

Impact of Biodiesel Fuels on Air Quality and Human Health: Task 1 Report

Incorporate Biodiesel Data into Vehicle Emissions Databases for Modeling

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Novato, California



NREL

National Renewable Energy Laboratory

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EXECUTIVE SUMMARY

BACKGROUND

Biodiesel fuels have been investigated for a number of reasons, such as an extender for petroleum-based fuels derived from a domestic renewable energy source, but lately the primary interest is the potential for a more environmentally benign fuel. One potential benefit of biodiesel is that it can biologically degrade, making spills and leaks less of a concern. However, the potential for exhaust emission reductions and reductions in emissions toxicity are of the most interest. Several studies have shown that large reductions in hydrocarbon, particulate, and carbon monoxide emissions are expected from its use either as a neat fuel or as a blend with petroleum-derived fuels.

There have been several studies regarding the effects of biodiesel fuels on exhaust emissions of NO_x, VOC, CO, and particulate matter (PM). Almost all of these studies have examined emissions from heavy-duty diesel truck (HDDT) engines. However, the effects of biodiesel use on ambient air quality have not been quantified. Thus, the National Renewable Energy Laboratory (NREL) has retained ENVIRON International Corporation to estimate the air quality and resultant toxic impacts from the use of biodiesel fuels in several cities in the United States.

Purpose

This document is the Task 1 report for the NREL “Impact of Biodiesel Fuels on Air Quality and Human Health” study. This report provides a discussion and analysis of the available biodiesel test data, and makes recommendations for how biodiesel effects on pollutant mass emissions as well as chemical composition should be incorporated into emission inventories for use in air quality modeling.

BIODIESEL EMISSION EFFECTS

The effects on emissions from truck and bus engines using biodiesel or a blend of biodiesel and standard diesel have been studied to investigate the effect on total hydrocarbon (THC), nitrogen oxides (NO_x), carbon monoxide (CO), and particulate matter (PM) emissions. Some studies have also investigated the chemical compositional effects such as toxic compounds. The effects of biodiesel fuel on emissions have been measured using both 2-stroke and 4-stroke engines for different model years that represent different levels of engine certification standards. These data were analyzed to obtain the mean effect of a 100% biodiesel fuel (B100) and a 20%/80% biodiesel/standard diesel fuel as shown in Table ES-1. The average of the biodiesel fuel effect was used to estimate the overall effect a B100 and B20 fuel would have on the Heavy Duty Diesel Vehicle (HDDV) fleet in the air quality modeling analysis.

Table ES-1. Emission effects by technology type from engine dynamometer testing due to biodiesel fuels compared against a standard diesel.

Engine Type/ Model Year	Fuel Pair	Engines	NOx	PM	CO	THC	THC + PM
20% Biodiesel Emission Effects							
2-Stroke < 1991	D-2 / B-20	6	3.2%	-1.8%	-13.9%	-20.9%	-14.8%
2-Stroke 1991+	D-2 / B-20	2	3.9%	-17.8%	-12.0%	-17.5%	-17.6%
4-Stroke <1991	D-2 / B-20	3	2.9%	-15.7%	-13.6%	-12.2%	-13.5%
4-Stroke 1991-3	D-2 / B-20	4	-0.9%	-15.7%	-12.0%	-2.8%	-12.0%
4-Stroke 1994+	D-2 / B-20	5	2.8%	-9.8%	-15.2%	-24.0%	-19.2%
Overall Average	D-2 / B-20	20	2.5%	-9.0%	-13.3%	-18.2%	-15.1%
Overall Average (w/o Sharp, 1998)	D-2 / B-20	17	2.4%	-8.9%	-13.1%	-17.9%	-14.8%
100% Biodiesel Emission Effects							
2-Stroke 1991+	D-2 / B-100	1	19.6%	-33.0%	-42.4%	-72.7%	-59.2%
4-Stroke 1991-3	D-2 / B-100	2	13.3%	-68.3%	-41.8%	-38.7%	-58.8%
4-Stroke 1994+	D-2 / B-100	5	9.9%	-36.6%	-41.5%	-76.3%	-62.8%
Overall Average	D-2 / B-100	8	11.8%	-51.0%	-42.0%	-69.7%	-61.5%
Overall Average (w/o Sharp, 1998)	D-2 / B-100	5	13.2%	-55.3%	-42.7%	-63.2%	-59.5%

Diesel particulate matter includes several known toxic compounds that fall into a class known as polyaromatic hydrocarbons (PAH) and nitro-PAH compounds. Studies that measured the PAH and nitro-PAH compounds in standard diesel and a B20 and B100 biodiesel fuel were compared to obtain an estimate of the reduction in these toxic compounds in the biodiesel fuel as shown in Table ES-2.

Table ES-2a. Relative fraction ($\times 10^6$) of selected PAH compounds to PM emissions from Sharp (1998) and Durbin (1999).

Compounds	Standard Diesel		B20		B100	
	Sharp	Durbin	Sharp	Durbin	Sharp	Durbin
Benzo(a)anthracene	1.59	1.01	1.51	0.43	1.37	1.11
Chrysene	2.21	1.01	1.32	0.65	1.04	0.89
Benzo(b)fluoranthene	0.96	0.50	0.97	0.22	0.77	0.22
Benzo(k)fluoranthene	1.01	*	0.92	*	0.73	*
Benzo(a)pyrene	1.12	0.25	0.69	1.72	0.49	0.00
Indeno(1,2,3-cd)pyrene	0.72	0.00	0.56	0.00	0.60	0.00
Dibenz(a,h)anthracene	0.21	0.00	0.19	0.00	0.13	0.00
Benzo(g,h,i)perylene	0.94	0.00	0.88	0.00	0.93	0.00
Total	8.76	2.77	7.04	3.02	6.06	2.22

* Included in Benzo(b)fluoranthene.

Table ES-2b. Relative fraction ($\times 10^6$) of selected Nitro-PAH compounds to PM emissions.

Compounds	D2	B20	B100
2-Nitrofluorene	0.14	0.11	0.09
1-Nitropyrene	0.11	0.11	0.02
7-Nitrobenz(a)anthracene	0.01	0.00	0.00
6-Nitrochrysene	0.00	0.00	0.00
6-Nitrobenz(a)pyrene	0.01	0.00	0.00
Total	0.27	0.22	0.11

Overall Effects of Biodiesel Fuel Use

The overall effects of the use of biodiesel fuel on emissions in the HDDV fleet are assumed to be the average effect from the engine dynamometer test data provided in Table ES-1. Based on the data in Table ES-2 and the dilution effect of the biodiesel fuel, the toxicity of the PM emissions from a B100 and B20 fuels were assumed to be 20 percent and 5 percent less than a standard diesel fuel.

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1. INTRODUCTION

BACKGROUND

Biodiesel fuels have been investigated for a number of reasons, such as an extender for petroleum-based fuels derived from a domestic renewable energy source, but lately the primary interest is the potential for a more environmentally benign fuel. One potential benefit of biodiesel is that it can biologically degrade, making spills and leaks less of a concern. However, the potential for exhaust emission reductions and reductions in emissions toxicity are of the most interest. Several studies have shown that large reductions in hydrocarbon, particulate, and carbon monoxide emissions are expected from its use either as a neat fuel or as a blend with petroleum-derived fuels.

Diesel particulate and, to a lesser extent, diesel hydrocarbon exhaust emissions, have garnered much scrutiny for their inherent toxicity. Diesel fuels are typically characterized by heavy hydrocarbons, which produce, through partial combustion, a variety of compounds commonly estimated to be toxic. The State of California has recently listed diesel particulates as a toxic substance. The recent Multiple Air Toxic Exposure Study in the South Coast Air Basin (MATES-II) estimated that 70 percent of the toxic risk in the South Coast (Los Angeles) Air Basin (SCAB) is due to diesel particulate emissions (SCAQMD, 1999). Therefore, the potential to reduce overall toxic emissions through fuel substitution is of great interest given the reduced toxicity of diesel particulates using biodiesel fuels.

Biodiesel has emission advantages for use in diesel engines because it can provide improvements to a number of important fuel properties, most importantly cetane and oxygen content. Generally, these properties are thought to be responsible for the improvement in emissions by improving ignition and distribution of oxidant. The effect of fuel substitution may be unique by engine type; with the Engine Manufacturers Association (EMA) has theorized that newer engines may show less benefit because of the more precise engine management currently used (EMA, 1995). Nonroad diesel engine lags highway engine technology, so emission benefits may be greatest for nonroad engines, which also have higher base emissions of HC and PM.

Most of the potential problems typically cited for the introduction of biodiesel blends are the lack of a running history for their use. Unforeseen complications arising from materials compatibility, consistent fuel quality, gumming, low temperature effects, and various other long durability factors not specifically listed are feared with the use of biodiesel blends and may affect the penetration into the nonroad market. Most of these concerns do not affect the emission testing results in the laboratory; and the lack of cold temperature testing is typical of emission testing for diesel, gasoline, or other types and makes of vehicles and engines.

The most consistent criticism of biodiesel is the low temperature and biologic stability and water sensitivity. The viscosity of biodiesel blends shows that the 20% blends show similar stability as more petroleum-based diesel fuels, while higher percentage blends of biodiesel show dramatic increases in low temperature kinematic viscosity (EMA, 1995). Cloud point, the cold temperature where a dramatic increase in the opacity of the fuel mixture occurs, is another variable thought to be a measure of the low temperature filter-plugging potential for a fuel. Likewise, biological and water stability is also of concern to ensure that the fuel does not produce gums and particles that could clog fuel filters.

Cost of an alternative fuel is always a concern, especially when the production facilities have neither been optimized nor can take advantage of economies of scale. The Department of Energy estimates that a fuel blend of 20% biodiesel and 80% diesel (known as B20) would cost approximately 30 to 40 cents a gallon more than regular diesel. This cost differential is significantly high to adversely affect the penetration of the market of biodiesel fuels. In most part, this price differential is due to the price of the base vegetable oil or tallow. In addition, there may be a small reduction in the fuel economy because biodiesel fuels have lower energy density than standard diesel fuels.

There have been several studies regarding the effects of biodiesel fuels on exhaust emissions of NO_x, VOC, CO, and particulate matter (PM). Almost all of these studies have examined emissions from heavy-duty diesel truck (HDDT) engines. However, the effect of biodiesel use on ambient air quality has not been quantified. Thus, the National Renewable Energy Laboratory (NREL) has retained ENVIRON International Corporation to estimate the air quality and resultant toxic impacts from the use of biodiesel fuels in several cities in the U.S.

