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Investigations of Emissions on the Deep Sea and in Port for Dated and Modern Ocean-Going Vessels

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

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in

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by

Thomas W. Eckel

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ABSTRACT OF THE DISSERTATION

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Currently, the shipping industry accounts for 5% of global fuel consumption. With the growing demand for electrification in land-based transportation and infrastructure, contributions to emissions inventories from large ocean-going vessels (OGVs) will continue to become more significant as they account for an even larger portion of global fuel consumption. The body of this work is an investigation of the real-world effects of modern emissions standards, and fuel regulations, on large ocean-going vessels (OGVs) used in the commercial maritime industry. This dissertation is comprised of sample system design and implementation, various studies on the effects of CARB regulated marine fuel, the difference between the regulated emission standards and the real-world emissions of Tier III OGVs, and the effect of vessel speed reduction (VSR) on Tier III emissions.

Emissions sampling systems were designed and deployed to two field campaigns included in this body of work. The first campaign consisted of in-use emissions measurements of a steam turbine driven container ship predating OGV emissions regulations. OGVs typically have an operational lifetime of 20 to 30 years. Therefore, a continued understanding of changes in emissions profiles for older vessels using new fuels is a critical part of future emissions modeling efforts. The second campaign evaluated the emissions profiles of two new build Tier III vessels, the newest EPA technology class for marine emissions standards. The primary emissions were measured and modal data was analyzed to determine the air quality effects of Tier III emissions control technology on deep sea and in port OGV emissions.

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1. INTRODUCTION

The following manuscript is a description of the relevant projects and investigations that comprise the Ph. D. dissertation of Thomas Ward Alexander Eckel. This work is motivated by the way that air quality and emissions control regulations have directly affected my health and welfare. I grew up in a small suburb called Palos Verdes, which is adjacent to the Port of Long Beach and the Port of Los Angeles. I can still clearly remember the smog layer around Los Angeles in the 90's, the unique sunsets, and the non-stop traffic around the ports and harbors in the South Bay. As a child, I was diagnosed with childhood onset asthma, which stayed with me until 2003. Only later on did I learn that the disappearance of my asthma coincided with the regulations that restricted emissions for heavy duty vehicles for land based commercial shipping in and out of ports. As a direct result, my goals as a scientist and a researcher have always been to benefit society, human health, and our quality of life. Thus, I chose to pursue air quality as a field of research after completing my undergraduate degree.

While in the process of completing this body of work, my research has deviated several times from the original path my advisor and I had envisioned, and the chapters in this document are a reflection of that. At the beginning of my time as a graduate student in 2019, my intended research plan was to use the indoor environmental chamber at CE-CERT APL to investigate viscosity and thermodynamic effects on secondary organic aerosol (SOA). In my first year, I began redesigning and building the next generation, large

volume, EPA environmental chambers housed at the APL. Simultaneously, I was invited to take part in 3 other projects. I evaluated the efficiency of a NO_x reduction coating for the consumer market, I investigated the secondary emissions from light duty vehicles using ethanol blended fuels, and I was put on a field team measuring primary emissions from a SuezMax class volatile liquid carrier (VLC). The fuel campaign gave me a much clearer idea of the contributors to ambient air pollution, and a better understanding of the aspects that drive SOA models and chamber research. My original intention was to conduct studies on particle viscosity and particle thermodynamics, then transition that research to a series of experiments based on precursors from combustion emissions.

The fuel study and chamber build were completed in the summer of 2020, at which point I was on track to begin working on experiments in the newly constructed environmental chamber. At the end of that summer, a series of field campaigns to investigate emissions from large commercial merchant vessels began, and was in need of a dedicated researcher. Recognizing what a rare opportunity this was, I radically shifted my research trajectory.

Immediately following this news, I began designing and constructing a sample system to measure emissions from ocean-going vessels (OGVs) that is in compliance with the EPA, International Standards Office, and Code of Federal Regulations guidelines on non-road, marine mobile source emissions testing. My time designing reactors and experimental apparati gave me the requisite experience to complete this build while meeting all the design goals for marine emissions sampling. The rest of the marine sampling campaigns started with a steam turbine driven vessel that predates modern emissions control

regulations, and serendipitously ended with diesel engine driven vessel that falls under the newest, and most strict, emissions technology class for OGVs.

