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Characterizing Emissions from the Combustion of Biofuels

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Abstract

Emissions from two biofuels, a soy-based biodiesel and an animal-based biodiesel, were measured and compared to emissions from a distillate petroleum fuel oil. The three fuels were burned in a small ($3.5x10^6$ Btu/hr) firetube boiler designed for use in institutional, commercial, and light industrial applications. Emissions were measured for carbon monoxide (CO), carbon dioxide (CO_2), oxides of nitrogen (NO_x), and sulfur dioxide (SO_2) using continuous emission monitors. Concentrations and size distributions of particulate matter (PM) were also measured. Flue gas samples were collected and analyzed to determine concentrations of aldehydes and other volatile organic compounds, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls. The boiler efficiency was also determined for operation using each of the three fuels. The most significant difference was for PM, where the distillate fuel oil had emissions roughly ten times higher than for either of the two biodiesel fuels. The particle size distributions (measuring particle volume) showed a mode near 1 μm for the two biodiesels and near 2.5 μm for the distillate fuel oil. All three fuels also had a mode near 20 nm. SO_2 was nearly four times higher for the distillate petroleum fuel oil than for either the soy or animal biodiesel. NO_x emissions were slightly higher for the distillate fuel oil than for the two biodiesels, but all three were within 6% of one another. CO and CO_2 concentrations were approximately the same for the three fuels. The differences in concentrations of the organic compounds were relatively small, with the emissions patterns being similar for all three fuels. Boiler efficiencies were also similar for the three fuels, with any difference being within the unit's measured variability range. In general, the two biodiesel fuels emitted less pollutants than the distillate fuel oil, and the low life-cycle CO_2 emissions for the biodiesels results in a net CO_2 reduction of nearly 75% when using these fuels compared to the petroleum distillate fuel.

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Nomenclature and Abbreviations

APCS	air pollution control system
APS	aerodynamic particle sizer
ASTM	American Society for Testing and Materials
B*n*	Biodiesel consisting of *n*% biodiesel and (100-*n*)% petroleum diesel
Btu	British Thermal Unit
CEM	continuous emission monitor
CO	carbon monoxide
CO_2	carbon dioxide
DOE	U.S. Department of Energy
dscm	dry standard cubic meter
EIA	DOE's Energy Information Administration
EPA	U.S. Environmental Protection Agency
FGR	flue gas recirculation
FOG	fats, oils, and greases
GHG	greenhouse gas
NO_x	oxides of nitrogen
NRMRL	National Risk Management Research Laboratory
O_2	oxygen
OAQPS	EPA's Office of Air Quality Planning and Standards, part of OAR
OAR	EPA's Office of Air and Radiation
PAH	polycyclic aromatic hydrocarbon
PM	particulate matter
$PM_{2.5}$	particulate matter smaller than 2.5 μm aerodynamic diameter
PM_{10}	particulate matter smaller than 10 μm aerodynamic diameter
ppb	parts per billion (10^9)
ppm	parts per million (10^6)
QA	quality assurance
QAPP	quality assurance project plan
SMPS	scanning mobility particle sizer
SO_2	sulfur dioxide
THC	total hydrocarbons
TSE	transmissible spongiform encephalopathy
UGa	University of Georgia
VOC	volatile organic compound

Characterizing Emissions from the Combustion of Biofuels

Background

The term "biofuels" typically refers to liquid fuels derived from biomass, although it is also used to describe solid or gaseous biomass-derived fuels. "Biomass" itself covers a broad range of biological feedstocks. The majority of these feedstocks tend to be waste materials from wood products, pulp processes, and agricultural production, or purpose-grown crops such as corn or soy. Biomass can also include food and municipal solid waste, solids from sewage treatment, and landfill gas, and liquid fuels from these sources are also considered to be biofuels. Biofuels are also a subset of the broader terms "renewable fuels" and "alternative fuels."

Biofuels have been of increasing interest as concern over reducing carbon dioxide (CO_2) emissions has grown due to CO_2's role in global climate change as well as rising concern over the stability of petroleum resource availability and price. This interest was emphasized when President Bush, in his 2007 State of the Union Address, called for the U.S. to reach the goal of producing 35 billion gallons of renewable and alternative fuels per year by 2017.

The U.S. Department of Energy (DOE) has projected that transportation biofuels, which are expected to make up the majority of liquid biofuel use, will increase by 5.5% annually through 2030, with other sectors (except biomass for electricity generation) increasing at a slower rate or remaining relatively constant, as shown in Figure 1 (U.S. Department of Energy 2007c). The same report projects biomass for electricity generation to increase by 4.8% annually over the same period. Between 1990 and 1995, transportation has been the only sector in which biomass consumption increased, and the rate of increase has been substantial at nearly 20% per year (U.S. Department of Energy 2006). Because transportation use of biomass is entirely via biofuel use, it is a valid conclusion to note that over the five year period from 2000 to 2005, nearly all of the increase in biomass-based energy consumption has been an increase in transportation biofuels. Consumption of ethanol blended into gasoline increased from 139 trillion Btu in 2000 to 340 trillion Btu in 2005.

The bulk of biofuel production and use has been for ethanol and biodiesel. Ethanol is currently used in oxygenated motor gasoline, and increasingly is seen as significant replacement for gasoline in "flex-fuel" vehicles. Nearly all commercial ethanol is made from corn, although efforts are being made to enable ethanol to be produced from cellulosic materials such as wood and agricultural wastes and fast-growing crops such as switchgrass. Biodiesel is generally produced from soy or palm oil, and is usually used in blends of biodiesel and conventional petroleum-based diesel fuel with little or no modification of the engine. However, there are processes that produce biodiesel from waste oils and fats such as used cooking oil, wastes from meat and poultry production, and other fats, oil, and grease (FOG) that are considered to be waste materials and are often discarded into sewage systems. In a few instances, engines have been modified for

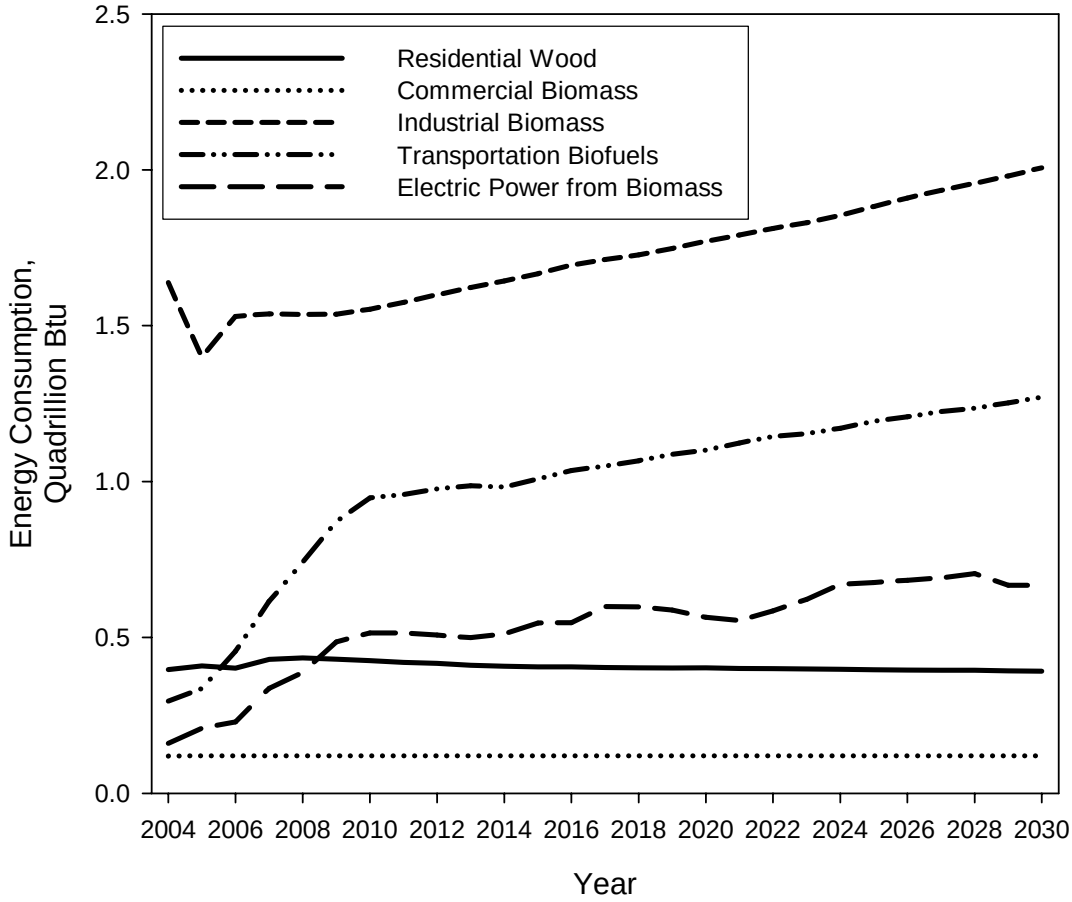

Figure 1. Projected bioenergy use by sector through 2030.

direct use of filtered but unprocessed vegetable oils, but this is not currently seen as a likely future approach to biofuel use.

As biofuel use has increased, the information on biofuel feedstocks and production methods has expanded, in terms of both level of understanding as well as extent of dissemination. This in turn has expanded interest in applying biofuels to applications beyond transportation to include biofuel combustion in boilers. As the technical understanding increases, more firms are venturing into biofuel use, including as boiler fuels.

The incentives to use biofuels in boilers are increasing, due to state-level requirements being placed on electricity generators. Data collected by the Database of State Incentives for Renewables & Efficiency (DSIRE) at North Carolina State University indicated that 31 states had some form of standard or regulation to increase the renewable energy use by electricity generators (North Carolina State University 2007). Although the renewable requirements can be met using wind, solar, or hydropower, co-firing fossil fuels with biomass or biofuels can be a technically attractive approach. These requirements

generally apply to electricity generators, but the focus on renewable energy resources also provides an incentive for increasing renewable energy use in other sectors.

The use of biofuels may have advantages in addition to reducing CO_2 emissions. An analysis by the New York State Energy Research and Development Authority noted that New York State now has adequate feedstock production capacity within the state to produce the full expected requirement for B2 fuel (2% biodiesel, 98% petrodiesel) for highway use. This analysis estimated that producing this relatively small amount of fuel within New York, rather than relying entirely on out-of-state supplies, would result in over 1100 new jobs in the state, even though the price of fuel increased due to mandated biofuel content (New York State Energy Research and Development Authority 2004). In addition, industries are working to be seen as environmentally responsible by voluntarily using increasing amounts of renewable energy, and are also facing possible "green energy" requirements or incentives to use renewable energy. These factors are providing incentives for growing biofuel consumption in stationary sources.

Biofuel Types for Boilers

Although the largest user of liquid biofuels is, and is projected to remain, the transportation sector, the expanding technical understanding of biofuel properties, production methods, and feedstocks, combined with the increased availability of (currently) low-cost glycerin from biodiesel production, has illuminated numerous opportunities for biofuel use in other applications, primarily as a fuel for small boilers. The DOE Energy Information Administration (EIA) estimates that, of the 5.9×10^{12} Btu (0.59 Quads) of biofuel energy consumption in the U.S. in 2005, the only non-transportation use of biofuels was in the industrial sector, and this consumption was in the form of biofuel losses and coproducts. This compares to the 2.13 Quads of wood energy and 0.58 Quads of waste biomass energy (which includes municipal solid waste, landfill gases, agriculture byproducts/crops, sludge waste, tires, and other biomass solids, liquids and gases) consumed in the U.S. during the same year (U.S. Department of Energy 2007c).

Even though the total biofuel consumption outside the transportation sector remains very small on a national scale, the emphasis on using renewable fuels has made the use of biofuels a relatively quick approach to increasing the fraction of renewable energy for owners and operators of boilers. Particularly where no significant modifications to fuel handling or combustion systems are needed, biofuels can be a relatively simple means to achieving a corporate or state goal for renewable energy production. Biofuels for boiler applications can include conventional biodiesel; waste fats, oils, and greases (FOGs) that have been treated but not put through the transesterification process to produce biodiesel; and glycerol generated from biodiesel production.[1]

Biodiesel use in boilers is very straightforward, as biodiesel is produced to have flow and combustion properties very similar to those of petroleum diesel, and both of which are

[1] It should be noted that most facilities do not consider the full life-cycle emissions of pollutants and CO_2 when substituting biofuels for fossil fuels.

generally similar to No. 2 distillate oil. Biodiesel is produced from oils and fats and its properties must meet American Society for Testing and Materials (ASTM) standard D 6751 before it can be accepted as an actual biodiesel. These properties are designed to ensure that any biofuel labeled for sale as biodiesel will perform properly in diesel engines without causing damage to the engine or the fuel system (American Society for Testing and Materials 2007). Boilers are typically able to burn fuels with wider ranges of fuel properties than internal combustion engines, so the ASTM standard is not as critical for boiler fuels as it is for vehicle fuels. Even so, using biodiesel in boilers does provide the operator with some assurance of fuel quality and performance, and therefore the operator may consider the additional cost of biodiesel compared to other biofuels to be a worthwhile premium.

Although it is technically possible to burn ethanol in a boiler, there is very little information about such use. It is likely that biodiesel is a preferred option because its properties are very similar to distillate fuel oil, so little adjustment to the boiler is required. Both ethanol and biodiesel are significantly more expensive than distillate fuel oil on a per unit energy basis. According to the EIA, wholesale distillate fuel oil prices were approximately $\$17.30/10^6$ Btu in late October 2007 (U.S. Department of Energy 2007b), compared to $\$23.00/10^6$ Btu for ethanol (priced on the Chicago Board of Trade spot market) (Ethanol Market 2007). These costs compare to $\$26.20/10^6$ Btu for biodiesel, as reported by DOE in July 2007 (U.S. Department of Energy 2007a).

For stationary sources other than internal combustion engines, forms of bioenergy other than biodiesel tend to be more commonly used because they tend to have lower costs. These lower costs are largely due to the fact that biodiesel requires considerable processing of the feedstock to meet the ASTM standards. The ASTM standards are largely designed to ensure that biodiesel fuels can be used in internal combustion engines. Other forms of bioenergy commonly used in stationary source combustion processes include woody biomass, such as waste wood, and waste FOGs. Liquid biofuels other than FOGs usually require considerably more processing to produce, and are therefore usually more expensive and less attractive as a biofuel option. However, biodiesel is being produced in increasing quantities, and because biodiesel fuels have been processed to meet ASTM specifications, they can have an advantage over other bioenergy sources, particularly for small boiler owners and operators who do not have the resources to evaluate fuel properties.

Review of the Literature

There have been relatively little data reported on performance of, or emissions from, the combustion of liquid biofuels in boilers. Although considerable research has been done to evaluate the use of solid biomass fuels in boilers, those results are outside the scope of this study. The vast majority of research to evaluate performance and emissions from liquid biofuel combustion has focused on the use of those fuels in internal combustion engines.

Two studies were found that measured emissions from residential and commercial space heating equipment using biodiesel blends, one published in 2001 and the second in 2003. Krishna tested emissions from, and performance of, two small boilers burning No. 2 fuel oil and four blends of biodiesel: B10, B20, B30, and a 50% biodiesel/50% kerosene blend designated BK50 (Krishna 2001).[2] The two boilers used were a residential wet-base boiler rated at 0.6 gph fuel flow (approximately 85,000 Btu/hr) and a larger commercial boiler rated at $1.8x10^6$ Btu/hr. The residential boiler was used to evaluate emissions during transient operation from a cold boiler state through steady state conditions. The initial water temperature at the cold boiler state was 55 °F, significantly lower than the usual 140-180 °F minimum water temperature maintained during normal operation. During the cold boiler start, the carbon monoxide (CO) emissions increased to approximately 250 ppm in about 30 s for the No. 2 oil, then settled down to 50-60 ppm after about 2 min. The four biodiesel blends followed the same temporal pattern, but the B30 fuel peaked at about 400 ppm CO and the BK50 at about 300 ppm CO. CO for the other two blends was about 250 ppm, similar to the No. 2 oil. At steady state, CO emissions for the biodiesel blends were consistently lower than the No. 2 oil by about 10 ppm for oxygen (O_2) concentrations between 4% and 6%. Above 6%, CO emissions began to increase for all the fuels.

Nitrogen oxide (NO_x) emissions from the residential boiler were also consistently lower for the biodiesel blends, with the differences ranging between about 2 ppm to about 20 ppm. Interestingly, the NO_x concentrations decreased with increasing O_2 concentration. For the commercial boiler (which was operated at steady state for these tests), NO_x emissions were measured at between 40 and 46 ppm for the No. 2 oil with O_2 concentrations near 8%. NO_x emissions from B100 were between 24 and 32 ppm, with NO_x emissions from the different blends falling between the two unblended fuels.