PURPOSE

This document is the Task 1 report for the NREL “Impact of Biodiesel Fuels on Air Quality and Human Health” study. This report provides a discussion and analysis of the available biodiesel test data, and makes recommendations for how biodiesel effects on pollutant mass emissions as well as chemical composition should be incorporated into emission inventories for use in air quality modeling. This document also contains a description of the current and upcoming emission factor models from the U.S. EPA and the California Air Resources Board (ARB), and the basis of heavy-duty diesel vehicle (HDDV) emission factors in these models. Along with this report we are also transmitting via email an electronic database of the biodiesel effects data collected and analyzed.

2. BIODIESEL EMISSION EFFECTS

The effect on emissions from truck and bus engines using biodiesel or a blend of biodiesel and typical highway diesel No. 2 has been investigated over the last several years. Many studies have investigated the effect on regulated emissions [total hydrocarbon (THC), nitrogen oxides (NO_x), carbon monoxide (CO), and particulate matter (PM)], and some of these have investigated chemical compositional effects such as toxic PAH and other compounds as well.

Starting with a review of the literature to date (Graboski and McCormick, 1998), and adding the most recent studies, a database of regulated emissions data was produced with data from the studies listed in Appendix A.. These studies investigated the engine emissions from a variety of diesel engines used in highway vehicles on the engine certification test for highway heavy-duty engines, and two studies investigated emissions on a chassis test cycle.

Missing from this list of data sources and the analysis below are several studies by students and professors at the University of Minnesota (Bickel, 1999) and ongoing work at the University of Idaho. Because only summary results were available, these have not been incorporated into the estimates below. However, the summary results indicate that the University of Minnesota was finding similar effects with biodiesel replacement as those detailed below for engine dynamometer data for mining equipment and other over the road trucks. This indicates that results found here are likely applicable to nonroad applications as well as highway vehicles.

REGULATED EMISSION EFFECTS

Emission testing can be performed either with the engine only or with the entire vehicle in the chassis configuration. The engine testing proceeds with the engine removed from the vehicle and loaded through the flywheel of the engine, and nearly all engine testing, including those studies reviewed here, uses the certification test cycle. The chassis testing loads the engine through the wheels, and two testing cycles -- the light-duty federal certification and heavy-duty evaporative preparation test cycles -- were used in the studies reviewed here.

The testing included repeat tests for each engine/vehicle/fuel combination. Repeat tests were averaged to produce a mass emissions estimate for each engine/vehicle/fuel combination. Overall mass emissions averages across engine/vehicle types were then produced for each biodiesel fuel blend and compared with those from the base fuel to produce the emission effects in percentage change.

Engine Emission Testing

The effect of biodiesel fuels either as blends or neat was first investigated for its effect on regulated emissions for a variety of possible engine types. The engine types investigated were defined as 2-stroke or 4-stroke engines of model years less-than-1991, 1991-1993, and 1994-and-later. These model years represent essentially precontrolled, NO_x-only controlled, and NO_x and PM-controlled engines based on the certification standards for those model years. Before 1994 some engines were 2-stroke diesel engines produced for various (but a limited number of)

applications preferring lighter and smaller engines like urban buses, fire trucks, and other specialty vehicles.

The most direct comparison of emission rates is to use fuel pair of standard highway diesel and 20%/80% biodiesel/diesel blends (D-2 / B-20) or diesel and 100% biodiesel (D-2 / B-100) to determine the emission effects of biodiesel. Table 2-1 shows paired results by technology type from the available engine dynamometer test data.

Table 2-1. Emission effects by technology type from changing diesel to biodiesel fuels for engine dynamometer testing.

Engine Type/ Model Year	Fuel Pair	Engines	NOx	PM	CO	THC	THC + PM
20% Biodiesel Emission Effects							
2-Stroke < 1991	D-2 / B-20	6	3.2%	-1.8%	-13.9%	-20.9%	-14.8%
2-Stroke 1991+	D-2 / B-20	2	3.9%	-17.8%	-12.0%	-17.5%	-17.6%
4-Stroke <1991	D-2 / B-20	3	2.9%	-15.7%	-13.6%	-12.2%	-13.5%
4-Stroke 1991-3	D-2 / B-20	4	-0.9%	-15.7%	-12.0%	-2.8%	-12.0%
4-Stroke 1994+	D-2 / B-20	5	2.8%	-9.8%	-15.2%	-24.0%	-19.2%
Overall Average	D-2 / B-20	20	2.5%	-9.0%	-13.3%	-18.2%	-15.1%
Overall Average (w/o Sharp, 1998)	D-2 / B-20	17	2.4%	-8.9%	-13.1%	-17.9%	-14.8%
100% Biodiesel Emission Effects							
2-Stroke 1991+	D-2 / B-100	1	19.6%	-33.0%	-42.4%	-72.7%	-59.2%
4-Stroke 1991-3	D-2 / B-100	2	13.3%	-68.3%	-41.8%	-38.7%	-58.8%
4-Stroke 1994+	D-2 / B-100	5	9.9%	-36.6%	-41.5%	-76.3%	-62.8%
Overall Average	D-2 / B-100	8	11.8%	-51.0%	-42.0%	-69.7%	-61.5%
Overall Average (w/o Sharp, 1998)	D-2 / B-100	5	13.2%	-55.3%	-42.7%	-63.2%	-59.5%

In order to determine overall effects, the data were averaged over all technology groups because the emission effects for the individual technology types were remarkably similar. For newer engines (4-strokes of model years 1994 and greater), the emission effects may seem to be different from the average effect for PM; however, the magnitude of the difference in relative or absolute terms was not great. For instance, with B20 replacement for the three newest technology engines, the emission effects for PM range from 0 to a 12 percent reduction, and for THC range from 17 to 27 percent reduction.. Though the THC effect for 4-stroke engine model years 1991-1993 is lower than on average, this group of engines represents a limited fraction of the in-use fleet.

Combining THC and PM reduces much of the variability between technology types and that might be explained by a variation in the gas/particulate partitioning of heavier unburned hydrocarbons. By combining THC and PM, the effect of heavier hydrocarbon condensation into the particulate phase that may occur preferentially with chassis testing (as demonstrated in the results below) is not apparent.

Because of the emissions measurement techniques¹, the total hydrocarbon and the particulate collection measurements may have measured some of the same compounds. The combined THC+PM measure may then have undercounted the benefit of biodiesel replacement of diesel fuel because the biodiesel fuels used were typically composed of heavier components than typical diesel fuel, so unburned or partially-burned fuel may be measured as both THC and particulate. Usually the PM measurement includes a secondary dilution tunnel, which may reduce condensation with that measure even though collection occurs at lower temperature.

For reasons that are described in more detail under the Chemical Composition section below, the hydrocarbon results in the Sharp (1998) study are considered to result in too great a THC reduction estimate, especially with 100 percent biodiesel replacement. Therefore the average emissions effects used in the work and shown in Table 2-1 for both 20% and 100% biodiesel replacement was without the three engines that were tested in the Sharp (1998) testing program. However, as shown in Table 2-1, ignoring these data does not demonstrably affect the estimate of emission effects.

Chassis Testing

Data from chassis testing were available for Light Heavy-Duty Diesel Vehicles tested on various biodiesel, blends, and standard diesel fuels (Durbin, et al. (1999), Peterson et al. (1999), and Peterson and Haines (1999)). The effects found for these chassis tests were somewhat different than that for engine tests, as shown in Table 2-2. The two pre-1994 model year vehicles show quite dissimilar effects to other chassis data for later model year vehicles. The particulate matter is found to increase with biodiesel use in contrast with the results of the engine testing. And there is a slight decrease in NO_x measured on chassis dynamometers as opposed to a slight increase measured on engine dynamometers.

However, the combined THC+PM effects are more similar between the later model year vehicles tested on the chassis and engine dynamometers. The chassis testing likely had more heavy hydrocarbon condensation into the particulate phase because the chassis testing requires that the emissions traverse the entire length of the exhaust system, often use smaller diameter and/or high-surface area accordion tubing before entering the dilution tunnel, and have lower dilution ratios. Therefore chassis measurements may have resulted in additional cooling resulting in greater condensation of heavy hydrocarbons. This was observed as the organic (soluble) carbon represented the entire increase in PM emissions that is shown in Table 2-2, while the elemental (soot) carbon decreased with biodiesel use. Engine dynamometer testing generally has shorter exhaust lengths and higher dilution ratios, perhaps resulting in less heavy hydrocarbon condensation.

The two pre-1994 vehicles show such dissimilar effects with biodiesel substitution that it does not seem appropriate to use these results. And of these two vehicles, only one engine was responsible for the majority of the percent change.

¹ Total hydrocarbons are measured with a heated flame-ionization detector and sampling systems that must be maintained at $191 \pm 11^\circ\text{C}$, while the particulate filters must be never exceed 51.7°C (Code of Federal Regulations 86-1310-90).

Table 2-2. Emission effects by technology type from changing diesel to biodiesel fuels for chassis dynamometer testing.

Engine Type/ Model Year	Fuel Pair	Engines	NOx	PM	CO	THC	THC + PM
20% Biodiesel Emission Effects							
<1994	D-2 / B-100	2	-0.9%	59.0%	0.6%	12.0%	26.2%
1994 +	D-2 / B-100	5	-4.0%	6.8%	-20.5%	-19.1%	-15.7%
Overall Average	D-2 / B-20	7	-3.4%	25.0%	-18.0%	-14.1%	-7.6%
100% Biodiesel Emission Effects							
<1994	D-2 / B-100	2	9.8%	131.0%	0.0%	-16.8%	27.8%
1994 +	D-2 / B-100	5	-6.4%	30.6%	-36.4%	-60.7%	-48.5%
Overall Average	D-2 / B-100	7	-3.4%	65.7%	-32.1%	-53.7%	-33.9%

CHEMICAL COMPOSITION

The chemical composition for emissions is important to determine the overall effect of diesel emissions on air quality. The chemical composition determined from the individual test results will be applied to the overall THC or the THC + PM emission estimates determined from modeling. The estimates derived from modeling will be modified to include the regulated pollutant emission effects detailed above.

Two studies measured chemical composition from biodiesel and diesel fueled tests (Sharp, 1998 and Durbin et al., 1999), and are compared here. There are two basic measurements taken for measuring chemical composition; a bag sample for lighter hydrocarbon, and two types of filters for heavier and particulate emissions. The lighter hydrocarbons are typically more difficult to determine because diesel fuel and therefore hydrocarbon emissions tend toward heavier compounds, which may adsorb on the bag surface and/or may be difficult to identify with a gas chromatograph. The two filters were the standard quartz-fiber filters followed by a polyurethane foam (PUF) resin-impregnated filter to trap semivolatile hydrocarbons. Both filters were then extracted, and measured for only polyaromatic hydrocarbons (PAH). Sharp (1998) combined the particulate and semivolatile filter extractions before analysis.

