**Impacts of Biodiesel Blends on PM_{2.5}, Particle Number and Size Distribution, and
Elemental/Organic Carbon from Nonroad Diesel Generators**

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Abstract

As an important alternative to diesel fuel, biodiesel is considered sustainable and environmentally friendly and has attracted increased interest over the last few decades. For the evaluation of biodiesel's impact on engine performance and emissions, most studies have focused on diesel vehicles and on-road diesel engines. There is also limited data available to assess the effect of biodiesels on emissions of unregulated pollutants, such as ultrafine particulate (UFP), particle number (PN) and size distributions. For developing successful emission control strategies, an understanding of biodiesel impact on emissions from both on-road and nonroad diesel engines is necessary. In this study, two nonroad diesel generators were tested with diesel and two biodiesel blends with 5% (v/v) (B5) and 20% (v/v) (B20) biodiesel under varied engine load conditions. The effects of engine load and biodiesel blends on emissions (g/min) and emission factor (g/kWh) of PM_{2.5}, PN, elemental and organic carbon (EC/OC), as well as particle size distribution were investigated. A method for the determination of EC/OC in overloaded filter samples was also developed and evaluated. While emissions (except OC) were found to increase with increasing load, emission factors of PN and OC decreased with increasing load while lowest emission factors for PM_{2.5} and EC were recorded under medium load. Although limited, the impacts on PM_{2.5}, PN, EC/OC, as well

as particle size distribution from biodiesel blends were more noticeable under the lowest and/or the highest engine load conditions and depended strongly on engine type.

KEYWORD: BIODIESEL, DIESEL GENERATOR, EMISSIONS, PM_{2.5}, ULTRAFINE, EC/OC

1. Introduction

Diesel particulate matter (PM) is generated from incomplete combustion of diesel fuels and mostly composed of carbonaceous aerosol or soot. In urban areas, diesel exhaust and PM are considered toxic pollutants with respect to human health and can cause or exacerbate respiratory, cardiovascular, or allergic health effects and even cancer [1-3]. Diesel PM from mobile sources contributes a significant fraction of ambient fine PM, especially in urban areas [4, 5]. In New York State, the carbon fraction is 55% of the primary fine particle or PM_{2.5} (PM with size of 2.5 micron or less aerodynamic diameter), where more than half of the carbonaceous aerosol is from mobile sources in urban areas [6]. As PM emission from on-road diesel vehicles has been reduced with more stringent regulations and new control technologies, PM emission from nonroad diesel engines has attracted more attention. The first federal emission standards (Tier 1) for nonroad diesel engines were not introduced until 1998 and the most recent emission standards (Tier 4) are scheduled to phase-in over the period of 2008-2015. The Tier 4 standards require that emissions of PM and NO_x be further reduced by about 90%, similar to those required by the 2007-2010 emission standards for highway engines.

In recent years, there has been an increasing interest in the development and use of alternative fuels due to increased environmental awareness and concerns regarding the depletion of petroleum resources. Biodiesel, as an alternative to diesel fuel, is considered sustainable and environmentally friendly. Several states and municipalities in the United States are mandating the use of low levels of biodiesel in diesel

fuel. The revised EPA Renewable Fuel Standard program (RFS2), effective July 1, 2010, requires biofuel production to grow from 11.1 billion gallons in 2009 to 36 billion gallons in 2022, with 21 billion gallons to come from "advanced biofuels", defined as renewable biomass non-corn starch ethanol-derived fuels such as biodiesel that achieve a 50% greenhouse gas reduction [7]. Unlike the renewable/green biodiesel which has a similar chemical composition to conventional petroleum-based diesel fuel, biodiesel is primarily composed of mono-alkyl esters of long-chain fatty acids organically derived from vegetable oils or animal fats through a transesterification process. Compared to petroleum-based diesel fuel, biodiesel has higher oxygen content, a higher cetane number, and increased lubricity. Biodiesel contains practically no sulfur or noxious compounds and has substantially less polycyclic aromatic hydrocarbons (PAHs), and is therefore considered less toxic than petroleum-based diesel fuel.

With increased usage of biodiesel, there is a need to address its impact on emissions, especially the composition/toxicity of PM and the development of emission profiles for PM emission control, atmospheric modeling, and source apportionment [8-11]. Most of the biodiesel studies in the literature come from chassis or engine dynamometer tests of on-road diesel engines and vehicles [12-15] while only limited studies have been carried out with nonroad diesel generator sets (gensets) [16-21]. Furthermore, there is insufficient data available to assess the effect of biodiesels on the emissions of unregulated pollutants, such as ultrafine particulate (UFP), particle number (PN) and size distributions [22]. Unlike modern automotive diesel engines that operate under variable load and speed with electronically controlled fuel injection systems designed to reduce fuel consumption and exhaust emissions, diesel gensets often operate with mechanically controlled fuel injection systems at a fixed RPM and varying electrical load. Emission characterization of nonroad diesel engine can be more complicated considering the hundreds of diesel engine types compared to the small number of on-road diesel engine manufacturers. Studies on diesel gensets' emissions are not only limited but also inconsistent with regard to PM emission, PM size distribution, and elemental and organic carbon (EC/OC) [19-21, 23-24]. While elevated PM emissions from diesel gensets under high engine load conditions have been reported [17,

