Title
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Journal
Environmental Science & Technology, 45(6)

ISSN
0013-936X 1520-5851

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Publication Date
2011-03-15

DOI
10.1021/es1026954

Peer reviewed

Environmental Science & Technology

ARTICLE

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Real-Time Gaseous, PM and Ultrafine Particle Emissions from a Modern Marine Engine Operating on Biodiesel

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Supporting Information

ABSTRACT: Emissions from harbor-craft significantly affect air quality in populated regions near ports and inland waterways. This research measured regulated and unregulated emissions from an in-use EPA Tier 2 marine propulsion engine on a ferry operating in a bay following standard methods. A special effort was made to monitor continuously both the total Particulate Mass (PM) mass emissions and the real-time Particle Size Distribution (PSD). The engine was operated following the loads in ISO 8178-4 E3 cycle for comparison with the certification standards and across biodiesel blends. Real-time measurements were also made during a typical cruise in the bay. Results showed the in-use nitrogen oxide (NOx) and $PM_{2.5}$ emission factors were within the not to exceed standard for Tier 2 marine engines. Comparing across fuels we observed the following: a) no statistically significant change in NO_x emissions with biodiesel blends (B20, B50); b) ~16% and ~25% reduction of $PM_{2.5}$ mass emissions with B20 and B50 respectively; c) a larger organic carbon (OC) to elemental carbon (EC) ratio and organic mass (OM) to OC ratio with B50 compared to B20 and B0; d) a significant number of ultrafine nuclei and a smaller mass mean diameter with increasing blend-levels of biodiesel. The real-time monitoring of gaseous and particulate emissions during a typical cruise in the San Francisco Bay (in-use cycle) revealed important effects of ocean/bay currents on emissions: NO_x and CO_2 increased 3-fold; $PM_{2.5}$ mass increased 6-fold; and ultrafine particles disappeared due to the effect of bay currents. This finding has implications on the use of certification values instead of actual in-use emission values when developing inventories. Emission factors for some volatile organic compounds (VOCs), carbonyls, and poly aromatic hydrocarbons (PAHs) are reported as supplemental data.

INTRODUCTION

Several studies[1−6] across the world indicate that the emissions from sources in ports adversely affect the air quality in the populated regions around them. These sources include ocean going vessels, harbor-craft, locomotives, cargo handling equipment, and trucks. Though ships are the largest contributors to port emissions, harbor-craft form a significant portion of the inventory. Harbor-crafts include ferries, excursion boats, tugboats, towboats, crew and supply vessels, work boats, fishing boats, barges, and dredge vessels.

Corbett's study[7] on waterborne commerce vessels in the United States shows that ~65% of the marine nitrogen oxide (NO_x) emissions, in the top 20 states with waterborne commerce, are from marine engines operating on inland waterways. Harbor-craft (e.g., barges and tow-boats) are the most common commercial vessels operating in these waterways.[8] Furthermore in regions like New York-New Jersey, Boston, or San Francisco, ferry transportation is a significant contributor to the local emissions inventory.[9,10] As a result harbor-craft emissions have significant effects on local and regional air quality even in inland areas.

Most harbor-craft are powered by marine compression ignition engines with a displacement <30 L cylinder^{-1}. Emissions from these engines are regulated by U.S Environmental Protection Agency's (EPA) code of federal regulation title 40 parts 85−94. Early studies on harbor-craft emissions focus on older engines operating on high sulfur fuels.[11,12] To meet current EPA standards, modern EPA Tier 2 engines are required to operate on low sulfur (<500 ppm S) diesel or ultralow sulfur diesel (ULSD) (<15 ppm S). However, emissions data Tier 2 marine engines is scarce.

One of the methods to reduce particulate matter (PM) emissions from diesel engines is the use of biodiesel. Most studies[13−23] on biodiesel fuels focus on engine/chassis dynamometer tests of on-road engines operating predominantly on transient cycles. These studies show small increases in NO_x emissions and large reductions in carbon monoxide (CO) and particulate matter (PM) mass emissions with increasing blend-levels of biodiesel. Research on biodiesel effects on marine diesel engines is limited, with one study [24] showing reductions in both NO_x and CO emissions.

