Longitudinal study of the performance characteristics and environmental impacts of renewable diesel fuels in marine engines

Final Report

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By

The Regents of the University of California
University of California, San Diego
Scripps Institution of Oceanography

Principal Investigator
Dr. T Bruce Appelgate Jr.
University of California – San Diego
9500 Gilman Drive, Dept 0210
La Jolla, CA, 92093-0210
tel 858-534-2220
fax 858-534-1635
email tba@ucsd.edu

Co-Principal Investigator
Professor Lynn Russell
University of California - San Diego
9500 Gilman Drive, Dept 0221
La Jolla, CA 92093-0221
Tel 858-534-4852
Fax 858-534-4851
Email lmrussell@ucsd.edu

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Executive Summary

This study monitored and assessed the operational viability, mechanical effects, and emissions of renewable drop-in marine diesel fuel in conventional marine diesel engines aboard a working oceanographic research vessel operated by Scripps Institution of Oceanography at the University of California, San Diego. Dr Lynn Russell conducted quantitative measurements to address fundamental questions about the environmental and performance characteristics resulting from sustained use of 100% (unblended) renewable diesel fuel. On an ongoing basis over the length of the study we monitored engine performance using autonomous ship-mounted instruments that measured criteria pollutants NOx and CO. We also conducted comprehensive organic and black carbon aerosol measurements to characterize the difference in aerosol emissions between conventional and renewable diesel fuels, using an existing seagoing containerized laboratory deployed twice during the study. Renewable diesel fuel holds potential for reducing pollutants and greenhouse gasses, and the results are being shared with stakeholders to evaluate the feasibility, costs and benefits of long-term use of renewable diesel fuel aboard seagoing vessels.

This program demonstrated that renewable diesel is viable as a drop-in fuel for regular use by vessels in California. Working with the fuel manufacturer and local fuel delivery services, we established a procurement pathway that evolved such that fuel could be regularly delivered in adequate quantities to support normal vessel operations using 100% renewable diesel. Over the 15-month duration of the project, R/V *Robert Gordon Sproul* used a total of 52,500 gallons. During this project, *Robert Gordon Sproul* conducted 39 regular oceanographic research and education missions, spanning 89 operational days at sea, covering more than 14,400 nautical miles, and involving 527 scientists and students.

An evaluation of gas and particle emissions from R/V Robert Gordon Sproul powered by diesel and biodiesel was conducted during 2014 and 2015, including two dedicated particle-sampling cruises: the 2014 cruise (29 September to 3 October in 2014) and the 2015 cruise (4 to 7 September and from 26 to 28 September in 2015). CO, CO_2, NOx were measured in the ship stack and particle number and mass concentrations, black carbon number and mass concentrations, and non-refractory organic mass concentrations were measured from ship plume using a suite of real-time instruments in an aerosol-measurement container van. The vessel was operated at different engine speeds (1600rpm, 1300rpm, 1000rpm and 700 rpm) to study the emissions characteristics of the vessel at various engine speeds when powered by diesel and biodiesel. The data obtained from these engine cycle tests were used to estimate the emission factors. Further, the changes in composition of non-refractory organic aerosol particles in the ship plume due to aging (photochemical reactions) in the atmosphere were also characterized.

The results indicate that NOx and CO emissions were lower for biodiesel compared to diesel at lower engine speeds (700 and 1000 rpm). A reduction of 20% CO and 13% NOx was observed with the usage of biodiesel when the engine was operated at 700 rpm. However, CO (Diesel: 4.01 ± 0.1 g/kg-fuel; Biodiesel: 3.91 ± 0. 2 g/kg-fuel) and NOx (Diesel: 51.06 ± 0.8 g/kg-fuel; Biodiesel: 50.65 ± 2 g/kg-fuel) emissions are nearly the same for both the fuels at 1600 rpm. Particle emissions increased by around 90% at 1600 rpm with usage of biodiesel and are nearly the same for both the fuels at 700 rpm. Particle number and mass emissions at 700 rpm are 1.25 ± 0.3 x 1016 (kg-fuel)-1 and 2.26 ± 0.05 (g/kg-fuel), respectively, for biodiesel and 1.34 ± 0.3 x 1016 (kg-fuel)-1 and 2.21 ± 0.5 (g/kg-fuel), respectively, for diesel. Black carbon number and

mass emission factors increased nearly by a factor of 2 and 1.5 times respectively with the usage of biodiesel at all engine speeds, indicating less complete combustion and more condensable emissions for biodiesel compared to diesel. While there are no significant composition changes in particle emissions from diesel and biodiesel, biodiesel has higher emissions of organic components compared to diesel. Slight differences in the composition of aged aerosols were observed between diesel and biodiesel emissions: carbonyl functional groups are increased in aged diesel particles but increases were not detectable for aged biodiesel particles.

To summarize, CO and NOx emissions were reduced for biodiesel at lower engine speeds, but the particle emissions are similar. Particle emissions increased for biodiesel at higher engine speeds, but CO and NOx emissions were nearly the same. These results indicate that biodiesel has lower emissions at lower engine speeds (700 and 1000 rpm) but diesel has lower emissions at higher engine speeds (1600 rpm).

The results of these studies are presented in posters at three scientific meetings (Price et al., 2015; Price et al., 2016a; Betha et al., 2016a) and in two manuscripts in preparation (Price et al., 2016b; Betha et al., 2016b). The sampling approach was also documented for the public in local periodicals by science journalist Judith Garfield (http://www.sdnews.com/pages/full_story/push?article-Scripps+research+on+biofuels+hits+close+to+home%20&id=26452067&instance=stories.).

General Approach

Our proposal called for using a variety of monitoring methods, in order to quantify as many products as the budget will allow. In order to characterize the difference in aerosol emissions between petroleum-based and renewable diesel fuels we conducted organic and black carbon aerosol measurements during a pair of dedicated sampling cruises, during which we were able to compare emissions from conventional ultra-low sulfur diesel with renewable diesel. For these cruises we deployed a seagoing containerized laboratory, developed by Dr. Russell for her research at Scripps Institution of Oceanography. The portable laboratory van is a converted ISO 20-foot shipping container that houses a suite of instruments, which can be craned onto research vessels and be secured on deck. During these dedicated cruises, we sampled the exhaust at the stack, and also sampled the exhaust plume after it had remained in the atmosphere for a length of time, which we accomplished by chasing the plume downwind with the ship in a manner similar to the 2011 E-PEACE program, which measured a plume of organic aerosol produced and emitted into the marine atmosphere from a research vessel [*Russell et al., 2012; Wonaschutz et al., 2013*]. By sampling the plume downwind, we could characterize the changes in composition of non-refractory organic aerosol particles in the ship plume due to aging (photochemical reactions) in the atmosphere.

Progress and Milestones

Milestone progress

Activity	Original	Revised	Actual
Procure renewable diesel fuel	Nov./Dec, 2013	SEP 2014	SEP 2014
Install instrumentation on the vessel	Nov./Dec, 2013	SEP 2014	SEP 2014
Begin fuel tests on board the vessel	Nov./Dec, 2013	SEP 2014	SEP 2014
End fuel tests on board the vessel	Nov. 2013 - TBD	OCT 2015	DEC 2015
Submit final report	Mid-March. 2015	JAN 2016	MAR 2016

Delays in the originally-planned schedule resulted from the timing of individual scientific research programs that use the ship, fuel availability, and factors beyond our direct control. The duration of our test period was longer than originally envisioned due to the unexpected low price of fuel, which enabled us to purchase a greater volume of fuel and operate for a longer period.

Phase 1. Baseline observations using ultra-low sulfur petroleum marine diesel

Complete. These observations were conducted during *Sproul* cruise SP1406.

Phase 2. Observations using 50:50 blend of fuels

Completed but inconclusive. These tests were conducted during *Sproul* cruise SP1406. However, due to a failure with the exhaust probe feeding the gas analyzers, the data from these tests did not meet quality standards for reporting.

Phase 3. Observations using 100% renewable diesel

Complete. Initial measurements were conducted during *Sproul* cruise SP1406, and continued uninterrupted through December 2015.

Phase 4. Observations using 100% algal-oil renewable diesel

Not achieved. No fuel vendor was capable of providing renewable diesel sourced from algal oil in the quantities required to meet this objective.

Phase 5: Final report.

Complete. This report constitutes the final report.

Fuel

Sourcing

We established two separate vendors, APEX/SoCo with a fuel depot in Los Angeles, and Neste Oil US Ltd with a fuel depot in Richmond, CA. Both vendors provide fuel produced by the Neste Oil refinery in Singapore.

Fuel loaded

Date	Vendor	Volume	Unit	Total Cost
16 SEP 2014	APEX/SoCo[1]	7,500 gallons	$3.28/gal	$24,614.28
14 NOV 2014	Neste Oil US, Inc	7,500 gallons	3.03/gal	22,761.00
05 FEB 2015	Neste Oil US, Inc	7,500 gallons	2.75/gal	20,601.75
28 APR 2015	Neste Oil US, Inc	7,500 gallons	3.09/gal	23,174.25
07 JUL 2015	Neste Oil US, Inc	7,500 gallons	2.80/gal	20,994.21
18 AUG 2015	Neste Oil US, Inc	7,500 gallons	2.40/gal	17,773.83
12 NOV 2015	Neste Oil US, Inc	7,500 gallons	2.30/gal	17,232.75
		52,500 gallons	2.80/gal	147,152.07

[1] Source of APEX fuel was Neste Oil

A fuel analysis of the renewable diesel is included as Appendix 1 to this report.

Overview of Vessel Operations

R/V ROBERT GORDON SPROUL

Figure 1. *The R/V Robert Gordon Sproul departing the Scripps Nimitz Marine Facility in San Diego Bay on a regular oceanographic research mission.*

The research vessel *Robert Gordon Sproul* (Figure 1) is a general-purpose oceanographic vessel owned by the University of California and operated by the Scripps Institution of Oceanography (a department of UC San Diego). Built as a mud boat in 1981, Scripps converted the ship for scientific service in 1986, and since then has operated regularly as the Institution's primary coastal and regional open-ocean platform. At 125 feet long, 32 feet wide and 696 long tons loaded displacement, the ship can carry twelve scientists and five crew on missions as long as 14 days, with a range of 4,300 nautical miles.

The vessel operates as part of the U.S. Academic Research Fleet within the auspices of the University-National Oceanographic Laboratory System (UNOLS), and as such is available on a shared-use basis by any federally-funded researcher in the United States, as well as by state, local, and nongovernmental agencies conducting research at sea. The ideal operational tempo for this class vessel is 75 to 150 operational days at sea.

Robert Gordon Sproul uses two Detroit Diesel 12V-149 engines at 675 hp, with two fixed-pitch propellers. Fuel capacity is 25,000 gallons in two main tanks, with consumption of 504 gallons per day (average) and 1,350 gallons per day (full speed). A diagram of the vessel's fuel system is shown in Figure 2.

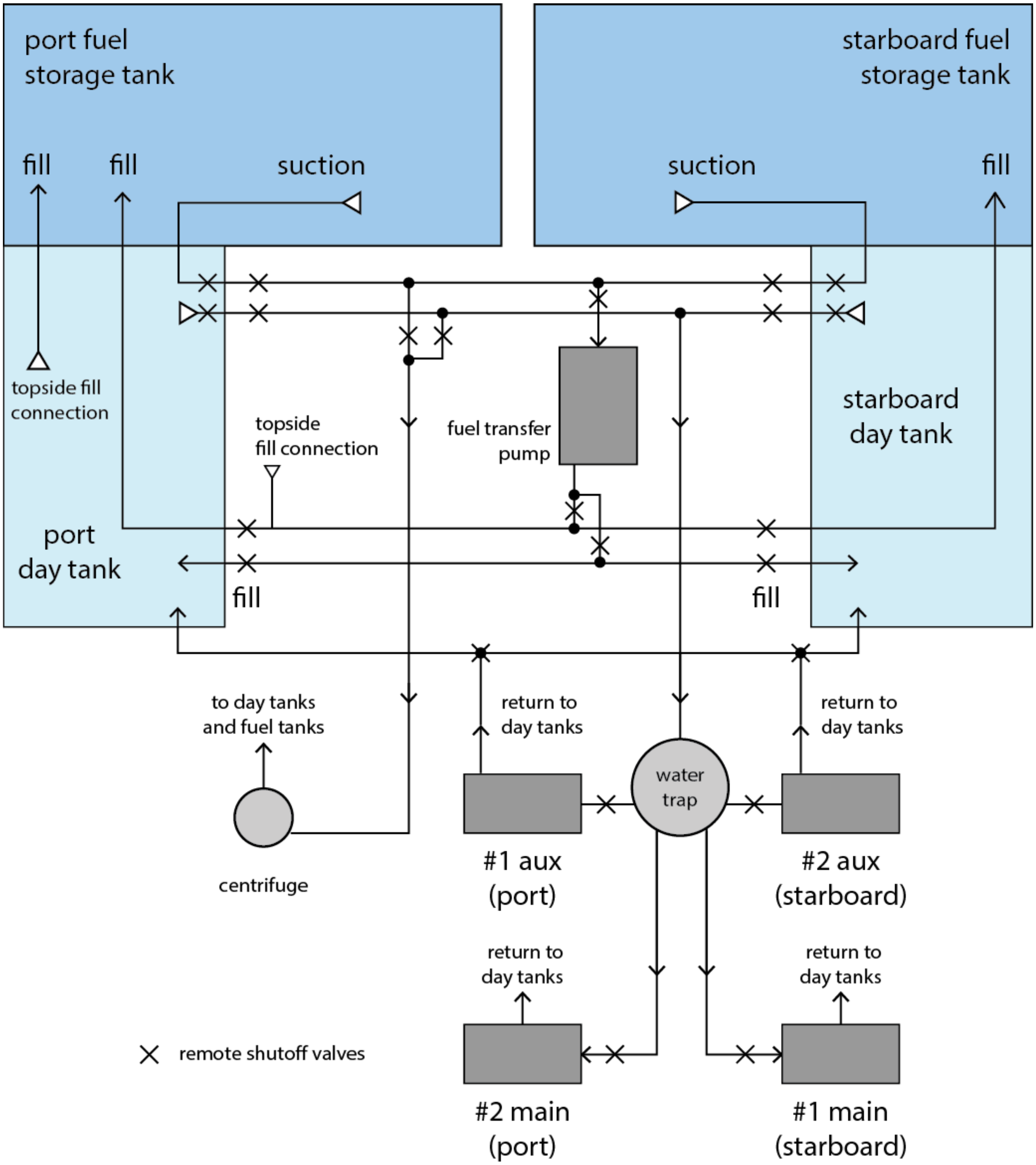

***Figure 2**. Layout of the fuel system aboard Robert Gordon Sproul. The main engines are 675 hp Detroit Diesel model 12V-149 engines.*