Lighter Hydrocarbons

In general, it is difficult to measure individual compounds for emissions from the bag samples, and the chemical species identified in these studies (Sharp, 1998 and Durbin et al., 1999) were much lower than the regulated hydrocarbon measurements. The measured emissions were typically quantified only up to carbon numbers of 12 (C12). Unburned diesel fuel (No. 2 fuel oil) is comprised of compounds predominately (>95 %) of C13 or greater (EPEFE, 1996). Biodiesel fuels are even less volatile where the T10, T50 and T90 points (temperature under which 10%, 50% and 90% of the fuel is distilled) are at considerably higher temperatures than for typical diesel fuels. The unknown and unidentified compounds are therefore likely heavier compounds related to unburned fuel, so are not explicitly determined. The detection of these heavier compounds is much more difficult because of the higher boiling temperatures (volatility), number of isomers, and lack of available reference standards.

The modeling for regulated pollutants relies on flame ionization detection (FID) measurements for THC emission estimates and is not completely compatible with the chemical compositional analysis. A review of the methods and data analysis is provided below.

The FID measures carbon content calibrated with propane, and this carbon content is converted to hydrocarbon mass by adding 1.85 atoms of hydrogen to each carbon atom (CFR, 1996) to determine the average molecular weight per carbon atom. The FID response varies only slightly per carbon atom for aromatic, olefin, and aliphatic carbon content, but is significantly less for alcohol carbons and practically unresponsive to carbonyl carbon atoms. So ketones, aldehydes and esters are undercounted generally, and in particular there is effectively no response for formaldehyde from the FID measurement. Therefore it is possible that the chemical speciation would estimate higher hydrocarbon emissions than the FID measurement.

The chemical compositional analysis in g/mile or g/hp-hr units is compared with the FID measurement in order to determine the mass of hydrocarbon that was not measured or identified. Only the weight of the noncarbonyl fraction (modified) of the ketones and aldehydes was added to the bag measurement of chemical composition and compared with the weight of the THC from the FID measurement. As shown in the equation below, any difference was ascribed to compounds that were neither identified nor measured and assumed to be of higher molecular weight than were measured by the chromatograph.

$$\text{Unknown/Unmeasured HC} = \text{FID} - (\text{Bag HC}) - (\text{modified Aldehyde \& Ketones})$$

The fraction of individual chemicals was then calculated by dividing the chemical composition with the THC measurement by the FID. This will result in a chemical composition that in total will be slightly more than 100 percent of the THC estimate because the aldehydes and ketones are now estimated at their full molecular weight. This higher value of hydrocarbons is comparable with the total organic gas (TOG) estimate defined by the California Air Resources Board (ARB) as the THC plus the total moles of all aldehydes added by weight as formaldehyde. The ARB TOG estimate was not used because it was derived from an approximate conversion of THC measurements, and this study used the data more directly.

Table 2-3 compares the measured chemical composition of hydrocarbons to the THC measurement by a heated flame ionization detector (FID). For most of the chemical composition measurements, it was possible to identify only 15 – 36 percent of the total hydrocarbons. In Sharp (1998), the total hydrocarbon measurement was extremely low for the 100 percent biodiesel runs, so it appears as if 100 percent of the hydrocarbons were determined. There are several reasons why this may have occurred, such as the exhaust composition tending toward the lighter side, or the FID was unable to measure unburned esters. But the likely explanation is that the THC measurement was too low, consistent with too low a sampling train temperature condensing the heavier unburned fuel components. This argues for a lower THC reduction estimate than that provided in Table 2-1.

Table 2-3. Percent unknown/unmeasured HC from two studies (100% - measured %).

Study	Diesel	20% Biodiesel	100% Biodiesel
Sharp (1998)	84.8	63.8	-1.7
Durbin (1999)	72.2	70.6	67.1

For the Sharp (1998) study in particular, the chemical composition shows higher percentages of the measured compounds with increasing biodiesel use, which was an artifact of the lower THC emission results for these vehicles. The increase in the fraction of certain pollutants of interest, such as 1,3 Butadiene, Benzene, Formaldehyde, and Acetaldehyde, can be mostly or wholly explained by the low THC measurement, which likely was a flawed measurement.

PAH Composition

The composition of the particulate and semivolatile phase PAH is distinctly different between the work of Sharp (1998) and Durbin (1999). The Sharp work only measured certain PAH and nitro-PAH compounds, while the Durbin work measured many PAH but not nitro-PAH compounds. Table 2-4 compares the percentage of total mass PM for the compounds that both studies measured. The Durbin work found a substantially lower quantity of these PAH compounds but with a similar trend in emission estimates. One odd measurement was the Benzo(a)pyrene quantity with the B20 run in the Durbin work, which was substantially higher than other estimates for similar PAH compounds. Otherwise the trend was for a lower fraction of PAH with increase use of biodiesel fuel.

Table 2-4. Relative fraction ($\times 10^6$) of selected PAH compounds to PM emissions from Sharp (1998) and Durbin (1999).

Compounds	D2		B20		B100	
	Sharp	Durbin	Sharp	Durbin	Sharp	Durbin
Benzo(a)anthracene	1.59	1.01	1.51	0.43	1.37	1.11
Chrysene	2.21	1.01	1.32	0.65	1.04	0.89
Benzo(b)fluoranthene	0.96	0.50	0.97	0.22	0.77	0.22
Benzo(k)fluoranthene	1.01	*	0.92	*	0.73	*
Benzo(a)pyrene	1.12	0.25	0.69	1.72	0.49	0.00
Indeno(1,2,3-cd)pyrene	0.72	0.00	0.56	0.00	0.60	0.00
Dibenz(a,h)anthracene	0.21	0.00	0.19	0.00	0.13	0.00
Benzo(g,h,i)perylene	0.94	0.00	0.88	0.00	0.93	0.00
Total	8.76	2.77	7.04	3.02	6.06	2.22

* Included in Benzo(b)fluoranthene.

These compounds were the heavier compounds, so would be more likely to be associated with the particulate phase than the semivolatile phase. In the Durbin work, more of the lighter PAH compounds were measured, which were more associated with THC measurements. This was especially true for the lightest PAH, naphthalene, which was measured in greater quantity in the bag sample than from the filter samples. Also, in the Durbin work, Benzo(a)pyrene was found in relatively large quantities (oddly in the semivolatile sample when all other PAH components shown here were found in the particulate sample) with 20 percent biodiesel and was barely

detectable from testing of other fuels; otherwise this sample would have shown a lower fraction of PAH than the diesel fueled testing samples.

Nitro-PAHs are compounds of some interest because of high specific toxicity. Sharp (1998) measured selected nitro-PAH with the results shown in Table 2-5. The table shows measurable reductions in the relative fraction of these compounds with increased biodiesel usage.

Table 2-5. Relative fraction ($\times 10^6$) of selected Nitro-PAH compounds to PM emissions.

Compounds	D2	B20	B100
2-Nitrofluorene	0.14	0.11	0.09
1-Nitropyrene	0.11	0.11	0.02
7-Nitrobenz(a)anthracene	0.01	0.00	0.00
6-Nitrochrysene	0.00	0.00	0.00
6-Nitrobenz(a)pyrene	0.01	0.00	0.00
Total	0.27	0.22	0.11

The relative fraction was lower for both PAH and nitro-PAH with increasing use of biodiesel. The lower fraction of PAH was found both for lower mass particulate (Sharp, 1998) and higher mass particulate (Durbin et al., 1999), which indicates that the fraction of PAH was not influenced by the mass emissions as the chemical composition was for the lighter hydrocarbons. This indicates that the toxicity of particulate matter would be reduced even without a change in the mass emissions of particulate.

RECOMMENDATIONS

We recommend that the average emission effects be derived from the engine dynamometer testing results. The primary reason for using engine data is that the sample sizes are larger. But the concern over whether the sampling method preferentially increases biodiesel particulate on the chassis tests also leads toward the engine test data, which typically use much shorter smooth exhaust pipes reducing the concern.

The use of engine test results to determine fuel effects is consistent with both ARB and EPA modeling efforts. EPA currently models emissions from data collected on engine tests. While ARB now uses chassis test results to determine basic emission rates, ARB estimates the effect of using California 'Clean Diesel' from engine test data.

From the data available, the chemical composition of lighter hydrocarbons (C12 and less) appears to be substantially unaffected by fuel used, so a base diesel chemical composition should be applied to the mass results shown here. The relative composition of the measured PAH and nitro-PAH compounds appears to be substantially decreased even as the particulate mass emissions are reduced. So inclusion of a lower relative fraction of PAH combined with overall PM reductions with biodiesel use is justified.

For the most likely in-use scenario, 20 percent biodiesel fuel use, there is substantially more data available showing consistent relative effects across a range of studies and engine technology types. The THC results remain suspect and may overstate reductions, especially with 100 percent biodiesel replacement as found in the Sharp study. Other studies used to determine the effect of

biodiesel replacement did not have the chemical composition concurrently measured, so the regulated emission measurements may have had similar measurement problems.

While the current data show higher particulate with biodiesel in chassis and lower particulate in engine testing results, this is the subject for further studies of the test methods. Because the combined THC+PM emission results are similar between engine and chassis testing, the likely explanation for the differences between chassis and engine testing results lie in the test methods with sampling line temperatures the most likely areas of study. For chassis testing, heavy hydrocarbon condensation is the likely basis for the increased particulate mass measurements for biodiesel replacement. Whether this is a real effect from the tailpipe or because of peculiarities of the test method deserves further study.

The chemical composition appears to show an increase in the relative contribution of the lighter hydrocarbon constituents. However, the uncertainty of the THC measurement in the Sharp (1998) work questions if the chemical composition is actually affected. We recommend not changing the chemical composition between fuel types; the mass emission changes recommended thus best reflect the mass emissions of these components as measured by Sharp.

For PAH compounds, the replacement of biodiesel is likely to result in emission reduction in addition to the particulate mass emissions reductions. The relative fraction of these PAH compounds measured in Sharp (1998) likely represent realistic fractions to apply to gross particulate emissions because the relative fraction decreased even as the mass particulate was reduced as well.

3. EMISSION FACTOR MODELS

Two regulatory models exist that estimate emission factors for on-road heavy-duty and light-duty diesel trucks and vehicles. These are MOBILE5 and EMFAC7G, developed respectively by EPA and the California Air Resources Board (ARB). There are planned revisions due this year to both of these models to be called MOBILE6 and EMFAC2000. EMFAC2000 is expected to be released in Spring 2000, and MOBILE6 is expected to be released by the end of 2000.