This research provides in-use gaseous and $PM_{2.5}$ emissions from a modern marine propulsion engine on a ferry operating on California ultra low sulfur diesel (B0) and blends of this diesel

Received: August 7, 2010
Accepted: January 12, 2011
Revised: December 16, 2010
Published: February 23, 2011

with biodiesel: B20 and B50. The paper includes an in-depth analysis of biodiesel effects on both regulated and unregulated emissions (e.g., elemental and organic carbon (EC/OC), PM number and size distribution, carbonyls, C_{10}-C_{30} hydrocarbons (HCs), and poly aromatic hydrocarbons (PAHs)). Additionally gaseous and particulate emissions were monitored during a typical cruise in the San Francisco bay providing valuable insight into the effects of ocean currents on in-use emissions. These results have significant implications on the use of certification values for emissions inventories.

EXPERIMENTAL DETAILS

Engine Specifications. The harbor-craft chosen for this test program has two propulsion and two auxiliary engines. The tested propulsion engine is a Category 1, four-stroke marine diesel engine meeting EPA Tier 2 emissions certification. Specifications of the test engine are as follows: Make/Model: 2007 Cummins QSK19-M, Maximum Power Rating: 500 hp, Rated Speed: 1900 rpm, Number of Cylinders: 6, Total Engine Displacement: 18.9 L, Engine hours at start of testing: 3550.

Engine parameters monitored during the testing include engine load and speed, intake air temperature and pressure, and instantaneous fuel flow. Values were continuously recorded from the engine's electronic control module (ECM) using the Cummins Inline 5 adapter and the Insite software Version 7.02.0.362.

Fuels. The engine was operated on three fuels: B0 and two blends of a soy-based biodiesel (B20 and B50). Selected fuel properties are provided in the Supporting Information (Tables SI-2 and SI-3).

Test Matrix. The engine was tested following the steady state load points in the ISO 8178-4 E3 duty cycle. Another steady state mode, idling in gear, was added to the test matrix (Table SI-4), as this mode forms a significant part of the activity of many harbor-craft. The steady state modes provide information on the in-use emissions factors and comparison of emissions across fuels and with the certification values.

The engine was tested while the harbor-craft sailed in the bay. With practical considerations of field testing, the actual load on the engine differed by up to ±5% from the target load. Biodiesel blends have lower energy content than diesel; therefore, the maximum achievable load with B50 was 94% rather than the 100% specified in ISO. To maintain uniformity and reduce uncertainty in the comparison of emissions across fuels, B20 and B0 were also tested at the 94% load instead of 100%.

Regulatory agencies are moving toward the use of in-use emissions. This research measured in-use gaseous and PM emissions from the engine during a typical cruise of the ferry in the San Francisco bay. Since the ferry is normally fueled with B20, the engine was operated on B20 during the in-use testing.

Emission Measurements. The gaseous and $PM_{2.5}$ mass emissions measurements were made using a partial dilution system equipped with a single venturi following the ISO 8178-1 protocol. Schematic of the test setup and details of the sampling and analysis are provided in the Supporting Information (SI).

Gaseous emissions, NO_x, CO, and CO_2, were measured in the raw and dilute exhaust. CO_2 measurements were used to determine the sample dilution ratio (DR). The CO_2 DR was verified to be within 10% of the NO_x DR per the ISO protocol. Sampling of $PM_{2.5}$ mass, carbonyls, C_{10} to C_{30} HCs, and PAHs were performed in the dilute exhaust. $PM_{2.5}$ mass was collected on 2-μm Teflo 47 mm filters for gravimetric analysis, while Pall Tissuquartz filters collected $PM_{2.5}$ for subsequent PM speciation. TSI's DustTrak was used on the dilute exhaust to provide a real-time measure of $PM_{2.5}$ mass.