20], reduced PM emissions with increasing engine load have also been observed by some researchers [18, 21]. The ratio of EC/OC has been found to increase with increasing engine load [17, 19, 25] while highest EC/OC ratio at medium load was also reported [16]. Furthermore, diesel genset emissions have been reported in different units such as g/min [16] and emission factors based on power output in g/kWh [18] or fuel consumption in g/L or g/gal [20, 25]. Some researchers have also studied genset emissions by measuring PM concentrations (mg/m^3) in the diluted exhaust [17, 20, 21]. This has made it more difficult to compare results from different studies. The objective of this study was to evaluate the impact of biodiesel blends on emissions (g/min) and emission factors (g/kWh) of $\text{PM}_{2.5}$, PN, EC/OC as well as particle size distribution from two diesel gensets. The diesel gensets were tested under various engine load conditions with ultra low sulfur diesel (ULSD) fuel and ULSD blended with 5 % (v/v) and 20 % (v/v) biodiesel (B5 and B20).

2. Experimental section

2.1 Diesel gensets and load bank

The two diesel gensets used in this study were SENTRY-Pro Gillette Generators (Elkhart, IN). The first is a 1999 genset equipped with a two cylinder 479 cc Kubota Z482E engine with rated power of 7000 watts. This genset meets the then existing 1995 California emission regulations for utility lawn and garden engines that have since been revised to “small nonroad engine” emission regulations. The second is a 2006 genset equipped with a one cylinder 401 cc Lombardini 15LD400 engine with rated power of 6000 watts. This genset meets the EPA/CARB Tier 2 emission standards.

A load bank designed to dissipate generated electricity as heat provided the proper engine load. The load bank was fabricated in-house and composed of five parallel wired pairs or “banks” of resistance heaters on two 120 VAC (nominal) circuits, allowing discrete load control in 20% increments. With all resistance banks (100% nominal), the average loads on the gensets were about 89% and 75% of the 7000 watt and

6000 watt maximum load ratings of G-1 and G-2, respectively. Genset testing was generally performed over five minute intervals with a fixed load configuration (1 to 5 resistance banks drawing current).

2.2 Fuels

One commercial ultra low sulfur diesel (ULSD) fuel and two biodiesel blend fuels (B5 and B20) were used in this study. The commercial ULSD was obtained from a local gas station. The biodiesel fuels were provided by the New York State Department of Transportation (DOT), which uses these fuels in DOT fleet vehicles. As the composition of diesel fuels varies seasonally, emission testing was performed with both winter and summer fuels on G-1 in February 2010 and April-May 2010, respectively. Emission testing on G-2 was carried out in summer of 2012 with summer fuel only. Fuel analyses were performed by the New York State Department of Agriculture and Markets, with detailed results presented in Table 1.

Table 1. Diesel and biodiesel fuel properties

As shown in Table 1, the S contents in the winter biodiesel blends (13 and 12 ppm for B5 and B20) were higher than the 8 ppm S in winter ULSD. This would not happen when preparing the biodiesel blends in house with stock ULSD and S free 100% biodiesel. However, this could happen with commercial fuel in practice (as in this case) due to several reasons including but not limited to: 1). The diesel stock used for blending at the refinery had a higher S content compared to that not used for blending; 2). Biodiesel blends after blending pick up more S during pipeline transportation as compared to diesel; and 3) 100% biodiesel used for blending might be produced with certain types of animal fat based or yellow grease based feedstock and was not S-free. This was one of the reasons to study the fuel impact with commercially available fuels actually used in the field instead of those prepared in the testing laboratory. The potential impact of elevated S content in winter biodiesel blends will be addressed in results and discussions.

2.3 Emission measurement and sample collection

A constant volume sampler (CVS) system was used to dilute the genset exhaust with filtered room air prior to PM_{2.5} sample collection. For the measurements of PN and size distribution, an in-house fabricated secondary dilution tunnel was used to further dilute the exhaust with a ratio of 20:1 to keep the measurements within the dynamic ranges of the PM instruments (Figure 1). A similar system was previously employed for vehicle emissions testing with details provided [26]. For emission testing, the genset was first operated for 30 min under max load to warm up the engine. It was then tested for emissions with two 5-min emission testing runs under engine loads from 20%-100% of max load with a 20% increment similar to the IOS 8178 Type D2 5-mode steady-state sequence. For each 5 minute testing under a specific genset loading, two replicate PM_{2.5} filter samples were collected using 47 mm Pallflex™ TX40 filters and Pallflex™ Tissuequartz filters for gravimetric PM_{2.5} and EC/OC analysis. The Pallflex™ Tissuequartz used for EC/OC analysis were pre-cleaned prior to sampling by baking at 550°C for 12 hours in individual aluminum foil envelopes and stored in them until actual use. The PM_{2.5} filter samples were collected according to a standard operation procedure developed in accordance to CFR Title 40 Part 1065.190 Particulate Filter Handling and Weighing. Prior to the test, all filters were conditioned for at least 60 min in an environmental chamber maintained at 22±1 °C and a dew point of 9.5±1°C. After stabilization, the filters were weighed by a Sartorius SE2-F microgram balance, specially modified for filter weighing with readability of 0.1 µg housed also in the environmental chamber. Weighed filters were stored in covered petri dishes in the environmental chamber until use. After sampling, filters were returned to the environmental chamber and conditioned for at least 60 minutes before being reweighed. Quartz PM_{2.5} filter samples were stored in the refrigerator before transport to the chemistry lab for EC/OC analysis. A Dekati Mass Monitor (DMM, Dekati Ltd, Tampere, Finland) was used to monitor PM mass concentrations and PM_{1.5} during emission testing of G-1. For testing of G-2, an Engine Exhaust Particle Sizer Spectrometer (TSI, Inc. Shoreview, MN) was used in place of DMM for particle size distribution.