In this section we describe the current and future models and approaches to estimating HDDV g/mile emission factors. While this focus here is on emission factors, it should be noted that both ARB and EPA have also updated their heavy-duty vehicle fleet mileage accumulation rates and age distributions.

MOBILE5

For MOBILE5, the methodology entails determination of a gram per mile (g/mi) emission factor by multiplying a work-specific emission level (in units of grams per horsepower-hour (g/bhp-hr)) by a conversion factor which converts work units into mileage units (bhp-hr/mi):

$$\text{Emission Factor (g/mi)} = \text{Work-Specific Emission Level (g/bhp-hr)} * \text{Conversion Factor (bhp-hr/mi)}$$

The work-specific emission factors have historically been determined using the Federal Test Procedure (FTP) for heavy-duty engines. This test procedure runs the engine that has been removed from the vehicle through a loaded cycle.

The conversion factor was determined from driver diaries of typical fuel economy (TIUS, 1988) coupled with manufacturers' estimates of engine efficiency and an estimate of the fuel density. The engine efficiency is measured as the brake specific fuel consumption (BSFC) in units of pounds of fuel per horsepower-hour. The calculation is shown in the equation below. Each of these individual estimations adds an element of uncertainty to the emission factor estimate, and the overall estimate for the conversion factor is implicitly based on the average driving behavior of all trucks and buses. The average speed for all driving is considered to be 20 miles per hour, and an adjustment is made to account for other average speeds (described briefly below).

$$\text{Conversion Factor (bhp-hr/mi)} = \text{Fuel density (lb/gal.)} / [\text{BSFC (lb/hp-hr)} * \text{Fuel economy (mi/gal.)}]$$

In MOBILE5, vehicle class, as determined by gross vehicle weight (GVW), was not distinguished, so the estimates relied on one average set of basic emission rates for all heavy-duty diesel vehicles. The vehicle class usually primarily affects the conversion factor estimate and especially the mile-per-gallon estimate because heavier vehicles require more fuel per mile while the fuel density is constant and the BSFC estimate changes only slightly with size of truck. Heavy-duty engine testing tends to be very costly. Due to the prohibitive costs involved in obtaining in-use emissions data on heavy-duty vehicles, very little recent test data existed at the time MOBILE5b was developed. Therefore, the heavy-duty emissions factors in MOBILE5b (1996) are the same ones that were developed for use in MOBILE4 (1989). The 1980 through

1990 model year emissions factors are based on data derived from a cooperative test program between EPA and engine manufacturers, involving 18 heavy-duty gasoline engines (model years 1979 to 1982) and 22 heavy-duty diesel engines from model years 1979 to 1984. In MOBILE5b, emission rates from the cooperative program were used unless the certification rate was higher than that produced from the test program. In cases where the certification results were greater, that rate was used instead.

MOBILE adjusts the basic emission rate to account for average speed and altitude. Average speed adjustments are intended to include vehicle stops, acceleration events, and idle time within a typical trip. Lower average speeds are characterized by more stop-and-go driving resulting in higher emissions per mile. Higher average speeds are characterized by less stop-and-go driving; however, added wind drag at very high speeds is modeled to affect higher fuel consumption and therefore higher emissions. Altitude adjustments are made to model the effect of lower barometric pressure ambient air, which reduces the amount of air available for combustion.

In order to calculate the most recent estimates for emissions of heavy-duty diesel emissions, EPA (1999) has provided a conversion from MOBILE5 estimates to MOBILE6 estimates described in more detail below. This conversion accounts for more recent information about the certification emission rates and conversion factors and includes the effect of engines that employ defeat devices. EPA discovered that some engine manufacturers employed defeat devices that would determine if the engine was operating on the certification test cycle (or a similar driving pattern), and if not to adjust the engine controls to improve fuel economy with a resulting increase in the NO_x emission rate.

MOBILE6

Based upon draft documentation, MOBILE6 is expected to use the same methodology as MOBILE5 for heavy-duty diesel vehicle emission estimates. Current public information about MOBILE6 indicates that they intend to revise the basic emission rates, conversion factors, and age and travel distributions however, so the numerical estimates may be different between MOBILE6 and MOBILE5. Also, the vehicle classes classified by GVW will be disaggregated into several individual classifications, shown in Table 3-1, in contrast to MOBILE5, which has only one set of emissions rates for all trucks.

Table 3-1. MOBILE6 heavy-duty vehicle classifications.

Designation	Description	Gross Vehicle Weight (lbs.)
Gasoline Vehicles		
HDGV (classes 2B-3)	<i>Heavy-duty gasoline vehicles</i>	8,501-14,000
HDGV (classes 4-8)	Heavy-duty gasoline vehicles	>14,000
Diesel Vehicles		
HDDV (class 2B)	Light heavy-duty diesel trucks	8,501-10,000
HDDV (class 3)	Light heavy-duty diesel trucks	10,001-14,000
HDDV (classes 4-5)	Light heavy-duty diesel trucks	14,001-19,500
HDDV (classes 6-7)	Medium heavy-duty diesel trucks	19,501-33,000
HDDV (class 8A)	Heavy heavy-duty diesel trucks	33,001-60,000
HDDV (class 8B)	Heavy heavy-duty diesel trucks	>60,000
Urban Buses		
HDGB (school)	Heavy-duty gasoline school buses	All
HDGB (transit)	Heavy-duty gasoline transit buses	All
HDDB (school)	Heavy-duty diesel school buses	All
HDDB (transit)	Heavy-duty diesel transit buses	All

The basic emission rates were determined for engines that have certification data including those engines produced after 1988. For engines before 1988, the 22 in-use engines, tested by EPA and used in MOBILE5, were used to estimate the average emission rates for the older engine types. Emission rates for newer engines were available only for the certification test. Emission rates generated on the engine dynamometer testing are available in units of grams per horsepower-hour need to be converted to grams per mile through energy conversion factors. The emission rates were only generally available by intended truck size; light, medium, heavy, or bus engine as shown in Table 3-1.

The revised conversion factor was determined from estimates of the brake specific fuel consumption (BSFC in units of lb/hp-hr), fuel density, and typical fuel consumption (in units of gallons/mile) (Arcadis, 1998). The BSFC was determined from manufacturers' estimates of fuel consumption by engine family and was sales weighted to produce an average BSFC value by model year and by truck and bus class. The fuel density was determined from in-use samples of diesel fuel. The typical fuel consumption was determined from driver/owner surveys of fuel consumption per mile and taken from the periodic Truck In-Use Survey (TIUS, 1993).

However, because MOBILE6 is not public, for purposes of this modeling the conversion of MOBILE5 estimates to reflect the currently expected changes in MOBILE6 will be used. The conversion of hydrocarbon emission estimates from MOBILE5 to MOBILE6 is a simple multiplicative factor (i.e. 0.413 for the in-use year 2007) applied to the MOBILE5 emission estimates. The conversion of NO_x emission estimates is more complicated because EPA estimates that defeat devices operation depends upon the average speed uniquely correlated to each roadway type (several subclasses of urban streets, arterial collectors, or limited access freeways). So for NO_x emissions, the conversion is applied to the emissions projected on each roadway type within a given region.

Deterioration rates in MOBILE6 are insignificant, so the zero-mile levels will determine the typical in-use emission rates except for the defeat device adjustment to in-use NO_x emissions. Zero-mile levels calculated using the certification emission rates and applying the conversion

factor for various truck classes are shown in Table 3-2 for the largest trucks (Class 8B), smallest trucks (Class 2B), and Urban Buses.

Table 3-2a. Estimates of MOBILE6 zero-mile emission rates in g/mile (w/o defeat device effects) for the class 8B trucks.

Model Year	HC (g/mile)	CO (g/mile)	NOx (g/mile)	PM (g/mile)
1988	1.53	4.37	20.49	1.44
1989	1.52	4.33	20.29	1.42
1990	1.66	5.79	15.52	1.22
1991	0.95	5.77	14.46	0.67
1992	0.94	5.72	14.32	0.66
1993	0.93	5.67	14.20	0.65
1994	0.52	3.30	14.22	0.25
1995	0.52	3.27	14.10	0.24
1996	0.52	3.24	13.97	0.24

Table 3-2b. Estimates of MOBILE6 zero-mile emission rates in g/mile (w/o defeat device effects) for class 2B trucks.

Model Year	HC (g/mile)	CO (g/mile)	NOx (g/mile)	PM (g/mile)
1988	0.71	1.33	4.79	0.49
1989	0.70	1.33	4.78	0.48
1990	0.57	1.99	5.33	0.42
1991	0.52	0.44	4.80	0.25
1992	0.51	0.44	4.80	0.25
1993	0.51	0.44	4.79	0.25
1994	0.22	1.30	4.46	0.10
1995	0.22	1.30	4.45	0.10
1996	0.22	1.30	4.45	0.10

Table 3-2c. Estimates of MOBILE6 zero-mile emission rates in g/mile (w/o defeat device effects) for urban buses.

Model Year	HC (g/mile)	CO (g/mile)	NO_x (g/mile)	PM (g/mile)
1988	2.16	6.17	28.90	2.02
1989	2.17	6.18	28.94	2.03
1990	2.40	8.36	22.39	1.75
1991	2.87	12.49	21.04	2.13
1992	2.87	12.51	21.09	2.13
1993	1.39	13.47	19.79	1.07
1994	0.37	4.93	22.72	0.28
1995	0.37	4.95	22.77	0.28
1996	0.37	4.96	22.83	0.19

EMFAC7G

EMFAC7G relied on the MOBILE5 heavy-duty diesel estimates for basic emission factors and average speed adjustments. EMFAC applied a deterioration estimate to account for tampering and malmaintenance for in-use vehicles and the effects of the inspection and maintenance program. This deterioration estimate was added as a percentage increase to the basic emission factors. California also added an adjustment to account for expected emission benefits of the reformulated diesel fuel program.

EMFAC2000

There has been considerable disagreement about how representative the converted engine testing is to in-use vehicle emissions. For that reason, ARB has revised the emission estimates for heavy-duty diesel vehicles by using the recently available emissions data collected with chassis-loaded diesel vehicles (ARB, 2000a).

Testing of heavy-duty vehicles to determine emissions may be performed in two ways. The first method involves removing the engine from the test vehicle's chassis (frame), mounting it on a test stand, and operating the engine on a testing apparatus known as an engine dynamometer. Data derived from engine dynamometers was the basis for the current emission estimates in MOBILE5 and EMFAC7G. The second method involves testing the engine while it is still in the vehicle by operating the entire vehicle on what is known as a chassis dynamometer. The latter method is very similar to the approach used to test light-duty vehicle and light-duty truck emissions. Emission levels produced on the engine dynamometer are measured in grams per brake horsepower-hour (g/bhp-hr) or grams per kilowatt-hour (g/kW-hr) for a given test cycle, while emissions produced on a chassis dynamometer are measured in grams per mile (g/mi) or grams per kilometer (g/km). The results of these emissions tests are used to develop emission factors for heavy-duty vehicles that are then used in mobile source modeling and inventory development.

