MSATs),[13] and hazardous air pollutants (HAPs).[14] Several VOCs have been prioritized due to their health risk by the U.S. Environmental Protection Agency (EPA), including benzene, 1,3-butadiene, formaldehyde, and acetaldehyde. These VOCs are known or suspected carcinogens. VOC concentrations vary considerably across space and time, and are affected by meteorology, season, road type, vehicle mix, traffic volume, traffic intensity and other factors.[15, 16] Seasonal, weekly and diurnal patterns in traffic volume, pollutant emissions and concentrations have been observed.[17-19]

Receptor models are used to identify and apportion sources of PM and VOCs. For example, chemical mass balance (CMB) models have been used for VOCs in Detroit, Chicago, Atlanta and Washington, D.C. in summers between 1984 and 1988,[20] in large-scale studies like the Southeast Michigan ozone study (SEMOS) in 1993,[21] in Los Angeles, Phoenix, Houston and elsewhere.[22] CMB models require *a priori* knowledge of source profiles, that is, the VOC compositions pertaining to vehicles, evaporative and fuel emissions, industrial emissions, and other source groups. Often, such profiles are unavailable or limited to a specific location.[20-22] A second class of receptor models called multivariate models, such as positive matrix factorization (PMF), do not require *a priori* knowledge of source profiles.[23-26] In comparison to other multivariate models, PMF is advantageous those only non-negative loadings are produced, and that the uncertainty in source profiles can be incorporated.[23-26] As a simpler alternative to receptor models, indicator compounds or ratios of compounds such as benzene, toluene, ethylbenzene and isomeric xylenes (BTEX) are sometimes used to indicate mobile sources.[27, 28]

The present study provides an apportionment of VOCs at a near-road location in Detroit, Michigan. In many ways, Detroit is an ideal city for research linking roadway exposures and health. The city has many high volume roads, several freight terminals,[29] a large minority and low socioeconomic status population, and high asthma prevalence, e.g., childhood asthma hospitalizations are twice the statewide average.[17, 30, 31] VOCs have been routinely monitored in Detroit (every six or 12 days) by Michigan Department of Natural Resources and Environment (MDNRE).[32] In addition, several studies have measured VOCs in Detroit, including the Detroit Air Toxics Initiative (DATI),[17, 29] the Detroit Exposure and Aerosol Research Study (DEAR),[33] the Mechanistic Indicators of Childhood Asthma (MICA) study in Detroit,[34] and Miller et al. (2010) monitored air toxics across both Detroit and Windsor, Canada.[35] The present study is part of a health study called "Role of Diesel and Other Vehicular Exhaust in Exacerbation of Childhood Asthma" which made daily measurements of VOCs with the aims of understanding the temporal variation of concentrations, and identifying emission sources.

5.4 Methods and Materials

5.4.1 Site description

VOC measurements were collected at the Herman Kiefer facility of the Detroit Department of Health and Wellness. The facility includes a number of buildings adjacent to the John C. Lodge Expressway (State Highway M-10) at Taylor Street in central Detroit (Figure 5.1). At this location, M-10 is a six lane freeway with an annual average daily traffic flow of 143,300 vehicles/day, and commercial traffic flow of 2,600 vehicles/day (2009 data).[36] The highway is oriented NNW to SSE, and is slightly below grade. Streets like Taylor cross via bridges. Two lane service roads parallel each side of the expressway. The sampling equipment drew air from a second story location in building facing the expressway, 25 m distant to a low traffic two lane service road, and 50 m distant to the freeway.

While the immediate area around the Kiefer facility is residential, the larger area contains many industrial facilities, including automobile manufacturing, iron/steel manufacturing, coke ovens, chemical plants, and refineries. Within a 4 km radius around the facility, 38 facilities release air pollutants based on U.S. EPA EnviroMapper data (shown in Appendix Table A5.2).[37] Further afield, southwest Detroit experiences heavy car and truck traffic, much of it traversing the Canada/U.S. border at the Ambassador Bridge. Based on the 2010 census,[38] Detroit has 713,777 residents of which 83% are African-American, and the metropolitan region has a population of 4 million.

5.4.2 Sample collection and analysis

VOCs samples were collected using adsorbent tubes and an 8-position automated sequential sampler. This sampler was designed for flow rates up to 10 mL/min, regulated using a mass flow controller and programmable logic controller (PLC) which controlled sampling timing and sequence. Outdoor air entered the sampler system at about 2 L/min via a rain shield, stainless steel insect screen, 6.35 mm dia Teflon tubing, a water trap, a manifold, and vacuum pump, and was discharged via a small muffler. Sampling tubes were inserted into the manifold and activated via solenoids controlled by the PLC.

In this study, 24-hr integrated samples were collected at a flow rate of 5 mL/min, giving a 7.2 L sample. 7 TDTs and 1 blank TDT were deployed each week from 9/01/2009 to 8/16/2010, representing a total of 350 samples and 50 blanks. Of the daily samples, 298 (85%) were deemed valid and used in this study.

Samples were collected using thermal desorption tubes (TDT, stainless steel, 10 cm x 4 mm; Scientific Instrument Services, Inc., Ringoes, NJ, USA) filled with 160 mg of Tenax GR (Scientific Instrument Services, Inc., Ringoes, NJ, USA) and 70 mg of Carbosieve SIII (Supelco Inc., Bellefonte, PA, USA). Prior to use, TDTs were placed in a conditioning oven (Scientific Instrument Services, Ringoes, NJ, USA) at 325ºC for 6 hours under 50 mL/min flow of ultra-high purity helium. Cleaned tubes were stored at 4 ^{o}C and transported in a clean glass jar containing a charcoal pack. After collection, TDTs were replaced in the jar, returned to the laboratory, and stored at 4 ^{o}C until analyses, which was completed within one week of collection. Further details of TDT preparation and analysis are provided elsewhere.[39-42]

Before analysis, each TDT was spiked with 2 μL of an internal standard (1 ng μL-1 each of fluorobenzene and p-bromofluorobenzene) using a TDT stainless-steel loader (Scientific Instrument Services, Inc., Ringoes, NJ, USA) and ultra-high purity grade helium flow (35 ml/min) through the loader and TDT. Samples were analyzed using an automated short-path thermal desorption system (Model 2000, Scientific Instrument Services, Ringoes, NJ, USA), on-column cryofocusing, gas chromatography, and mass spectrometry (GC/MS, Model 6890/5973, Chemstation, G1701BA, Version B.01, Hewlett– Packard, Palo Alto, CA, USA). The GC was equipped with a 60 m × 0.25 mm id. capillary column with 1.4 μm film thickness (DB-VRX J&W Scientific, Agilent

Technologies, Santa Clarita, CA, USA). The MS was set to scan mode for ions 29 - 270 amu with 3 scans/s and 0.1 amu step size.

Target analytes included over 100 compounds (e.g., aromatics, halogenated, alkanes), each using authentic standards and calibrations. These compounds were selected on the basis of their health significance and frequency of occurrence, and include several Hazardous Air Pollutants (HAPs), e.g., benzene, toluene, ethylbenzene, xylenes, styrene, 1,4-dichlorobenzene.[14] Method detection limits (MDLs), established using seven low concentration spiked samples, ranged from 0.008 to 1 $\mu g/m^{-3}$ depending on the VOC. The quality assurance and quality control (QA/QC) program included laboratory and field blanks and spiked samples. All laboratory and field blanks were clean. For VOC analysis, spiked (standard mixture) samples were analyzed to check the calibration of GC/MS. The method and its performance have been detailed elsewhere.[39-42]

5.4.3 Data analysis

The total target VOC (TTVOC) concentration was computed as the sum of target VOCs. Descriptive statistics were computed for each VOC, including mean, median, standard deviation, detection frequency, and trend plots. Spearman rank correlation was used to determine the linear correlations among variables, including ΣBTEX, defined as the sum of benzene, toluene, ethylbenzene and p-,m-,o-xylene concentrations. Kruskal-Wallis tests and a significance level $\alpha = 0.05$ were used to determine the significance of day-of-week, weekday-weekend, and seasonal differences for fall 2009 (Sept.-Nov.), winter 2010 (Dec. 2009-Feb. 2010), spring 2010 (Mar.-May) and summer 2010 (June-Aug.). Data handling and statistical analyses used Excel (Microsoft, Seattle, WA, USA) and SPSS 17 (IBM Corp., Somers, NY, USA).

5.4.4 Source apportionment modeling

The selected receptor model was positive matrix factorization (PMF) 3.0, obtained from U.S. EPA.[43] PMF is a multivariate modeling tool that decomposes the sample data matrix **X** into two matrices:

$$\mathbf{X}_{ij} = \sum_{k=1}^{p} \mathbf{G}_{ik}\ \mathbf{F}_{kj} + \mathrm{e}_{ij} \qquad (1)$$

where $\mathbf{X}_{ij}$ = ith observation i of the jth chemical species, p = number of factors, **F** = factor profile matrix, **G** = factor contributions matrix, and e_{ij} = residual error. Factors represent source classes, e.g., vehicles, and are derived in a manner such that profiles are orthogonal to one another. Factors can be rotated to simplify results (i.e. "Fpeak" runs in PMF model). PMF allows users to define the uncertainty associated with the observations, including values below MDLs. PMF uses an objective function that minimizes Q:

$$\mathrm{Q} = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{\mathbf{X}_{ij} - \sum_{k=1}^{p} \mathbf{G}_{ik}\,\mathrm{F}_{kj}}{\mathrm{U}_{ij}} \right]^2 \qquad (2)$$

where **X**, **G** and **F** are taken from eq. (1), and u_{ij} is the uncertainty of ith observation for the jth chemical species. PMF accepts two types of uncertainty, i.e., sample-specific and equation-based. Additionally, PMF keeps each element of the factor profile matrix **F** non-negative and thus physically plausible.

Steps used to examine input data and obtain robust solutions included the following: determination of signal-to-noise ratio (S/N); display of scatter plots between two species; and analysis of trend plots to identify extreme data or unusual events (data can be excluded in this step). After conducting the "base run", Q values, residual analyses, observed/predicted (O/P) scatter plots, "Fpeak" runs (factor rotation if needed), and bootstrap runs can be used to examine the fit of the solution. Detailed descriptions of

PMF and these procedures are provided by Paatero and Tapper,[23] PMF 3.0 user guide,[43] and elsewhere.[44]

The number of factors was selected following guidance from the PMF user's guide[43] and Hopke[45]: (1) if additional factors or rotations (Fpeaks runs) significantly increased Q values; (2) whether the distribution of residuals (errors) was symmetrical and if scaled residuals were within ±3 standard deviations; and (3) whether factors were interpretable and corresponded to realistic physical phenomena.

Source apportionments were estimated seasonally. Non-detects were replaced by one-half of the MDL, and measurements below MDLs were maintained (not replaced by half of MDLs). All valid samples (298) were included and no outliers were excluded (only few VOCs had scaled residuals exceeded ±3 standard deviations). Equation-based uncertainty was used, i.e., 15% error to account for sampling and analytical errors (using the default equation), and an additional 5% error for model uncertainty. (10 and 15% errors were also explored as a sensitivity analysis, but Q values were not significantly altered and thus these results are not further discussed). VOCs with detection frequencies below 5% were excluded (placed in the PMF's “bad” category); VOCs with detection frequencies greater than 5% but less than 15% were included in PMF in the “weak” category, which is given three times the default uncertainty; and VOCs with detection frequencies greater than 15% were included in the “strong” category, which is given the default uncertainty. Up to 9 factors were explored for each season.

5.5 Results and discussion

5.5.1 VOC levels and temporal variation

A total of 41 VOCs were identified at the Kiefer site, most with detection frequencies exceeding 50% (Table 5.1). Many VOCs were detected in nearly every sample, e.g., benzene, toluene, ethylbenzene and p-m-o-xylene, 4-ethyl toluene, trimethyl benzene, naphthalene and C_{7}-$_{15}$ n-alkanes; these VOCs have been associated with exhaust and evaporative emissions from mobile sources. Less commonly detected VOCs have been associated with a variety of sources: biogenic emissions, e.g., α-pinene;[46] wastes, e.g., p-isopropyl toluene;[47] solvents and industrial emissions, e.g., chlorobenzene, cyclohexane, and methylene chloride; and biomass burning, e.g., benzene and methylene chloride.[48]

The TTVOC concentration averaged 14.0±8.2 μg/m^3 (range from 2.6 to 59.2 μg/m^3; 24-hr integrated samples), and the ΣBTEX (benzene, toluene, ethylbenzene and p-,m-,o-xylenes) concentration averaged 6.3±3.9 μg/m^3 (0.9 to 30.0 μg/m^3). Concentrations of different species often were highly correlated, e.g., toluene, ethylbenzene, p-,m-,o-xylenes and TTVOC had correlation coefficients exceeding 0.80 (Table 5.2). Benzene had lower correlation (r=0.40-0.58) with other BTEX compounds and TTVOC, suggesting that a number of sources other than mobile sources contribute to benzene or the other BTEX compounds.