Total PM_{2.5} number emission was measured with a condensation particle counter (CPC, Model 3022, TSI, Inc. MN).

Figure 1. Diesel genset testing sampling diagram

Measurements of EC and OC in PM_{2.5} filter samples were performed using an EC/OC analyzer from Sunset Laboratory, Inc. Because of the large range of PM_{2.5} emission rates under various engine load conditions, the optimal sampling rate designated for PM_{2.5} organic analysis (data not shown) resulted in excessive loading with regard to EC/OC analysis, especially for samples collected under high engine load conditions. To accommodate analysis of heavily loaded samples, it was necessary to develop a method capable of introducing a smaller size of punched sample. Compared to the conventional filter punch of 1.625 cm diameter with total filter area of 2.1 cm² (deposit area 1.06 cm²) required by the EC/OC instrument, a smaller punch with 0.81cm diameter (total filter area of 0.52 cm²) was used, as in the SRM 8785 inter-comparison study [27]. The smaller punch must be squeezed between two blank regular size punches into a sandwich to be able to stay in place when inserted into the quartz tube for analysis. Consequently, EC and OC blanks, especially OC even at trace levels, from these two blank punches have to be corrected for accurate sample OC measurements. This was achieved by firing the two blank punches before making the sample sandwich. Furthermore, a correction factor must be applied to the instrument's calculated results as its software makes EC/OC calculations based on the conventional punch size. The thermal protocol used was a modified STN-NIOSH protocol with increased hold time from 120s to 150s at 920 °C. This was to ensure complete separation of the CO₂ peaks generated from EC and the calibration standard.

3. Results and discussions

3.1. PM_{2.5} Emissions

Engine load, among other factors, plays an important role in $PM_{2.5}$ emission from diesel gensets. Comparisons of gravimetric $PM_{2.5}$ emissions and emission factors from G-1 and G-2 running on diesel and biodiesel blends under various engine load conditions are shown in Figure 2. Emissions of $PM_{2.5}$ from G-1 stayed constant under loadings from 20% to 60% followed by a moderate increase under 80% load and a sharp increase under 100% load (Figure 2A). A gradual increase in $PM_{2.5}$ emission from 20% to 80% load, however, was observed for G-2 followed by a sharp increase under 100% load like G-1. Concentrations of PM measured in mg/m^3 have been found to increase with increased loadings [17, 20] while reduced PM concentration has also been reported [21]. For on-road diesel engines, it has been found that PM emissions increase with engine load [13, 28]. For $PM_{2.5}$ emission factors, emission factor was at the highest level under 20% load and would decrease with increased loadings up to 60% for G-1 and 80% for G-2 before a moderate increase under 100% load (Figure 2B). A reduction in $PM_{2.5}$ emission factor with increased loadings, as reported by others [18], would be concluded if the 100% data is excluded. Our results show that impact of engine load on genset $PM_{2.5}$ emissions can be very different from that with emission factors.

Figure 2. Emissions (A) and emission factors (B) of $PM_{2.5}$ from G-1 (solid) and G-2 (dotted)

Compared to diesel fuel, biodiesel blends had similar $PM_{2.5}$ emissions under three low load conditions of $\leq 60\%$ for both gensets (Figure 2A). Slightly reduced $PM_{2.5}$ emissions with biodiesel blends were observed under 80% and 100% loads, especially for B20 with G-1 and B5 with G-2. The absence of reduced $PM_{2.5}$ emission with B20 under 100% load on G-1 might be caused by changes in engine operation conditions. A similar conclusion can be drawn from the emission factor results shown in Figure 2B where high uncertainties were recorded with the 20% load data sets. Reduced PM emissions with biodiesel have been reported by others [20-21]. Our results show that the impact of biodiesel on $PM_{2.5}$ emission varied with genset load conditions. This will not be a problem for engine testing with a designated test cycle, such as the ISO 8178 C1, 8-mode steady-state test cycle or equivalent, where

emissions are composited results from weighed emissions under different load conditions. However, caution should be exercised when interpreting in-use data from genset testing performed under a single load or multiple but non-cycle load conditions.

Interestingly, the newer G-2 exhibited higher $PM_{2.5}$ emissions and emission factors than G-1 as shown in Figure 2. The G-1, although an earlier model year genset, is equipped with a two cylinder engine and water cooling. The newer G-2 is equipped with a one cylinder engine and less efficient air cooling. The lower $PM_{2.5}$ emission produced by G-1 might be caused by more complete combustion compared to G-2. In addition to $PM_{2.5}$, G-1 also exhibited lower emissions of regulated gaseous of total hydrocarbons (THC), carbon monoxide (CO), and nitrogen oxides (NO_x) compared to G-2 (data not shown).