The following three chapters are what I feel are the most impactful investigations I have taken part in since beginning my time in graduate school. They cover chamber design (Chapter 2) and the two of the most impactful vessel sampling campaigns (Chapters 3 and 4).

2. NOVEL DESIGN FOR ATMOSPHERIC INDOOR REACTION CHAMBER WITH REDUCED WALL LOSSES

ABSTRACT

Environmental simulation photoreactors, more commonly known as environmental chambers, have been the preeminent method of determining the effects of photochemistry and atmospheric processes on criteria pollutants, greenhouse gases, volatile organic compounds, and aerosols for over 50 years. The following work is the evolution of the reactor system originally described in Carter et al. (2005). Motivated by goals to reduce particle wall-loss, lower experimental background, and improve experimental precision, a drastic approach to redesigning the environmental chambers at UCR was taken. By completely redesigning the chamber geometry, the enclosure infrastructure, adding a soft x-ray, and electronically insulating the reactor, dramatic improvements in experiment lifetime, particle decay rate, and data volume correction were achieved. The particle decay has been minimized to ~0.3/day (greater than tenfold improvement), the volume correction is as low as ~6% for a twelve-hour experiment, the 12-hour particle background is more than tenfold lower, and experimental lifetime has reached in excess of 50 hours.

2.1 BACKGROUND

2.1.1 Indoor Environmental Reactors and the UCR CE-CERT System

Environmental simulation photoreactors, more commonly known as environmental chambers, are the preeminent method of determining the effects of photochemistry and atmospheric processes on criteria pollutants, greenhouse gases, volatile organic compounds, and aerosols for over 50 years (Jeffries et al., 1982, Jeffries et al., 1985a, Jeffries et al., 1985b, Jeffries et al., 1985c, Jeffries et al., 1990; Gery et al., 1988; Hess et al., 1992; Simonaitis and Bailey, 1995; Simonaitis et al., 1997; Carter et al., 1995a; Carter, 2000; Dodge, 2000 and references therein; Odum et al., 1996, Odum et al., 1997; Griffin et al., 1999a, Griffin et al., 1999b; Kleindienst et al., 1999; Barnes and Sidebottom, 2000; Cocker et al., 2001a, Cocker et al., 2001b, Cocker et al., 2001c; Jang and Kamens, 2001; Seinfeld and Pankow, 2003 and references therein, Johnson et al., 2004; Montserrat and Wirtz, 2005). Experimental observations are then used to develop chemical mechanisms and inform regional atmospheric air quality models. A comprehensive overview of the purpose and impacts of chamber experiments can be found in Carter et al. 2005.

The work described in this paper is a continuation of the reactor system originally described in "A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation," by Carter et al. (2005). Since the original configuration, there have been many evolutions for indoor chambers, and this reactor specifically. Typically, advances in chamber design and technology are motivated by needs arising in different studies in the aerosol field, as with the design approach described in

this body of work. From 2018 to 2023, chamber groups at UCR and Cal-Tech conducted a collaborative study on the properties used in modeling analysis and SOA formation of select volatile chemical products (VCP) documented in a report prepared for the ARB (2023). Due to the use of different reactors at different locations, it was important to standardize testing protocols between the research groups to ensure the quality of data. This was verified by running a series of control experiments in both chambers and comparing results and data treatment methodology. In the process of standardizing research protocols, some inconsistencies in results between the two reactor systems appeared. After the user and methodology discrepancies were addressed, certain differences in the raw data appeared, indicating enhanced particle losses in the UCR chamber. These types of losses are common in environmental chambers of this type, and are accounted for in a data correction figure known as the decay rate (days-1) (Carter et al. 2005). The decay rate of particles in the previous generation of chambers was reported at ~7 d^{-1} (Carter et al. 2005). An in-depth description of the particle losses in chambers can be found in Cocker et al. (2001a). While the results of the collaborating chamber groups agreed after data treatment, this decay rate was found to be up to 2 times higher than the decay rate in the Cal-Tech chamber.