Seasonal variation was significant ($p < 0.05$) for all compounds except α-pinene (p=0.55; Kruskal-Wallis test, Appendix Table A5.3). TTVOC concentrations were highest in fall 2009 (17.0±9.3 μg/m^3) and lowest in summer 2010 (8.8±4.6 μg/m^3; Figure 5.2). Most VOCs followed the pattern seen for TTVOC, however, the highest levels occurred in winter (rather than fall) for benzene, 4-ethyl toluene, 2-ethyl toluene, 1,3,5-

trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethyl benzene, naphthalene, α-pinene and methylene chloride.

Day-of-week variation was not significant for any VOC (Kruskal-Wallis test), possibly due to small systematic differences and large temporal variation. However, tests comparing weekday (Monday to Friday) and weekend (Saturday and Sunday) showed significantly ($p < 0.05$) higher levels of 13 target VOCs on weekdays, including toluene, ethylbenzene, and p-,m-,o-xylene (Kruskal-Wallis test, Appendix Table A5.4). No differences were seen for TTVOC and 24 target VOCs including benzene, naphthalene, 1,4-dichlorobenzene, and C_{7-15} n-alkanes (Kruskal-Wallis test, Appendix Table A5.4). Although the concentration differences between weekdays and weekends were small, these results suggest temporal changes in source contributions, specifically a pattern that differs by weekend and weekday.

Recent monitoring (2004-2009) at regulatory, school and residential sites in the Detroit area shows fairly comparable ΣBTEX levels (4.1-17.1 $\mu g/m^3$), although benzene levels at Kiefer (0.71 ± 0.40 $\mu g/m^3$) were lower than levels measured at other sites (1.0-2.8 $\mu g/m^3$; Table 5.3).[17, 32-34, 49, 50] Recent regulations on benzene content in fuel (<0.62% vol) in 2011 may help explain the relatively low benzene levels seen at the Kiefer site since many refineries used early removals to earn benzene credit reductions in the preceding (2007-2010) period.[51] At a regulatory site in Detroit (N. Delray), benzene levels dropped from 1.39 $\mu g/m^3$ in 2006-2007 to 0.97 $\mu g/m^3$ in 2009,[29, 32] supporting this hypothesis.

Temporal trends and coverage, and spatial variability among sites may also explain differences. In particular, the MICA study collected samples outside residences in winter only, while the DEARS took samples in only winter and summer.[33, 34]

Although MDNRE and DATI studies (phase 2) encompassed over a year (April 2006-April 2007 and 2009), VOC samples were only collected at one site in Detroit (N. Delray, a population-oriented site as defined by MDNRE) with limited number of samples.[29, 32] The initial phase of the DATI study (April 2001 to April 2002) monitored VOC levels at five sites in Detroit, and indicated significant differences in VOC levels between sites for target VOCs except for 1,4-dichlorobenzene.[17] Miller et al. (2010) also noted that the degree of spatial variation of TTVOC and ΣBTEX across 64 Detroit monitoring sites, as compared to 38 sites in Windsor, Canada using both passive and active monitoring conducted in September 2008.[35]

Other emission sources near the Kiefer site may contribute to measured VOC concentrations. This may include evaporative emissions from vehicles in parking lots at the facility (mainly at the other side of the building), which can be strong sources of toluene, ethylbenzene and xylene.[18] As noted earlier, several dozen facilities within a 4 km radius are listed as air emission sources (Appendix Table A5.2), however, no releases of air toxics from these facilities are shown in air emission reports and the Toxic Release Inventory for 2009.[37, 52]

Both indoor air and outdoor studies have shown strong correlation among BTEX compounds, including urban and near roadway studies.[53-55] Miller et al. (2010) reported high correlation among BTEX compounds and TTVOC (r=0.92-0.96) at Detroit sites, suggesting the influence of mobile sources.[36] Seasonal, diurnal (rush hour), and weekday/weekend trends in urban pollutants, including PM, CO and BTEX, have been shown in urban and roadway settings, as well as associations with traffic density and vehicle type.[18, 19, 53, 55-57] With respect to seasonal variation, VOC levels are expected to be higher in the winter due to calm and stable atmosphere conditions and more frequent inversions, which hinder pollutant dispersion, and due to cold starts from vehicles, which increase emissions.[32] In addition, biomass burning, which includes benzene emissions, is more frequent in winter time.[58, 59]

5.5.2 BTEX ratios

The toluene/benzene (T/B) ratios at the Kiefer site ranged widely (0.02-21.2) and averaged of 4.33±2.74 (median=3.71). T/B ratios varied seasonally (Kruskal-Wallis test p=0.00, Table 5.4). Overall, the annual average T/B ratio exceeded those at other Detroit studies (1.6-3.6)[17, 32-34, 49, 50] as well as ratios other urban and roadway sites (1.0 to 3.0).[10-12, 34] All of this may indicate additional toluene sources or lower benzene levels.

Other ratios are sometimes used to indicate sources including toluene/ m-,p-,o-xylene (T/X) and m-,p- xylene/ethylbenzene. The annual average T/X ratio at Kiefer were 1.25, very similar to ratios reported along highways in commercial, residential and industrial areas in Detroit (T/X=1.18).[15]

For comparison, T/B and T/X ratios seen in liquid gasoline (<10% ethanol) in Chapter 2 were 2.5 and 1.1, respectively; these ratios were 3.6 and 0.4 for ultra-low sulfur diesel (ULSD), respectively. However, these ratios differed in their vapors (Chapter 2), T/B and T/X ratios seen in gasoline vapors were 1.3 and 15.1; these ratios were 2.2 and 1.1 for ULSD vapors, respectively. Furthermore, T/B and T/X ratios seen in diesel engine exhaust using ULSD fuel (Chapter 4) were differed from liquid ULSD and vapors, and also depended on the specific engine. T/B (0.2-0.4) and T/X (2.9-3.4) ratios were seen for the 1.7 L diesel engine operating under idle and three load conditions;

T/B (0.6-1.1) and T/X (1.0-1.3) ratios were seen for the 6.4 L diesel engine operating under idle and two load conditions (2004 calibration).

At Kiefer, the m-,p-xylene/ethylbenzene ratio was 3.2, which is consistent with the ratios from other Detroit studies (2.9-3.3) except for the data from MDNRE (8.2 due to low ethylbenzene concentration in Table 5.3).[17, 32-34, 49, 50] Ratios of m-,p-xylene/ethylbenzene have been shown to be relatively constant (2.8-4.6) among vehicle exhaust, solvent petroleum, and fuel evaporation sources.[28, 53] For comparison (Chapter 2 and 4), the m-,p-xylene/ethylbenzene ratios were also consistent with the literature for liquid gasoline (3.0) and ULSD (3.4), gasoline vapor (3.2), ULSD vapor (2.7), and diesel engine exhaust using ULSD (2.0-3.2).

At Kiefer, while the annual average ratios match, ratios varied widely and seasonally, possibly reflecting sources that vary in emissions or composition, e.g., seasonal variation of motor vehicle fuels, emissions from other sources, and photochemical reactions. Moreover, these ratios do not indicate other sources that might contribute to VOC levels.

5.5.3 Receptor modeling results

Initial analyses use a full year of measurements (298 daily samples), but results varied seasonally (Appendix Figure A5.1), thus, apportionments were estimated seasonally. Depending on season, 35 to 38 VOCs were used in the PMF models (Appendix Table A5.1), and 6 to 8 factors were resolved. Model fit was good: R^2 exceeded 0.91 for the reconstructed TTVOC with small residuals (>90% of observations had residuals within ±3.00 standard deviations); bootstrap analyses showed good fits of the solutions (>90% samples can be reconstructed); and factors were interpretable (described later). The first five factors explained most of the variation and were identified as the following: (1) vehicle exhaust (22-44% of TTVOC, including gasoline and diesel vehicles) based on BTEX and C_{7-9} n-alkanes contributions; (2) diesel vehicle exhaust (6-11%) based on C_{10-16} n-alkanes; (3) fuel evaporative emissions (16-23%) based on toluene, ethylbenzene, xylene and trimethyl benzene; (4) industrial emissions (15-22%)with solvents based on methylene chloride, toluene, xylenes, trimethylbenzene and others; and (5) biomass burning (0-17%), tentatively identified due to benzene and methylene chloride. Generally, the remaining factors provided small contributions. These included: (6) unknown sources (4-13%), e.g., indoor or other industrial emissions due to 1,4-dichlorobenzene; (7) biogenic emissions (2-5%) associated with α-pinene; and (8) other multiple sources due to a combination of VOCs. Essentially similar factors were resolved in fall 2009, spring 2009 and winter 2010 (illustrated in Appendix Figure A5.2-5).

In summer (2010), the source apportionments differed from those in three other seasons. Fuel evaporation (22%) was the top contributor, exceeding contributions from diesel exhaust (15%), and other unknown sources (13%). Also, the biomass burning factor disappeared.

The PMF results are somewhat comparable with apportionments obtained earlier for Detroit using chemical mass balance (CMB) receptor models in summer of 1993 (a part of Southeast Michigan ozone study) and in summer of 1988 (a part of 39-city of ozone precursors) which identified vehicle exhaust (28-38%), refineries (7-17%), gasoline vapor (2-9%), solvent-based architectural coatings (3-5%), solvent-based graphic arts (4-5%), and coke ovens (3-4%) as dominant sources, leaving 35% of the variation as unexplained (Table 5.6).[20, 21] In comparison to the Detroit emission inventory, the unexplained sources were attributed to industrial surface coatings (solvent use), sources that were not available to include in the model.[20, 21] Also, this CMB model application is relatively old and ambient samples were collected in only one season (summer) using a short sampling time (1-2 hr). Therefore, these results may not be fully relevant to this study, and there is a need to update the source profiles and monitored data.

The PMF results also resemble the 2005 VOC emission inventory prepared for Wayne County, which encompasses Detroit (Table 5.7), constructed using EPA-approved emission factors and models (MOVES for on-road vehicles and NONROAD for non-road vehicles, equipment and engines). On road vehicles (43%) , solvent use (32%), and non-road equipment (10%) were the top three sources, accounting for 85% of TTVOC emissions.[60] While such inventories are considered robust, they do not apply to specific locations and do not reflect temporal variation.

In the present study, the PMF model differentiated diesel exhaust based on C_{10-16} n-alkanes. As shown in Chapters 2 and 4, these species were often the dominant VOCs in diesel fuel, vapor and exhaust. Previous studies have utilized more volatile VOCs in receptor models, and differentiating gasoline and diesel exhaust was often difficult. As examples, Brown et al. (2008) found six factors using PMF at two sites in Los Angeles (VOCs sampled from July-September from 2001-2003), which were broken down as evaporative emissions (31-34%), motor vehicle exhaust (22-24%), liquid/unburned gasoline (13-27%), coatings or industrial process losses (15-17%), and biogenic emissions (1-3%).[61] Troussier et al. (2008) found 5-7 factors using PMF at three sites in France (summer and winter of 2001 and 2003), which showed that automobile exhaust source was the dominant source (35-61%) followed by gasoline evaporation (10-26%), gas leaks (9-19%), biogenic (0.7-2%), domestic heating (0.3-10%), solvent use (5-20%) and printing (0.5-4%) depended on season and city.[62] Leuchner and Rappenglück (2010) identified eight factors using PMF at an urban site in Houston (August-September 2006), and identified sources included natural gas/crude oil (27%), industrial liquefied petroleum gas (17%), vehicular exhaust (15%), fuel evaporation (14%), aromatics (13%), petrochemical emissions (4-5%), and biogenic emissions (4%).[26] A few CMB studies have differentiated diesel exhaust, for example, e.g., in Los Angeles in 1995, gasoline exhaust was the most abundant source (38-50%) followed by gasoline vapor (15-29%), diesel exhaust (11-15%), and liquid gasoline (0.6-11%).[22]