Emissions and emission factors of $PM_{1.5}$ measured on G-1 have similar trends as $PM_{2.5}$ (data not shown) with diesel and biodiesel blends under various load conditions. The measured $PM_{1.5}$ emission has shown a good correlation ($R^2 = 0.96$) with $PM_{2.5}$ emission. Emission of $PM_{1.5}$ was found approximately 23% lower than $PM_{2.5}$ emission due to the fact that the DMM only measures particles up to the size of 1.5 μm while filters collected PM up to the size of 2.5 μm . Thus, the observed results may indicate that $\sim 3/4$ of total $PM_{2.5}$ emitted from the genset were $PM_{1.5}$ or about 1/4 of total $PM_{2.5}$ were in the 1.5 to 2.5 μm size range.

3.2 PN emissions

Total PN emissions and emission factors from both gensets under various engine load conditions are depicted in Figure 3. PN emissions increased with increasing load on both gensets. Furthermore, PN emission also experienced a sharp increase under 100% load similar to that with $PM_{2.5}$ emission shown in Figure 2A. The higher than expected emission for G-2 with B20 under 80% engine load might be caused by changes in engine operation conditions. Emission factors of PN, however, decrease sharply when engine load increased from 20% to 40%, especially for G-1 (Figure 3B). The PN emission factors would then decrease from 40% to 80% load and flatten out at 100% load. The absence of a moderate increase in

PN emission factors under 100% load, as with $PM_{2.5}$ emissions factors shown in Figure 2B, might indicate the presence of more large particles (further discussion below). In a recent study, Zhang et al. [24] has reported the lowest PN emission factor observed under 50% load. As our data show in Figure 3, PN emissions under various load conditions have a very different pattern compared to PN emission factors. The PN emissions increased with increasing engine load while PN emission factor decreased with increasing load.

Figure 3. Emissions (A) and emission factors (B) of PN from G-1 (solid) and G-2 (dotted)

For the impact of biodiesel on PN emissions, we have noticed a small but consistent reduction in PN emission with biodiesel blends compared to diesel on G-1 over the loading range. Greater reduction of PN emission was recorded with B20 compared to B5. In contrast, biodiesel blends exhibited an increase in PN emissions compared to diesel on G-2 (Figure 3A). As for PN emission factors, the impact from biodiesel blends is unnoticeable on G-1 (Figure 3B). However, a slight increase has been observed with biodiesel blends compared to diesel on G-2, especially under 20% engine load. The impact of biodiesel on the PN emission factors may depend as much on engine load like those for $PM_{2.5}$ (Figure 2B) but rather on engine types. An increase in PN emission factor with biodiesel has been also reported by Zhang et al. [24]. Notably G-1, which had a lower $PM_{2.5}$ emission compared to G-2, exhibited higher PN than G-2.

3.3 PM size distribution

Particle size distribution was measured on G-2 only. Although the sampling was carried out after a $PM_{2.5}$ cyclone, the $PM_{2.5}$ size distribution reported here should represent PM size distribution from the genset as most PM from diesel engines are UFPs. An example of PM size distributions from G-2 with diesel fuel under different load conditions is shown in Figure 4A. Particle size distributions were recorded with a single mode at about 50 to 80 nm under different engine load conditions. Similar particle size distributions were observed with biodiesel blends (data not shown). As shown in Figure 4A, PM

concentration increased with increasing load as that shown in Figure 3A for PN emissions. Also of note is that the diameter of PM with maximum concentration increased with increasing load as shown in Figure 4B. In other words, there are relatively more large particles under elevated load conditions. This is in agreement with the increased PM size under elevated engine load conditions reported by other researchers [19, 24].

Figure 4. PM size distributions with diesel (A) and peak size (B) under various engine load conditions

For the impact of biodiesel blends on particle size distribution, we have noted that more large particles were produced with the use of B20 under high load conditions (Figure 4B). Particle size distributions from G-2 running on diesel, B5 and B20 under 100% load are compared in Figure 5. An increase in PN concentration of larger particles was clearly seen with B20 compared to that with diesel. Increased emissions of smaller particles with biodiesel have been reported by others [19, 23], who also reported that particles generated with biodiesel are more compact than particles generated with diesel fuel. Morphology study of particles is scheduled in our future genset emission testing to investigate this discrepancy.

Figure 5. PM size distribution with diesel and biodiesel blends on G-2 under 20% engine load

3.4 $PM_{2.5}$ EC/OC Emissions

3.4-1 $PM_{2.5}$ EC/OC measurement

As mentioned in the experimental section, a method was developed to analyze heavy load filter samples for EC/OC by introducing a sandwich-type small punch. To evaluate the method, commercially available reference materials with reference EC/OC values were analyzed. The reference materials analyzed include standard reference materials (SRM) developed by the US National Institute of Standard and Technology (NIST) and performance evaluation reference materials from Sunset Laboratory Inc. and KulTech Inc. We analyzed two SRMs from NIST. The SRM 8785 was developed by re-suspending the

NIST Urban Dust SRM 1649a and filtering it with a quartz filter [27]. The SRM 1650 is a diesel PM reference material in non-filter (powder) form and has to be transported onto a filter punch to be introduced into the EC/OC analyzer. Thus, a similar method as that used by Han et al. [29] was employed for sample introduction of SRM 1650. Instead of weighing a small amount of the SRM 1650 directly onto a filter punch, we weighed a small amount of it into a donut-shape hole ($\sim 0.35 \text{ cm}^2$) created at the center of a regular size (2.1 cm^2) quartz punch, which was laid on top of another same size quartz filter punch. After weighing, it was then covered by a third regular quartz filter punch to make a PM sandwich sample ready for EC/OC analysis. In this manner, analysis of the SRM 1650 was carried out by the same method as real samples. The analyses of these reference materials are provided in Table 2 together with their reference EC/OC values.