After evaluating potential causes, the determination was made to design and construct a new generation of environmental chamber addressing the decay rate, and other known shortcomings of the previous system.

2.1.2 Previous Generation of UCR Environmental Reactor

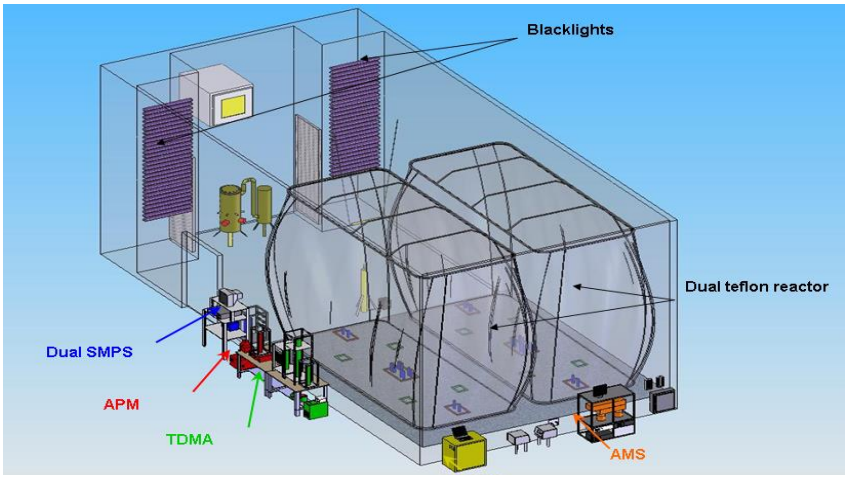

Figure 1. Schematic of Previous Generation Environmental Chambers and Enclosure (Peng et al. 2018)

Figure 1 is a schematic of the previous environmental reactor system and the reactor enclosure at UCR CE-CERT. An in-depth description of the enclosure, reactors, and infrastructure can be found in Carter et al. (2005), who described the system as two collapsible 90 m^3 FEP Teflon film reactors on pressure-controlled moveable frameworks inside a temperature-controlled enclosure flushed with purified air.

2.1.3 Inherent Design Flaws

The design flaws in the previous system can be broken down into three categories: enhanced electrostatic effects, higher than desired particle background, and limited reactor integrity. The primary contributor to particle decay rate is electrostatic effects on the FEP chamber surface (Cocker et al. 2001a). The variable volume system used to force positive pressure, and the floating floor to conceal the exhaust and mixing systems, were a great source of electric charge to the reactor surface. As shown in Figure 1, the bottoms of both

reactors are sealed directly to the floating floor via aluminum injection and sampling plates. This grounds the chamber walls and provides an "infinite" source of electrons. Furthermore, the dual reactor system is in constant contact with the walls of the enclosure and the adjacent reactor. These electrostatic particle losses can lead to data corrections for final SOA yield of up to 600% for particle volume concentration.

The variable reactor high and constant forcing of positive pressure in the reactors also negatively impacted the integrity of the reactor walls and seams. The reactor material is 0.002-inch-thick Teflon FEP, which is not a robust material. In the process of making these reactor bags, long strips of Teflon FEP are press sealed together with a pneumatic heat sealer. While this creates a perfect air tight seal, it also removes some of the elasticity from the material, and creates predictable strain and failure points in the reactors. These failure points require frequent maintenance, and the integrity failures get progressively worse over the lifespan of the bag. While the reactor chambers themselves are not permanent features of the build, previous generations would need to be rebuilt in sometimes as little as six months when the experimental variability and the reactor integrity would get progressively worse.

The experimental SOA background, defined as the SOA production inherent to the reactor itself without injected hydrocarbons, was also higher than originally expected. This may have been due to system integrity issues or the use of non-FEP material in parts of the chamber mixing systems. Regardless, the new system was designed to limit introduction of SOA formation precursors.