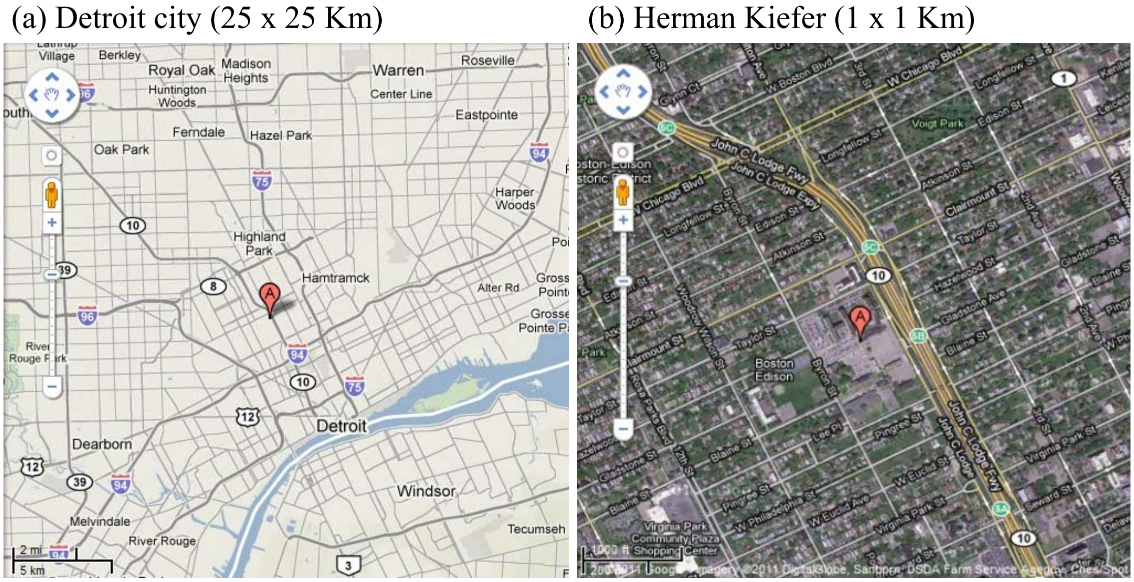
The PMF apportionments have several limitations. Only VOCs between C_6 and C_{16} were considered. Including very volatile VOCs can increase robustness and enhance interpretations, e.g., isopentane has been identified as a gasoline vapor tracer,[20, 22, 48] halo-alkenes are tracers of chemical plants,[48] isoprene and halo-alkanes are biomass burning tracers,[48, 59] and ethylene and propylene are components of gasoline and diesel exhausts, respectively.[20, 21, 48] Receptor models require several strong assumptions. Ideally, each source type has unique tracers, however, many source profiles are similar and often collinear.[22] Chapter 2 shows that compositions of gasoline fuel and vapor are collinear, moreover, gasoline and diesel exhaust, liquid and evaporated gasoline, and fugitive refinery emissions share many VOCs.[15] However, these sources may be resolved if profiles are sufficiently different. Source profiles are assumed to remain constant, both from source to receptor and over time. In reality, profiles can change on daily and seasonal scales due to meteorology, photochemical reactions,[28, 63] and selective washout during precipitation events. In addition, on a seasonal basis, fuel formulations vary, and temperature affects both the magnitude and composition of evaporative and exhaust emissions.

Apportionment studies are widely used in air quality management to confirm emission inventories, to understand sources affecting particular receptors, and for other purposes. Recently, receptor model results have been used in epidemiological studies, a potentially attractive approach if health impacts associated with pollutants are better explained by contributions from specific emission sources than by levels of individual pollutants. For example, source apportionments for particulate matter was associated with cardiovascular and mortality outcomes using receptor modeling.[64-66] This suggests that receptor modeling can provide reliable insights into those source components that contribute to health effects.

5.6 Conclusions

In this study, daily VOCs were collected for a year near a major expressway in Detroit. Concentrations were low (TTVOC averaged 13.9±8.8 $\mu g/m^3$), and showed systematic seasonal and weekly variation. TTVOC concentrations were highest in fall and lowest in summer; benzene concentrations peaked in winter. These results are generally comparable with monitoring elsewhere in Detroit, although benzene concentrations were lower, possibly reflecting recent regulations for gasoline.

Source apportionments were derived on a seasonal basis using PMF models, which identified contributing factors including vehicle exhaust, diesel exhaust, fuel evaporation, solvent-based industrial emissions, biomass burning, biogenic emissions, and indoor sources. Emission contributions from diesel-powered vehicles were differentiated based on C_{10-16} n-alkanes. Generally, these results at the Kiefer site are comparable to those found in other Detroit studies using CMB models and emission inventories. VOC levels vary by location, meteorological condition, study period, season, atmospheric half-life, and other factors. This information is useful for air quality management purposes, including estimating ozone precursors, and potentially as an explanatory variable in epidemiology studies.



(a) Detroit city (25 x 25 Km)

(b) Herman Kiefer (1 x 1 Km)

Figure 5.1 Maps of the sampling location at the Herman Kiefer facility in Detroit, Michigan, USA. From Google maps.

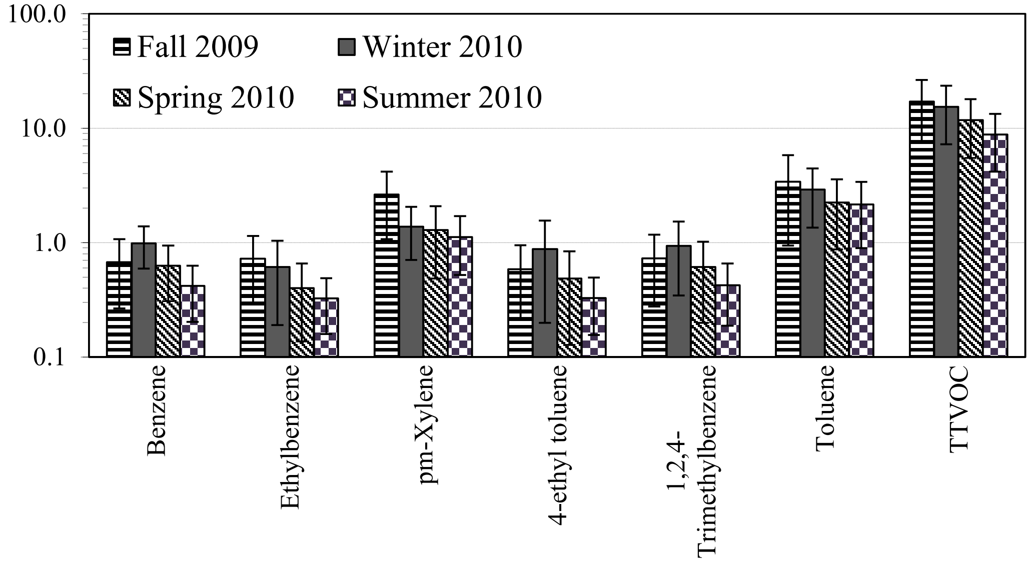


Figure 5.2 Concentrations of selected VOCs by season (μg/m^3) at Herman Kiefer, Detroit.

Table 5.1 Summary statistics for 41 VOCs measured at the Kiefer site from September 1, 2009 to August 16, 2010; 24-hr integrated samples.

Name	MDL $(\mu g/m^3)$	Det. Freq. (%)	Mean $(\mu g/m^3)$	St.Dev $(\mu g/m^3)$	Min $(\mu g/m^3)$	50 th $(\mu g/m^3)$	Max $(\mu g/m^3)$
Benzene	0.032	100%	0.71	0.40	0.11	0.61	2.94
Ethylbenzene	0.014	100%	0.54	0.39	0.07	0.43	2.79
pm-Xylene	0.016	100%	1.69	1.20	0.26	1.33	10.48
o-Xylene	0.015	100%	0.62	0.43	0.10	0.49	3.78
4-ethyl toluene	0.072	100%	0.60	0.49	0.07	0.48	4.15
1,3,5-Trimethylbenzene	0.010	100%	0.23	0.17	0.03	0.19	1.37
1,2,4-Trimethylbenzene	0.012	100%	0.71	0.49	0.10	0.59	3.72
Naphthalene	0.027	100%	0.22	0.13	0.03	0.20	1.21
Toluene	0.018	100%	2.76	1.86	0.27	2.26	12.36
n-Octane	0.032	100%	0.31	0.18	0.08	0.28	1.95
2-ethyl toluene	0.010	100%	0.25	0.20	0.03	0.19	1.69
1,2,3-trimethyl benzene	0.011	100%	0.26	0.21	0.03	0.21	1.74
n-Heptane	0.030	99%	0.74	0.58	0.15	0.60	7.13
n-Propylbenzene	0.010	98%	0.15	0.12	0.02	0.12	1.01
Methyl cyclohexane	0.012	97%	0.20	0.13	0.04	0.18	1.23
Styrene	0.020	97%	0.15	0.11	0.02	0.12	0.69
n-Dodecane	0.026	97%	0.15	0.11	0.02	0.13	0.67
1,4-Dichlorobenzene	0.008	96%	0.45	0.67	0.03	0.22	6.04
n-Undecane	0.028	95%	0.14	0.10	0.02	0.12	0.63
n-Tetradecane	0.089	91%	0.28	0.21	0.02	0.24	2.31
2-methylnaphthalene	0.040	88%	0.09	0.04	0.01	0.08	0.27
Tetrachloroethene	0.035	87%	0.14	0.09	0.02	0.11	0.51
n-Nonane	0.245	79%	0.57	0.37	0.10	0.48	2.85
n-Decane	0.124	76%	0.31	0.21	0.05	0.26	1.65
1-Methylnaphthalene	0.034	69%	0.05	0.03	0.00	0.05	0.18
n-Pentadecane	0.061	69%	0.16	0.14	0.01	0.13	1.17
n-Butylbenzene	0.013	68%	0.05	0.03	0.01	0.04	0.20
Isopropylbenzene	0.021	56%	0.06	0.04	0.01	0.05	0.26
n-Tridecane	0.045	54%	0.16	0.14	0.02	0.13	1.42
Carbontetrachloride	0.233	49%	0.25	0.12	0.02	0.23	0.87
Phenol	0.561	39%	0.64	0.52	0.08	0.53	5.24
p-Isopropyltoluene	0.009	34%	0.05	0.04	0.01	0.04	0.30
α-Pinene	0.012	32%	0.18	0.21	0.03	0.13	1.86
Methylene chloride	0.204	21%	1.99	2.97	0.23	0.71	17.67
n-Hexadecane	0.139	15%	0.14	0.13	0.03	0.11	1.10
Cyclohexane	0.306	13%	0.33	0.16	0.11	0.30	0.85
Chlorobenzene	0.021	11%	0.07	0.05	0.01	0.05	0.24
Limonene	0.228	5%	0.16	0.19	0.03	0.11	1.41
Trichloroethylene	0.040	4%	0.08	0.03	0.02	0.08	0.14
Methyl methacrylate	0.291	3%	0.38	0.32	0.06	0.31	1.23
sec-Butylbenzene	0.010	1%	0.34	0.61	0.02	0.04	1.26
TTVOC	**-**	**-**	**13.95**	**8.18**	**2.63**	**11.80**	**59.21**

Table 5.2 Spearman correlation coefficients for BTEX and TTVOC (sample size = 298).

Spearman's Correlation	Benzene	Toluene	Ethylbenzene	p-/m-Xylene	o-Xylene	TTVOC
Benzene	1	.58**	.50**	.40**	.40**	.53**
Toluene	-	1	.86**	.82**	.82**	.90**
Ethylbenzene	-	-	1	.92**	.92**	.93**
p-/m-Xylene	-	-	-	1	1.00**	.85**
o-Xylene	-	-	-	-	1	.85**
TTVOC	-	-	-	-	-	1

** Correlation is significant at the 0.01 level (2-tailed)

Table 5.3 Comparison of outdoor BTEX concentrations with literature.