The chassis-derived data available from several studies are now considered sufficient to estimate emissions. The emission factors were developed by ARB separately for three sets of diesel vehicles: (1) heavy heavy-duty and medium heavy-duty, (2) light heavy-duty vehicles, and (3)

urban buses, with the ARB weight classifications shown in Table 3-3. Each of these three groups of vehicles had emission factors estimates from totally separate testing programs with different test procedures, as described below. In EMFAC2000, diesel-powered trucks with a gross vehicle weight of 8,501 pounds or greater are classified in the following manner:

Table 3-3. ARB heavy-duty trucks weight classes by Gross Vehicle Weight (GVW).

GVW in lbs	Vehicle Class
8,501 to 14,000	Light-Heavy Duty Trucks (LHDT)
14,001 to 33,000	Medium-Heavy Duty Trucks (MHDT)
> 33,000	Heavy-Heavy Duty Trucks (HHDT)

The chassis test cycles on which the emissions should be based is a point of debate. While several were considered, the urban dynamometer driving schedule (UDDS) (EPA, 1996) was used for medium-heavy and heavy-heavy-duty vehicles because it was developed based on the same data set used to produce certification engine test cycle and it was the only heavy-duty cycle intended to represent actual in-use driving behavior. The light-duty Federal Test Procedure (FTP) testing cycle was used for the light-heavy-duty vehicles because the cycle was considered appropriate for the lighter trucks represented by pickup trucks, sport-utility, and vans typically used in the role of more traditional light-duty applications. For urban buses, chassis data were only available on the central business testing cycle (CBD), which is a series of successive acceleration, cruise, braking, and idle typical of urban bus behavior.

For heavy-heavy (HHDDV) and medium-heavy trucks (MHDDV), data from three sources were used to derive the chassis dynamometer based emission rates in EMFAC2000. The first data set, made available by U.S. EPA, was obtained from the New York State Department of Environmental Conservation and Energy (NYSDEC). Under sub-contract to Energy and Environmental Analysis, Inc. (EEA), U.S. EPA and NYSDEC, the West Virginia University (WVU) Department of Mechanical and Aerospace Engineering conducted chassis dynamometer based emissions tests on 35 heavy-heavy and medium-heavy diesel trucks on various chassis test cycles. The second data set was Graboski (1998), which tested 21 trucks and buses on various test procedures under hot and cold start conditions. Test data from a total of 11 heavy-heavy and medium-heavy diesel trucks tested on the UDDS cycle under hot start conditions were obtained from the database. The tests were conducted at high altitude; altitude correction factors were therefore applied before emissions test results were merged with other data for this analysis. The altitude correction factors were taken from EPA (1998) and are shown in Table 3-4. The third data set was obtained directly from WVU and included tests performed on four heavy-heavy diesel trucks on the UDDS cycle.

Table 3-4. EPA heavy-duty diesel vehicle high altitude adjustment factors.

HC	CO	NOX	PM
2.05	2.46	1.02	1.47

Two data sources were used to derive the emissions rates for light-heavy diesel trucks (LHDDV). The first data set was obtained from the U.S. EPA. The tests were conducted by the College of Engineering, Center for Environmental Research and Technology (CE-CERT) in Riverside under contract to the U.S. EPA with the objective to investigate the effect of payload on exhaust emissions. It included bag specific results from five trucks tested over the Federal Test Procedure and three different payloads. Staff used data obtained from testing the trucks at

the equivalent test weight (ETW). The ETW is the test weight equal to the empty weight of the vehicle plus 40 percent fuel fill in the tank. Vehicles in this data set were tested with California reformulated diesel fuel in the tank at the time the vehicle was received. The second data set was obtained from Norbeck (1998) and included bag specific FTP test results from 15 trucks tested at the equivalent test weight. Vehicles in this data set were tested with the Federal certification diesel fuel, Type 2-D. Fuel correction factors explained in more detail below were applied to the first data set before they were merged with the second data set.

For HHDDV and MHDDV, regression equations were used to calculate the average emission rates for model years that were within the data points, i.e. model years 1981 to 1998 for HHDDV and 1985 to 1999 for MHDDV. Model years prior to 1981 or 1985 were assumed to have the same average emission rate as the 1981 or 1985 model year. For HHDDV of model years 1999 and later, an average emission rate was calculated by multiplying the average emission rate of the 1991-93 model year group by the ratio of the standards of the 1999+ model year to the 1991-93 model year groups. The 1991-93 model year group was considered as a basis for calculating the 1999+ model year average emissions because this group had the lowest NOx emissions and therefore was considered to be free of off-cycle (defeat device) NOx increases. For MHDDV of model years 2000 and later, average emission rates were calculated by taking the ratio of standards with respect to the 1998-99 model year estimates and multiplying by the 1998-99 model year group average emission rate because no off-cycle NOx increases were observed for this vehicle class.

For LHDDV, two average set of emission rates were calculated -- one for model years before 1990 and a second for model years after 1990 -- because the data naturally fell into these two groups. These averages were applied for model years that are within the data set, i.e. 1982 to 1996. Model years prior to 1982 were assumed to have the same average emission rate as the 1982 model year. For model years after 1996, the average emission rates were calculated using the ratio of standards and the average emission rate of the 1991-93 model year group.

For urban (transit) buses, a data set from West Virginia University under contract to the Department of Energy's National Renewable Energy Laboratory was available to estimate emissions from 1988-1996 model year urban buses. Regression curves by model year were developed with buses of model years 1988 and earlier having the same emission rate. For 1999 and later model years, the emission factors were determined from a ratio of emission standards from 1991-1993 model years to avoid including off-cycle emission effects.

Deterioration was considered by ARB by employing an estimate of the frequency of occurrence and an emissions effect of failure of one or more given engine components. The type, frequency of occurrence, and emission effect are specific to each model year engine and are combined to produce a percentage increase in emissions. Because the available data showed no correlation of emissions with odometer, ARB does not estimate deterioration for urban buses.

Table 3-5. ARB estimated maximum percentage increase in emissions from engine deterioration (tampering and malmaintenance).

Vehicle	Pollutant	Pre88	88-90	Model Year Group			
				91-93	94-97	98-02	2002+
HHDDV	NOx	3.4	5.5	9.8	7.6	5.6	5.8
	HC	226.9	343.7	332.1	525.8	512.4	240.9
	PM	125.1	107.3	138.3	200.2	169.8	100.6

MHDDV	NO _x	5.2	4.2	10.0	7.6	5.6	5.8
	HC	227.6	342.1	325.9	525.8	512.4	240.9
	PM	95.5	89.8	130.7	206.5	170.7	101.3
LHDDV	NO _x	4.0	3.3	10.0	7.6	5.6	5.8
	HC	257.6	388.0	325.9	525.8	512.4	240.9
	PM	92.7	82.0	102.0	206.5	170.7	101.3

Because the average emission rates determined from the data set included engines that had some deterioration, a method was devised where the average deterioration was estimated by averaging the emission effects of tampering (which can occur immediately upon purchase) with the emission effects of tampering and malmaintenance (due to wear just prior to rebuild). By applying this average deterioration to the emission estimates from the in-use data, a zero-mile level could be calculated.

In addition, ARB accounts for the use of California diesel (so called “Clean Diesel”), which is a diesel fuel that restricts the aromatics content in addition to the lower sulfur requirement found with Federal (or 49 state) diesel. Emission effects for this fuel were taken from the testing of two heavy-duty diesel engines using fuels that varied by sulfur and aromatic content (ARB, 2000b), and the effects modeled are shown in Table 3-6. California diesel fuel was implemented statewide in October 1993, and diesel engines were certified on the lower (0.05%) sulfur Federal diesel fuel for the 1993 model year. So whether an in-use adjustments was made due to lower sulfur and aromatics or lower aromatics only depended upon the model year and the in-use year of interest.

Table 3-6. Emissions reduction due to lower sulfur and aromatic content.

Model Year	Reduction Due to Low Sulfur (0.28 to 0.05 % by weight)	Reduction Due to Low Aromatic (30 to 10 % by volume)	Reduction Due to Low Aromatic (30 to 10 % by volume)	Combined Effect of Lower Sulfur and Aromatic Contents
	PM	PM	NO _x	PM
Pre 1991	3.86%	16.73%	5.57%	20.59%
1991+	22.70%	10.07%	12.4%	32.77%

The final emission factor for trucks and buses are shown in Table 3-7. These emission factors include the adjustments described above, and zero-mile levels can be compared with the estimates for MOBILE6 except for the off-cycle (defeat device) effects on NOx emissions. In general, the zero-mile emission rates are surprisingly comparable (given the differing data sources) with the MOBILE6 estimates. However there are some significant differences such as late model urban buses where EMFAC2000 estimates much higher HC and PM emissions than MOBILE6. And engine deterioration of HC and PM emissions make the EMFAC2000 estimates generally higher than the MOBILE6 estimates.

Table 3-7a. EMFAC2000 zero-mile emission (ZM) and deterioration (DR) rates (g/mi per 10k mi) – HHDDV.

MY Group	HC		CO		NOx		PM	
	ZM	DR	ZM	DR	ZM	DR	ZM	DR
Pre 1975	1.60	0.018	8.36	0.095	28.52	0.012	1.98	0.016
1975-76	1.45	0.018	7.81	0.098	27.17	0.013	1.85	0.016
1977-79	1.45	0.019	7.81	0.101	27.17	0.013	1.85	0.017
1980-83	1.45	0.020	7.81	0.108	27.17	0.014	1.85	0.018
1984-86	0.74	0.011	4.87	0.074	20.18	0.011	1.18	0.012
1987-90	0.34	0.009	2.48	0.065	16.79	0.015	0.84	0.008
1991-93	0.28	0.009	1.74	0.056	15.97	0.030	0.51	0.009
1994-97	0.19	0.016	0.84	0.068	19.06	0.042	0.32	0.010
1998	0.18	0.014	0.63	0.049	23.01	0.037	0.26	0.007
1999-02	0.18	0.009	0.63	0.031	13.36	0.013	0.21	0.003
2003	0.14	0.003	1.01	0.023	6.68	0.007	0.26	0.003
2004	0.14	0.003	1.01	0.023	6.68	0.007	0.26	0.003

Table 3-7b. EMFAC2000 zero-mile emission (ZM) and deterioration (DR) rates (g/mi per 10k mi)– MHDDV.