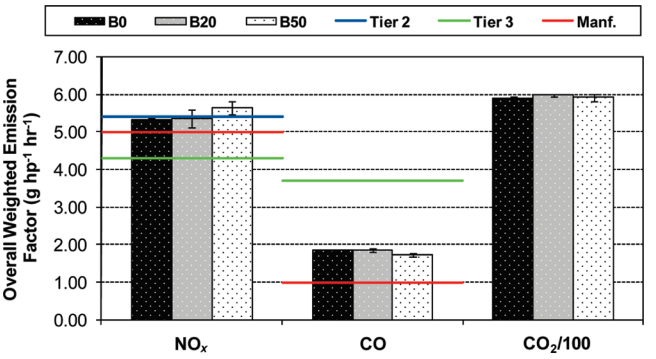

Figure 1. Overall weighted emissions factors (g hp^{-1} h^{-1}). **Note:** Tier 2 and 3 standard shown on the NOx bars are for NO_X+THC, Tier 2 and Tier 3 standard for CO are the same, Manf.: Manufacturer's typical values for this engine family.[26]

Particle size distribution (PSD) was measured using a fast Scanning Mobility Particle Sizer (fSMPS).[25] The concentration in the dilute exhaust (DR ~3.0) was too high for PSD sampling; therefore, a point mixing secondary dilution system provided an overall dilution of 24 ± 2.5. Filtered ambient air without temperature or humidity control was used for dilution. Raw and dilute NO_x measurements were used to determine this overall DR. PSD is dependent on DR and other dilution parameters; therefore, PSD data obtained in this study may vary from PSD in the harbor-craft plume.

Volume concentration data obtained from the fSMPS was plotted against the gravimetric PM mass to determine the effective density of the PM. Calculation details for this effective density, gaseous and PM emission factors (g hp^{-1} h^{-1}), and in-use emissions (g h^{-1}) are provided in the SI.

RESULTS AND DISCUSSION

Steady State Loads. The first stage of this study involved the in-use testing of the propulsion engine on three fuels B0, B20, and B50 following the steady state load points in the ISO certification cycle. This testing was used to determine the effect of biodiesel on engine exhaust emissions as well as to evaluate whether the engine meets the EPA Tier 2 standard in its real-world application (engines are certified on an engine dynamometer).

Gaseous Emissions. Figure 1 shows the overall weighted average emission factors for CO_2, NO_x, and CO. The modal data are provided in Figure SI-4. Duplicate readings were taken at each load point. The error bars in the figures indicate the range of measurement.

CO_2 emissions factors range from 557 to 601 g hp^{-1} h^{-1}, typical of four stroke diesel engines. No significant variation in the CO_2 emission factors was observed across fuels.

NO_x emission factors varied from 5.2 to 5.7 g hp^{-1} h^{-1} across engine loads and fuels. The measured overall weighted average NO_x emission factor 5.33 ± 0.04 g hp^{-1} h^{-1} (for B0) was greater than the manufacturer's engine family value [26] of 4.99 g hp^{-1} h^{-1}. It is important to note that engine manufacturer's typically test their engines under highly controlled conditions on an engine dynamometer. This study, however, was performed on an in-use engine operating on a harbor-craft. As a result, the emission

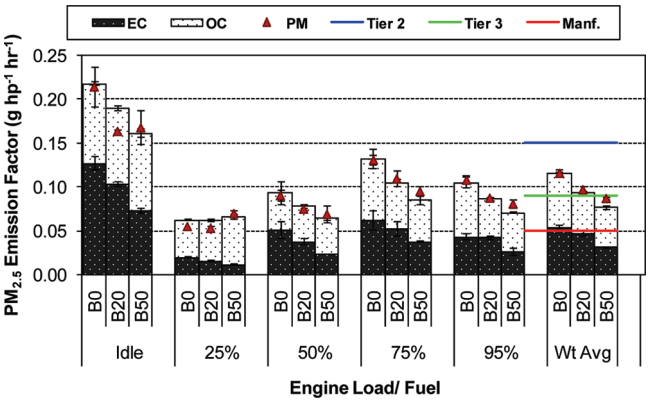

Figure 2. Total and speciated $PM_{2.5}$ mass emission factors (g hp^{-1} h^{-1}). **Note**: Manf.: Manufacturer's typical values for this engine family.[26]

factors measured in this study for NO_x, CO (below), and $PM_{2.5}$ (below) are significantly higher than the typical values reported by the manufacturer from engine dynamometer testing (Figures 1 and 2).