Study	Location	Sites	Period	# of Sites	# of Sample	Concentration in $\mu g/m^3$, Mean (St.Dev)					
						Benzene	Toluene	Ethyl benzene	m-/p-Xylene	o-Xylene	ΣBTEX
This study	Detroit	Near roadway	Sep. 2009 - Aug. 2010	1	298	0.71 (0.40)	2.76 (1.86)	0.54 (0.39)	1.69 (1.20)	0.62 (0.43)	6.32
MDNRE[A]	Detroit (N.Delray)	Regulatory	Jan. 2009 - Dec. 2009	1	39	0.97	1.85	0.12	0.99	0.21	4.14
DATI-2[B]	Detroit (N.Delray)	Regulatory	Apr. 2006- Apr 2007	1	28	1.39	2.37	0.51	NA	0.52	4.79
MICA[C]	Detroit/ Dearborn	Outside Resident	Nov.-Dec. 2006	77	39	1.53 (0.89)	4.11 (2.79)	0.78 (0.52)	2.56 (1.78)	0.96 (0.65)	9.94
DEARS[D]	Detroit	Outside Resident	Jan.-March 2005-2007	145	616	1.73 (1.25)	3.20 (2.41)	0.83 (0.48)	2.47 (1.65)	0.82 (0.56)	9.05
DEARS[D]	Detroit	Regulatory and Non-Residential	July-Aug. 2004-2006	145	94	2.04 (1.34)	4.52 (2.15)	0.87 (0.74)	2.56 (2.65)	0.82 (0.69)	10.82
DEARS[D]	Detroit	Outside Resident	July-Aug. 2004-2006	145	687	2.75 (1.92)	7.54 (6.41)	1.30 (0.87)	4.12 (3.34)	1.35 (0.96)	17.06
DEARS[D]	Detroit	Regulatory and Non-Residential	Jan.-March 2005-2007	145	87	1.37 (0.93)	2.22 (1.92)	0.61 (0.30)	1.78 (1.00)	0.61 (0.35)	6.59
Mukerjee et al.[E]	Detroit/ Dearborn	Outside School	July-Aug. 2005	25	300	1.47 (0.35)	5.28 (1.28)	0.87 (0.22)	2.74 (0.74)	0.91 (0.22)	11.26

A: Michigan Department of Natural Resources and Environment (MDNRE).[32] B: Detroit air toxics initiative (DATI)-phase two.[29] C: The Mechanistic Indicators of Childhood Asthma (MICA).[34] D: Detroit Exposure and Aerosol Research Study (DEARS)[33] E: Mukerjee et al. (2009).[67]

Table 5.4 Ratios of BTEX concentrations.

Period	Annul	Fall 2009	Winter 2010	Spring 2010	Summer 2010
Sample size	298	90	84	81	43
Ratio					
Toluene/Benzene	4.33	5.07	2.93	3.57	5.16
Benzene/p-,m-,o-Xylene	0.38	0.19	0.52	0.36	0.27
Toluene/p-,m-,o-Xylene	1.25	0.95	1.53	1.27	1.41
Ethylbenzene/p-,m-,o-Xylene	0.24	0.20	0.32	0.23	0.21
p-,m-Xylene/Ethylbenzene	3.19	3.65	2.24	3.24	3.43

Table 5.5 Possible sources identified by PMF model.

Fall 2009			**TTVOC**	
Factor[A]	Possible source[B]	Featured species[C]	(%)[D]	(µg/m^3)[E]
1	Vehicle exhaust	BTEX, trimethyl benzene, C_{7-10} n-alkanes	34.4	5.85
3	Fuel evaporation and biogenic source	TEX, α-Pinene	18.7	3.19
4	Biomass burning	Benzene, methylene chloride	16.5	2.81
2	Industrial source	Styrene, xylenes, methylene chloride	15.6	2.65
5	Diesel exhaust	C_{10-16} n-alkanes	11.0	1.88
6	Unknown source	1,4-Dichlorobenzene	3.8	0.65
Winter 2010			**TTVOC**	
Factor[A]	Possible source[B]	Featured species[C]	(%)[D]	(µg/m^3)[E]
1	Vehicle exhaust	BTEX, trimethyl benzene, C_{7-10} n-alkanes	28.8	4.43
2	Fuel evaporation and biomass burning	BTEX, trimethyl benzene	20.5	3.15
3	Industrial source	Chlorobenzene, styrene, C_{14-16} n-alkanes	16.2	2.50
4	Diesel exhaust	BTEX, C_{10-16} n-alkanes	10.0	1.54
5	Unknown source	1,4-Dichlorobenzene	8.6	1.33
6	Industrial source	Methylene chloride	8.0	1.24
7	Biogenic and unknown source	p-Isopropyltoluene, 1,4-dichlorobenzene	5.9	0.91
8	Biogenic source	α-Pinene, p-isopropyltoluene	2.0	0.30
Spring 2010			**TTVOC**	
Factor[A]	Possible source[B]	Featured species[C]	(%)[D]	(µg/m^3)[E]
1	Vehicle exhaust	BTEX, trimethyl benzene, C_{7-10} n-alkanes	29.2	3.43
2	Industrial source	Chlorobenzene, styrene, trimethyl benzene, C_{14-15} n-alkanes	22.5	2.65
3	Biomass burning	Benzene, methylene chloride	17.1	2.01
4	Fuel evaporation and industrial source	BTEX, trimethyl benzene, methylene chloride	13.9	1.64
5	Diesel exhaust	BTEX, C_{10-16} n-alkanes	6.4	0.75
6	Unknown source	1,4-Dichlorobenzene and p-isopropyltoluene	6.0	0.70
7	Biogenic source	α-Pinene	4.8	0.57
Summer 2010			**TTVOC**	
Factor[A]	Possible source[B]	Featured species[C]	(%)[D]	(µg/m^3)[E]
1	Fuel evaporation	BTEX, trimethyl benzene	22.0	1.93
2	Vehicle exhaust	BTEX, trimethyl benzene, C_{7-10} n-alkanes	20.5	1.80
3	Industrial and biogenic source	Styrene, α-pinene	15.2	1.33
4	Diesel exhaust	C_{10-16} n-alkanes	14.8	1.30
5	Industrial source	Styrene, xylenes, n-heptane, n-tetradecane, n-hexadecane	14.6	1.29
6	Unknown source	1,4-Dichlorobenzene, p-Isopropyltoluene, BTEX, alkanes	12.9	1.14

A: Factors resolved by PMF model. B: Interpretation for possible source based on featured VOCs. C: Featured VOCs dominated in that factor. D: Factor contributions (%) of TTVOC (sum of all factors = 100%). E: Factor contributions presented in concentration (µg/m^3) of TTVOC.

Table 5.6 Source apportionments for Detroit based on CMB models.

References	Scheff et al.,1996		Kenski et al., 1995	
Location	Detroit, MI. Three urban sites were located in Wayne city.		Detroit, MI. I94 service drive at Grande West.	
Period and Measurements	July and August in 1993. 8 days data of 2-hour canister samples at 6 am, 10 am and 2 pm.		July and August in 1988. 39 weekdays of hourly canister samples at 6 am, 8 am, 12 pm, 2 pm and 10 pm.	
Sample size	97		192	
Source catogories	CMB (% of NMOC)	Emission Inventory[a]	CMB (% of NMOC)	Emission Inventory
Vehicle exhaust	38.4	37.7	28.2	32.9
Industry (refinery)	7.0	0[b]	16.5	0.7
Gasoline vapor	1.8	9.1	9.4	6.9
Solvent (architectural coating)	4.9	0.6	2.5	3.8
Solvent (graphic arts)	4.1	6.3	4.7	0.7
Industry (coke ovens)	2.9	1.9	3.7	2.0
Liquid gasoline	6.1	-	-	-
Others (100% - above)	34.8	44.4	34.5	53.0

- : not reported. NMOC = sum of chromatographic peaks. [a] 1993 southeast Michigan ozone study (SEMOS) modeling at Wanye county monitor locations. [b] The Marathon refinery is located in Wanye county, but is outside of the grid cells of SEMOS study.

Table 5.7 VOC emission inventory for Wayne county, Michigan for 2005 from EPA.[60]

Rank	Source sector	Total Emissions (tons)	(%)
1	On road vehicles	35,267	43.1
2	Solvent use	25,991	31.8
3	Non road equipment	8,437	10.3
4	Miscellaneous	6,962	8.5
5	Industrial processes	3,594	4.4
6	Fossil fuel combustion	804	1.0
7	Waste disposal	531	0.6
8	Electricity generation	149	0.2
9	Residential wood combustion	117	0.1

Available online: http://www.epa.gov/air/emissions/voc.htm

5.7 Appendix

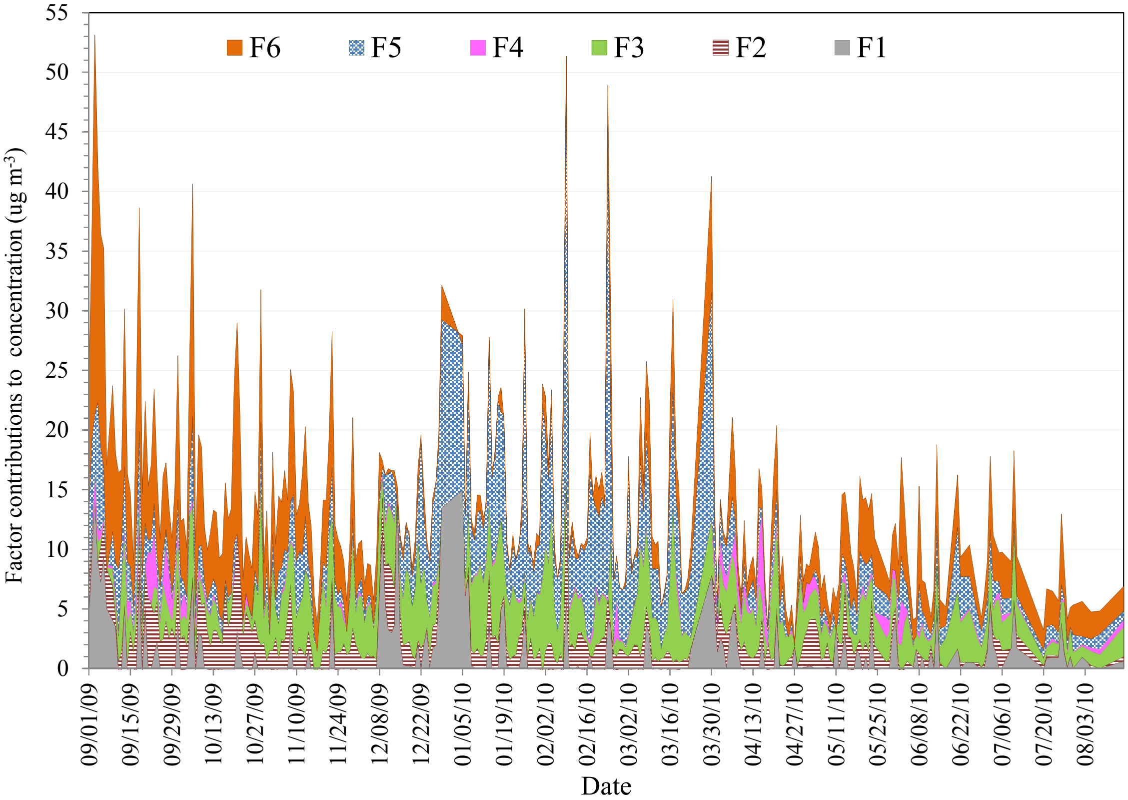


Figure A5.1 Trends of contributions for 6 factors resolved by PMF at Herman Kiefer, Detroit, Michigan, USA (9/01/2009 to 8/16/2010).