INITIAL SETUP AND CHARACTERIZATION CRUISE

From December 2013 to August 2014, the Russell group ordered the required instrumentation and supplies. Russell developed plans for making continuous long-term measurements using permanently-installed sensors. Calibration and operation protocols were developed and tested.

During September 2014, the Russell group installed the shipboard instrumentation to measure NO, NO2, NOx, CO, and CO2 in the stack emissions. The installation included gas analyzers that were mounted in instrument racks in the ship's computer laboratory. A heated inlet was installed from the stack to the instruments to transfer the gases to the instruments, which required the installation of additional air-conditioning within the laboratory space.

In September 2014 the Russell group aerosol van was loaded on the ship to begin integration and testing before the initial test/calibration cruise. Ship support by the SIO marine operations staff at the Port of San Diego's Tenth Avenue Marine Terminal was very good despite the required security and access issues of the off-site location (the Scripps Nimitz Marine Facility is closed during 2015 for reconstruction of its wharf and pier). These preparations included dockside engine tests to test flow rates and to validate instrument response.

From 29 September to 03 October 2014 the R/V *Robert Gordon Sproul* conducted engine testing underway at sea during cruise SP1406. The ship operations included engine testing using both diesel and biofuel, as well as measurements of the plume as it evolved in the atmosphere. An example of the test regimen is shown in Figure 3.

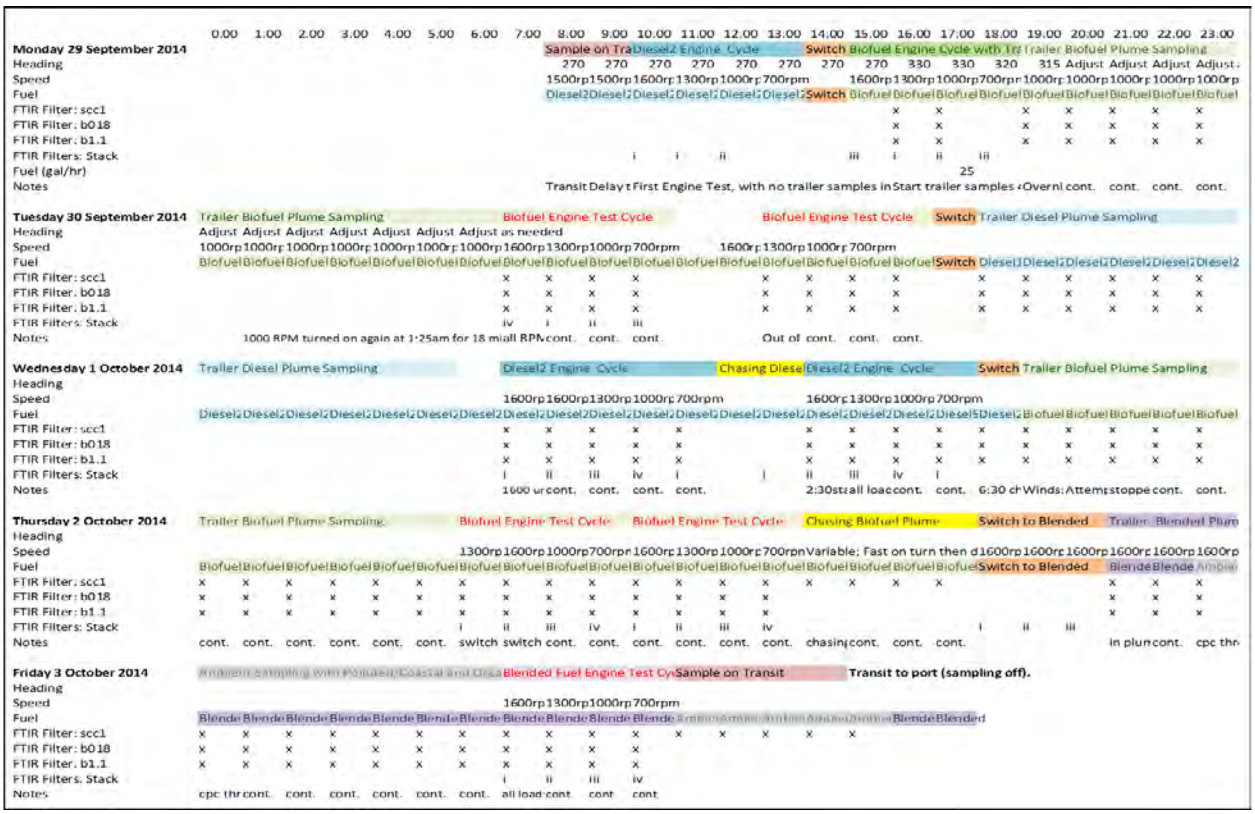

Figure 3. *Chronology of vessel activities during initial characterization cruise aboard R/V Robert Gordon Sproul (cruise ID SP1406) showing fuel type, consumption rate, engine speed, sampling (FTIR) source, and vessel heading. Vessel heading is significant because the heading and prevailing winds determine how well the exhaust plume is sampled by the snorkel mounted on the aft deck from the Russel laboratory van.*

During cruise SP1406, the following goals were achieved

- Installed, tested, and calibrated CO, CO_2, and NO_x monitors on stack
- Verified measurements of criteria pollutants and PM2.5
- Measured stack and plume with advanced PM instruments in aerosol van
- Checked air flow velocity at stack
- Tracked fuel usage with speed
- Tested biofuel, diesel, and blended mixture
- Tracked diesel and biofuel plumes downwind for one hour to characterize changes to the plume through time caused by photochemical reactions.

Following the completion of SP1406, the Russel laboratory van was removed from the vessel, but all of the ship-installed sensors remained up and running and acquiring data. From October 2014 through December 2015 we continuously monitored stack emissions during normal research and education operations. During this period the ship exclusively used 100% renewable diesel fuel. During this period, technicians from the Russel lab visited the vessel between every deployment to conduct routine system checks on the shipboard instruments.

In September 2015, almost exactly one year after the initial biofuel cruise, the aerosol van was re-installed back on the ship to conduct a second detailed sampling and calibration cruise. The mission plan for this cruise was intended to be as close to identical to the SP1406 as possible, but a failure of the shipboard mass spectrometer required the mission to be cut short, and then resumed later in the month. For this reason, the second detailed sampling suite involved data acquired from two cruises, SP1517 and SP1521. Despite this interruption, all of the goals of this second sampling program were achieved, duplicating those of SP1406.

CHRONOLOGY OF VESSEL DEPLOYMENTS DURING THIS PROJECT

All vessel operations during the study period (SEP 2014 through DEC 2015) used 100% renewable diesel fuel supported by this project, and emissions data were sampled and recorded continuously. As a Scripps research vessel, each underway period is designated with a project identifier (cruise ID), and scientific operations on board are the responsibility of a Chief Scientist. With a home port at the Nimitz Marine Facility in San Diego Bay, most of the research and educational activities of *Robert Gordon Sproul* occur in the Southern California Bight, although during the study period the ship ventured for an extended project in northern California, with port calls in Moss Landing, CA. Typical operational profile of a research cruise involves transiting to a research location at 9 knots, conducting whatever scientific operations are required, and then transiting to the next study site. Many scientific activities involve stopping and loitering at a site (for instance to conduct vertical water profiles using CTD casts, or taking bottom samples), or moving at slow speed while towing instruments behind the vessel (for instance towed sonars or nets). Depending on the nature of the science mission, every cruise is slightly different in duration, location, and activity profile. A complete list of all underway periods is presented in Table 1.

Table 1. Listing of all scientific mission completed during the 15-month duration of this project. Every underway period is assigned a Cruise Identifier (e.g. SP1406). The vessel spent 89 days at sea, in total.

Year	Cruise	Chief Sci	Port	Departure	Port	Arrival
2014	SP1406	Russell	San Diego	29 SEP 2014	San Diego	03 OCT 2014
2014	SP1407	Bresnahan	San Diego	22 OCT 2014	San Diego	22 OCT 2014
2014	SP1408	Checkley	San Diego	01 NOV 2014	San Diego	01 NOV 2014
2014	SP1409	Checkley	San Diego	02 NOV 2014	San Diego	02 NOV 2014
2014	SP1410	Brothers	San Diego	15 NOV 2014	San Diego	23 NOV 2014
2014	SP1411	Katz	San Diego	01 DEC 2014	San Diego	02 DEC 2014
2014	SP1412	Alford	San Diego	05 DEC 2014	San Diego	08 DEC 2014
2014	SP1405	Russell	San Diego	29 SEP 2014	San Diego	03 OCT 2014
2014	SP1406	Bresnahan	San Diego	22 OCT 2014	San Diego	22 OCT 2014
2014	SP1407	Checkley	San Diego	01 NOV 2014	San Diego	01 NOV 2014
2014	SP1408	Checkley	San Diego	02 NOV 2014	San Diego	02 NOV 2014
2014	SP1409	Brothers	San Diego	15 NOV 2014	San Diego	23 NOV 2014
2014	SP1410	Katz	San Diego	01 DEC 2014	San Diego	02 DEC 2014
2014	SP1411	Alford	San Diego	05 DEC 2014	San Diego	08 DEC 2014
2015	SP1501	Appelgate	San Diego	26 FEB 2015	San Diego	26 FEB 2015
2015	SP1502	Katz	San Diego	03 MAR 2015	San Diego	04 MAR 2015
2015	SP1503	Babcock	San Diego	06 APR 2015	San Diego	06 APR 2015
2015	SP1504	Semmens	San Diego	11 APR 2015	San Diego	11 APR 2015
2015	SP1505	Sirovic	San Diego	12 APR 2015	San Diego	12 APR 2015
2015	SP1506	Taylor	San Diego	18 APR 2015	San Diego	18 APR 2015
2015	SP1507	Send	San Diego	30 APR 2015	San Diego	30 APR 2015
2015	SP1508	Hazard	San Diego	12 MAY 2015	San Diego	13 MAY 2015
2015	SP1509	Alford	San Diego	02 JUN 2015	San Diego	02 JUN 2015
2015	SP1510	Nickels	San Diego	11 JUN 2015	San Diego	17 JUN 2015
2015	SP1511	Lankhorst	San Diego	18 JUN 2015	San Diego	19 JUN 2015
2015	SP1512	Coale	San Diego	20 JUN 2015	Moss Landing	23 JUN 2015
2015	SP1513	Coale	Moss Landing	24 JUN 2015	Moss Landing	30 JUN 2015
2015	SP1514	Coale	Moss Landing	01 JUL 2015	San Diego	03 JUL 2015
2015	SP1515	Rouse	San Diego	11 JUL 2015	San Diego	11 JUL 2015
2015	SP1516	Doran	San Diego	05 AUG 2015	San Diego	08 AUG 2015
2015	SP1517	Russell	San Diego	04 SEP 2015	San Diego	07 SEP 2015
2015	SP1518	Hardin	San Diego	11 SEP 2015	San Diego	17 SEP 2015
2015	SP1519	Laxton	San Diego	19 SEP 2015	San Diego	19 SEP 2015
2015	SP1520	Laxton	San Diego	21 SEP 2015	San Diego	21 SEP 2015
2015	SP1521	Russell	San Diego	26 SEP 2015	San Diego	28 SEP 2015
2015	SP1522	Gallimore	San Diego	07 OCT 2015	San Diego	12 OCT 2015
2015	SP1523	Franks	San Diego	17 OCT 2015	San Diego	17 OCT 2015
2015	SP1524	Franks	San Diego	18 OCT 2015	San Diego	18 OCT 2015
2015	SP1525	Lankhorst	San Diego	22 OCT 2015	San Diego	22 OCT 2015
2015	SP1526	Levin	San Diego	07 NOV 2015	San Diego	07 NOV 2015
2015	SP1527	Send	San Diego	12 NOV 2015	San Diego	13 NOV 2015
2015	SP1528	Levin	San Diego	14 NOV 2015	San Diego	14 NOV 2015
2015	SP1529	Doran	San Diego	17 NOV 2015	San Diego	20 NOV 2015
2015	SP1530	Baumann	San Diego	01 DEC 2015	San Diego	05 DEC 2015
2015	SP1531	Hazard	San Diego	08 DEC 2015	San Diego	09 DEC 2015
2015	SP1532	Klimek	San Diego	12 DEC 2015	San Diego	17 DEC 2015

ENGINE HOURS

Over the duration of this project we logged 6,985 hours of engine time using 100% renewable diesel fuel on *Robert Gordon Sproul's* four engines as shown below. Routine maintenance was performed, with no engine problems encountered.