Summing up the measured NO_x emission factor with the manufacture's typical value[26] for total hydrocarbon (THC) emissions of 0.14 g hp^{-1} h^{-1}, we get a NO_x+THC emission factor of 5.47 g hp^{-1} h^{-1}. This emission factor is greater than EPA Tier 2 emissions standard for NO_x + THC 5.4 g hp^{-1} h^{-1} but lower than the 6.48 g hp^{-1} h^{-1} not to exceed standard.

Studies of on-road[13−23] engines show NO_x increases of −5.9% to 6.6% for B20 and 2% to 17% for B50. Roskilly et al., 2008 shows a 1.1 to 24.3% reduction in NO_x emissions with B100 on two marine engines.[24] Due to variability in in-use testing (standard deviation/range of up to 6%), no statistically significant change was observed in the weighted average NO_x emission factor across fuels (t test p value = 0.96 for B20, 0.38 for B50).

Modal CO emission factors were <1.0 g hp^{-1} h^{-1} for all engine loads except at 75% where it was ∼2.7 g hp^{-1} h^{-1}. The observed trend (including the 75% load) is consistent with the data trend obtained for the engine family provided by the engine manufacturer. The measured overall weighted CO emission factor of 1.84 ± 0.04 (for B0) was almost twice the manufacturer's typical value[26] of 0.99 g hp^{-1} h^{-1} but well below the Tier 2 and Tier 3 standard of 3.7 g hp^{-1} h^{-1}. Research on on-road engines[13−23] show CO reductions of 3−30% with B20, 18−40% with B50 while one study[24] on marine engines shows small increases (<3.3%) in CO emissions. The weighted average CO emission factor of the test engine did not change significantly when switching to B20 (p = 0.92); it did however decrease by 7% with B50 (p = 0.07).

Total $PM_{2.5}$ Mass Emissions. The $PM_{2.5}$ mass emission factors at ISO loads (Figure 2) range from 0.053 to 0.131 g hp^{-1} h^{-1}. The emission factor at idle was higher (0.164 to 0.214 g hp^{-1} h^{-1}). The weighted average $PM_{2.5}$ emission factor 0.116 ± 0.004 g hp^{-1} h^{-1} (for B0) was double the manufacturer's typical value[26] of 0.05 g hp^{-1} h^{-1} but less than the Tier 2 PM standard of 0.15 g hp^{-1} h^{-1}. When operated on B50, the engine attained the Tier 3 PM standard but exceeded the Tier 3 NO_x+THC standard.

The weighted average $PM_{2.5}$ emission factor reduces by 16% with B20 and 25% with B50. On-road engine studies[13−23] across different engine technologies show a wide range of PM reductions with biodiesel (4% to 37% with B20 and 4% to 63% with B50). The results of this study are comparable to US EPA's[16] report on comprehensive analysis on biodiesel effects, which predominately consists of 4-stroke diesel engines.

The modal data for the ISO load points (25% to 94%) show that the percent reduction in PM increases with increase in engine load. In fact, at the 25% load point, PM emissions do not change with B20 and increase by 28% with B50. The percent reductions at idle (B20 and B50) were similar to that at high engine loads. Chang et al., 1998[27] observed similar trends of increasing PM at low engine loads with biodiesel.