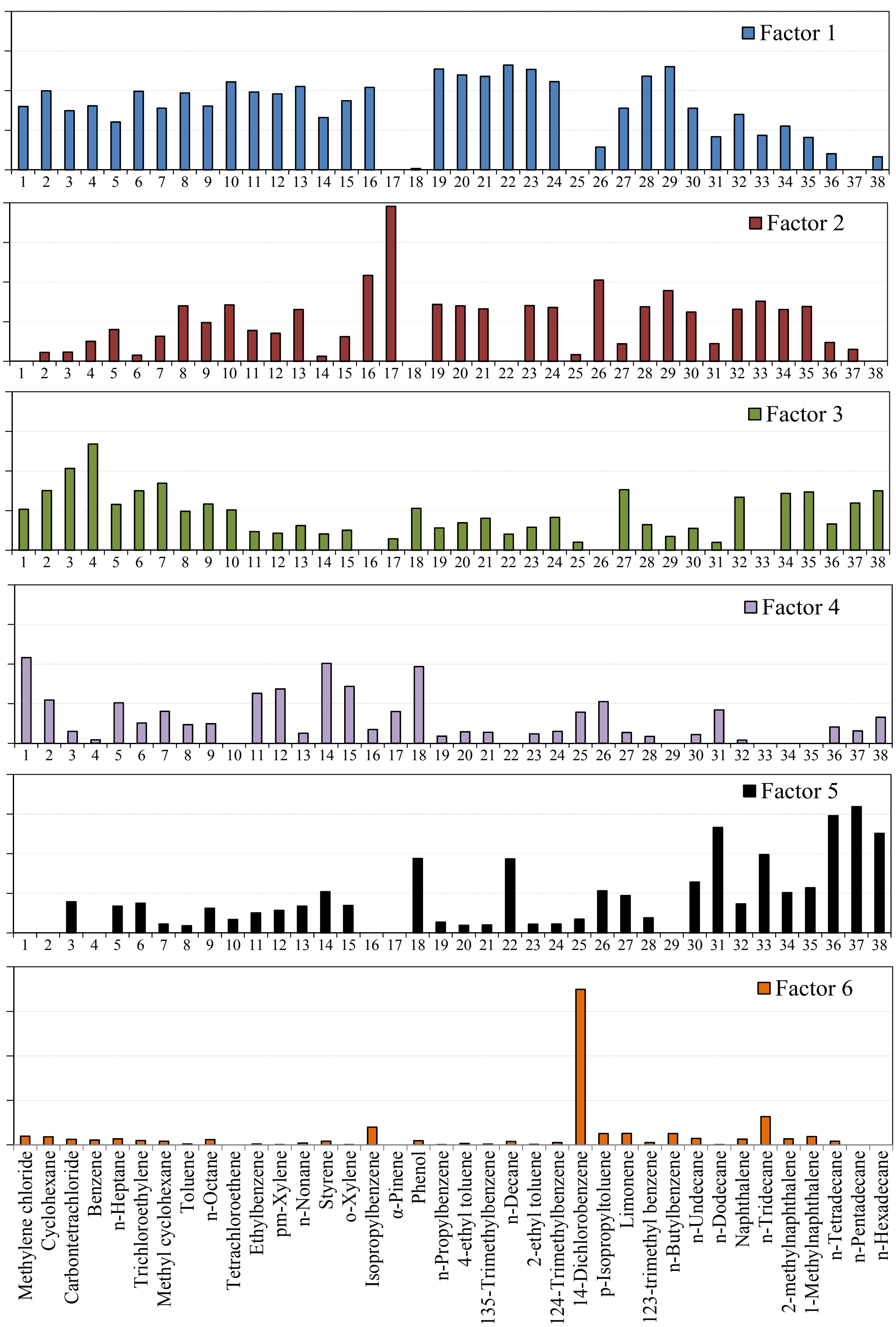


Figure A5.2 Factor profiles (% of species total) for fall 2009.

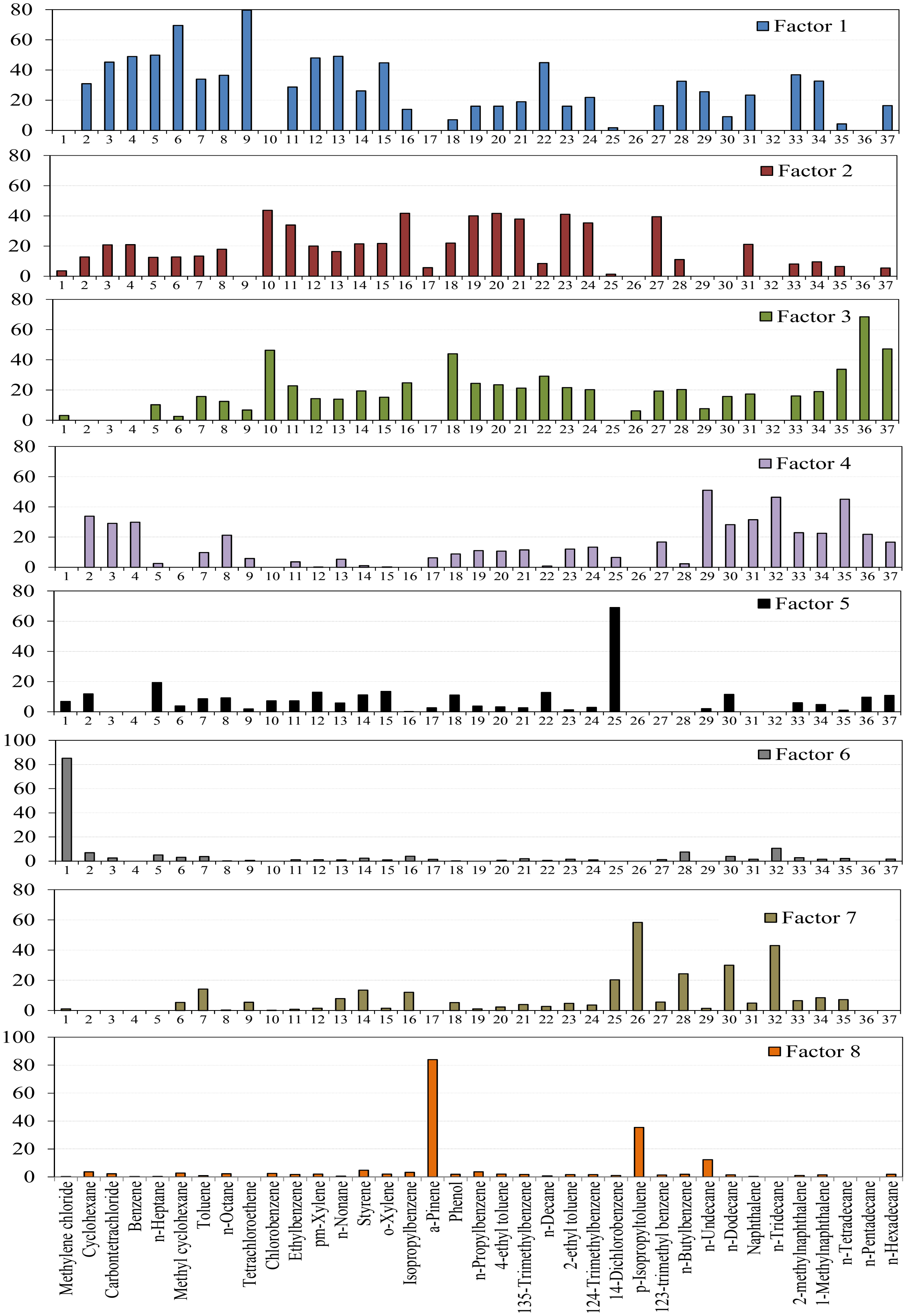


Figure A5.3 Factor profiles (% of species total) for winter 2010.

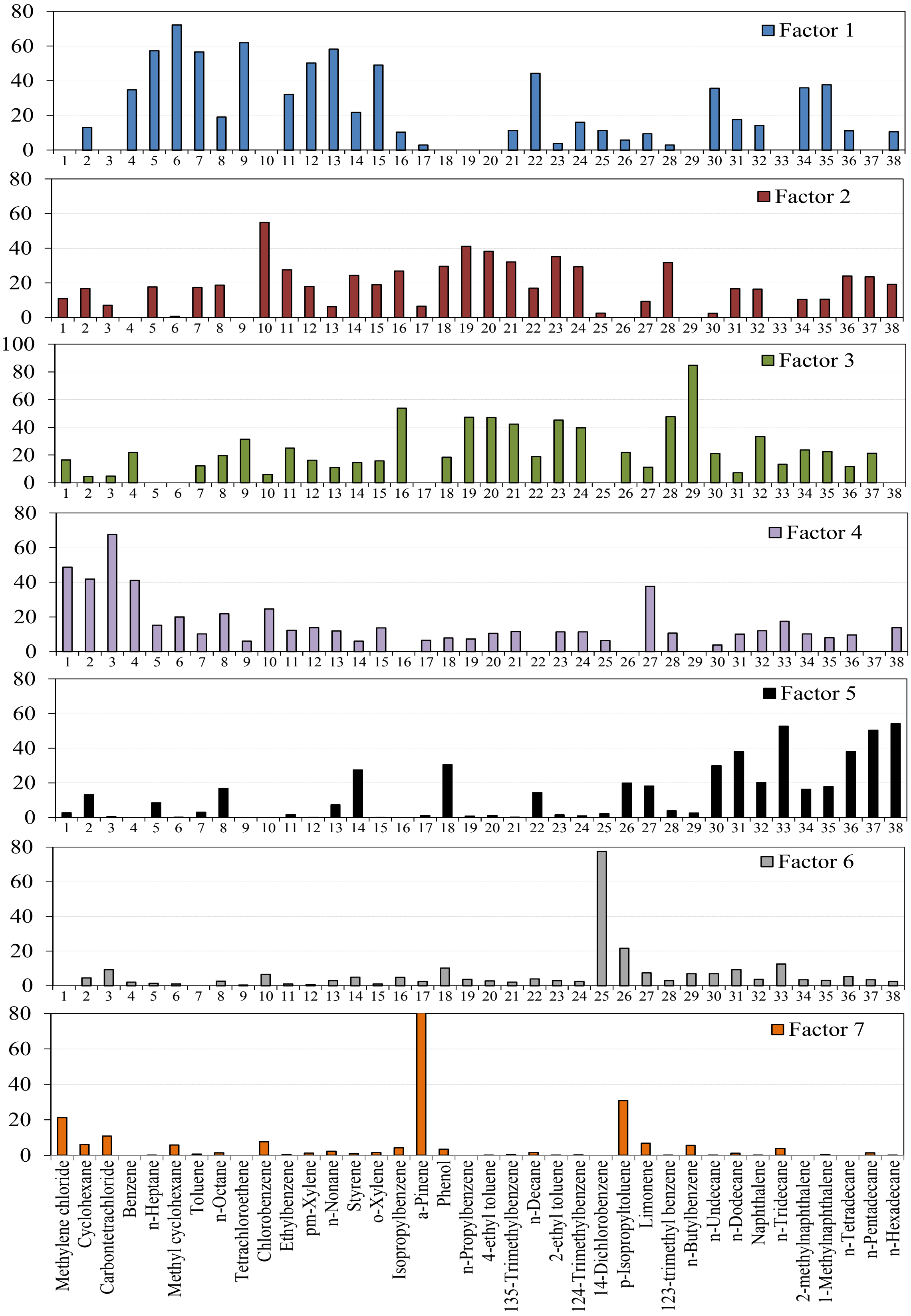


Figure A5.4 Factor profiles (% of species total) for spring 2010.

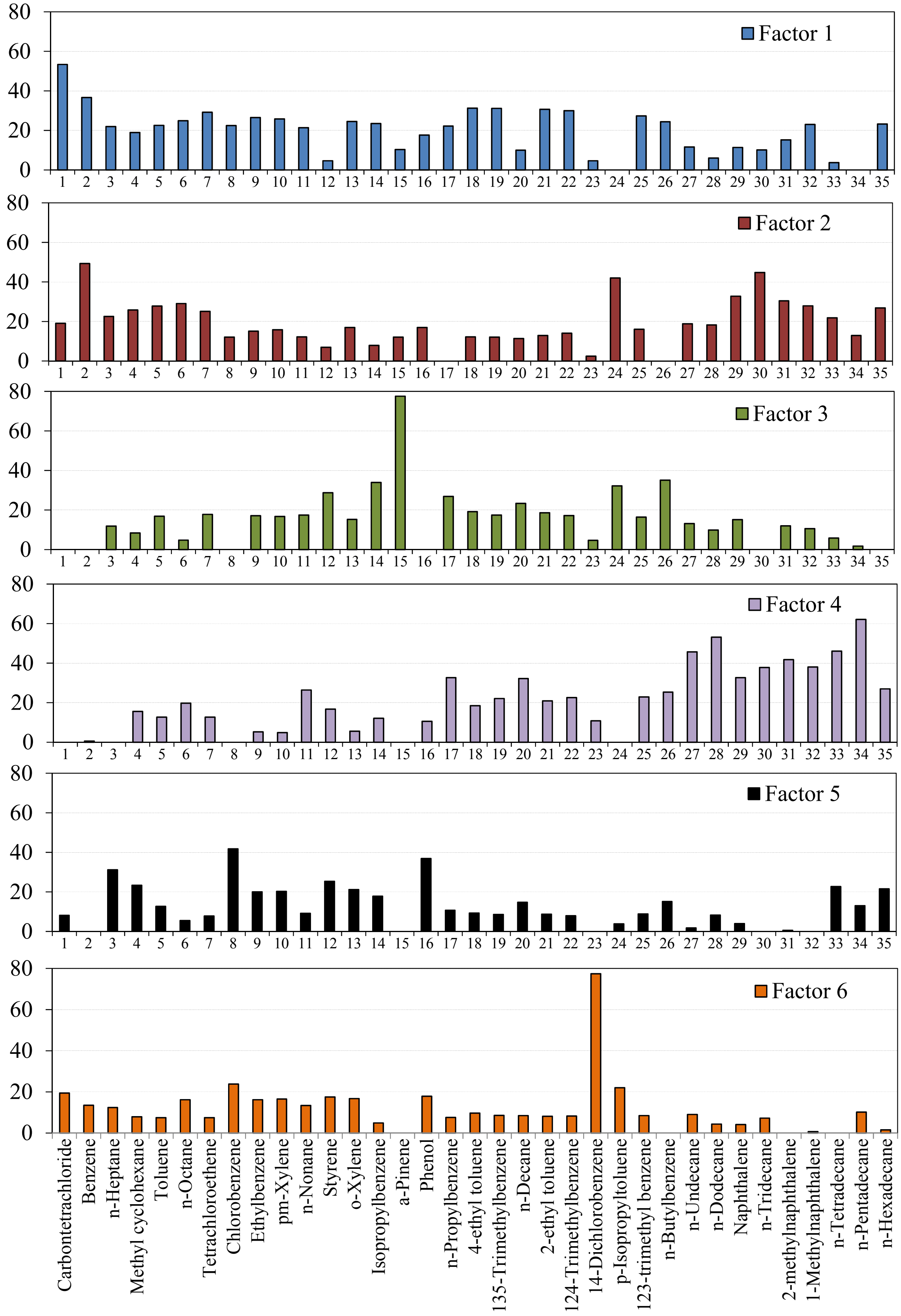


Figure A5.5 Factor profiles (% of species total) for summer 2010.