2.2 Design Approach

2.2.1 Design Objectives

There were three specific design goals with this generation of environmental chamber: 1) minimizing electrostatic effects, 2) increase experiment lifetime, and 3) retain reactor purge efficiency. The most efficient way to achieve these goals was to alter the reactor geometry and completely overhaul the enclosure infrastructure. The next generation chamber swaps the dual reactor system to a single, fixed partial frame, large volume reactor. To support this change, the enclosure floating floor needed to be removed and the larger components of the chamber infrastructure needed to get shifted out of the enclosure. By doing this, most of the charge sources can be removed. Soft x-ray devices were permanently deployed in the enclosure to minimize the remaining surface charging effects. Their usage has since been implemented in the experimental SOP.

The other design constraints are the given aspects of the system infrastructure, locations of fill air and exhaust ducts, the FEP reactor material itself, and the enclosure footprint.

2.3 Chamber Design and Construction

2.3.1 New Chamber Design

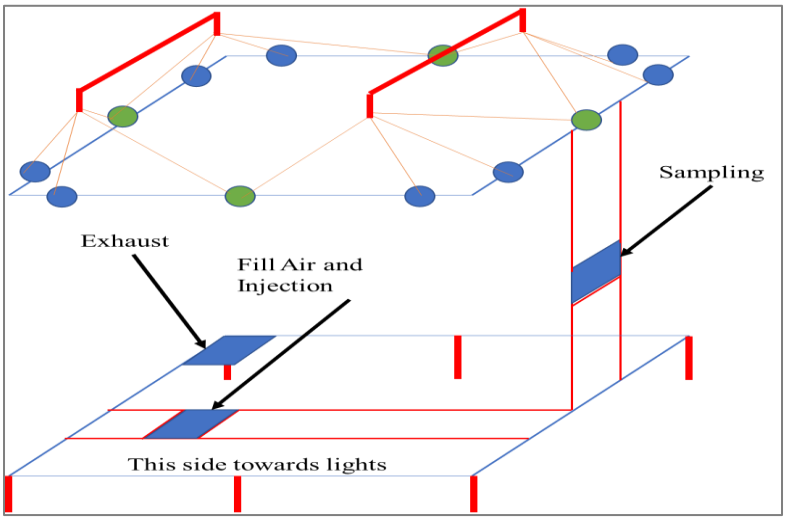

Figure 2. New Generation Chamber Frame

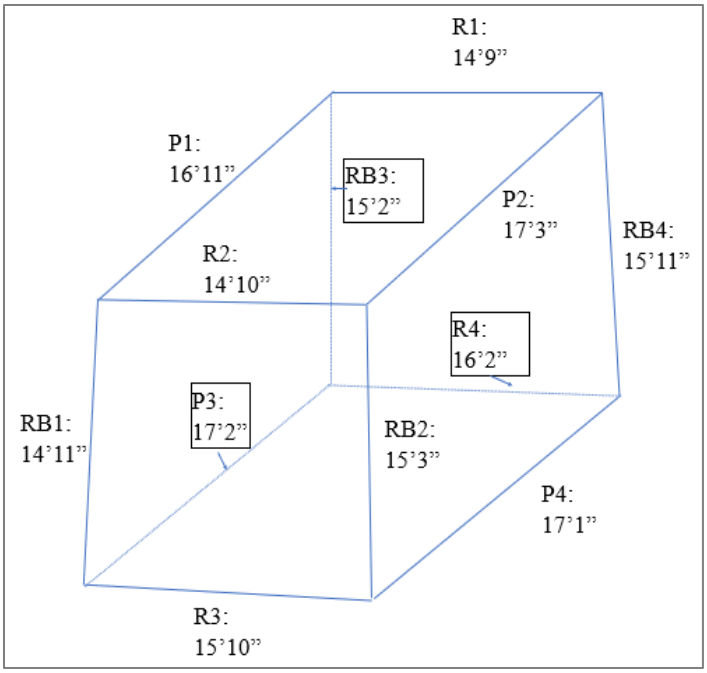

Figure 3. Final Teflon Bag Dimensions

Figure 2 above is a general diagram for the partial frame. The actual frame pieces were constructed from 8020TM utility rail. The top frame is suspended from the ceiling using the elevator system from the previous reactors. The bottom frame is electrically insulated from the metal enclosure floor with ½" thick Teflon pucks. The

utility rail for the frame was cut to size based on the actual FEP reactor bag measurements in Figure 3 on the left.