Elemental and Organic Carbon fractions of $PM_{2.5}$ Mass Emissions. $PM_{2.5}$ emissions from diesel exhaust were speciated into elemental and organic carbon. The EC emission factors at ISO modes range from 0.012 to 0.062 g hp^{-1} h^{-1}; the OC emission factors ranged from 0.040 to 0.071 g hp^{-1} h^{-1}. As expected emission factors at idle were higher: 0.073 to 0.128 g hp^{-1} h^{-1} for EC and ∼0.089 g hp^{-1} h^{-1} for OC (Figure 2).

An ∼23% reduction in EC was observed with B20 at engine loads ≤50%. No significant change was observed at the higher loads. B50 reduced EC by 38% to 53% across all loads. Other researchers have observed reductions in soot,[17,28] nonvolatile PM,[21] and EC[29] with biodiesel blends. OC showed similar trends with B20 and B50: 27% to 33% reduction at the two highest loads, no significant change at idle and 50%, and an 8% (B20) and 28% (B50) increase at the 25% load. This behavior of the OC resulted in the no reduction/increase in PM at the 25% load with B20 and B50 biodiesel blends, respectively. Chang et al., 1998 observed increases in soluble organic fraction of PM mass which resulted in increase of PM at low engine loads.[27] The overall weighted average emission factors show the following: 14% and 42% reduction in EC; 23% and 27% reduction in OC, for B20 and B50, respectively.

$PM_{2.5}$ mass from B0 and B20 had similar OC/EC ratios: ∼2.5 at 25% load and ∼1.0 at all other loads. $PM_{2.5}$ mass from B50 had a higher OC/EC ratio: ∼4.5 at 25% load and ∼1.4 at other loads. Previous research has also shown increased OC/EC ratios,[29] soluble organic fractions,[20,27,28] and volatile organic fractions[17,21,30] of PM mass with biodiesel content.

A high resolution Time of Flight Atomic Mass Spectrometer (ToF-AMS) was used to estimate the OM/OC ratio of the water-soluble organic fraction of PM mass (see the SI for details). The OM/OC ratio in the $PM_{2.5}$ mass increased from ∼1.22 (B0) to ∼1.36 (B50) with increasing biodiesel blends. Other studies have shown/used similar OM/OC ratio of 1.2 to 1.3 for diesel particulate.[31,32] Using the measured OM/OC factor, OM was determined for each sample point. An excellent correlation (r^2 = 0.99) was obtained between total gravimetric $PM_{2.5}$ mass and the sum of EC and OM for all three fuels (Figure SI-5). The total $PM_{2.5}$ mass was found to be 10% less than the sum of the EC and OM. This can be attributed to the positive adsorption artifact of Tissuquartz filters used for the carbon analysis.[32,33]

PM Size Distribution. Figure 3 shows the particle size distribution (PSD) for three engine loads. Data for Idle and 94% loads are provided in the SI (Figure SI-6). The number concentration curves in Figure 3 represent seven minute averages of fSMPS data. The dN/dlogDp standard deviation (not shown) was ±10%. Volume concentration curves show a log-normal fit of instrument data.

All three fuels show particles in the accumulation mode with number electrical mobility mean diameters ranging from 63 to 82 nm at the ISO modes and 89−99 nm at Idle (Figures 3 and SI-6). The accumulation mode particles primarily consist of carbonaceous soot agglomerates formed during direct combustion.[34]