In the second study, Batey tested a series of residential furnaces burning B20 (20% soy, 80% low sulfur highway diesel fuel) and a No. 2 distillate heating oil alone (Batey 2003). He tested six different furnaces with fuel flow ratings from 0.75 to 2.5 gph of oil (roughly 100,000 to 325,000 Btu/hr), and measured O_2, NO_x, CO, and sulfur dioxide (SO_2) flue gas concentrations and smoke number. NO_x emissions using the B20 fuel were frequently lower than those measured for the No. 2 oil. Batey reported that NO_x was about 20% lower when using B20, although the data were all in graphical format and the 20% figure could not be verified. CO emissions tended to be consistently lower when using B20 compared to the No. 2 oil, and for some units, the CO was substantially lower when using B20. The optimum operations (low NO_x and CO) typically occurred at 4-8% O_2. Batey also reported that SO_2 emissions were reduced by 83% when using B20 compared to the No 2 oil. He reported that smoke number was usually lower when using B20 than the No. 2 oil when operating at the same burner setting.

Batey identified several research needs, including additional tests to evaluate a broader range of blends (different biofuel content and blends with ultralow sulfur distillate fuel), determine boiler and furnace fouling rates, evaluate cold-flow characteristics of the

[2] Biodiesel-gasoline blends are designated by the letter "B" followed by the percent biodiesel content. A blend of 20% biodiesel and 80% gasoline is thus designated "B20."

biodiesel and biodiesel blends, and conduct tests of furnaces using biodiesel mixes in real-world settings.

Adams and colleagues at the University of Georgia (UGa) Engineering Outreach Service conducted a series of tests to evaluate the combustion performance of biofuels in an industrial boiler rated at 100,000 lb/hr of 250 psig saturated steam (roughly 100 mmBtu/hr thermal energy output). The steam-atomizing burner nozzle was a late 1950s design without modification for low NO_x operation, but the boiler was modified for flue gas recirculation (FGR) to reduce NO_x emissions. Neither the boiler nor the nozzle were modified for the biofuel tests. The UGa tests consisted of 173 separate test runs, burning natural gas, No. 2 fuel oil, choice white grease, tallow, yellow grease, chicken fat, and four blends, each with 67% No 2 fuel oil and 33% of the fats or greases.

Emissions measured during the tests of the unblended fuels showed PM to be lower for the yellow grease and tallow, but higher for the choice white grease and chicken fat compared to No. 2 fuel oil, with the majority of the difference being in the filterable fraction of the PM. NO_x emissions followed the same pattern, with yellow grease and tallow NO_x emissions being lower than from No. 2 fuel oil, and NO_x from choice white grease and chicken fat being higher. FGR reduced NO_x emissions for all fuels tested. In general, NO_x emission concentrations for the fuels ranged from 75-120 ppm, with most of the measurements falling in the 90-100 ppm range. SO_2 emissions were below 5 ppm for all the fats and greases, increasing to 87 ppm for the No. 2 fuel oil and 127 ppm for the No. 2 fuel oil with FGR. SO_2 emissions for the blends ranged from 20 ppm to 87 ppm without FGR, and up to 109 ppm with FGR for the No 2 fuel oil/white grease blend. CO emissions were lower for all the fats and greases compared to the No. 2 fuel oil, with the maximum being 14 ppm for the white grease. CO emissions increased slightly when operating with FGR, to a maximum of 39 ppm for the No. 2 fuel oil/white grease blend.

More recently, Duke Energy conducted a series of tests to evaluate the performance of biodiesel fuel in a large (90 MWe) combustion turbine. The tests were conducted at the Duke Energy Mill Creek Station in mid-2007, in collaboration with the Electric Power Research Institute (EPRI), and complete emissions and performance data have not yet been published.

These studies have shown the potential for biofuels to be used in ways that can be beneficial from the perspective of direct stack emissions of pollutants. However, it should be noted that the range of fuels and combustion equipment tested is very limited, and the studies were conducted under well-controlled conditions. Further work is needed to fully understand the potential impacts of biofuel combustion in stationary sources, both in research studies and in longer-term evaluations. The current study is designed to evaluate emissions from biofuel combustion in a different type of boiler.

Health and Safety Issues

Safety issues for biodiesel are generally the same as for petroleum-based diesel fuels, even though the health and safety indicators for biodiesel are consistently less hazardous

than for petroleum diesel fuels (Tyson 2001). Even so, biodiesel is a fuel and needs to be handled with care.

In general, there have been no reported health issues associated with vegetable-based biodiesel fuels. Oils derived from soybeans or other crops are typically used in foods, and although the oils may not be food-grade, they are the same feedstocks that are used for food-grade products. However, there are health concerns associated with animal-based biofuels. Waste animal products can contain microbial, other organic, or inorganic contaminants that may pose health risks to the general public if they are present in the fuel. Greene et al. reviewed the literature associated with potential contaminants in animal-based biofuel feedstocks to evaluate the potential for human health risks associated with each contaminant. They concluded that there was "little or no known risk to human and animal health and to the environment relative to inherent microbial, organic or inorganic agents in animal fats destined for biodiesel production"(Greene, Dawson et al. 2007). Although they noted that it is impossible to establish a zero risk assessment for any fat used in biodiesel production, the authors did find that the literature indicated that the production processes and the ultimate biodiesel combustion significantly reduced any risk associated with microbial contaminants. They included evaluations of studies of bacteria, viruses, fungi, yeast, parasites, and microbial toxins in animal material and the potential of these microbial contaminants to survive through the production and use processes. Greene et al. also concluded that metals and metalloids would not lead to significant safety issues because of the low levels of these elements in animal fats (Greene, Dawson et al. 2007). It should be noted, however, that long term use of animal-based biofuels, particularly in one location, could result in measurable increases in any metals consistently present in waste animal fats, and in instances where such feedstocks are being contemplated for long term use, the trace element content of the feedstocks should be carefully monitored.

One issue that may be of particular health concern associated with using waste animal fat as the feedstock for biodiesel is the possible contamination with proteinaceous infectious particles, or prions. Prions are the cause of transmissible spongiform encephalopathy (TSE), forms of which include bovine spongiform encephalopathy (more familiarly known as mad cow disease) and Creutzfeldt-Jakob disease in humans, and are only present (although rarely) in brain and nerve tissue of certain animals. The question of whether prions can contaminate biodiesel has been studied to determine whether this is in fact a problem. Seidel et al. concluded that each biodiesel processing step resulted in a significant reduction in prion viability, leading to the end result that biodiesel, "even from material with a high concentration of pathogenic prions, can be considered as safe"(Seidel, Alm et al. 2005). A report prepared for the International Energy Agency's (IEA's) Committee on Advanced Motor Fuels echoed the Seidel et al. report by concluding that, "Biodiesel produced from animals infected with TSE poses a negligible risk to animal and public health" (Baribeau, Bradley et al. 2006). Recommendations of the Baribeau et al. report included approaches to minimize the potential for prion-contaminated material to enter the feedstock stream and research needs associated with reducing the uncertainties in their conclusions.

In summary, the literature does not identify any significant health risks associated with the production and use of animal-based biodiesel fuels.

Emissions Test Study

Because of the increased interest in and use of biofuels in stationary combustion systems, there has been a similar increase in questions regarding emissions in a regulatory context. Equipment owners and operators and regulatory agencies have expressed interest in information that would provide guidance regarding how emissions would change if petroleum fuels were replaced with biofuels in an effort to reduce net greenhouse gas emissions. This study was designed to answer some of these questions for a specific combination of fuels and combustion equipment.

Quality Assurance

The project was conducted under NRMRL's Quality Management Plan, as a Level III project. A Level III Quality Assurance (QA) Project Plan (QAPP) was developed and approved prior to beginning measurements. The QAPP describes the tests to be conducted, the measurements to be used, and the applicability of the measurements; specifies the QA objectives for the measurements (such as completeness, accuracy, and precision); defines the requirements for maintaining a chain of custody of samples; and provides for the means to document discrepancies and deviations from the plan.

Approach and Equipment

The tests were conducted on a firetube package boiler located in EPA's research facilities in Research Triangle Park, NC. The boiler is a 2.94×10^6 Btu/hr (860 kW), 3-pass wetback Scotch Marine package boiler manufactured by Superior Boiler Works, Inc. (see Figure 2). The boiler can fire natural gas or a variety of fuel oils from distillate (No. 2) fuel oil to residual (No. 6) fuel oil. The boiler's burner is a low pressure, air atomizing nozzle designed to generate a fuel spray to ensure proper air-fuel mixing. The unit can be set to fire automatically or manually at any desired rate between the minimum and the maximum firing rates. An electric heater is used to maintain proper fuel oil temperature and therefore, viscosity. Both fuel and atomizing air flows can be varied to achieve proper oil atomization. The boiler has 355 ft^2 (33 m^2) of heating surface and generates up to 2,400 lb/hr (1,090 kg/hr) of saturated steam at pressures up to 15 psig (103 kPa). Fuel flow is measured with a liquid volume totalizing meter and stoichiometric ratios are determined by measuring stack O_2 and carbon dioxide (CO_2) concentrations.

The boiler is fully instrumented with continuous emission monitors (CEMs) for measuring concentrations of CO_2, CO, NO_x, O_2, and SO_2. A computerized data acquisition system (DAS) records CEM measurements as well as exit steam and flue gas temperatures. The flue gas from the boiler passes through a manifold to an air pollution control system (APCS) consisting of a natural-gas-fired secondary combustion chamber, a fabric filter, and an acid gas scrubber to ensure proper removal of pollutants emitted by the research facility's combustion units. Particle size distributions (PSDs) are measured using a TSI Inc. model 3080/3022A scanning mobility particle sizer (SMPS) and a TSI

Figure 2. Photograph of the burner end of the firetube package boiler used in the biofuel tests.

Inc. aerodynamic particle sizer (APS). All flue gas concentration and size distribution measurements are taken prior to the APCS.

The stack of the boiler has several ports available for collecting gas and particle samples, as shown in Figure 3. The vertical section of the 8 in (20 cm) diameter steel stack is sufficient in length and free of flow disturbances so that PM can be sampled at an axial location that meets EPA Method 1A sampling requirements. Several sampling ports are located along the horizontal section of the duct approximately 9 ft (2.7 m) above the facility catwalk. The horizontal section of the duct (8-in steel pipe) is sufficient in length and free of flow disturbances so that particulate matter can be sampled at an axial location that meets EPA Method 1A particulate matter sampling requirements.

For the current tests, the boiler was operated at the lowest stack O_2 concentration that would ensure acceptable NO_x and CO concentrations over a full day of operation. "Acceptable" in this case was not determined a priori, but was determined by reducing O_2

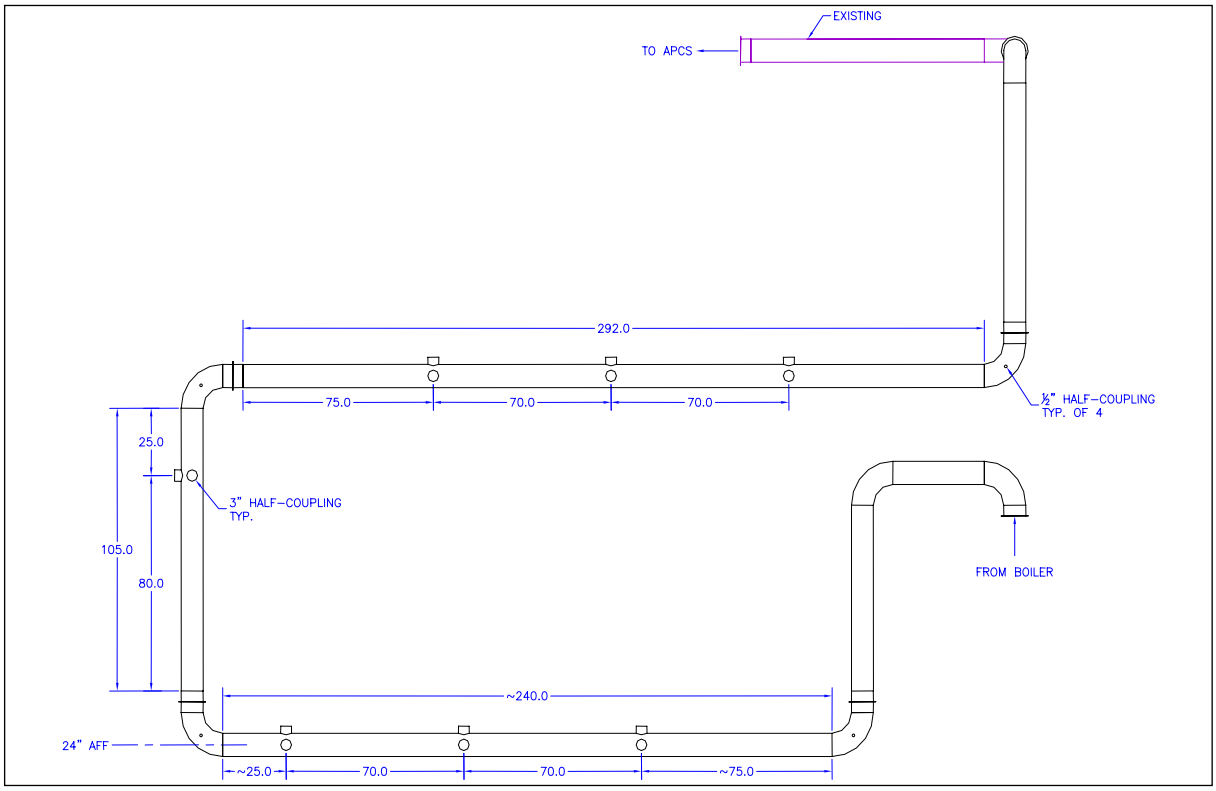

Figure 3. Exhaust gas sampling locations.

until CO began to increase and then increasing the O_2 level by about 0.5%. It was anticipated that the stack O_2 level would be no lower than 3% for the tests. Measured stack O_2 levels will be discussed in more detail below. The boiler can use flue gas recirculation to reduce NO_x emissions, but the recirculation was set to zero for these tests.

The boiler load was set to maintain a steady flame and boiler water level. The boiler is designed to automatically turn the burner off when steam pressure increases above a set point (12 psig in this case), and then turn the burner on again as the steam pressure decreases below a minimum (9 psig). This cycling typically occurs for lower load conditions, but can also occur when the steam load varies. In situations where the boiler load and pressure are too high, the steam flow can exceed the capacity of the condensate sump tank, resulting in a loss of boiler water and a drop in the boiler water level. This requires additional water to be injected into the boiler at a lower temperature than the recirculating condensate, which results in transient boiler conditions. After a series of initial scoping runs to determine the range between these two situations (burner cycling and condensate makeup), the target boiler load for the tests was set at approximately $2x10^6$ Btu/hr, roughly 2/3 of the maximum boiler capacity.

Prior to starting the tests, the boiler tubes were physically cleaned to remove residues that had accumulated during a previous series of tests to evaluate the potential formation of polychlorinated dibenzo-d-dioxins (PCDDs). The previous study involved co-firing No. 2 fuel oil and a mixture of 1,2 dichlorobenzene and copper naphthenate. The boiler was

operated at conditions that were designed to form significant levels of soot and create a high-soot, high-chlorine residue along the boiler tubes to simulate long-term operation as a waste incineration unit. Residues were removed from each end of the boiler, where the combustion gases exit one series of boiler tubes, change direction, and enter the subsequent series of tubes. Residues were also removed from the boiler tubes. No analyses were conducted on the removed residues before they were disposed of as hazardous waste.

For the current tests, three fuels were chosen for comparison – a non-road diesel fuel (similar to a commercial No. 2 petroleum fuel oil, hereafter referred to as No. 2 fuel oil), a biodiesel produced from soy oil, and a biodiesel produced from animal fats. The fuels were delivered in drums to EPA's test facilities, with several drums each of the three fuels. To account for any possible variability in composition, a sample was collected from each drum and combined with other samples of the same fuel from the other drums prior to analysis. Table 1 provides the ultimate analyses and physical properties for the three fuels. Note that the oxygen content, the flashpoint, and the kinematic viscosity of the biofuels is considerably higher, and the fuel higher heating value is lower, than that of the No. 2 fuel oil.

Table 1. Ultimate analyses and thermochemical properties of the three fuels tested.

	No. 2 Fuel Oil	Soy Biodiesel	Animal Biodiesel
Karl Fischer Water	<0.03 %	0.087 %	0.076 %
Carbon	84.15 %	76.30 %	74.82 %
Hydrogen	12.67 %	11.95 %	11.76 %
Nitrogen	<0.5 %	<0.5 %	<0.5 %
Sulfur	<0.05 %	<0.05 %	<0.05 %
Chlorine	<20 ppm	<20 ppm	<20 ppm
Ash	0.25 %	0.12 %	<0.10 %
Oxygen (by difference)	2.93 %	11.63 %	13.42 %
Fuel Higher Heating Value (Btu/lb)	19,318	16,972	17,084
Flashpoint-Pensky Martens	64 °C	> 160 °C	> 160 °C
Pour Point	- 16 °C	4 °C	8 °C
Viscosity-Kinematic at 37.8 °C	2.845 cSt	4.475 cSt	4.609 cSt
Viscosity-Kinematic at 40 °C	2.726 cSt	4.278 cSt	4.399 cSt
Specific Gravity	0.8493	0.8776	0.8745

The content of trace elements was also determined for the three fuels, as shown in Table 2. The only trace element measured above detection level was iron in the No. 2 fuel oil.

