UC Riverside UC Riverside Electronic Theses and Dissertations

Title

Analytical Framework to Evaluate Emission Control Systems for Marine Engines

Permalink https://escholarship.org/uc/item/5tg226g7

Author Jayaram, Varalakshmi

Publication Date 2010

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA RIVERSIDE

Analytical Framework to Evaluate Emission Control Systems for Marine Engines

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Chemical and Environmental Engineering

by

Varalakshmi Jayaram

December 2010

Dissertation Committee: Dr. David R. Cocker III, Chairperson Dr. J. Wayne Miller Dr. Joseph Norbeck

Copyright by Varalakshmi Jayaram 2010 The Dissertation of Varalakshmi Jayaram is approved:

Committee Chairperson

University of California Riverside

Acknowledgements

First and foremost I would like to thank my advisors Dr. David Cocker and Dr. Wayne Miller for providing me with the opportunity, knowledge and resources to become a PhD, for giving me the independence to plan and manage entire projects and for pushing me beyond my comfort zone to broaden my perspective and develop an extensive skill set.

Next I would like to thank Dr. Joseph Norbeck for his valuable comments during my qualifying exam and for being a part of my final thesis committee. Also Dr. Heejung Jung for sharing his insight on my work and overseeing the progress of the transfer line study.

A special thanks to William A Welch for being there on every field expedition, providing an on-hands training in the field and showing me the importance of being positive and staying calm under tremendous pressure.

I shall always be grateful to Kathy Cocker, Kent Johnson, Charles Bufalino, Mr. Kurt Bumiller, Don Pacocha and Joe Valdez, for accepting me as a part of the CE-CERT family, entertaining even my craziest ideas and providing me with the means and methods of making each project happen. To all the graduate and undergraduate students (Harshit Agrawal, Ajay Chowdry, Abhilash Nigam, M Yusuf Khan, Poornima Dixit, Karel Johnson, Cristina Hall, Mary Sheppy, Antony Turgman, James Gutierrez, David Torres, Charles Wardle, Sindhuja Ranganathan) who trained me or whom I trained, thank you all for providing me with the analytical and technical support.

A special thanks to California Air Resources Board for providing the financial support without which none of this research could have happened.

Finally I would like to thank my family and friends: my parents for taking turns staying with me during the most demanding periods of my program; my dear son, Krishna for being patient when I worked long hours and filling me with joy even in the dullest moments, Kavita Kothakonda and her beautiful daughters Vaishnavi and Vaibhavi for entertaining Krishna while I wrote several parts of this dissertation and my best friends Harshit Agrawal, Rajwant Bedi, Sindhuja Ranganathan and Bill Welch for talking me through the bad times and celebrating the good ones with me.

The text of Chapter 3 of this dissertation, in part or in full, is a reprint of the material as it appears in the Journal of Air Waste Management Association Volume 60, December 2010, DOI:10.3155/1047-3289.60.12.1.

I dedicate this work to my parents Gomathy and Jayaram Rangan for providing me with the courage, support and encouragement to become a strong independent individual capable of supporting my son. Thank you Amma and Appa, you made this dissertation happen.

ABSTRACT OF THE DISSERTATION

Analytical Framework to Evaluate Emission Control Systems for Marine Engines

by

Varalakshmi Jayaram

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering University of California, Riverside, December 2010 Dr. David R. Cocker III, Chairperson

Emissions from marine diesel engines are mainly uncontrolled and affect regional air quality and health of people living near ports. Many emission control strategies are evolving to reduce these emissions and their impacts. This dissertation characterizes the effectiveness of new technologies for reducing NO_x and $PM_{2.5}$ emissions from a range of marine diesel engines. Researchers, regulators and policy makers require these characterizations to develop emission inventories and suitable mitigation strategies.

Three NO_x control technologies were analyzed: injection timing retard, water in fuel emulsion, and selective catalytic reduction (SCR). Each significantly reduced NO_x emissions. The SCR, however, increased $PM_{2.5}$ emissions by 150-380% indicating a need for technology modification before implementation. Additionally, two fuel control strategies for $PM_{2.5}$ based on cleaner burning fuels were evaluated: the effects of switching from high-sulfur heavy fuel oil to lower-sulfur marine distillate oil and switching from diesel to biodiesel blends were tested. Results showed significant $PM_{2.5}$ reductions with minimal change in NO_x ; however, the biodiesel fuel increased formation of nucleation mode particles.

In-use emission benefits of a diesel-electric hybrid tug were characterized. Activity data showed that the average load factors of tug boat engines were up to 83% lower than that specified in the certification cycles typically used for developing emission inventories. Reductions of 73% for $PM_{2.5}$, 51% for NO_x and 27% for CO_2 were seen in comparison to a similar conventional tug. The majority of these reductions were attributed to the hybrid tug's energy management system, which directs use of auxiliary power for propulsion. Additional in-use harbor-craft measurements showed significant ocean current effects with a three to six fold increase gaseous and $PM_{2.5}$ emissions.

Overall this research showed that 1) new control technologies should be evaluated in the pilot stage to ensure that they do not increase emissions, 2) use of certification cycle load factors can significantly overestimate emissions from marine applications, and 3) actual in-use measurements are needed for accurate localized inventories. Finally, a new activity and emissions based protocol was developed to establish emission benefits of a multi-powered diesel-electric hybrid system.

Table of Contents

1	Intro	oduc	tion 1
1	.1	Em	issions from Marine Diesel Engines 1
	1.1.	1	Oxides of Nitrogen (NO _x)
	1.1.	2	Oxides of Sulfate (SO _x)
	1.1.	3	Particulate Matter (PM)
	1.1.	4	Carbon monoxide and Hydrocarbons
	1.1.	5	Carbon dioxide
1	.2	Cor	trol Technologies4
1	.3	Out	line of Dissertation ϵ
2	Effe	ect of	f Adding Water to Fuel on Emissions from a Large Marine Engine
2	.1	Cha	pter Summary 8
2	.2	Intr	oduction
2	.3	Exp	perimental Methods
	2.3.	1	Test Engine
	2.3.	2	Test Fuels11
	2.3.	3	Test Cycle
	2.3.	4	Sampling and Analysis
	2.3.	5	Calculating Exhaust Flow Rates
	2.3.	6	Calculating Emission Factors
2	.4	Res	ults and Discussions
	2.4.	1	Gaseous Emissions
	2.4.	2	Total and Speciated PM _{2.5} Mass Emissions
2	.5	Ack	znowledgements
3	Effe	ectiv	eness of Emission Control Technologies for Auxiliary Engines on Ocean
-	Gon	ng-∨	Zessels
3.	.1	Cha	apter Summary
3.	.2	Intr	oduction
3.	.3	Exp	perimental Details

3.3	3.1	Engine and Fuel Specifications	28
3.3	3.2	Test Cycle	29
3.3	3.3	Emission Measurements	29
3.3	3.4	Modal & Overall Emission Factors	30
3.3	3.5	Emission Control Technologies	31
	3.3.5	1 Cleaner Burning Fuels	31
	3.3.5	2 Low NO _x Mode	31
	3.3.5	3 Selective Catalytic Reduction	31
3.4	Res	ults and Discussions	32
3.4	4.1	Transfer Line Loss	32
3.4	4.2	Baseline Emissions	33
3.4	4.3	Cleaner Burning Fuels	40
3.4	4.4	Low NO _x Mode	41
3.4	4.5	Selective Catalytic Reduction	42
3.5	Acl	nowledgements	43
4 Re	al-Ti	ne Gaseous, PM and Ultrafine Particle Emissions from a Modern Mari	ne
En	gine	Operating on Biodiesel	45
4.1	Cha	pter Summary	45
4.2	Intr	oduction	46
4.3	Exp	erimental Details	48
4.3	3.1	Engine Specifications	48
4.3	3.2	Fuels	48
4.3	3.3	Test Matrix	50
4.3	3.4	Emission Measurements	51
	4.3.4	1 Gaseous Emissions	52
	4.3.4	2 Total PM _{2.5} Mass Emissions	53
	4.3.4	3 Elemental and Organic Carbon in PM _{2.5} mass	53
	4.3.4	4 Carbonlys	54
	434	5 C_{10} to C_{20} hydrocarbons. Naphthalene and Poly aromatic	

4.3.4	.6 Organic Mass to Organic Carbon Ratio	55
4.3.4	.7 Particle Number and Size Distribution	55
4.3.4	.8 Real-Time PM Mass Emissions	56
4.3.5	Calculating Effective Density of PM _{2.5} Mass	57
4.3.6	Calculating Modal & Overall Emission Factors	58
4.3.7	Calculating In-Use Emissions (g hr ⁻¹)	58
4.4 Re	sults and Discussion	59
4.4.1	Steady State Loads	59
4.4.1	.1 Gaseous Emissions:	59
4.4.1	.2 Total PM _{2.5} Mass Emissions	62
4.4.1	.3 Elemental and Organic Carbon fractions of PM _{2.5} Mass Emiss	sions.
		63
4.4.1	.4 PM Size Distribution	65
4.4.1		70
4.4.1	.6 C_{10} to C_{30} Hydrocarbons, Naphthalene & Poly Aromatic	
	Hydrocarbons	 71
442	In-Use Cycle	71
4.5 Ac	knowledgements	72
5 Protoco	Development and Use for Determining the Benefits of a Hybrid Tug	76
5.1 Ch	apter Summary	76
5.2 Int	roduction	77
5.3 Ex	perimental Methods	78
5.3.1	Test Boats.	78
5.3.1	.1 Conventional tug (CT)	79
5.3.1	.2 Hybrid Tug (HT)	80
5.3.2	Activity and Emissions Based Approach	82
5,3,3	Data Logging Procedure	85
534	Calculating Operating Mode Weighting Factors	00 90
5 3 5	Calculating the Engine Load	رد ۵۵
5.5.5	Calculating the Elignic Load	90

	5.3.5	.1 Load Correction for Main Engine on Conventional Tug	91
	5.3.6	Developing Engine Histograms	93
5.3.7 Calculat		Calculating the Average Load required for a Tug Operation	94
	5.3.8	Emissions Testing	95
	5.3.8	.1 Emissions Testing Phase 1	98
	5.3.8	.2 Emissions Testing Phase 2	100
	5.3.9	Determining Exhaust Flow Rates	101
	5.3.9	.1 Intake Air Method	101
	5.3.9	.2 Carbon Balance Method	101
	5.3.10	Calculating of Emissions in g hr ⁻¹	102
	5.3.11	Calculating Modal and Overall Weighted Average Emission Factors	103
5	.4 Res	sults and Discussion	103
	5.4.1	Tug Operating Mode Weighting Factors	103
	5.4.2	Engine Histograms	105
	5.4.2	.1 Conventional Tug (CT)	105
	5.4.2	.2 Hybrid Tug	105
	5.4.3	Emissions Profiles	112
	5.4.4	Overall In-Use Emissions	120
	5.4.4	.1 Retrofit Scenarios	122
	5.4.5	Acknowledgements	125
6	Conclus	ions and Recommendations	126
7	Bibliog	raphy	132
Ap	pendix A	A Determining Particulate Matter Losses in Raw Gas Heated Transfer Li	ne
			145
А	A.1 Inti	roduction	145
А	.2 Exp	perimental Details	146
	A.2.1	Transfer Line	146
	A.2.2	Test Engines	148
	A.2.3	Test Fuels	148

A.2.	4 Emissio	n Measurements	149
А	.2.4.1	Gaseous Measurements	151
А	.2.4.2	Particulate Matter Measurements	152
А	.2.4.3	Particle Size Distribution	153
A.3	Results and I	Discussions	153
A.3.	1 4-Stroke	e Engine	153
A.3.	2 2-Stroke	e Engine	158
A.4	Conclusions		162
A.5	Acknowledg	ements	162

Table of Figures

Figure 2-1	Picture of Water in Fuel Emulsion Unit	12
Figure 2-2	Schematic of the Sampling System	14
Figure 2-3	Gaseous Emission Factors a)Nitrogen Oxides b)Carbon Monoxide c)Total Hydrocarbons d) Carbon dioxide	18
Figure 2-4	PM _{2.5} Mass Emission Factors a)Total PM _{2.5} Gravimetric Mass b)Elemental Carbon Fraction c)Organic Carbon Fraction d) Hydrated Sulfate Fraction :	21
Figure 2-5	PM _{2.5} Mass Balance for the 50% Engine Load Point	22
Figure 2-6	PM _{2.5} Mass Balance Across all Loads and Fuels	23
Figure 3-1	Effect of Fuel Switching on Gaseous Emission Factors a)NO _x b)CO ₂ c)CO d)Weighted NO _x	34
Figure 3-2	Effect of Fuel Switching on Total & Speciated PM Emission Factors a)Total PM b)EC c)OC d)H ₂ SO ₄ .6.5H ₂ O	35
Figure 3-3	Effect of SCR on Emission Factors a)Gases for HFO b)Gases for MDO c)Total & Speciated PM for HFO d)Total & Speciated PM for MDO	38
Figure 3-4	PM _{2.5} Mass Closure for AE#2 and AE#3	39
Figure 3-5	Effect of Low NOx Mode on Emission Factors of AE#3 @ 27% Engine Loa Point	d 42
Figure 4-1	Schematic of Sampling System	52
Figure 4-2	Correlation between DustTrak PM _{2.5} and Gravimetric PM _{2.5} for B20	57
Figure 4-3	Overall Weighted Emissions Factors (g hp ⁻¹ hr ⁻¹)	60
Figure 4-4	Modal Gaseous Emission Factors (g hp ⁻¹ hr ⁻¹)	61
Figure 4-5	Total and Speciated PM _{2.5} Mass Emission Factors (g hp ⁻¹ hr ⁻¹)	63
Figure 4-6	PM _{2.5} Mass Balance	65
Figure 4-7	Particle Size Distribution-1	67
Figure 4-8	Particle Size Distribution-2	68

Figure 4-9	Density-Shape Factor of Diesel/Biodiesel PM	70
Figure 4-1	0 Carbonyl Emission Factors	71
Figure 4-1	1 C_{10} to C_{30} Hydrocarbons, Naphthalene and Poly-Aromatic Hydrocarbons	72
Figure 4-1	2 Real Time Emissions Trace on a Typical Cruise a)Approximate Route for Cruise b)Gaseous and PM emissions c)Particle Size Distribution	74
Figure 5-1	Schematic of Power-Train on the Hybrid Tug	81
Figure 5-2	Schematic of the Data Logging System on the Conventional Tug	87
Figure 5-3	Schematic of the Data Logging System on the Hybrid Tug	88
Figure 5-4	ECM Load versus CO ₂ Emissions for A)Main Engine Conventional Tug CA 3512 C B)Auxiliary Engine Conventional Tug JD 6081 C)Main Engine Hybrid Tug Cummins QSM50 D)Auxiliary Engine Hybrid Tug Cummins QSK11 M	T 92
Figure 5-5	Load Correction for Main Engine on Conventional Tug	93
Figure 5-6	Schematic of Sampling System for Emissions Testing Phase 1	97
Figure 5-7	Schematic of Test Setup for Emissions Testing Phase 2	97
Figure 5-8	Weighting Factors for Tug Operating Modes 10	04
Figure 5-9	Main Engine Histograms for Conventional Tug	06
Figure 5-1	0 Engine Histograms for Hybrid Tug – 1 10	07
Figure 5-1	1 Engine Histograms for Hybrid Tug – 2 10	38
Figure 5-1	2 Engine Histograms for Hybrid Tug without Batteries -1	10
Figure 5-1	3 Engine Histograms for Hybrid Tug without Batteries– 2 1	11
Figure 5-1	4 PM _{2.5} Mass Balance for A)Main Engine Conventional Tug CAT 3512 C B)Auxiliary Engine Conventional Tug JD 6081 C) Main Engine Hybrid Tug Cummins QSM50 D) Auxiliary Engine Hybrid Tug Cummins QSK11 M	g 14
	······································	

Figure 5-15	Emission Profile of A)Auxiliary Engine on Conventional Tug B)Main Engine on Conventional Tug C)Auxiliary Engine on Hybrid Tug D)Main	
	Engine on Hybrid Tug	5
Figure 5-16	Comparison of Phases 1 & 2 for Main Engine on Conventional Tug CAT 3512 C	7
Figure 5-17	Comparison of Phases 1 & 2 for Main Engine of Hybrid Tug Cummins QSK50 M 118	3
Figure 5-18	Comparison of Phases 1 & 2 for Auxiliary Engine on Hybrid Tug Cummins QSM11)
Figure A-1	Picture of Transfer Line 146	5
Figure A-2	Schematic of Thermocouple Positions (A to E) 147	1
Figure A-3	Schematic of Sampling System	Ĺ
Figure A-4	PM Emissions from 4-Stroke Engine155	5
Figure A-5	Mass Balance for 4-Stroke Engine 156	5
Figure A-6	Particle Size Distribution for 4-Stroke Engine	7
Figure A-7	PM Emissions from 2-Stroke Engine159)
Figure A-8	Mass Balance for Detroit 2-Stroke Engine 160)
Figure A-9	Particle Size Distribution for 2-Stroke Engine	Ĺ

Table of Tables

Table 1-1 NO _x Emission Limits ³⁷	5
Table 1-2 Fuel Sulfur Limits ³⁷	5
Table 2-1 Selected Properties of Heavy Fuel Oil 1	1
Table 2-2 Test Matrix 12	3
Table 2-3 Details of Exhaust Gas Analyzers 1	5
Table 2-4 Overall Weighted Average Emission Factors 19	9
Table 3-1 Test Matrix 23	8
Table 3-2 Selected Fuel Properties 29	9
Table 3-3 Effect of Transfer Line on Emissions from AE#3	3
Table 4-1 Certificate of Analysis Provided by Fuel Supplier for B100 44	9
Table 4-2 Selected Fuel Properties 50	0
Table 4-3 Test Matrix 50	0
Table 4-4 Details of Horiba PG-250 52	3
Table 5-1 Tug Boat Specifications 7	9
Table 5-2 Engine Specifications for Conventional Tug 79	9
Table 5-3 Engine Specifications for Hybrid Tug	0
Table 5-4 Details of Data Logger	6
Table 5-5 Test Matrix for Data Logging	9
Table 5-6 Selected Fuel Properties 90	6
Table 5-7 Test Matrix for Emissions Testing 90	6
Table 5-8 Details of Horiba PG-250	9

Table 5-9 Weekly Variation in Weighting Factors for Operating Modes of Conventional Tug
Table 5-10 Weekly Variation in Weighting Factors for Operating Modes of Hybrid Tug
Table 5-11 Average Load Requirements for Each Operating Mode 112
Table 5-12 Emission Factors in g kW ⁻¹ hr ⁻¹ from Emissions Testing Phase 1 113
Table 5-13 In-Use Emissions of the Hybrid and Conventional Tug at each Tug Operating Mode
Table 5-14 Emission Factors for Shore Power ¹⁴²⁻¹⁴³ 121
Table 5-15 Overall In-Use Emission for the Conventional and Hybrid Tugs 122
Table 5-16 In-Use Emissions of the Hybrid and Conventional Tug at each Tug OperatingMode for Retrofit Scenario 1124
Table 5-17 In-Use Emissions of the Hybrid and Conventional Tug at each Tug OperatingMode for Retrofit Scenario 2124
Table A-1 Temperature Profile of the Transfer Line 147
Table A-2 Engine Specifications 148
Table A-3 Test Fuel Properties 149
Table A-4 Test Matrix 150
Table A-5 Details of Horiba PG-250

List of Acronyms

%	percentage
°C	degree Centigrade
°F	degree Fahrenheit
μm	micro meter
μΩ	micro ohm
AE	Auxiliary Engine
APES	Analytical Procedure for Elemental Separation
ASTM	American Society for Testing Materials
B0	Ultra Low Sulfur Diesel
B20	20% Biodiesel 80% Ultra low sulfur diesel
B50	50% Biodiesel 50% Ultra low sulfur diesel
BC	Black Carbon
BTU	British Thermal Unit
CARB	California Air Resources Board
CAT	Caterpillar
CFO	Critical Flow Orifice
CFR	Code of Federal Regulations
СО	Carbon monoxide
CO ₂	Carbon dioxide
CPC	Condensation Particle Counter
CSV	Comma separated Value

cSt	centistoke
СТ	Conventional Tug
DAD	Diode Array Detector
DAF	Dilution Air Filter
DDI	ultrapure water with conductivity of 18 milliohm
DNPH	2,4 dinitrophenylhydrazine
DR	Dilution Ratio
DT	Dilution Tunnel
EC	Elemental Carbon fraction of particulate matter
ECA	Emission Control Areas
ECM	Electronic Control Module
EGA	Exhaust Gas Analyzer
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
fSMPS	fast Scanning Mobility Particle Sizer
g	gram
GC-MS	Gas Chromatograph – Mass Spectrometer
НС	hydrocarbon
HCLD	Heated Chemiluminescence Detector
HEPA filter	High Efficiency Particulate Filter
HFO	Heavy Fuel Oil
hp	horsepower

hr	hour
HR-ToF-AMS	High Resolution Time of Flight Aerosol Mass Spectrometer
HT	Hybrid Tug
IC	Ion Chromatograph
IMO	International Maritime Organization
ISO	International Organization for Standardization
ITR	Injection Timing Retard
JD	John Deere
kg	kilogram
km	kilometer
kW	kilowatt
1	liter
lb	pound
LC	Liquid Chromatograph
LC-ToF-MS	Liquid Chromatograph – Time of Flight – Mass Spectrometer
m	meter
m/m	mass/mass
MDO	Marine Distillate Oil
ME	Main Engine
MGO	Marine Gas Oil
ml	milliliter
MI	Michigan

min	minute
MW	Megawatt
MYr	Manufactured Year
Ν	Nitrogen
NDIR	Non-Dispersive Infra Red
NIOSH	National Institute for Occupational Safety and Health
nm	nano meter
NO	Nitrogen monoxide
NO _x	oxides of nitrogen
N_2O	nitrous oxide
NO ₂	Nitrogen dioxide
OC	Organic Carbon fraction of Particulate Matter
OGV	Ocean-going vessel
ОМ	Organic Mass
OR	Oregon
РАН	Poly Aromatic Hydrocarbon
PIKA	Peak Integration by Key Analysis
PM	Particulate Matter
PM ₁₀	Particulate Matter with diameters ≤ 10 micrometer
PM _{2.5}	Particulate Matter with diameters ≤ 2.5 micrometer
ppm	parts per million
PSD	Particle Size Distribution

PTFE	Teflo [®] filter
PUF	Poly Ureathane Foam
RH	Relative Humidity
rpm	revolutions per minute
S	Sulfur
SAE	Society of Automotive Engineers
scf	standard cubic feet
SCR	Selective Catalytic Reduction
SO _x	oxides of sulfate
SO ₂	Sulfur dioxide
SO ₃	Sulfur trioxide
SOC	State of Charge
SP	Sampling Probe
TDMA	Tandem mobility particle sizer
Tg	Teragram or 10 ¹² grams
THC	Total hydrocarbon
TT	Transfer Tube
TL	Transfer Line
ULSD	Ultra Low Sulfur Diesel
US EPA	United States Environmental Protection Agency
VN	Venturi
VNC	Virtual Network Computing

WFE	Water in Fuel Emulsion
XAD	an absorbent resin used for hydrocarbon sampling
yr	year

1 Introduction

The international shipping industry is a significant source of global anthropogenic emissions¹⁻⁵. Recent research show that ship emissions have adverse effects on air quality near ports and high traffic shipping lanes⁶⁻¹⁰. About 70% of global ship emissions occur within 400 km of land². Studies¹¹⁻¹² have linked the particulate matter (PM) emissions from ships to increased number of premature deaths.

The global ocean-going fleet is broadly classified into two categories: transport and non transport². The transport fleet predominantly consists of large ocean-going vessels (OGVs)². These vessels typically have one low to medium speed main propulsion engine, three to five auxiliary engines and a boiler. The non-transport fleet consists of military vessels and harbor-craft (e.g: fishing vessels, tug boats, ferries and service vessels)². Harbor-craft have medium to high speed main and auxiliary engines. On most harbor-craft the main engines are used to move the vessel over the water while the auxiliary engines are used for hotelling and other unique vessel equipment needs.

1.1 Emissions from Marine Diesel Engines

95% of the global ocean-going fleet is powered by marine diesel engines². Emissions from marine diesel engines include oxides of nitrogen (NO_x), oxides of sulfur (SO_x), particulate matter (PM_{2.5}), carbon monoxide (CO), hydrocarbons and carbon dioxide (CO₂).

1.1.1 Oxides of Nitrogen (NO_x)

NO_x emissions are formed in the engine from intake air nitrogen and oxygen due to the high temperatures and pressures during the combustion reaction¹³. NO_x is a precursor to the formation of ozone which leads to smog^{14-15} . It is also a significant contributor to formation of nitric acid and nitrate aerosol¹⁴⁻¹⁵. Ships emit 5.0 to 6.9 teragrams (Tg or 10^{12} g) of NO_x as N per year which is about 15% of the global NO_x emissions^{3, 5, 11, 16}. NO_x emissions can be controlled by primary or secondary methods¹⁷⁻¹⁹. Primary methods including injection timing retardation, fuel nozzle adaptation/fuel injection, exhaust gas recirculation, water emulsification of fuel and direct injection of water into combustion chamber can reduce NO_x emissions by 10% to 50%¹⁷⁻¹⁹. Secondary methods like selective catalytic reduction (SCR) involve exhaust gas after treatment and can achieve reductions greater than 95%¹⁷⁻¹⁹.