MY Group	HC		CO		NOx		PM	
	ZM	DR	ZM	DR	ZM	DR	ZM	DR
Pre 1975	0.34	0.011	3.17	0.100	18.50	0.032	1.07	0.016
1975-76	0.34	0.011	3.17	0.100	18.50	0.032	1.07	0.016
1977-79	0.34	0.011	3.17	0.100	18.50	0.032	1.07	0.016
1980-83	0.34	0.011	3.17	0.100	18.50	0.032	1.07	0.016
1984-86	0.33	0.014	2.99	0.131	17.91	0.043	1.00	0.021
1987-90	0.21	0.016	1.80	0.140	15.74	0.034	0.73	0.017
1991-93	0.18	0.018	1.43	0.139	13.11	0.078	0.45	0.022
1994-97	0.11	0.017	0.78	0.121	11.55	0.048	0.27	0.018
1998	0.09	0.014	0.64	0.097	10.52	0.032	0.24	0.012
1999-02	0.09	0.014	0.64	0.097	10.52	0.032	0.24	0.012
2003	0.09	0.007	1.04	0.074	5.79	0.018	0.29	0.009
2004+	0.09	0.006	1.04	0.074	5.48	0.017	0.29	0.009

Table 3-7c. EMFAC2000 zero-mile emission (ZM) and deterioration (DR) rates (g/mi per 10k mi) – LHDDV.

MY Group	HC		CO		NO_x		PM	
	ZM	DR	ZM	DR	ZM	DR	ZM	DR
Pre 1975	0.19	0.007	0.74	0.025	3.94	0.005	0.23	0.003
1975-76	0.19	0.007	0.74	0.028	3.94	0.006	0.23	0.003
1977-79	0.19	0.008	0.74	0.030	3.94	0.006	0.23	0.003
1980-83	0.19	0.009	0.74	0.033	3.94	0.007	0.23	0.004
1984-86	0.19	0.010	0.74	0.037	3.94	0.008	0.23	0.004
1987-90	0.15	0.013	0.57	0.051	3.99	0.007	0.23	0.005
1991-93	0.22	0.016	0.68	0.052	6.67	0.031	0.07	0.002
1994	0.16	0.019	0.50	0.060	6.86	0.022	0.05	0.003
1995	0.16	0.019	0.50	0.060	6.86	0.022	0.05	0.003
1996-97	0.16	0.019	0.50	0.060	6.86	0.022	0.05	0.003
1998-99	0.02	0.002	0.44	0.052	2.43	0.006	0.03	0.001
2000-01	0.02	0.002	0.44	0.052	2.43	0.006	0.03	0.001
2002-03	0.03	0.001	0.71	0.039	1.56	0.004	0.04	0.001
2004+	0.02	0.001	0.71	0.039	1.56	0.004	0.04	0.001

Table 3-7d. EMFAC2000 diesel urban bus emission factors (g/mile)

Model Year	HC	CO	NO_x	PM
Pre 1987	2.06	18.19	46.18	1.29
1987-90	2.05	16.28	40.20	1.22
1991-93	2.02	9.71	25.49	1.16
1994-95	1.99	6.50	29.84	1.41
1996-98	1.98	5.10	39.17	1.69
1999-02	1.98	5.10	20.39	0.58
2003	0.84	4.05	10.20	0.12
2004-06	0.84	4.05	2.55	0.12
2007	0.84	4.05	1.02	0.12
2008	0.75	4.05	0.90	0.10

4. INCORPORATING BIODIESEL EMISSION EFFECTS INTO MODELING DATA BASES

The effects of biodiesel on mass emissions in HDDV's need to be incorporated into the emission inventory data bases that are used in air quality modeling. We describe here how this is done for the different modeling data bases to be used in the air quality modeling tasks. Information about other components of the air quality modeling to be performed can be found in the project Air Quality Modeling Plan.

NORTHEAST CORRIDOR AND CHICAGO OZONE MODELING

The Emissions Modeling System version 1995 (EMS95) is the emissions processing system used in the Northeast Ozone Transport Region (OTR) and Chicago area ozone modeling data bases. EMS95 is a large and complex modeling system that is written using the Statistical Analysis System (SAS7). In standard EMS95 emissions modeling, a composite fleet emission factor is calculated using MOBILE5. This composite emission factor is a function of speed and VMT by roadway type (e.g., rural interstate, urban arterial), vehicle class fleet mix, temperature, fuel parameters, and Inspection and Maintenance (I/M) program parameters input for each county in the modeling domain. Average speed and VMT inputs are across all vehicle categories.

For the air quality modeling to be performed in this study, we have updated the EMS95 modeling system to include adjustments that reflect what is expected in MOBILE6. Specifically, we will use the MOBILE6 adjustments that EPA developed for the modeling performed for the Tier 2 vehicle/sulfur standards final rulemaking (Koupal and Dolce, 1999). While these adjustments do not include all changes being made to MOBILE6, they do include many of the more significant effects. Adjustments are made to:

- Light-duty vehicle (passenger cars and trucks) and heavy-duty gasoline vehicle emission factors for exhaust HC and NO_x. The adjustments depend on fuel type (reformulated or conventional) and Inspection and Maintenance program type, and are made to each county using county-specific data. For the 2007 modeling year, these adjustments are all substantial, typically in the range of 20 to 70 percent reductions. Additional adjustments (additive) were made to account for increases in NO_x emissions for air conditioning usage as modeled in MOBILE6 (dependent on county-specific ambient temperatures).
- Evaporative emissions adjustments to reflect the benefits of Tier 2 vehicle controls only; these are small, only a few percent reduction. MOBILE6 will have significant revisions to all categories of evaporative HC emissions in light-duty vehicles, but the emissions modeling approach is so different from MOBILE5 that it was not possible to develop simple adjustment factors.
- Heavy-duty diesel vehicle NO_x emissions for the effects excess NO_x emissions from the so-called "defeat device". These adjustments differ by roadway type and speed, with the largest increases on interstates.
- HDDV VOC and NO_x emissions for other changes in MOBILE6 – new emissions standards, revised conversion factors (for converting engine dynamometer g/bhp-hr measurements to g/mile), and revised fleet characterization (age and mileage accumulation distributions).

As the first step in the emissions processing, EMS95 generates a very large lookup table of MOBILE5 output emission factors, with the MOBILE6 adjustments described above, by vehicle class as a function of I/M program parameters, fuel parameters, speed (typically in 5 mph increments), and temperature (typically in 2°F increments). Emission factors by vehicle class are then interpolated using the county-specific I/M program parameters and temperature, and average speed inputs for each roadway type. To incorporate the biodiesel emission effects into the inventory, the MOBILE5/6 HDDV emission factors in this lookup table will be multiplied by the engine dynamometer biodiesel effects by pollutant as shown in Table 2-1 (using the overall average without the Sharp, 1998 data). EMS95 then calculates the on-road fleet average emissions by taking a weighted average of the vehicle class emission factors (weighted by fleet mix and vehicle class-specific VMT).

LAS VEGAS CO MODELING

The carbon monoxide emission inventory used in the Clark County (Las Vegas) SIP was developed using a combination of the Emissions Preprocessor System version 2 (EPS2.0) and the Direct Travel Impact Model version 2 (DTIM2). The DTIM2 system used in the Las Vegas modeling combines link specific traffic activity data from the TRANPLAN transportation model with emission factors from MOBILE5 to produce gridded hourly emissions estimates for on-road mobile sources. The EPS2.0 system then reads the inventory generated by the DTIM2 model and performs the final tasks needed in preparation for use in air quality modeling.

For the CO modeling in the Las Vegas region, the biodiesel emission effects shown in Table 2-1 will be multiplied by the MOBILE5 emission factors for HDDVs prior to running the DTIM2/EPS2 system.

LOS ANGELES OZONE AND PM MODELING

The emission processing system adopted by the South Coast Air Quality Management District (SCAQMD) to generate the inventories used in the Los Angeles 1987 Southern California Air Quality Study (SCAQS) domain uses the DTIM2 system to generate a gridded hourly on-road mobile source emission inventory. However, the emission factor model used was the EMFAC7 model developed by the California Air Resources Board (CARB). Also, because of historic precedent, the SCAQMD uses an earlier version of the EPS2.0 system. This system, as used by SCAQMD, consists primarily of the program CENTEMS, which is responsible for chemical speciation and temporal allocation of emissions estimates, as well as application of any growth or controls.

The methodology we will use in the Los Angeles area for ozone and PM modeling will be similar to that adopted for CO modeling in the Las Vegas region. The mobile source emission factor model that we will use will be EMFAC2000 version 2.0, which has not yet been released by ARB. The EMFAC2000 emission factors for HDDV will be adjusted using the biodiesel effects shown in Table 2-1. The adjusted emission factors will be used in the DTIM2 processing to generate on-road mobile emission estimates that will then be processed by the CENTEMS program to generate the mobile source emissions inventory estimates to be used in the ozone and PM air quality modeling.

5. HEALTH EFFECTS IMPACT MODELING PLAN

OBJECTIVE

Introduction of biodiesel on a large-scale basis has the potential to provide public health benefits associated with decreased toxicity of diesel PM emissions. Benefits from decreases in the total mass of primary and possibly secondary PM emissions are also possible. A health impact modeling analysis will be performed as part of the project to quantify the potential health benefits.

BACKGROUND

Exhaust from conventional fueled diesel vehicles contains numerous known and suspected human carcinogens. Diesel exhaust was recently classified as a Toxic Air Contaminant by the California Air Resources Board (ARB, 1998); was the subject of an EPA health risk assessment (EPA, 1998), and a critical review by the Health Effects Institute (1995) which is sponsoring ongoing work in this area. One of the potential benefits of biodiesel fuel use is a decrease in the overall toxicity of PM emissions. This is a result of the elimination or reduction of certain toxic components of diesel exhaust which are present in conventional fuels but not in biodiesel. Additional benefits may be associated with potential reductions in the total mass of particulate matter in the exhaust.

TECHNICAL APPROACH

An assessment will be made of the potential health benefits impact of each biodiesel use scenario considered for the Los Angeles area PM modeling to be performed in PM₁₀ modeling as described in the previous section. Results from a survey of available data on differences in toxicity between biodiesel and conventional diesel exhaust PM emissions will be used to develop appropriate toxicity adjustments factors to apply to the PM emission estimates. PM model results from the biodiesel PM₁₀ impact modeling will be combined with an exposure model to estimate population exposures in Los Angeles to diesel exhaust under each fuel scenario. These results will take into account movement of people between various microenvironments including time spent indoors. Resulting exposure estimates will then be combined with toxicity factors to estimate differences in cancer incidence and morbidity/mortality rates between each fuel use scenario. Finally, costs associated with the computed morbidity/mortality rates will be estimated using cost factors for various outcomes developed for the PM NAAQS Regulatory Impact Analysis (EPA, 1997).