Extensive flue gas sampling was conducted to measure CO, CO_2, NO_x, SO_2, organic compound, and PM emissions for each of the three fuels. Three separate test runs were made for each fuel, with each run lasting approximately three hours. Manual samples were also taken for each test run to determine concentrations of volatile organic compounds (VOCs), aldehydes, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs). Shorter tests were planned to evaluate possible changes associated with blends of biofuels. During the tests of the blends, only CEM measurements were planned, with no extractive flue gas samples.

Table 2. Trace element content of the three fuels tested in ppm.

	No. 2 Fuel Oil	Soy Biodiesel	Animal Biodiesel
Calcium	<23	<23	<24
Potassium	<51	<52	<54
Zinc	<9	<9	<9
Iron	44	<9	<9
Silicon	<196	<183	<178
Nickel	<9	<9	<9
Magnesium	<9	<9	<9
Copper	<9	<9	<9
Chromium	<9	<9	<9
Manganese	<9	<9	<9
Cerium	<9	<9	<9
Platinum	<9	<9	<9
Lead	<5	<5	<5
Phosphorus	<9	<9	<9

Table 3 shows a summary of the tests planned for each of the fuels and blends.

Table 3. Matrix of planned tests.

Test Number	Fuel	Constituent Composition (volume %)			Test Duration (hours at steady state)	CEM[(1)]	Manual Methods[(2)]
		#2 Fuel Oil	Vegetable-based Biodiesel	Animal-based Biodiesel			
1	#2 Fuel Oil	100	0	0	10	Yes	Yes
2	Vegetable Biodiesel	0	100	0	10	Yes	Yes
3	Animal Biodiesel	0	0	100	10	Yes	Yes
4	B20[c]	80	20	0	4	Yes	No
5	B40	60	40	0	4	Yes	No
6	B60	40	60	0	4	Yes	No
7	B80	20	80	0	4	Yes	No

Notes:
1. CEM measurement for O_2, CO_2, CO, NOx , SO_2, and total hydrocarbons (THC)
2. Manual sampling method for particulate matter, particle size distribution, VOCs, aldehydes, PAHs, PCBs

Results

The tests of the three unblended biofuels were completed without significant problems, although one sampling train was damaged during the soy biodiesel test and an additional test run was required to obtain the three semivolatile samples needed (see QA Discrepancies below). Prior to the scoping runs, the plan was to operate the unit at rated load (2.9×10^6 Btu/hr); however, the boiler was only able to maintain 1.89×10^6 to 1.94×10^6 Btu/hr fuel input. It is unclear why the fuel feed rate could not be increased, but the unit's operation was stable at the lower load and there were no indications of unusual emissions based on the CEM data, so the tests proceeded at the reduced load. Steam temperatures were steady at between 225 and 229 °F. Three tests were conducted for

each of the three unblended fuels, and the required number of samples was collected for subsequent analysis.

The tests of the blends were not completed because of residues that built up in the fuel system, apparently from the fuel. Additional information on this problem is provided in the QA Discrepancies section below.

Continuous Emission Monitor Measurements

Average flue gas concentrations from combustion of the three fuels tested are shown in Table 4. The average values and standard deviations were calculated using all CEM data collected during steady state operation at each test condition. Figure 4, Figure 5, and Figure 6 show the average concentrations of O_2 and CO_2, CO and HC, and NO_x and SO_2, respectively. The O_2 levels for the two biodiesels were slightly lower than for the No. 2 fuel oil, even though the CO levels changed very slightly. The boiler was able to be operated at very low O_2 levels with the biodiesels with no indication of CO increases or visible sooting. As expected, the CO_2 concentrations were approximately the same for all three fuels. NO_x concentrations were nearly identical for the three fuels, at 110 ppm (corrected to 3% O_2). Concentrations of SO_2 were found to be quite low, with the No. 2 fuel oil being the highest at nearly 17 ppm and the two biodiesels each being below 5 ppm. Hydrocarbon concentrations were at or below the instrument detection level, resulting in negative readings for the concentrations.

Table 4. Average flue gas concentrations of combustion gases for the tested fuels as measured by CEM (dry conditions). All values except O_2 are corrected to 3% O_2. Values in parentheses are standard deviations for the CEM data.

	O_2 (%)	CO_2 (%)	CO (ppm)	NO_x (ppm)	SO_2 (ppm)	THC (ppm)
No. 2 (Distillate) Fuel Oil	1.9 (0.13)	13.4 (0.10)	2.2 (0.14)	110. (2.4)	16.9 (1.6)	0.70 (2.1)
Soy Biodiesel	1.4 (0.40)	13.6 (0.14)	2.7 (1.0)	110. (4.0)	4.4 (0.48)	-0.40 (7.5)
Animal Biodiesel	1.7 (0.21)	13.5 (0.35)	3.1 (0.35)	110. (1.8)	3.1 (0.37)	-2.9 (26.)

With the exception of O_2, all the results are corrected to 3% O_2. Emission rates are presented in Table 5 and emission factors are given in Table 6.

Table 5. Gaseous pollutant emission rates, lb/hr.

	O_2	CO_2	CO	NO_x	NO	SO_2	HC
No. 2 Distillate (Standard Deviation)	31.9 (2.24)	317 (1.63)	3.28E-03 (2.48E-04)	1.88E-01 (4.13E-03)	1.82E-01 (3.75E-03)	5.82E-02 (2.68E-03)	6.03E-04 (3.68E-03)
Soy Biodiesel (Standard Deviation)	28.3 (3.98)	268 (2.76)	5.39E-03 (1.99E-03)	2.10E-01 (7.87E-03)	2.08E-01 (1.85E-02)	8.73E-03 (9.48E-04)	-7.94E-04 (1.47E-02)
Animal Biodiesel (Standard Deviation)	34.2 (4.17)	271 (6.93)	6.11E-03 (6.96E-04)	2.21E-01 (3.53E-03)	2.19E-01 (3.89E-03)	6.13E-03 (7.35E-04)	-5.77E-03 (5.21E-02)

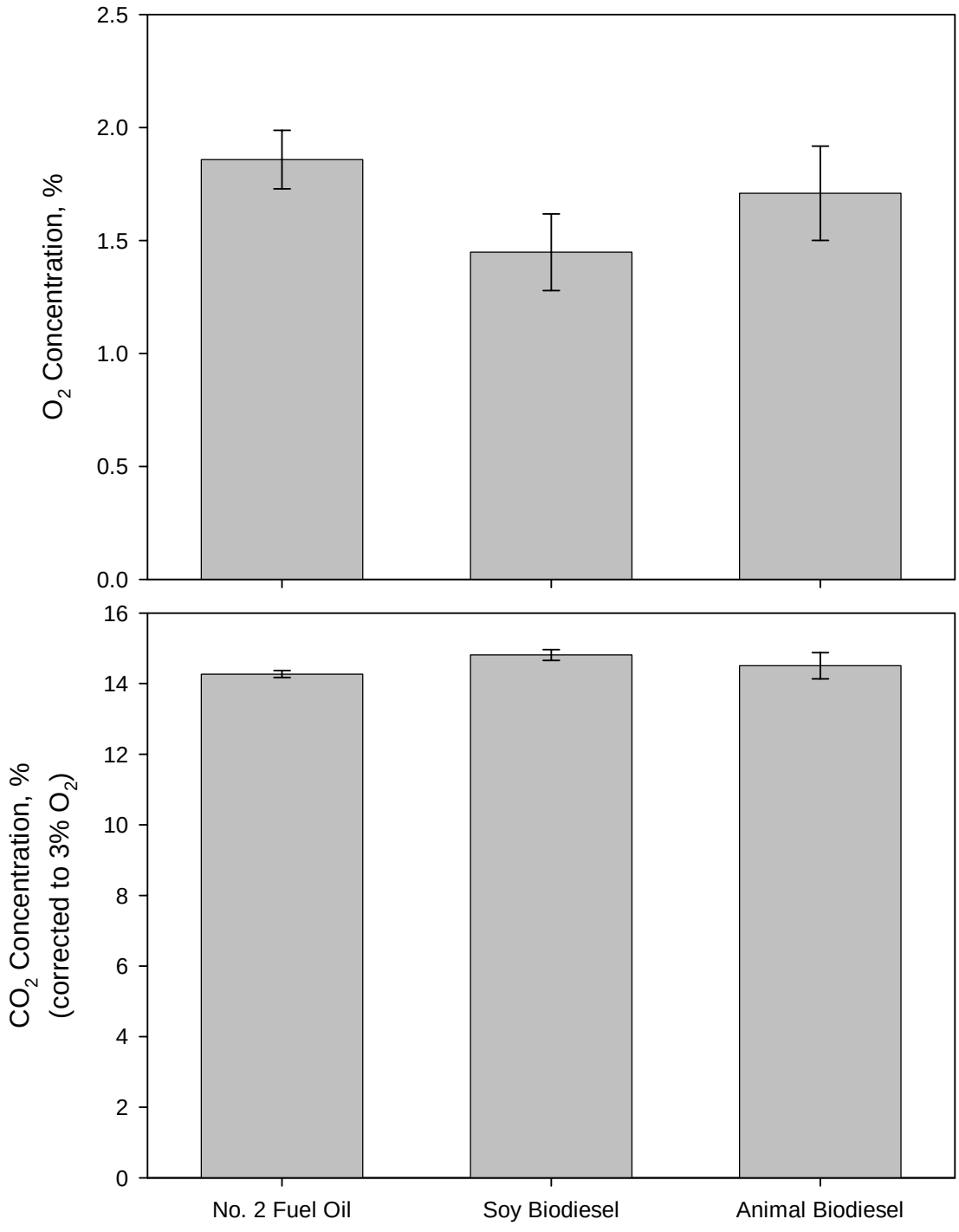

Figure 4. Concentrations of O_2 and CO_2 for the three tested fuels in ppm.

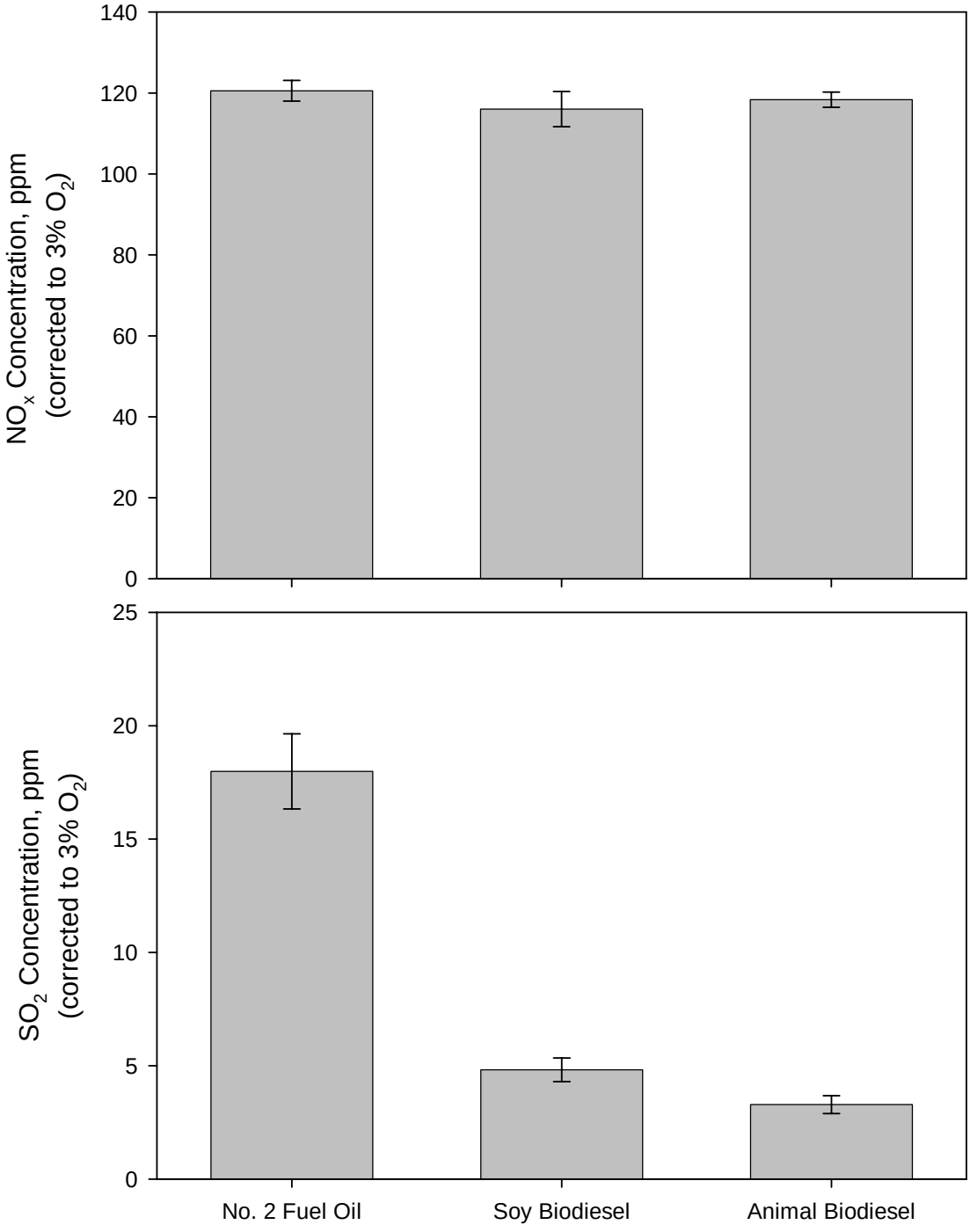

Figure 5. Concentrations of NO_x and SO_2 for the three fuels tested.

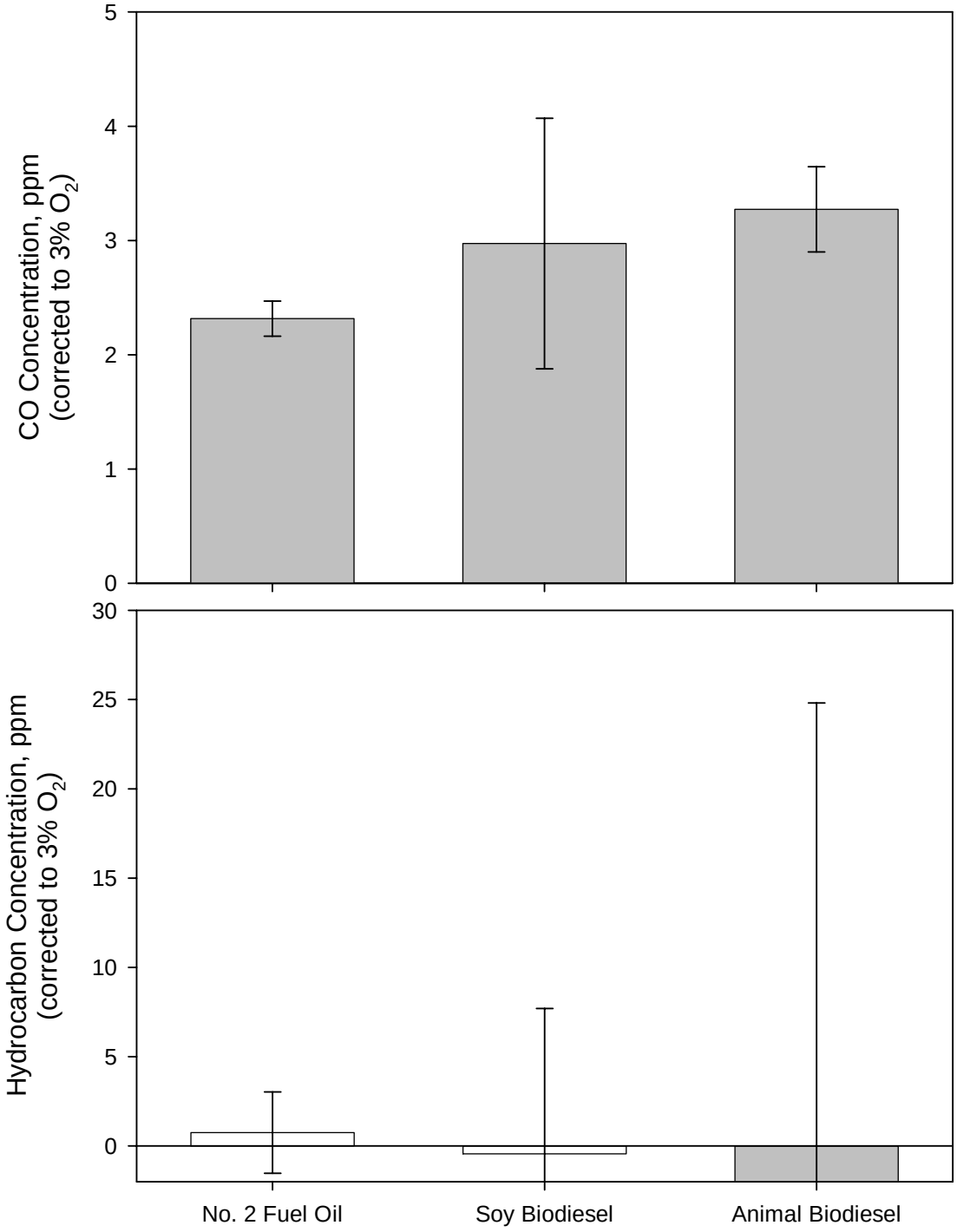

Figure 6. Concentrations of CO and THC for the three fuels tested.