Table 2. Reference materials EC/OC results

As shown in Table 2, our carbon results (EC, OC and TC) agree reasonably well with the values for both Sunset Laboratory Inc. and KulTech Inc. reference filters. For the five replicate SRM 8785 filters, our average EC, OC, and TC values are slightly higher than the NIST values but are in better agreement with those reported recently by Yang et al. [30] where a different temperature protocol other than the STN-NIOSH was employed. Our analysis of the NIST diesel PM SRM 1650 has shown an OC content of 0.347 g/g, 0.466 g/g of EC, 0.814 g/g of TC, and an EC/TC ratio of 0.57. There are no reference EC/OC values for the SRM 1650 from NIST. Compared to results reported by Han et al [29], our results exhibited higher OC, lower EC, and lower EC/TC ratio. This is expected due to the reported difference between the IMPROVE method measurements and the NIOSH method measurements [8]. The difference in these techniques has also been reflected in the reported EC, OC, and TC results for SRM 8785 by NIST.

3.4-2 PM_{2.5} OC and EC emissions

Emissions and emission factors of OC from G-1 running on diesel, B5, and B20 under various load conditions are shown in Figure 6. Emissions and emission factors of OC from G-2 have similar patterns as G-1 (data not shown). For both gensets, OC emissions varied only slightly under different load conditions (Figure 6A). Similar results for genset OC emissions have been reported by others [17]. For emission factors, a reduction with increasing load was observed as shown in Figure 6B. The highest and most variable OC emission factors were produced under the lowest (20%) load. Emission factor of OC decreased sharply when engine load increased from 20% to 40% with much smaller decrease from 40% to 100% load.

Figure 6. OC emissions (A) and emission factors (B) under various load conditions

The use of biodiesel had limited impact on OC emissions and emission factors as shown in Figure 6. It seems OC emissions were slightly increased with the biodiesel blends under elevated load conditions (Figure 6A). This is in agreement with results reported by Chung et al. [19]. The impact of biodiesel on OC emission factor as shown in Figure 6B was not as obvious as that with OC emissions.

Emissions and emission factors of EC from G-1 running on diesel, B5, and B20 under various load conditions are shown in Figure 7. Emissions of EC from G-2 have similar patterns to G-1 (data not shown). Unlike OC emissions, genset EC emissions elevated as load increased with a sharp increase from 80% to 100% (Figure 7A). This is in accordance with the sharply increased PM_{2.5} emission from 80% to 100% load shown in Figure 2A. Liu et al. [17] also reported a sharp increase of EC emission under maximum genset load. Emission factors of EC exhibited an inverted bell-shape pattern, similar to the PM_{2.5} emission factors shown in Figure 2B, with high emissions at both ends of the loading range (Figure 7B). This is expected as combustion was optimized for the genset to be running most efficiently under medium load conditions.

Figure 7. EC emissions (A) and emission factors (B) under various load conditions

For the impact of biodiesel on EC emissions, moderate reductions were recorded only under 80 and 100% loadings (Figure 7A). A decrease in EC emission factors with biodiesel was also observed over the loading range with minimal reduction under medium load, especially with B20 (Figure 7B). Such clear decrease in EC emission factors wasn't observed with G-2 (data not shown) indicating the dependence on engine type.

3.4-3 $PM_{2.5}$ EC/OC Ratios

The PM EC/OC ratio is source specific and has been used in PM source apportionment studies [9-10, 31-33]. It has also been reported that EC/OC ratios from different mobile sources were variable depending on combustion condition, fuel, and even EC/OC analytical method [9, 16, 32]. A recent European study has suggested over-prediction of direct mobile source OC emissions with the employment of minimum OC/EC ratio of about 1.0 from remote and rural sites [10]. Ratios of $PM_{2.5}$ EC/OC under different engine load conditions are shown in Figure 8 for both gensets with diesel, B5 and B20. There is a clear trend of increasing EC/OC ratio with increased engine load. This is in good agreement with that reported by others [17, 19, 25] but different from that reported by Shah et al. [16] who reported a bell-shaped curve with the highest EC/OC ratio observed at ~ 50% engine load. For the two gensets we tested, EC/OC ratios varied from 0.22 to 4.0 for G-1 and 0.48 to 4.7 for G-2 under different engine load conditions. Our EC/OC ratios are comparable to those reported by others [16-17, 19] for diesel gensets. The low EC/OC ratio of < 0.35 under different load conditions reported by Zhu et al. [25] on 30-kw military diesel gensets might indicate high OC emissions due to rich combustion from these military diesel gensets. An average EC/OC ratio of 1.69 was obtained with our combined EC/OC data from both gensets. This value is close to the average EC/OC ratio of 1.24 reported for nonroad diesel buses but substantially lower than the

EC/OC ratio from on-road diesel vehicles possibly due to the difference between on-road and nonroad diesel engines [33].