1.1.2 Oxides of Sulfate (SO_x)

 SO_x emissions are formed by the oxidation of fuel sulfur during combustion. The two main oxides formed are SO_2 and SO_3 . Ships typically operate on high sulfur (up to 4.5% mass/mass), high viscosity heavy fuel oil (HFO) which is the residual fraction of crude oil refining. Therefore ship exhausts have high concentrations of SO_x . Annual global SO_x emission estimates for the shipping industry range from 4.7 to 6.5 Tg of SO_x as $S^{3, 5, 11, 16}$. This is approximately 5-7% of the global SO_x emissions^{3, 5, 11, 16}. SO_x emissions can be controlled by cleaning the exhaust using a scrubber or switching to lower sulfur fuels such as marine distillate oil (MDO) and marine gas oil (MGO)¹⁷.

1.1.3 Particulate Matter (PM)

 $PM_{2.5}$ emissions are formed from fuel sulfur, ash and un-burnt or partially burnt fuel/lubricating oil¹⁷. $PM_{2.5}$ can penetrate deep into the lungs. Some studies associate fine particulate exposure with increased risk of lung cancer, pulmonary and cardiovascular disease (Lloyd & Pope). Recent studies¹¹⁻¹² have linked ship $PM_{2.5}$ mass emissions to ~60,000 cardiopulmonary and lung cancer deaths annually. Annual PM_{10} emission from ships is estimated to be 1.2 to 1.6 Tg^{3, 5, 11, 16}. Global emission estimates of some of the components of primary ship PM are as follows: 0.35 to 0.77 Tg yr⁻¹ of sulfate, 0.05 to 0.10 Tg yr⁻¹ of black carbon (BC) and 0.13 to 1.06 Tg yr⁻¹ of organic carbon (OC)^{3, 5, 11, ¹⁶. Ship PM can have significant effects on the radiative budget of the earth's atmosphere - the sulfate fraction showing a negative effect and BC a positive effect^{2, 20-22}. The primary method employed to reducing PM emissions from ships is the use of the lower sulfur MDO/MGO in place of the high sulfur HFO. Smaller vessels like harbor-craft may employ diesel particulate filters when the PM regulations become stringent.}

1.1.4 Carbon monoxide and Hydrocarbons

CO and total hydrocarbon (THC) emissions are a result of incomplete combustion. The concentration of these two species in diesel exhaust is low¹³; therefore this work will not focus on CO and THC emissions.

1.1.5 Carbon dioxide

 CO_2 is the most important greenhouse gas emitted by ships both in terms of quantity and global warming potential²³. Current estimates of annual CO_2 emissions from shipping are

~1046 Tg which is ~3.3% of global CO_2 emissions²³. Use of hybrid systems that incorporate solar, wind and water power are under consideration to reduce energy requirements of marine diesel engines thereby leading to lower in-use CO_2 emissions.

1.2 Control Technologies

One of the key challenges faced by researchers and regulators in developing emission inventories is the availability of reliable emission factors and activity data. Recent research on emissions has primarily focused on establishing gaseous and PM emission factors for uncontrolled marine engines²⁴⁻³⁴. Data on effects of control technologies is limited ^{30-31, 35-36}.

Introduction of control technologies is primarily regulation driven. The International Maritime Organization (IMO) regulates fuel sulfur content and NO_x emissions from marine engines (Tables 1-1 and 1-2)³⁷. High shipping activity regions located near heavily populated coastlines are designated as emission control areas (ECAs). Regulations for ships operating in these ECAs are more stringent. IMO's marine environment protection committee is currently finalizing a regulation for the control of greenhouse gas emissions by the introduction of several mandatory technical and operational strategies ³⁸.

Tier	Date	NO _x Limit, g kW ⁻¹ hr ⁻¹		
		n < 130	$130 \le n < 2000$	$n \ge 2000$
Tier I	2000	17.0	$45 * n^{-0.2}$	9.8
Tier II	2011	14.4	$44 * n^{-0.23}$	7.7
Tier III	2016 ^a	3.4	$9 * n^{-0.2}$	1.96

 Table 1-1 NO_x Emission Limits³⁷

Note: n is rated speed of engine in rpm, ^a In NO_x Emission Control Areas (Tier II standards apply outside ECA)

Date	Sulfur Limit in Fuels (% m/m)		
	SO _x ECA	Global	
2000	1.5%	1.50/	
July 2010	1.00/	4.3%	
2012	1.0%	2.50/	
2015	0.1%	5.5%	
2020 ^a		0.5%	

 Table 1-2 Fuel Sulfur Limits³⁷

Note: ^a alternative date is 2025, to be decided by a review in 2018

NO_x and PM emission factors of marine engines are significantly greater than that of onroad diesel engines. Several control technologies employed on these on-road engines (e.g: exhaust gas recirculation, injection timing retard, selective catalytic reduction) are currently being adapted for use in marine engines. Most studies^{18, 36} estimate reductions from these technologies based on their experiences for on-road engines. However, actual reductions may vary due to the engine technology and the use of high sulfur fuels in marine engines. This research focuses on quantifying the effect of several emission control technologies on gaseous and $PM_{2.5}$ emissions from a variety of in-use marine engines.

1.3 Outline of Dissertation

Four control technologies: 1) water in fuel emulsion (WFE), 2) cleaner burning fuels, 3) injection timing retardation and 4) selective catalytic reduction (SCR) were evaluated on in-use marine engines operating on PanMax and post Panamax class container vessels (Chapter 2 & 3). Detailed gaseous (NO_x, CO, CO₂) and PM_{2.5} (total mass, elemental carbon (EC), OC, sulfate) emissions were measured to quantify the effects of each control strategy on target pollutants as well as other emissions from these engines.

Two control technologies for harbor-craft were evaluated: an alternative fuel, biodiesel (Chapter 4) and a diesel electric hybrid system (Chapter 5). A modern marine propulsion engine on a ferry/excursion boat was tested while operating on ultra low sulfur diesel (B0) and two blends of diesel with biodiesel (B20, B50) to evaluate the impacts of biodiesel on gaseous (NO_x, CO, CO₂), PM_{2.5} (total mass, EC, OC, size distribution) and selected hydrocarbon (carbonyls, aldehydes, poly aromatics, C_{10} to C_{30} alkanes) emissions. Also, real-time monitoring of gaseous and PM_{2.5} emissions were conducted during a typical cruise in the San Francisco bay. Analysis of the data from the cruise revealed significant effects of ocean currents on emissions from these engines.

One of the prevalent technology solutions for reduction of CO_2 emissions is the diesel electric hybrid system. Evaluating the emission benefits of a hybrid system can be quite

challenging. The common thread seen in testing of hybrid vehicles is proper accounting of energy from all sources. The final study in this dissertation (Chapter 5) involved the development and implementation of an activity and emissions based model to determine real world gaseous ($NO_x CO_2$) and total $PM_{2.5}$ mass emission benefits of a hybrid system on a tug boat. A data acquisition system capable of continuously monitoring and logging second by second data from four engines and batteries on two tugs (conventional and hybrid) was utilized for a period of one month each to obtain activity data. A series of emission tests were then performed to determine the emission profiles of main and auxiliary engines on the tugs. Next, activity and emission data were combined to determine the overall in-use emissions from each tug. Finally the emission benefits of the hybrid system are presented.

Chapter 6 details the major findings of this dissertation and provides recommendations for future work. Additionally, Appendix A presents some preliminary analyses on the losses associated with a heated line used for sampling PM from diesel engines.

2 Effect of Adding Water to Fuel on Emissions from a Large Marine Engine

2.1 Chapter Summary

Large two-stroke low-speed marine propulsion engines operated on ocean going vessels are significant contributors to global anthropogenic NO_x and PM_{2.5} mass emissions. This study evaluates the effectiveness of water in fuel emulsion (WFE) NO_x control technology on the propulsion engine of a PanaMax class container vessel. In-use measurements of gaseous (NOx, CO, CO2, total hydrocarbons) and PM2.5 (total and speciated) emissions were made based on the ISO 8178-1 protocol while operating on different blends of WFEs. The overall weighted average NO_x and PM_{2.5} mass emission factors with HFO (3.61% sulfur) were found to be 16.6 g kW⁻¹ hr⁻¹ and 1.95 g kW⁻¹ hr⁻¹. The reduction in weighted average NO_x emissions were found to be ~12% with 20% water to fuel ratio and ~23% with 33% water to fuel ratio. Overall the change in total PM_{2.5} mass varied from -16% to 45% with the water addition. The organic carbon fraction of PM_{2.5} increased by a factor of 1.8 to 3.5; elemental carbon fraction increased by 0.8 to 4.8. The WFE changed the speciation of the PM_{2.5} mass from 0.2% EC, 4% Ash, 8% OC and 93% hydrated Sulfate to 0.6% EC, 3% Ash, 22% OC and 66% hydrated sulfate.

2.2 Introduction

Ships are significant contributors of the global anthropogenic nitrogen oxides (NO_x) and particulate matter $(PM_{2.5})$ emissions^{2-5, 11}. These emissions adversely affect air quality

near ports and high traffic shipping lanes⁶⁻¹⁰. The sources of emissions on a ship include a main propulsion engine, three to seven auxiliary engines and an auxiliary boiler; the most significant of these being the propulsion engine. The propulsion engines on ocean going vessels are typically large, low-speed, two-stroke marine diesel engines.

Oxides of nitrogen are mainly formed from intake air nitrogen and oxygen during combustion reactions in the engine. This NO_x formation reaction explained by the Zeldovich mechanism is driven by high temperatures of combustion. Some NO_x is also formed from the fuel nitrogen. NO is the most abundant nitrogen oxide in the exhaust of a two-stroke low-speed engine followed by NO₂ (~5%) and N₂O (~1%)¹⁷. NO_x emissions are one of the precursors for the formation of ozone which causes adverse health effects. NO_x is also known to react with other compounds in the atmosphere to form nitric acid and nitrate aerosol ¹⁴.

PM_{2.5} emissions in ship exhaust originate from partial burned or unburned fuel and lubricating oil, fuel sulfur and ash¹⁷. Sulfates form the most significant component of ship PM_{2.5} emissions followed by organic carbon (OC), elemental carbon (EC) and ash^{25-27, 39}. These fine particles can lodge deep into the lungs causing increased respiratory symptoms, chronic bronchitis and irregular heart-beat¹⁴. Recent research has linked the PM_{2.5} mass emissions from ships to a significant number of premature deaths particularly along coastlines¹¹⁻¹². These emissions also affect the atmospheric radiation budget. EC or black carbon (BC) absorbs solar radiation while sulfate scatters it. BC is also known to

deposit on snow thereby reducing albedo. Sulfate particles aid in the formation of clouds which scatter solar radiation. Current studies^{2, 20-22} show an overall negative radiative effect from ship $PM_{2.5}$.

The International Maritime Organization (IMO) regulates NO_x emissions from marine engines ³⁷. The current NO_x emission standard for low speed (<130 rpm) marine engines is 17.0 g kW⁻¹ hr⁻¹. The Tier II standard of 14.4 g kW⁻¹ hr⁻¹ will come into effect in 2011. Several NO_x control technologies^{17-19, 36} like injection timing retardation, modifications to fuel nozzle/fuel injection, exhaust gas recirculation, WFEs, water injection in combustion chamber, humidification of intake air and selective catalytic reduction are being considered for achieving the Tier II and Tier III IMO standards.

Emissions data for low-speed two-stroke marine engines are limited. The most referenced data set is that published by Llyod's register ²⁴. Recent studies²⁵⁻³⁰ have primarily focused on characterizing gaseous and particulate matter emissions from uncontrolled engines. In-use data on these engines equipped with NO_x control technologies are scarce.

This study evaluates the effectiveness of a water in fuel emulsion (WFE) unit in reducing NO_x emissions from a large two-stroke low-speed marine propulsion engine. It also assesses the effect of this control technology on other gaseous and $PM_{2.5}$ emissions - carbon dioxide (CO₂), carbon monoxide (CO), total hydrocarbons (THC), total $PM_{2.5}$ mass emissions and the EC, OC and sulfate fractions of $PM_{2.5}$ mass. For this purpose in-

use measurements were made following the load points in the ISO 8178 E3 cycle while the engine operated on several blends of water and heavy fuel oil (HFO).

2.3 Experimental Methods

2.3.1 Test Engine

Emissions testing was performed on the 48,826 kW Hyundai MAN B&W 11K90MC-C main propulsion engine of a PanaMax class container vessel. This is an eleven cylinder large two-stroke low-speed (104 rpm) marine diesel engine manufactured in 1995 with a total engine displacement of 16095 liters.

2.3.2 Test Fuels

This test engine was operated on the normal fuel of operation, 3.61% heavy fuel oil (HFO) that met the ISO 8217 specifications. A sample of the fuel obtained from the ship was analyzed for some selected properties (Table 2-1). This high viscosity HFO is preheated to reduce viscosity before injection into the engine.

r r	
Density @15°C	0.9865 g ml^{-1}
Viscosity @ 50°C	382.9 cSt
Sulfur Content	3.61 % mass
Carbon Content	85% mass
Hydrogen Content	10.4% mass
Ash	0.029 % mass

Table 2-1 Selected Properties of Heavy Fuel Oil
Testing was also performed while the engine operated on three WFEs: 20% water 80% HFO, 33% water 67% HFO and 48% water 52% HFO. These emulsions were made by spraying a controlled amount of pre-heated water into the fuel followed by mixing in a homogenizer. Figure 2-1 shows a picture of the experimental WFE unit installed by MAN B&W Diesel on the test engine. Addition of water to the fuel increases its viscosity, thereby increasing the required pre-heating before injection. The amount of water that can be added to fuel was limited to 33% at high load by the capacity of the fuel heater and 48% at low loads by the maximum allowed temperature of fuel injection.



Figure 2-1 Picture of Water in Fuel Emulsion Unit

2.3.3 Test Cycle

In-use emission testing was carried out during a sea voyage from the Los Angeles to Dutch Harbor following the load points in the ISO 8178-4 E3 cycle. Due to practical considerations, the engine was not operated at the 100% engine load, 75% engine load for the 48% water WFE and 8% load for the 33% water WFE. Table 2-2 lists the load points measured for each test fuel. The engine load in this study was determined from the readings on the control panel of the engine control room. Due to operational constraints, the actual load on the engine varied by $\pm 5\%$ from the target load.

Fuel	Percent of Max. Engine Load					
	75%	50%	25%	8%		
Base Fuel: 100% HFO	\checkmark	\checkmark	\checkmark	\checkmark		
20% Water 80% HFO	\checkmark	\checkmark	\checkmark	\checkmark		
33% Water 67% HFO	\checkmark	\checkmark	\checkmark	×		
48% Water 52% HFO	×	\checkmark	\checkmark	\checkmark		

 Table 2-2 Test Matrix

2.3.4 Sampling and Analysis

Gaseous and Particulate Matter ($PM_{2.5}$) sampling methods conformed to ISO 8178-1 protocols. Figure 2-2 shows a schematic of the sampling system. A partial dilution system with a single venturi was used for $PM_{2.5}$ mass sampling. A one meter long heated transfer line maintained at 250°C was used to transfer the raw exhaust from the stack to the dilution tunnel.

Exhaust gas analyzers were used to measure the concentrations of nitrogen oxides (NO_x) , carbon monoxide (CO), carbon dioxide (CO₂) and total hydrocarbons (THC) in the raw exhaust. CO₂ measurements were also made in the dilution tunnel. Details of the gas

analyzers are provided in Table 2-3. A two point calibration of each gas analyzer was performed before and after each test condition. The concentrations of CO_2 measured in the raw and the dilute exhaust were used to determine the dilution ratio for $PM_{2.5}$ sampling. During this test program a dilution ratio of 22 to 32 was used.



Figure 2-2 Schematic of the Sampling System

 $PM_{2.5}$ mass was sampled on two parallel filters: a pre-weighed 47 mm diameter 2µm pore Teflo[®] filter (Pall Gelman, Ann Arbor, MI) and a 47 mm 2500 QAT-UP Tissuquartz filter (Pall Gelman, Ann Arbor, MI) preconditioned at 600°C for five hours. The Teflo[®] filters were used for measurement of the total gravimentric $PM_{2.5}$ mass and sulfate

analysis while the Tissuquartz filters were used for elemental and organic carbon analysis.

Table 2-3 Details of Exhaust Gas Analyzers						
Gaseous Component	Manufacturer / Model	Measurement Principle	Measuring Range	Location		
Nitrogen oxides	EcoPhysics/ CLD 82 M hrv2	Chemiluminescence	0-2500ppm	Raw Exhaust		
Carbon dioxide/ Carbon monoxide	Siemens/ AG Ultramat 23	Non Dispersive Infra Red	0-500ppm / 0-10%	Dilute Exhaust		
Carbon dioxide/ Carbon monoxide	Siemens/ AG Ultramat 23	Non Dispersive Infra Red	0-1% / 0-10%	Raw Exhaust		
Hydrocarbons	HORIBA/ MEXA 1170HFID	Hydrogen Flame Ionization Detector	0-500ppmC1	Raw Exhaust		
Oxygen	M&C Instruments/ PMA 10	Paramagnetic	0-30%	Raw Exhaust		

Teflo[®] filters were weighted before and after sampling using a Mettler Toledo UMX2 microbalance to determine their net gains. As per the weighing procedures described in the Code of Federal Regulations (CFR), these filters were conditioned for a period of at least 24 hours in an environmentally controlled room (Relative Humidity of 40% and Temperature of 25°C) and weighed daily until two consecutive weight measurements were within 3mg. After completion of the gravimentric analysis, these filters were extracted with ultrapure (DDI) water (Conductivity 18 M Ω cm) and isopropyl alcohol. The water extract was analyzed in a Dionex ICS-1000 ion chromatography system for sulfate ions.

The preconditioned Tissuquartz filters were stored in sealed petridishes at temperatures less than 4°C before and after sampling. These filters were analyzed for elemental and organic carbon (EC/OC) in a Sunset Laboratory (Forest Grove, OR) Thermal/Optical Carbon Aerosol Analyzer according to the NIOSH 5040 reference method.

2.3.5 Calculating Exhaust Flow Rates

The exhaust flow rate at each test mode was calculated using MAN B&W's, proprietary method that provide an accurate value for the total exhaust flow, including both the combustion and the scavenger air flows. This proprietary method is based on the load and the operating conditions of the engine and the turbochargers. The method was checked by the manufacturer against stoichiometric calculations based on carbon and oxygen balances.

2.3.6 Calculating Emission Factors

Total and speciated $PM_{2.5}$ mass concentrations in the raw exhaust are calculated using the measured mass on the filter, total sample volume flown through the filter and the dilution ratio during sampling. The gaseous and $PM_{2.5}$ mass concentrations are converted to emissions in g hr⁻¹ using the calculated exhaust flow rates. Finally the modal emission factors in g kW⁻¹ hr⁻¹ are determined as the ratio of the emissions in g hr⁻¹ to the observed engine load in kW. The overall weighted emission factors were calculated based on the weighted factors specified in the ISO 8178- E3 test cycle.

2.4 **Results and Discussions**

A single fifteen minute $PM_{2.5}$ emission measurement consisting of two parallel filter samples was made at each test mode. Gaseous measurements were made during filter sampling. Two five minute average CO₂, CO and THC measurements and one five minute average measurement each NO_x and NO emissions are reported in this study.

2.4.1 Gaseous Emissions

Figure 2-3 shows a comparison of the modal gaseous emissions factors across fuel types. The error bars represent the range of measurement. A comparison of overall weighted average emission factors in g kW⁻¹ hr⁻¹ for NO_x, CO, CO₂, THC and PM_{2.5} measured in this program versus those used by California Air Resources Board⁴⁰⁻⁴¹ (CARB) and U.S. Environmental Protection Agency⁴² (EPA) for their emission inventory calculations is presented in Table 2-4. The overall weighted average NO_x emission factor of 16.6 g kW⁻¹ hr⁻¹ for engine operating on HFO was 2.3% less than IMO Tier I standard of 17.0 g kW⁻¹ hr⁻¹. and 8.3% lower than the CARB⁴⁰⁻⁴¹ and EPA⁴² emission factor of 18.9 g kW⁻¹ hr⁻¹. ~98% of the total NO_x emissions was found to be NO. The measured emission factors for CO₂, CO and THC were found to be similar to those reported in literature^{17, 25-28}.



Figure 2-3 Gaseous Emission Factors a)Nitrogen Oxides b)Carbon Monoxide c)Total Hydrocarbons d) Carbon dioxide

	Base Fuel HFO	20% Water 80% HFO	33% Water 67% HFO	CARB ⁴⁰⁻⁴¹	EPA^{42}
NO _x	16.6	14.6	12.7	18.1	18.1
СО	0.32	0.48	0.45	1.38	1.40
CO ₂	625	642	613	620	620.62
THC	0.13	0.34	0.34	0.69	0.60
PM _{2.5}	1.95	1.86	2.37	2.11 ^a	2.19 ^a

Table 2-4 Overall Weighted Average Emission Factors

Note: ^a Corrected for Fuel Sulfur

The WFE is primarily used for NO_x emission control. The water in the fuel absorbs the heat and reducing the temperature of combustion in the engine, thereby reducing the formation of NO_x in the engine. Corbett et. al 2002,¹⁸ estimates a nominal NO_x reduction of 42% with WFE while other studies suggest a 1% NO_x reduction for every 1% water to fuel ratio. In this study the reduction in NO_x emissions was found to increase with increasing water to fuel ratio at all engine loads (Figure 2-3a). The reduction in the overall weighted average NO_x emission factor was found to be ~12% with 20% water addition and ~23% with 33% water (Table 2-4). Results show that the WFE unit when optimized for water to fuel ratio (between 20% and 33% for this engine) can be used effectively for meeting the IMO Tier 2 standard of 14.4g kW⁻¹ hr⁻¹.

Use of WFEs increased CO emissions by 53% to 336% at all by the 25% engine load point where they decreased by 38% to 53%. THC emissions increased by a factor of 2.2 to 4.6. In spite of the large increases observed in CO and THC emissions with WFEs,

they were still low (<1.5 g/kW-hr). No significant change was observed in CO_2 emissions with water addition.

2.4.2 Total and Speciated PM_{2.5} Mass Emissions

Figure 2-4 shows a comparison of the total and speciated $PM_{2.5}$ mass emission factors across the test fuels at each engine load. EC, OC, ash and hydrated sulfate (H₂SO₄.6.5H₂O) were found to be the major constituents of total $PM_{2.5}$ mass. Total $PM_{2.5}$ mass emission factors for the base fuel HFO ranged from 1.47 to 2.47g kW⁻¹ hr⁻¹. The $PM_{2.5}$ mass was found to contain 0.2% EC, 4% Ash, 8% OC, 93% hydrated Sulfate. Other studies^{25-28, 43} on marine propulsion engines operating on HFO have seen a speciation of <2% EC, 3-18% ash, 7-29% OC and 33-84% hydrated sulfate. Overall 2.2% to 3.9% of the sulfur in the fuel was converted to sulfate in the $PM_{2.5}$ mass emissions. Other researchers^{25-26, 28, 44} have shown similar conversions of 1.1% to 5.0% for main propulsion engines operating on HFO.

Total $PM_{2.5}$ mass emissions increased with the addition of water at most engine loads. The change in total $PM_{2.5}$ mass varied -16% to 45%. Addition of water increased the EC fraction by a factor of 1.1 to 4.8 at all but the one test mode (8% engine load with 48% water and 52% HFO). The OC fraction was also found to increase by a factor of 1.8 to 3.5 with water addition. The differences in hydrated sulfate fraction varied from 18% to -93% with the addition of water. The use of WFEs altered the $PM_{2.5}$ mass speciation to 0.6% EC, 3% Ash, 22% OC, 66% hydrated sulfate.



Figure 2-4 PM_{2.5} Mass Emission Factors a)Total PM_{2.5} Gravimetric Mass b)Elemental Carbon Fraction c)Organic Carbon Fraction d) Hydrated Sulfate Fraction

Figures 2-5 and 2-6 shows the mass balance between the total gravimetric $PM_{2.5}$ mass collected on the Teflo filter versus the sum of the speciated fractions of $PM_{2.5}$ mass. Overall the sum of the speciated mass was found to be about 7% lower than the total mass. This gap in the mass balance is most likely attributable to the uncertainty in the multiplication factor needed to convert the organic carbon fraction into organic mass.



Figure 2-5 PM_{2.5} Mass Balance for the 50% Engine Load Point



Figure 2-6 PM_{2.5} Mass Balance Across all Loads and Fuels

2.5 Acknowledgements

Co-authors Ole Peter Fredrickson (MAN Diesel, Research and Development Department, Copenhagen, Denmark), William A Welch, J. Wayne Miller, David R Cocker III. California Air Resources Board and the major shipping company for their financial support, Charles Bufalino for his efforts in the test preparation, the ships' crew for their generous help on-board the PanaMax vessel and Virgilio Afan, Harshit Agrawal, Kathalena Cocker, Heather Donnelly, Cristina Hall, Karel Jansen, Irina Malkina, Anthony Turgman and Mary Sheppy for their analytical support.