Engine	9/12/14	12/31/15	hours on renewable
#1 Main	7,512	9,534	2,022
#2 Main	7,485	9,723	2,238
#1 Aux	17,141	17,894	753
#2 Aux	5,252	7,224	1,972

Results

PART 1: EXPERIMENTAL METHODS

Gas and particle emissions from the *R/V Robert Gordon Sproul* were measured using a suite of real-time instruments (Table 2), before and after a one-year period of using biodiesel. The first set of detailed particle measurements underway were carried out from 29 September to 3 October in 2014 aboard SP1406 ("2014 cruise"). The second set of measurements was carried out from 4 to 7 September and from 26 to 28 September in 2015 aboard SP1517 and SP1521 ("2015 cruise"). In addition, stack emissions were measured on throughout the entire year of 2015, during normal scientific and educational deployments of the vessel.

Table 2. *Real-time particle instrumentation used to measure gases and physicochemical properties of particle emissions.*

Location	Instrument	Measured Parameters	Resolution
Stack	CO and NOx Analyzers	CO, CO_2, NO and NO_x gas concentrations	1 sec
Aerosol Sampling Van	High Resolution – Time of Flight - Aerosol Mass Spectrometer (HR-ToF-AMS)	Non-refractory particle component types: organic, sulfate, nitrate, ammonium, and chloride	2 min
Aerosol Sampling Van	Single Particle Soot Photometer (SP2)	Black carbon number and mass concentrations and size distributions	1 min
Aerosol Sampling Van	Scanning Electrical Mobility Sizer (SEMS), Aerodynamic Particle Sizer (APS), Optical Particle Sizer (OPS)	Particle number concentrations and size distributions	5 min

Measurements of Stack Gases

CO, CO_2 and NOx emissions were measured from the stack using a custom-designed probe, heated inlet, and water-removal system (Figure 4) during all available cruises in late 2014 and all of 2015. The engine exhaust was sampled through a sampling probe inserted into the main stack vent of the starboard engine. The exhaust was filtered for particles using a particle filter at the upstream of sampling line. The filtered exhaust was passed through a heated line to the condenser/cooling unit to remove the moisture and filter any residual particles. A portion of the exhaust was directed to CO Analyzer (Model: T300, Teledyne API, USA) to measure CO and CO_2 concentrations. The remaining portion of the sampled exhaust was diluted with zero air and NOx gas concentrations were measured using a NOx analyzer (Model: T200M, Teledyne API, USA).

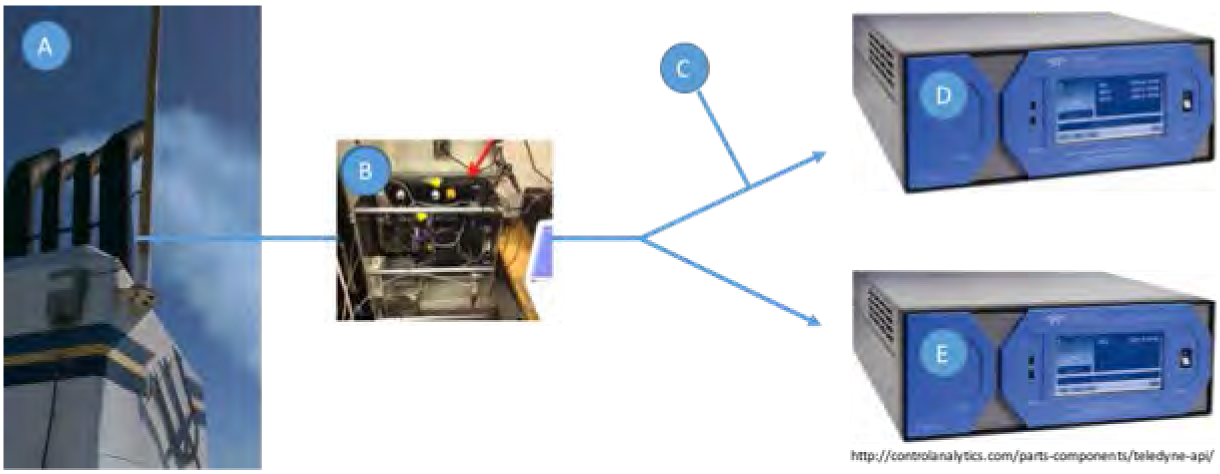

Figure 4. *Schematic for measurement of stack gases from starboard engine: A) Sampling probe connected to heated inlet line, B) Cooling unit with water trap, C) Dilution line, D) NO and* NO_x *analyzer (Teledyne T200M), E) CO and* CO_2 *analyzer (Teledyne T300).*

Particle Measurements in Aerosol Sampling Van

During the dedicated 2014 and 2015 aerosol sampling cruises, particle emissions from *R/V Robert Gordon Sproul* were measured using the plume intercept method (also known as the "sniffer" method), wherein concentrations of the pollutants are measured in a plume that is intercepted downwind of the vessel. The rationale to use the plume intercept method for particle emissions is that atmospherically relevant dilution factors and temperatures are achieved by the time the plume is sampled. The plume was sampled using an isokinetic inlet mounted on the sampling trailer (Figure 5). It is then directed to the suite of real time instruments housed in the trailer to measure the physicochemical properties of the particles in the plume.

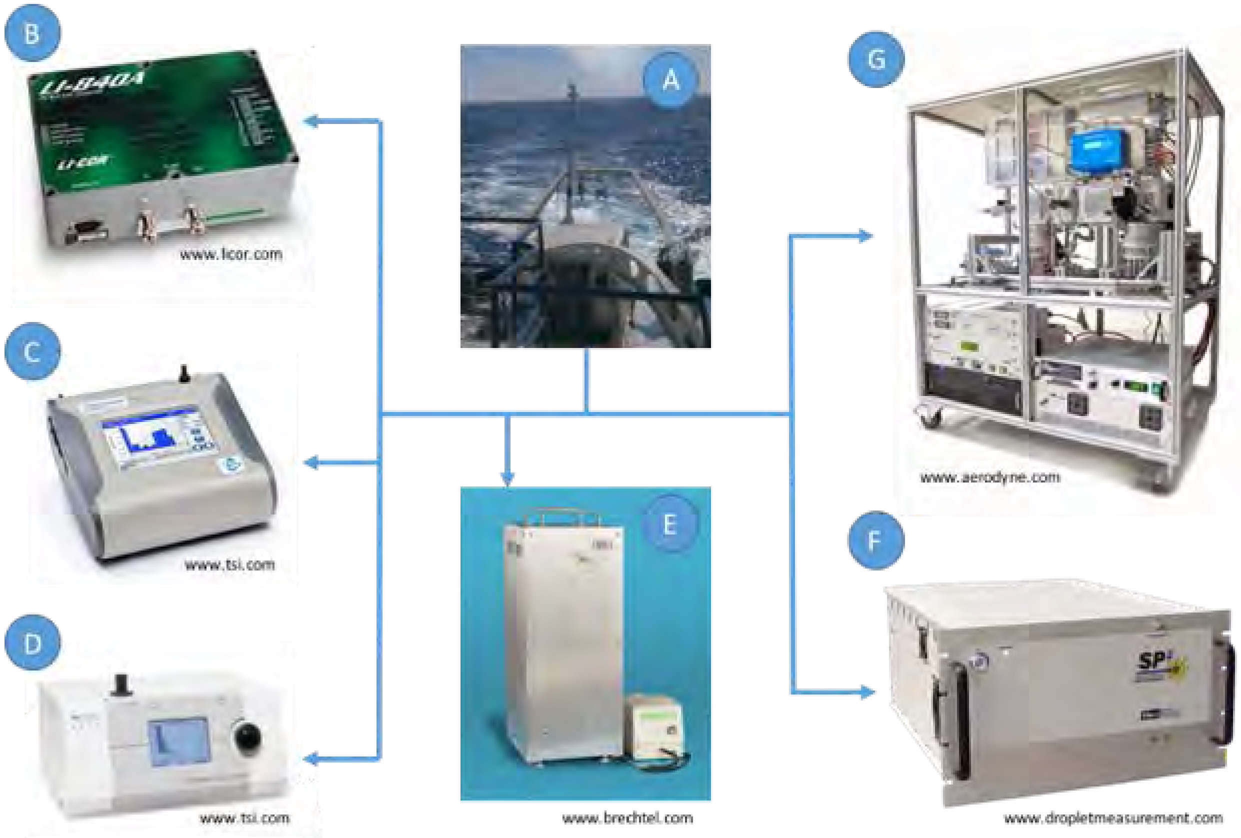

Figure 5. *Schematic for particle measurement in the sampling trailer. A) Isokinetic, plume-facing, aerosol-sampling inlet, B) CO_2 analyzer (Licor 840A), C) OPS (TSI 3330), D) APS (TSI 3320), E) SEMS (Brechtel), F) SP2 (Droplet Measurement Technologies), G) HR-ToF-AMS (Aerodyne Research Inc.).*

Table 2 lists the instruments used in this study and the particle properties they measure. The HR-ToF-AMS measures the chemical composition of aerosol particles in real time. It measures aerosol organic, sulfate, chloride, nitrate, and ammonium components in "non-refractory" particles. The size distributions of particles in the plume were measured over a large size range (0.01 – 10 µm) using different particle sizing instruments. Submicrometer particles (0.01 - 1 µm) were measured with a scanning electrical mobility spectrometer (SEMS, Model 138 2002, Brechtel Manufacturing Inc., USA) while larger particles were measured using an aerodynamic particle sizer (APS, Model 3321, TSI Inc., USA; size range 0.5– 20 µm) and an optical particle sizer (OPS, Model 330, TSI Inc., USA; size range 0.3–10 µm). The single particle soot photometer (SP2) was used to measure light-absorbing black carbon (BC, or soot) mass in individual aerosol particles. It also provides size distributions of black carbon (BC) aerosol particles (0.07 – 0.4 µm). In addition to the above real-time instruments, size selected (1 µm and 0.18 µm) particles from the plume were collected on filters and analyzed in the lab using Fourier Transform Infrared (FTIR) spectroscopy for alkane, amine, hydroxyl, carbonyl and carboxylic acid functional groups.

The APS and OPS measurements are not included in this report because the ship plume did not have distinguishable concentrations of particles in the APS and OPS size ranges (0.5– 20 µm and 0.3–10 µm, respectively).

PART 2: EMISSION FACTORS FOR BIODIESEL AND DIESEL

During each set of measurements, biodiesel and diesel were used and their emission factors were estimated for these two fuel types. In addition, the dependence of emission factors on engine speed and other conditions was investigated.

CO and NOx Emissions

CO and NOx emission factors (EFs) were calculated from automated stack measurements of CO_2, CO and NOx concentrations during the scheduled research cruises of the R/V *Robert Gordon Sproul.*

- CO and NOx emission factors varied from 1.26 – 13.1 g/kg-fuel (5.5 ± 2.4 g/kg-fuel) and 29 -142 g/kg-fuel (64.4 ± 30.9 g/kg-fuel), respectively (Figure 6).
- These EFs are comparable to EFs of ocean going vessels reported in the literature. Beecken et al. [2014] measured emissions from 87 different vessels and reported average NOx emissions of 66.6 ± 23.4 g/kg-fuel.
- The variability in the emissions between cruises depends mainly on engine load and operating speeds, which in turn varies with overall laden weight of the ship and sea state.