Table 6. Gaseous pollutant emission factors, lb/10^{12} Btu.

	O_2	CO_2	CO	NO_x	NO	SO_2	HC
No. 2 Distillate (Standard Deviation)	16.9 (1.18)	168 (0.86)	1.73E-03 (1.31E-04)	9.92E-02 (2.19E-03)	9.65E-02 (1.98E-03)	3.07E-02 (1.42E-03)	3.19E-04 (1.94E-03)
Soy Biodiesel (Standard Deviation)	15.0 (2.11)	142 (1.46)	2.85E-03 (1.05E-03)	1.11E-01 (4.16E-03)	1.10E-01 (9.77E-03)	4.62E-03 (5.01E-04)	-4.20E-04 (7.80E-03)
Animal Biodiesel (Standard Deviation)	17.6 (2.15)	139 (3.56)	3.14E-03 (3.58E-04)	1.14E-01 (1.82E-03)	1.13E-01 (2.00E-03)	3.15E-03 (3.78E-04)	-2.97E-03 (2.68E-02)

Particulate Matter

Particulate matter emissions were measured using Method 202, which provides information on filterable and condensable PM, with the condensable PM further distinguished between organic and inorganic fractions (U.S. Environmental Protection Agency 2005). Results of the tests are shown in Figure 7.

Total PM was significantly higher for the No. 2 fuel oil than for the two biodiesel fuels, with the largest difference in the results seen in the condensable inorganic fraction as seen in Table 7. This is not surprising, given that most of the condensable inorganic PM is likely to be composed of sulfur compounds. Although the fuel sulfur contents were all below the measurement detection level of 0.05% (500 ppm), the emissions of SO_2 were roughly an order of magnitude higher for the No. 2 fuel oil than for either of the two biodiesels. This indicates that the sulfur content of the No. 2 fuel oil was also significantly higher, and the most likely source of the condensable inorganic PM. For the No. 2 fuel oil, the condensable inorganic PM was found to be 8-16 mg/dscm over the three test runs, while for the two biodiesels, the condensable inorganic PM was between 0.3 and 2.0 mg/dscm.

Condensible organic PM was the lowest component of the total PM. For the No. 2 fuel oil, the condensable organic PM was between 0.12 and 0.46 mg/dscm. For the two

Table 7. Measured particulate matter concentrations, mass emission rates, and emission factors.

	Mass Concentration, mg/dscm			
	Filterable PM	Condensable Organic PM	Condensable Inorganic PM	Total PM
No. 2 Fuel Oil	5.43 (0.43)	0.27 (0.17)	12.3 (3.82)	18.0 (3.88)
Soy Biodiesel	2.40 (1.61)	0.11 (0.00)	1.08 (0.85)	3.48 (2.27)
Animal Biodiesel	2.52 (1.91)	0.15 (0.07)	1.37 (0.19)	3.89 (1.73)
	Emission Rate, lb/hr			
No. 2 Fuel Oil	6.90E-3 (8.18E-4)	3.36E-4 (2.03E-4)	1.56E-2 (4.65E-3)	2.28E-2 (4.64E-3)
Soy Biodiesel	3.20E-3 (2.13E-3)	1.52E-04 (2.52E-6)	1.45E-3 (1.13E-3)	4.82E-3 (3.01E-3)
Animal Biodiesel	3.52E-3 (2.66E-3)	2.03E-4 (8.89E-5)	1.93E-3 (3.00E-4)	5.65E-3 (2.41E-3)
	Emission Factors, lb/10^6 Btu			
No. 2 Fuel Oil	3.65E-3	1.78E-4	8.23E-3	1.21E-2
Soy Biodiesel	1.70E-3	8.02E-5	7.69E-4	2.55E-3
Animal Biodiesel	1.81E-3	1.05E-4	9.91E-4	2.91E-3

biodiesels, the condensable organic PM was below the method detection limit of 0.11-0.22 mg/dscm for all runs.

The filterable PM results were slightly higher for the No. 2 fuel oil than for the two biodiesels. For the No. 2 fuel oil, the filterable PM data were consistent across all three runs, with an average of 5.4 mg/dscm. The two biodiesels had filterable PM similar to one another, with each biodiesel having one run at a significantly lower level than the other two. Even if the low runs are ignored, the biodiesel filterable PM results were still lower than that for the No. 2 fuel oil.

The PSDs measured during the tests indicate that the majority of particle mass as indicated by volume are larger than 1 μm in aerodynamic diameter. Figure 8 shows the PSDs measured for the three fuels tested, and shows that the majority of particle volume is in the range of 0.5-10 μm. These measurements are of electrical mobility diameter and not strictly aerodynamic diameter, although the two are related. The mass measurements using Method 202 and the mass values estimated from the PSDs are consistent in terms of magnitude for all three fuels, as shown in Figure 7.

The diamond symbols show the estimated mass based on the integrated volume measured by the APS, assuming a 1 g/cc mass density for the particles. The integrated volume and the Method 202 results show excellent agreement. There is some discrepancy, however, between the size distribution results and the Method 202 fractions, particularly for the No. 2 fuel oil results. The size distributions (see Figure 8) show that nearly all the PM volume (and therefore mass) is larger than about 0.5 μm in aerodynamic diameter for all three fuels. For the soy and animal biodiesel fuels, the integrated mass is about the same as the filterable mass as measured by Method 202. This makes physical sense, as the filterable particles are likely to be in these larger size ranges. On the other hand, the condensable mass, whether organic or inorganic, is more likely to be much smaller – near 0.1 μm or less in aerodynamic diameter. The APS data for the No. 2 fuel oil show the majority of the volume (mass) as being well above what would be expected for condensable particles. It is unclear why the APS and Method 202 data match as well as they do for the No. 2 fuel oil.

Aldehydes

Aldehyde concentrations were measured for each of the test conditions, with three samples collected from the exhaust from each of the three fuels. The highest concentration levels were for formaldehyde, acetaldehyde, and acetone, each of which had concentrations of over 1 ppm for one of the three fuels. Formaldehyde and acetaldehyde concentrations were measured at 3.4 and 2.5 ppm, respectively, from the soy biodiesel, and acetone was measured at 1.8 ppm from the No. 2 fuel oil. Figure 9 shows the average measured concentrations of the 12 aldehydes. Given the relatively high variability in the measurements, the significance of the differences in emissions for the three fuels is questionable. Even though the formaldehyde and acetaldehyde from the soy biodiesel appear to be significantly higher than the respective concentrations

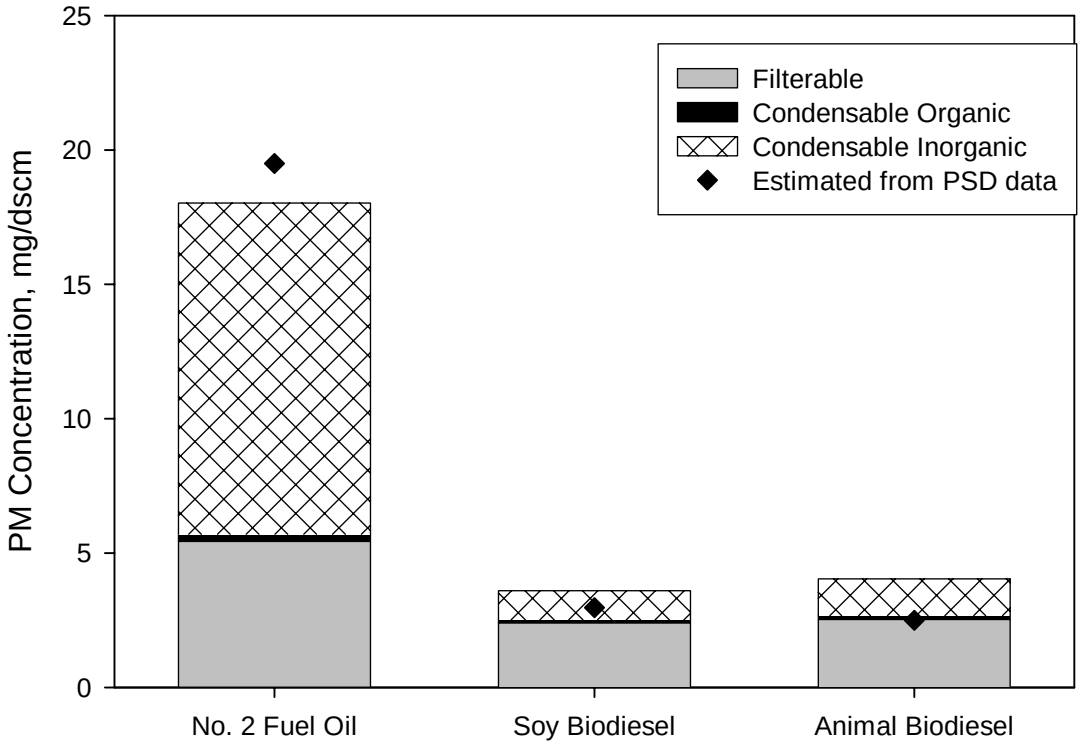

Figure 7. PM concentrations from the three fuels tested.

measured for the other two fuels, the relative standard deviation for these two measurements were over 100%, making it impossible to state definitively that the increases would be consistent in the absence of a larger number of measurements.

Table 8 presents the aldehyde concentrations, emission rates are given in Table 9, and Table 10 gives the aldehyde emission factors for the three fuels. Those values shown as being less than the stated value are based on using zero for those samples in which the compound was not detected at a level of about 0.6 ppm.

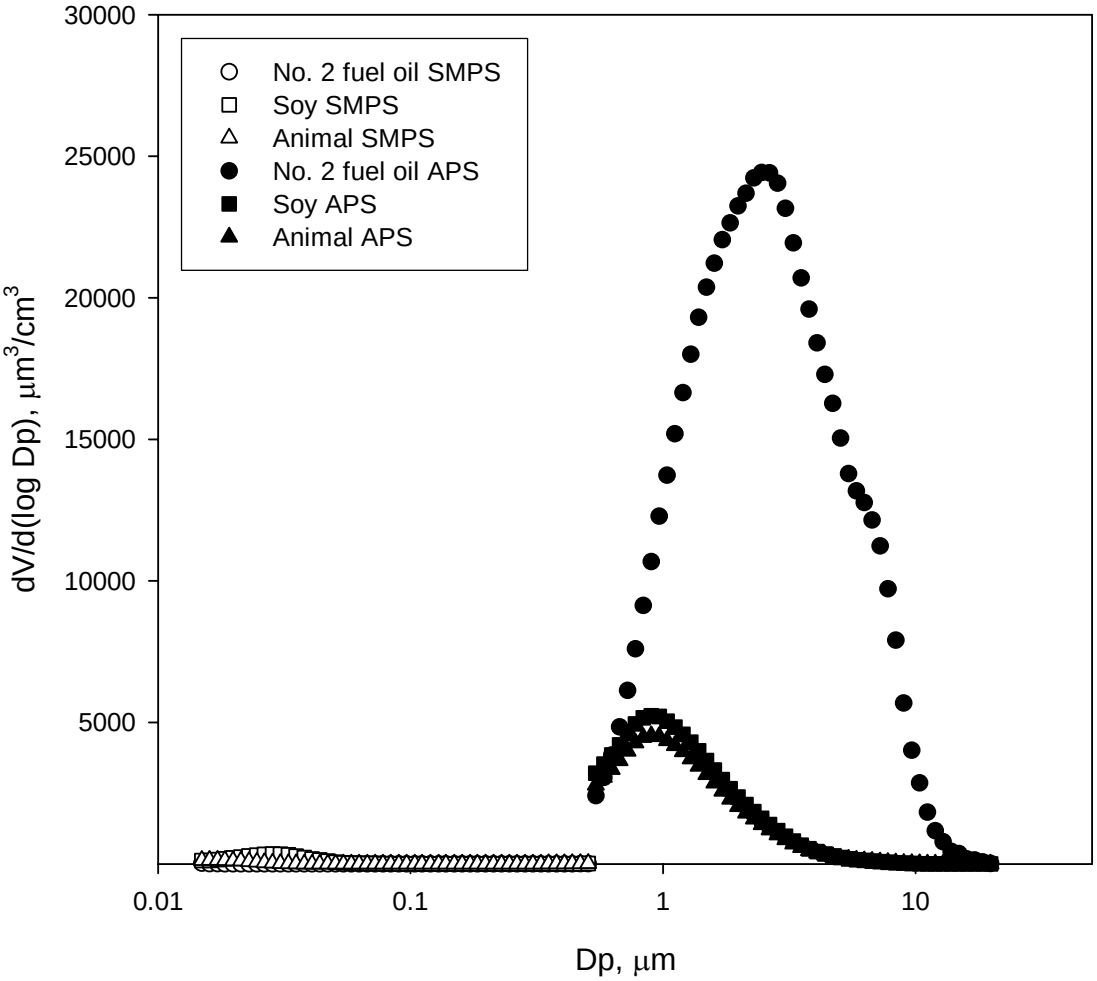

Figure 8. Particle size distributions for the three fuels tested.

Table 8. Measured concentrations of aldehydes from the three fuels, in ppm.

	Mass Concentration, ppm (standard deviation in parentheses)		
	No. 2 Fuel Oil	Soy Biodiesel	Animal Biodiesel
Formaldehyde	$8.34x10^{-2}$ ($1.57x10^{-2}$)	$3.40x10^{0}$ ($5.80x10^{0}$)	$3.26x10^{-1}$ ($2.68x10^{-2}$)
Acetaldehyde	$3.02x10^{-2}$ ($4.04x10^{-3}$)	$2.53x10^{0}$ ($4.35x10^{0}$)	$3.29x10^{-2}$ ($2.24x10^{-2}$)
Acetone	$1.77x10^{0}$ ($2.87x10^{0}$)	$3.97x10^{-1}$ ($1.62x10^{-1}$)	$2.47x10^{-1}$ ($9.23x10^{-2}$)
Propionaldehyde	< $2.87x10^{-3}$ ($4.98x10^{-3}$)	ND[(a)]	ND
Crotonaldehyde	< 4.31x10-03 (3.77x10-03)	ND	< $1.95x10^{-3}$ ($3.37x10^{-3}$)
Butylaldehyde	< $2.02x10^{-3}$ ($3.49x10^{-3}$)	ND	ND
Benzaldehyde	< 2.48 $x10^{-3}$ ($4.30x10^{-3}$)	ND	ND
Iso-Veraldehyde	< $1.10x10^{-2}$ ($1.13x10^{-2}$)	< $1.05x10^{-2}$ ($9.95x10^{-3}$)	< $2.20x10^{-3}$ ($3.81x10^{-3}$)
Veraldehyde	< $2.39x10^{-3}$ ($4.13x10^{-3}$)	ND	ND
Tolualdehyde	< $7.33x10^{-3}$ ($1.27x10^{-2}$)	ND	ND
Hexanal	< $2.31x10^{-3}$ ($4.00x10^{-3}$)	ND	ND
2,5-Dimethy-benzaldehyde	< $1.70x10^{-3}$ ($2.94x10^{-3}$)	ND	ND

(a) Not detected

Table 9. Emission rates of aldehydes from the three fuels, lb/hr.

	Emission Rates, lb/hr (standard deviation in parentheses)		
	No. 2 Fuel Oil	Soy Biodiesel	Animal Biodiesel
Formaldehyde	1.32×10^{-4} (2.11×10^{-5})	5.83×10^{-3} (9.93×10^{-3})	5.73×10^{-4} (5.55×10^{-5})
Acetaldehyde	7.01×10^{-5} (7.13×10^{-6})	6.40×10^{-3} (1.10×10^{-2})	8.44×10^{-5} (5.69×10^{-5})
Acetone	5.63×10^{-3} (9.15×10^{-3})	1.30×10^{-3} (5.40×10^{-3})	8.42×10^{-4} (3.26×10^{-5})
Propionaldehyde	< 9.13×10^{-6} (1.58×10^{-5})	ND[(a)]	ND
Crotonaldehyde	< 1.63×10^{-5} (1.43×10^{-5})	ND	< 7.90×10^{-6} (1.37×10^{-5})
Butylaldehyde	< 7.97x10-6 (1.38×10^{-5})	ND	ND
Benzaldehyde	< 1.44×10^{-5} (2.50×10^{-5})	ND	ND
Iso-Veraldehyde	< 5.12×10^{-5} (5.31×10^{-5})	< 5.13×10^{-5} (4.91×10^{-5})	< 1.10×10^{-5} (1.90×10^{-5})
Veraldehyde	< 1.13×10^{-5} (1.95×10^{-5})	ND	ND
Tolualdehyde	< 4.83×10^{-5} (8.37×10^{-5})	ND	ND
Hexanal	< 1.27×10^{-5} (2.19×10^{-5})	ND	ND
2,5-Dimethy-benzaldehyde	< 1.79×10^{-5} (3.09×10^{-5})	ND	ND

(a) Not detected

Table 10. Emission factors for aldehydes from the three fuels, lb/10^6 Btu.