Figure 8. Gensets PM_{2.5} EC/OC ratios under various load conditions for G-1 (A) and G-2 (B)

As for the impact of biodiesel on EC/OC ratios, no consistent trend was found for the two gensets tested. While a slight decrease in EC/OC ratio with biodiesel blends has been observed on G-1 compared to that with diesel fuel, especially under high load conditions (Figure 8A), no such decrease was observed on G-2 (Figure 8B) indicating the dependence on engine type. Decreased EC/OC ratios with biodiesel compared to regular diesel have been reported with diesel genset [19] and engines [34-15]. Although source apportionment studies have taken into consideration different EC/OC ratios from various sources as well as different aspects of each source, such as on-road and nonroad gasoline and diesel engines of mobile sources, the impact of biodiesel on EC/OC ratio shouldn't be ignored with consideration of increased biodiesel usage. As the impact of biodiesel depends on gensets' engine types, studies with a relatively large number of gensets are needed to establish the overall impact from biodiesel fuels.

3.5 Impact of sulfur in biodiesel blend

We noted the S contents in the winter biodiesel blends were slightly higher than the 8 ppm S in winter ULSD (Table 1). This could be caused by several reasons as discussed in section 2.2. In commercial practice, the S content may vary between different batches at the refinery but is kept below 10 ppm. This is to ensure the final S content at the pump station is < 15 ppm in compliance with regulation, taking potential contamination during pipeline transportation into consideration. As shown in Table 1, all the diesel fuels and biodiesel blends used in this study have S contents < 15 ppm. As S in fuel contributes to the formation of PM, a logical question is what (if any) effect the slightly higher S content in biodiesel will have on the impact of biodiesel on emissions, especially PM_{2.5} and PN. A comparison of the impacts between winter and summer biodiesel blends on PM_{2.5} and PN emissions is shown in Figure 9.

For both winter and summer fuels, reduced $PM_{2.5}$ and PN emissions were observed with biodiesel blends compared to diesel. Furthermore, similar reductions in $PM_{2.5}$ and PN emissions have been achieved with winter and summer biodiesel blends when compared to diesel. This is expected as: 1) the S content in winter biodiesel blends are only slightly higher (several ppm) than that in diesel; and 2) contributions from fuel S to the formation of $PM_{2.5}$ and PN are limited on diesel engine not equipped with an aftertreatment device such as a diesel particle filter (DPF). Unlike diesel engine with a DPF where sulfate is a major component of PM as most carbonaceous particle are removed by the DPF, $PM_{2.5}$ and PN emitted from gensets tested in this study are mostly carbonaceous with minor contribution from fuel S. In conclusion, no impacts on $PM_{2.5}$ and PN emissions from the slightly higher S content in winter biodiesel blends compared to that in winter diesel were observed.

It is also possible that other component (s) in biodiesel blend may be different from that in diesel stock, such as trace elements. While trace elements are outside the scope of this study, a significant impact from potential differences in other components/properties of the fuel is not expected, based on the almost identical fuel analysis results provided in Table 1.

4. Conclusion

Emissions of $PM_{2.5}$, PN, and EC have been found to increase with increasing load while engine load has limited impact on OC emissions. The ratio of EC/OC was also found to increase with engine load. For emissions factors, however, an “L” or “U” shaped emission pattern was generally observed under various engine load conditions. Emission factor would decrease with increasing load (PN, OC) and then increase under higher load conditions ($PM_{2.5}$, EC). Slight reductions have been observed for $PM_{2.5}$ in both emissions and emissions factors with biodiesel blends, especially under high engine load conditions. While a decrease in PN emission was recorded on G-1 with biodiesel blends, such a reduction was absent

in PN emission factor. Furthermore, an increase in PN emission as well as emission factor with biodiesel blends has been observed on G-2. Biodiesel blends have also been found to have limited impact on OC emission and emissions factor while a reduction in EC emission/emission factor has been recorded, especially under high (80 and 100%) engine load conditions.

Our data with limited testing from two diesel gensets have shown that emissions exhibited different, sometimes reversed, patterns under various engine load conditions compared to those from emission factors. Furthermore, the nonlinear response of emissions to engine load may indicate potential large variations in emissions as a result of small changes in the determined engine load, or as a result of fluctuating loads in response to demand. The impact on emission and emission factor from biodiesel blends was found to depend on not only engine load but also engine type. The fact that engine load and biodiesel may have a very different impact on emission and emission factor asks for precautions to be taken when interpreting emission data. Future studies with relatively large number of gensets and biodiesel of different stocks are needed to address the overall impact from biodiesel fuels.