Our analysis will focus on health effects associated with the toxicity of primary diesel particulate emissions although available dose/response data do not always distinguish between diesel particulate and whole exhaust. Effects associated specifically with primary vapor phase toxic emissions such as benzene and secondary pollutants (ozone, formaldehyde, secondary particulate such as secondary organic aerosols, etc.) will not be considered although this would be necessary

for a complete health risk assessment. We also note that our emphasis will be on health effects associated with long-term, non-occupational exposures. Biodiesel use may also reduce the potential for adverse health consequences associated with both short-term (acute) exposures to “hot spot” concentrations and occupational exposures.

Exposure Modeling

EPA’s Office of Air Quality Planning and Standards (OAQPS) has recently enhanced the pNEM/CO (probabilistic NAAQS Exposure Model for Carbon Monoxide) and applied it to Denver and Los Angeles (Johnson et al., 1999). This new version of the pNEM/CO model represents the current state-of-the-art in estimating CO exposures. Application of pNEM/CO to Los Angeles using 1995 data is currently undergoing some refinements to better account for the spatial variation in ambient CO; revised results along with a comprehensive report are expected to be available within the next month which will allow sufficient time for them to be used in the biodiesel health impact analysis. EPA’s Clean Air Scientific Advisory Committee is scheduled to review the pNEM/CO analysis in Spring, 2000.

The pNEM is usually run with indoor sources included to get a total exposure estimate. However the, results of a model run for Los Angeles with indoor sources turned off are available in this case. The output of pNEM/CO with indoor sources turned off will be adapted to provide seasonal CO exposure estimates for various age/gender/occupation population cohorts. These results will then be rescaled by the ratio of diesel PM emissions to total outdoor CO emissions to obtain diesel PM exposure estimates. This is the same methodology used in the EPA/OMS diesel PM exposure study (EPA, 1999).

Health Impacts

In addition to cancer, non-cancer health effects have been associated with chronic exposure to PM emissions in general and diesel exhaust in particular. Acute effects from short-term exposures have also been identified. Estimates of both an approximate “no effects” level for acute effects and a lifetime cancer unit risk factor have been published by EPA and ARB for diesel exhaust PM as a marker for whole diesel exhaust. Similar information is available for many known toxic components of diesel exhaust. However, quantitative exposure/response relationships for outcomes such mortality, respiratory illnesses, etc. have only been developed for urban ambient PM and not specifically for diesel exhaust. Nevertheless, results for urban ambient PM could be used to approximate diesel exhaust health effects.

Annual average exposure estimates obtained from pNEM/CO as described above will be combined with published unit risk factors for conventional diesel and biodiesel to estimate cancer incidence rates attributable to diesel exhaust for the total population and sensitive subgroups for each of the fuel use scenarios used. Both a “best estimate” and a range of values will be generated based on the range of published unit risk factors. PM exposure/response relationships developed as part of the Regulatory Impact Analysis (RIA) for EPA’s 1997 PM NAAQS rule making will be used to estimate incidents of mortality associated with long-term exposures to diesel exhaust at ambient concentrations under each scenario. These relationships are summarized in Appendix I of the RIA (EPA, 1997).

Cost Estimates for Biodiesel Health Impacts

Costs associated with the morbidity and mortality estimates described above will be based on cost factors from EPA's 1997 PM RIA (EPA, 1997). Table 5-1 lists health effects for which quantified benefit estimates are available from the PM RIA along with those for which quantitative estimates are not available. Given the high cost factors associated with mortality, it is reasonable to expect that changes in mortality will dominate the cost comparison between fuel use scenarios as it did in the PM NAAQS scenarios. We will therefore focus our cost comparison on changes in mortality. Our mortality benefits estimate will consider both value of a statistical life saved and the value of a statistical life-year extended as used in the PM RIA. Note that cost factors are not available in the RIA for cancer so we will not attempt to quantify costs for this outcome.

Table 5-1. PM benefits categories.

	Unquantified Benefit Categories	Quantified Benefit Categories (incidences reduced and/or dollars)
Health Categories	Changes in pulmonary function Morphological changes Altered host defense mechanisms Cancer Other chronic respiratory disease Infant Mortality Mercury Emission Reductions	Mortality (acute and long-term) Hospital admissions for: all respiratory illnesses congestive heart failure ischemic heart disease Acute and chronic bronchitis Lower, upper, and acute respiratory symptoms Respiratory activity days Minor respiratory activity days Shortness of breath Moderate or worse asthma Work loss days

HEALTH EFFECTS IMPACT REPORTING

A comprehensive draft interim report will be prepared describing the data sources, methods, assumptions used in the health effects impact modeling along with the modeling results. Revisions as needed in response to reviewer comments will be incorporated into a document which will appear as a chapter integrated into the project final report.

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Appendix B

Bag Hydrocarbon Chemical Composition
(values in **red** were not explicitly measured)

Chemical Composition	Sharp (1998)			Durbin et al. (1999)		
	B100	B20	2D	B100	B20	2D
METHANE	2.3%	0.4%	0.4%	0.5%	1.3%	1.2%
ETHANE	0.5%	0.1%	0.1%	0.2%	0.1%	0.1%
ETHENE	37.3%	10.5%	9.4%	9.3%	6.0%	5.4%
PROPANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
PROPENE	5.7%	2.4%	2.4%	2.3%	1.9%	1.9%
ETHYNE	8.3%	2.2%	2.0%	1.9%	1.3%	1.3%
PROPADIENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
BUTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
T-2-BUTENE	0.1%	0.1%	0.1%	0.0%	0.0%	0.0%
1-BUTENE	2.3%	0.7%	0.7%	0.5%	0.2%	0.1%
2-METHYLPROPENE	0.9%	0.6%	0.6%	0.4%	0.4%	0.4%
2,2-DIMETHYLPROPANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
PROPYNE	0.3%	0.1%	0.2%	0.0%	0.0%	0.0%
1,3-BUTADIENE	3.3%	1.0%	0.8%	0.9%	0.5%	0.5%
2-METHYLPROPANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1-BUTYNE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
METHANOL	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C-2-BUTENE	0.0%	0.1%	0.1%	0.0%	0.0%	0.0%
3-METHYL-1-BUTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
ETHANOL	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2-METHYLBUTANE	0.2%	0.1%	0.1%	0.0%	0.0%	0.0%
2-BUTYNE	0.0%	0.0%	0.1%	0.2%	0.3%	0.1%
1-PENTENE	0.7%	0.0%	0.3%	0.2%	0.2%	0.2%
2-METHYL-1-BUTENE	0.3%	0.1%	0.1%	0.1%	0.0%	0.0%
PENTANE	0.1%	0.2%	0.1%	0.0%	0.0%	0.0%
UNIDENTIFIED C5 OLEFINS	0.0%	0.0%	0.2%	0.0%	0.0%	0.0%
2-METHYL-1,3-BUTADIENE	0.2%	0.0%	0.1%	0.1%	0.1%	0.0%
T-2-PENTENE	0.0%	0.0%	0.1%	0.0%	0.1%	0.0%
3,3-DIMETHYL-1-BUTENE	0.0%	0.0%	0.0%	0.1%	0.1%	0.1%
C-2-PENTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2-METHYL-2-BUTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
T-BUTANOL	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
CYCLOPENTADIENE	0.0%	0.0%	0.0%	0.1%	0.0%	0.0%
2,2-DIMETHYLBUTANE	0.0%	0.0%	0.1%	0.0%	0.1%	0.0%
CYCLOPENTENE	0.0%	0.0%	0.1%	0.1%	0.0%	0.0%
4-METHYL-1-PENTENE	0.0%	0.0%	0.1%	0.1%	0.1%	0.0%
3-METHYL-1-PENTENE	0.0%	0.0%	0.0%	0.1%	0.1%	0.1%
CYCLOPENTANE	0.0%	0.0%	0.0%	0.2%	0.1%	0.1%
2,3-DIMETHYLBUTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Methyl-t-Butyl-Ether	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
4-METHYL-C-2-PENTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2-METHYLPENTANE	0.1%	0.1%	0.2%	0.1%	0.0%	0.1%
4-METHYL-T-2-PENTENE	0.0%	0.0%	0.0%	0.1%	0.2%	0.1%
3-METHYLPENTANE	0.2%	0.1%	0.1%	0.0%	0.1%	0.1%
2-METHYL-1-PENTENE	0.5%	0.2%	0.2%	0.0%	0.0%	0.0%
1-HEXENE	0.5%	0.2%	0.2%	0.4%	0.1%	0.1%
HEXANE	0.7%	0.1%	0.0%	0.1%	0.1%	0.1%
UNIDENTIFIED C6 OLEFINS	0.0%	0.2%	0.3%	0.0%	0.0%	0.0%
T-3-HEXENE	0.0%	0.0%	0.0%	0.6%	0.0%	0.0%