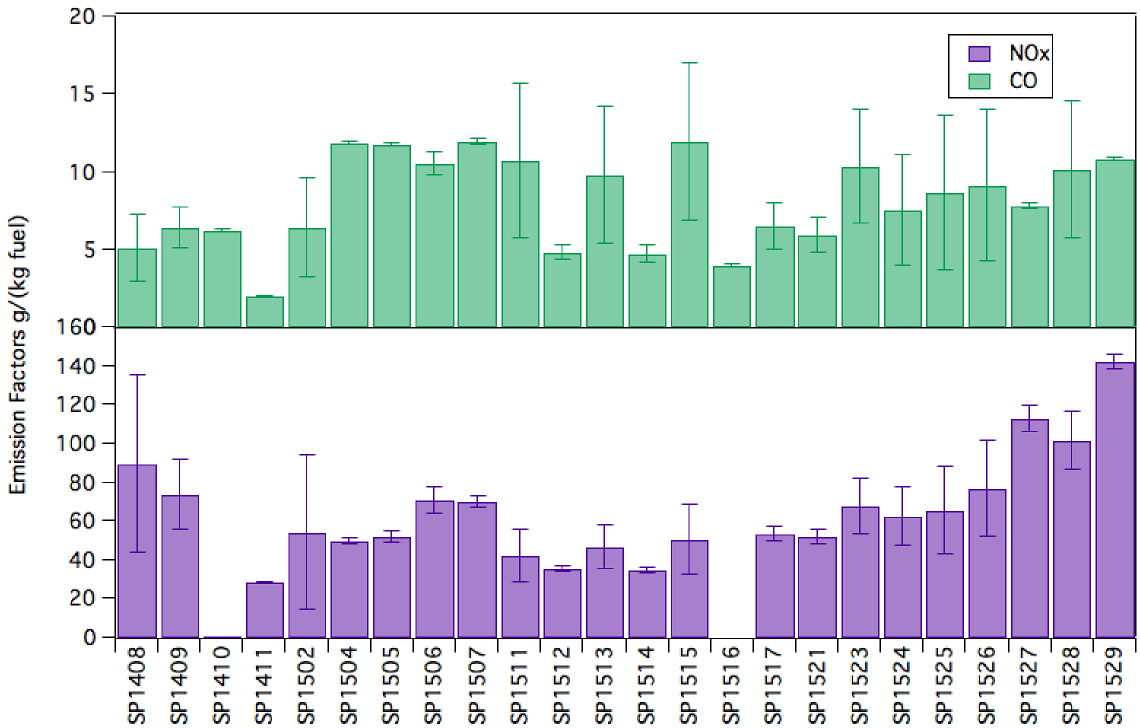

Figure 6. *Emission factors (EFs) of CO and NOx during different cruises of R/V Robert Gordon Sproul between 11/15/14 – 11/20/15. (Cruise numbers are provided on x-axis)*

Variation of CO and NOx Emissions with Engine Speed

Dependence of CO and NOx emissions on engine speeds was investigated further. Engine speeds were varied from 1600rpm to 700rpm. The engines were operated at specific speeds for one hour at a time, during which the stack CO and NOx emissions were measured and averaged. These test cycles were repeated 12 times with biodiesel and 4 times with diesel during the 2014 and 2015 cruises.

- Biodiesel has lower CO and NOx emissions compared to diesel. EF of CO ranged from 3.9 – 9.3 g/kg-fuel with biodiesel while it is in the range of 4 -11.7 g/kg-fuel with diesel for engine speeds between 700 and 1600 rpm (Figure 7). EFs of NOx are in the range of 47 – 55 g/kg fuel for biodiesel and 51 – 64 g/kg-fuel for diesel.
- EFs of CO and NOx increased with decreasing engine speed. EF of CO increased by nearly 200% when engine speed decreased from 1600 to 700 rpm for biodiesel while it increase by 300% for diesel. EFs of NOx, on the other hand increased by only 10% for biodiesel and 25% for diesel when changing engine speeds from 1600 to 700 rpm.

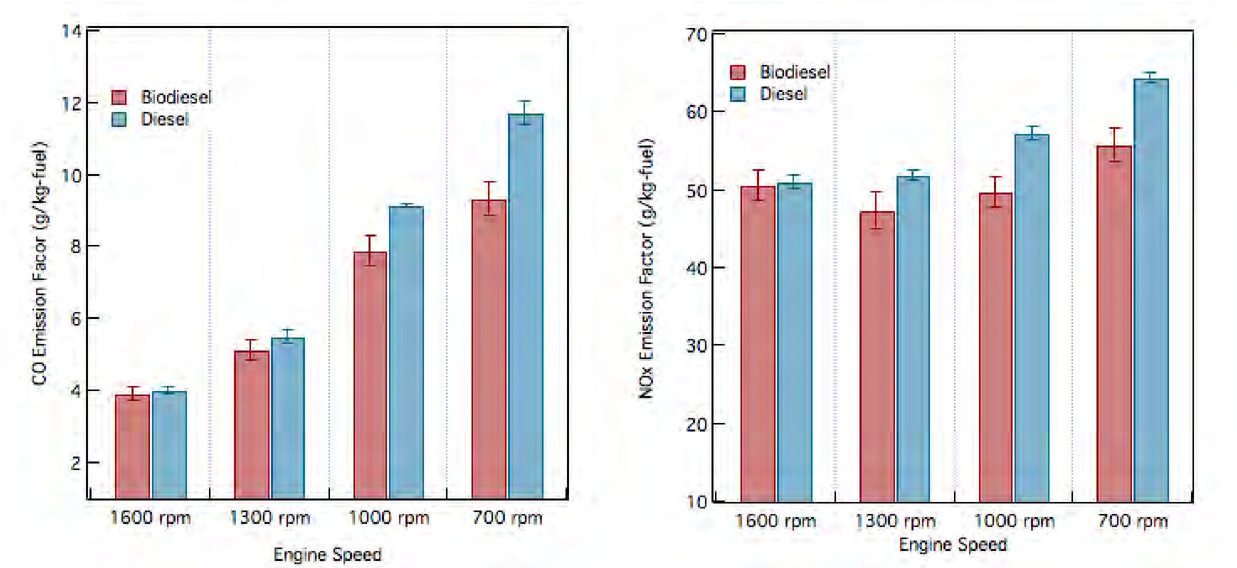

Figure 7. *EFs of CO and NOx from R/V Robert Gordon Sproul at different engine speeds when powered by diesel and biodiesel. Each mean represents the average of a number of one-hour test periods (n=7 for biodiesel; n=2 for diesel). The average was calculated over different engine cycle tests conducted during the 2015 cruise (9/4/15-9/6/15 and 9/26/15-9/28/15).*

CO and NOx emissions from *R/V Gordon Sproul* were reduced for biodiesel. However, the reduction is significant only at lower engine speeds (1000 rpm and 700 rpm). CO emissions were reduced by 14% and 20% at 1000 rpm and 700rpm, respectively, for biodiesel. NOx emissions were reduced by 13% and 13.4% at 1000 rpm and 700 rpm, respectively. When compared to the other studies found in the literature the reduction in NOx emissions for biodiesel is high in this study. Gysel et al. [2014] observed an overall reduction of 4% in NOx emissions from a Stalwart class marine vessel for biodiesel derived from sugarcane. Jayaram et al. [2011] did not see any change in NOx emissions when a mixture of ultra-low sulfur diesel (ULSD) and soy-based biodiesel was used.

Particle Emissions

In addition to the measurements of stack gases, particle number concentrations and size distributions were measured from the fresh plume released into atmosphere. These particles were sampled approximately 20 m downwind from emission in an instrumented van with an

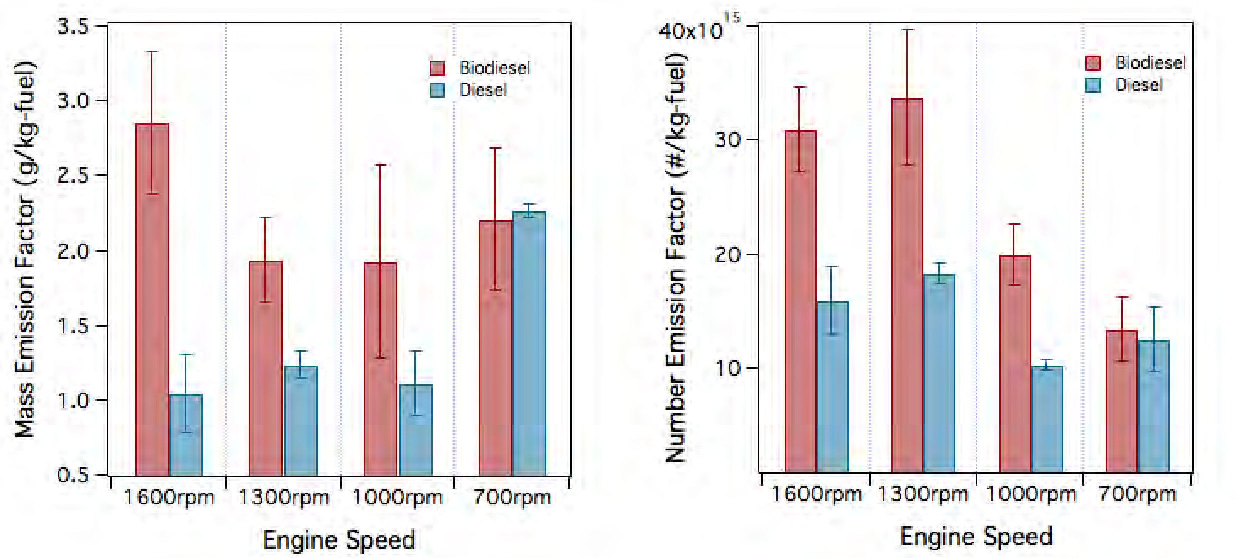

Figure 8. *Number and mass emission factors of submicron particles. Each mean represents the average of a number of one-hour test periods (after eliminating measurements that did not meet the criteria in Table 3: n=5 for biodiesel and n=3 for diesel at 1600 rpm; n=7 for biodiesel and n=3 for diesel at 1300 rpm; and n=7 for biodiesel and n=3 for diesel at1000 rpm; and n=9 for biodiesel and n=2 for diesel at 700 rpm). The averages were calculated over different engine cycle tests conducted during the 2014 cruise (9/29/14 – 10/3/14) and the 2015 cruise (9/4/15 – 9/6/15 and 9/26/15 – 9/28/15).*

Table 3. *Criteria used to determine measurements in plume.*

Instrument	**Measurement**	**Criteria used to determine measurements in plume**
Licor	CO_2	$\Delta CO_2 > 10$ ppm
HR-ToF-AMS	Mass fragments of organic particle components and their distribution	Organic mass concentration > 2 □g r (> 0.5 for aged).
SEMS	Particle number size distributions	SEMS number concentration > 10^5 cm^{-3}.
CPC	Particle concentrations	CPC number concentration > 10^4 cm^{-3}.
SP2	Black carbon number, mass concentrations, and size distributions	Black carbon number > 4000 cm^{-3}, Black carbon mass > 4 □g m

isokinetic inlet. The selection criteria for data from various instruments used to identify times when the plume was being sampled is shown in Table 3.

- Biodiesel has higher number and mass emission factors compared to diesel. Submicron particle number emission factors varied from 1.8 - 1.1 x 10^{16} (kg-fuel)$^{-1}$ for biodiesel and 1.3

– 0.6x10^{16} (kg-fuel)$^{-1}$ for diesel. While mass emission factors varied from 1.93 – 2.85 g/kg-fuel for biodiesel and 1 – 2.2 g/kg-fuel for diesel.

- With increasing speed, particle number emissions increased for both diesel and biodiesel (Figure 9. While the highest mass emissions for biodiesel is at the highest engine speed (1600 rpm), the highest mass emissions for diesel was at the lowest engine speed (700 rpm).