	Emission Factors, lb/10^6 Btu (standard deviation in parentheses)		
	No. 2 Fuel Oil	Soy Biodiesel	Animal Biodiesel
Formaldehyde	6.96×10^{-5} (1.12×10^{-5})	3.08×10^{-3} (5.25×10^{-3})	2.95×10^{-4} (2.86×10^{-5})
Acetaldehyde	3.70×10^{-5} (3.77×10^{-5})	3.38×10^{-3} (5.82×10^{-3})	4.34×10^{-5} (2.93×10^{-5})
Acetone	2.98×10^{-3} (4.84×10^{-3})	6.88×10^{-4} (2.86×10^{-4})	4.33×10^{-4} (1.68×10^{-4})
Propionaldehyde	< 4.83×10^{-6} (8.36×10^{-6})	ND[(a)]	ND
Crotonaldehyde	< 8.60×10^{-6} (7.56×10^{-6})	ND	< 4.06×10^{-6} (7.04×10^{-6})
Butylaldehyde	< 4.21×10^{-6} (7.30×10^{-6})	ND	ND
Benzaldehyde	< 7.63×10^{-6} (1.32×10^{-5})	ND	ND
Iso-Veraldehyde	< 2.71×10^{-5} (2.81×10^{-5})	< 2.71×10^{-5} (2.60×10^{-5})	< 5.64×10^{-6} (9.77×10^{-6})
Veraldehyde	< 5.96×10^{-6} (1.03×10^{-5})	ND	ND
Tolualdehyde	< 2.56×10^{-5} (4.43×10^{-5})	ND	ND
Hexanal	< 6.70×10^{-6} (1.16×10^{-5})	ND	ND
2,5-Dimethy-benzaldehyde	< 9.45×10^{-6} (1.64×10^{-5})	ND	ND

(a) Not detected

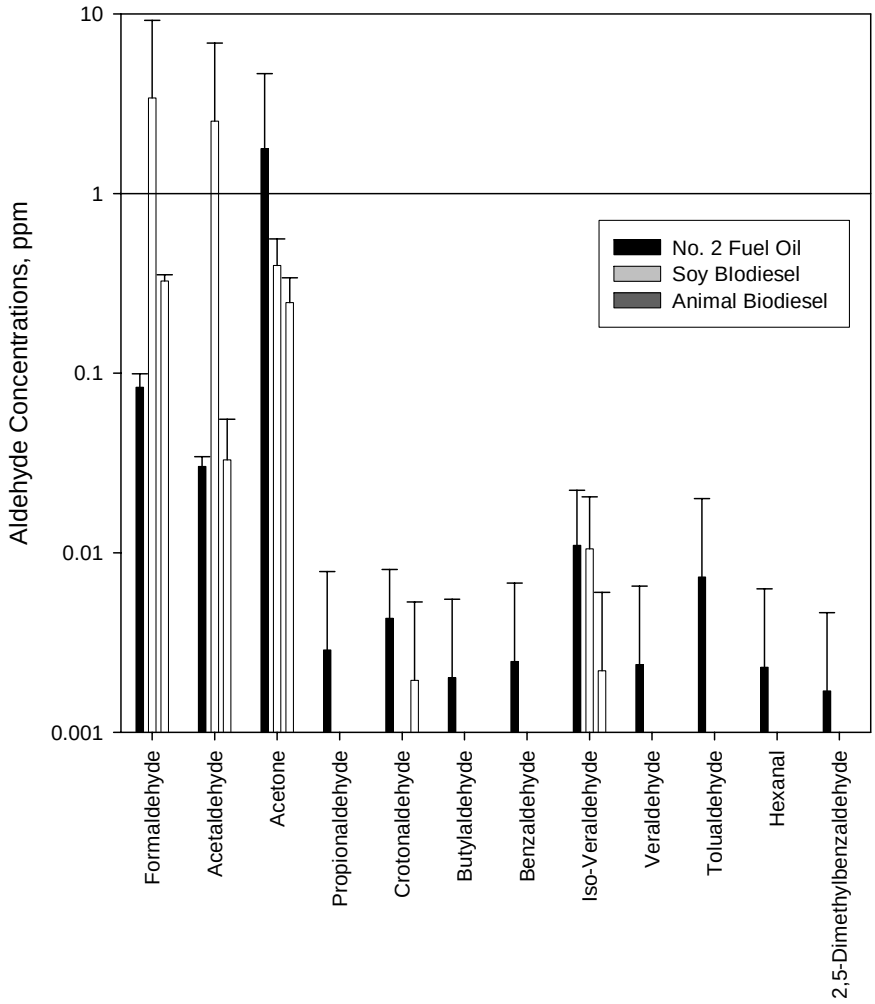

Figure 9. Concentrations of aldehydes from the three fuels tested.

Volatile and Semivolatile Organic Compounds

Samples from the exhaust of each of the three fuels were analyzed for 60 volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs). Thirty three VOCs and SVOCs were detected in at least one of the nine samples analyzed (three for each fuel). Ten compounds were not detected in any of the runs for at least one of the three fuels, and seven additional compounds were detected but at levels below the method detection level for at least one of the three fuels. Table 11 shows the concentrations of detected VOCs and SVOCs measured in the collected samples. Table 12 gives the average emission rate in lb/hr and Table 13 shows the emission factors in lb/10^{12} Btu for all the compounds detected in at least one sample. The stated values were determined using zero for those samples in which the compound was not detected, and using the detection level of 0.5 ppb for those samples in which the compound was detected, but at levels below the 0.5 ppb detection level.

Table 11. Average concentrations of volatile organic compounds in ppb (standard deviation shown in parentheses).

	No. 2 Fuel Oil Average (Standard Deviation)	Soy Biodiesel Average (Standard Deviation)	Animal Biodiesel Average (Standard Deviation)
Chloromethane	0.860 (1.49)	ND[a]	ND
Bromomethane	0.267 (0.462)	ND	1.07 (1.85)
Chloroethane	0.557 (0.964)	1.03 (1.78)	0.633 (1.10)
Ethanol	23.6 (25.8)	72.6 (86.2)	193 (324)
Carbon disulfide	21.7 (24.8)	70.6 (81.9)	199 (332)
Isopropyl alcohol	< 2.64[b] (1.94)	1.84 (2.49)	7.90 (9.03)
Acetone	33.7 (6.08)	37.8 (10.0)	62.1 (45.3)
Methyl-t-butyl ether	ND	0.383 (0.664)	< 1.00 (1.32)
Vinyl acetate	ND	ND	2.76 (2.39)
Cyclohexane	< 1.76 (1.09)	4.72 (2.96)	3.46 (2.06)
Chloroform	0.563 (0.575)	< 1.02 (0.553)	1.12 (0.563)
Ethyl acetate	5.65 (5.07)	3.97 (4.27)	4.68 (4.14)
Tetrahydrofuran	1.84 (0.637)	1.26 (0.406)	5.54 (5.14)
2-Butanone	6.22 (10.8)	2.50 (4.34)	13.1 (22.6)
Benzene	3.15 (2.06)	3.09 (1.12)	19.0 (27.9)
Trichloroethylene	1.43 (1.24)	1.61 (2.79)	2.81 (1.34)
1,4 Dioxane	ND	ND	< 0.863 (1.09)
Toluene	0.920 (0.817)	0.300 (0.520)	3.89 (1.02)
4-Methyl-2-pentanone	1.35 (0.289)	11.71 (16.04)	1.67 (0.644)
2-Hexanone	6.36 (1.27)	3.08 (2.74)	ND
Ethylbenzene	< 0.873 (0.530)	< 0.853 (0.307)	1.31 (0.803)
Chlorobenzene	1.00 (0.887)	0.560 (0.970)	2.13 (2.82)
m,p-Xylene	1.56 (0.890)	1.65 (0.759)	2.88 (2.55)
o-Xylene	< 0.517 (0.525)	ND	1.02 (0.779)
Styrene	< 0.500 (0.000)	0.727 (0.049)	0.250 (0.433)
Tribromomethane	0.917 (1.59)	1.90 (1.66)	1.15 (1.18)
1,1,2,2-Tetrachloroethane	ND	ND	1.14 (1.98)

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Table 11 (Continued)

1-Ethyl-4-methyl benzene	< 0.500 (0.000)	< 0.167 (0.289)	< 0.167 (0.289)
1,3,5-Trimethylbenzene	< 0.520 (0.530)	< 0.167 (0.289)	0.517 (0.480)
1,2,4-Trimethylbenzene	1.12 (0.698)	0.220 (0.381)	0.800 (0.904)
1,3-Dichlorobenezene	1.05 (1.82)	ND	0.743 (1.29)
1,4-Dichlorobenezene	1.13 (1.96)	ND	1.36 (1.26)
1,2-Dichlorobenzene	293 (88.8)	546 (271)	139 (78.3)

(a) Not detected
(b) Concentrations shown as less than the stated value had one or more measurements below the method detection level. Average values are calculated using the method detection level.

Figure 10 illustrates the concentrations of the detected VOCs and SVOCs. In general, the animal biodiesel has higher concentrations of the organic compounds compared to the other two fuels, although the high variability in concentrations results in differences that are not statistically significant in many cases. The semi-log plot makes the magnitude of the variability difficult to see, but the data in Table 12 demonstrate the high standard deviations relative to the average. There were only six compounds (acetone, cyclohexane, tetrahydrofuran, ethylbenzene, m,p-xylene, and 1,2-dichlorobenzene) for which the relative standard deviations were less than one for all three fuels.

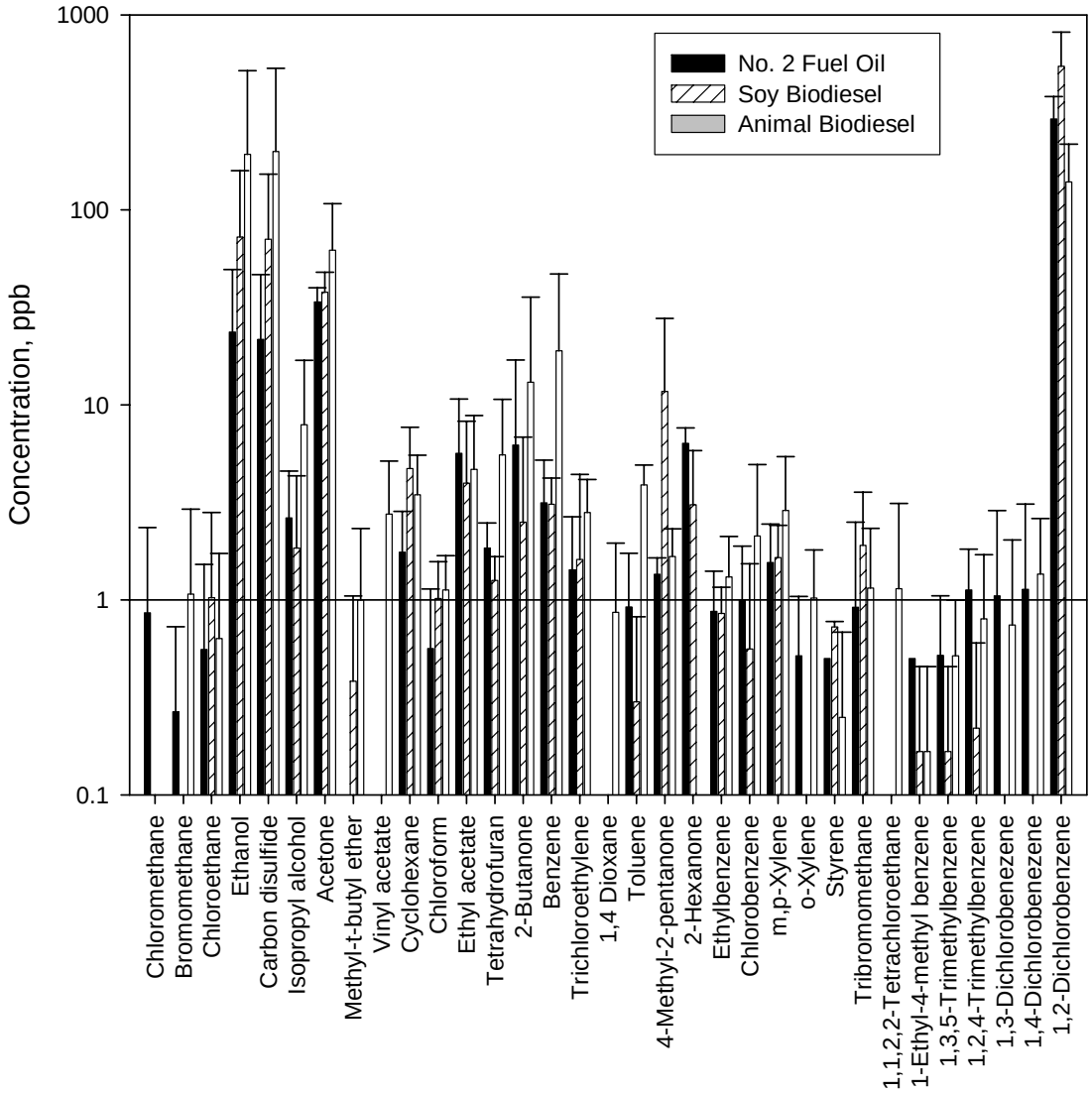

Figure 10. Concentrations of detected VOCs and SVOCs, in ppb.

Table 12. Emission rates of volatile and semivolatile organic compounds, in lb/hr.

	No. 2 Fuel Oil Average (Standard Deviation)	Soy Biodiesel Average (Standard Deviation)	Animal Biodiesel Average (Standard Deviation)
Chloromethane	2.20E-06 (3.82E-06)	ND[a]	ND
Bromomethane	1.39E-06 (2.40E-06)	ND	6.06E-06 (1.05E-05)
Chloroethane	1.82E-06 (3.16E-06)	3.67E-06 (6.36E-06)	2.37E-06 (4.10E-06)
Ethanol	5.59E-05 (6.04E-05)	1.87E-04 (2.22E-04)	5.15E-04 (8.66E-04)
Carbon disulfide	8.45E-05 (9.54E-05)	3.01E-04 (3.48E-04)	8.79E-04 (1.46E-03)
Isopropyl alcohol	< 8.23E-06[b] (6.03E-06)	6.22E-06 (8.33E-06)	2.75E-05 (3.14E-05)
Acetone	1.03E-04 (1.46E-05)	1.23E-04 (3.24E-05)	2.10E-04 (1.51E-04)
Methyl-t-butyl ether	ND	1.94E-06 (3.36E-06)	< 5.23E-06 (6.97E-06)
Vinyl acetate	ND	ND	1.37E-05 (1.19E-05)
Cyclohexane	< 7.80E-06 (4.85E-06)	2.25E-05 (1.43E-05)	1.72E-05 (1.05E-05)
Chloroform	3.60E-06 (3.78E-06)	< 6.83E-06 (3.69E-06)	7.89E-06 (4.10E-06)
Ethyl acetate	2.58E-05 (2.33E-05)	1.95E-05 (2.11E-05)	2.39E-05 (2.11E-05)
Tetrahydrofuran	7.06E-06 (2.60E-06)	5.13E-06 (1.74E-06)	2.36E-05 (2.22E-05)
2-Butanone	2.28E-05 (3.94E-05)	1.00E-05 (1.73E-05)	5.46E-05 (9.45E-05)
Benzene	1.31E-05 (9.06E-06)	1.36E-05 (5.13E-06)	8.80E-05 (1.30E-04)
Trichloroethylene	9.70E-06 (8.45E-06)	1.18E-05 (2.05E-05)	2.17E-05 (1.07E-05)
1,4 Dioxane	ND	ND	< 4.41E-06 (5.57E-06)
Toluene	4.39E-06 (3.93E-06)	1.53E-06 (2.65E-06)	2.09E-05 (5.29E-06)
4-Methyl-2-pentanone	7.12E-06 (1.34E-06)	6.71E-05 (9.25E-05)	9.75E-06 (3.65E-06)
2-Hexanone	3.34E-05 (5.41E-06)	1.72E-05 (1.53E-05)	ND
Ethylbenzene	< 4.88E-06 (2.95E-06)	< 5.11E-06 (1.88E-06)	8.13E-06 (4.93E-06)
Chlorobenzene	5.83E-06 (5.20E-06)	3.52E-06 (6.10E-06)	1.42E-05 (1.89E-05)
m,p-Xylene	8.70E-06 (4.97E-06)	9.91E-06 (4.75E-06)	1.78E-05 (1.56E-05)
o-Xylene	< 2.94E-06 (2.94E-06)	ND	6.33E-06 (4.76E-06)
Styrene	< 2.74E-06 (1.05E-07)	4.26E-06 (2.18E-07)	1.55E-06 (2.69E-06)
Tribromomethane	1.22E-05 (2.11E-05)	2.73E-05 (2.39E-05)	1.72E-05 (1.77E-05)
1,1,2,2-Tetrachloroethane	ND	ND	1.11E-05 (1.93E-05)
1-Ethyl-4-methyl benzene	< 3.17E-06 (1.20E-07)	< 1.11E-06 (1.92E-06)	< 1.16E-06 (2.01E-06)

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Table 12 (Continued)

1,3,5-Trimethylbenzene	< 3.25E-06 (3.36E-06)	< 1.11E-06 (1.92E-06)	3.64E-06 (3.36E-06)
1,2,4-Trimethylbenzene	7.15E-06 (4.44E-06)	1.47E-06 (2.54E-06)	5.57E-06 (6.29E-06)
1,3-Dichlorobenezene	8.47E-06 (1.47E-05)	ND	6.33E-06 (1.10E-05)
1,4-Dichlorobenezene	8.77E-06 (1.52E-05)	ND	1.16E-05 (1.07E-05)
1,2-Dichlorobenzene	2.29E-03 (7.76E-04)	4.54E-03 (2.35E-03)	1.19E-03 (6.59E-04)

(a) Not detected
(b) Concentrations shown as less than the stated value had one or more measurements below the method detection level. Average values are calculated using the method detection level.