Table A5.1 VOCs used in PMF model, showing detection frequency and variable classification by season.

Season	Sample size		Season	Sample size		Season	Sample size		Season	Sample size	
Fall 2009	90		Winter 2010	84		Spring 2010	81		Summer 2010	43	
Species	% ≥MDL	Categories	Species	% ≥MDL	Categories	Species	% ≥MDL	Categories	Species	% ≥MDL	Categories
Benzene	100%	Strong	Benzene	100%	Strong	Benzene	100%	Strong	Benzene	100%	Strong
n-Heptane	100%	Strong	n-Heptane	100%	Strong	n-Heptane	98%	Strong	n-Heptane	100%	Strong
Toluene	100%	Strong	Toluene	100%	Strong	Toluene	99%	Strong	Toluene	100%	Strong
n-Octane	100%	Strong	n-Octane	100%	Strong	n-Octane	99%	Strong	n-Octane	100%	Strong
Ethylbenzene	100%	Strong	Ethylbenzene	100%	Strong	Ethylbenzene	100%	Strong	Ethylbenzene	100%	Strong
p-,m-Xylene	100%	Strong	p-,m-Xylene	100%	Strong	p-,m-Xylene	100%	Strong	p-,m-Xylene	100%	Strong
o-Xylene	100%	Strong	o-Xylene	100%	Strong	o-Xylene	100%	Strong	o-Xylene	100%	Strong
4-ethyl toluene	100%	Strong	4-ethyl toluene	100%	Strong	4-ethyl toluene	100%	Strong	4-ethyl toluene	100%	Strong
1,3,5-Trimethylbenzene	100%	Strong	1,3,5-Trimethylbenzene	100%	Strong	1,3,5-Trimethylbenzene	100%	Strong	1,3,5-Trimethylbenzene	100%	Strong
1,2,4-Trimethylbenzene	100%	Strong	1,2,4-Trimethylbenzene	100%	Strong	1,2,4-Trimethylbenzene	100%	Strong	1,2,4-Trimethylbenzene	100%	Strong
Naphthalene	100%	Strong	Naphthalene	100%	Strong	Naphthalene	100%	Strong	Naphthalene	100%	Strong
Methyl cyclohexane	100%	Strong	Methyl cyclohexane	95%	Strong	Methyl cyclohexane	95%	Strong	Methyl cyclohexane	100%	Strong
2-ethyl toluene	99%	Strong	2-ethyl toluene	100%	Strong	2-ethyl toluene	100%	Strong	2-ethyl toluene	100%	Strong
1,2,3-trimethyl benzene	99%	Strong	1,2,3-trimethyl benzene	100%	Strong	1,2,3-trimethyl benzene	100%	Strong	1,2,3-trimethyl benzene	100%	Strong
Styrene	98%	Strong	Styrene	100%	Strong	Styrene	99%	Strong	Styrene	88%	Strong
n-Propylbenzene	98%	Strong	n-Propylbenzene	100%	Strong	n-Propylbenzene	98%	Strong	n-Propylbenzene	95%	Strong
n-Dodecane	98%	Strong	n-Dodecane	100%	Strong	n-Dodecane	99%	Strong	n-Dodecane	84%	Strong
n-Tetradecane	98%	Strong	n-Tetradecane	99%	Strong	n-Tetradecane	95%	Strong	n-Tetradecane	56%	Strong
Tetrachloroethene	98%	Strong	Tetrachloroethene	74%	Strong	Tetrachloroethene	85%	Strong	Tetrachloroethene	91%	Strong
1,4-Dichlorobenzene	97%	Strong	1,4-Dichlorobenzene	98%	Strong	1,4-Dichlorobenzene	93%	Strong	1,4-Dichlorobenzene	95%	Strong
n-Undecane	97%	Strong	n-Undecane	98%	Strong	n-Undecane	90%	Strong	n-Undecane	95%	Strong
2-methylnaphthalene	96%	Strong	2-methylnaphthalene	98%	Strong	2-methylnaphthalene	85%	Strong	2-methylnaphthalene	58%	Strong
n-Nonane	91%	Strong	n-Nonane	79%	Strong	n-Nonane	73%	Strong	n-Nonane	65%	Strong
n-Pentadecane	86%	Strong	n-Pentadecane	60%	Strong	n-Pentadecane	80%	Strong	n-Pentadecane	35%	Strong
n-Decane	82%	Strong	n-Decane	77%	Strong	n-Decane	72%	Strong	n-Decane	65%	Strong
n-Butylbenzene	78%	Strong	n-Butylbenzene	83%	Strong	n-Butylbenzene	47%	Strong	n-Butylbenzene	60%	Strong
n-Tridecane	78%	Strong	n-Tridecane	74%	Strong	n-Tridecane	28%	Strong	n-Tridecane	16%	Strong
1-Methylnaphthalene	73%	Strong	1-Methylnaphthalene	81%	Strong	1-Methylnaphthalene	69%	Strong	1-Methylnaphthalene	40%	Strong
Isopropylbenzene	63%	Strong	Isopropylbenzene	73%	Strong	Isopropylbenzene	41%	Strong	Isopropylbenzene	35%	Strong
p-Isopropyltoluene	48%	Strong	p-Isopropyltoluene	36%	Strong	p-Isopropyltoluene	21%	Strong	p-Isopropyltoluene	28%	Strong
Phenol	41%	Strong	Phenol	54%	Strong	Phenol	36%	Strong	Phenol	14%	Weak
a-Pinene	28%	Strong	a-Pinene	32%	Strong	a-Pinene	28%	Strong	a-Pinene	49%	Strong
Carbontetrachloride	18%	Strong	Carbontetrachloride	68%	Strong	Carbontetrachloride	70%	Strong	Carbontetrachloride	37%	Strong
Cyclohexane	18%	Strong	Cyclohexane	17%	Strong	Cyclohexane	9%	Weak	Cyclohexane	2%	Bad
n-Hexadecane	14%	Weak	n-Hexadecane	7%	Weak	n-Hexadecane	27%	Strong	n-Hexadecane	9%	Weak
Methylene chloride	7%	Weak	Methylene chloride	42%	Strong	Methylene chloride	27%	Strong	Methylene chloride	2%	Bad
Limonene	7%	Weak	Limonene	2%	Bad	Limonene	7%	Weak	Limonene	0%	Bad
Trichloroethylene	6%	Weak	Trichloroethylene	4%	Bad	Trichloroethylene	4%	Bad	Trichloroethylene	2%	Bad
sec-Butylbenzene	4%	Bad	sec-Butylbenzene	0%	Bad	sec-Butylbenzene	0%	Bad	sec-Butylbenzene	0%	Bad
Chlorobenzene	1%	Bad	Chlorobenzene	25%	Strong	Chlorobenzene	7%	Weak	Chlorobenzene	9%	Weak

Table A5.2 Air pollutant sources near the Kiefer site (4 km radius).

Facility name	City	State	Zip
American Axle & Manufacturing Incorporated	DETROIT	MI	48212
Arco Alloys Corporation	DETROIT	MI	48211
Basf Corp	HAMTRAMCK	MI	48212
Caraco Pharmaceutical Lab Ltd	DETROIT	MI	48202
City Concrete & Asphalt Crushing Llc	DETROIT	MI	48211
City Of Detroit Dept Of Transportation	DETROIT	MI	48208
Commercial Steel Treating Corp	DETROIT	MI	48204
Continental Baking	DETROIT	MI	48238
Continental Metal Company (Sb)	DETROIT	MI	48211
Deluxe Hard Chrome Service	DETROIT	MI	48238
Detroit Chrome Electro Forming Company	DETROIT	MI	48238
Detroit Forge Plant	DETROIT	MI	48212
Detroit Pub Schl Ne	DETROIT	MI	48207
Detroit Thermal Blvd Heating Plant	DETROIT	MI	48226
Detroit Thermal Llc	DETROIT	MI	48226
Detroit Thermal Willis Heating Plant	DETROIT	MI	48226
Doric Vault Detroit Inc	DETROIT	MI	48204
Empire Iron Works, Inc.	DETROIT	MI	48240
Ferrous Processing And Trading Schlaefer	DETROIT	MI	48211
Focushope Center	DETROIT	MI	48238
Fpt/Schlafer (Ferrous Processing) (Sb)	DETROIT	MI	48211
Gateway Additive Company	DETROIT	MI	48204
General Motors Mlcg Detroit-Hamtramck Assembly Center	DETROIT	MI	48211
Gmc Saginaw Detroit Forge	DETROIT	MI	48212
Greater Detroit Resource Recovery Facili	DETROIT	MI	48211
Henry Ford Hospital	DETROIT	MI	48202
Master Alloys Corp	DETROIT	MI	48211
Michigan Piano Company	DETROIT	MI	48211
Michigan Waste Services	HAMTRAMCK	MI	48211
Moses Baptist Temple	DETROIT	MI	48202
Msx International Special Vehicles Lynch	DETROIT	MI	48202
Msx Intl Special Vehicles	DETROIT	MI	48211
Progressive Poletown Properties	HAMTRAMCK	MI	48212
Recycled Polymeric Materials Inc	DETROIT	MI	48204
Seibert Oxidermo Incorporated	DETROIT	MI	48211
Trimtech Llc	DETROIT	MI	48202
Usl City Environmental Incorporated	DETROIT	MI	48211
Wayne State University	DETROIT	MI	48202

* U.S. EPA. Envirofacts. http://www.epa.gov/emefdata/em4ef.home; last update: Feb. 2011.

Table A5.3 Average concentration ($\mu g/m^3$) of target VOCs, and tests for differences by season (Kruskal-Wallis test).