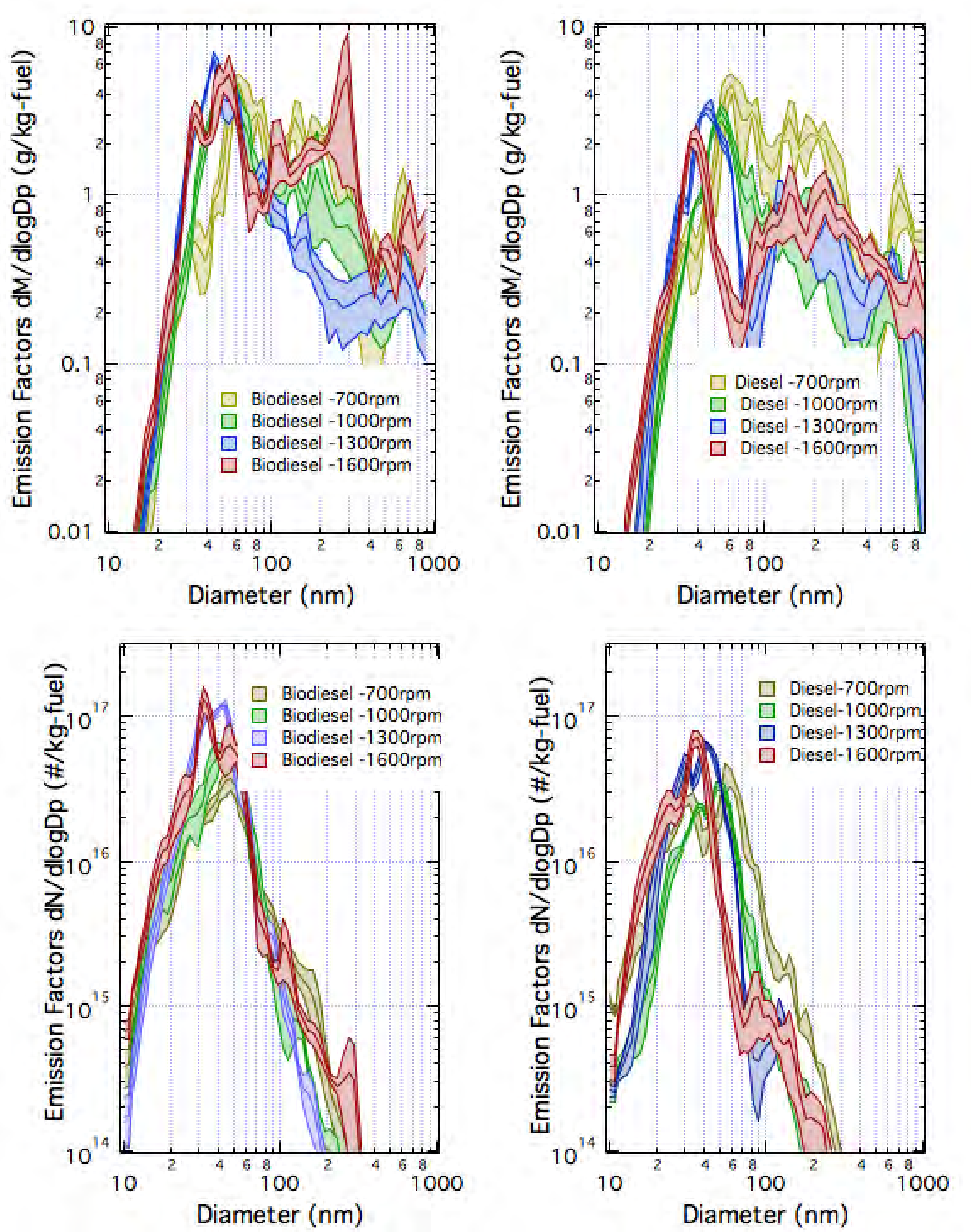

Figure 9. *Mass and number size distribution of particles measured in the plume at 1600 rpm, 1300 rpm, 1000 rpm, and 700 rpm for biodiesel and diesel. (The shaded area indicates standard error of the mean value at each diameter.) The reported size distributions were measured during the 2014 cruise (9/29/14 – 10/3/14) and the 2015 cruise (9/4/15 – 9/6/15 and 9/26/15 – 9/28/15).*

- For typical underway engine speeds, particle mass and number emissions generally increased at higher engine speed, but their emission factors were quite variable for each engine speed.
- The variability in emissions at different engine speeds results from several other factors that contribute to engine load. As shown in Figure 10, the emission factors tend to decrease with increasing engine speed, with decreasing variability in pitch (estimated as the standard deviation (SD) of the reported pitch), and with decreasing roll for the same engine speed. While roll and pitch indicate the sea state, lower vessel speed for the same engine speed also provides a measure of the load.

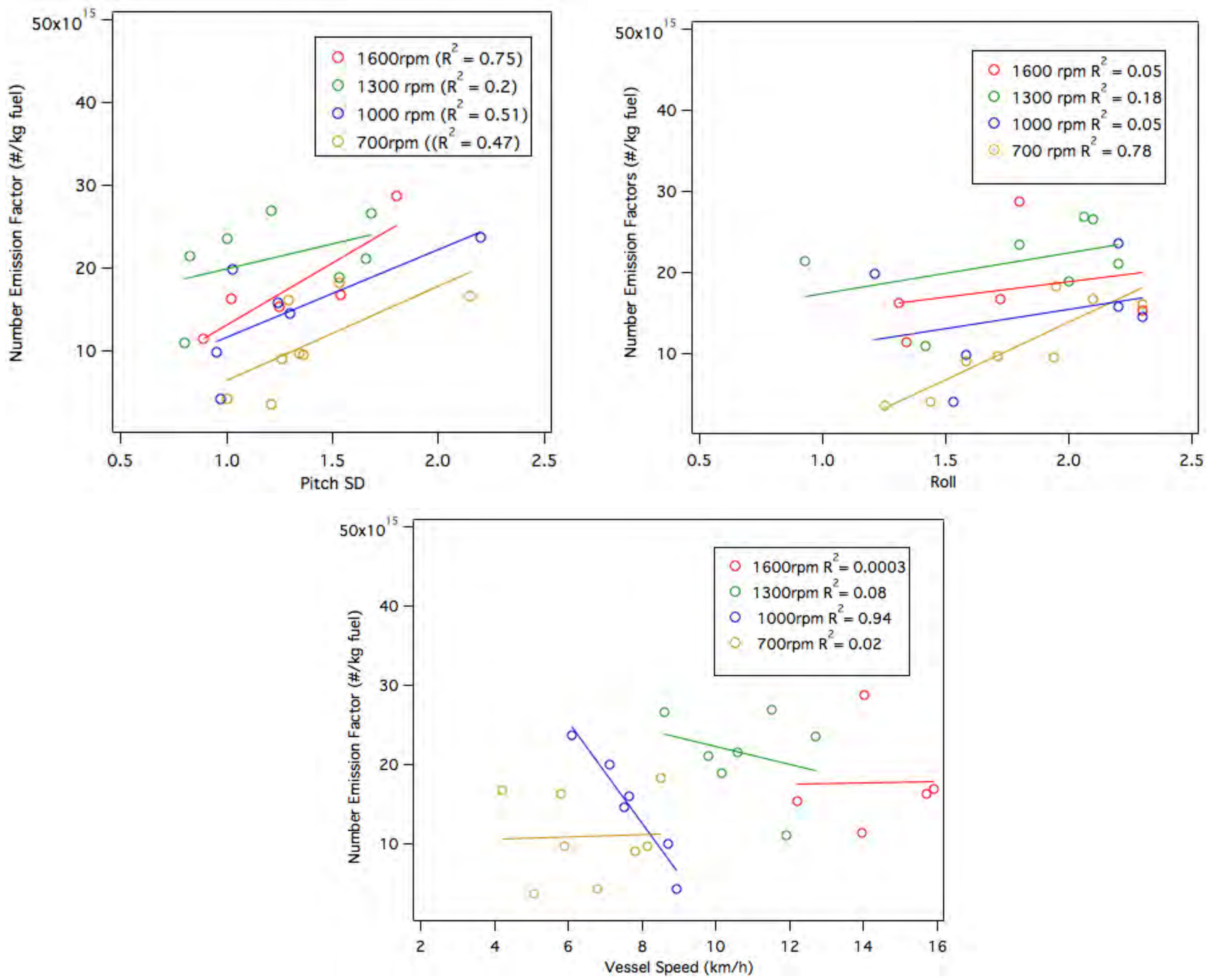

***Figure 10**. Particle emission factors at 1600 rpm, 1300 rpm, 1000 rpm, and 700 rpm as functions of vessel speed, variability in pitch (indicated as standard deviation, SD, of pitch), and roll measured during the 2014 cruise (9/29/14 – 10/3/14) and the 2015 cruise (9/4/15 – 9/6/15 and 9/26/15 – 9/28/15).*

- Emission factors of particle mass size distributions are estimated from particle number assuming particle density of 1.2 g/cc.
- The modal diameter of the smaller mode of the particle size distributions increased with decreasing engine speed, i.e. at higher engine speeds, a larger fraction of smaller number of particles was observed.
- A bimodal mass size distribution was observed at high engine speeds, with the smaller mode between 40 and 60 nm. The peak diameter of the smaller mode increased with decreasing speed. The second mode was observed to peak at approximately 200 nm. This mode was invariant with engine speed.

Number and mass emission factors for the *R/V Robert Gordon Sproul* using diesel and biodiesel indicate that the particle emissions increased for biodiesel. However, the increase in particle emissions is larger at higher engine speeds. At lower engine speeds (700 rpm) particle emissions are similar for both diesel and biodiesel. The majority of studies have indicated an increase in particle number and decrease in particle mass with the usage of biodiesel (Jayaram et al., 2011; Lapeurta et al., 2008). This increase in particle number and decrease in particle mass was primarily attributed to the increase in nucleation mode (diameter > 50 nm) and decrease in accumulation mode particles for biodiesel. In this study, we observed an increase in small mode particle emissions for biodiesel at higher engine speeds leading to an increase in the total particle number. However, the estimated particle mass for biodiesel was higher than for diesel. A few studies have also reported an increase in particle mass for biodiesel similar to these observations from the R/V *Sproul* (Hansen et al., 1997; Peterson et al., 1996).

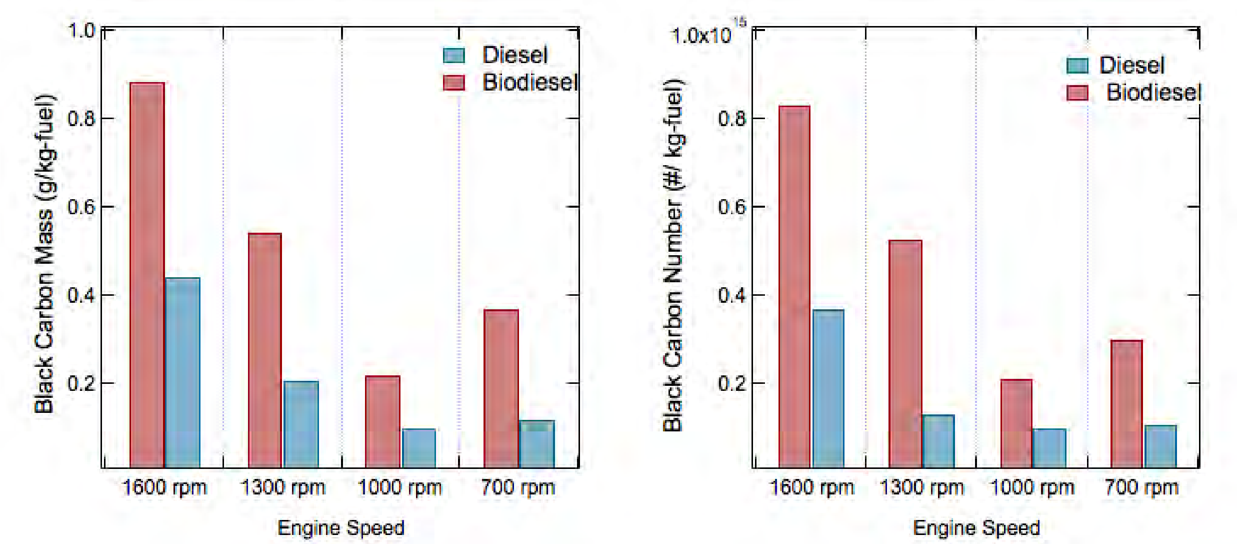

Figure 11. *Black carbon mass and number emission factors estimated from the black carbon measurement using SP2 during the 2015 cruise (9/4/15 – 9/6/15 and 9/26/15 – 9/28/15). (This instrument was not available during the 2014 cruise.)*

Black Carbon Emissions

Black carbon (BC) emissions were measured using a single particle soot photometer (SP2). Figure 11 shows the black carbon number and mass concentrations. The criteria for selecting the data for analysis is show in Table 3.

- BC emissions are higher for biodiesel compared to diesel. BC concentrations range from 0.2 to 1 g/kg-fuel for biodiesel and from 0.1 to 0.44 g/kg-fuel for diesel. Higher BC emissions indicate less complete combustion for biodiesel compared to diesel.
- BC number and size distributions were shown for particles in the size range of 100 to 400 nm (Figure 12).
- Particles larger than 400 nm were associated primarily with other (non-ship) particle sources, so that their variability reflected differences in the background atmospheric aerosol concentrations during the cruises.
- BC number and mass emissions generally decrease with decreasing engine load. The lowest BC emissions, i.e. the most complete combustion of BC, were observed at 1000 rpm for both diesel and biodiesel.

In summary, BC emissions were higher for biodiesel compared to diesel. Prior studies have reported a decrease in soot production for biodiesel. Jayaram et al. (2011) observed 23% reduction in elemental carbon for biodiesel. The higher BC emission in this study indicates less complete combustion for biodiesel. The lowest BC emissions were observed at 1000 rpm for both diesel and biodiesel.

Summary of Emission Factors for Biodiesel and Diesel Results

The emission factors of gases and particles indicate that the biodiesel used in this study has gas emissions lower than the ultra-low sulfur diesel for the R/V *Robert Gordon Sproul*. However, the particle and BC emissions for both number and mass were higher for biodiesel compared to diesel.