3 Effectiveness of Emission Control Technologies for Auxiliary Engines on Ocean Going-Vessels

3.1 Chapter Summary

Large auxiliary engines operated on ocean going vessels in transit and at berth impact the air quality of populated areas near ports. This research presents new information on the comparison of emission ranges from three alike engines and the effectiveness of three control technologies: switching to cleaner burning fuels, operating in the low NO_x mode and Selective Catalytic Reduction (SCR). In-use measurements of gaseous (NOx, CO, CO_2) and $PM_{2.5}$ (total and speciated) emissions were made on three auxiliary engines on post-PanaMax class container vessels following the ISO-8178-1 protocol. The in-use NO_x emissions for the MAN B&W 7L32/40 engine family vary from 15.0 g kW⁻¹ hr⁻¹ to 21.1 g kW⁻¹ hr⁻¹ for HFO and 8.9 g kW⁻¹ hr⁻¹ to 19.6 g kW⁻¹ hr⁻¹ for MDO. Use of cleaner burning fuels resulted in NO_x reductions ranging from 7% to 41% across different engines and a PM_{2.5} reduction of up to 83%. The NO_x reductions are a consequence of fuel nitrogen content and engine operation; the PM_{2.5} reduction is attributed to the large reductions in the hydrated sulfate and organic carbon (OC) fractions. As expected, operating in the low NO_x mode reduced NO_x emissions by approximately 32% and nearly doubled elemental carbon (EC) emissions. However, PM_{2.5} emission factors were nearly unchanged since the EC emission factor is only ~5% of the total PM_{2.5} mass. SCR reduced the NO_x emission factor to < 2.4 g kW⁻¹ hr⁻¹, but increased the PM_{2.5} emissions by a factor of 1.5 to 3.8. This increase was a direct consequence of the conversion of SO_2

to sulfate emissions on the SCR catalyst. The EC and OC fractions of $PM_{2.5}$ reduced across the SCR unit.

3.2 Introduction

Recent research has shown that ship emissions are a significant contribution to the global emission inventory ^{1, 3, 5, 16, 45-48} and impact local and regional air quality in highly populated areas located near ports ⁶⁻¹⁰. Particulate Matter (PM) emissions from ships have been linked to increased cardiopulmonary and lung cancer deaths across the world, most of which occur near the coastline ¹¹. All of these studies indicate that the forecasted increase in port activity and growth of ports will result in greater emissions from ships near coastlines and potentially a more adverse health impact for the communities located near them. Therefore, a number of emission control technologies are being investigated for marine engines.

Ships, the largest source of port emissions ⁴⁹, generally have one main propulsion engine and three to seven Auxiliary Engines (AEs). AEs, typically medium speed 4-stroke marine diesel engines, are operated near/at the port to provide power for cargo refrigeration, hotelling, maneuvering, etc. Hence, AEs can have a significant impact on air quality near the ports.

Emissions from marine engines and fuel sulfur content are regulated by the International Maritime Organization (IMO) 50 . IMO caps the fuel sulfur content at 4.5% m/m worldwide and requires fuels with <1.5% m/m sulfur in 'Sulfur Emission Control Areas'.

The IMO emission standard for nitrogen oxides (NO_x) is determined by the rated speed of the engine. Amendments to this regulation, that would introduce progressive reduction in fuel sulfur content and NO_x emissions to come into effect as early as July 2010, were approved by the Marine Environmental Protection Agency of IMO ⁵¹. Also, the U.S Environmental Protection Agency has adopted regulations that would progressively reduce the particulate matter (PM) and NO_x emissions on marine auxiliary engines by 90% and 80%, respectively on ships that are flagged or registered in the U.S. ⁵². Several emission control technologies are being explored to attain these new emission standards. These include switching from high-sulfur Heavy Fuel Oil (HFO) to cleaner burning lower-sulfur Marine Distillate Oil (MDO), water injection into fuels or combustion chamber, Injection Timing Retard (ITR), common rail injection and Selective Catalytic Reduction (SCR) ^{18, 36, 48, 53}.

Emissions data for marine auxiliary engines are limited. The most referenced data set is that published by Llyod's register ²⁴. Studies by Cooper et al. present in-use emissions data of criteria pollutants on auxiliary engines and 4-stroke medium speed diesel propulsion engines on ferries ³¹⁻³⁴. Sarvi et al. 2008 ³⁵ presents a comparison of NO_x, carbon-monoxide (CO) and total PM emissions from an auxiliary engine operating on a test-rig with HFO and MDO. In-use testing of gaseous and total PM emissions from an SCR installed on an auxiliary engine has been reported by several researchers ^{30-31, 36}.

PM emissions from ships have a considerable effect on the atmospheric radiation budget. Two of the major components of PM, elemental or black carbon that absorbs solar radiation and sulfate particles that scatter sunlight, display opposite radiative forcing effects ², ²⁰⁻²². Current studies show that the overall radiative effect from ship PM is negative ², ²⁰⁻²². Most research on in-stack measurements of PM composition has focused on main engines ²⁵⁻²⁹ with little data on auxiliary engines ^{26, 43}. PM size distribution data on main ²⁷⁻²⁹ and auxiliary engines ^{30, 43, 54-55} are limited. Several plume studies help determine the composition of PM emitted from ships ^{27, 39, 43, 56}. All these studies give an idea on the composition of PM from an uncontrolled engine. Control technologies for PM and NO_x may change the speciation of the PM. Research on the effect of controls on PM are scarce.

This research helps to improve the understanding of the baseline emissions from auxiliary engines and the potential for emission reductions when adding various control technologies: cleaner burning fuels, operating in low NOx mode and SCR. Measured emissions included NO_x , CO, carbon-dioxide (CO₂) and total and speciated $PM_{2.5}$ mass emissions.

3.3 Experimental Details

In-use emissions testing was performed on uncontrolled marine auxiliary engines and engines with various control technologies for PM and NO_x during a total of six test expeditions (Table 3-1).

3.3.1 Engine and Fuel Specifications

Three auxiliary engines AE#1, AE#2 and AE#3 aboard post-PanaMax class container vessels were tested. Each of the engines, MAN B&W 7L32/40 (Manufacture Year 1999), were seven cylinder 4-stroke medium speed (720 rpm) marine diesel engines with a maximum power rating of 3500 kW and a maximum generated power output of 3125 kW. Engine parameters including load (kW), speed (rpm), intake manifold temperature and pressure were monitored manually during testing. Each engine was tested on typical supplies of high-sulfur HFO and a lower-sulfur MDO. Selected fuel properties are provided in Table 3-2.

			Transfor	Control Technology	Target ISO Engine			Emissions	
Engine	Campaign	Fuel	Line		Load Points			Measured	
					25%	50%	75%	Gases	PM
	#1	HFO		×	\checkmark			\checkmark	×
		MDO	\checkmark	×	\checkmark		\checkmark	\checkmark	×
۸ <u>۳</u> #1		HFO	I	×					
AE#1	#2		N	SCR	\checkmark			\checkmark	\checkmark
	#3	MDO	\checkmark	×	\checkmark				
				SCR	\checkmark			\checkmark	\checkmark
AE#2	#2	MDO		×	\checkmark				
		HFO	\checkmark	×	\checkmark		\checkmark	\checkmark	\checkmark
AE#3	#4 —	LIEO		×	Х		×	\checkmark	
		mo	×	×	\checkmark		×	\checkmark	\checkmark
		MDO		×	×		×		
			×	×	\checkmark		×	\checkmark	\checkmark
	#5	MDO	00 ×	×	$\overline{\mathbf{v}}$	×	×		
				ITR	\checkmark	×	×	\checkmark	

 Table 3-1 Test Matrix

Note: Gases = NO_x, CO, CO₂; PM = Total & Speciated PM mass

Engine	Campaign	Fuel Type	Density @ 15°C (kg m ⁻³)	Viscosity @ 50°C mm ² s ⁻¹	Sulfur Content (%m/m)	Ash Content (%m/m)
AE#1	#1	HFO	966.5	449	3.8	0.03
	#1	MDO	855.1	n/a	0.263	n/a
	#3	HFO	989.5	389	3.8	0.02
		MDO	846.9	n/a	0.160	n/a
AE#2	#2	HFO	989.5	400	2.7	0.05
		MDO	830.1	2.5^{1}	0.05	0.01
AE#3	#4	HFO	988.8	n/a	3.30	n/a
		MDO	847.3	n/a	0.159	n/a
	#5	MDO	845.9	2.9^{1}	0.11	< 0.005

Table 3-2 Selected Fuel Properties

Note: n/a = not available; ¹@ 40°C

3.3.2 Test Cycle

Marine auxiliary engines are basically generating-sets that operate at constant speed with intermittent load. Hence, they were tested following the engine load points in the ISO 8178-D2 cycle⁵⁷. Due to practical considerations the engines could not be tested at the 10% and 100% load points. Fortunately, these points have the lowest weighting factor when calculating the overall weighted average emission factor. Triplicate measurements were conducted at each load point.

3.3.3 Emission Measurements

Methods for sampling and analysis of gaseous, total and speciated $PM_{2.5}$ conformed to ISO 8178-1 test methods ⁵⁸. Continuous monitoring of gaseous emissions (NO_x, CO₂ and CO) was performed using a Horiba PG-250 portable multi-gas analyzer. A schematic of the test setup and details of sampling and analysis are provided elsewhere²⁵⁻²⁶. Briefly,

 $PM_{2.5}$ sampling used a partial dilution system with a single venturi. The dilution ratio (DR) was measured based on the CO₂ measurements in the raw and diluted exhaust. The DR was within 10% of the DR determined using NO_x emissions, as per ISO 8178-1. $PM_{2.5}$ was collected on two types of filters – 47 mm diameter 2 µm pore Teflo filters for gravimetric mass and hydrated sulfate analysis, and 47 mm diameter 2500 QAT-UP Tissuquartz filters for elemental and organic carbon analysis. Details of analysis are provided elsewhere ²⁵⁻²⁶.

Early campaigns used a 5 m heated raw gas transfer line to connect the probe sampling the raw exhaust to the dilution tunnel, as allowed by the ISO method. Later efforts (Campaign #4) show the transfer line introduces significant $PM_{2.5}$ losses: ~40% for HFO, ~30% for MDO (See Supplemental Data). A deeper inspection of the $PM_{2.5}$ fractions indicated the primary line loss was hydrated sulfate with little to no change in OC and EC. Thus the absolute measured $PM_{2.5}$ data, from Campaigns #2 and #3 only, are biased low. However, the relative shift in PM levels measured with a transfer line is indicative of emission benefits. Later test setups shifted to a close coupling of the main exhaust and dilution tunnel.

3.3.4 Modal & Overall Emission Factors

The emission factors in g kW^{-1} hr⁻¹ were calculated using the recorded engine load, measured concentrations and calculated exhaust flow. The exhaust flow was calculated as equal to the intake air flow which was determined from manufacturer reported cylinder volume and recorded engine speed and inlet air temperature and pressure. Overall weighted average emission factors were calculated as per the ISO-8178 E3 cycle.

3.3.5 Emission Control Technologies

3.3.5.1 Cleaner Burning Fuels

Few control systems are as easily implementable on existing vessels as switching from the high-sulfur HFO to cleaner burning low-sulfur MDO. Expected benefits include a large reduction in PM due to reduced fuel sulfur content and small reduction in NO_x from reduced fuel nitrogen content. All three AEs were tested on both fuels to access the emission reduction potential of fuel switching. The engines were not modified during fuel switching.

3.3.5.2 Low NO_x Mode

The engine family for these vessels could operate in the low NO_x mode with injection timing retard (ITR). The expected benefit was a 25% reduction in NO_x and an increase in PM because of the NO_x PM tradeoff ^{13, 59}. AE#3 was tested to determine the effect of ITR.

3.3.5.3 Selective Catalytic Reduction

SCRs are installed on many combustion sources and can reduce NO_x emissions by over 90%. However, data on SCRs retrofitted on large ocean going vessels is scarce ^{30, 36}. For this study, the silencer on AE#1 was removed and retrofitted with a SINO_x Urea-SCR

control. The SCR system used urea injection and a vanadium catalyst impregnated on titanium oxide bed ⁶⁰⁻⁶¹. No Diesel Oxidation Catalyst (DOC) was installed downstream of the catalyst due to lack of space. The urea injection rate was adjusted by the SCR control system based on the exhaust gas temperature before the SCR and the concentration of NO_x after it. No modifications were made to the engine. The exhaust gas temperature at the SCR inlet ranged from 327°C to 363°C. The temperature rise across the SCR was ~11°C.

3.4 Results and Discussions

3.4.1 Transfer Line Loss

The ISO 8178-1 protocol is proven effective for particulate measurements from engines using fuels with a maximum sulfur content of 0.8%. The sulfur content of the fuels we tested ranged from 0.05% to 3.8%. The protocol allows the use of a 5 m long heated stainless steel line for transferring the raw exhaust from the sampling probe to the dilution tunnel. Our transfer lines used during the initial tests were unable to achieve the required ISO specified temperature of 250°C and were maintained at a temperature of 210°C. During Campaign #4 the effect of the transfer line on the emission factors of AE#3 was assessed for both HFO and MDO at the target ISO engine load of 50%. The results are provided in Table 3-3. As expected there was no significant change in the gaseous emission factors. There was, however, a significant reduction in PM_{2.5} mass due to thermophoretic losses in the transfer line: ~40% for HFO and ~30% for MDO (Table 3-3). A deeper inspection of the PM mass fractions indicated the primary line loss was the hydrated sulfate fraction: 44% for HFO and 70% for MDO. The OC fraction was reduced

slightly for HFO and the EC fraction did not change significantly for either fuel. The data were examined for a common factor to scale the PM data where a transfer line was used but none was found. Thus the absolute measured $PM_{2.5}$ data, from the Campaigns #2 and #3 only, are biased low and need to be used with caution. However, the relative shift in PM levels measured with a transfer line is indicative of emission benefits.

Table 5-5 Effect of Transfer Line on Emissions from AE#5							
Fuel	HF	0	MI	MDO			
Engine Load	47% 45%		41%	43%			
Transfer Line	With	Without	With	Without			
CO ₂	794 ±20	776 ± 12	781 ± 4	766 ± 3			
CO	0.88 ± 0.13	0.78 ± 0.08	0.66 ± 0.04	0.61 ± 0.03			
NO _x	18.8 ± 2.0	16.6 ± 0.7	15.6 ± 0.5	14.4 ± 0.4			
PM	1.06 ± 0.05	1.77 ± 0.05	0.23 ± 0.02	0.32 ± 0.01			
EC	0.015 ± 0.003	0.023 ± 0.002	0.013 ± 0.002	0.021 ± 0.010			
OC	0.226 ± 0.007	0.38 ± 0.02	0.16 ± 0.02	0.16 ± 0.01			
H ₂ SO ₄ .6.5H ₂ O	0.62 ± 0.03	1.12 ± 0.04	0.008 ± 0.004	0.033 ± 0.006			

Table 3-3 Effect of Transfer Line on Emissions from AE#3

Note: All emission factors reported in $g kW^{-1} hr^{-1}$

3.4.2 Baseline Emissions

All three engines were tested on HFO and MDO to determine baseline gaseous and $PM_{2.5}$ emissions (Figure 3-1 and Figure 3-2). Most measurements were made in triplicate, so the error bars in the figures indicate the standard deviation in the measurement.

 NO_x emission factors were the highest for AE#2 ranging across engine loads from 16.5 to 21.2 g kW⁻¹ hr⁻¹, followed by AE#3 with 14.4 to 15 g kW⁻¹ hr⁻¹ and AE#1 with 8.9 to 17.6



Figure 3-1 Effect of Fuel Switching on Gaseous Emission Factors a)NO_x b)CO₂ c)CO d)Weighted NO_x

Note: MYr Manufacture Year, AE#1 Emission factors averaged across Campaigns #1 and #3. AE#3 Emission factors at 25% load with MDO averaged across Campaigns #4 and #5. Error bars indicate standard deviation of measurement





Note: *PM data biased low due to transfer line loss (See Supplemental Data, AE#1 Emission factors are from Campaign #3, AE#3 Emission factors at 25% load with MDO averaged across Campaigns #4 and #5, Error bars indicate standard deviation of measurement.

g kW⁻¹ hr⁻¹ (Figure 3-1a). AE#1 showed a significantly greater decline in NO_x emission NO_x reduction for AE#1 coupled with the lower NO_x emissions rates are indicative of factors with increasing engine load while operating on MDO as compared to HFO. The engine wear, which leads to lower cylinder compression ratio with MDO versus HFO. Communications with the manufacturer confirmed this (refer to the last two paragraphs of this section). MAN B&W reports NO_x emission factors in the range of 14.2 to 12.4 g kW⁻¹ hr⁻¹ with HFO for the same engine model ⁶².

A comparison of the weighted overall NO_x emission factors of AE#1, AE#2 and the engine tested by MAN B&W Diesel is provided in Figure 3-1d. The differences in the NO_x emissions from these engines can be attributed to the maintenance and operation of the engines. Cooper, 2003, ³² also observed significant differences in emissions from different engines of the same model. Figure 3-1d also shows the current IMO NO_x regulation ⁵⁰ for a marine engine with a rated speed 720 rpm speed applicable to marine engine manufactured after Jan 1, 2000 and the estimated auxiliary engine NO_x emission factors used by Entec UK Ltd, 2002 ²⁴. These estimates were developed based on data from the Lloyd's register. The same estimates are used by the California Air Resources Board ⁶³ and the U.S. Environmental Protection Agency ⁶⁴.

The modal CO_2 emission factors across all engines and fuels varied from 659 to 894 g kW⁻¹ hr⁻¹ (Figure 3-1b). CO₂ emission factors decreased with the increase in engine load showing that these engines operated more efficiently at the higher load points. The CO

emission factor, as expected, was low ranging from 0.5 to 2.0 g kW⁻¹ hr⁻¹ (Figure 3-1c). It was somewhat higher for AE#1, consistent with the condition of the engine.

 $PM_{2.5}$ emissions consist of four main components elemental carbon (EC), organic carbon (OC), hydrated sulfate (H₂SO₄.6.5H₂O) and ash. Reasonably good agreement is seen between the sum of these fractions and the total gravimetric $PM_{2.5}$ mass for each of these engines (Figures 3-3b, 3-3d, 3-4). For HFO the hydrated sulfate is ~72% of the reported $PM_{2.5}$ mass, followed by OC at ~32%, the ash at ~13% and the EC fraction <2%. For MDO, OC is the largest fraction (~53%) followed by hydrated sulfate (~20%); the EC fraction averaged 5% and ash ~8%. Other studies on HFO have shown similar speciation of 71.7% hydrated sulfate, 21.4% OC, 4.2% ash and 2.7% EC for an auxiliary engine ⁴³ and 33-84% hydrated sulfate, 7-29% OC, 3-18% ash and <2% of EC ^{25-28, 43} for main engines. Also $PM_{2.5}$ from an auxiliary engine operating on MDO was reported to contain about 43% hydrated sulfate, 23% OC and 7% EC ²⁶.

As mentioned earlier, AE#1 has a lower NO_x and somewhat higher CO emissions compared to other AEs. It also emits higher OC and EC than AE#2. These findings are consistent with an engine operating at lower efficiency due to engine wear. The loss in efficiency is expected to be and is more pronounced for the less viscous fuel; consistent with the higher OC and much lower NO_x emission factors for MDO versus HFO for AE#1.



Figure 3-3 Effect of SCR on Emission Factors a)Gases for HFO b)Gases for MDO c)Total & Speciated PM for HFO d)Total & Speciated PM for MDO

Note: PM Data biased low due to transfer line loss (See Supplemental Data); Error bars indicate standard deviation of measurement





AE#1, though operating less efficiently than the other auxiliary engines, was a fully operational engine on-board the vessel. Results in this section establish that there could be significant differences in the in-use emissions among different engines of the same model. This is a significant finding that should be considered while determining emission factors for any inventory. Other researchers ^{39, 65} also suggest that engine maintenance and operating parameters like turbo feed pressure, wear on nozzles, maladjustments in injection and injection pressures could influence the level of emissions of an in-use engine.

3.4.3 Cleaner Burning Fuels

All three engines showed a reduction in NO_x (Figure 3-1a) when switching from HFO to MDO: 21% to 41% for AE#1, 7% to 10% for AE#2 and 13% for AE#3 at the 50% load point. There was no NO_x reduction observed at the 25% load point for AE#3. The difference in the nitrogen contents of the fuels can account for a NO_x emission increase of around 1 g kW⁻¹ hr⁻¹ (calculated from typical fuel nitrogen compositions - MDO 0%, HFO 0.4% m/m). The NO_x reduction seen in AE#2 and AE#3 are consistent with the changes in fuel nitrogen content; however AE#1 showed a much higher NO_x reduction due to engine wear considerations discussed earlier. Sarvi et al. 2008, ³⁵ also shows slight reduction in NO_x for medium speed diesel engines by switching from HFO to MDO. No significant CO₂ or CO emission benefits were observed from fuel switching.

Fuel switching significantly reduces the total $PM_{2.5}$ mass emissions (Figure 3-2a): 34% to 38% for AE#1 at higher loads, 46% to 67% for AE#2 and 82% to 83% for AE#3. The $PM_{2.5}$ emission benefit for switching from HFO to MFO for AE#1 and AE#2 is likely underestimated due to greater thermophoretic losses of $PM_{2.5}$ in the transfer line for HFO versus MDO (Section 2.4.1).

The primary reason for the reduction in $PM_{2.5}$ with fuel switching is the 72% to 97% reduction in hydrated sulfate fraction of the $PM_{2.5}$ (Figure 3-2d), which is directly attributable to the sulfur content of the fuel. The OC fraction reduces by 26% to 68% across loads for AE#2 and AE#3 while EC does not change much. AE#1 behaves

differently. The OC for AE#1 did not change with fuel switching at the higher loads; however, at the 25% load OC increases. In fact, the decrease in hydrated sulfate fraction is cancelled by the increase in EC and OC at this test point, so no $PM_{2.5}$ reduction is observed. The OC behavior for AE#1 leads to lower measured emission benefits from fuel switching for AE#1 compared to AE#2.

3.4.4 Low NO_x Mode

AE#3 was tested at the 27% load point to determine the effect of low NO_x mode or Injection Timing Retard (ITR) on gaseous and PM_{2.5} emissions (Figure 3-5). ITR reduced the NO_x emission factor from 17.0 g kW⁻¹ hr⁻¹ to 11.5 g kW⁻¹ hr⁻¹ and increased CO emissions from 0.77 g kW⁻¹ hr⁻¹ to 0.89 g kW⁻¹ hr⁻¹; the CO₂ emission factor was unchanged. Corbett et al., 2002 ¹⁸ estimated a 11% increase in PM with ITR while Cooper, 2004 ³⁶ estimates negligible change in PM with ITR. At this load point we did not see a statistically significant change in total PM_{2.5} mass emissions. Studies on diesel engines generally report an increase in the amount of smoke with ITR⁵⁹. Looking at the speciated PM, the EC fraction increased from 0.0369 \pm 0.001 to 0.072 \pm 0.019 g kW⁻¹ hr⁻¹, the hydrated sulfate fraction did not change. The small increase in the EC was not enough to change the overall PM mass.



Figure 3-5 Effect of Low NOx Mode on Emission Factors of AE#3 @ 27% Engine Load Point *Note:* Error bars indicate standard deviation of measurement

3.4.5 Selective Catalytic Reduction

The SCR installed in the exhaust of AE#1 was tested with both HFO and MDO (Figure 3-3). Due to the lack of space in the exhaust system, a DOC was not installed downstream of the SCR. Some studies referred to in this section explicitly state the presence of a DOC after the SCR.

The NO_x emission factor downstream of the SCR was 1.4 to 2.4 g kW⁻¹ hr⁻¹, which corresponds to a reduction of 90-91% for HFO and 82-84% for MDO (Figures 3-3a and 3-3c). Other researchers have reported similar NO_x benefit ^{30-31, 36}. The CO emissions, though low, increased by a factor of 1.4 to 2.0 downstream of the SCR (Figures 3-3a and 2-3c). Other studies have shown both increases ^{30, 61} and decreases in CO emissions ^{61, 66}. Several researchers have reported a reduction in hydrocarbons and carbonaceous PM

matter (EC and OC) across the SCR catalyst $^{30, 36, 60-61, 67-68}$. The SCR on AE#1 reduced OC by as much as 77% -91%.; while the EC fraction reduced by 17% – 63% (Figures 3-3b and 3-3d). The ratio of OC to EC reduces from 8:1-22:1 to 1:1-8:1 across the SCR. The partial oxidation of OC, EC as well as hydrocarbons across the SCR catalyst could attribute to the increase in the CO emission factor that was observed.

The total $PM_{2.5}$ emission increased 1.5 to 3.8 times downstream of the SCR except at the 25% load point with MDO (Figures 3-3b and 3-3d). Examination of the $PM_{2.5}$ fractions showed increases in the hydrated sulfate fraction of $PM_{2.5}$: 68% to 87% for HFO and 89% to 92% for MDO. Vanadium catalyst used in the SCR is known to promote the oxidation of SO₂ to SO₃⁶⁹, which in turn gets converted to sulfate. Increase in hydrated sulfate is much greater than the decrease in the OC and EC fractions of $PM_{2.5}$ except at the 25% load point with MDO (a decrease in total $PM_{2.5}$ is seen for this test point). Studies ^{60-61, 67-68} with low sulfur content (<0.03% m/m) reported reductions in PM across the SCR. Cooper, 2004 ³⁶ reported no change in PM emissions downstream of the SCR while engines operated on the HFO and MDO based on the Lloyds database while Fridell et al., 2008 ³⁰ reported a reduction in PM with the use of HFO. Power plants using high-sulfur coals (3 to 5% m/m) have reported an increase in PM emissions and sulfuric acid emission downstream of SCRs ⁷⁰.

3.5 Acknowledgements

Co-authors Abhilash Nigam, William A. Welch, J. Wayne Miller, David R Cocker III. California Air Resources Board and the major shipping company for their financial support, Charles Bufalino for his efforts in the test preparation, the ships' crew for their generous help on-board the post-PanaMax vessels and Virgilio Afan, Harshit Agrawal, Ajay Chaudhary, Kathalena Cocker, Heather Donnelly, Cristina Hall, Karel Jansen, Irina Malkina, Anthony Turgman and Mary Sheppy for their analytical support.