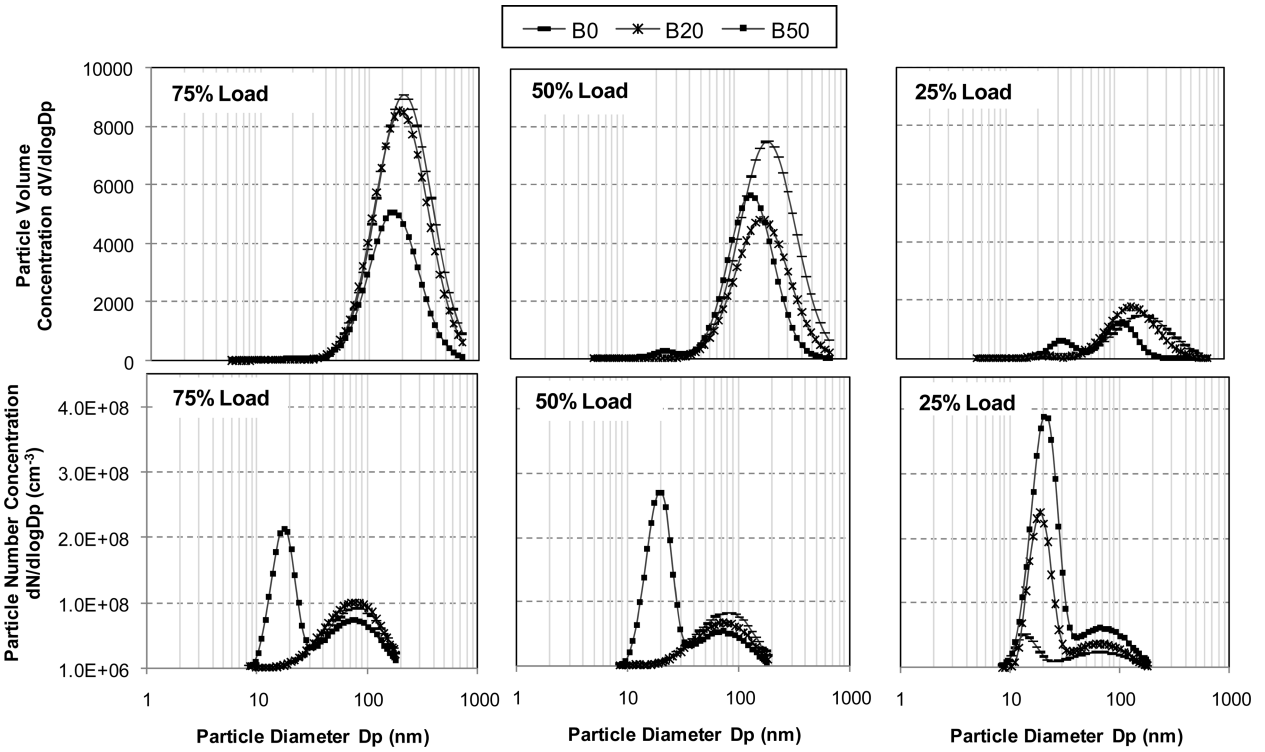

Figure 3. Particle size distribution. **Note**: Particle number concentration curves are instrument readings, particle volume concentration curves are log-normal fit of the instrument reading. The curves represent averages over a 7 min sample time. Standard deviation of measurement over the 7 min period were ±10%.

Particles in this mode are the primary contributors to the total $PM_{2.5}$ mass. Results show reductions in the volume mean diameter and total number concentration in the accumulation mode with increasing biodiesel blends. This is consistent with trends seen in gravimetric $PM_{2.5}$ mass emissions. Other researchers have observed a similar trend of particle size and number reduction in accumulation mode with biodiesel.[35,36]

Nucleation mode particles (<50 nm) consist primarily of volatile hydrocarbon and sulfate particles[34] along with some nonvolatile ash/carbonaceous particles.[35,37] Since fuels used in this program had <15 ppm of sulfur, it is reasonable to assume that most of the nuclei will be formed by volatile hydrocarbons. The formation of these nuclei is very sensitive to sampling and dilution conditions.[38] Dilution conditions were kept constant during the test program, to help provide a robust data set for comparative analysis across fuels and engine loads. Bimodal PSDs with nucleation mode particles in 14−26 nm range were observed with B0 and B20 at the 25% engine load and with B50 at all loads (Figures 3 and SI-6). As discussed earlier, these engine load/fuel conditions had a higher OC/EC ratio. This indicates that there may not be sufficient solid carbonaceous agglomerates to adsorb volatile hydrocarbons, thereby facilitating the formation of fresh nuclei. This theory is corroborated by previous research[38] that suggests suppression of the nucleation mode by adsorption of volatile hydrocarbon on the solid carbonaceous agglomerates in the accumulation mode.