PART 3: CHEMICAL COMPOSITION OF ORGANIC PARTICLE EMISSIONS

To compare the differences in particle emissions from biodiesel and diesel, we investigated the detailed changes in organic particles at different speeds and after aging in the atmosphere. In this section, we provide a summary of the results from HR-ToF-AMS, including event trigger (ET) modes for single particle composition, and FTIR measurements.

Organic Mass Concentration Dependence on Vessel Speed

There is a general trend of increasing organic particle mass concentration with decreasing vessel speed for both the 2014 and 2015 cruises.

- At higher loads (and lower vessel speeds for the same engine speeds), more emissions are produced (Figure 13). For a given engine speed, vessel speed is an indicator of sea state as well as ship load and balance. For example, at the same engine speed, rough seas will slow the actual speed of the vessel.

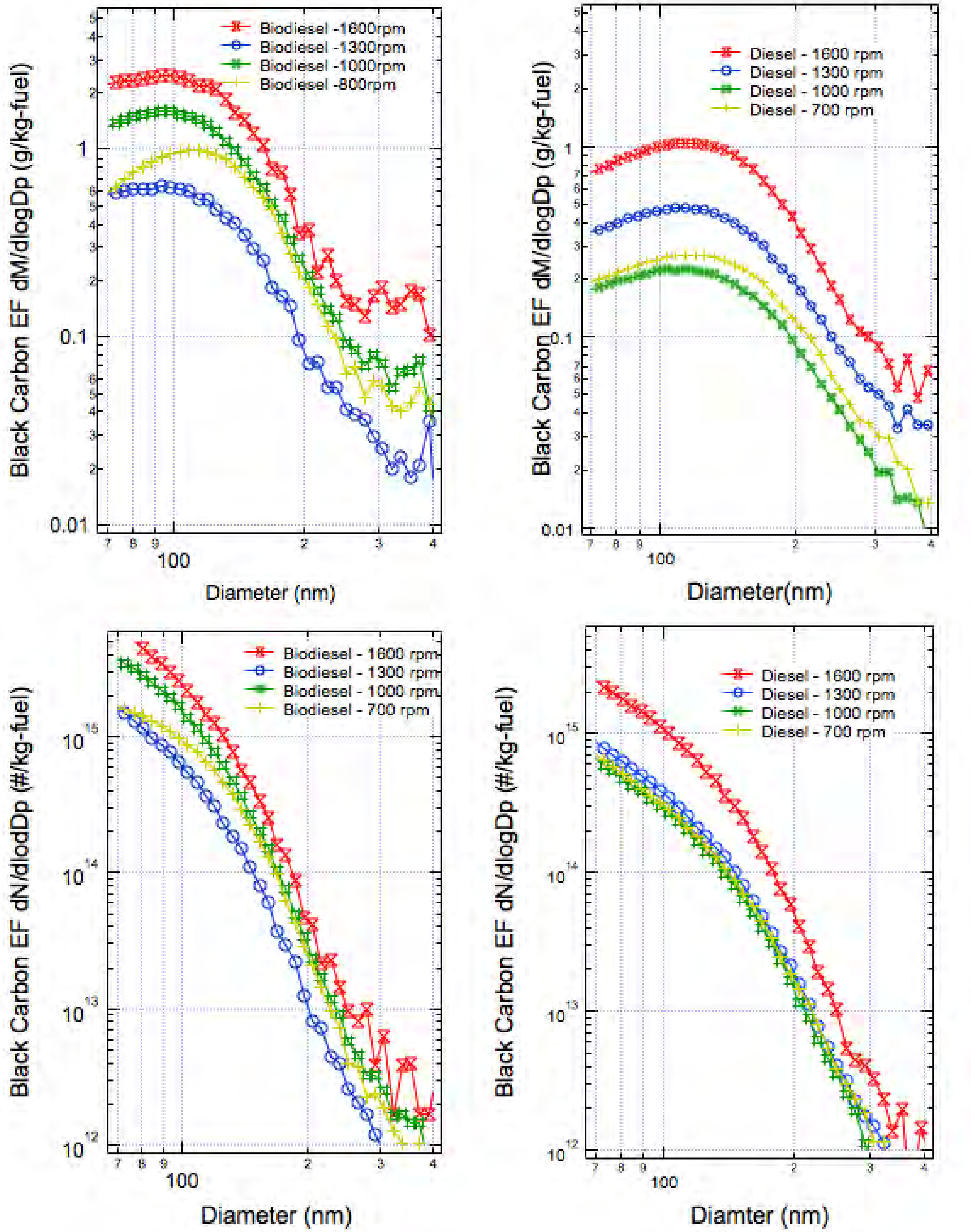

Figure 12. *Emission factors of black carbon mass and number size distributions estimated from the SP2 measurements during the 2015 cruise (9/4/15 – 9/6/15 and 9/26/15 – 9/28/15). (This instrument was not available during the 2014 cruise.)*

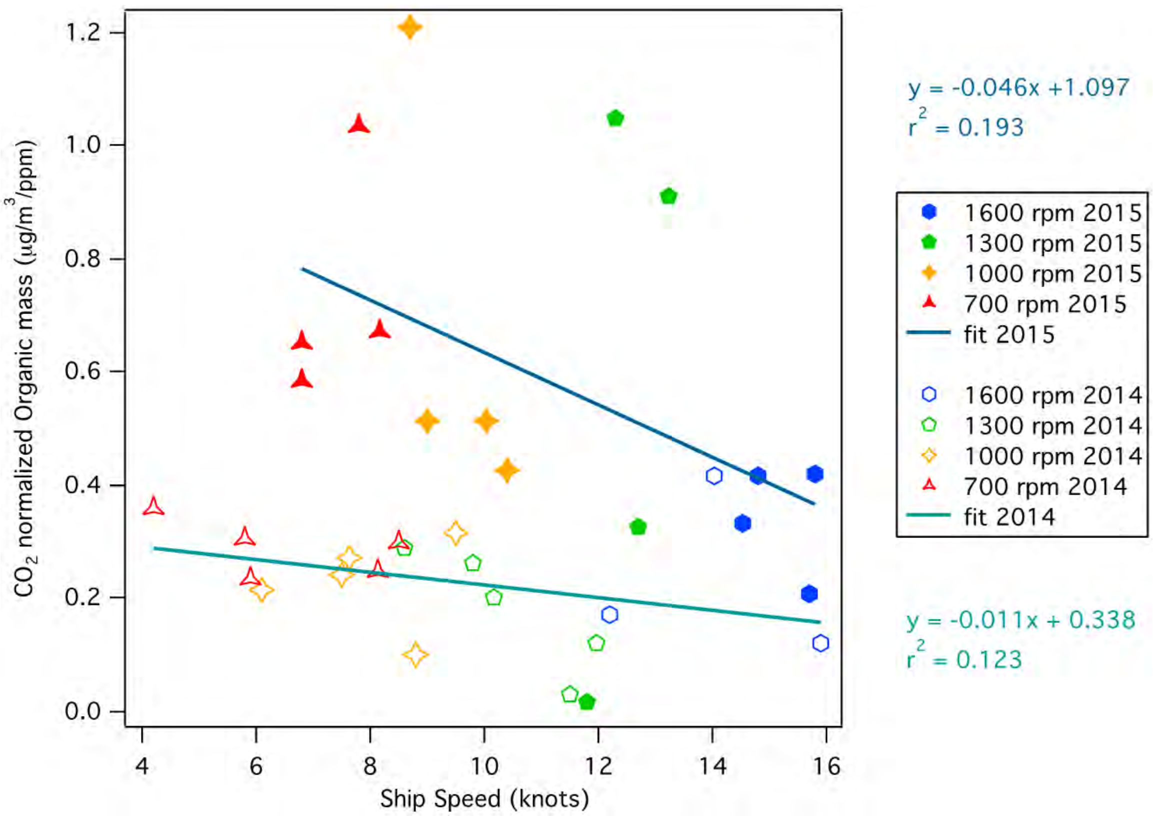

***Figure 13**. CO_2 normalized HR-ToF-AMS organic mass concentrations (CE=1) for biodiesel emissions at 700, 1000, 1300, and 1600 rpm engine speeds versus vessel speed (km/h) measured during Cruise 1 (9/29/14 – 10/3/14) and Cruise 2 (9/4/15 -9/6/15 and 9/26/15 – 9/28/15)*

Differences in Particle MS Composition between Fuels, Speeds, and Aging

The spectra in Figures 14, 15, and 16 are background subtracted and normalized to *m/z* 43 (which was either the 1st or 2nd highest peak). The ratio between *m/z* 43, 55, and 69 appeared similar between fresh and aged for both fuels, while peaks like *m/z* 27 and 57 would vary between fresh and aged. By normalizing the mass spectra to *m/z* 43, the differences between the biodiesel and diesel, fresh and aged plumes, and 700 and 1300 rpm can be compared.

- While the spectra are quite similar, the difference between biodiesel and diesel (Figure 11) shows that there is a more abundant hydrocarbon series in the diesel mass spectra (*m/z* 57, 71, 85, 97, 111) than in the biodiesel mass spectra (*m/z* 55, 69, 83, 95, 109).
- The fresh emissions contain higher relative amounts of alkane/cyclic fragments (C_nH_{2n+1}, C_nH_{2n-1}) and the aged emissions contain higher relative amounts of alkene or aromatic fragments (C_nH_{2n-3} to C_nH_{2n-13}) (Figure 12). This result provides an indication that alkanes may have oxidized more quickly than aromatics.
- The difference spectra between two engine speeds (Figure 16) show that there is an increase in higher *m/z* peaks relative to *m/z* 43 at 1300 rpm compared to 700 rpm. This result indicates a shift in concentration for one or more of the hydrocarbon components of the organic aerosol. The results are consistent with higher relative amounts of larger, unburnt hydrocarbons at the higher engine speeds.

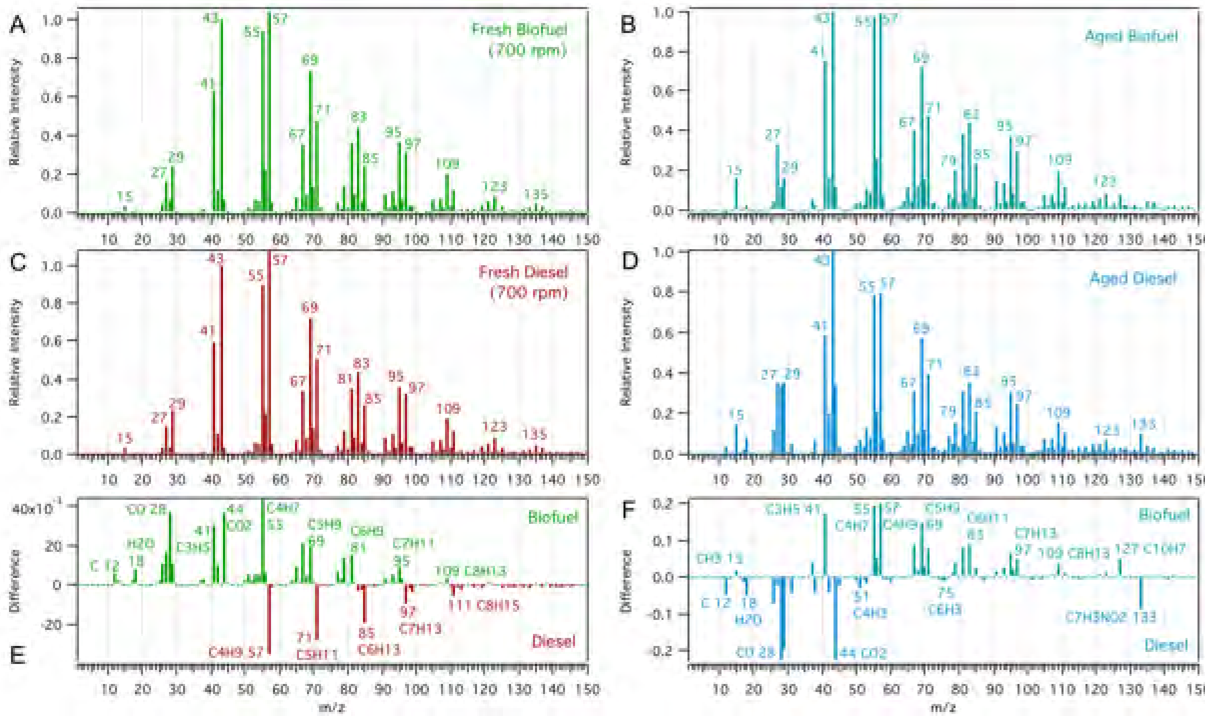

Figure 14. *Background-subtracted HR-ToF-AMS mass spectra (normalized to m/z 43) for fresh and aged biodiesel emissions (A-B), fresh and aged diesel emissions (C-D), and the difference between biodiesel and diesel emissions (E-F) HR-ToF-AMS spectra from the 2015 cruise (9/4/15 – 9/6/15 and 9/26/15 – 9/28/15) were used for the analysis.*