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References

1. Bell, M. Assessment of the health impacts of particulate matter characteristics. Health Effects Institute Research Report 161 2012.
2. Krewski, D., Jerrett, M., Burnett, R., Ma, R., Hughes, E., Shi, Y., et al. Extended follow-up and spatial analysis of the American cancer society study linking particulate air pollution and mortality. Health Effects Institute Report 2009.
3. Garshick, E., Smith, T., Laden, F. Research directions to improve estimates of human exposure and risk from diesel exhaust. Health Effects Institute Special Report, 113-150, 2002.
4. Gertler, A., Gillies, J., Pierson, W..An assessment of the mobile source contribution to PM10 and PM2.5 in the United States. Water, Air, and Soil Pollution 2000. 123:203-214.
5. HEI. Mobile-source air toxics: a critical review of the literature on exposure and health effects. Health Effects Institute Special Report 16, 2007.
6. NYSERDA. Assessment of carbonaceous PM2.5 for New York and the region. New York State Energy Research and Development Authority Report 08-01, 2008.
7. USEPA . Finalizes regulations for the national renewable fuel standard program for 2010 and beyond. EPA-420-F-10-007, 2010.
8. Schauer, J.. Evaluation of elemental carbon as a marker for diesel particulate matter. Journal of Exposure Science and Environmental Epidemiology 2003.13:443-453.
9. Fujita, E., Campbell, D., Arnott, W., Chow, J., Zielinska, B. Evaluations of the chemical mass balance method for determining contributions of gasoline and diesel exhaust to ambient carbonaceous aerosols. Journal of the Air Waste Management Association 2007. 57,721-740.
10. Pio, C., Cerqueira, M., Harrison, R., Nunes, T., Mirante, F., Alves, C., et al. OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon. Atmospheric Environment 2011.45:6121-6132.
11. Sahu, M., Hu, S., Ryan, P., Le Masters, G., Grinshpun, S., Chow, J., et al. Chemical compositions and source identification of PM2.5 aerosols for estimation of a diesel source surrogate. Science of the Total Environment 2011. 409:2642-2651.

12. Lapuerta, M., Armas, O., Rodriguez-Fernandez, J. Effect of biodiesel fuels on diesel engine emissions. *Progress in Energy and Combustion Science* 2008. 34:198-223.
13. Enweremadu, C., Rutto, H. Combustion, emission and engine performance characteristics of used cooking oil biodiesel-A review. *Renewable and Sustainable Energy Reviews* 2010. 14:2863-2873.
14. Xue, J., Grift, T., Hansen, A. Effect of biodiesel on engine performances and emissions. *Renewable and Sustainable Energy Reviews* 2011. 15:1098-1116.
15. Fazal, M., Haseeb, A., Masjuki, H. Biodiesel feasibility study: An evaluation of material compatibility; performance; emission and engine durability. *Renewable and Sustainable Energy Reviews* 2011. 15:1314-1324.
16. Shah, S., Cocker III, D., Miller, J., Norbeck, J. Emission rates of particulate matter and elemental and organic carbon from in-use diesel engines. *Environmental Science & Technology* 2004. 38:2544-2550.
17. Liu, Z., Lu, M., Birch, M., Keener, T., Khang, S., Liang, F.. Variations of the particulate carbon distribution from a non-road diesel generator. *Environmental Science & Technology* 2005. 39:7840-7844.
18. Shah, S., Cocker III, D., Johnson, K., Lee, J., Soriano, B., Miller, W. Emissions of regulated pollutants from in-use diesel back-up generators. *Atmospheric Environment* 2006. 40:4199-4209.
19. Chung, A., Lall, A., Paulson, S. Particulate emissions by a small non-road diesel engine: Biodiesel and diesel characterization and mass measurements using the extended idealized aggregates theory. *Atmospheric Environment* 2008. 42:2129-2140.
20. Tsai, J., Chen, S., Huang, K., Lin, Y., Lee, W., Lin, C., et al. PM, carbon, and PAH emissions from a diesel generator fuelled with soy-biodiesel blends. *Journal of Hazardous Materials* 2010. 179:237-243.

21. Lee, W., Liu, Y., Mwangi, F., Chen, W., Lin, S., Fukushima, Y., et al. Assessment of energy performance and air pollutant emissions in a diesel engine generator fueled with water-containing ethanol-biodiesel-diesel blend of fuels. *Energy* 2011. 36:5591-5599.
22. Anderson, L. Effects of using renewable fuel on vehicle emissions. *Renewable and Sustainable Energy Reviews* 2015. 47:162-172.
23. Lin, Y., Tsai, C., Yang, C., Wu, C.J., Wu, T., Chang-Chien, G. Effects on aerosol size distribution of polycyclic aromatic hydrocarbons from the heavy-duty diesel generator fueled with feedstock palm-biodiesel blends. *Atmospheric Environment* 2008. 42:6679-6688.
24. Zhang, Z., Balasubramanian, R. Physicochemical and toxicological characteristics of particulate matter emitted from a non-road diesel engine: Comparative evaluation of biodiesel-diesel and butanol-diesel blends. *Journal of Hazardous Materials* 2014. 264:395-402.
25. Zhu, D., Nussbaum, N., Kuhns, H., Chang, M., Sodeman, D., Uppapalli, S., et al. In-plume emission test stand 2: emission factors for 10-to 100-kw US military generators. *Journal of the Air Waste Management Association* 2009. 59:1446-1457.
26. Tang, S., LaDuke, G., Whitby, R., Li, M., Mazurek, M. Comparison of regulated and PM_{2.5} EC/OC emissions from light-duty gasoline, diesel and CNG vehicles over different driving cycles. *SAE International Journal of Fuels and Lubricants* 2009. 1:1290-1306.
27. Klouda, G., Filliben, J., Parish, H., Chow, J., Watson, J., Cary, R. Reference material 8785: Air particulate matter on Filter media. *Aerosol Science & Technology* 2005. 39:173-183.
28. Xue, J. Combustion characteristics, engine performances and emissions of waste edible oil biodiesel in diesel engine. *Renewable and Sustainable Energy Reviews* 2013. 23:350-365.
29. Han, Y., Cao, J., Chow, J., Watson, J., An, Z., Jin, Z., et al. Evaluation of the thermal/optical reflectance method for discrimination between char- and soot-EC. *Chemosphere* 2007. 69:569-574.
30. Yang, F., Huang, L., Duan, F., Zhang, W., He, K., Ma, Y., et al. Carbonaceous species in PM_{2.5} at a pair of rural/urban sites in Beijing, 2005-2008. *Atmos Chem Phys* 2011. 11:7893-7903.