Name	Fall 2009		Winter 2010		Spring 2010		Summer 2010		Kruskal Wallis
	Mean	St.Dev	Mean	St.Dev	Mean	St.Dev	Mean	St.Dev	Test (p*)
Benzene	0.67	0.40	0.99	0.40	0.62	0.32	0.42	0.21	0.00
Ethylbenzene	0.72	0.43	0.61	0.42	0.40	0.26	0.32	0.17	0.00
pm-Xylene	2.62	1.54	1.38	0.67	1.29	0.80	1.11	0.59	0.00
o-Xylene	0.95	0.53	0.52	0.26	0.47	0.29	0.41	0.23	0.00
4-ethyl toluene	0.58	0.37	0.88	0.68	0.48	0.36	0.33	0.17	0.00
1,3,5-Trimethylbenzene	0.21	0.13	0.33	0.23	0.20	0.14	0.13	0.07	0.00
1,2,4-Trimethylbenzene	0.72	0.45	0.94	0.59	0.61	0.41	0.42	0.24	0.00
Naphthalene	0.20	0.11	0.29	0.15	0.20	0.11	0.15	0.11	0.00
Toluene	3.39	2.45	2.90	1.55	2.23	1.36	2.15	1.25	0.00
n-Octane	0.43	0.26	0.28	0.10	0.26	0.10	0.20	0.07	0.00
2-ethyl toluene	0.23	0.14	0.38	0.28	0.20	0.14	0.13	0.07	0.00
1,2,3-trimethyl benzene	0.24	0.14	0.41	0.28	0.21	0.14	0.13	0.07	0.00
n-Heptane	1.14	0.82	0.52	0.22	0.58	0.31	0.58	0.35	0.00
n-Propylbenzene	0.14	0.09	0.23	0.17	0.13	0.09	0.09	0.04	0.00
Methyl cyclohexane	0.26	0.16	0.17	0.07	0.18	0.12	0.16	0.12	0.00
Styrene	0.19	0.11	0.16	0.11	0.12	0.09	0.08	0.06	0.00
n-Dodecane	0.22	0.12	0.15	0.11	0.12	0.05	0.06	0.03	0.00
1,4-Dichlorobenzene	0.62	0.75	0.20	0.29	0.57	0.86	0.33	0.49	0.00
n-Undecane	0.21	0.12	0.13	0.08	0.12	0.06	0.08	0.04	0.00
n-Tetradecane	0.36	0.19	0.32	0.28	0.23	0.11	0.12	0.07	0.00
2-methylnaphthalene	0.10	0.05	0.09	0.04	0.08	0.04	0.06	0.03	0.00
Tetrachloroethene	0.15	0.09	0.12	0.07	0.17	0.11	0.10	0.05	0.00
n-Nonane	0.82	0.49	0.45	0.20	0.50	0.25	0.36	0.14	0.00
n-Decane	0.49	0.27	0.25	0.13	0.27	0.14	0.19	0.09	0.00
1-Methylnaphthalene	0.05	0.03	0.06	0.02	0.05	0.02	0.04	0.02	0.00
n-Pentadecane	0.18	0.12	0.20	0.22	0.14	0.09	0.07	0.06	0.00
n-Butylbenzene	0.05	0.03	0.06	0.03	0.05	0.02	0.03	0.01	0.00
Isopropylbenzene	0.07	0.04	0.08	0.05	0.05	0.03	0.03	0.01	0.00
n-Tridecane	0.21	0.17	0.18	0.11	0.10	0.06	0.04	0.02	0.00
Carbontetrachloride	0.17	0.08	0.30	0.12	0.31	0.10	0.22	0.13	0.00
Phenol	0.63	0.36	0.73	0.76	0.60	0.27	0.45	0.34	0.00
p-Isopropyltoluene	0.04	0.02	0.09	0.06	0.05	0.02	0.03	0.01	0.00
α-Pinene	0.18	0.10	0.24	0.36	0.17	0.10	0.09	0.07	0.55
Methylene chloride	0.79	0.46	2.44	2.70	1.68	3.69	0.43	-	0.00
n-Hexadecane	0.12	0.08	0.29	0.32	0.16	0.09	0.10	0.07	0.00
Cyclohexane	0.40	0.20	0.35	0.10	0.27	0.10	0.23	0.12	0.03
Chlorobenzene	0.06	-	0.07	0.06	0.09	0.06	0.05	0.02	0.00
Limonene	0.14	0.08	0.14	0.11	0.26	0.33	0.07	0.03	0.00
Trichloroethylene	0.08	0.03	0.08	0.02	0.11	0.03	0.06	0.05	0.00
Methyl methacrylate	-	-	0.33	0.25	0.77	0.65	-	-	0.00
sec-Butylbenzene	0.34	0.61	-	-	-	-	-	-	0.00
TTVOC	17.03	9.31	15.40	8.17	11.76	6.25	8.78	4.61	0.00

* significant level 0.05.

Table A5.4 Summary statistics of VOC concentration ($\mu g/m^3$) by weekdays and weekend, and tests for differences by these periods (Kruskal-Wallis test).

	Monday to Friday (n=215)					Saturday and Sunday (n=83)					Kruskal Wallis
Compound	Mean	St Dev	Min	50 th	Max	Mean	St Dev	Min	50 th	Max	Test (p*)
Benzene	0.71	0.42	0.11	0.61	2.94	0.71	0.36	0.12	0.58	1.86	0.72
Ethylbenzene	0.58	0.42	0.07	0.45	2.79	0.47	0.27	0.13	0.40	1.50	**0.05**
pm-Xylene	1.77	1.27	0.26	1.37	10.48	1.49	1.00	0.45	1.22	5.33	**0.03**
o-Xylene	0.65	0.45	0.10	0.50	3.78	0.55	0.35	0.19	0.46	1.94	**0.03**
4-ethyl toluene	0.64	0.55	0.07	0.51	4.15	0.50	0.30	0.12	0.45	1.43	**0.04**
1,3,5-Trimethylbenzene	0.25	0.19	0.03	0.20	1.37	0.19	0.11	0.05	0.17	0.54	**0.02**
1,2,4-Trimethylbenzene	0.75	0.53	0.10	0.61	3.72	0.60	0.35	0.16	0.54	1.75	**0.02**
Naphthalene	0.22	0.14	0.03	0.19	1.21	0.21	0.11	0.05	0.21	0.52	0.85
Toluene	2.84	1.88	0.27	2.31	12.36	2.54	1.80	0.69	2.03	9.97	**0.05**
n-Octane	0.31	0.16	0.09	0.27	0.99	0.31	0.23	0.08	0.28	1.95	0.75
2-ethyl toluene	0.26	0.22	0.03	0.21	1.69	0.20	0.13	0.06	0.18	0.62	**0.04**
1,2,3-trimethyl benzene	0.28	0.23	0.03	0.22	1.74	0.22	0.14	0.05	0.18	0.70	0.07
n-Heptane	0.76	0.62	0.19	0.62	7.13	0.68	0.45	0.15	0.58	2.39	0.13
n-Propylbenzene	0.16	0.14	0.02	0.13	1.01	0.13	0.07	0.03	0.12	0.36	0.05
Methyl cyclohexane	0.21	0.14	0.04	0.18	1.23	0.18	0.10	0.04	0.16	0.47	0.08
Styrene	0.15	0.12	0.02	0.12	0.69	0.13	0.07	0.02	0.12	0.32	0.52
n-Dodecane	0.15	0.11	0.02	0.12	0.67	0.15	0.10	0.03	0.13	0.47	0.75
1,4-Dichlorobenzene	0.46	0.72	0.03	0.22	6.04	0.40	0.54	0.03	0.22	3.41	0.94
n-Undecane	0.15	0.10	0.02	0.13	0.63	0.14	0.09	0.02	0.12	0.56	0.90
n-Tetradecane	0.27	0.22	0.02	0.24	2.31	0.29	0.17	0.04	0.25	0.99	0.24
2-methylnaphthalene	0.09	0.05	0.01	0.08	0.27	0.08	0.04	0.02	0.08	0.26	0.66
Tetrachloroethene	0.15	0.09	0.04	0.12	0.51	0.12	0.08	0.02	0.09	0.39	**0.01**
n-Nonane	0.57	0.35	0.14	0.51	2.12	0.58	0.44	0.10	0.46	2.85	0.42
n-Decane	0.31	0.22	0.05	0.26	1.65	0.32	0.21	0.08	0.27	1.07	0.75
1-Methylnaphthalene	0.05	0.03	0.00	0.05	0.18	0.05	0.02	0.01	0.05	0.13	0.50
n-Pentadecane	0.16	0.16	0.01	0.12	1.17	0.16	0.09	0.04	0.14	0.44	0.44
n-Butylbenzene	0.05	0.03	0.01	0.04	0.20	0.05	0.03	0.01	0.04	0.15	0.31
Isopropylbenzene	0.06	0.05	0.01	0.05	0.26	0.06	0.04	0.02	0.05	0.16	**0.02**
n-Tridecane	0.16	0.15	0.02	0.12	1.42	0.16	0.10	0.04	0.13	0.47	0.33
Carbontetrachloride	0.25	0.12	0.02	0.24	0.87	0.24	0.11	0.04	0.21	0.51	0.36
Phenol	0.67	0.60	0.08	0.53	5.24	0.57	0.25	0.17	0.53	1.10	0.88
p-Isopropyltoluene	0.06	0.05	0.01	0.04	0.30	0.04	0.02	0.02	0.04	0.09	0.09
α-Pinene	0.19	0.23	0.03	0.14	1.86	0.13	0.08	0.04	0.10	0.30	**0.04**
Methylene chloride	2.23	3.23	0.23	0.88	17.67	1.33	2.05	0.29	0.60	7.76	0.64
n-Hexadecane	0.14	0.14	0.03	0.10	1.10	0.15	0.09	0.04	0.13	0.45	**0.05**
Cyclohexane	0.33	0.16	0.11	0.30	0.85	0.33	0.12	0.19	0.33	0.53	0.17
Chlorobenzene	0.08	0.05	0.02	0.06	0.24	0.03	0.01	0.01	0.03	0.04	**0.03**
TTVOC	14.51	8.62	2.63	12.36	59.21	12.50	6.72	3.73	10.79	37.37	0.08

*Bold values are statistically significantly ($p<0.05$)

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Chapter 6

Conclusions

The overall goal of this research was to investigate consequences of using the new motor vehicle fuels, including bioethanol and biodiesel blends, and specifically, to improve the understanding of fuel composition, permeation rates, diesel exhaust emissions, and contributions from gasoline and diesel vehicles at a near highway site using source apportionment analyses. The research had four specific aims: (1) Characterizing compositions of current motor vehicle fuels and vapors, and performing a collinearity analysis for receptor modeling; (2) Evaluating permeation of fuels through personal protective equipment (PPE) in order to understand the dermal exposures and aid the selection of PPE materials; (3) Characterizing exhaust emissions from diesel engines at various loads and speeds for different fuels, and; (4) Investigating the levels and sources of VOCs at a near road site in Detroit, Michigan.

Compositions of the new motor fuels (petroleum fuels and biofuel blends) differ from previous fuels, and thus exposures and risks associated with these fuels likely also differ. Overall, the experimental studies conducted for aims 1 to 3 showed that the formulation of motor fuels significantly alters the magnitude and composition of evaporative and exhaust emissions, permeation rates, and the fuel- and vehicle-related source profiles. Emissions were fuel-, PPE- and vehicle-specific, but distinct profiles for gasoline and diesel fuels and vapors were observed. In aim 4, VOCs monitored at a near highway site for a one year period were used in source apportionment models to identify important sources, an ambient setting relevant to understanding of exposures of the general public. In addition, the chemical compositions of these fuels and sources characterized in this dissertation have significant implications for both environmental and occupational exposures associated with the fuel cycle, and considerable relevance to source apportionment and general air quality management.

This chapter summarizes the major findings, significance and limitations of this research. Each chapter, which focuses on one of the specific aims, is discussed in turn. This is followed by recommendations for further research.

6.1 Composition of current motor vehicle fuels and vapors and collinearity analysis for receptor modeling

The VOC composition of four commercial motor vehicle fuels and their headspace vapors, including gasoline (<10% ethanol), E85 (85% bioethanol and 15% gasoline), ultra-low sulfur diesel (ULSD) and B20 (20% soy methyl ether with 80% ULSD), was presented in Chapter 2. Gasoline and E85 were dominated by aromatics and n-heptane (including both liquid fuel and headspace vapor), and E85 and gasoline compositions differed considerably. Despite E85's low gasoline content, vapor concentrations of many VOCs (e.g., n-octane, ethyl benzene, p-, m-,o-xylene, n-nonane at 5 ^{o}C, and 15 VOCs at 40 ^{o}C) exceeded levels in gasoline vapor. Additionally, the partial pressures of 17 target VOCs in E85 increased faster with temperature than gasoline, further shifting the VOC composition. ULSD and B20 had similar liquid and vapor compositions, and were dominated by C_9 to C_{16} n-alkanes, followed by aromatics.

VOC concentrations in the diesel fuels were low compared to gasoline. Gasoline showed compositions were generally comparable to those in the literature, but scant data exist in the open literature regarding the composition of E85, ULSD and B20.

Headspace compositions predicted using the fuel's composition, vapor-liquid equilibrium theory, and activity coefficients (when available) had reasonable correlation to measured values, although predictions for fuels other than gasoline showed large biases. For E85, systematic underprediction of headspace vapor concentrations suggests that activity coefficients in the range of 1.5 to 2.0 are needed. While predictions are potentially simple and cost-efficient, measurements remain necessary given these limitations of availability of activity coefficients, approximations in the Antoine equation, and variation or experimental errors in the composition of fuel. Collinearity among profiles was evaluated using singular value variance-decomposition (SVD) analyses, which showed strong correlation among B20 and ULSD fuels and headspace vapors, but distinct profiles for gasoline and diesel fuels and vapors. These results can be used to help estimate fuel related emissions and exposures, particularly as profiles in receptor models that identify and apportion emission sources. Importantly, the collinearity analysis suggests that gasoline- and diesel-related emissions can be distinguished, as demonstrated in Chapter 5.

6.2 Permeation through personal protective equipment (PPE)

Motor fuels are complex mixtures of hydrocarbons that include toxic compounds such as benzene and other toxic compounds, and require controls to limit inhalation and dermal exposures. Chapter 3 measured breakthrough times (BTs), permeation rates (PRs), and the VOC composition of permeants for four fuels (gasoline, E85, ULSD and

B20) through three types of gloves (neoprene, nitrile Sol-Vex and Viton) commonly used as PPE, three types of gloves (latex, nitrile and vinyl) used in laboratory settings, and a reference material (neoprene sheet).