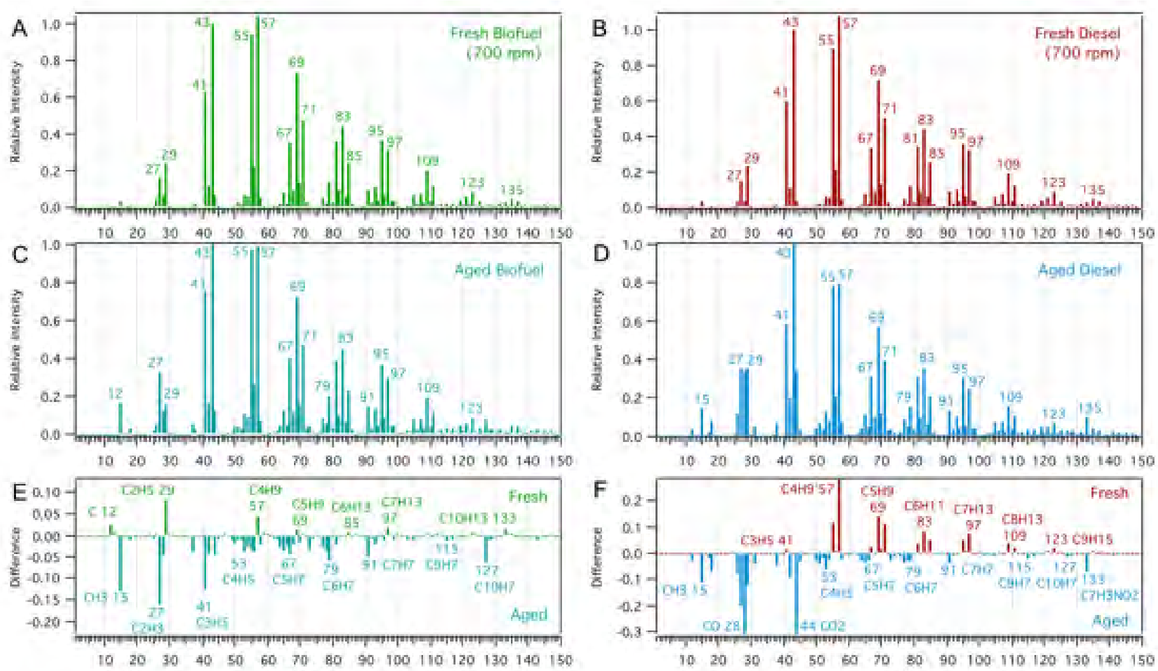

Figure 15. *Background-subtracted HR-ToF-AMS mass spectra (normalized to m/z 43) for fresh biodiesel and diesel emissions (A-B), aged biodiesel and diesel emissions (C-D), and the difference between fresh and aged for both fuels (E-F). HR-ToF-AMS spectra from the 2015 cruise (9/4/15 -9/6/15 and 9/26/15 – 9/28/15) were used for the analysis.*

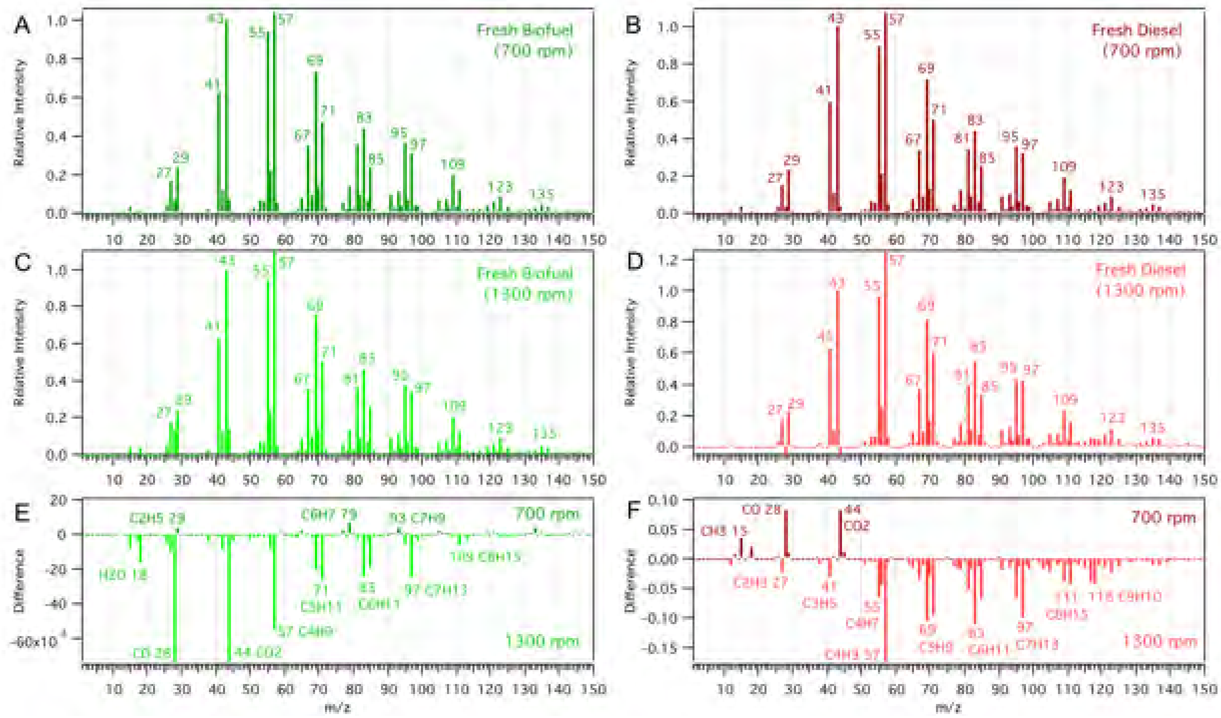

Figure 16. *Background-subtracted HR-ToF-AMS mass spectra (normalized to m/z 43) for fresh biodiesel and diesel emissions at 700 rpm engine speed (A-B), fresh biodiesel and diesel emissions at 1300 rpm engine speed (C-D), and the difference between 700 and 1300 rpm engine speeds for both fuels (E-F). HR-ToF-AMS spectra from the 2015 cruise (9/4/15 – 9/6/15 and 9/26/15 – 9/28/15) were used for the analysis.*

Differences in Particle Types

The single particle cluster analysis (Figure 17) confirms that there are differences in the hydrocarbon composition.

- Three clusters with hydrocarbon fragmentation patterns were observed for the fresh biodiesel emissions at 700 and 1000 rpm.
- Two clusters with hydrocarbon fragmentation patterns were observed for the fresh biodiesel emissions at 1300 rpm. These clusters were similar to two of the clusters for lower engine speeds.
- Two MS clusters with hydrocarbon fragmentation patterns were observed for the fresh biodiesel emissions at 1600 rpm. These clusters were similar to two of the clusters for 700 and 1000 rpm but one of the clusters was different from those found at 1300 rpm.
- The number of particles (Np) corresponding to each cluster are shown. The most abundant cluster changes with increasing speed, corroborating the findings from the difference spectra.

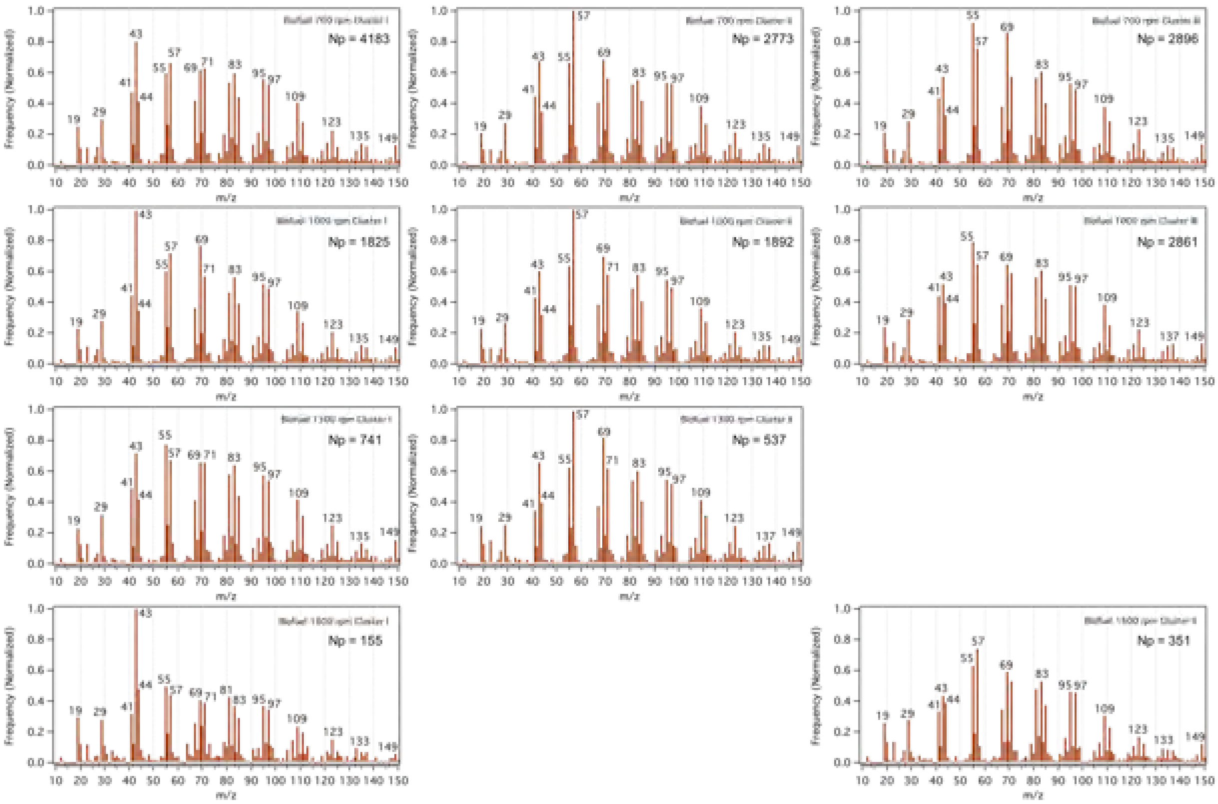

Figure 17. *HR-ToF-AMS single particle mass spectra cluster analysis for biodiesel plume emissions at 700, 1000, 1300, and 1600 rpm engine speeds. Np = number of particles. (CE=1). HR-ToF-AMS spectra the 2015 cruise (9/4/15 – 9/6/15 and 9/26/15 – 9/28/15) were used for the cluster analysis.*

Comparison of Elemental Ratios of Organic Particles

- The elemental ratios show that the ship emissions consist of highly reduced aerosol. Typically the ship emissions had elemental ratios of O/C~0 and H/C~2, with OM/OC~1.2. These metrics are consistent with most of the organic mass consisting of C_nH_{2n} molecules with a large number of alkane fragments.
- The ambient marine aerosol is more oxidized. Typically the background aerosol had elemental ratios of O/C=0.7 – 0.8 and H/C=1.2 – 1.3, with OM/OC=2.2 – 3.0.

Changes in Mass Size Distribution with Engine Speed

- The slight differences observed in the mass spectra are corroborated by the size distribution profiles for the organic mass emissions at different engine speeds (Figure 19), which show a shift of the smaller organic particle mode to larger diameter particles with decreasing engine speed.
- Two size modes are observed. The second size mode remains at 100 nm while the smaller size mode shifts to larger diameters with decreasing engine speed. The smaller size mode appears to overlap the second size mode at 700 rpm engine speed.