31. Zielinska, B., Sagebiel, J., McDonald, J., Whitney, K., D.R., L. Emission rates and comparative chemical composition from selected in-use diesel and gasoline-fueled vehicles. *J Air Waste Manage Assoc* 2004. 54:1138-1150.
32. Lough, G., Schauer, J.J. Sensitivity of source apportionment of urban particulate matter to uncertainty in motor vehicle emissions profiles. *J Air Waste Manage Assoc* 2007. 57:1200-1213.
33. Green, M., Chow, J., Chang, M., Chen, L.A., Kuhns, H., Etyemezian, V., et al. Source apportionment of atmospheric particulate carbon in Las Vegas, Nevada, USA. *Particuology* 2013. 11:110-118.
34. Zhang, J., He, K., Shi, X., Zhao, Y. Comparison of particle emissions from an engine operating on biodiesel and petroleum diesel. *Fuel* 2011. 90:2089-2097.
35. Gangwar, J., Gupta, T., Agarwal, A. Composition and comparative toxicity of particulate matter emitted from a diesel and biodiesel fuelled CRDI engine. *Atmospheric Environment* 2012. 46:472-481.

Table 1. Diesel and biodiesel fuel properties

Property	ASTM Method	Diesel		B5		B20	
		Winter	Summer	Winter	Summer	Winter	Summer
Cetane Index, calculated	D975	45.9	45.8	47.3	46.3	45.0	47.3
API Gravity @ 60 °F	D287	35.4	34.9	34.8	35.2	36.6	34.3
Flash Point*, °F	D93	137	134	123	122	155	132
Distillation 50% (D), °F	D86-DIES	496	502	515	502	476	523
Distillation 90% (D), °F	D86-DIES	597	603	626	613	628	627
Aromatic Content (wt %)	D1319-AR	30.9	29.0	27.7	31.2	35.3	29.4
Sulfur# (wt %)	D7039	0.0008	0.0007	0.0013	0.0008	0.0012	0.0007
Fatty Acid Methyl Ester (vol %)		<0. 25	<0. 25	5.0	5.1	16.7	17.8

*PMCC Pensky-Martens Closed Cup

Monochromatic Wavelength Dispersive–X-ray Florescence Spectrometry

Table 2. Reference materials EC/OC results

SRMs	Number of Samples (n)	OC (g/g)	EC (g/g)	TC (g/g)	EC/TC
SRM8785	5	0.196	0.081	0.277	0.293
	Info. Value	0.169	0.067	0.236	0.279
SRM1650	8	0.347	0.466	0.814	0.572
	Han et al. (2007)	0.232	0.495	0.727	0.681
Sunset Lab Inc.		OC μg	EC μg	TC μg	EC/TC
	3	130.7	25.0	155.7	0.16
	Info. Value	131.1	27.2	158.3	0.17
KulTech Inc.	Sample ID	OC $\mu\text{g}/\text{cm}^2$	EC $\mu\text{g}/\text{cm}^2$	TC $\mu\text{g}/\text{cm}^2$	EC/TC
	7EC07A11-3	11.39	3.29	14.67	0.22
	Info. Value	11.66	3.41	15.07	0.23
	7EC08C10-1*	18.99	2.73	21.71	0.13
	Info. Value	21.73	2.78	24.52	0.11
	7EC05A04-1	8.77	5.57	14.35	0.39
	Info. Value	7.35	5.92	13.27	0.45
	7EC07B07-1	19.02	6.06	25.09	0.24
	Info. Value	21.97	6.99	28.96	0.24

* Special samples made from diesel PM samples provided by CARB

Figure 1

Figure 2. Emissions (A) and emission factors (B) of PM_{2.5} from G-1 (solid) and G-2 (dotted)

Figure 3. Emissions (A) and emission factors (B) of PN from G-1 (solid) and G-2 (dotted)

Figure 4. PM size distributions with diesel (A) and peak size (B) under various engine load conditions

Figure 5. PM size distribution with diesel and biodiesel blends on G-2 under 20% engine load

Figure 6. OC emissions (A) and emission factors (B) under various load conditions

Figure 7. EC emissions (A) and emission factors (B) under various load conditions

Figure 8. Gensets PM_{2.5} EC/OC ratios under various load conditions for G-1 (A) and G-2 (B)

Figure 9. Comparisons of winter and summer biodiesels on PM2.5 (A) and PN (B) emissions