Laboratory studies[28,35,36,39] on PSD from diesel engines show similar bimodal distribution with biodiesel and biodiesel blends. These studies also observe an increase in particle number concentration in the nucleation mode and reduction in the accumulation mode with increasing blends of biodiesel. This study confirms the finding for an in-use marine engine showing a 1.7 to 3.5 times increase in the total particle number with B50 compared to B0.

Studies[40,41] on health effects of nanoparticles suggest that smaller particles have increased biological activity because of larger specific surfaces. This indicates a need for further research on the nature and health effects of these nucleation particles formed by diesel versus biodiesel.

PM from B0 (volume mean diameter ~212 nm) was found to have an effective density of 0.53 (calculation details in the SI). Park et al., 2003[42] observed a similar effective density of 0.39 to 0.55 for diesel PM having a mobility mean diameter of 220 nm. B20 and B50 PM show effective densities of 0.49 and 0.77, respectively (Figure SI-2). The increase in effective density with B50 can be attributed to a reduction of particle mean diameter[42] and increase in the OC/EC ratio (indicative of a larger semivolatile OM fraction) with biodiesel PM. (Semivolatile OM can be adsorbed into the surface and voids of the carbonaceous agglomerate particles making them more dense.)

Carbonyls. The total carbonyl emission factor varied from 0.005 to 0.060 g hp^{-1} h^{-1} across engine loads and fuels (Figure SI-7). These values are in line with carbonyl emission factors observed by other researchers.[30,43−45] These emissions were the lowest at the 75% engine load and highest at Idle. Formaldehyde and acetaldehyde were the most significant fractions accounting for >75% of the total carbonyls. Studies on biodiesel effects on carbonyl emissions show varied results. Some[30,43,46,47] see an increase in carbonyl emissions with increasing biodiesel blends, few others[44,45] show reductions, and one study[48] shows increase in formaldehyde along with a reduction in acetaldehyde. In this study, no statistically significant changes (p < 0.05, 95% confidence limit) were observed in the total carbonyl emissions with increasing blends of biodiesel, except at the 94% engine load. At

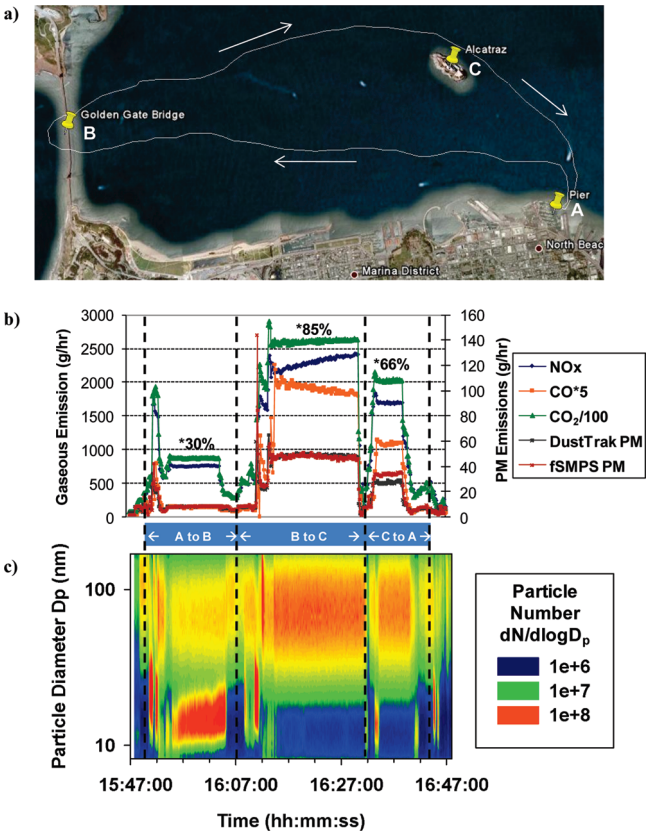

Figure 4. Real time emissions trace on a typical cruise a) approximate route for cruise, b) gaseous and PM emissions, and c) particle size distribution. **Note:** *Engine load.

this load B20 had no effect, but the total carbonyl emission factor doubled for B50.