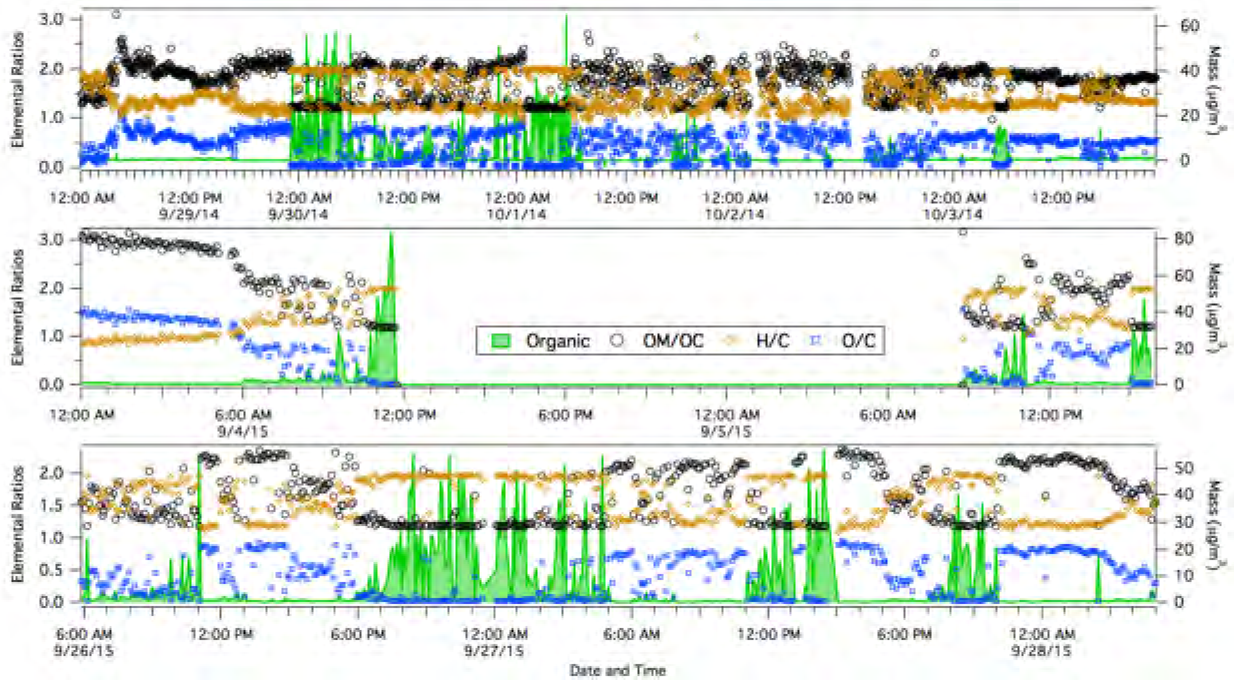

Figure 18. *HR-ToF-AMS elemental ratios and organic mass concentration (CE=1) over time for the 2014 cruise (9/29/14 – 10/3/14) and the 2015 cruise (9/4/15 – 9/6/15 and 9/26/15 – 9/28/15).*

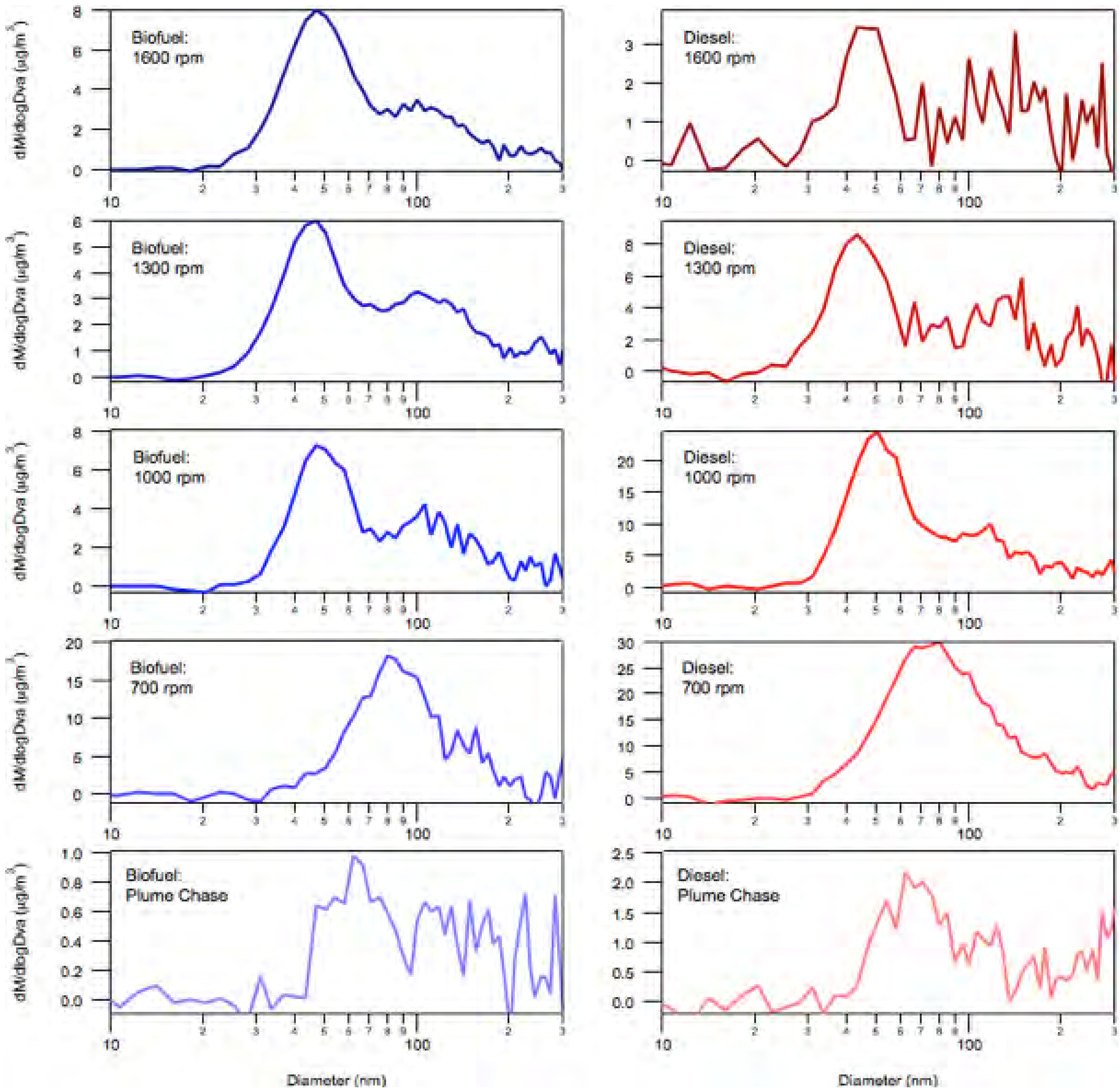

Figure 19. *HR-ToF-AMS size distribution profiles for biodiesel (9/26/15) and diesel (9/5/15) emissions at different engine speeds and aged emissions. (CE=1)*

Differences in Particle FTIR Composition between Fuels, Speeds, and Aging

- There is a large hydrocarbon signal at wave numbers 2800-3000 in all of the samples of ship emissions.
- The ratio between the hydrocarbon peaks is very consistent for fresh emissions at each speed; the ratio is slightly greater with the diesel emissions:
    - Average biodiesel ratio (700 – 1300 rpm): 1.635
    - Average diesel ratio (700 – 1300 rpm): 1.766
    - Average biodiesel ratio (aged): 1.338
    - Average diesel ratio (aged): 1.449

- There is a small increase in the carbonyl fraction for the aged diesel compared with the fresh emissions of diesel. This change in oxidation with aging of the diesel emissions is consistent with the observed increase in *m/z* 44. The biodiesel aged sample has too little signal above background to detect change.

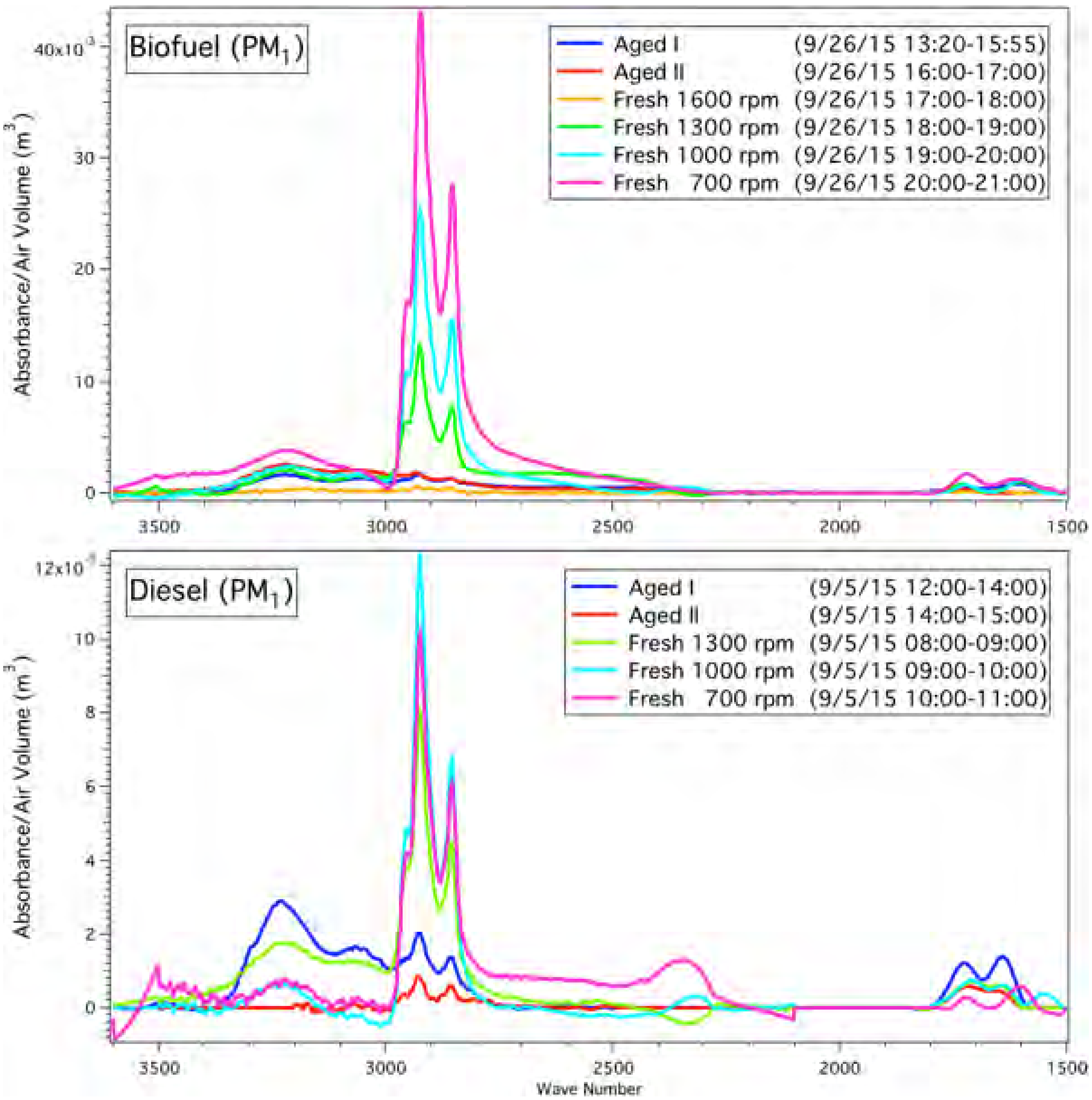

Figure 20. *FTIR spectra (normalized to air volume) for PM_1 size cutoff samples for biodiesel (9/26/15) and diesel emissions (9/5/15) at 700, 1000, 1300, and 1600 rpm engine speeds.*

For both fuels, the organic mass emissions increased at lower ship speeds. The organic chemical composition of particles from diesel and biodiesel are similar in this study. Both HR-ToF-AMS and FTIR spectra as well as the HR-ToF-AMS elemental analysis indicate the ship exhaust is mainly composed of alkane-like hydrocarbons. Only slight differences in composition are observed. The HR-ToF-AMS mass spectra and FTIR hydrocarbon peak ratio suggest different types of alkane hydrocarbons are present for both fuels. The HR-ToF-AMS single particle spectra show some composition changes for different engine speeds. Comparison of fresh and aged HR-ToF-AMS and FTIR spectra indicates that alkane aerosol was oxidized more quickly relative to aromatic aerosols. There was also an observed increase in the carbonyl functional groups in the aged diesel emissions.

PART 4: OUTCOMES OF THIS STUDY

The results of these emission studies are presented in posters at three scientific meetings (Price et al., 2015; Price et al., 2016a; Betha et al., 2016a) and in two manuscripts in preparation (Price et al., 2016b; Betha et al., 2016b). The sampling approach was also documented for the public in local periodicals by science journalist Judith Garfield (http://www.sdnews.com/pages/full_story/push?article-Scripps+research+on+biofuels+hits+close+to+home%20&id=26452067&instance=stories). These products are listed below.

- 34th Annual American Association for Aerosol Research Conference: Characterization of fresh and aged emissions from a marine vessel fueled with diesel and biodiesel (presented 13 October 2015).
- 33rd Informal Symposium on Kinetics and Photochemical Processes in the Atmosphere: Comparison of diesel and biodiesel organic aerosol emissions from a marine vessel (to be presented 24 March 2016).
- 33rd Informal Symposium on Kinetics and Photochemical Processes in the Atmosphere: Gaseous and particulate emissions from a marine vessel powered by diesel and biodiesel. (to be presented 24 March 2016).
- Characterization of organic aerosol emissions from a marine vessel powered by diesel and biodiesel. Derek J. Price, Chia-li Chen, Maryam A. Lamjiri, Raghu Betha, Lynn M. Russell (2016 in preparation).
- Emission factors of CO, NO_x and Particles from a marine vessel powered by diesel and biodiesel. Raghu Betha, Maryam A. Lamjiri, Chia-li Chen, , Derek, J. Price. Lynn M. Russell (2016 in preparation).
- Scripps research on biofuels hits close to home, Judith Garfield, http://www.sdnews.com/pages/full_story/push?article-Scripps+research+on+biofuels+hits+close+to+home%20&id=26452067&instance=stories.

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Appendix 1. Fuel Analysis of Renewable Diesel

Appendix 2. Fuel Analysis: Sulfur, Carbon and Nitrogen