Original dimensions were chosen to give the new reactor 2 feet of standoff between the enclosure walls and reactor surface in any direction. Variation in actual reactor dimension is caused by material non-uniformity after press sealing.

2.3.2 New Enclosure Design

Figures 4 and 5 below are the reactor footprints inside the enclosure before and after the redesign. Not shown is the exhaust system, which used to reside under the false floor shown in Figure 4. That exhaust system was moved out of the enclosure completely, and ducting was extended from the reactor exhaust to the new exhaust blower system.

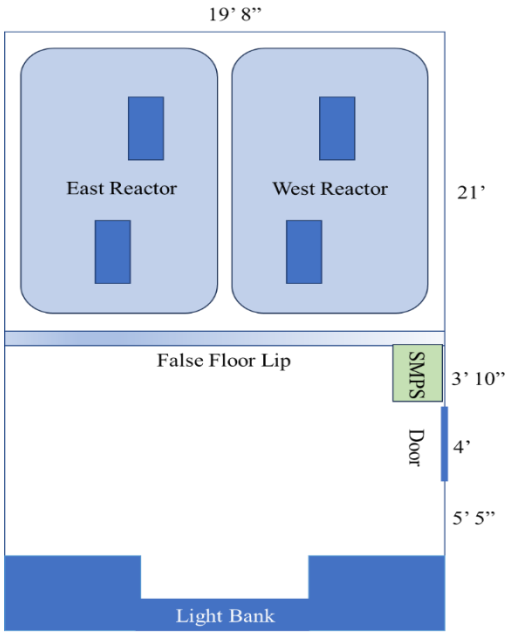

Figure 4. Previous Enclosure Floor Plan

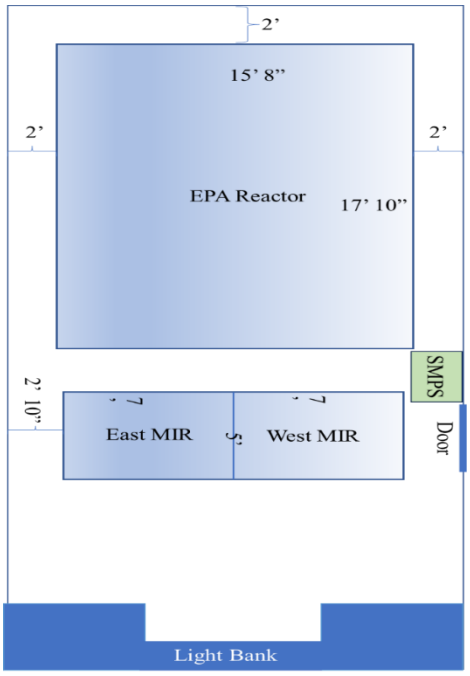

Figure 5. New Enclosure Floor Plan

The decision to add two more smaller reactors to continue performing maximum incremental reactivity (MIR), and other comparative studies, was made after removing the old infrastructure and false floor. It was not implemented until after this work was complete.

2.3.3 Soft X-Ray

Three Hamamatsu soft X-ray PhotoIonizers that were tested to fully cover the whole 118 m^3 Teflon bag and discharge the bag from over ±10000V to within ±10V in 2 minutes. The PhotoIonizers are located on the enclosure walls, above the reactor, on either side of the enclosure. These effects are evaluated in detail in ARB (2023).

2.3.4 Reactor Exhaust

In order to compensate for the single reactor and the fixed volume, a completely automated exhaust system was designed and installed. A 2-blower setup capable of moving 3000 cubic feet per hour was attached to the reactor with a low pressure, 1-way check valve to prevent downstream contamination during experiments. The blowers are controlled by an OmegaDyne™ PID with an OmegaDyne™ pressure transducer as a data source. This allows the reactor to be cleaned automatically during off hours.

2.4 Results

2.4.1 Chamber specification comparison

The complete summary of the physical specifications of the new chamber and old chambers are tabulated (Table 1) on the next page. Some important features from the overview are the changes in surface area to volume ratio, surface charge, and SOA background.