C_{10} to C_{30} Hydrocarbons, Naphthalene, and Poly Aromatic Hydrocarbons. Total gas and particle phase emissions factors for the C_{10} to C_{30} HCs and PAHs are provided in Figure SI-8. Emission factors of these compounds are similar to those reported in other studies.[43,44,49] No significant trends were seen across fuel types. A larger variation in emissions was observed at Idle probably due to changes in engine load (31 kW for B0, 28 kW for B20, and 45 kW for B50). Previous studies[43,44,49−51] on on-road engines have shown a reduction in PAH emissions with biodiesel.

In-Use Cycle. Engine certification cycles are not always representative of the activity of the engine in its real world application. As a result regulatory agencies are moving toward establishing in-use duty cycles to improve the accuracy of emissions inventories.

During this study, an attempt was made to understand the actual in-use emissions of the propulsion engine on the ferry during its standard operation. For this purpose, gaseous and PM emissions were monitored on a second by second basis during a typical cruise in the San Francisco Bay. The engine was operated on B20, the fuel used on the vessel for daily operations. The ferry sailed from the San Francisco pier to the Golden Gate Bridge to Alcatraz and back (Figure 4a). The direction of the bay/ocean currents was outward from the pier to the bridge.

A real-time trace of the gaseous and $PM_{2.5}$ emissions in g h^{-1} is shown in Figure 4b. Total $PM_{2.5}$ emissions obtained using the fSMPS and DustTrak were in good agreement. The bay current had a significant effect on the engine load during the cruise. Though the boat was sailing at a constant speed, the engine load was 30% when the ferry sailed from the pier to the bridge, 85% from the bridge to Alcatraz, and 66% from Alcatraz back to the pier. Comparing emissions (in g h^{-1}) from the pier to the Golden Gate Bridge to those from the bridge to Alcatraz, we found a 3-fold increase in NO_x and CO_2, a 13-fold increase in CO, and a 6-fold increase in the total $PM_{2.5}$ mass emissions. The same comparison on a fuel basis (g per kg fuel) showed no significant change in NO_x and CO_2, four and a half-fold increase in CO, and a 2-fold increase in $PM_{2.5}$ mass. The differences in these values would make a significant change in the inventories which typically report emissions in g h^{-1}.

The effect of ocean current, which translates to change in engine load, is also seen in the real-time PSD (Figure 4c). The bulk of particles are found in the 75−80 nm range, the total number varying as a result of the engine load. During the journey from the pier to the bridge a large number of ultrafine particles (∼17 nm) were seen because the engine was operating at a low load (near 25%) where the OC/EC ratio is high enough to induce nucleation.

This analysis clearly shows that the effect of ocean currents is a major factor that needs to be considered during the development of emission inventories, and in-use measurements provide the necessary data for accurate inventories.

■ ASSOCIATED CONTENT

Supporting Information. A detailed description of emissions measurement methods; calculations of modal and overall emission factors, in-use emissions (g h^{-1}) and effective density of PM; list of references for test methods and certification standards; tables showing fuel properties and the test matrix; figures displaying modal gaseous emission factors, PSD for 94% load and Idle, correlation for real-time PM mass from DustTrak, effective density of PM, emissions of carbonyls, PAHs and C_{10} to C_{30} HCs. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

The authors would like to thank California Air Resources Board for their financial support, Mr. Charles Bufalino and Mr. Kurt Bumiller for their efforts in the test preparation, the ferry crew and administrative staff for their generous help on-board the vessel, and Mr. Virgilio Afan, Ms. Kathalena Cocker, Mr. James Theodore Gutierrez, Mr. Mohammad Yusuf Khan, and Dr. Sindhuja Ranganathan for their support in preparation and analysis of the sample media.

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