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

4.1 Chapter Summary

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 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: 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 CO₂ increased three-fold; PM_{2.5} mass increased six-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

4.2 Introduction

Several studies⁶⁻¹¹ 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 study⁷¹ 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 waterways⁷². Furthermore in regions like New York-New Jersey, Boston, or San Francisco, ferry transportation is a significant contributor to the local emissions inventory⁷³⁻⁷⁴. 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 85-94⁷⁵. Early studies on harbor craft emissions focus on older engines operating on high sulfur fuels ^{31, 34}. To meet current EPA standards, modern EPA Tier 2 engines are required to operate on low sulfur (<500ppm S) diesel or ultra-low sulfur diesel (ULSD) (<15ppm 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 studies⁷⁶⁻⁸⁶ 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 study⁸⁷ 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 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, C₁₀-C₃₀ 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.

4.3 Experimental Details

4.3.1 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 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.

4.3.2 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 Tables 4-1 and 4-2.

Property	Method	Specification	Result
Visual Appearance	ASTM D4178	2.0 max	1.0
Acid Number	ASTM D554	$0.80 \text{ max mg KOH g}^{-1}$	$0.13 \text{ mg KOH g}^{-1}$
Flash Point	ASTM D2500	Report °C	-1°C
Cloud Point	ASTM D93	130 min. °C	189 °C
Water Sediment	ASTM D2709	0.050 max %vol	0.000 %vol
Free Glycerin	ASTM D6584	0.020 max %vol	0.002 %vol
Total Glycerin	ASTM D6584	0.240 max %vol	0.013 %vol
Monoglycerides	ASTM D6584	Report %	0.414 %vol
Diglycerides	ASTM D6584	Report %	0.095 %vol
Triglycerides	ASTM D6584	Report %	0.070 %vol
Sulfated Ash	ASTM D874	0.020% max. mass %	0.005 mass %
Carbon Residue	ASTM D4530	0.050% max. mass %	<0.005 mass %
Cetane	ASTM D613	47 min.	50
Copper Strip Corrosion	ASTM D130	3 max.	1
Phos Content	ASTM D4951	10 max. ppm	<1 ppm
Sulfur Content	ASTM D4951	0.00-15.00 ppm	1.30 ppm
Kinematic Viscosity	ASTM D445	$1.90-8.00 \text{ mm}^2 \text{ s}^{-1}$	4.08 mm ² s ⁻¹
Moisture (Karl Fischer)	Volumetric	Report %	0.014%
Cold Soak Filtration	Annex A1	200 s max.	64 s
Oxidative Stability	EU 14112	3 hr min.	7.7 hr
Group I Metals	EU 14538	6 ppm max.	<1.0 ppm
Group II Metals	EU 14538	8 ppm max.	<1.0 ppm
Vacuum Distillation	ASTM D1160	360°C max @ 90%	362.0 °C

Table 4-1 Certificate of Analysis Provided by Fuel Supplier for B100

Fuel	API Gravity @ 60°F	Density @ 25°C (kg m ⁻³)	Volume % of Methyl Ester
B0	37.2	838.4	n/a
B20	35.3	848.1	22.6
B50	33.1	859.0	46.4

Table 4-2 Selected Fuel Properties

4.3.3 Test Matrix

The engine was tested following the steady state load points in the ISO 8178 E3 duty cycle⁵⁷. Another steady state mode, idling in gear, was added to the test matrix (Table 4-3), 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.

Day	Fuel	Engine Loads	
Day 1 -	B50	<i>RT & GS</i> :	94%, 75%, 50%, 25%, Idle
	B0	<i>RT & GS</i> :	94%, 75%, 50%, 25%, Idle
	B50	<i>RT & GS</i> :	94%, 75%, 50%, 25%
	B20	<i>RT & GS</i> :	94%, 75%, 50%, 25%, Idle
	B20	<i>RT & GS</i> :	94%, 75%, 75%, 50%, 25%, Idle
	B50	<i>RT & GS</i> :	94%, 75%, 75%, 50%, 25%, Idle
	B0	<i>RT & GS</i> :	94%, 75%, 75%, 50%, 25%, Idle
	B20	RT:	Typical cruise of harbor-craft in the bay

Table 4-3 Test Matrix

Note: *RT*: Real Time Monitoring and Recording of Gaseous emission, total $PM_{2.5}$ mass emissions, particle size distribution; *GS*: Grab samples for total and speciated $PM_{2.5}$ mass, carbonyls, C_{10} to C_{30} hydrocarbons, including naphthalene and polyaromatic hydrocarbons, 1,3 butadiene, benzene, toluene, ethylbenzene and xylenes

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 $\pm 5\%$ 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 towards 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.

4.3.4 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 protocol⁵⁸. Schematic of the test setup is provided in Figure 4-1. Gaseous emissions, NO_x, CO and CO₂, were measured in the raw and dilute exhaust. CO₂ measurements were used to determine the sample dilution ratio (DR). The CO₂ DR was verified to be within 10% of the NO_x DR per the ISO protocol. Sampling of PM_{2.5} mass, carbonyls, C₁₀ to C₃₀ HCs and PAHs were performed in the dilute exhaust. PM_{2.5} mass was collected on 47 mm Teflo[®] 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 4-1 Schematic of Sampling System

Details of sampling and measurement of the following species: Carbon dioxide, nitrogen oxides, carbon monoxide, total $PM_{2.5}$ mass, elemental and organic carbon in $PM_{2.5}$ mass, carbonyls, C_{10} to C_{30} hydrocarbons, naphthalene and poly aromatic hydrocarbons are provided elsewhere²⁵⁻²⁶. A brief description is given below for convenience.

4.3.4.1 Gaseous Emissions

A Horiba PG-250 five gas analyzer was used for sampling CO_2 , NO_x and CO in the raw and dilute exhaust. A three point calibration was performed on the gas analyzer at the start and end of each day of testing. Details of the analyzer are provided in Table 4-4..

Component	Detector	Ranges
Nitrogen Oxides (NOx)	Heated Chemiluminescence Detector (HCLD)	0-25, 50, 100, 250, 500, 1000, & 2500 ppmv
Carbon Monoxide (CO)	Non dispersive Infrared Absorption (NDIR)	0-200, 500, 1000, 2000, & 5000 ppmv
Carbon Dioxide (CO ₂)	Non dispersive Infrared Absorption (NDIR)	0-5, 10, & 20 vol%
Sulfur Dioxide (SO ₂)	Non dispersive Infrared Absorption (NDIR)	0-200, 500, 1000, & 3000 ppmv
Oxygen	Zirconium oxide sensor	0-5, 10, & 25 vol%

Table 4-4 Details of Horiba PG-250

4.3.4.2 Total PM_{2.5} Mass Emissions

PM_{2.5} mass was sampled a 2µm pore 47 mm Teflo[®] filters (Pall, Ann Arbor, MI). Net weight on the Teflo[®] filters was determined using a Mettler Toledo UMX2 microbalance following the guidelines in the code of federal regulations⁸⁸. Before and after sampling, filters were conditioned for at least 24 hours in an environmentally controlled room (RH = 40%, T = 25 C) and weighed daily until two consecutive weight measurements were within 3 µg.

4.3.4.3 Elemental and Organic Carbon in PM_{2.5} mass

 $PM_{2.5}$ mass was also collected on 47mm 2500 QAT-UP Tissuquartz filters (Pall, Ann Arbor, MI). These filters were preconditioned for 5 hours at 600°C and stored at temperatures <4°C before and after sampling and analysis. EC/OC analysis on the

Tissuquartz filters was performed according to the NIOSH method⁸⁹ using Sunset Laboratories Thermal/Optical Carbon Aerosol Analyzer.

4.3.4.4 Carbonlys

Carbonyls were sampled downstream of the Teflo[®] filters on 2,4 dinitrophenylhydrazine (DNPH) coated silica cartridges (Waters Corp., Milford, MA). The flow through the DNPH cartridges was maintained at 1.7 lit min⁻¹ using a critical flow orifice. Sampled cartridges were extracted using 5ml of acetonitrile and injected into Agilent 1200 series Liquid Chromatograph (LC) equipped with a Diode Array Detector (DAD) and an LC-ToF-MS 6210. A 5µm Deltabond AK resolution column was used for the analysis. The LC sample injection and operating conditions were set up according to the specifications of SAE 930142HP protocol⁹⁰. Quantification was performed using the ultra violet spectrum obtained from the DAD. The masses of the target compounds were verified with the LC-ToF-MS.

4.3.4.5 C_{10} to C_{30} hydrocarbons, Naphthalene and Poly aromatic compounds

The diluted exhaust was collected through a Tissuquartz filter and into a column packed with polyurethane foam (PUF)/XAD-4 resin. A portion of the Tissuquartz filter was used to analyze for the elemental and organic carbon, as described in the previous section. Both the PUF/XAD-4 cartridge and the remainder of quartz filter was extracted with methylene chloride and analyzed using a modified method EPA TO13A protocol (GC-

MS analysis) to determine total emission rates for PAHs and n-alkanes. Details on the analysis method are found in Shah et al., 2005⁹¹.

4.3.4.6 Organic Mass to Organic Carbon Ratio

After completing gravimetric analysis, the Teflo[®] filters were sonicated at 60°C for 1hr 15min in 5ml of double distilled water (conductivity 18.2 μ \Omega) to extract the water soluble organic carbon. The water sample was filtered through a 1 μ m Whatman syringe filter to remove large insoluble particles. These samples were then nebulized and injected into an Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS)⁹² operating in the high resolution V-mode⁹³. The OM/OC ratio of aerosol was determined following the Peak Integration by Key Analysis (PIKA) and Analytical Procedure for Elemental Separation (APES) template⁹³⁻⁹⁴.

4.3.4.7 Particle Number and Size Distribution

Particle size distribution (PSD) was measured using a fast Scanning Mobility Particle Sizer (fSMPS)⁹⁵. The concentration in the dilute exhaust (DR ~3.0) was too high for PSD sampling; therefore, a secondary dilution system was installed to provide an overall dilution of 24 ± 2.5 . Raw and dilute NO_x measurements were used to determine this overall DR. Data from the fSMPS were also used to determine the effective density of the PM. Details of the design and operation of the fSMPS are provided elsewhere⁹⁵. During this test program the fSMPS was operated in the size range of 7 to 188nm with a five

second scan time. The instrument was calibrated for size and number using a Tandem Mobility Particle Sizer (TDMA) and an ultrafine Condensation Particle Counter (CPC).

4.3.4.8 Real-Time PM Mass Emissions

Two instruments were used for monitoring the real time PM mass emissions: fSMPS and TSI's DustTrak Aerosol Monitor Model 8520. The DustTrak was sampling from the primary dilution tunnel while the fSMPS used the secondary dilution. An average dilution ratio across all the steady state engine load points was used for calculation of the real-time PM from these two instruments.

The DustTrak provides a real-time mass concentration measurement based on 90° light scattering principle. It is typically calibrated by TSI using Arizona road dust. During this test the 2.5 μ m impactor was connected to the inlet of the DustTrak to ensure that the PM sampled in this instrument matches that collected on the Teflo[®] filters. Since the DustTrak is not a reference method for measuring diesel PM, a correlation between the DustTrak measurements and the total gravimetric PM_{2.5} mass measurements (from the Teflo[®] filters) was determined across the steady state modes (Figure 4-2). This correlation was used to obtain the real-time PM mass concentration from the DustTrak during the in-use testing.

To determine the PM mass concentration from the fSMPS, a log normal curve was fit to the PSD obtained from the fSMPS. The total volume concentration was determined using the log normal curve. This was then multiplied by the effective density of B20 PM to obtain the total PM mass concentration.



Figure 4-2 Correlation between DustTrak PM_{2.5} and Gravimetric PM_{2.5} for B20

4.3.5 Calculating Effective Density of PM_{2.5} Mass

A log normal curve was fit to the PSD and the total volume of the particles was determined from this fit. Using this particle volume and assuming a particle density of 1 g cm⁻³ the total mass from the fSMPS was calculated. This assumed fSMPS mass was plotted versus the total gravimetric $PM_{2.5}$ mass obtained from Teflo[®] filters. The slope of

the straight line fit to this data gives an estimate of the effective density of the particulate matter.

4.3.6 Calculating Modal & Overall Emission Factors

The emission factors in g hp⁻¹ hr⁻¹ were calculated using the measured concentration, calculated exhaust flow and the engine load obtained from the engine ECM. The exhaust flow in turn was calculated as equal to the intake air flow. Intake air flow was determined using the manufacturer provided engine displacement along with the following parameters obtained from the engine ECM: engine speed, inlet air temperature and pressure. The overall weighted emissions factors in g hp⁻¹ hr⁻¹ were calculated as per the ISO 8178-E3 cycle⁵⁷.

4.3.7 Calculating In-Use Emissions (g hr⁻¹)

As mentioned in previous sections the concentrations of NO_x , CO and CO_2 were measured using the Horiba PG250; $PM_{2.5}$ mass concentrations were determined using TSI's DustTrak and the fSMPS; PM number concentration and size distribution was logged using the fSMPS. The emissions in g hr⁻¹ were calculated based on the measured concentration and the calculated exhaust flow. The exhaust flow was calculated as equal to the intake air flow.

4.4 **Results and Discussion**

4.4.1 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).

4.4.1.1 Gaseous Emissions:

Figure 4-3 shows the overall weighted average emission factors for CO_2 , NO_x and CO. The modal data is provided in Figure 4-4. 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 hr⁻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 hr⁻¹ across engine loads and fuels. The measured overall weighted average NO_x emission factor 5.33 ± 0.04 g hp⁻¹ hr⁻¹ (for B0) was greater than the manufacturer's engine family certification value⁹⁶ of 4.99 g hp⁻¹ hr⁻¹. Summing up the measured NO_x emission factor with the manufacture's certification value⁹⁶ for total hydrocarbon (THC) emissions of 0.14 g hp⁻¹ hr⁻¹, we get a NO_x + THC emission factor of 5.47 g hp⁻¹ hr⁻¹. This emission factor is greater than EPA Tier 2

emissions standard⁹⁷ for NO_x + THC 5.4 g hp⁻¹ hr⁻¹ but lower than the 6.48 g hp⁻¹ hr⁻¹ not to exceed standard⁹⁸.



Figure 4-3 Overall Weighted Emissions Factors (g hp⁻¹ hr⁻¹)

Note: Tier 2 & 3 standard shown on the NOx bars are for NO_X +THC, Tier 2 and Tier 3 standard for CO are the same, Manf. Cert.: Manufacturer's certification of that engine family⁹⁶

Studies of on-road⁷⁶⁻⁸⁶ 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 engines⁸⁷. In this study, no statistically significant change was observed in the 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 hr⁻¹ for all engine loads except at 75% where it was ~ 2.7 g hp⁻¹ hr⁻¹. The observed trend (including the 75% load) is consistent with the data trend obtained for the engine family certification provided by the engine



Figure 4-4 Modal Gaseous Emission Factors (g hp⁻¹hr⁻¹)

manufacturer. The measured overall weighted CO emission factor of 1.84 ± 0.04 (for B0) was almost twice the manufacturer's engine family certification value⁹⁶ of 0.99 g hp⁻¹ hr⁻¹ but well below the Tier 2 and Tier 3 standard of 3.7 g hp⁻¹ hr⁻¹. Research on on-road engines⁷⁶⁻⁸⁶ show CO reductions of 3-30% with B20, 18-40% with B50 while one study⁸⁷ 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).

4.4.1.2 Total PM_{2.5} Mass Emissions

The PM_{2.5} mass emission factors (Figure 4-5) range from 0.053 to 0.131 g hp⁻¹ hr⁻¹. The emission factor at idle was higher (0.164 to 0.214 g hp⁻¹ hr⁻¹). The weighted average PM_{2.5} emission factor 0.116 \pm 0.004 g hp⁻¹ hr⁻¹ (for B0) was double the manufacturer's certification value⁹⁶ of 0.05 g hp⁻¹ hr⁻¹ but less than the Tier 2 PM standard of 0.15 g hp⁻¹ hr⁻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 studies⁷⁶⁻⁸⁶ following transient/steady state cycles also show reductions in PM with biodiesel ranging from 4% to 37% with B20 and 4% to 63% with B50.

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, 1998⁹⁹ observed similar trends of increasing PM at low engine loads with biodiesel.

4.4.1.3 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 hr⁻¹; the OC emission factors ranged from 0.040 to 0.071 g hp⁻¹ hr⁻¹. As expected emission factors at idle were higher: 0.073 to 0.128 g hp⁻¹ hr⁻¹ for EC and ~0.089 g hp⁻¹ hr⁻¹ for OC (Figure 4-5).



Figure 4-5 Total and Speciated PM_{2.5} Mass Emission Factors (g hp⁻¹ hr⁻¹) **Note:** Manf. Cert.: Manufacturer's certification of that engine family⁹⁶

A ~23% reduction in EC was observed with B20 at engine loads \leq 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^{80, 100}, non-volatile PM⁸⁴ and EC¹⁰¹ 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 loads⁹⁹. The overall weighted average emission factors show: 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 ratios¹⁰¹, soluble organic fractions^{83, 99-100} and volatile organic fractions^{80, 84, 102} 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. 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 particulate¹⁰³⁻¹⁰⁴. 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 4-6). 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 analysis¹⁰⁴⁻¹⁰⁵.



Figure 4-6 PM_{2.5} Mass Balance

4.4.1.4 PM Size Distribution

Figures 4-7 and 4-8 show the particle size distribution (PSD) for all three fuels across all engine loads. The number concentration curves in these figures represent seven minute averages of fSMPS data. The dN/dlogDp standard deviation (not shown) was $\pm 10\%$. 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 63-82 nm at the ISO modes and 89-99 nm at Idle (Figures 4-7 and 4-8). The accumulation mode particles primarily consist of carbonaceous soot agglomerates formed during direct combustion¹⁰⁶. 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 biodiesel¹⁰⁷⁻¹⁰⁸.

Nucleation mode particles (<50nm) consist primarily of volatile hydrocarbon and sulfate particles¹⁰⁶ along with some non-volatile ash/carbonaceous particles^{107, 109}. Since fuels used in this program had <15ppm 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 conditions¹¹⁰. Dilution conditions were kept constant during the test program, to help provide a robust dataset 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 4-7 and 4-8). 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



Figure 4-7 Particle Size Distribution-1

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 minute period were $\pm 10\%$



Figure 4-8 Particle Size Distribution-2

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 7min sample time. Standard deviation of measurement over the 7 minute period were $\pm 10\%$

nuclei. This theory is corroborated by previous research¹¹⁰ that suggests suppression of the nucleation mode by adsorption of volatile hydrocarbon on the solid carbonaceous agglomerates in the accumulation mode.

Laboratory studies^{100, 107-108, 111} 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.

Studies¹¹²⁻¹¹³ 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 ~212nm) was found to have an effective density of 0.53. Park et al, 2003^{114} observed a similar effective density of 0.39 to 0.55 for diesel PM having a mobility mean diameter of 220nm. B20 and B50 PM show effective densities of 0.49 and 0.77 respectively (Figure 4-9). The increase in effective density with B50 can be attributed to a reduction of particle mean diameter¹¹⁴ and increase in the OC/EC ratio (indicative of a larger semi-volatile OM fraction) with biodiesel PM. (Semi-volatile OM

can be adsorbed into the surface and voids of the carbonaceous agglomerate particles making them more dense.)



Figure 4-9 Density-Shape Factor of Diesel/Biodiesel PM

4.4.1.5 Carbonyls

The total carbonyl emission factor varied from 0.005 to 0.065 g hp⁻¹ hr⁻¹ across engine loads and fuels (Figure 4-10). These values are in line with carbonyl emission factors observed by other researchers^{102, 115-117}. 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^{102, 115, 118-119} see an increase in carbonyl emissions with increasing biodiesel blends, few others¹¹⁶⁻¹¹⁷ show reductions and one study¹²⁰ 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 this load B20 had no effect but the total carbonyl emission factor doubled for B50.



Figure 4-10 Carbonyl Emission Factors

4.4.1.6 C₁₀ to C₃₀ Hydrocarbons, Naphthalene & Poly Aromatic Hydrocarbons

Total gas and particle phase emissions factors for the C_{10} to C_{30} HCs and PAHs are provided in Figure 4-11. Emission factors of these compounds are similar to those reported in other studies^{115-116, 121}. No significant trends were seen across fuel types. A larger variation in emissions was observed at Idle probably due to changes in engine load (31kW for B0, 28kW for B20 and 45kW for B50). Previous studies^{115-116, 121-123} on on-road engines have shown a reduction in PAH emissions with biodiesel.



Figure 4-11 C₁₀ to C₃₀ Hydrocarbons, Naphthalene and Poly-Aromatic Hydrocarbons

4.4.2 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 towards 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 4-12 a). 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 hr⁻¹ is shown in Figure 4-12 b. 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 from the pier to the Golden Gate Bridge to those from the bridge to Alcatraz we found a three-fold increase in NO_x and CO₂, a thirteen-fold increase in CO and a six-fold increase in the total $PM_{2.5}$ mass emissions. The differences in these values would make a significant change in the inventories.

The effect of ocean current, which translates to change in engine load, is also seen in the real-time PSD (Figure 4-12 c). 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 (~17nm) were seen because the engine



Figure 4-12 Real Time Emissions Trace on a Typical Cruise a)Approximate Route for Cruise b)Gaseous and PM emissions c)Particle Size Distribution **Note:** *Engine Load

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.

4.5 Acknowledgements

Co-authors Dr. Harshit Agrawal, Mr. Willaim A Welch, Dr. J Wayne Miller and Dr. David R Cocker III. 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, 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.

5 Protocol Development and Use for Determining the Benefits of a Hybrid Tug

5.1 Chapter Summary

Modern mobile sources are expected to simultaneously reduce emissions of criteria pollutants, toxics and greenhouse gases. One common technological solution available today is hybrid technology. The in-use emissions benefits of replacing a conventional tug boat with a hybrid one was quantified by performing a side by side comparison. A continuous data-logging system capable of monitoring the energy systems on the tugs while they performed similar operations (shore power, dock, transit, standby, barge move and ship assist) was utilized to determine the weighting factors for each tug operating mode and engine histograms of the four EPA Tier 2 tug diesel engines. The average operating loads of these engines were found to up to 83% lower than the load factors specified in the certification cycles highlighting the need for development of in-use duty cycles. The second stage was an emissions testing program that established the emission profiles of these engines. These profiles were coupled to actual engine histograms and weighting factors to calculate overall in-use emissions of each tug. Significant reductions of 73% for PM_{2.5}, 51% for NO_x and 27% for CO₂ were observed with the hybrid technology. The bulk of the overall reductions were found to occur in the transit mode. The hybrid tug's energy management system that directs the use of auxiliary power for propulsion was found to be the primary cause for emission reductions as opposed to the energy storage device. The CO_2 reductions were in good agreement with the eight month fuel savings measured by the tug owner. The activity and emissions based model developed in this research can be used to estimate the benefits of various scenarios, including retrofits of existing tugs.

5.2 Introduction

Modern mobile sources are required to simultaneous reduce criteria pollutants, toxics and green-house gas emissions thereby addressing the issues of air quality, energy sustainability and global climate change. One prevalent technology solution to achieve this goal is the use of two or more propulsion sources also known as hybrid technology. A common application of hybrid technology today is passenger vehicles. Hybrid diesel electric systems have been used in submarines as early as 1904¹²⁴. More recently several emerging hybrid technologies¹²⁵⁻¹²⁹ that harness power from water, wind and sun are being implemented on boats and even large ships.

Calculating the emissions benefits of a hybrid technology is quite challenging¹³⁰⁻¹³² as they operate quite differently from conventional technology. Test protocols developed for conventional systems have to be adapted appropriately based on application¹³³⁻¹³⁵. Several researchers¹³⁶⁻¹³⁹ are evaluating hybrid systems in their real world applications instead of engine dynamometers. The common thread in developing new test protocols is to ensure that energy used from multiple sources is properly accounted for.

The goal of this research was to develop and implement an activity based approach that quantifies the benefits of using diesel electric hybrid system on a tug boat using a three step process. First the in-use activity of the conventional and hybrid tug boat was established and engine histograms and weighting factors were identified for each tug. Secondly, the gaseous (nitrogen oxide NO_x and carbon monoxide CO_2) and particulate matter ($PM_{2.5}$) emissions from the main and auxiliary engines on the tug boats was measured to: a) verify that each engine met the EPA Tier 2 standard during typical operation and b) determine the emissions profile for these engines. Finally, the activity and emissions data were combined to determine the differences between total emissions from the hybrid and conventional tug boat.

5.3 Experimental Methods

5.3.1 Test Boats

Two tugs were chosen, one conventional and the other hybrid, operating in the San Pedro bay ports (Table 5-1). Both tug boats have four EPA Tier 2 certified diesel engines - two main propulsion engines and two auxiliary generators (Tables 5-2 and 5-3). Besides these, the hybrid tug has two soft-gel lead acid battery arrays. Each array has sixty-three batteries with a total energy capacity of 170.1kW-hr at full charge.

Tug Boat	Conventional	Hybrid
Gross Ton	144	144
Length	78'	78'
Breath	34'	34'
Height	14'	14'
Rated Horsepower	5,580	5,000
Bollard Pull	134,000	124,000
Propeller	Two US 205 FP Rolls Royce ASD	Two Rolls Royce US205 Azimuthing Stern Drives
Main Engines	Two CAT 3512 C	Two Cummins QSK50
Auxiliary Engines	Two JD 6081	Two Cummins QSM11

 Table 5-1 Tug Boat Specifications

5.3.1.1 Conventional tug (CT)

Both 1902 kW main engines are connected by a mechanical drive shaft to a single propeller. Therefore, both main engines must be operated to move and maneuver the tug. The 195 kW auxiliary engines provide power for the winch motor and other hotelling requirements.