Table 13. Emission factors for volatile and semivolatile organic compounds, in lb/10^{12} Btu.

	No. 2 Fuel Oil Average (Standard Deviation)	Soy Biodiesel Average (Standard Deviation)	Animal Biodiesel Average (Standard Deviation)
Chloromethane	1.16E+00 (2.02E+00)	ND[a]	ND
Bromomethane	7.33E-01 (1.27E+00)	ND	3.12E+00 (5.40E+00)
Chloroethane	9.64E-01 (1.67E+00)	1.94E+00 (3.36E+00)	1.22E+00 (2.11E+00)
Ethanol	2.95E+01 (3.19E+01)	9.91E+01 (1.17E+02)	2.65E+02 (4.46E+02)
Carbon disulfide	4.47E+01 (5.05E+01)	1.59E+02 (1.84E+02)	4.52E+02 (7.54E+02)
Isopropyl alcohol	< 4.35E+00[b] (3.19E+00)	3.29E+00 (4.41E+00)	1.42E+01 (1.62E+01)
Acetone	5.45E+01 (7.73E+00)	6.53E+01 (1.72E+01)	1.08E+02 (7.75E+01)
Methyl-t-butyl ether	ND	1.03E+00 (1.78E+00)	< 2.69E+00 (3.59E+00)
Vinyl acetate	ND	ND	7.07E+00 (6.14E+00)
Cyclohexane	< 4.13E+00 (2.56E+00)	1.19E+01 (7.58E+00)	8.83E+00 (5.39E+00)
Chloroform	1.90E+00 (2.00E+00)	< 3.61E+00 (1.95E+00)	4.06E+00 (2.11E+00)
Ethyl acetate	1.36E+01 (1.23E+01)	1.03E+01 (1.11E+01)	1.23E+01 (1.09E+01)
Tetrahydrofuran	3.73E+00 (1.37E+00)	2.71E+00 (9.21E-01)	1.21E+01 (1.14E+01)
2-Butanone	1.20E+01 (2.08E+01)	5.29E+00 (9.17E+00)	2.81E+01 (4.86E+01)
Benzene	6.95E+00 (4.79E+00)	7.22E+00 (2.72E+00)	4.53E+01 (6.70E+01)
Trichloroethylene	5.13E+00 (4.47E+00)	6.25E+00 (1.08E+01)	1.12E+01 (5.52E+00)
1,4 Dioxane	ND	ND	< 2.27E+00 (2.87E+00)
Toluene	2.32E+00 (2.08E+00)	8.10E-01 (1.40E+00)	1.08E+01 (2.72E+00)
4-Methyl-2-pentanone	3.76E+00 (7.06E-01)	3.55E+01 (4.89E+01)	5.02E+00 (1.88E+00)

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Table 13 (continued)

2-Hexanone	1.77E+01 (2.86E+00)	9.09E+00 (8.11E+00)	ND
Ethylbenzene	< 2.58E+00 (1.56E+00)	< 2.70E+00 (9.94E-01)	4.18E+00 (2.54E+00)
Chlorobenzene	3.08E+00 (2.75E+00)	1.86E+00 (3.23E+00)	7.31E+00 (9.75E+00)
m,p-Xylene	4.60E+00 (2.63E+00)	5.24E+00 (2.51E+00)	9.15E+00 (8.03E+00)
o-Xylene	< 1.56E+00 (1.55E+00)	ND	3.26E+00 (2.45E+00)
Styrene	< 1.45E+00 (5.55E-02)	2.25E+00 (1.15E-01)	7.99E-01 (1.38E+00)
Tribromomethane	6.45E+00 (1.12E+01)	1.44E+01 (1.26E+01)	8.84E+00 (9.12E+00)
1,1,2,2-Tetrachloroethane	ND	ND	5.72E+00 (9.91E+00)
1-Ethyl-4-methyl benzene	< 1.67E+00 (6.35E-02)	< 5.87E-01 (1.02E+00)	< 5.97E-01 (1.03E+00)
1,3,5-Trimethylbenzene	< 1.72E+00 (1.78E+00)	< 5.87E-01 (1.02E+00)	1.87E+00 (1.73E+00)
1,2,4-Trimethylbenzene	3.78E+00 (2.35E+00)	7.75E-01 (1.34E+00)	2.87E+00 (3.24E+00)
1,3-Dichlorobenezene	4.48E+00 (7.75E+00)	ND	3.26E+00 (5.64E+00)
1,4-Dichlorobenezene	4.64E+00 (8.03E+00)	ND	5.94E+00 (5.52E+00)
1,2-Dichlorobenzene	1.21E+03 (4.10E+02)	2.40E+03 (1.24E+03)	6.11E+02 (3.39E+02)

(a) Not detected
(b) Concentrations shown as less than the stated value had one or more measurements below the method detection level. Average values are calculated using the method detection level.

Table 14 shows those compounds for which the samples were analyzed, but were not detected in any of the samples. For these compounds, the emission rate is reported as 0 lb/hr and the emission factor as 0 lb/10^{12} Btu. At the detection limit of 0.5 ppb, the emission rate would be about 2.7×10^{-6} lb/hr and the emission factor would be about 1.5 lb/10^{12} Btu.

Table 14. Compounds not detected in any sample.

Dichlorodifluoromethane	Hexane	Bromodichloromethane
1,2-Chloro-1,1,2,2-Tetrafluoroethane	1,1-Dichloroethane	cis-1,3-Dichloropropene
Vinyl Chloride	cis-1,2-Dichloroethene	t-1,3-Dichloropropene
1,3 Butadiene	1,1-trichloroethane	Tetrachloroethylene
Trichloromonofluoromethane	Carbon tetrachloride	1,1,2-Trichloroethane
1,1-Dichloroethene	Heptane	Dibromochloromethane
1,1,2-Trichloro-1,2,2-trichloromoethane	1,2-Dichloroethane	Benzyl chloride
Methylene chloride	1,2-Dibromoethane	1,1,2,3,4,4-Hexachloro-1,3-butadiene
t-1,2-Dichloroethene	1,2-Dichloropropane	1,2,4-Trichlorobenzene

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbon concentrations were collected using EPA Method 0010 (U.S. Environmental Protection Agency 1986) and analyzed according to California Air Resources Board (CARB) Method 429 (California Air Resources Board 1997). Three samples were collected for each fuel, with one sample collected per test run. The analyses determined concentrations of 19 PAHs, of which two were found to be below the detection limit for all three fuels. Figure 11 shows the concentrations of the 19 PAHs for the three fuels. In general, the relative pattern of PAH concentration is consistent across all three fuels, with phenanthrene being the PAH with the highest concentration and perlyene being the PAH with the lowest concentration for all three fuels. In all three fuels, both fluorene and dibenzo(a,h)anthracene were below detection limits (at approximately 1 ppm) in the flue gases of the three fuels.

As can be seen in Figure 11, the PAH concentrations for the animal biodiesel are all lower than those for the soy biodiesel. Of the 17 PAHs measured above the detection level, 5 were higher for the No. 2 fuel oil than for the soy biodiesel and 12 were lower. Eight of the 17 detected PAHs were higher for the animal biodiesel than for the No. 2 fuel oil.

Table 15 shows the concentrations in ng/Nm^3, Table 16 gives the emission rate results in g/hr, and Table 17 provides the emission factor results in lb/10^{12} Btu for the 19 PAHs.

Field blank samples were taken during each of the three test conditions. Field blank PAH levels were an average of 19% of the sample levels for the No. 2 fuel oil and 16% of sample levels for the soy biodiesel. The field blank levels were highest for naphthalene for both these fuels, at 41% of sample value for the No. 2 fuel oil and 65% for the soy biodiesel. For the animal biodiesel, the field blank levels averaged 54%, with blank levels exceeding sample levels for ideno(1,2,3-cd)pyrene and benzo(ghi)perylene.

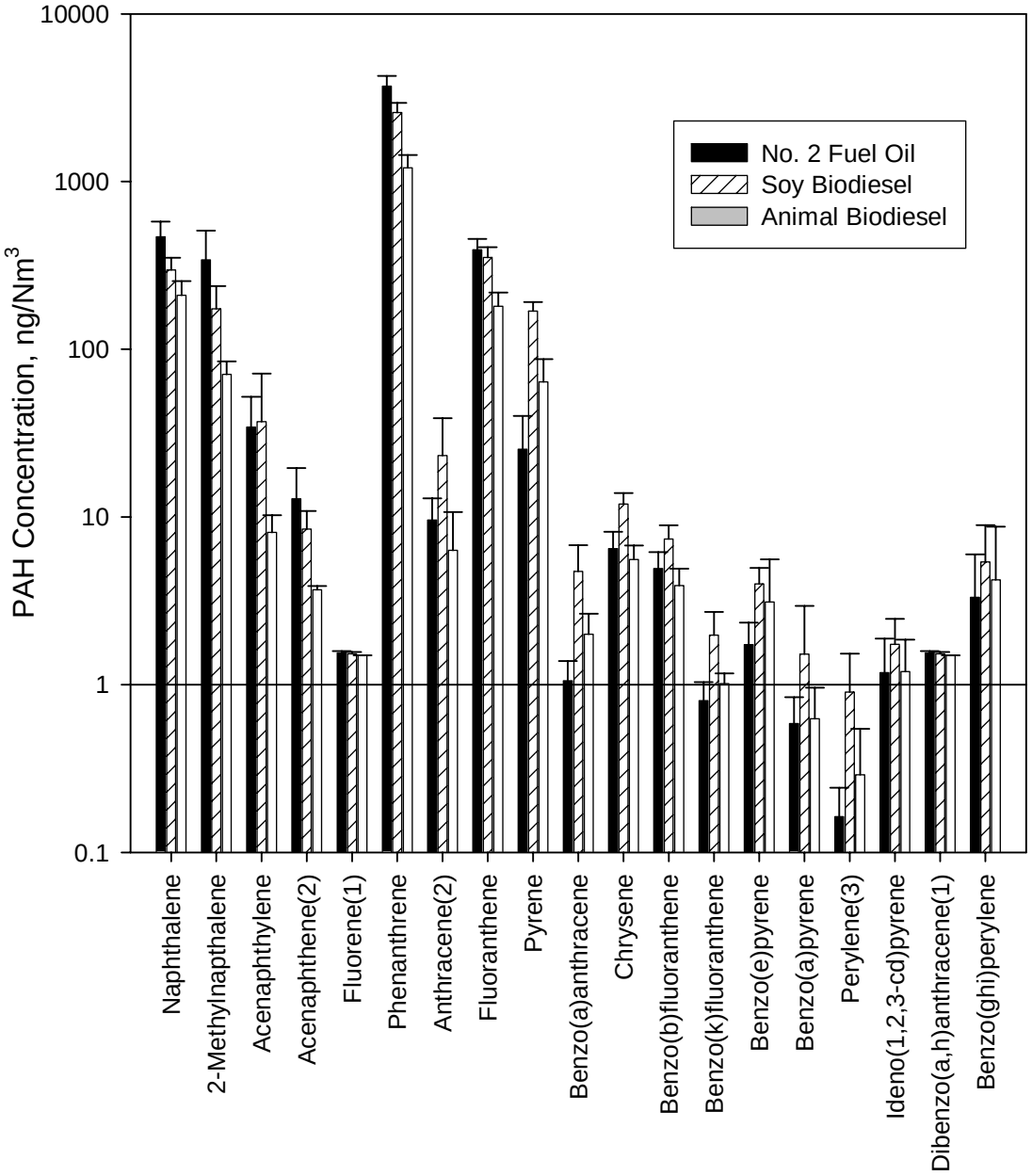

Figure 11. Concentrations of PAHs from the three fuels, in ng/Nm^3. (1) No samples were above the detection limit; (2) one sample was below the detection limit; (3) two samples (one each for soy and animal biodiesel) were below the detection limit.

Table 15. Concentrations of PAHs in ng/Nm^3.

	No. 2 Fuel Oil	Soy Biodiesel	Animal Biodiesel
	Average (Standard deviation)	Average (Standard deviation)	Average (Standard deviation)
Naphthalene	469 (109)	297 (54.0)	210 (45.0)
2-Methylnapthalene	341 (168)	174 (64.2)	71.0 (13.6)
Acenaphthylene	34.4 (17.8)	37.0 (34.7)	8.09 (2.15)
Acenaphthene	12.8 (6.7)	<8.48 (a) (2.37)	3.68 (0.19)
Fluorene (b)	<1.55 (c) (0.04)	<1.53 (0.04)	<1.49 (0.01)
Phenanthrene	3706 (558)	2580 (364)	1210 (232)
Anthracene	<10 (a) (3)	23.3 (15.6)	6.32 (4.38)
Fluoranthene	393 (62.0)	353 (52.7)	181 (37.0)
Pyrene	25.4 (14.6)	169 (22.1)	64.0 (23.4)
Benzo(a)anthracene	1.06 (0.33)	4.74 (2.05)	2.00 (0.65)
Chrysene	6.48 (1.69)	11.9 (1.98)	5.57 (1.18)
Benzo(b)fluoranthene	4.93 (1.24)	7.37 (1.56)	3.90 (1.01)
Benzo(k)fluoranthene	0.80 (0.23)	1.97 (0.75)	1.01 (0.15)
Benzo(e)pyrene	1.73 (0.61)	3.99 (0.98)	3.11 (2.49)
Benzo(a)pyrene	0.59 (0.26)	1.52 (1.43)	0.63 (0.33)
Perylene	0.16 (0.08)	<0.90 (a) (0.63)	<0.29 (a) (0.26)
Ideno(1,2,3-cd)pyrene	1.18 (0.70)	1.74 (0.73)	1.20 (0.66)
Dibenzo(a,h)anthracene (b)	<1.55 (0.04)	<1.53 (0.04)	<1.49 (0.01)
Benzo(ghi)perylene	3.32 (2.67)	5.40 (3.53)	4.22 (4.54)

(a) One of three samples were below detection limit.
(b) All samples were below detection limit.
(c) Concentrations shown as less than the stated value had one or more measurements below the method detection level. Average values are calculated using the method detection level.

Table 16. PAH emission rates in g/hr.

	No. 2 fuel oil	Soy Biodiesel	Animal Biodiesel
Naphthalene	2.65E-04 (5.40E-05)	1.82E-04 (3.05E-05)	1.33E-04 (2.86E-05)
2-Methylnapthalene	1.92E-04 (8.91E-05)	1.07E-04 (3.82E-05)	4.48E-05 (8.65E-06)
Acenaphthylene	1.93E-05 (9.46E-06)	2.26E-05 (2.10E-05)	5.11E-06 (1.37E-06)
Acenaphthene	7.22E-06 (3.59E-06)	<5.20E-06 (a) (1.39E-06)	2.32E-06 (1.23E-07)
Fluorene (b)	<8.77E-07 (c) (3.54E-08)	<9.39E-07 (9.46E-09)	<9.43E-07 (4.56E-09)
Phenanthrene	2.10E-03 (2.63E-04)	1.58E-03 (2.02E-04)	7.62E-04 (1.47E-04)
Anthracene	<5.41E-06 (a) (1.76E-06)	1.42E-05 (9.38E-06)	3.99E-06 (2.77E-06)
Fluoranthene	2.22E-04 (3.01E-05)	2.17E-04 (2.92E-05)	1.14E-04 (2.35E-05)
Pyrene	1.43E-05 (7.90E-06)	1.04E-04 (1.20E-05)	4.04E-05 (1.48E-05)
Benzo(a)anthracene	5.96E-07 (1.69E-07)	2.90E-06 (1.22E-06)	1.26E-06 (4.14E-07)
Chrysene	3.66E-06 (8.59E-07)	7.32E-06 (1.11E-06)	3.52E-06 (7.48E-07)
Benzo(b)fluoranthene	2.78E-06 (6.26E-07)	4.53E-06 (8.95E-07)	2.46E-06 (6.44E-07)
Benzo(k)fluoranthene	4.53E-07 (1.18E-07)	1.21E-06 (4.42E-07)	6.40E-07 (9.81E-08)
Benzo(e)pyrene	9.77E-07 (3.17E-07)	2.45E-06 (5.70E-07)	1.96E-06 (1.57E-06)
Benzo(a)pyrene	3.30E-07 (1.35E-07)	9.27E-07 (8.66E-07)	3.96E-07 (2.10E-07)
Perylene	9.18E-08 (4.21E-08)	<5.59E-07 (a) (3.94E-07)	<1.83E-07 (a) (1.61E-07)
Ideno(1,2,3-cd)pyrene	6.62E-07 (3.77E-07)	1.07E-06 (4.32E-07)	7.56E-07 (4.18E-07)
Dibenzo(a,h)anthracene (b)	<8.77E-07 (3.54E-08)	<9.39E-07 (9.46E-09)	<9.43E-07 (4.56E-09)
Benzo(ghi)perylene	1.86E-06 (1.44E-06)	3.31E-06 (2.14E-06)	2.67E-06 (2.87E-06)

(a) One of three samples were below detection limit.
(b) All samples were below detection limit.
(c) Concentrations shown as less than the stated value had one or more measurements below the method detection level. Average values are calculated using the method detection level.