Table 1. UCR Environmental Chamber Specs

Terms	UCR collapsible chamber	UCR new fixed-volume chamber
Size	~90m^3 × 2	~118m^3
Dimensions	Collapsible ~ 6m(H) × ~3m(W) × ~5m(D)	~ 4.6m(H) × ~4.9m(W) × ~5.3m(D)
Surface area to volume ratio	Start at 1.43 m^{-1}, gradually increase to 2.68 m^{-1}	~1.22 m^{-1}
Material	FEP Teflon	FEP Teflon
Temperature	~5- 40°C ±1°C	~5- 40°C ±1°C
Relative humidity	0-100%	0-100%
Clean air source	Compressed air purified by canisters of Purafil, heated Carulite 300, and particle filter pack	Compressed air purified by canisters of Purafil, heated Carulite 300, and particle filter pack
Shortest distance from chamber to light	~16 ft	~14.3 ft
[1]Enclosure purge air	Up to 1,600 SCFH	Up to 1,000 SCFH
Pressure differential (inside minus outside)	>0.01 inH_2O	0.008-0.012 inH_2O during cleaning; dilution correction according to tracer level
Black lights	Sylvania BL350 115 W	Sylvania BL350 115 W
Light intensity	$k_{NO2\rightarrow NO}$=0.402 min^{-1}	$k_{NO2\rightarrow NO}$=0.402 min^{-1}
UV peak wavelength	350nm(main), 435nm, 545nm, 577nm	350nm(main), 435nm, 545nm, 577nm
Chamber surface charge	Charged due to Teflon film rubbing with reflective aluminum sheeting material and other reactor; average surface voltage is unknown	"Neutral"; Teflon reactor is isolated from the aluminum wall/ground with Teflon mat underneath each frame feet; Soft X-ray PhotoIonizers to discharge bag to "neutral"; surface voltage around ±10V; minimal mechanical agitation throughout experiments
SOA background	<0.1 $\mu m^3/cm^3$ formed for 8hr (at 1ppm H_2O_2)	<0.01 $\mu m^3/cm^3$ formed for 8hr (at 2ppm H_2O_2)

2.4.2 Decay Rate Comparison

In order to quantify the results of the chamber re-design, two experiments with *m*-xylene and H_2O_2, which are common starting compounds for chamber SOA experiments, were replicated in the new chamber with the x-ray engaged throughout the experiment. The conditions and decay rates for all 4 are located in Tables 2 and 3 and Figures 6-9. The tabulated results also have the starting compounds and their concentrations listed.

Table 2. Results of First Decay Rate Comparison

	m-xylene Concentration	H_2O_2 Concentration	Vol Corr % At 470 Minutes	Decay Rate ($days^{-1}$)
Old Run EPA 1860	120 ppb	1 ppm	407%	7.30
New Run EPA 2619	144 ppb	1 ppm	35%	1.66