Table 5-2 Engine Specifications for Conventional Tug		
	Main Engine	Auxiliary Engine
Manufacturer /Model	CAT 3512C	John Deere 6081 AFM75
Manufacture Year	2008	2008
Technology	4-Stroke Diesel	4-Stroke Diesel
Max. Power Rating	1902 kW	-
Prime Power	-	195 kW
Rated Speed	1800 rpm	1800 rpm
# of Cylinders	12	6
Total Displacement	58.6 lit	8.1 lit

Table 5-2 Engine Specifications for Conventional Tug

	Main Engine	Auxiliary Engine
Manufacturer /Model	Cummins QSK50 M	Cummins QSM11
Manufacture Year	2007	2007
Technology	4-Stroke Diesel	4-Stroke Diesel
Max. Power Rating	1342 kW	-
Prime Power	-	317 kWm
Rated Speed	1800 rpm	1800 rpm
# of Cylinders	16	6
Total Displacement	50 lit	10.8 lit

Table 5-3 Engine Specifications for Hybrid Tug

5.3.1.2 Hybrid Tug (HT)

Energy from the main engines, auxiliary engines and batteries can be used for propulsion. As a result the main engines have a 29% lower power rating and the auxiliary engines have a 63% higher power rating when compared to the CT. A schematic of the drive-train on the HT is provided in Figure 5-1. Briefly, the main engines on the HT are linked mechanically to the propellers. One motor-generator unit is mounted between the shaft of each engine and propeller. These units allow the use of battery and auxiliary power for propulsion. They also provide regenerative power from freewheeling propellers and main engines for charging batteries, operating the winch motor and hotelling.

The batteries during these tests were predominately charged by the auxiliary engines. (They have the capability of being charged by shore power; however, during this test



Figure 5-1 Schematic of Power-Train on the Hybrid Tug

program sufficient shore power was not available.) The HT has an energy management system that determines which power sources to use during tug operation. The captain on the HT uses a switch in the wheelhouse to communicate the tug operating mode (dock, transit, standby or assist) or load requirements to the energy management system.

5.3.2 Activity and Emissions Based Approach

An activity and emissions based approach was developed to determine the in-use emission benefits of the HT. A step by step description of the approach is provided below.

The emission benefits of a hybrid tug is calculated as follows

Emission Reduction
$$\% = \frac{TE_c - TE_h}{TE_c} \times 100$$
 --------Equation 5-1

where, TE_c is the total in-use emissions for CT in g hr⁻¹ and TE_h is the total in-use emissions for HT in g hr⁻¹.

The total in-use emissions TE of any gaseous or particulate matter species in g hr⁻¹, is calculated as a linear combination of the weighting factors on emissions for each operating mode:

$$TE = \sum_{i=1}^{n} [W_i \sum_{j=1}^{m} (E_{ij})]$$
 -------Equation 5-2

where, *n* is the total number of tug operating modes, *m* is the total number of engines on the tug, W_i is the weighting factor for i^{th} tug operating mode (Equation 3) and E_{ij} is the total in-use emissions in g hr⁻¹ from the j^{th} engine for the i^{th} tug operating mode (Equation 4).

The modes of operation of a typical tug were determined as follows:

Shore Power: The tug is at dock plugged into shore power for its utilities. None of the engines are operating during this mode.

Dock: During this operation the tug is at dock with one auxiliary engine powering the lights and air-conditioning. The HT switches between the auxiliary engine and batteries during this mode. The state of charge of the batteries arrays are maintained above 60%.

Standby: In this mode the tug is idling in the water waiting for a call to start or transit to a job. The CT operates two main and one auxiliary engine during while the HT switches between the batteries and one auxiliary engine.

Transit: This mode refers to the movement of the tug between jobs and to and from different docks. The CT boat operates two main and one auxiliary engine. The HT uses batteries and one auxiliary engine for slow speeds (<6.0 knots) and two auxiliary engines for higher speeds.

Ship Assist and Barge Moves Tug boats typically perform two kinds of jobs in the ports: 1) assisting ships from berth to sea and vice-versa and 2) moving barges from one
location to another. The CT operates two main and one auxiliary engine while the HT operates all four engines for a job.

The weighting factor for each tug operating mode is calculated as follows:

$$W_i = \frac{t_i}{t_{total}}$$
------Equation 5-3

where, W_i is the weighting factor for the i^{th} tug operating mode, t_i is the time spent by the tug in the i^{th} tug operating mode and t_{total} is the total sample time for the tug.

To determine the total in-use emissions from each engine on the tug the following equation can be used:

$$E_{ij} = \sum_{k=1}^{p} [WL_{ijk} EL_{jk}]$$
 ------Equation 5-4

where, E_{ij} is the total in-use emissions in g hr⁻¹ from the j^{th} engine for the i^{th} tug operating mode, p is the total number of operating modes for the j^{th} engine. These modes are based on the % of maximum engine load: off, 0 to <10%, 10% to <20%, 20% to <30%, and so on until 90% to <100% and 100%, WL_{ijk} is the fraction of time spent by the j^{th} engine at its k^{th} operating mode during the i^{th} tug boat operating mode (obtained from the engine histogram) and EL_{jk} is the emissions in g hr⁻¹ for the j^{th} engine at its k^{th} operating mode (obtained from the engine's emission profile).

Based on guidelines provided in the hybrid electric vehicle testing protocols of the Society of Automotive Engineers¹⁴⁰ (SAE) and California air resources board¹⁴¹ (CARB), the state of charge of the batteries at the end of each sample period, used for developing

engine histograms of the HT, was returned to original state of charge at commencement of the sample period. This helps to eliminate biases in emissions caused by the use of the auxiliary engine for charging the batteries.

To use this activity based approach, testing was performed in two stages. The first stage involved one month of data logging on each tug to establish tug operating mode weighting factors and engine histograms. The second stage was two phase in-use emissions testing program of engines on the tugs to determine their emissions profiles. Details of the testing procedures and calculations are provided in the following sections.

5.3.3 Data Logging Procedure

A Labview program was developed to interface with four electronic control modules (ECMs), a GPS and batteries to continuously retrieve and store engine operating parameters. Table 5-4 lists the details of the devices used for interfacing between the power sources and the data logger along with the parameters that were logged. Schematics of the data-logging setup are provided in Figures 5-2 and 5-3. Briefly, the data logger was placed on the workbench in the engine room. Data from the main and auxiliary engine ECMs were obtained using four Dearborn Protocol Adapters. These Dearborn adapters were powered by engine startup batteries. A Garmin GPS was installed on the top of the mast on the tug boat to provide data on location and speed of the tug. An event logger (a circular switch with an analog output) that provides information on the operating mode of the tug was installed in the wheelhouse of the CT.

	СТ	HT	Devices Used	Parameters Logged
GPS	V	V	• Garmin GPS 18 PC receives wireless signal from satellite and transmits it through a serial port to the data logger	Date, Time, Latitude, Longitude, Speed, Course
Two main propulsion engines and two auxiliary engines	V	\checkmark	 4 Dearborn Protocol Adapters Model DG-DPAIII/i that receives J1939 signal from the engine's electronic control module (ECM) 4 Dearborn Protocol Adapter cables (DG-J1939-04- CABLE) that convert the J1939 signal to serial/RS232 signal, One USB2-4COM-M that receives 4 serial signals and transmits them through one USB port to the data logger 	Engine speed (rpm), Engine load (% of max load at the engine speed), instantaneous fuel flow rate (cc min ⁻¹), inlet manifold temperature (°F) and pressure (kPa)
Event Logger	V	×	• Omega's USB-1608FS box that receives five analog from the event logger located in the wheelhouse and transmits them through a single USB cable to the data logger	Operating modes: Dock, Standby, Slow Transit, Fast Transit and Assist
Wheel house Switch	×	V	 5 Philmore 86-124 (24 vDC, 10 A) SPDT relays convert the signals from wheelhouse switch to digital voltage signals. Omega's USB-1608FS box receives these five digital signals from the relays and transmits them through a single USB cable to the data logger. 	Operating Modes: Shorepower, Dock, Standby, Transit, Fast Transit, Assist
Battery Arrays	×		• Omega's USB-1608FS box that receives six analog signals from the battery arrays and transmits them through a single USB cable to the data logger.	State of charge, voltage in volts and current in amps for each battery array.

Table 5-4 Details of Data Logger

CT: Conventional Tug, HT: Hybrid Tug



Figure 5-2 Schematic of the Data Logging System on the Conventional Tug



Figure 5-3 Schematic of the Data Logging System on the Hybrid Tug

Captains were provided with instructions on operating the switch. As mentioned in the earlier the HT had a wheelhouse switch that communicates the operating mode to the energy management system. Signals from this switch were transmitted to the data logger. Also analog signals indicating the voltage, current and state of charge of the battery arrays were obtained from the energy management system. Remote access to the data-logger using VNC server and client application was provided by the tug company. The port engineer uploaded the CSV data files and scanned copies of the tug's paper logs on a weekly basis to a FTP site.

Table 5-5 shows the test matrix for the data-logging procedure. Activity data was collected for a total time of \sim 34 days on the CT, \sim 48 days on the HT and \sim 1.5 days on the HT with the batteries disconnected from the drive train.

Tug Boat	Start Time	End Time
Conventional	1/8/2010 17:04:41	2/12/2010 13:10:22
	3/4/2010 17:24:32	3/21/2010 4:59:58
	3/26/2010 14:45:40	4/2/2010 10:30:53
Hybrid	4/30/2010 8:19:46	5/11/2010 11:53:23
	5/19/2010 9:52:13	5/24/2010 8:14:29
	6/8/2010 10:02:04	6/17/2010 12:22:25

 Table 5-5 Test Matrix for Data Logging

5.3.4 Calculating Operating Mode Weighting Factors

Using the paper logs, GPS data and engine data the operating mode signals from the even-logger switch on the CT and the wheelhouse switch on the HT were verified and corrected wherever necessary. A Python 2.6 code was written to read the corrected CSV data files and calculate the total time spend by each tug in the different operating modes. Following Equation 4-3 from the main article the weighting factor for each tug operating mode was calculated as the ratio of the time spent in that mode to the total sample time.

5.3.5 Calculating the Engine Load

The CSV data files obtained from the data logger had information on engine speed in rpm and engine load as a percentage of the maximum load at that engine speed. The auxiliary engines are constant speed engines, so the percentage load obtained from the ECM was multiplied by the maximum rated power of the engine to determine the engine load. The main propulsion engines are variable speed engines. For these engines the percentage load obtained from the ECM was multiplied by the maximum load at that engine speed. This maximum load was obtained from the lug curves provided by the respective engine manufacturers.

Engine ECMs do not measure the actual load on the engine. They use an algorithm to estimate the load. This proprietary algorithm varies from one manufacturer to another. Engine ECMs typically provide good load estimates at high loads and deviate from actual numbers at lower loads. This is particularly true for marine engines whose ECMs are not regulated. The ratio of the carbon-dioxide (CO_2) emissions to the load on the engine is an indication of its thermal efficiency. Since this efficiency tends to be relatively constant across the entire range of engine operation, we would expect a straight line relationship between the engine load and the CO_2 emissions. Significant deviations from a straight line relationship will be indicative an errors in the ECM load readings.

Figure 5-4 show plots of engine ECM load versus the measured CO_2 emissions in kg hr⁻¹ (from Emissions Testing Phases 1 & 2) for one auxiliary and one main engine on each tug. A good straight line correlation is observed for all but one engine. Therefore a load correction was applied to this engine, details of which are provided below.

5.3.5.1 Load Correction for Main Engine on Conventional Tug

In the case of emissions testing Phases 1 and 2, the engine load for the main engine on the CT for the low loads $\leq 25\%$ of the maximum rated power were calculated using the measured CO₂ emissions in g hr⁻¹ and the equation for fit to the ECM load versus CO₂ emissions provided in Figure 5-4 A.

The data-logger however, collects only engine speed and percentage load data from the ECM and not real-time CO_2 emissions data. Therefore the equation of the straight line fit cannot be used to correct activity data. Corrections to the activity data can be made only based on the engine speed. So, a correlation was developed between the CO_2 corrected engine load and engine speed (Figure 5-5) was used to calculate the load on the CAT 3512

main engines for speeds below 1300rpm. For all higher speeds, the percent load obtained from the ECM was used.



Figure 5-4 ECM Load versus CO₂ Emissions for **A**)Main Engine Conventional Tug CAT 3512 C **B**)Auxiliary Engine Conventional Tug JD 6081 C)Main Engine Hybrid Tug Cummins QSM50 D)Auxiliary Engine Hybrid Tug Cummins QSK11 M



Figure 5-5 Load Correction for Main Engine on Conventional Tug

5.3.6 Developing Engine Histograms

The calculated loads of the main and the auxiliary engines were then split into twelve bins as shown below:

Bin Off	Engine is Off
Bin 1	0 to <10%
Bin 2	10 to <20%
Bin 3	20 to <30%
Bin 4	30 to <40%
Bin 5	40 to <50%
Bin 6	50 to <60%
Bin 7	60 to <70%
Bin 8	70 to <80%

Bin 9	80 to <90%
Bin 10	90 to <100%

Bin 11 100%

A Python 2.6 code was written to calculate the total time spent by the engine in each bin for each operating mode. The fraction of time spent by the engine in any bin for a particular operating mode was calculated as the ratio of time spent in that bin to the total time spent by the boat in that operating mode. These fractions were then plotted to get the engine histograms at each operating mode. While calculating the engine histograms for the HT care was taken to ensure that the state of charge of the battery at the start and end time of each sample period was the same.

5.3.7 Calculating the Average Load required for a Tug Operation

For the CT, the total energy used in kW-sec for each operating mode during the data logging period was obtained by summing up the kWs on all four engines for every second of time spent in that operating mode. This value was then divided by the total time spent in that operating mode to get the average load needed to perform that operation.

On the HT, the energy from the batteries was also taken into account. The following equation was used to calculate the energy in kW-sec drawn from each battery array.

$$E_{battery} = (SOC_{start} - SOC_{end}) \times 170.1 \times 3600$$
 -------Equation 5-5

where, $E_{battery}$ is energy drawn from or into the battery array, SOC_{start} is state of charge of the array at the start of the chosen sample time, SOC_{end} is state of charge of the array at the end of the chosen sample time, 170.1 is the total energy content of the battery array in kW hr and 3600 is the number of seconds in an hour

The average load required to perform a particular operating mode on the HT was calculated as the sum of the total energy drawn from all four engines and two battery arrays during that operation divided by the total time spent in that operating mode.

5.3.8 Emissions Testing

Each tug has two main and two auxiliary engines. Since the main engines on each tug were the same make, model and manufacture year only one main engine on each tug was tested for emissions. The same was done for the auxiliary engines, only one auxiliary engine was tested on each tug. The engine specifications of the test engines are provided in Tables 5-2 and 5-3. All four test engines were operated on the normal fuel of operation, red dye ultra low sulfur diesel during emissions testing. Table 5-6 provides selected properties of fuel samples obtained from the tugs. Emission testing was performed in two phases (Test Matrix Table 5-7). Schematics of the sampling systems for each phase are provided in Figures 5-6 and 5-7.

Fuel	Analysis Method	Diesel from Conventional Tug	Diesel from Hybrid Tug	
API Gravity @60 °F	ASTM D4052	38.2	38.7	
Specific Gravity @50 °F	ASTM D4052	0.8338	0.8316	
Density @ 15.525 °C (kg m ⁻³)	ASTM D4052	0.8333	0.8311	
Sulfur, ppm	ASTM D 2622	9.2	17.4	
Carbon wt%	ASTM D 5291	86.14	86.02	
Hydrogen %	ASTM D 5291	13.56	13.60	

 Table 5-6 Selected Fuel Properties

 Table 5-7 Test Matrix for Emissions Testing

Tug Boat	Engine	Date	Engine Speeds (rpm)/ Load (% max)					
Emissions Testing Phase 1								
Constitution	JD 6081	01/14/10	<i>RT & ISO</i> : 75%,50%,25%, 10%					
Conventional	CAT 3512C	01/15/10	<i>RT</i> & <i>ISO</i> : 100%,75%,50%,25%, Idle					
II. had	Cummins QSM11	03/03/10	<i>RT</i> & <i>ISO</i> : 75%, 50%, 25%					
пурна	Cummins QSK50	03/04/10	<i>RT</i> & <i>ISO</i> : 100%, 75%, 50%, 25%, Idle					
	Em	issions Test	ing Phase 2					
Conventional	CAT 3512C	07/08/10	<i>RTP</i> : 1780, 1655, 1542, 1434, 1301, 1142, 1000, 900, 800, 700, Idle					
	Cummins QSM11	06/08/10	<i>RTP</i> : 75%, 60%, 50%, 40%, 25%, 20%					
Hybrid	Cummins QSK50	06/08/10	<i>RTP</i> : 1780, 1700, 1600, 1525, 1424, 1300, 1142, 1050, 950, 850, 750, Idle					

Note: RT- Real Time Monitoring and Recording of Gaseous Emissions, ISO- Filter Samples taken in accordance with ISO 8178-4 E3/D2 cycles, RTP- Real Time Monitoring and Recording of Gaseous and PM Emission



Figure 5-6 Schematic of Sampling System for Emissions Testing Phase 1



Figure 5-7 Schematic of Test Setup for Emissions Testing Phase 2

5.3.8.1 Emissions Testing Phase 1

The goal of Phase 1 of testing was to establish if the engines meet the EPA Tier 2 standard when in-use. For this purpose gaseous (CO₂ and NO_x) and particulate matter (PM_{2.5}) emissions measurements were made based on the ISO 8178-1 protocols. The main engine was tested following the load points in the ISO 8178-4 E3 while the auxiliary engine was tested based on the ISO 8178-4 D2 cycle. The steady state load points on the main engines of both tugs and the auxiliary engine of the HT were achieved by pushing against a pier. The auxiliary engine on the CT typically operated at a load of 10-12% of its maximum rated power. A load bank was used for testing the higher load points. Due to practical considerations the actual load on the engines could differ by $\pm 5\%$ from the target load. Also some loads in the test cycles could not be achieved.

Details of sampling and measurement of the gaseous and $PM_{2.5}$ measurement methods are provided elsewhere²⁵⁻²⁶. A brief description is given below for convenience.

Gaseous Emissions: A Horiba PG-250 five gas analyzer was used for sampling CO_2 , NO_x and CO in the raw and dilute exhaust. A three point calibration was performed on the gas analyzer at the start and end of each day of testing. Details of the analyzer are provided in Table 5-8.

Component	Detector	Ranges
Nitrogen Oxides (NOx)	Heated Chemiluminescence Detector (HCLD)	0-25, 50, 100, 250, 500, 1000, & 2500 ppmv
Carbon Monoxide (CO)	Non dispersive Infrared Absorption (NDIR)	0-200, 500, 1000, 2000, & 5000 ppmv
Carbon Dioxide (CO ₂)	Non dispersive Infrared Absorption (NDIR)	0-5, 10, & 20 vol%
Sulfur Dioxide (SO ₂)	Non dispersive Infrared Absorption (NDIR)	0-200, 500, 1000, & 3000 ppmv
$Oxygen(O_2)$	Zirconium oxide sensor	0-5, 10, & 25 vol%

Table 5-8 Details of Horiba PG-250

 $PM_{2.5}$ Emissions: A partial dilution system with a single venturi was used for PM sampling. Dilution ratio was calculated as the ratio of the CO₂ concentration in the raw exhaust to that in the dilution system. This dilution ratio was verified to be within 10% of the dilution ratio calculated from NO_x concentrations. PM_{2.5} mass was sampled on two parallel filters - 2µm pore 47 mm Teflo[®] filters (Pall, Ann Arbor, MI) and 47mm 2500 QAT-UP Tissuquartz filters (Pall, Ann Arbor, MI).

The Teflo[®] filters were used for gravimetric analysis. Net weight on the these filters was determined using a Mettler Toledo UMX2 microbalance following the guidelines in the code of federal regulations⁸⁸. Before and after sampling, filters were conditioned for at least 24 hours in an environmentally controlled room (RH = 40%, T = 25 C) and weighed daily until two consecutive weight measurements were within 3 µg.

The Tissuquartz filters were preconditioned for 5 hours at 600°C and stored at temperatures <4°C before and after sampling and analysis. Elemental Carbon (EC) and Organic Carbon (OC) analysis of these filters was performed according to the NIOSH method⁸⁹ using Sunset Laboratories Thermal/Optical Carbon Aerosol Analyzer.

5.3.8.2 Emissions Testing Phase 2

The goal of this phase was to determine the emissions profile of the test engines over their entire operating range. The auxiliary engine on the CT always operated at a steady load of ~12%. Since this load point was already tested during phase 1 this engine was not tested again. The other three engines were tested at several steady state loads including the ones from Phase 1 to a good idea about the varying of gaseous and $PM_{2.5}$ mass emissions as a function of engine load. As in the case of Phase 1, the load points were achieved while pushing against the pier. Gaseous measurements were once again made using a Horiba PG-250.

A simple partial dilution system (Figure 5-7) was used for measuring the real-time PM emissions using TSI's DustTrak. The ratio of the CO_2 concentrations in the raw versus the dilute was used to determine the dilution ratio for these PM measurements. The DustTrak provides a real-time mass concentration measurement based on 90° light scattering principle. It is typically calibrated by TSI using Arizona road dust. A 2.5µm impactor was connected to the inlet of the DustTrak to ensure that the PM sampled in this

instrument matches that collected in Phase 1 of testing. Since the DustTrak is not a reference method, these real-time $PM_{2.5}$ measurements were used only to determine the trends in the PM concentration as a function of load.

5.3.9 Determining Exhaust Flow Rates

5.3.9.1 Intake Air Method

This method is widely used for calculating exhaust flow rates of diesel engines. It assumes that the engine is an air pump, so the flow of air into the engine will be equal to the exhaust flow out of the engine. The flow rate of intake air is determined from engine speed, inlet air temperature and pressure and the engine displacement. Engine speed and inlet air temperature and pressure are obtained from the engine ECM.

5.3.9.2 Carbon Balance Method

The method is used when the fuel flow rate is known. Since almost all the carbon in the fuel goes to CO_2 emissions, we can assume that all of the carbon in the fuel is converted to CO_2 in the exhaust. The exhaust flow rate can be calculated using the fuel flow rate readings from the ECM along with the measured CO_2 concentrations.

The engine ECMs of the auxiliary engine on the HT (Cummins QSK11) and main engines on both tugs (CAT 3512C, Cummins QSK50 M) provided engine speed and intake air temperature and pressure readings. Therefore exhaust flow rates for these engines were calculated using the intake air method. The calculated exhaust flow rates for

the main engines were found to be in good agreement with that provided by the engine manufacturer. Personal communication with the engine manufacturer revealed that the calculated flow rates for the auxiliary engine on the HT were significantly larger than the manufacturer's numbers due to issues with the intake air pressure readings. Therefore, for this engine alone the exhaust flow measurements provided by the manufacturer were used.

The data-logger was unable to retrieve the intake manifold temperature and pressure data from the ECM of the auxiliary engine on CT. Only engine speed, load and instantaneous fuel flow data were obtained. Since, the engine manufacturer did not provide any exhaust flow data; exhaust flow calculations for this engine were performed following the carbon balance method.

5.3.10 Calculating of Emissions in g hr⁻¹

Mass emissions of CO_2 and NO_x in g hr⁻¹ were calculated using the calculated exhaust flows and the measured concentrations in the exhaust. In the case of $PM_{2.5}$ mass emissions, the concentration in the dilute exhaust was calculated as a ratio of the measured filter weight to the total sample flow through the filter. This was then converted to a concentration in the raw exhaust by multiplying with the CO_2 dilution ratio. This raw $PM_{2.5}$ concentration was used along with the exhaust flow to determine the mass emissions in g hr⁻¹.

5.3.11 Calculating Modal and Overall Weighted Average Emission Factors

The emission factor at each mode is calculated as the ratio of the calculated mass flow (g hr^{-1}) in the exhaust to the reported engine load (kW). An overall single emission factor representing the engine is determined by weighting the modal data according to the ISO 8178 E3 or ISO 8178 D2 cycle requirements and summing them. The equation used for the overall emission factor is as follows:

$$A_{WM} = \frac{\sum_{i=1}^{n} (g_i \times WF_i)}{\sum_{i=1}^{n} (P_i \times WF_i)}$$
-------Equation SI-2

Where A_{WM} is the overall weighted average emission factor in g kW⁻¹ hr⁻¹, *n* is the total number of modes in the ISO duty cycle, g_i is the calculated mass flow in g hr⁻¹ for the *i*th operating mode, WF_i is the weighting factor for the for the *i*th operating mode and P_i is the engine load in kW for the *i*th operating mode

5.4 **Results and Discussion**

5.4.1 Tug Operating Mode Weighting Factors

Figure 5-8 shows the observed individual and average tug operating mode weighting factors. Individual weighting factors for all operating modes were similar (Tables 5-9 and 5-10). On an average the dolphin class tug spends about ~54% of its total operating time at dock (including shore power), ~7% in standby, ~17% in transit, ~17% in ship assist and ~5% making barge moves. The HT spends a third of its time at dock plugged into shore power compared to the CT which spends 1% plugged in.