Both BTs and PRs showed the dependence on the fuel-PPE material combination. Gasoline tended to have the highest PR among the four fuels, and only the Viton glove gave excellent protection (BT > 8 hr). Diesel and B20 had low PRs, and both Viton and nitrile Sol-Vex materials gave good protection; neoprene also could give acceptable protection. The compositions of permeants differed from neat fuels, and also depended strongly on the glove-fuel combination. Importantly, permeants were "enriched" in lighter aromatic VOCs (e.g., benzene), and "depleted" in the heavier alkanes, relative to the composition of the neat fuel. Due to the toxicities of permeants, workers protected by PPE may have larger exposures of these enriched toxics than expected based on the fuel composition or the total PR.

Among the scenarios, inhalation and dermal exposures estimated for fuel delivery workers, service station attendants and laboratory workers can exceed guidelines. Although simplified and representing only a subset of occupational settings where PPE is worn, the scenarios demonstrate the importance of selecting and wearing appropriate PPE.

6.3 Characterization of exhaust emissions from two diesel engines using B20 and ULSD fuels.

Chapter 4 investigated regulated and unregulated emissions from two diesel engines (1.7 and 6.4 L displacement) using B20 and ULSD fuels. The engines were equipped with various exhaust aftertreatment systems, including a diesel oxidation catalyst (DOC), a catalyzed diesel particle filter (DPF), and exhaust gas recirculation (EGR). Tests were performed at idle and load conditions. The B20 and aftertreatment systems did not significantly affect engine performance (e.g., power and fuel consumption). For both engines under load, B20 generally reduced emissions of particulate matter (PM), non-methane hydrocarbons (NMHCs) and target VOCs, however, nitrogen oxides (NO_x) and formaldehyde emissions sometimes increased. The DOC and catalyzed DPF converted a high fraction of carbon monoxide (CO), NMHC, formaldehyde, target VOCs and PM (with DPF only) when the operating temperature was reached (> 250 ^{o}C). Importantly, for the DOC-equipped 2002 1.7 L engine, B20 gave lower DOC conversion efficiencies than ULSD, resulting in higher emissions of formaldehyde and several VOCs. This did not occur for the catalyzed DPF-equipped 2007 6.4 L engine.

Idle emissions have attracted considerable attention, especially for school buses. Idle emissions depended on the engine, emission calibration and aftertreatment systems. For the 1.7 L engine, DOC had little effect on emissions at idle. Importantly, idle emissions of NMHC and formaldehyde were 4-15 times higher than at load conditions (based on emissions expressed as mass/hour); CO was higher than medium-low load only (600 kPa BMEP) by 3-4 times, and PM_{10} was higher than low load only (200 kPa BMEP) by 1.5-2 times. Idle emissions of other pollutants (BC, EC, NO_x and total target VOCs) were lower than at load. For the 6.4 L engine at idle using the 2004 calibration without the catalyzed DPF, formaldehyde emissions were at similar levels to under load conditions; all other emissions were lower. For the 6.4 L engine with the 2007 calibration and catalyzed DPF, only CO emissions were higher at idle than load condition. The tests with the older engine help to confirm the significance of idle emissions.

With respect to the use of biodiesel on idle emissions, B20 tended to increase emissions of PM_{10}, EC and formaldehyde from the 1.7 L engine (with and without the DOC), and also from the 6.4 L engine (under 2004 calibration) compared to ULSD. B20 also increased total target VOC emissions from the DOC-equipped 1.7 L engine compared to ULSD.

Engine combustion and other processes that form or affect emissions are very complex, e.g., affected by emission control strategies (EGR, oxidation catalyst, and particulate filter). The unregulated emissions, which usually comprise a small fraction of gaseous and particulate emissions, can be important due to their known or potential toxicity and health impact. The emission profiles are useful for both emission inventories and receptor modeling, and which represent different approaches to identify and apportion emission sources.

6.4 VOC characteristics and source apportionments: A case study in Detroit, Michigan.

Chapter 5 characterizes speciated VOCs measured on a daily basis at a near road site in Detroit from September 1st 2009 to August 16th 2010. 41 target VOCs were detected, most of which are considered to be hazardous air pollutants (HAP).[1] On average, concentrations of total target VOCs were generally low (13.9±8.8 $\mu g/m^3$). The highest concentrations occurred in fall 2009 (average=17.0±9.3 $\mu g/m^3$), but the highest benzene concentration occurred in winter 2010 (0.99±0.40 $\mu g/m^3$). Seasonal variation was significant ($p < 0.05$) except for α-pinene. Weekday and weekend variations were also observed for most VOCs. These results are generally comparable with monitoring elsewhere in Detroit, although benzene concentrations were lower, possibly reflecting recent regulations that lowered its content in gasoline.

Source apportionments were resolved on a seasonal basis using positive matrix factorization (PMF), a receptor model technique that decomposes measurements into a smaller number of composite variables that represent source categories. The sources identified in the present application were vehicle exhaust (explained 21-29% of total target VOCs), diesel exhaust (6-15%), fuel evaporation (17-22%), solvent-related industrial emissions (15-30%), biomass burning (0-17%), biogenic emissions (2-5%), and unknown (4-13%), with contributions that depended on season.

The apportionment described above is generally comparable to estimate using local emission inventories,[2] and are also similar to predictions using chemical mass balance (CMB) receptor models that have been previously applied in Detroit.[3, 4] However, the CMB studies for Detroit was not be able to apportion diesel exhaust and samples were collected only on summer with 1-2 hr sampling time.[3, 4] The results also are useful for understanding emission-exposure relationships, temporal trends of pollutants, ozone formation potential, and other applications in air quality management.

6.5 Significance

Changes in fuel composition impact all aspects of fuel-related emissions and exposures. Information regarding the new motor fuels (e.g., blends using ethanol, ULSD, and biodiesel) is very limited in the literature. This study provides new information on several aspects of current and newer fuels.

Chapter 2 provides speciated VOC compositions of liquid and vapors for four fuels, which can be used to describe leaks and emissions from fuel- and vehicle-related sources (e.g., storage tanks, vehicle refueling, hot soaks, running and evaporative losses). It provides a set of source profiles that can be used in receptor models aimed at apportioning emission sources. This information can also be used to estimate exposures and risks related to fuel or vapor exposure, as performed in Chapter 3.

Biofuels can hasten the degradation of many elastomers and can significantly increase permeation and evaporation rates.[5-7] Current information regarding permeation rates and permeant compositions for biofuel blends through PPE materials is very limited. Chapter 3 provides unique information detailing permeant composition through various PPE materials, which have significant implications for exposure and risk assessments. Occupational exposures were estimated for three scenarios, and recommendations of suitable PPE were made.

Vehicle exhaust emissions depend strongly on fuel formulation and many other factors, e.g., engine type, engine operating conditions, and aftertreatment technologies. Currently, limited information exists regarding emissions of many pollutants, such as benzene and other speciated hydrocarbons, and the effects of using biodiesel blends and aftertreatment systems together on emissions are still unclear. This study is unique in examining and comparing emissions from diesel engines using biodiesel blends and current ULSD fuels. In addition, this study also examined idle emissions, which have not been well characterized and which have attracted considerable attention at schools and other locations due to potential exposures. The emission profiles developed in this study, which reflect the new fuels, engine calibrations and emission control systems, can be used to update emission profiles used in receptor modeling and inventory studies, and potentially in exposure, health and risk studies.

Air pollution epidemiology studies addressing traffic have focused on PM and ozone; however, VOCs are important since many VOCs are ozone precursors,[8] mobile-source air toxics,[9] and HAPs.[1] In addition, speciated VOCs are rarely monitored on a daily basis at near-road sites, although monitoring data is available for the ozone season, at regulatory (compliance) sites, and in special studies. Monitoring of a wide range of VOCs at a near-road site in this work included analysis of several species rarely reported, namely, C_{12-16} straight chain alkanes that help to identify diesel exhaust emissions. Previous studies have mostly collected light (very volatile) VOCs, and have found it difficult to differentiate gasoline and diesel exhaust, which was accomplished in the work present in Chapter 5. These results demonstrate the ability of VOC receptor models, and the need for seasonal analyses.

6.6 Limitations

The fuel cycle (from well/feedstock-to-wheels) is enormously large and complex, and this study is recognized to have a number of limitations. In the work in Chapter 2, only four fuels were examined. This sample does not represent the variation expected due to brand, season and location. Due to the sample size, statistical tests may not be very useful. Assumptions used to predict concentrations of headspace vapors also have limitations due to the lack of activity coefficients available, approximations in the Antoine equation, and variation or experimental errors in the fuel composition.

In Chapter 3, the test materials used in the permeation tests also represent a limited cross-section of available materials, although the tests are expected to give reasonable guidance for that material type. Again, only four fuels were examined. The scenario assumptions were simplified and limited to the available combinations of test PPE materials and fuels.

Chapter 4 used bench tests of two types of diesel engines and two fuels, i.e., B20 and ULSD fuels. This limited sample cannot represent the range of emissions due to different engine brands, model years, engine calibrations, aftertreatment systems, fuel type, and other factors. Moreover, only bench tests at steady-state conditions were conducted.

The VOC analyses in Chapter 5 and throughout this research accommodate a wide range of VOCs, but still include only a subset of VOCs. The absorbent used in sampling is sensitive to moisture, which can occupy active sites and cause the failures and biases. In the field study in Chapter 5, limitations arise from practical issues associated with the study design, sampling and analysis, including the potentially limited representativeness of the single study site; the potential for sampling errors, e.g., systematic flow errors; the lack of replicates due to limited number of samplers; subjective judgment regarding the identification of potential sources; and modest sample sizes.

6.7 Recommendations for further study

Motor fuels continue to evolve and represent complex mixtures with hundreds of compounds, including VOCs. Their composition differs widely, and these differences may be expected to increase as new fuels emerge. Thus, there will be a continuing need to evaluate impacts of fuels across the fuel lifecycle, potentially including the extraction, refining, distribution and use phases.

There is a continuing need to provide VOC speciations of liquid fuel, fuel vapors, evaporative emissions, and exhaust emissions. Updates on the VOC composition is needed to understand the potential to form ozone and to assess the significance of human exposure and toxicity. Such analyses can also be used as source profiles in emission estimates, source apportionment modeling and air pollutant management.

With respect to motor fuels, tests should encompass multiple brands, seasons and locations, and include both conventional and alternative fuels. Potentially a national testing program can be developed, augmenting existing programs (i.e. bulk proprieties of fuels e.g., benzene, total aromatics, total olefins, total saturates based on ASTM D1319 and D5769),[10, 11] which include measurements of VOCs and other components beyond the bulk composition measurements currently reported in the limited testing taking place. Because vapor compositions depend on temperature; measurements of vapor composition under a wide range of temperature are needed. If vapor predictions are used, then appropriate activity coefficients should be derived that account for the non-ideal behavior of VOCs in mixture.

Fuel formulations affect permeation and thus affect exposures, especially occupational exposures. It is recommended that multiple types of PPE be tested for various types of fuels. Further, the existing National Institute for Occupational Safety and Health (NIOSH) PPE recommendations[12] should be revisited and updated for these new fuels, which can demonstrate significantly higher permeation rates. These tests are relatively straightforward and should follow standard methods.

This work demonstrates that different fuels and aftertreatment technologies produce large changes in the composition of diesel exhaust emissions. Emissions depend strongly on fuel formulation, engine type, engine operating conditions, aftertreatment technologies, engine wear and maintenance, and many other factors. It is recommended to test multiple engines with various brands, model years, aftertreatment systems, and various fuels. Testing should extend beyond the regulated pollutants, and should include toxic compounds such as benzene, formaldehyde, and polycyclic aromatic hydrocarbons (PAHs) like benzo(a)pyrene and nitro-PAHs that are associated with health risks.

Mobile sources are widely considered to be the principal pollutant sources in most urban settings. Apportionments of sources, especially considering changes in fleet emissions, would benefit from additional pollutant measurements at multiple locations, including studies evaluating the effects of different types of roads and distances to the road. Both historical monitoring data (if available) and new data could be incorporated, especially since long-term trends and exposures are needed to understand chronic exposures and health risks. In addition to the receptor modeling approach used here (positive matrix factorization), other techniques are available to identify sources and apportion contributions, e.g., chemical mass balance (CMB) receptor modeling. Comparisons might use multiple techniques to help confirm results. Lastly, larger and better characterized emission sources could be tracked using meteorological data, trajectory analysis, dispersion modeling, and possibly geographic information system analyses, which would also complement the statistical apportionments provided by receptor modeling.

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