Table 17. Emission factors for PAHs in lb/10^{12} Btu.

	No. 2 fuel oil	Soy Biodiesel	Animal Biodiesel
	Average (Standard deviation)	Average (Standard deviation)	Average (Standard deviation)
Naphthalene	3.08E-01 (6.29E-02)	2.12E-01 (3.56E-02)	1.50E-01 (3.24E-02)
2-Methylnapthalene	2.23E-01 (1.04E-01)	1.24E-01 (4.45E-02)	5.08E-02 (9.80E-03)
Acenaphthylene	2.25E-02 (1.10E-02)	2.63E-02 (2.44E-02)	5.79E-03 (1.55E-03)
Acenaphthene	8.41E-03 (4.18E-03)	<6.06E-03 (a) (1.62E-03)	2.63E-03 (1.40E-04)
Fluorene (b)	<1.02E-03 (c) (4.13E-05)	<1.09E-03 (1.10E-05)	<1.07E-03 (5.17E-06)
Phenanthrene	2.44E+00 (3.06E-01)	1.85E+00 (2.36E-01)	8.64E-01 (1.67E-01)
Anthracene	<6.30E-03 (a) (2.05E-03)	1.66E-02 (1.09E-02)	4.52E-03 (3.14E-03)
Fluoranthene	2.59E-01 (3.50E-02)	2.53E-01 (3.40E-02)	1.29E-01 (2.66E-02)
Pyrene	1.66E-02 (9.20E-03)	1.21E-01 (1.40E-02)	4.58E-02 (1.68E-02)
Benzo(a)anthracene	6.94E-04 (1.97E-04)	3.38E-03 (1.42E-03)	1.43E-03 (4.69E-04)
Chrysene	4.26E-03 (1.00E-03)	8.52E-03 (1.29E-03)	3.99E-03 (8.48E-04)
Benzo(b)fluoranthene	3.24E-03 (7.29E-04)	5.27E-03 (1.04E-03)	2.79E-03 (7.30E-04)
Benzo(k)fluoranthene	5.28E-04 (1.37E-04)	1.41E-03 (5.15E-04)	7.26E-04 (1.11E-04)
Benzo(e)pyrene	1.14E-03 (3.69E-04)	2.85E-03 (6.64E-04)	2.23E-03 (1.78E-03)
Benzo(a)pyrene	3.84E-04 (1.57E-04)	1.08E-03 (1.01E-03)	4.49E-04 (2.38E-04)
Perylene	1.07E-04 (4.90E-05)	<6.51E-04 (a) (4.59E-04)	<2.08E-04 (a) (1.83E-04)
Ideno(1,2,3-cd)pyrene	7.71E-04 (4.39E-04)	1.24E-03 (5.03E-04)	8.56E-04 (4.74E-04)
Dibenzo(a,h)anthracene (b)	<1.02E-03 (4.13E-05)	<1.09E-03 (1.10E-05)	<1.07E-03 (5.17E-06)
Benzo(ghi)perylene	2.16E-03 (1.68E-03)	3.86E-03 (2.49E-03)	3.02E-03 (3.25E-03)

(a) One of three samples were below detection limit.
(b) All samples were below detection limit.
(c) Concentrations shown as less than the stated value had one or more measurements below the method detection level. Average values are calculated using the method detection level.

Polychlorinated Biphenyls

PCBs were sampled using EPA Method 0010 (U.S. Environmental Protection Agency 1986) and analyzed using CARB Method 428 (California Air Resources Board 1990). Concentrations of PCBs are shown in Figure 12. The concentrations measured in these tests were substantially higher than expected, which is likely to be the result of the previous testing done to evaluate the potential for dioxin formation during co-firing of chlorinated wastes in small boilers. Total PCB concentrations were as much as two orders of magnitude higher than the PAHs, which is extremely high given the lack of significant chlorine in the three fuels (all less than the 20 ppm detection limit as seen in

Table 1). As with the PAHs, PCBs concentrations from the animal biodiesel were lower in each case than those from the soy biodiesel or the No. 2 fuel oil. PCB concentrations were higher than those from the soy biodiesel for total chlorinated biphenyls up to and including total pentachlorinated biphenyls, and were lower than those from the soy biodiesel for total PCBs with six or more chlorine atoms.

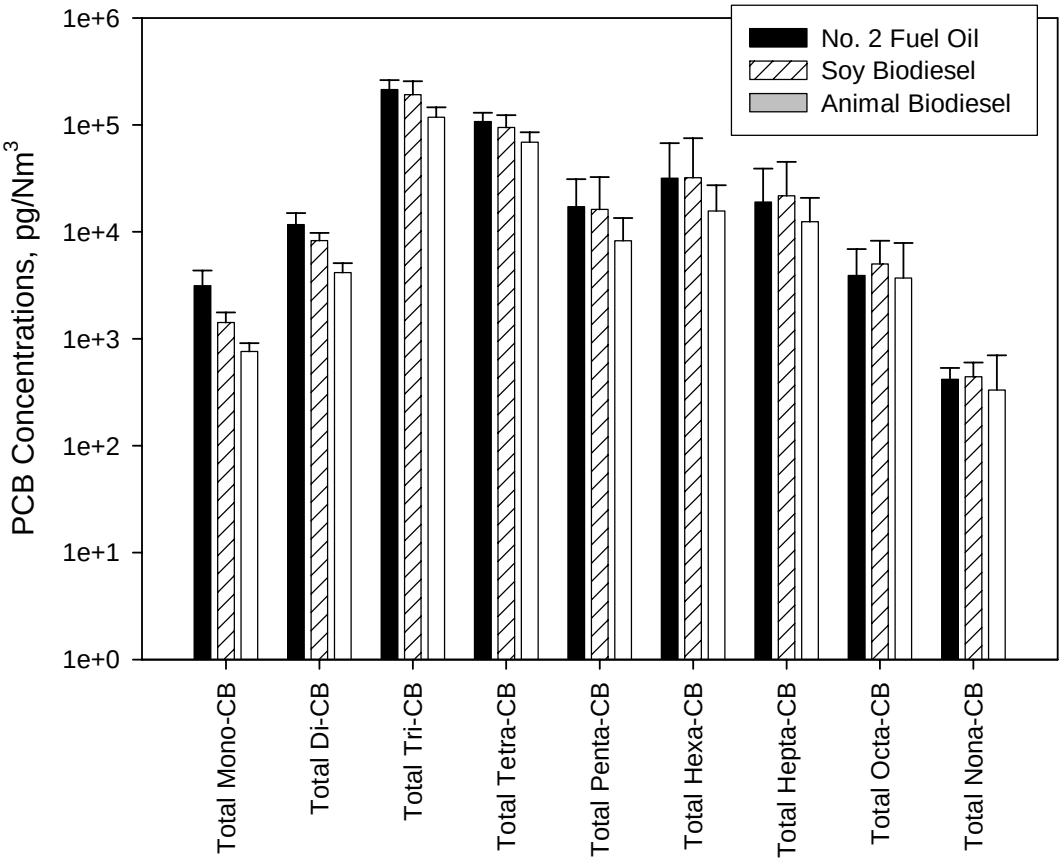

Figure 12. Concentrations of PCBs for each of the three fuels tested.

Concentrations (in pg/Nm^3) of 12 individual PCBs and total PCBs by chlorine content are shown in Table 18. Emission rates in lb/hr are given in Table 19, and emission factors in lb/10^{12} Btu are provided in Table 20.

Table 18. Concentrations of PCB for the three fuels tested, in pg/Nm^3.

	No. 2 Fuel Oil	Soy Biodiesel	Animal Biodiesel
	Average (Standard Deviation)	Average (Standard Deviation)	Average (Standard Deviation)
3,3',4,4' Tetrachlorobiphenyl	709 (123)	587 (109)	362 (34.0)
3,4,4',5 Tetrachlorobiphenyl	191 (50.9)	131 (24.6)	78.1 (9.40)
2,3,3',4,4' Pentachlorobiphenyl	263 (39.8)	215 (70.0)	128 (7.10)
2,3,4,4',5 Pentachlorobiphenyl	71.9 (15.4)	50.2 (15.5)	31.0 (4.00)
2,3',4,4',5 Pentachlorobiphenyl	594 (192)	534 (307)	313 (67.2)
2,3',4,4',5' Pentachlorobiphenyl	63.3 (9.7)	47.1 (20.1)	26.8 (4.00)
3,3',4,4',5 Pentachlorobiphenyl	259 (153)	183 (48.0)	96.8 (17.5)
2,3,3',4,4',5 Hexachlorobiphenyl	238 (62.6)	176 (66.1)	105 (41.2)
2,3',4,4',5,5' Hexachlorobiphenyl	121 (28.2)	101 (53.0)	62.2 (29.9)
3,3',4,4',5,5' Hexachlorobiphenyl	90.3 (35.9)	56.6 (16.3)	28.8 (6.20)
2,3,3',4,4',5,5' Heptachlorobiphenyl	107 (40.5)	72.2 (19.3)	38.5 (17.3)
2,2',3,3',4,4',5,5',6,6' Decachlorobiphenyl	119 (32.6)	82.3 (19.0)	48.8 (25.3)
Total Mono-CB	3140 (1210)	1420 (344)	760 (146)
Total Di-CB	11700 (3270)	8270 (1500)	4150 (950)
Total Tri-CB	214000 (47600)	191000 (64800)	118000 (28100)
Total Tetra-CB	107000 (22400)	94400 (28800)	69000 (16500)
Total Penta-CB	17200 (13900)	16200 (16200)	8250 (5220)
Total Hexa-CB	31700 (35600)	32000 (43000)	15600 (11600)
Total Hepta-CB	18900 (20200)	21700 (23400)	12500 (8320)
Total Octa-CB	3920 (3000)	4990 (3240)	3700 (4160)
Total Nona-CB	417 (115)	441 (159)	332 (367)

Table 19. Emission rates of PCBs for the three fuels tested, in lb/hr.

	No. 2 Fuel Oil	Soy Biodiesel	Animal Biodiesel
	Average (Standard Deviation)	Average (Standard Deviation)	Average (Standard Deviation)
3,3',4,4' Tetrachlorobiphenyl	4.01E-04 (6.22E-05)	3.61E-04 (7.03E-05)	2.29E-04 (2.16E-05)
3,4,4',5 Tetrachlorobiphenyl	1.08E-04 (2.60E-05)	8.03E-05 (1.46E-05)	4.93E-05 (6.01E-06)
2,3,3',4,4' Pentachlorobiphenyl	1.49E-04 (2.27E-05)	1.32E-04 (4.26E-05)	8.10E-05 (4.36E-06)
2,3,4,4',5 Pentachlorobiphenyl	4.07E-05 (8.39E-06)	3.08E-05 (9.30E-06)	1.96E-05 (2.52E-06)
2,3',4,4',5 Pentachlorobiphenyl	3.38E-04 (1.15E-04)	3.28E-04 (1.86E-04)	1.97E-04 (4.21E-05)
2,3',4,4',5' Pentachlorobiphenyl	3.58E-05 (5.12E-06)	2.89E-05 (1.21E-05)	1.69E-05 (2.48E-06)
3,3',4,4',5 Pentachlorobiphenyl	1.46E-04 (8.21E-05)	1.13E-04 (2.84E-05)	6.11E-05 (1.11E-05)
2,3,3',4,4',5 Hexachlorobiphenyl	1.34E-04 (3.23E-05)	1.08E-04 (4.00E-05)	6.61E-05 (2.60E-05)
2,3',4,4',5,5' Hexachlorobiphenyl	6.88E-05 (1.62E-05)	6.19E-05 (3.22E-05)	3.93E-05 (1.89E-05)
3,3',4,4',5,5' Hexachlorobiphenyl	5.09E-05 (1.88E-05)	3.48E-05 (9.68E-06)	1.82E-05 (3.95E-06)
2,3,3',4,4',5,5' Heptachlorobiphenyl	6.02E-05 (2.12E-05)	4.44E-05 (1.15E-05)	2.43E-05 (1.10E-05)
2,2',3,3',4,4',5,5',6,6' Decachlorobiphenyl	6.70E-05 (1.65E-05)	5.06E-05 (1.14E-05)	3.08E-05 (1.60E-05)
Total Mono-CB	1.77E-03 (6.30E-04)	8.69E-04 (1.99E-04)	4.80E-04 (9.27E-05)
Total Di-CB	6.60E-03 (1.72E-03)	5.10E-03 (1.02E-03)	2.62E-03 (6.02E-04)
Total Tri-CB	1.21E-01 (2.70E-02)	1.18E-01 (4.22E-02)	7.44E-02 (1.78E-02)
Total Tetra-CB	6.07E-02 (1.30E-02)	5.83E-02 (1.88E-02)	4.36E-02 (1.04E-02)
Total Penta-CB	9.82E-03 (8.09E-03)	9.91E-03 (9.87E-03)	5.21E-03 (3.28E-03)
Total Hexa-CB	1.82E-02 (2.06E-02)	1.96E-02 (2.62E-02)	9.85E-03 (7.33E-03)
Total Hepta-CB	1.09E-02 (1.17E-02)	1.33E-02 (1.42E-02)	7.87E-03 (5.26E-03)
Total Octa-CB	2.24E-03 (1.74E-03)	3.08E-03 (1.99E-03)	2.34E-03 (2.63E-03)
Total Nona-CB	2.37E-04 (6.75E-05)	2.72E-04 (9.93E-05)	2.10E-04 (2.32E-04)

Table 20. Emission factors for PCBs from the three fuels, lb/10^{12} Btu.

	No. 2 Fuel Oil	Soy Biodiesel	Animal Biodiesel
	Average (Standard Deviation)	Average (Standard Deviation)	Average (Standard Deviation)
3,3',4,4' Tetrachlorobiphenyl	4.67E-01 (7.25E-02)	4.21E-01 (8.19E-02)	2.59E-01 (2.45E-02)
3,4,4',5 Tetrachlorobiphenyl	1.25E-01 (3.02E-02)	9.35E-02 (1.70E-02)	5.59E-02 (6.81E-03)
2,3,3',4,4' Pentachlorobiphenyl	1.73E-01 (2.64E-02)	1.54E-01 (4.97E-02)	9.18E-02 (4.94E-03)
2,3,4,4',5 Pentachlorobiphenyl	4.74E-02 (9.77E-03)	3.59E-02 (1.08E-02)	2.22E-02 (2.86E-03)
2,3',4,4',5 Pentachlorobiphenyl	3.94E-01 (1.34E-01)	3.82E-01 (2.17E-01)	2.24E-01 (4.77E-02)
2,3',4,4',5' Pentachlorobiphenyl	4.17E-02 (5.97E-03)	3.37E-02 (1.41E-02)	1.92E-02 (2.81E-03)
3,3',4,4',5 Pentachlorobiphenyl	1.70E-01 (9.56E-02)	1.31E-01 (3.31E-02)	6.93E-02 (1.26E-02)
2,3,3',4,4',5 Hexachlorobiphenyl	1.57E-01 (3.76E-02)	1.26E-01 (4.66E-02)	7.50E-02 (2.95E-02)
2,3',4,4',5,5' Hexachlorobiphenyl	8.01E-02 (1.88E-02)	7.21E-02 (3.75E-02)	4.45E-02 (2.15E-02)
3,3',4,4',5,5' Hexachlorobiphenyl	5.93E-02 (2.19E-02)	4.05E-02 (1.13E-02)	2.06E-02 (4.48E-03)
2,3,3',4,4',5,5' Heptachlorobiphenyl	7.01E-02 (2.46E-02)	5.17E-02 (1.34E-02)	2.76E-02 (1.24E-02)
2,2',3,3',4,4',5,5',6,6' Decachlorobiphenyl	7.80E-02 (1.93E-02)	5.89E-02 (1.32E-02)	3.50E-02 (1.81E-02)
Total Mono-CB	2.06E+00 (7.33E-01)	1.01E+00 (2.32E-01)	5.44E-01 (1.05E-01)
Total Di-CB	7.69E+00 (2.00E+00)	5.94E+00 (1.19E+00)	2.97E+00 (6.82E-01)
Total Tri-CB	1.41E+02 (3.15E+01)	1.38E+02 (4.92E+01)	8.43E+01 (2.02E+01)
Total Tetra-CB	7.07E+01 (1.51E+01)	6.79E+01 (2.18E+01)	4.94E+01 (1.18E+01)
Total Penta-CB	1.14E+01 (9.42E+00)	1.15E+01 (1.15E+01)	5.90E+00 (3.72E+00)
Total Hexa-CB	2.12E+01 (2.40E+01)	2.28E+01 (3.05E+01)	1.12E+01 (8.31E+00)
Total Hepta-CB	1.26E+01 (1.36E+01)	1.55E+01 (1.66E+01)	8.91E+00 (5.96E+00)
Total Octa-CB	2.61E+00 (2.03E+00)	3.58E+00 (2.32E+00)	2.65E+00 (2.98E+00)
Total Nona-CB	2.76E-01 (7.86E-02)	3.16E-01 (1.16E-01)	2.38E-01 (2.63E-01)

Results for total PCBs were surprisingly high, particularly for the tri- and tetra-chlorinated biphenyls (CBs). Comparison with field blank results showed that the values for these two congener classes were well above blank levels. For the No. 2 fuel oil, the mono- through penta-CBs all had blank levels lower than 10% of the sample values. The remaining blank levels were 19% for hexa-CBs, 39% for the hepta-CBs, 65% for the octa-CBs, and 40% for the nona-CBs. For the soy biodiesel, the blank levels were below 10% for all the total CBs other than hepta-CBs, for which the blank was 10% of the average sample mass. For the soy biodiesel, only the tri- and tetra-CB blank levels were

below 10% of the sample mass. The other blank levels were 14% for the mono-CBs, 57% for the di-CBs, 102% for the penta-CBs, 103% for the hexa-CBs, 61% for the hepta-CBs, 30% for the octa-CBs, and 18% for the nona-CBs.