Figure 5-8 Weighting Factors for Tug Operating Modes

Table 5-9 Weekly Variation in Weighting Factors for Operating Modes of Conventional Tug

Sample Time (Days)	8.7	8.7	8.7	8.7	Average
Shore Power + Dock	57%	54%	52%	55%	55% ± 2%
Standby	6%	7%	8%	6%	$7\%\pm1\%$
Transit	16%	15%	15%	19%	$16\%\pm2\%$
Barge Move	2%	3%	8%	7%	$5\% \pm 3\%$
Assist	19%	20%	17%	13%	$17\%\pm3\%$

Table 5-10 Weekly Variation in Weighting Factors for Operating Modes of Hybrid Tug

Sample Time(Days)	9.4	7.1	6.8	11.1	4.9	8.8	Average
Shore Power	19%	23%	16%	14%	20%	20%	$19\%\pm3\%$
Dock	38%	32%	36%	38%	34%	28%	$34\% \pm 4\%$
Standby	8%	6%	6%	6%	5%	7%	$6\% \pm 1\%$
Transit	15%	18%	19%	18%	19%	19%	$18\% \pm 1\%$
Barge Move	5%	5%	6%	6%	4%	6%	$5\% \pm 1\%$
Ship Assist	15%	16%	15%	17%	19%	20%	$17\%\pm2\%$

5.4.2 Engine Histograms

5.4.2.1 Conventional Tug (CT)

For all operating modes (except shore power), the conventional boat has one auxiliary engine operating at 10%-12% of its rated power and the other auxiliary engine off. The main engines on the CT are off when the tug is at dock and at 5% of their maximum rated power when the CT is at standby. Figure 5-9 shows engine histograms of both main engines for other operating modes. The average load required on the CT was found to be 718 kW for transit, 608 kW for ship assist and 754 kW for a barge move. Typically two to three tugs help maneuver the ship, during a ship assist, along with the ship's main propulsion engine. Barges (no propulsion engines) are typically moved by a single tug leading to the larger average load requirement for a barge move than a ship assist.

5.4.2.2 Hybrid Tug

The HT required a load of ~28 kW for hotelling power at dock. When not plugged into shore power, this tug was powered by batteries (~78% of the time at dock) or one auxiliary engine (~22% of time at dock). Figures 5-10 and 5-11 show the engine histograms for all four HT engines at the other operating modes. During standby mode we find that the HT is powered by only batteries ~30% of the time, one auxiliary engine ~53% of the time, and more than one auxiliary engine ~17% of time. The HT uses two auxiliary engines when transiting at speeds >6.0 knots (~30% of time). The main engines are generally operated only for a ship assist or barge move. However, we find that they are sometimes on during standby and transit modes; e.g, the five minute main engine cool



Figure 5-9 Main Engine Histograms for Conventional Tug Note: ME1- Main Engine 1, ME2- Main Engine 2







Figure 5-11 Engine Histograms for Hybrid Tug – 2 **Note:** AE1- Auxiliary Engine 1, AE2- Auxiliary Engine 2, ME1-Main Engine 1, ME2-Main Engine 2

down periods after a job or for safety concern like dense fog when captain chooses to keep all engines on. The average load required for the HT to transit (~278 kW) is 39% lower than that required by the CT because the HT's energy management system directs use of auxiliary and battery power for propulsion during transit. The average load required for ship assist and barge moves for the HT were similar (508 kW and 507 kW, respectively), lower than the CT due to significant use of auxiliary engines on the HT.

The HT was operated for a period of ~ 1.5 days with the batteries disconnected from the diesel electric drive train to determine the effect of the energy management system versus the energy storage device (batteries). The tug performed four ship assists and six barge moves during this time. Figures 5-12 and 5-13 show engine histograms for the HT operating without batteries.

Table 5-11 provides average load requirements for each operating mode for the CT and the HT with and without the batteries. This data shows that >46% of the reduction in load at the standby, transit, barge move and ship assist modes occur due to the diesel electric drive train.



Figure 5-12 Engine Histograms for Hybrid Tug without Batteries -1 **Note:** AE1- Auxiliary Engine 1, AE2- Auxiliary Engine 2, ME1-Main Engine 1, ME2-Main Engine 2



Figure 5-13 Engine Histograms for Hybrid Tug without Batteries– 2 **Note:** AE1- Auxiliary Engine 1, AE2- Auxiliary Engine 2, ME1-Main Engine 1, ME2-Main Engine 2

Onerating	Average Load (kW)				
Modes	Conventional Hybrid Tug		Hybrid Tug		
	Tug	without Batteries	myonia Tug		
Dock	22	34	29		
Standby	184	111	74		
Transit	718	409	278		
Assist	608	476	508		
Barge Move	754	641	507		

 Table 5-11 Average Load Requirements for Each Operating Mode

Overall, we find that the average loads on the main and auxiliary engines of the CT are 16% and 12% of the maximum rated power; for the HT average loads of main and auxiliary engines were 12% and 34% of the rated power. These are well below the load factors of the standard ISO duty cycles. The engines on the HT are still operating in their inefficient zone suggesting the need for a larger energy storage system and smaller main engines in the next generation of hybrid tugs.

5.4.3 Emissions Profiles

Table 5-12 shows the modal and overall weighted average emission factors of CO₂, NO_x and total and speciated PM_{2.5} mass from emissions testing Phase 1. This table also lists the manufacturer's published emission factors and the EPA Tier 2 standard for each test engine family. Duplicate/triplicate measurements were made at steady state test modes with a range/standard deviation of <5% for gases and <11% for PM_{2.5} mass emissions. Figure 5-14 shows a comparison of PM_{2.5} mass emissions in g hr⁻¹ made by two separate methods – gravimetric measurements of Teflo[®] filters and total carbon analysis of Tissuquartz filters. The total carbon measurements were 3% to 19% greater than the

gravimetric measurements attributable to the positive artifact associated with sorption of semi-volatile gases to Tissuquartz filters.

Target	Actual	NO	CO.	PM _e -	FC	00			
Load	Load	NO _x	CO_2	1 112.5	EC	UC			
Main Engine on the Conventional Tug CAT 3512 C									
Idle	7%	17.5	704	0.045	0.012	0.038			
25%	30%	8.5	704	0.164	0.034	0.161			
50%	52%	7.8	682	0.195	0.090	0.105			
75%	75%	6.6	705	0.068	0.038	0.036			
100%	100%	7.4	697	0.091	0.036	0.064			
Wt. Avg.		7.1	701	0.097	0.047	0.059			
Manf. Wt Av	g. Nominal	6.31	657	0.10	n.a	n.a			
Manf. Wt Av	g. NTE	7.57	n.a	0.12	n.a	n.a			
EPA Tier 2 St	td	7.2*	n.a.	0.20	n.a	n.a			
	Auxiliary Eng	gine on the (Convention	al Tug JD 6	6081				
10%	11%	5.9	771	0.38	0.19	0.19			
25%	26%	7.3	774	0.20	0.11	0.13			
50%	40%	8.9	773	0.20	0.05	0.14			
75%	71%	7.3	746	0.24	0.01	0.21			
Wt Avg		7.7	772	0.24	0.09	0.15			
EPA Tier 2 St	td	7.2*	n.a	0.20	n.a	n.a			
Ν	1ain Engine o	n the Hybri	d Tug Cun	nmins QSK	50 M				
Idle	7%	11.0	792	0.101	0.077	0.049			
25%	26%	7.7	756	0.028	0.018	0.020			
50%	49%	8.2	823	0.075	0.055	0.033			
75%	75%	7.9	799	0.058	0.039	0.029			
100%	99%	7.7	812	0.041	0.022	0.028			
Wt. Avg.		7.8	798	0.053	0.034	0.026			
Manf. Wt Av	g.	6.53	n.a	0.09	n.a	n.a			
EPA Tier 2 St	td	7.2*	n.a	0.20	n.a	n.a			
Auxiliary Engine on Hybrid Tug Cummins QSM11									
25%	27%	7.0	765	0.116	0.078	0.048			
50%	51%	7.4	725	0.050	0.026	0.034			
75%	73%	7.5	749	0.039	0.021	0.028			
Wt. Avg.		7.41	744	0.058	0.034	0.034			
Manf. Wt Av	g.	6.289	n.a	0.134	n.a	n.a			
EPA Tier 2 St	td	7.2*	n.a	0.20	n.a	n.a			

Table 5-12 Emission Factors in g kW⁻¹ hr⁻¹ from Emissions Testing Phase 1

Note: EC Elemental Carbon fraction of PM_{2.5}, OC Organic Carbon fraction of PM_{2.5}

Manf. Wt Avg. Manufacturer's Weighted Average, NTE Not to Exceed

* Standard if for the sum of nitrogen oxides and total hydrocarbon emissions



Figure 5-14 PM_{2.5} Mass Balance for A)Main Engine Conventional Tug CAT 3512 C B)Auxiliary Engine Conventional Tug JD 6081 C) Main Engine Hybrid Tug Cummins QSM50 D) Auxiliary Engine Hybrid Tug Cummins QSK11 M

The overall weighted average NO_x emission factors for these engines range from 7.1 to 7.8 g kW⁻¹ hr⁻¹. These factors are just below (for CAT 3512 C) or above the EPA Tier 2 standard (NO_x plus total hydrocarbon (THC) emissions of 7.2 gkW⁻¹ hr⁻¹). The overall

weighted average $PM_{2.5}$ mass emission factors, for three out of the four engines, were well below the EPA Tier 2 standard of 0.20 g kW⁻¹ hr⁻¹. The measured emissions factors for the CAT 3512 C engine are comparable to the manufacturer's published values. For the Cummins engines, we find that the measured NO_x emission factors are larger and $PM_{2.5}$ emission factors smaller than the manufacturer's numbers.

Figure 5-15 shows the emission profiles of all four engines. Data for the auxiliary engine of the CT are obtained from Phase 1, for other three engines from Phase 2. In Phase 2 several steady state load points, including the ones in Phase 1, were tested. A three to five minute average of the real time gaseous and $PM_{2.5}$ mass emissions were made. The standard deviation in the CO₂ measurement at each test mode was <2%. A comparison of the load, gaseous emissions and $PM_{2.5}$ concentrations from Phase 1 and 2 are provided in Figures 5-16 through 5-18. Gaseous measurements in Phase 2 were found to be slightly greater than that of Phase 1 due to an overall increase in engine load. TSI's DustTrak was used for $PM_{2.5}$ measurements in Phase 2 to aid extrapolation of PM filter measurements between load points. Since the DustTrak is not a reference method, results from Phase 2 were figures 5-16 through 5-18).



Figure 5-15 Emission Profile of A)Auxiliary Engine on Conventional Tug B)Main Engine on Conventional Tug C)Auxiliary Engine on Hybrid Tug D)Main Engine on Hybrid Tug



Figure 5-16 Comparison of Phases 1 & 2 for Main Engine on Conventional Tug CAT 3512 C



Figure 5-17 Comparison of Phases 1 & 2 for Main Engine of Hybrid Tug Cummins QSK50 M



Figure 5-18 Comparison of Phases 1 & 2 for Auxiliary Engine on Hybrid Tug Cummins QSM11
5.4.4 Overall In-Use Emissions

The engine histograms were coupled with the emission profiles (Equation 4) to determine the total emissions of $PM_{2.5}$, NO_x and CO_2 emissions for each tug at every tug operating mode (Table 5-13). The emissions for the shore power mode for each tug were calculated as the product of its load requirement at dock (Table 5-11) and the emission factors of a conventional natural gas fired steam plants with selective catalytic reduction (SCR) for NO_x control and with no CO catalyst (Table 5-14). The total in-use emissions from each tug (calculated using Equation 2) based on individual and average tug operating mode weighting factors are shown in Table 5-15.

The overall reductions of $PM_{2.5}$, NO_x and CO_2 emissions with the HT were found to be 73%, 51% and 27% respectively. The CO_2 reductions are in good agreement with the fuel savings of 25-28% observed by the tug owner over an eight month period. The transit mode was found to be the largest contributor to the overall emission reductions ~50% for $PM_{2.5}$, ~53% for NO_x , ~78% for CO_2 . In this mode the HT was powered by one or two auxiliary engines and batteries while the CT used one auxiliary and two main engines.

The emission reductions results for the HT operating without batteries show that the bulk of the emission savings (97% for $PM_{2.5}$, 95% for NO_x , 70% for CO_2) is a result of the diesel electric drive train and not the batteries. The diesel electric drive train allows the use of auxiliary and battery power for propulsion thereby reducing the load requirements for each tug operation.

Operating Mode	PM _{2.5} (g hr ⁻¹)			NO _x (g hr ⁻¹)			CO ₂ (kg hr ⁻¹)		
moue	Con.	Hyb_NB	Hyb.	Con.	Hyb_NB	Hyb.	Con.	Hyb_NB	Hyb.
Shore Power	0.0009	0.0013	0.0012	0.0011	0.0017	0.0015	0.014	0.021	0.018
Dock	5.1	3.2	1.1	156	309	89	16	33	10
Standby	26.6	8.7	7.3	3757	832	677	176	83	68
Transit	114.8	16.9	15.5	7633	2683	2371	530	276	240
Barge Move	133.1	42.1	36.4	7666	5588	4659	555	569	457
Ship Assist	82.0	36.4	38.3	6452	4270	4541	424	423	450

 Table 5-13 In-Use Emissions of the Hybrid and Conventional Tug at each Tug Operating Mode

Table 5-14 Emission Factors for Shore Power						
		Emission Factor				
	Lbs $(10^{6} \text{scf})^{-1}$	Lbs $MW^{-1} hr^{-1 a}$	$g kW^{-1} hr^{-1}$			
<i>PM</i> _{2.5}	7.6	0.087	29			
NO_x	10	0.117	74			
CO_2	120000	1371	278			

^a heating value of natural gas = 1,050 Btu scf⁻¹, power generation heat rate = 12,000 Btu $kW^{-1} hr^{-1}$

	PM _{2.5}		l	NO _x	CO_2			
	$g hr^{-1}$	Reduction	$g hr^{-1}$	Reduction	$g hr^{-1}$	Reduction		
Actual Emis	Actual Emissions Based on Individual Operating Mode Weighting Factors							
Conventional Tug	44.1	n.a.	3088	n.a.	208	n.a		
Hybrid Tug without Batteries	13.2	70%	1676	46%	169	19%		
Hybrid Tug	12.1	73%	1528	51%	153	27%		
Actual Em	issions Bas	ed on Average	Operating	Mode Weight	ing Facto	ors		
Conventional Tug	45.2	n.a.	3153	n.a	213	n.a		
Hybrid Tug without Batteries	13.6	70%	1708	46%	173	19%		
Hybrid Tug	12.2	73%	1523	52%	152	29%		
Retrofit Scenario	1 Emission	ns Based on A	verage Operating Mode Weighting Factor			g Factors		
Conventional Tug	42.1		3238	n.a	215	n.a.		
Hybrid Tug without Batteries	20.7	51%	2160	33%	165	23%		
Hybrid Tug	17.6	58%	1966	39%	145	32%		
Retrofit Scenario 2 Emissions Based on Average Operating Mode Weighting Factors								
Conventional Tug	44.1	n.a.	3088	n.a.	208	n.a.		
Hybrid Tug without Batteries	20.4	54%	2132	31%	162	22%		
Hybrid Tug	17.5	60%	1976	36%	146	30%		

Table 5-15 Overall In-Use Emission for the Conventional and Hybrid Tugs

5.4.4.1 Retrofit Scenarios

Since the CT and the HT have engines from different engine manufacturers with different power ratings a couple of retrofit scenarios were modeled.

Retrofit Scenario 1: This scenario assumes that both tugs have the same set of engines - CAT 3512 C main engines and Cummins QSK11-M auxiliary engines. For this scenario the reductions in the overall in-use emissions calculated based on average weighting factors was found to be 58%, 39%, 32% for $PM_{2.5}$, NO_x and CO_2 respectively (Table 5-15). The reductions in NO_x and $PM_{2.5}$ increased while that of CO_2 increased when compared to the actual numbers. The bulk of the reductions still occur in the transit mode. Also most of the reductions are a result of the diesel electric drive train rather than the batteries.

Retrofit Scenario 2: Conventional tugs typically have auxiliary engines with a lower power rating (e.g., the JD 6081 tested in this work). Therefore, a more realistic scenario might be: Conventional tug powered by CAT 3512 C main engines and the JD 6081 auxiliaries; Hybrid tug powered by CAT 3512 C main engines and the Cummins QSK11-M auxiliaries. The reductions in the overall in-use emissions seen in Retrofit Scenario 2 were similar to that of Retrofit Scenario 1 (Table 5-15).

Operating Mode	PM _{2.5} (g hr ⁻¹)		NO _x (g hr ⁻¹)			$CO_2 (kg hr^{-1})$			
	Con.	Hyb_NB	.Hyb	Con.	Hyb_NB	Hyb.	Con.	Hyb_NB	Hyb.
Shore Power	0.0009	0.0013	0.0012	0.0011	0.0017	0.0015	0.014	0.021	0.018
Dock	1.9	3.2	1.1	241	309	89	18	33	10
Standby	23.5	8.7	7.1	3842	1127	886	178	84	69
Transit	111.6	24.4	19.0	7718	3021	2679	531	270	235
Barge Move	130.0	75.7	55.3	7751	7289	6421	557	534	435
Ship Assist	78.8	59.8	60.4	6537	5934	6197	426	394	422

Table 5-16 In-Use Emissions of the Hybrid and Conventional Tug at each Tug Operating Mode for Retrofit Scenario 1

 Assumption: Both tugs have CAT 3512 C main engines and Cummins QSK11 auxiliaries

 Table 5-17 In-Use Emissions of the Hybrid and Conventional Tug at each Tug Operating Mode for Retrofit Scenario 2

 Assumption: Conventional tug has CAT 3512C mains and JD 6081 auxiliaries; hybrid tug has CAT 3512 C mains and Cummins QSK11 auxiliaries

Operating Mode	Р	PM _{2.5} (g hr	¹)	I	NO _x (g hr ⁻¹)	C	CO ₂ (kg hr	¹)
Moue	Con.	Hyb_NB	Hyb.	Con.	Hyb_NB	Hyb.	Con.	Hyb_NB	Hyb.
Shore Power	0.0009	0.0013	0.0012	0.0011	0.0017	0.0015	0.014	0.021	0.018
Dock	5.1	3.2	1.1	156	309	89	16.0	32.8	9.9
Standby	27	9	7	3757	1127	886	176	84	69
Transit	115	24	19	7633	3021	2679	530	270	235
Barge Move	133	76	55	7666	7289	6421	555	534	435
Ship Assist	82	60	60	6452	5934	6197	424	394	422

5.4.5 Acknowledgements

The authors would like to thank CARB for their financial support; A technical working group (members from CARB, Foss Maritime Company, Pacific Merchant Shipping Association, Ports of Los Angeles and Long Beach, South Coast Air Quality Management District and U.S. Environmental Protection Agency) for overseeing the progress of the project; Edward Sun and Wayne McMahon of CARB for their input on HEV testing; Foss Maritime Company, Aspin Kemp and Associates and Startcrest Consulting LLC for their for their generous help on-board the vessels; Charles Bufalino, Kurt Bumiller, Mac MacClanahan and Ed Sponsler for their efforts in the test preparation; Kathalena Cocker, Poornima Dixit, James Theodore Gutierrez, Sindhuja Ranganathan, Letia Solomon, David Torres and Charles Wardle for their support in preparation and analysis of the sample media; Alex Vu for his help in developing Python 2.6 codes for data analysis; Kyle Loggins for preparing the schematic of the hybrid boat's diesel electric drive train.

6 Conclusions and Recommendations

The goal of this research was to develop and implement protocols that characterize the effectiveness of several existing and emerging control technologies on a variety of in-use marine diesel engines. Overall, four control technologies for marine engines on ocean-going vessels and two for those on harbor-craft were evaluated.

A WFE unit installed on a low-speed two-stroke marine propulsion engine of a PanaMax class vessel was tested during a voyage from Los Angeles to Dutch Harbor. The reduction in weighted average NO_x emissions was found to be ~12% with 20% water to fuel ratio and ~23% with 33% water to fuel ratio. This reduction is lower than the estimates of 1% reduction for every 1% increase in the water to fuel ratio used by other researchers^{17, 19}. In general the total PM_{2.5} mass increased with the water addition. The PM_{2.5} mass increase can be attributed predominantly to the 1.8 to 3.5 factor increase in organic carbon fraction and to some extent to the 0.8 to 4.8 factor increase the elemental carbon. Overall the WFE changed the speciation of the PM_{2.5} mass from 0.2% EC, 4% ash, 8% OC, 93% hydrated sulfate to 0.6% EC, 3% ash, 22% OC, 66% hydrated sulfate. A caveat to these findings is that only one measurement was made for each test load on a single vessel. Therefore the results from this study should be verified with additional measurements.

Three controls were evaluated on a series of large four-stroke medium-speed auxiliary engines operating on two Post PanaMax class container vessels at berth: cleaner burning fuels, low NO_x mode and selective catalytic reduction (SCR). Switching from high sulfur HFO to lower sulfur marine distillate oil resulted in PM_{2.5} reductions of up to 83% due to significantly lower emissions of sulfate and OC particles. Minor reductions in NO_x were also observed. Operating in the low NO_x mode reduced NO_x emissions by 32% and nearly doubled the EC emissions. However, the total PM_{2.5} emission factors were unchanged since the EC emission factor is only ~5% of the total PM_{2.5} mass. The selective catalytic reduction unit reduced the NO_x emission factor to < 2.4 g kW⁻¹ hr⁻¹, but increased the PM_{2.5} emissions by a factor of 1.5 to 3.8. This increase was a direct consequence of the conversion of SO₂ to sulfate particles over the SCR catalyst. The EC and OC fractions of PM_{2.5} were reduced across the SCR unit.

IMO regulates NO_x emissions from ships. Current technology solutions that help attain the Tier 2 standard that comes into effect in 2011 include low NO_x mode and WFE. The most promising control technology available to attain the Tier 3 NO_x standard is SCR. Results from these studies show that WFE and SCR control increase $PM_{2.5}$ mass emissions and also change the PM speciation. These findings suggest the need for implementation of a mix of $PM_{2.5}$ control methods like cleaner burning fuels in conjunction with the NO_x controls to prevent increase in global and regional ship $PM_{2.5}$ emissions. Total and speciated $PM_{2.5}$ mass emissions from ships have significant effects on chemical composition of the atmosphere, climate and human health. Results from these studies should be used to model changes in these effects resulting from the penetration of these technologies into current and future fleets. No in-use emissions data on the effect of SCR on low-speed two-stroke main propulsion engines are currently available. Since SCR is the only viable technology solution for attaining the IMO Tier 3 NO_x standard, there is a additional need to establish the effect of SCR on total and speciated $PM_{2.5}$ mass emissions from these engines.

Biodiesel blends are known to reduce $PM_{2.5}$ mass emissions along with minimal increase in NO_x emissions. No significant change in NO_x emissions were observed with ULSD/biodiesel blends (B20, B50) on a four-stroke high-speed modern marine propulsion engine. $PM_{2.5}$ mass emissions were reduced by ~16% and ~25% with B20 and B50 blends, respectively. Speciation of the PM emissions showed increased OC to EC ratios with the B50 blend. An increased formation of nucleation mode particles and a smaller mass mean diameter was observed with increasing ratios of biodiesel to diesel fuel. Studies¹¹²⁻¹¹³ on health effects of nanoparticles suggest that smaller particles have increased biological activity because of larger specific surfaces; the findings of this study show that the size and nature of the PM emitted by biodiesel are different from diesel indicating a need for further research on the nature and health effects of particles formed by the combustion of diesel versus biodiesel fuels.

The California Air Resources Board is assessing the need for the development of a vessel speed reduction (VSR) program that requires ocean going vessels to reduce their speed to 12 knots during arrival and departure from ports¹⁴⁴. This program is expected to significantly

reduce emissions of CO_2 , NO_x , SO_x and PM. Results from the biodiesel study show significant effects of bay/ocean currents on engine load and emissions. Six-fold increase in $PM_{2.5}$ mass emissions and three-fold increases in NO_x and CO_2 emissions were observed for the ferry sailing against versus along the bay current. This finding presents the need for the development of a model that calculates the engine load and emissions from marine engines based on vessel/engine type and frictional/residual resistances due to waves, ocean currents and wind speed. Such a model will help accurately predict the emission benefits of the VSR program. In-use emissions data from a range of large ocean-going vessels operating at low speeds of 10 to 15 knots during various ocean and wind conditions is required to validate the model.

The final phase of this research involved the development and implementation of an activity and emissions based model that estimates the overall in-use emission reductions of a complex hybrid system (four engines and an energy storage device: batteries) on a tug boat. Significant emission reductions were observed: 73% for $PM_{2.5}$, 51% for NO_x and 27% for CO_2 . The primary cause for these reductions was the energy management system on the hybrid tug that directs the use of auxiliary and battery power for propulsion. The observed CO_2 reductions were in good agreement with the eight month fuel savings measured by the tug owner.

The energy storage device on the hybrid tug provides supplemental power during high acceleration periods allowing the load on the engines to increase gradually. This eliminates the puff or sudden increase in the $PM_{2.5}$ mass emissions associated with

accelerations. The model developed for the evaluation of the hybrid system uses engine histograms and discrete in-use emissions data to estimate emission benefits. Therefore savings in $PM_{2.5}$ mass due to elimination of the puff are not captured by the model. This presents a unique opportunity for developing a complex model similar to that presented by Feng et. al. 1995¹³² that provides a better estimate of the total emission reductions of the hybrid technology.

The primary goal of energy storage devices on hybrid systems is to supply excess energy needed during accelerations and all energy during low load operations, thereby allowing the use of a smaller engine that operates predominantly in its efficient zone. The hybrid system employed on the tug boat was the first of its kind. Activity data collected during this study shows that the hybrid system increased the average operating load on the auxiliary engines of the tug from 12% to 34% of its maximum power rating. However, the average load on the main engines of the hybrid tug was found to be only 12%. These main engines are still operating in inefficient zone suggesting the need for a larger energy storage system and smaller main engines in the next generation of hybrid tugs.

During the hybrid study activity data was collected from a total of eight engines on two tugs: a conventional and a hybrid one. Data revealed that the average operating load of engines on the conventional tug were 73% to 77% less than those specified in the standard ISO duty cycles. On the hybrid tug the average operating load of the main and auxiliary engines were ~83% and ~28% lower. Most regional and global emission

inventories are calculated based on the load factors of standard duty cycles. The load factors obtained in this study can be used to improve the accuracy of these inventories. Also the data logger developed in the study can be employed on other marine vessels to determine the activity of those engines to establish accurate load factors that can be used for improving emission inventories and air quality models.