Chemical Composition	Sharp (1998)			Durbin et al. (1999)		
	B100	B20	2D	B100	B20	2D
C-3-HEXENE	0.0%	0.0%	0.0%	0.1%	0.1%	0.0%
DI-ISOPROPYL ETHER	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
T-2-HEXENE	0.0%	0.0%	0.0%	0.0%	0.1%	0.0%
3-METHYL-T-2-PENTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2-METHYL-2-PENTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3-METHYLCYCLOPENTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C-2-HEXENE	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%
Ethyl-t-Butyl-Ether	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3-METHYL-C-2-PENTENE	0.0%	0.0%	0.0%	0.2%	0.1%	0.1%
2,2-DIMETHYLPENTANE	0.3%	0.0%	0.0%	0.0%	0.0%	0.0%
METHYLCYCLOPENTANE	0.3%	0.0%	0.0%	0.1%	0.0%	0.0%
2,4-DIMETHYLPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,2,3-TRIMETHYLBUTANE	0.0%	0.0%	0.0%	0.1%	0.0%	0.0%
3,4-DIMETHYL-1-PENTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1-METHYLCYCLOPENTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
BENZENE	5.2%	1.1%	0.9%	1.1%	0.4%	0.3%
3-METHYL-1-HEXENE	0.0%	0.0%	0.0%	0.1%	0.4%	0.3%
3,3-DIMETHYLPENTANE	0.2%	0.0%	0.0%	0.0%	0.0%	0.0%
CYCLOHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2-METHYLHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,3-DIMETHYLPENTANE	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%
1,1-DIMETHYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
TERT-AMYL METHYL ETHER	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
CYCLOHEXENE	0.1%	0.1%	0.0%	0.0%	0.0%	0.0%
3-METHYLHEXANE	0.0%	0.0%	0.0%	0.2%	0.1%	0.1%
C-1,3-DIMETHYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3-ETHYLPENTANE	0.6%	0.4%	0.0%	0.0%	0.0%	0.0%
T-1,2-DIMETHYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
c-1,3-Dimethylcyclopentane	0.1%	0.0%	0.1%	0.0%	0.0%	0.0%
1-HEPTENE	0.0%	0.0%	0.0%	0.2%	0.0%	0.0%
2,2,4-TRIMETHYLPENTANE	0.6%	0.3%	0.2%	0.1%	0.2%	0.1%
2-METHYL-1-HEXENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
T-3-HEPTENE	0.0%	0.0%	0.0%	0.3%	0.1%	0.0%
HEPTANE	0.3%	0.1%	0.0%	0.0%	0.0%	0.0%
C-3-HEPTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
UNIDENTIFIED C7	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2-METHYL-2-HEXENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3-METHYL-T-3-HEXENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
T-2-HEPTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3-ETHYL-C-2-PENTENE	0.5%	0.0%	0.0%	0.0%	0.0%	0.0%
2,4,4-TRIMETHYL-1-PENTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,3-DIMETHYL-2-PENTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C-2-HEPTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
METHYLCYCLOHEXANE	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%
C-1,2-DIMETHYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,2-DIMETHYLHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1,1,3-TRIMETHYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,4,4-TRIMETHYL-2-PENTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,2,3-TRIMETHYLPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,5-DIMETHYLHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Chemical Composition	Sharp (1998)			Durbin et al. (1999)		
	B100	B20	2D	B100	B20	2D
ETHYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,4-DIMETHYLHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1-T-2-C-4-TRIMETHYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3,3-DIMETHYLHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1-T-2-C-3-TRIMETHYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,3,4-TRIMETHYLPENTANE	0.0%	0.1%	0.1%	0.0%	0.0%	0.0%
2,3,3-TRIMETHYLPENTANE	0.0%	0.1%	0.0%	0.0%	0.0%	0.0%
TOLUENE	2.1%	1.0%	0.5%	0.3%	0.3%	0.3%
2,3-DIMETHYLHEXANE	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%
1,1,2-TRIMETHYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2-METHYLHEPTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3,4-DIMETHYLHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
4-METHYLHEPTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3-METHYLHEPTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1C,2t,3-TRIMETHYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.3%	0.1%	0.0%
C-1,3-DIMETHYLCYCLOHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
T-1,4-DIMETHYLCYCLOHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3-ETHYLHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,2,5-TRIMETHYLHEXANE	0.4%	0.0%	0.1%	0.0%	0.0%	0.0%
T-1-METHYL-3-ETHYLCYCLOPENTANE	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%
C-1-METHYL-3-ETHYLCYCLOPENTANE	0.0%	0.2%	0.2%	0.0%	0.0%	0.0%
1,1-DIMETHYLCYCLOHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
TRANS-1-METHYL-2-ETHYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1-METHYL-1-ETHYL-CYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,4,4-TRIMETHYLHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,2,4-TRIMETHYLHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
TRANS-1,2-DIMETHYLCYCLOHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1-OCTENE	0.0%	0.0%	0.0%	0.1%	0.1%	0.1%
T-4-OCTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
OCTANE	0.1%	0.1%	0.1%	0.0%	0.0%	0.0%
UNIDENTIFIED C8	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
T-2-OCTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
T-1,3-DIMETHYLCYCLOHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C-2-OCTENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
ISOPROPYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,2-DIMETHYLHEPTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,3,5-TRIMETHYLHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C-1-METHYL-2-ETHYLCYCLOPENTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,4-DIMETHYLHEPTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
4,4-DIMETHYLHEPTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C-1,2-DIMETHYLCYCLOHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
ETHYLCYCLOHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,6-DIMETHYLHEPTANE	0.0%	0.2%	0.2%	0.0%	0.0%	0.0%
1,1,3-TRIMETHYLCYCLOHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,5-DIMETHYLHEPTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3,3-DIMETHYLHEPTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3,5-DIMETHYLHEPTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
ETHYLBENZENE	0.1%	0.3%	0.3%	0.0%	0.0%	0.0%
2,3,4-TRIMETHYLHEXANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,3-DIMETHYLHEPTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Chemical Composition	Sharp (1998)			Durbin et al. (1999)		
	B100	B20	2D	B100	B20	2D
m-& p-XYLENE	0.3%	0.3%	0.4%	0.0%	0.0%	0.0%
4-METHYLOCTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3,4-DIMETHYLHEPTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
4-ETHYLHEPTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2-METHYLOCTANE	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%
3-METHYLOCTANE	0.0%	0.1%	0.0%	0.0%	0.0%	0.0%
STYRENE	0.0%	0.0%	0.0%	0.2%	0.1%	0.1%
o-XYLENE	0.0%	0.2%	0.2%	0.0%	0.1%	0.1%
1-NONENE	0.0%	0.1%	0.0%	0.1%	0.1%	0.0%
T-3-NONENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C-3-NONENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
NONANE	0.0%	0.2%	0.2%	0.0%	0.0%	0.0%
T-2-NONENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
I-PROPYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,2-DIMETHYLOCTANE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
2,4-DIMETHYLOCTANE	0.0%	0.1%	0.1%	0.1%	0.1%	0.1%
n-PROPYLBENZENE	0.0%	0.0%	0.1%	0.0%	0.1%	0.1%
1-METHYL-3-ETHYLBENZENE	0.0%	0.0%	0.1%	0.1%	0.3%	0.2%
1-METHYL-4-ETHYLBENZENE	0.0%	0.0%	0.1%	0.0%	0.1%	0.0%
1,3,5-TRIMETHYLBENZENE	0.0%	0.0%	0.1%	0.0%	0.1%	0.1%
1-METHYL-2-ETHYLBENZENE	0.0%	0.0%	0.1%	0.0%	0.1%	0.1%
1,2,4-TRIMETHYLBENZENE	0.0%	0.1%	0.1%	0.1%	0.4%	0.4%
T-BUTYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1-DECENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
DECANE	0.0%	0.1%	0.1%	0.0%	0.1%	0.1%
I-BUTYLBENZENE	0.0%	0.1%	0.1%	0.1%	1.3%	1.2%
1,3,-DIMETHYL-5-ETHYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
s-BUTYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1-METHYL-3-I-PROPYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.1%
1,2,3-TRIMETHYLBENZENE	0.0%	0.1%	0.0%	0.0%	0.1%	0.0%
1-METHYL-4-I-PROPYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
INDAN	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1-METHYL-2-I-PROPYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1,3-DIETHYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.1%	0.1%
1,4-DIETHYLBENZENE	0.0%	0.1%	0.0%	0.0%	0.3%	0.3%
1-METHYL-3-N-PROPYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1-METHYL-4-N-PROPYLBENZENE	0.0%	0.0%	0.1%	0.0%	0.1%	0.1%
1,2-DIETHYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.1%
1-METHYL-2-N-PROPYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.3%	0.3%
1,4-DIMETHYL-2-ETHYLBENZENE	0.0%	0.1%	0.0%	0.0%	0.0%	0.0%
1,3-DIMETHYL-4-ETHYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1,2-DIMETHYL-4-ETHYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.3%	0.2%
1,3-DIMETHYL-2-ETHYLBENZENE	0.0%	0.0%	0.0%	0.1%	0.0%	0.0%
UNDECANE	0.0%	0.7%	0.6%	0.1%	0.1%	0.1%
1,2-DIMETHYL-3-ETHYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.1%	0.0%
1,2,4,5-TETRAMETHYLBENZENE	0.0%	0.0%	0.2%	0.8%	0.4%	0.5%
2-METHYL-BUTYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
3,4 DIMETHYL-I-PROPYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1,2,3,5-TETRAMETHYLBENZENE	0.0%	0.4%	0.1%	0.0%	0.0%	0.0%
T-1-BUTYL-2-METHYLBENZENE	0.0%	0.1%	0.1%	0.0%	0.0%	0.0%

Chemical Composition	Sharp (1998)			Durbin et al. (1999)		
	B100	B20	2D	B100	B20	2D
1,2,3,4-TETRAMETHYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
N-PENT-BENZENE	0.0%	0.1%	0.2%	0.0%	0.0%	0.0%
T-1-BUTYL-3,5-DIMETHYLBENZENE	0.0%	0.1%	0.1%	0.0%	0.0%	0.0%
T-1-BUTYL-4-ETHYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
NAPHTHALENE	0.0%	0.0%	0.1%	0.0%	0.1%	0.1%
DODECANE	0.0%	0.5%	0.4%	0.2%	0.1%	0.1%
1,3,5-TRIETHYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
1,2,4-TRIETHYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
HEXYLBENZENE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
UNIDENTIFIED C9-C12+	0.0%	0.9%	1.2%	0.0%	0.0%	0.0%
Unknown (C1-C4)	0.0%	0.0%	0.0%	0.6%	0.8%	1.0%
Unknown (C4-C12)	0.0%	0.0%	0.0%	3.9%	4.1%	4.6%
FORMALDEHYDE	43.0%	13.8%	12.5%	9.6%	7.0%	7.0%
ACETALDEHYDE	15.8%	5.6%	5.1%	3.8%	3.7%	2.8%
ACROLEIN	8.7%	1.8%	2.0%	0.9%	1.5%	1.1%
ACETONE	2.7%	1.5%	1.6%	0.5%	0.3%	0.2%
METHACROLEIN	0.0%	0.0%	0.0%	0.2%	0.3%	0.2%
PROPIONALDEHYDE	4.2%	2.0%	1.3%	0.8%	0.6%	0.5%
CROTONALDEHYDE	3.8%	1.5%	1.4%	0.3%	0.2%	0.2%
ISOBUTYRALDEHYDE, NOTE H	1.3%	0.4%	0.4%	0.0%	0.0%	0.0%
METHYL ETHYL KETONE, NOTE H	1.3%	0.4%	0.4%	0.3%	0.1%	0.1%
BENZALDEHYDE	1.6%	0.4%	0.5%	0.4%	0.6%	0.4%
ISOVALERALDEHYDE	2.3%	0.4%	0.3%	0.0%	0.0%	0.0%
VALERALDEHYDE	1.1%	0.4%	0.4%	0.4%	0.2%	0.3%
O-TOLUALDEHYDE	1.4%	0.3%	0.2%	0.0%	0.0%	0.0%
M/P-TOLUALDEHYDE	3.4%	1.1%	1.3%	0.1%	0.1%	0.2%
HEXANALDEHYDE	1.8%	0.3%	0.2%	0.8%	0.3%	0.2%
DIMETHYLBENZALDEHYDE	0.2%	0.3%	0.3%	0.0%	0.0%	0.0%

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