Based on these values, only the penta- and hexa-CBs from the animal biodiesel are questionable in terms of their presence in the flue gases. The high overall levels across all three fuels is likely a consequence of the fact that the boiler was used as a test bed for dioxin formation tests prior to use in the current tests. Although over a year had passed since those tests were performed, and even though the boiler itself was cleaned prior to the biofuel tests, it is likely that residues from the earlier tests resulted in the high PCB values reported here. It is not believed that these values are representative of PCB emissions from No. 2 fuel oil or biofuels in general.

Boiler Efficiency

The thermal efficiency of the boiler was estimated during operation with each of the three fuels. A complete efficiency analysis was not conducted for these tests, but an input/output analysis was conducted to estimate differences in boiler efficiency. The input energy was determined from the fuel heat of combustion (reported as the higher heating value) and fuel mass flow, and the output energy was calculated from the change in temperature of the boiler cooling water loop and the cooling water flow. Measurements of fuel energy input and cooling water energy output were made for each test run, providing three values for each of the three fuels. Table 21 provides the energy input and output values, the calculated thermal efficiencies, and the standard deviation of the efficiency estimates for each of the three fuels.

Table 21. Results of boiler efficiency measurements.

Fuel	Energy Input, 10^6 Btu/hr	Energy Output, 10^6 Btu/hr	Thermal Efficiency, %	Standard Deviation, %
No. 2 Fuel Oil	1,890,000	1,610,000	85.1%	5.95%
Soy Biodiesel	1,890,000	1,580,000	83.8%	6.86%
Animal Biodiesel	1,940,000	1,670,000	85.7%	6.31%

The lower average value for the soy biodiesel is not significant, as the range for the soy biodiesel overlaps the ranges for the other two fuels. The difference is most likely due to normal measurement variability, as suggested by the overlap in average plus or minus standard deviation. A brief examination of the combustion gas concentrations does not provide any indication that other factors are involved in the difference. The O_2 level was lower for the soy biodiesel compared to the other two fuels, and the CO level was below 3 ppm, both of which would indicate that the difference in efficiency is not due to excess combustion air or poor fuel burnout.

Life Cycle Analysis

When evaluating biofuels as a means to reduce greenhouse gas (GHG) emissions, it is important to understand the emissions over the fuel lifecycle, e.g., the entire production and use of the fuel. This is because GHGs are unlike criteria pollutants, which tend to be relatively short-lived and at unhealthy concentrations over relatively local spatial scales. GHGs, on the other hand, tend to be quite long-lived and therefore act over global scales. Thus, GHG emissions at any point in the production and use cycle contribute to the

effects of increased GHG concentration, and emissions from any part of the lifecycle are therefore of concern.

The lifecycle of biodiesel includes the production of the feedstock, the transport of the feedstock to the biodiesel production facility, the conversion of the feedstock to biodiesel, the transport of the biodiesel to the end user, and the combustion of the biodiesel. Each of the steps from production to transport to the end user requires some level of energy input, which may be in the form of direct energy (such as fuel to generate steam in a conversion process) or indirect energy (such as the energy content of the natural gas used to produce nitrogen fertilizer). These energy inputs are required for both biodiesel and No. 2 distillate oil, although many of the processes will be significantly different.

There have not been any studies that compare distillate heating oil to biodiesel, but there have been studies that have compared lifecycle emissions of highway diesel fuel (very similar to No. 2 distillate oil) to biodiesel. Sheehan et al. evaluated the lifecycle energy inputs for a highway diesel fuel and a soy-based biodiesel in a 1998 report, *Life Cycle Inventory of Biodiesel and Petroleum Diesel for Use in an Urban Bus* (Sheehan, Camobreco et al. 1998). They estimated that biodiesel requires 1.24 units of energy input to produce fuel with 1 unit energy (including feedstock production energy inputs), while petroleum diesel fuel requires 1.20 units of energy input to produce fuel with 1 unit of energy content. However, the fossil energy input requirements were significantly different, because of the fact that the biodiesel feedstock is soy oil rather than a fossil energy source (crude oil). Therefore, the ratio of fossil energy input to fuel energy output is just under 1.20 for the diesel fuel compared to 0.31 for the biodiesel.

More recently, Hill et al. reported similar results, with a "net energy balance" of 0.73, based on 1 unit of fuel energy (Hill, Nelson et al. 2006). The net energy balance is calculated by subtracting the total energy used in biofuel production from the energy present in the fuel. To directly compare the net energy balance to the results of Sheehan et al. requires one to assume that all the production input energy is in the form of fossil energy, which may not be the case. However, given the probable increases in process efficiencies between 2000 and 2006, and the likelihood of agricultural and conversion processes to be almost entirely fueled by fossil energy, it seems reasonable to directly compare these two results. Direct comparison shows the Hill et al. value is very close to, but slightly higher than, the Sheehan et al. result, which would convert to a net energy balance value of 0.69.

MacLean et al. report that biodiesel vehicles would consume 843 GJ of fossil energy, and 864 GJ of total energy, over the entire fuel lifecycle and vehicle operation (MacLean, Lave et al. 2000). However, they estimate that the vehicle operation would consume 612 GJ of energy over the vehicle's lifetime, and their calculations evidently assume this 612 GJ is entirely fossil energy. If the fuel being analyzed is B100 (100% biodiesel), then there should be no fossil energy consumption during vehicle operation. The MacLean et al. results contradict the results of Sheehan et al. discussed above, although MacLean et al. cite the Sheehan et al. study as a key source of information on biodiesel lifecycle energy use. It would appear that the MacLean et al. study erroneously includes the 612

GJ as fossil energy, which would result in a fossil fuel input requirement of 231 GJ and a total energy consumption of 864 GJ, which would result in a net fossil energy input to fuel energy output ratio of 0.27, much more in line with the Sheehan et al. results. In terms of the net energy balance, this would translate to 0.73, the same as Hill et al. and slightly higher than Sheehan et al.

Sheehan et al. is the only study to estimate net (direct and indirect) CO_2 emissions explicitly, as opposed to inferring emissions based on the energy balance. It should be noted that their analysis is for a different fossil fuel – highway diesel fuel – than what is used in the boiler tests reported here. However, the lifecycle assessment to the point of end use will be largely the same, given the similarities between highway diesel fuel and No. 2 distillate oil. They estimated that highway diesel fuel would emit a net 633 g-CO_2/bhp-h, compared to 136 g-CO_2/bhp-h for the soy biodiesel (Sheehan, Camobreco et al. 1998).

This is a significant reduction in net CO_2 emissions, and it should be expected that a similar percent reduction would be possible when using biodiesel in a boiler, since all the fossil energy input is upstream of the end use. If the thermal efficiency of the unit does not change when using the biodiesel compared to using the No. 2 distillate oil, the net change in CO_2 will be entirely associated with the reduction in fuel production and conversion. Assuming a similar percent reduction, the net CO_2 emissions would drop by about 79% when using the biodiesel compared to the No. 2 distillate oil.

For these tests in particular, one can evaluate the total conversion of fossil energy to steam energy as a means to compare the potential CO_2 impacts of using biodiesel as a boiler fuel. Based upon the fossil fuel inputs to fuel energy output ratios estimated by Sheehan et al., petroleum diesel requires 1.2 units of fossil fuel input per unit of useful fuel energy output, while soy-based biodiesel requires 0.31 units of fossil fuel input. Using the boiler efficiency values presented in Table 21, the net fossil fuel input per steam energy output for this boiler can be seen in Table 22 below.

Table 22. Fossil fuel input required per unit of thermal energy output for the boiler tested.

Fuel	
No. 2 Fuel Oil	1.41
Soy Biodiesel	0.37
Animal Biodiesel	0.36[(a)]

(a) Assumes the fossil fuel input for animal biodiesel is the same as the soy biodiesel fossil fuel input.

The values above assume the average fossil fuel input for both this particular soy biodiesel and animal biodiesel; however, the significant reduction in total fossil fuel content indicates that the net CO_2 emissions using biodiesel will be significantly reduced in comparison to petroleum distillate fuel.

QA Discrepancies

Several differences occurred during the tests between the actual conduct of the tests and the planned methods or approaches as stated in the QAPP. These are noted below, along with corrective actions (if any) and impacts on the results of the tests.

Discrepancy: The QAPP states that, "if the 'past-optimum' O_2 concentration is below 3%, the tests will be run with flue gas O_2 concentration at 3%" (the "past-optimum" O_2 concentration was defined as the O_2 concentration at which the CO began to increase significantly as O_2 level was reduced). In practice, the boiler was operated at O_2 levels well below 3% for all three fuels (see Table 4), at between 1.4% and 1.9%. The CO concentrations for these O_2 levels were very low (less than 5 ppm), indicating that higher O_2 levels would have resulted in reduced boiler efficiency without any improvement in combustion efficiency due to the increased mass of combustion air being used.
Resolution: No corrective actions were taken. Operation at the lower O_2 concentrations was appropriate and reflects actual boiler operation; therefore the results when using the lower O_2 concentrations are appropriate and represent the conditions the tests were designed to evaluate.

Discrepancy: The QAPP states that manual sampling will be conducted only when steady state conditions have been reached (and presumably maintained, although this second criterion was not explicitly stated), as determined by flue gas O_2 concentration remaining within 0.3%, boiler steam temperatures within 3 °F, boiler steam pressure within 0.5 psig, and heat exchanger cooling water temperature rise within 2 °F over a period of 20 minutes. In practice, manual sampling was conducted during periods when each of these criteria varied outside the stated bounds. Flue gas O_2 concentrations changed by up to 0.7%; boiler steam temperature changed by 4 °F in one instance, boiler steam pressure changed by as much as 2 psig, and heat exchanger cooling water (outlet) changed as much as 5 °F within 15 minutes (these changes occurred distinct from one another).
Resolution: There is no evidence from measurements that the transient conditions had any major impact on the emissions of concern. Although there are instances where transient changes in O_2 concentration coincide with changes in CO concentration, the CO concentrations never exceeded 20 ppm, and the highest excursions only lasted for about 90 seconds. The remaining criteria did not appear to have any influence on emissions, although the boiler and cooling water temperatures will influence boiler efficiency calculations. Although the conditions under which the sampling was started each day need to be more clearly communicated in future tests, the samples collected during periods when boiler was operating outside the steady state criteria still represent valid data that will be representative of actual unit operation.

Discrepancy: During a ten-minute period on the second test day (November 1, 2007), several CEM values appear to be at monitor calibration levels for a short period. At 8:39, the SO_2 concentrations rose rapidly from 1.7 ppm to about 140 ppm (the concentration of the SO_2 calibration gas), stayed near that concentration for about three minutes, and then dropped back down to 2.8 ppm at 8:42. From that point, the SO_2 concentration never rose above 6 ppm. At 8:44, O_2, CO_2, NO_x, and NO concentrations suddenly dropped to

near zero, and then returned to their previous levels about five minutes later. During this period, no significant change was seen in the CO concentration, which would indicate that the O_2 concentration in the boiler had not changed significantly.
Resolution: Based on the step changes in recorded concentrations to either zero or to the level of the calibration gas, and the absence of any evidence of operational upset, it is clear that these transient excursions were due to changes in the valve settings to the CEMs, and not to any changes in the boiler operation. The data during these transient periods will not be used in the calculations of average concentrations or concentration variability. In addition, the brief period of the excursions and the rapid return to pre-excursion levels indicate that simply excluding these data will result in an accurate reflection of the boiler's actual emissions.

Discrepancy: During testing on November 5, 2007, CEM data were not stored by the data acquisition system during the first test run of the day. The data were recorded from 8:00:33 to 8:03:52, at which point the recorded data end until data logging was resumed at the beginning of the second test run. CEM data were then recorded from 11:10:16 through the end of the day's testing at 21:03:21.
Resolution: The collection of data for nearly 10 hours is adequate to determine the emissions of those gases measured by CEM (O_2, CO_2, CO, NO_x, NO, SO_2 and HC), and meets the stated test duration in Table 2 of the QAPP. Comparison of these gas concentrations to the measurements using other fuels is therefore not compromised.

The largest impact of the loss of the CEM data is the inability to identify short-term transient excursions in the measured gases. Although hand-written data sheets provide data on these gas concentrations at 15 minute intervals during the period of data loss, they do not provide guidance with respect to possible transient excursions that may have lasted less than 15 minutes. No such excursions were noticed by the operators.

Discrepancy: A Method 10 sampling train was dropped and a glass impinger was broken as the sampling train was being recovered after the first test run on November 5, 2007 (animal biodiesel test).
Resolution: A fourth test run was conducted on November 5 to allow an additional Method 10 sample to be collected. This additional run provides the necessary three samples required in the QAPP, and there was no loss of data for the November 5 tests.

Discrepancy: Tests of the blends of soy biodiesel and No. 2 fuel oil were not conducted due to problems with the fuel system "gumming up" and preventing adequate fuel flow. As the unit was being prepared for initial testing of the first biofuel blend (B20), problems were noted with the fuel flow. A semi-solid, gelatin-like material was found to be impeding flow through the fuel lines and the fuel filter. Repeated attempts to operate the unit were not successful, and the tests had to be halted.
Resolution: This problem was not resolved. No data were collected for the biofuel/fuel oil blends. These data will need to be collected in future testing.

Conclusions

In general, use of biodiesel as a replacement for petroleum distillate fuel appears to have little, if any, disadvantage from an environmental perspective. Emissions of all pollutants measured in this study are roughly the same or lower for the biofuels than for the petroleum distillate fuel.

For the gas-phase criteria pollutants, there was little difference in CO or NO_x emissions across the emissions from the three fuels, with the CO emissions being less than 5 ppm and the NO_x emissions near 110 ppm for all three fuels. The largest difference was for SO_2, where the No. 2 fuel oil had emission concentrations of about 17 ppm and the two biodiesels each had less than 5 ppm. Total hydrocarbon emissions were below the detection level of the instrument for all three fuels.

PM emissions were highest for the No. 2 fuel oil, at 18 mg/dscm. Most of the PM mass for the No. 2 fuel oil was in the condensed phase. The two biodiesel fuels each had total PM mass emission concentrations between 3 and 4 mg/dscm, with the majority of that (approximately 2.5 mg/dscm) in the filterable fraction.

Aldehydes were significantly higher for the soy biodiesel compared to the No. 2 fuel oil and the animal biodiesel. However, the variability measured over the three runs was high enough that significant uncertainty remains with respect to this conclusion.

Other volatile and semivolatile organic emissions suggest that these compounds may be at higher concentrations in the animal biodiesel compared to the other two fuels. In all cases, the emissions were roughly of the same order of magnitude, which indicates that there were no fundamental differences in emissions. However, as for the other organic compounds (aldehydes, PAHs, and PCBs), the variability in the measurements was significant for all compounds and all three fuels. The significance of the differences in VOC and SVOC concentrations remain highly uncertain.

General trends in the distributions of PAHs and PCBs were very similar, indicating that there are no significant differences in the formation pathways for these compounds that depend on the characteristics of these three fuels. PCB emissions seem particularly high, likely to be a consequence of the previous series of tests. In general, there was little significant difference between petroleum and biodiesel fuels noted for PAH and PCB emissions.

Potential problems in boiler operation were noted at the start of the tests of petro/biodiesel blends. It is unclear whether these problems were specific to the fuel blends, or are a more general problem with biodiesel fuels in general. The length of operating time on unblended soy and animal biodiesels suggest that the issue may be specific to the blends, but additional study is needed to determine whether this is indeed the case or not. Such problems could impact emissions, particularly with respect to unburned fuel, CO, and organic compounds.

Although the average boiler efficiency for the soy biodiesel was lower than for the other two fuels, the variability in the results was such that it is not possible to determine whether there were significant differences in boiler efficiency when using the three fuels. The difference in boiler efficiency was relatively small, although over long-term operation, such differences can be significant in terms of total emissions.

CO_2 emissions when using biodiesel are estimated to be significantly lower than for petroleum distillate fuel, based on the previous life cycle analyses evaluated for this study. The stack concentrations of CO_2 were nearly the same for all three fuels, but the two biofuels had CO_2 emission factors 15-17% lower than the No. 2 fuel oil. The life cycle CO_2 emissions for biodiesel are difficult to determine for boiler applications, but one estimate for life cycle CO_2 emissions for mobile sources estimated that the total CO_2 emissions for soy biodiesel were only about 22% those for highway diesel fuel.

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