Overall this research highlights the need for characterizing emerging control technologies in the pilot phase. Some control technologies though effective for the target pollutant, increase the emissions of other pollutants. Analyses of these technologies at an early stage can help rectify such issues before large scale implementation. This work also shows the importance of in-use measurements and the need to develop in-use duty cycles that are representative of the real world emissions from marine engines. The activity and emissions based model developed within this dissertation for estimating real world emission benefits of hybrid systems can be employed on other emerging hybrid systems.

7 Bibliography

- 1. Dalsoren, S. B.; Eide, M. S.; Endresen, O.; Mjelde, A.; Gravir, G.; Isaksen, I. S. A., Update on emissions and environmental impacts from the international fleet of ships: the contribution from major ship types and ports. *ACP* **2009**, *9* (6), 2171-2194.
- 2. Capaldo, K.; Corbett, J. J.; Kasibhatla, P.; Fischbeck, P.; Pandis, S. N., Effects of ship emissions on sulphur cycling and radiative climate forcing over the ocean. *Nature* **1999**, *400* (6746), 743-746.
- 3. Corbett, J. J.; Koehler, H. W., Updated emissions from ocean shipping. *JGR-Atmospheres* **2003**, *108* (D20).
- 4. Sinha; P., Emissions of trace gases and particles from two ships in the southern Atlantic Ocean. *Atmos. Environ.* **2003**, *37* (15), 2139-2148.
- 5. Eyring, V.; Kohler, H. W.; van Aardenne, J.; Lauer, A., Emissions from international shipping: 1. The last 50 years. *JGR-Atmospheres* **2005**, *110* (D17).
- 6. Deniz, C.; Durmusoglu, Y., Estimating shipping emissions in the region of the Sea of Marmara, Turkey. *Sci. Total Environ.* **2008**, *390* (1), 255-261.
- 7. Lucialli, P.; Ugolini, P.; Pollini, E., Harbour of Ravenna: The contribution of harbour traffic to air quality. *Atmos. Environ.* **2007**, *41* (30), 6421-6431.
- 8. Saxe, H.; Larsen, T., Air pollution from ships in three Danish ports. *Atmos. Environ.* **2004**, *38* (24), 4057-4067.
- 9. Schrooten, L.; De Vlleger, I.; Panis, L. I.; Styns, K.; Torfs, R., Inventory and forecasting of maritime emissions in the Belgian sea territory, an activity-based emission model. *Atmos. Environ.* **2008**, *42* (4), 667-676.
- 10. Vutukuru, S.; Dabdub, D., Modeling the effects of ship emissions on coastal air quality: A case study of southern California. *Atmos. Environ.* **2008**, *42* (16), 3751-3764.
- Corbett, J. J.; Winebrake, J. J.; Green, E. H.; Kasibhatla, P.; Eyring, V.; Lauer, A., Mortality from ship emissions: A global assessment. *Environ. Sci. Technol.* 2007, 41 (24), 8512-8518.
- 12. Winebrake, J. J.; Corbett, J. J.; Green, E. H.; Lauer, A.; Eyring, V., Mitigating the Health Impacts of Pollution from Oceangoing Shipping: An Assessment of Low-Sulfur Fuel Mandates. *Environ. Sci. Technol.* **2009**, *43* (13), 4776-4782.
- 13. Heywood, J., Internal Combustion Engine Fundamentals. March 31st 1998.

- 14. U.S. Environmental Protection Agency What are the Six Common Air Polluants? http://www.epa.gov/air/urbanair/ (accessed 05/03/2008).
- 15. John H, S.; Syros N, P., *Atmospheric Chemistry and Physics: From Air Pollution* to Climate Change. John Wiley Hoboken NJ: 2006.
- 16. Endresen, O.; Sorgard, E.; Sundet, J. K.; Dalsoren, S. B.; Isaksen, I. S. A.; Berglen, T. F.; Gravir, G., Emission from international sea transportation and environmental impact. *JGR-Atmospheres* **2003**, *108* (D17).
- 17. MAN B&W Diesel, Emission Control Two-Stroke Low-Speed Diesel Engine. 1996.
- 18. Corbett, J. J.; Fischbeck, P. S., Commercial marine emissions and life-cycle analysis of retrofit controls in a changing science and policy environment. *Naval Engineers Journal* **2002**, *114* (1), 93-106.
- 19. Goldsworthy, L. Design of Ship Engines for Reduced Emissions of Oxides of Nitrogen 2002. http://www.flamemarine.com/files/AMCPaper.pdf.
- Lauer, A.; Eyring, V.; Corbett, J. J.; Wang, C. F.; Winebrake, J. J., Assessment of Near-Future Policy Instruments for Oceangoing Shipping: Impact on Atmospheric Aerosol Burdens and the Earth's Radiation Budget. *Environ. Sci. Technol.* 2009, 43 (15), 5592-5598.
- 21. Lauer, A.; Eyring, V.; Hendricks, J.; Jockel, P.; Lohmann, U., Global model simulations of the impact of ocean-going ships on aerosols, clouds, and the radiation budget. *ACP* **2007**, *7* (19), 5061-5079.
- Eyring, V.; Stevenson, D. S.; Lauer, A.; Dentener, F. J.; Butler, T.; Collins, W. J.; Ellingsen, K.; Gauss, M.; Hauglustaine, D. A.; Isaksen, I. S. A.; Lawrence, M. G.; Richter, A.; Rodriguez, J. M.; Sanderson, M.; Strahan, S. E.; Sudo, K.; Szopa, S.; van Noije, T. P. C.; Wild, O., Multi-model simulations of the impact of international shipping on Atmospheric Chemistry and Climate in 2000 and 2030. *ACP* 2007, 7, 757-780.
- Buhaug, Ø.; Corbett, J. J.; Eyring, V.; Endresen, Ø.; Faber, J.; Hanayama, S.; Lee, D. S.; Lee, D.; Lindstad, H.; Markowska, A. Z.; Mjelde, A.; Nelissen, D.; Nilsen, J.; Pålsson, C.; Wanquing, W.; Winebrake, J. J.; Yoshida, K. Control of Greenhouse Gas Emissions from Ships engaged in International Trade: Second IMO GHG Study 2009 2009. http://www.seas-at-risk.org/1mages/MEPC%2059-INF.10%20(The%20Second%20IMO%20GHG%20Study%202009).pdf (accessed 11/02/2010).
- 24. Entec UK Ltd., Quantification of Emissions from Ships Associated with Ship Movements Between Ports in the European Community. 2002.

- 25. Agrawal, H.; Malloy, Q. G. J.; Welch, W. A.; Miller, J. W.; Cocker, D. R., In-use gaseous and particulate matter emissions from a modern ocean going container vessel. *Atmos. Environ.* **2008**, *42* (21), 5504-5510.
- 26. Agrawal, H.; Welch, W. A.; Miller, J. W.; Cocker, D. R., Emission Measurements from a Crude Oil Tanker at Sea. *Environ. Sci. Technol.* **2008**, *42*, 7098–7103.
- Murphy, S. M.; Agrawal, H.; Sorooshian, A.; Padro, L. T.; Gates, H.; Hersey, S.; Welch, W. A.; Jung, H.; Miller, J. W.; Cocker, D. R.; Nenes, A.; Jonsson, H. H.; Flagan, R. C.; Seinfeld, J. H., Comprehensive Simultaneous Shipboard and Airborne Characterization of Exhaust from a Modern Container Ship at Sea. *Environ. Sci. Technol.* 2009, 43 (13), 4626-4640.
- 28. Moldanova, J.; Fridell, E.; Popovicheva, O.; Demirdjian, B.; Tishkova, V.; Faccinetto, A.; Focsa, C., Characterisation of particulate matter and gaseous emissions from a large ship diesel engine. *Atmos. Environ.* **2009**, *43* (16), 2632-2641.
- 29. Kasper, A.; Aufdenblatten, S.; Forss, A.; Mohr, M.; Burtscher, H., Particulate emissions from a low-speed marine diesel engine. *Aerosol Sci. Technol.* **2007**, *41* (1), 24-32.
- 30. Fridell, E.; Steen, E.; Peterson, K., Primary particles in ship emissions. *Atmos. Environ.* **2008**, *42* (6), 1160-1168.
- 31. Cooper, D. A., Exhaust emissions from high speed passenger ferries. *Atmos. Environ.* **2001**, *35* (24), 4189-4200.
- 32. Cooper, D. A., Exhaust emissions from ships at berth. *Atmos. Environ.* 2003, *37* (27), 3817-3830.
- 33. Cooper, D. A., HCB, PCB, PCDD and PCDF emissions from ships. *Atmos. Environ.* 2005, *39* (27), 4901-4912.
- 34. Cooper, D. A.; Peterson, K.; Simpson, D., Hydrocarbon, PAH and PCB emissions from ferries: A case study in the Skagerak-Kattegatt-Öresund region. *Atmos. Environ.* **1996**, *30* (14), 2463-2473.
- 35. Sarvi, A.; Fogelholm, C. J.; Zevenhoven, R., Emissions from large-scale mediumspeed diesel engines: 2. Influence of fuel type and operating mode. *Fuel Process. Technol.* **2008**, *89* (5), 520-527.
- 36. Cooper, D. A., Methodology for Calculating Emissions from Ships: 1. Update of Emission Factors. 2004, Assignment for Swedish Environmental Protection Agency.

- 37. International Maritime Organization, Annex 13, Resolution MEPC.176(58), Amendments to the Annex of the Protocol of 1997 to amed the International Convention for the Prevention of Pollution from Ships, 1973, as Modified by the Protocol of 1978 Relating Thereto. 2008.
- 38. International Maritime Organization Greenhouse Gas Emissions. http://www.imo.org/OurWork/Environment/PollutionPrevention/AirPollution/Pag es/GHG-Emissions.aspx (accessed 11/02/2010).
- 39. Lack, D. A.; Corbett, J. J.; Onasch, T.; Lerner, B.; Massoli, P.; Quinn, P. K.; Bates, T. S.; Covert, D. S.; Coffman, D.; Sierau, B.; Herndon, S.; Allan, J.; Baynard, T.; Lovejoy, E.; Ravishankara, A. R.; Williams, E., Particulate emissions from commercial shipping: Chemical, physical, and optical properties. *JGR-Atmospheres* **2009**, *114*.
- 40. California Air Resources Board. Emissions Estimation Methodology for Ocean-Going Vessels. 2008. http://www.arb.ca.gov/regact/2008/fuelogv08/appdfuel.pdf (accessed 11/1/2010).
- 41. California Air Resources Board. A Critical Review of Ocean-Going Vessel Particulate Matter Emission Factors 2007. http://www.arb.ca.gov/msei/offroad/pubs/ocean_going_vessels_pm_emfac.pdf (accessed 11/1/2010).
- 42. U.S. Environmental Protection Agency. Current Methodologies in Preparing Mobile Source Port-Related Emission Inventories - Final Report 2009. http://www.epa.gov/cleandiesel/documents/ports-emission-inv-april09.pdf (accessed Nov 1,2010).
- 43. Petzold, A.; Hasselbach, J.; Lauer, P.; Baumann, R.; Franke, K.; Gurk, C.; Schlager, H.; Weingartner, E., Experimental studies on particle emissions from cruising ship, their characteristic properties, transformation and atmospheric lifetime in the marine boundary layer. *ACP* **2008**, *8* (9), 2387-2403.
- 44. Petzold, A.; Weingartner, E.; Hasselbach, J.; Lauer, P.; Kurok, C.; Fleischer, F., Physical Properties, Chemical Composition, and Cloud Forming Potential of Particulate Emissions from a Marine Diesel Engine at Various Load Conditions. *Environ. Sci. Technol.* **2010**, *44* (10), 3800-3805.
- 45. Corbett, J. J.; Fischbeck, P., Emissions from ships. Science **1997**, 278 (5339), 823-824.
- 46. Corbett, J. J.; Fischbeck, P. S.; Pandis, S. N., Global nitrogen and sulfur inventories for oceangoing ships. *JGR-Atmospheres* **1999**, *104* (D3), 3457-3470.

- 47. Endresen, O.; Sorgard, E.; Behrens, H. L.; Brett, P. O.; Isaksen, I. S. A., A historical reconstruction of ships' fuel consumption and emissions. *JGR-Atmospheres* **2007**, *112* (D12).
- 48. Eyring, V.; Kohler, H. W.; Lauer, A.; Lemper, B., Emissions from international shipping: 2. Impact of future technologies on scenarios until 2050. *JGR-Atmospheres* **2005**, *110* (D17).
- 49. Business Transportation and Housing Agency; California Environmental Protection Agency. Goods Movement Action Plan Phase I: Foundations 2005. http://www.arb.ca.gov/gmp/docs/finalgmpplan090205.pdf (accessed 09/02/08).
- 50. International Maritime Organization, Annex VI of MARPOL 73/78 Regulations for the Prevention of Air Pollution from Ships and NOx Technical Code. 1997.
- 51. IMO. IMO environment meeting approves revised regulations on ship emissions 2008. http://www.imo.org/Safety/mainframe.asp?topic_id=1709&doc_id=9123.
- 52. U.S. Environmental Protection Agency, Control of Emissions of Air Pollution From Locomotive Engines and Marine Compression-Ignition Engines Less Than 30 Liters per Cylinder; Final Rule - 40 CFR Parts 9, 85. **2008**.
- 53. Corbett, J. J.; Chapman, D., An environmental decision framework applied to marine engine control technologies. *J. Air Waste Manage. Assoc.* **2006**, *56* (6), 841-851.
- 54. Lyyranen, J.; Jokiniemi, J.; Kauppinen, E., The effect of Mg-based additive on aerosol characteristics in medium-speed diesel engines operating with residual fuel oils. *J. Aerosol Sci* **2002**, *33* (7), 967-981.
- 55. Lyyränen, J.; Jokiniemi, J.; Kauppinen, E.; Joutsensaari, J.; Auvinen, A., Particle formation in medium speed diesel engines operating with heavy fuel oils. *J. Aerosol Sci* **1998**, *29* (Supplement 2), S1003-S1004.
- 56. Lack, D.; Lerner, B.; Granier, C.; Baynard, T.; Lovejoy, E.; Massoli, P.; Ravishankara, A. R.; Williams, E., Light absorbing carbon emissions from commercial shipping. *Geophys. Res. Lett.* **2008**, *35* (13), 6.
- 57. International Organization for Standardization, ISO 8178-4 Reciprocation internal combustion engines Exhaust emission measurement Part 4: Test cycles for different engine applications. 1996; Vol. First Edition 1996-08-15.
- 58. International Organization for Standardization, ISO 8178-1 Reciprocating internal combustion engines Exhaust emission measurement Part 1: Test-bed measurement of gaseous and particulate exhaust emissions. 1996; Vol. First Edition 1996-08-15.

- 59. Abdel-Rahman, A. A., On the emissions from internal-combustion engines: A review. *Int. J. Energy Res.* **1998**, 22 (6), 483-513.
- 60. Amon, B.; Keefe, G., On-Road Demonstration of Nox Emission Control for Heavy-Duty Diesel Trucks Using SINOx Urea SCR Technology - Long-Term Experience and Measurement Results. *Society of Automotive Engineers* 2001, *SAE 2001-01-1931*.
- 61. Fritz, N.; Mathes, W.; Mueller, R.; Zuerbig, J., On-Road Demonstration of NOx Emission Control for Diesel Trucks With SINOx Urea SCR System. *Society of Automotive Engineers* **1999**, *SAE 1999-01-0111*
- 62. MAN B&W Diesel A/S, R. D. B. R. E., Dept. 2431, Emission Measurement Results A.P. Moeller - Sine Maersk Hitachi, MAN B&W - 12K90MC mk6, Holeby Genset 7L32/40, Sea trial 9-11 February 2004. 2004.
- 63. California Air Resources Board. Emissions Estimation Methodology for Ocean-Going Vessels. 2005. http://www.arb.ca.gov/regact/marine2005/appd.pdf.
- 64. U.S. Environmental Protection Agency. Current Methodologies and Best Practices in Preparing Port Emission Inventories - Final Report 2006. http://www.epa.gov/sectors/ports/bp_portemissionsfinal.pdf (accessed Sept 9,2008).
- 65. Grados, C. V. D.; Uriondo, Z.; Clemente, M.; Espadafor, F. J. J.; Gutierrez, J. M., Correcting injection pressure maladjustments to reduce NOx emissions by marine diesel engines. *Transportation Research Part D-Transport and Environment* **2009**, *14* (1), 61-66.
- 66. M.J Bradley & Associates, Staten Islan Ferry Alice Austen Vessel SCR Demonstration Project Final Report. 2006; Vol. Prepared for the Port Authority of New York and New Jersey and New York City Department of Transportation.
- 67. Amon, B.; Fischer, S.; Hofmann, L.; Zurbig, R., The SINOx system for trucks to fulfill the future emission regulations. *Top. Catal.* **2001**, *16* (1-4), 187-191.
- 68. Rusch, K.; Hofmann, L.; Zuerbig, J.; Scarnegie, B., PM Reduction by SCR Catalyst. *Society of Automotive Engineers* **2003**, *SAE* 2003-01-0777
- 69. Svachula, J.; Alemany, L. J.; Ferlazzo, N.; Forzatti, P.; Tronconi, E.; Bregani, F., Oxidation of SO₂ to SO₃ Over Honeycomb Denoxing Catalysts. *Industrial & Engineering Chemistry Research* **1993**, *32* (5), 826-834.
- 70. Morita, I.; Nagai, Y.; Kato, Y.; Franklin, H. N.; Cooper, J., Development and Operating Results of Low SO2 to SO3 Conversion Rate Catalyst for DeNOx Application. In *ICAC's Clean Air Technologies and Strategies Conference & Workshop*, Baltimore, MD, 2005.

- 71. Corbett, J. J.; Fischbeck, P. S., Emissions from Waterborne Commerce Vessels in United States Continental and Inland Waterways. *Environ. Sci. Technol.* **2000**, *34* (15), 3254-3260.
- 72. Corbett, J. J.; Robinson, A. L., Measurements of NOx Emissions and In-Service Duty Cycle from a Towboat Operating on the Inland River System. *Environ. Sci. Technol.* **2001**, *35* (7), 1343-1349.
- 73. Farrell, A. E.; Redman, D. H.; Corbett, J. J.; Winebrake, J. J., Comparing air pollution from ferry and landside commuting. *Transportation Research Part D: Transport and Environment* **2003**, *8* (5), 343-360.
- 74. Farrell, A. E.; Corbett, J. J.; Winebrake, J. J., Controlling air pollution from passenger ferries: cost-effectiveness of seven technological options. *J. Air Waste Manage. Assoc.* **2002**, *52* (12), 1399-1410.
- 75. U.S. Environmental Protection Agency. Final Rule: Control of Emissions of Air Pollution from Locomotives and Marine Compression-Ignition Engines Less Than 30 Liters per Cylinder 2008, p. Parts 85-94. http://www.epa.gov/sectors/ports/bp_portemissionsfinal.pdf.
- 76. McCormick, R. L.; Tennant, C. J.; Hayes, R. R.; Black, S.; Ireland, J.; McDaniel, T.; Williams, A.; Frailey, M.; Sharp, C. A., Regulated Emissions from Biodiesel Tested in Heavy-Duty Engines Meeting 2004 Emission Standards. Society of Automotive Engineers 2005, SAE 2005-01-2200.
- 77. Sze, C.; Whinihan, J. K.; Olson, B. A.; Schenk, C. R.; Sobotowski, R. A., Impact of Test Cycle and Biodiesel Concentration on Emissions. *Society of Automotive Engineers* **2007**, *SAE* 2007-01-4040.
- 78. McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R., Effects of Biodiesel Blends on Vehicle Emissions. *National Renewable Enegy Laboratory* **2006**, *NREL/MP-540-40554*.
- 79. U.S. Environmental Protection Agency, A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions. *Draft Technical Report* **2002**, *EPA420-P-02-001*.
- 80. Sharp, C. A.; Howell, S. A.; Jobe, J., The Effect of Biodiesel Fuels on Transient Emissions from Modern Diesel Engines, Part I Regulated Emissions and Performance. *Society of Automotive Engineers* **2000**, *SAE 2000-01-1967*.
- 81. Graboski, M. S.; Ross, J. D.; McCormick, R. L., Transient Emissions from No. 2 Diesel and Biodiesel Blends in a DDC Series 60 Engine. *Society of Automotive Engineers* **1996**, *SAE 961166*.

- 82. Schumacher, L. G.; Borgelt, S. C.; Fosseen, D.; Goetz, W.; Hires, W. G., Heavyduty engine exhaust emission tests using methyl ester soybean oil/diesel fuel blends. *Bioresour. Technol.* **1996**, *57* (1), 31-36.
- 83. Alam, M.; Song, J.; Acharya, R.; Boehman, A., Combustion and Emissions Performance of Low Sulfur, Ultra Low Sulfur and Biodiesel Blends in a DI Diesel Engine. *Society of Automotive Engineers* **2004**, *SAE* 2004-01-3024.
- 84. Cheng, A. S.; Buchholz, B. A.; Dibble, R. W., Isotopic Tracing of Fuel Carbon in the Emissions of a Compression-Ignition Engine Fueled with Biodiesel Blends. *Society of Automotive Engineers* **2003**, *SAE* 2003-01-2282.
- 85. Durbin, T. D.; Cocker Iii, D. R.; Sawant, A. A.; Johnson, K.; Miller, J. W.; Holden, B. B.; Helgeson, N. L.; Jack, J. A., Regulated emissions from biodiesel fuels from on/off-road applications. *Atmos. Environ.* **2007**, *41* (27), 5647-5658.
- Eckerle, W. A.; Lyford-Pike, E. J.; Stanton, D. W.; LaPointe, L. A.; Whitacre, S. D.; Wall, J. C., Effects of Methyl Ester Biodiesel Blends on NOx Emissions. Society of Automotive Engineers 2008, SAE 2008-01-0078.
- 87. Roskilly, A. P.; Nanda, S. K.; Wang, Y. D.; Chirkowski, J., The performance and the gaseous emissions of two small marine craft diesel engines fuelled with biodiesel. *Appl. Therm. Eng.* **2008**, *28* (8-9), 872-880.
- 88. Code of Federal Regulations *Protection of the Environment 40 CFR 86*.
- 89. NIOSH NIOSH Manual of Analytical Methods National Istitute of Occupational Safety and Health, Cincinnati, OH; 1996.
- 90. Siegl, W. O.; Richert, J. F. O.; Jensen, T. E.; Schuetzle, D.; Swarin, S. J.; Loo, J. F.; Prostak, A.; Nagy, D.; Schlenker, A. M., Improved Emissions Speciation Methodology for Phase II of The Auto/Oil Air Quality Improvement Research Programs Hydrocarbons and Oxygenates. SAE Technical Paper 1993, Serial No. 930142, Special Publication SP-1000.
- 91. Shah, S. D.; Ogunyoku, T. A.; Miller, J. W.; Cocker, D. R., On-Road Emission Rates of PAH and n-Alkane Compounds from Heavy-Duty Diesel Vehicles. *Environ. Sci. Technol.* **2005**, *39* (14), 5276-5284.
- 92. Jayne, J. T.; Leard, D. C.; Zhang, X.; Davidovits, P.; Smith, K. A.; Kolb, C. E.; Worsnop, D. R., Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles. *Aerosol Sci. Technol.* 2000, 33 (1), 49 - 70.
- 93. DeCarlo, P. F.; Kimmel, J. R.; Trimborn, A.; Northway, M. J.; Jayne, J. T.; Aiken, A. C.; Gonin, M.; Fuhrer, K.; Horvath, T.; Docherty, K. S.; Worsnop, D.

R.; Jimenez, J. L., Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer. *Anal. Chem.* **2006**, 78 (24), 8281-8289.

- 94. Aiken, A. C.; DeCarlo, P. F.; Kroll, J. H.; Worsnop, D. R.; Huffman, J. A.; Docherty, K. S.; Ulbrich, I. M.; Mohr, C.; Kimmel, J. R.; Sueper, D.; Sun, Y.; Zhang, Q.; Trimborn, A.; Northway, M.; Ziemann, P. J.; Canagaratna, M. R.; Onasch, T. B.; Alfarra, M. R.; Prevot, A. S. H.; Dommen, J.; Duplissy, J.; Metzger, A.; Baltensperger, U.; Jimenez, J. L., O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Timeof-Flight Aerosol Mass Spectrometry. *Environ. Sci. Technol.* 2008, 42 (12), 4478-4485.
- Shah, S.; Cocker, D., A Fast Scanning Mobility Particle Spectrometer for Monitoring Transient Particle Size Distributions. *Aerosol Sci. Technol.* 2005, 39 (6), 519 - 526.
- 96. Cummins Inc. Marine Performance Curves. http://marine.cummins.com/attachments/public/marine/Products/Commercial%20 Propulsion/QSK19_T2/fr4462.pdf (accessed 08/03/2010).
- 97. Code of Federal Regulations *Protection of the Environment 40 CFR 1042*.
- 98. Code of Federal Regulations *Protection of the Environment 40 CFR 94*.
- 99. Chang, D. Y.; Van Gerpen, J. H., Determination of Particulate and Unburned Hydrocarbon Emissions from Diesel Engines Fueled with Biodiesel. *Society of Automotive Engineers* **1998**, *SAE* 982527.
- 100. Zhu, L.; Zhang, W.; Liu, W.; Huang, Z., Experimental study on particulate and NOx emissions of a diesel engine fueled with ultra low sulfur diesel, RME-diesel blends and PME-diesel blends. *Sci. Total Environ.* **2010**, *408* (5), 1050-1058.
- 101. Zhang, J.; He, K.; Shi, X.; Zhao, Y., Effect of SME biodiesel blends on PM2.5 emission from a heavy-duty engine. *Atmos. Environ.* **2009**, *43* (15), 2442-2448.
- Ballesteros, R.; Hernández, J. J.; Lyons, L. L.; Cabañas, B.; Tapia, A., Speciation of the semivolatile hydrocarbon engine emissions from sunflower biodiesel. *Fuel* 2008, 87 (10-11), 1835-1843.
- 103. Japar, S. M.; Szkarlat, A. C.; Gorse, R. A.; Heyerdahl, E. K.; Johnson, R. L.; Rau, J. A.; Huntzicker, J. J., Comparison of solvent extraction and thermal-optical carbon analysis methods: application to diesel vehicle exhaust aerosol. *Environ. Sci. Technol.* **1984**, *18* (4), 231-234.
- 104. Shah, S. D.; Cocker, D. R.; Miller, J. W.; Norbeck, J. M., Emission Rates of Particulate Matter and Elemental and Organic Carbon from In-Use Diesel Engines. *Environ. Sci. Technol.* **2004**, *38* (9), 2544-2550.

- Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T., Measurement of Emissions from Air Pollution Sources. 2. C1 through C30 Organic Compounds from Medium Duty Diesel Trucks. *Environ. Sci. Technol.* **1999**, *33* (10), 1578-1587.
- 106. Kittelson, D. B., Engines and nanoparticles: a review. *J. Aerosol Sci* **1998**, *29* (5-6), 575-588.
- 107. Heikkilal[^], J.; Virtanen, A.; Rol[^]nkkol[^], T.; Keskinen, J.; Aakko-Saksa, P. i.; Murtonen, T., Nanoparticle Emissions from a Heavy-Duty Engine Running on Alternative Diesel Fuels. *Environ. Sci. Technol.* **2009**, *43* (24), 9501-9506.
- Jung, H.; Kittelson, D. B.; Zachariah, M. R., Characteristics of SME Biodiesel-Fueled Diesel Particle Emissions and the Kinetics of Oxidation. *Environ. Sci. Technol.* 2006, 40 (16), 4949-4955.
- 109. Kittelson, D. B.; Watts, W. F.; Savstrom, J. C.; Johnson, J. P., Influence of a catalytic stripper on the response of real time aerosol instruments to diesel exhaust aerosol. *J. Aerosol Sci* **2005**, *36* (9), 1089-1107.
- Kittelson, D. B.; Watts, W. F.; Johnson, J. P., On-road and laboratory evaluation of combustion aerosols--Part1: Summary of diesel engine results. *J. Aerosol Sci* 2006, *37* (8), 913-930.
- 111. Krahl, J.; Baum, K.; Hackbarth, U.; Jeberien, H. E.; Munack, A.; Schutt, C.; Schroder, O.; Walter, N.; Bunger, J.; Muller, M. M.; Weigel, A., Gaseous Compounds, Ozone Presursors, Particle Number and Particle Size Distributions, and Mutagenic Dggects Due to Biodiesel. *Transactions of the American Society of Agricultural Engineers* 2001, 44 (2), 179-191.
- 112. Donaldson, K.; Li, X. Y.; MacNee, W., Ultrafine (nanometre) particle mediated lung injury. *J. Aerosol Sci* **1998**, *29* (5-6), 553-560.
- Oberdorster, G.; Oberdorster, E.; Oberdorster, J., Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles. *Environ Health Perspect* 2005, 113 (7).
- Park, K.; Cao, F.; Kittelson, D. B.; McMurry, P. H., Relationship between Particle Mass and Mobility for Diesel Exhaust Particles. *Environ. Sci. Technol.* 2002, *37* (3), 577-583.
- 115. Turrio-Baldassarri, L.; Battistelli, C. L.; Conti, L.; Crebelli, R.; De Berardis, B.; Iamiceli, A. L.; Gambino, M.; Iannaccone, S., Emission comparison of urban bus engine fueled with diesel oil and [`]biodiesel' blend. *Sci. Total Environ.* 2004, 327 (1-3), 147-162.

- 116. Sharp, C. A.; Howell, S. A.; Jobe, J., The Effect of Biodiesel Fuels on Transient Emissions from Modern Diesel Engines, Part II Unregulated Emissions and Chemical Characterization. *Society of Automotive Engineers* **2000**, *2000-01-1968*.
- Peng, C.-Y.; Yang, H.-H.; Lan, C.-H.; Chien, S.-M., Effects of the biodiesel blend fuel on aldehyde emissions from diesel engine exhaust. *Atmos. Environ.* 2008, 42 (5), 906-915.
- 118. He, C.; Ge, Y.; Tan, J.; You, K.; Han, X.; Wang, J.; You, Q.; Shah, A. N., Comparison of carbonyl compounds emissions from diesel engine fueled with biodiesel and diesel. *Atmos. Environ.* **2009**, *43* (24), 3657-3661.
- 119. Corrêa, S. M.; Arbilla, G., Carbonyl Emissions in Diesel and Biodiesel Exhaust. *Atmos. Environ.* **2008**, *42*, 769-775.
- 120. Di, Y.; Cheung, C. S.; Huang, Z., Experimental investigation on regulated and unregulated emissions of a diesel engine fueled with ultra-low sulfur diesel fuel blended with biodiesel from waste cooking oil. *Sci. Total Environ.* **2009**, *407* (2), 835-846.
- Ballesteros, R.; Hernández, J. J.; Lyons, L. L., An experimental study of the influence of biofuel origin on particle-associated PAH emissions. *Atmos. Environ.* 2010, 44 (7), 930-938.
- 122. Corrêa, S. M.; Arbilla, G., Aromatic hydrocarbons emissions in diesel and biodiesel exhaust. *Atmos. Environ.* **2006**, *40* (35), 6821-6826.
- 123. Lapuerta, M.; Armas, O.; Rodríguez-Fernández, J., Effect of biodiesel fuels on diesel engine emissions. *Prog. Energy Combust. Sci.* **2008**, *34* (2), 198-223.
- 124. Potter, J. The History of Fuel-Electric Hybrid Propulsion. http://www.escapekeygraphics.com/2007/07/the-history-of-fuel-electric-hybrid-propulsion-3/ (accessed 10/18/2010).
- 125. Calder, N. Water Power. http://www.sailmagazine.com/boatworks/engines-and-systems/hydroelectric_power_cruising/ (accessed 10/18/2010).
- 126. Saltmarsh, M., A fuel-saving system for ships relies on kites Business International Herald Tribune. *The New York Times* 08/09/2009, 2009.
- 127. Dove, T. Lagoon 440. http://www.sailmagazine.com/boat-reviews/Lagoon440/ (accessed 10/18/2010).
- 128. Hornblower Hybrid. http://www.alcatrazcruises.com/website/hybrid.aspx (accessed 10/18/2010).

- 129. Hybrid Boat Debuts in San Francisco. http://www.steyrmotors.com/products/products.htm (accessed 10/18/2010).
- 130. Silva, C.; Ross, M.; Farias, T., Evaluation of energy consumption, emissions and cost of plug-in hybrid vehicles. *Energy Convers. Manage.* **2009**, *50* (7), 1635-1643.
- 131. Duoba, M.; Spencer, Q.; LeBlanc, N.; Larsen, R., Testing Hybrid Electric Vehicle Emission and Fuel Economy at the 1994 DOE/SAE Hybrid Electric Vehicle Challenge. *Society of Automotive Engineers* **1995**, *950177*.
- 132. An, F.; Barth, M., Critical Issues in Quantifying Hybrid Electric Vehicle Emissions and Fuel Consumption. *Society of Automotive Engineers* **1995**, *981902*.
- 133. Clark, N. N.; Xie, W.; Gautam, M.; Lynos, D. W.; Norton, P.; Balon, T. H., Hybrid Diesel-Electric Heavy Duty Bus Emissions: Benefits of Regeneration and Need for State of Charge Correction. *Society of Automotive Engineers* **2000**, 2000-01-2955.
- 134. McKain, D. L.; Clark, N. N.; Balon, T. H.; Moynihan, P. J.; Lynch, S. A.; Webb, T. C., Characterization of Emissions from Hybrid-Electric and Conventional Transit Buses. *Society of Automotive Engineers* **2000**, *2000-01-2011*.
- 135. Brodrick, C.-J.; Sperling, D.; Dwyer, H. A.; Becker, C., Emissions from Conventional and Hybrid Electric Transit Buses Tested on Standard and San Francisco Specific Driving Cycles. *Society of Automotive Engineers* **2002**, 2002-01-3117.
- 136. Takada, Y.; Ueki, S.; Saito, A., Study on Fuel Economy and NOx Emissions of Medium Duty Hybrid Truck in Real Traffic Conditions. *Society of Automotive Engineers* **2004**, *2004-01-1086*.
- 137. Takada, Y.; Ueki, S.; Saito, A., Investigation into Fuel Economy and NOx Emissions of Light Duty Hybrid Truck in Real Traffic Conditions. *Society of Automotive Engineers* 2005, 2005-01-0265.
- 138. Martini, G.; Bonnel, P.; Manfredi, U.; Carriero, M.; Krasenbrink, A.; Franken, O.; Rubino, L.; Bartoli, G. B.; Bonifacio, M., On-road Emissions of Conventional and Hybrid Vehicles Running on Neat or Fossil Fuel Blended Alternative Fuels. Society of Automotive Engineers 2010, 2010-01-1068.
- 139. Qin, K.; Li, M.; Gao, J.; Gao, J.; Ai, Y., On-Road Test and Evaluation of Emissions and Fuel Economy of the Hybrid Electric Bus. *Society of Automotive Engineers* 2009, 2009-01-1866.

- 140. Society of Automotive Engineers. Recommended Practices for Measuring Exhaust Emissions and Fuel Economy of Hybrid Electric Vehicles 1999. http://www.imo.org/Safety/mainframe.asp?topic_id=1709&doc_id=9123.
- 141. California Air Resources Board. California Exhaust Emission Standards and Test Procedures for 2009 and Subsequent Model Zero-Emission Vehicles, and Hybrid Electric Vehicles, In the Passenger Car, Light-Duty Truck and Medium-Duty Vehicle Classes 2009. http://www.imo.org/Safety/mainframe.asp?topic_id=1709&doc_id=9123.
- 142. Environ International Corporation. Cold Ironing Cost Effectiveness Study 2004. http://www.imo.org/Safety/mainframe.asp?topic_id=1709&doc_id=9123.
- 143.U.S. Environmental Protection Agency. AP-42 Compilation of Air Pollutant
Emission Factors 2004.
http://www.imo.org/Safety/mainframe.asp?topic_id=1709&doc_id=9123.
- 144. California Air Resources Board Vessel Speed Reduction for Ocean-Going Vessels. http://www.arb.ca.gov/ports/marinevess/vsr/vsr.htm (accessed 11/10/2010).
- 145. Cocker, D. R.; Flagan, R. C.; Seinfeld, J. H., State-of-the-Art Chamber Facility for Studying Atmospheric Aerosol Chemistry. *Environ. Sci. Technol.* **2001**, *35* (12), 2594-2601.

Appendix A Determining Particulate Matter Losses in Raw Gas Heated Transfer Line

A.1 Introduction

The ISO 8178-1 protocol⁵⁸ allows the use of a heated line up to 5 m long to transfer raw emissions from a stack to the dilution tunnel for sampling PM_{2.5} mass emissions from an engine operating on a fuel with a sulfur content <0.8% mass/mass (m/m). ISO also requires that the temperature of the gas at the exit of the transfer line (TL) should not be less than 87% of the inlet temperature, thereby ensuring that the thermophoretic losses in the line are <5%. However, marine engines on ocean going vessels operate on high sulfur heavy fuel oil with sulfur content of up to 4.5% m/m. Significant losses (Chapter 3) in PM_{2.5} mass of ~30% and ~40% were observed in the TL while testing some marine auxiliary engines on Post Panamax class container vessels that were operating on fuels with sulfur contents 0.16% m/m and 3.3% m/m. These losses were found to occur primarily in the sulfate fraction of the PM with additional losses in the organic carbon (OC) fraction.

This study is aimed towards investigating the losses associated with the use of a heated transfer line during $PM_{2.5}$ mass sampling from diesel engines. Towards this goal two engines were tested on a variety of fuels with a range of sulfur contents with and without the use of a TL. The TL was also operated at several different temperatures. This section includes a description of the experiments conducted and a preliminary analysis of the data obtained from these experiments. Further analyses are required to develop a

theoretical model to estimate PM losses in the TL as a function of line length, temperature of operation, PM composition, size distribution and PM concentration.

A.2 Experimental Details

A.2.1 Transfer Line

To investigate the influence of a heated transfer line on emission measurement a 20 ft (6 m) long transfer line with an 8.1 mm inner diameter was used. This TL is similar to Technical Heaters, Inc model 212-6-15 (San Fernando, CA) but with a core inner tube comprised of slightly flexible stainless steel tube. This tube is covered by a high density stainless over-braid, heating element, electrical insulation, thermal insulation and external jacket as shown Figure A-1.



Figure A-1 Picture of Transfer Line

The TL was equipped with five thermocouples (A through E) along its length as shown in Figure A-2, which were used to monitor the temperature profile of the TL during the experiments. The thermocouple closest to the exit (E) of the transfer line was connected to a temperature controller to set the desired temperature of operation. Table A-1 details the recorded temperature profile of the transfer line during the experiments.



Figure A-2 Schematic of Thermocouple Positions (A to E)

Campaion	Fuel	Exhaust Temp	Temperature Profile (°C)					
Cumpuign	T uti	(°C)	Α	В	С	D	E	
			346	336	325	316	316	
	ULSD	380	302	267	242	221	214	
			273	211	168	137	118	
#1		380	343	336	268	319	311	
	Spiked ULSD		310	277	250	229	216	
	Sooppin S		276	218	174	143	121	
		378	344	340	332	324	313	
	Spiked ULSD		303	270	243	225	214	
	270 5		270	210	167	139	119	
	ULSD	194	237	273	303	314	314	
#2	Spiked ULSD	105	239	275	303	314	315	
	0.8% S	195	154	142	133	126	121	
	Spiked ULSD	104	240	276	305	316	314	
	2% S	194	155	142	133	127	121	

Table A-1 Temperature Profile of the Transfer Line

Note: The Thermocouple E is the set-point

A.2.2 Test Engines

Two diesel engines were chosen: one with EC rich PM (4-stroke) and the other OC rich PM (2-stroke). The 4-stroke CAT 3406 C back-up generator was operated at 50% of its maximum rated power using a load bank. The 2-stoke Detroit 12V-71TI marine propulsion engine was operated on an engine dynamometer at 25% of its maximum load to ensure a high OC to EC. Table A-2 lists engine specifications.

Table A-2 Engine Specifications							
Engine Model	CAT 3406 C	Detroit 12V-71TI					
Technology	4-stroke	2-stroke					
Rated Speed	1800 rpm	2030 rpm					
Rated Power	350 kW	515 hp					
# of Cylinder	6	12					
Engine Displacement	14.6 liter	17 liter					

Table A-2 Engine Specifications

A.2.3 Test Fuels

One of the parameters hypothesized to affect the behavior of the transfer line is the composition of the PM. The OC to EC ratio was varied by choice of engine; the PM sulfur content was varied by operating each engine on fuels with varying sulfur levels. CARB ULSD fuel was spiked with appropriate quantities of methyl-disulfide to obtain fuels with sulfur contents of up to 2% m/m. Table A-3 lists selected properties of the test fuels. The ULSD fuel was used as the base fuel for testing in all three campaigns.

Test Date	Fuel Sample	API Gravity	APISpecificGravityGravity@ 60 °F@ 60 °F		Sulfur Content
Campaigns #1 & #2	ULSD	38.0	0.8346	0.8340	(ppm) 13.2
Campaign #1 April 2010	Spiked ULSD 500 ppm S	37.4	0.8376	0.8371	509
	Spiked ULSD 2% S	36.4	0.8429	0.8324	20097
Campaign #2 June 2010	Spiked ULSD 0.8% S	37.6	0.8367	0.8362	8597.6
	Spiked ULSD 2% S	37.0	0.8397	0.8392	19702.7

Table A-3 Test Fuel Properties

A.2.4 Emission Measurements

The transfer line was tested in two campaigns (Table A-4). The sampling methods followed the ISO 8178-1 protocol⁵⁸ except for TL. Figure A-3 shows a schematic of the sampling system. Briefly a partial dilution system (primary dilution) with a venturi was used for PM sampling. This dilution system was connected to the raw gas sampling probe with and without the transfer line to determine effects of the transfer line. A secondary dilution using an ejector dilutor was used to obtain particle size distribution using scanning mobility particle sizers (SMPS). An exhaust gas analyzer measured the CO₂ and NO_x concentrations in the raw, primary and secondary dilute exhaust. Primary dilution ratio was determined from the concentrations of CO₂ and was verified to be within 10% of the NO_x dilution ratio. NO_x concentrations were used for determining the secondary dilution ratio since the CO₂ concentrations were too low. Details of the gas sampling and PM mass and size distribution sampling are provided in the subsequent sections.

Test Campaign	Test Engine	Fuel	Transfer Line (TL)	TL Temperature Set Point (°F)	# of Filter Samples
			×	n/a	5
		ULSD		600	5
		(<15 ppm S)		425	5
				250	4
			×	n/a	5
Campaign #1	CAT 3406 C	Spiked ULSD		600	5
April 2010 @50% load		(500 ppm S)		425	5
				250	5
			×	n/a	5
		Spiked ULSD (2% S)		600	5
				425	5
				250	5
		ULSD	×	n/a	2
		(<15 ppm S)		600	2
		Smiled III SD	×	n/a	2
Campaign #2	Detroit	(0.8% ppm S)		600	2
June 2010	2^{-12} 0^{-71} 1^{-10}	(0.0% ppin 3)		250	2
	C 20 /0 1000	Spiked III SD	×	n/a	2
		(2% S)		600	2
		(270 3)		250	2

Table A-4 Test Matrix



Figure A-3 Schematic of Sampling System

A.2.4.1 Gaseous Measurements

A Horiba PG-250 five gas analyzer (Table A-5) was used for sampling CO_2 , NO_x and CO in the raw exhaust and the primary and secondary dilution systems. A three point calibration was performed on the gas analyzer at the start and end of each day of testing.

Component	Detector	Ranges
Nitrogen Oxides (NOx)	Heated Chemiluminescence Detector (HCLD)	0-25, 50, 100, 250, 500, 1000, & 2500 ppmv
Carbon Monoxide (CO)	Non dispersive Infrared Absorption (NDIR)	0-200, 500, 1000, 2000, & 5000 ppmv
Carbon Dioxide (CO ₂)	Non dispersive Infrared Absorption (NDIR)	0-5, 10, & 20 vol%

A.2.4.2 Particulate Matter Measurements

 $PM_{2.5}$ mass was sampled from the primary dilution system on two parallel filters a 2µm pore 47 mm Teflo[®] filters (Pall, Ann Arbor, MI) for gravimetric and sulfate analysis and a 47mm 2500 QAT-UP Tissuquartz filters (Pall, Ann Arbor, MI) for elemental and organic carbon analysis. The dilution ratio ranged from 4 to 8.

Net weight on the Teflo[®] filters was determined using a Mettler Toledo UMX2 microbalance following the guidelines in the code of federal regulations⁸⁸. Filters were conditioned for at least 24 hours in an environmentally controlled room (RH = 40%, T = 25 C) and weighed daily until two consecutive weight measurements were within 3 µg. After completing the gravimetric analysis, these filters were extracted in 5ml of ultrapure water (conductivity = $18\mu\Omega$). Two drops of isopropyl alcohol were used to wet filter surface and aid in ion extraction. This extract was analyzed for sulfate ions using an ion chromatograph Dionex ICS 1000.

The Tissuquartz filters were preconditioned for 5 hours at 600°C and stored at temperatures <4°C before and after sampling and analysis. EC/OC analysis of these filters were performed according to the NIOSH method⁸⁹ using Sunset Laboratories Thermal/Optical Carbon Aerosol Analyzer.

A.2.4.3 Particle Size Distribution

Particle size distribution (PSD) was measured using Scanning Mobility Particle Sizers (SMPSs). A fast Scanning Mobility Particle Sizer (fSMPS) was used while testing the 4stroke engine and a cylindrical SMPS was used for the Detroit 2-stroke engine. Details of the design and operation of the fSMPS and SMPS are provided elsewhere^{95, 145}. During this test program the fSMPS was operated in the size range of 7 to 188nm with a five second scan time. The cylindrical SMPS measured particles in the size range 20 to 441nm over a one minute scan time. Both instruments were calibrated for size and number using polystyrene latex (PSL) particles. The secondary dilution system used for PSD sampling provided an overall dilution of 17 to 34.

A.3 Results and Discussions

A.3.1 4-Stroke Engine

Figure A-4 compares the measured concentrations of $PM_{2.5}$ mass and its components (EC, OC and hydrated sulfate) for the 4-stroke engine tested with and without the transfer line for each fuel. A reduction in the total measured $PM_{2.5}$ mass of 18% for TL at 600 °F, 23% for TL at 425°F and 25% for TL at 250°F were observed for ULSD when compared to the measurement without the TL. However, no statistically significant change was seen in EC and OC measurements for ULSD.

Total measured $PM_{2.5}$ mass did not change with the use of TL for 500ppm S diesel fuel. A look at the speciated data shows no change in EC and a 29% to 44% reduction in OC at lower TL temperatures (425°F and 250°F). A 39% reduction was observed in measured total $PM_{2.5}$ mass with the use of TL at 250°F for the 2% S diesel. Speciated $PM_{2.5}$ mass results show a 33% to 43% increase in EC at higher TL temperatures (600°F and 425°F), a 47% to 56% reduction in OC with TL and an 8% to 12% increase in hydrated sulfate for all but the 250°F TL temperature, where a 44% decrease was observed.

Figure A-5 shows the mass balance for the 4-stroke engine. A good correlation between the sum of the individual components and total $PM_{2.5}$ was observed for all fuels.

Figure A-6 shows the particle size distributions measured on the 4-stroke engine for all test conditions. No significant change was observed in the PSD with the use of TL for ULSD and the 500ppm S diesel. However, the use of a TL resulted in formation of nucleation mode particles in the 40nm range for 2% S diesel fuel when operated at higher temperatures (600 °F and 450°F). This could be a result of increased formation of hydrated sulfate particles as seen in the speciation data. At 250°F TL temperature we see a smaller nucleation mode at ~20nm along with decreased number concentration in the accumulation mode. This finding when coupled with the observed reductions seen in OC and sulfate suggests significant thermophoretic losses of these species in the TL for all fuels.



Figure A-4 PM Emissions from 4-Stroke Engine


Figure A-5 Mass Balance for 4-Stroke Engine



Figure A-6 Particle Size Distribution for 4-Stroke Engine

A.3.2 2-Stroke Engine

Figure A-7 shows the total and speciated PM measurements with and without the TL for a 2-stroke diesel engine operating at 25% of its maximum load. A 42% to 66% reduction in $PM_{2.5}$ mass measurements were observed with the TL when compared to measurements made without the TL for all three fuels (ULSD, 0.8% S diesel, 2% S diesel). These reductions can be attributed to 34% to 68% reduction in OC (for all fuels) and 34% to 41% reduction in EC (for ULSD and 0.8% S diesel). Results of hydrated sulfate fraction are not available for this engine. The difference in total measured PM mass and the sum of EC and OC fractions provides an estimate of the hydrated sulfate concentrations (Figure A-8). This data indicates a 60 to 75% reduction in sulfate fraction with the use of TL for 0.8% S and 2% S fuels.

Figure A-9 shows the particle size distribution seen with and without the TL for the 2stroke engine. Significant reductions in both size and number concentration of particles were observed for the use of the TL at 600°F (315°C). This TL line temperature was chosen to maintain consistency between the tests for the 4-stroke and 2-stroke engines. However, it is 61% greater than the 2-stroke engine's exhaust temperature of ~195°C (Table A-1). As a result, it is expected that some of the OC particles evaporated and moved into the gas phase resulting in the large reductions in total PM_{2.5} mass. No change was observed in the particle diameter for the TL temperature of 250°F; though a significant reduction in number was observed for all three fuels. This indicates



Figure A-7 PM Emissions from 2-Stroke Engine



Figure A-8 Mass Balance for Detroit 2-Stroke Engine



Figure A-9 Particle Size Distribution for 2-Stroke Engine

thermophoretic loss of PM mass in the TL similar to that seen in the 4-stroke engine. The 2% S diesel showed formation of nucleation mode particles for the 250°F TL temperature.

A.4 Conclusions

The results from this study show that $PM_{2.5}$ mass measurements are extremely sensitive to the TL temperature (relative to the exhaust temperature) and the composition of PM (OC rich or sulfate rich). PM losses of up to 55% for 2% S fuel and up to 66% for fuels with <0.8%S were observed with the use of TL. This indicates a need to eliminate the use of transfer line and adopt direct coupling of the dilution tunnel to the sampling probe for measuring PM emissions from marine engines. However, sufficient space may not be available near the sampling port for direct coupling of the dilution tunnel to the sampling port. In such cases the only option may be the use of a heated transfer line. Therefore it is recommended that a theoretical model to predict transfer line losses be developed using in part the data collected from this study.

A.5 Acknowledgements

Co-authors Poornima Dixit, M. Yusuf Khan, William A Welch, Heejung Jung, J Wayne Miller, David R Cocker. California Air Resources Board for their financial support. Charles Bufalino, Kent Johnson, Joe Valdez, Don Pacocha, Shunsuke Nakao, Xioachen Tang, Ping Tang, Kurt Bumiler, Hansheng Pang for their help with the test preparation and setup. Kathy Cocker, James Guiterrez, Charles Wardle, David Torres for preparation and analysis of sample media.