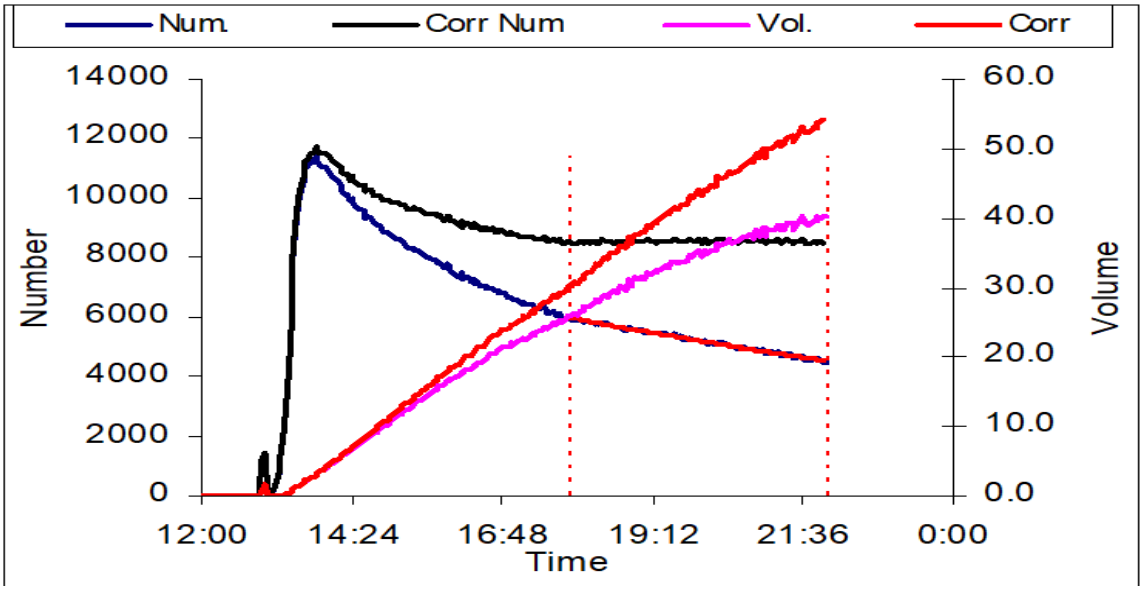

Figure 6. EPA 2619: New Chamber; M-Xylene 144 ppb + 1ppm H_2O_2; with X-Ray

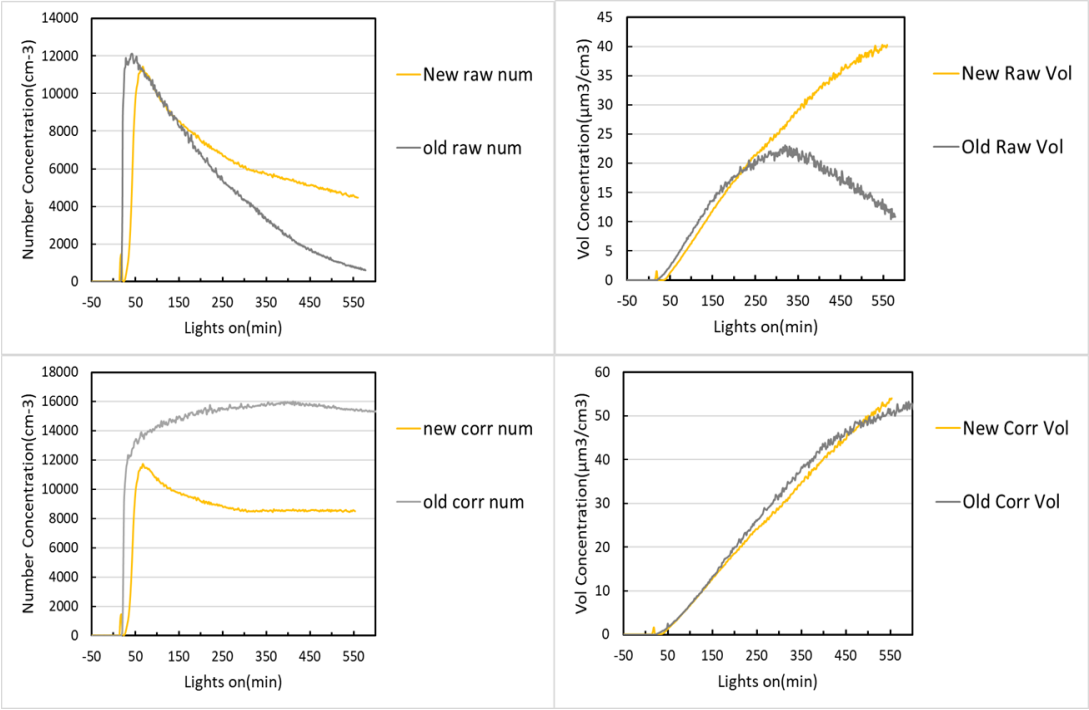

Figure 7. Chamber Comparison 1 EPA 2619 (New) and EPA 1860 (Old)

Table 3. Results of Second Decay Rate Comparison

	m-xylene Concentration	H_2O_2 Concentration	Vol Corr % At 470 Minutes	Decay Rate ($days^{-1}$)
Old Run EPA 2534	34 ppb	1 ppm	110%	5.30
New Run EPA 2620	47 ppb	1 ppm	25%	1.81

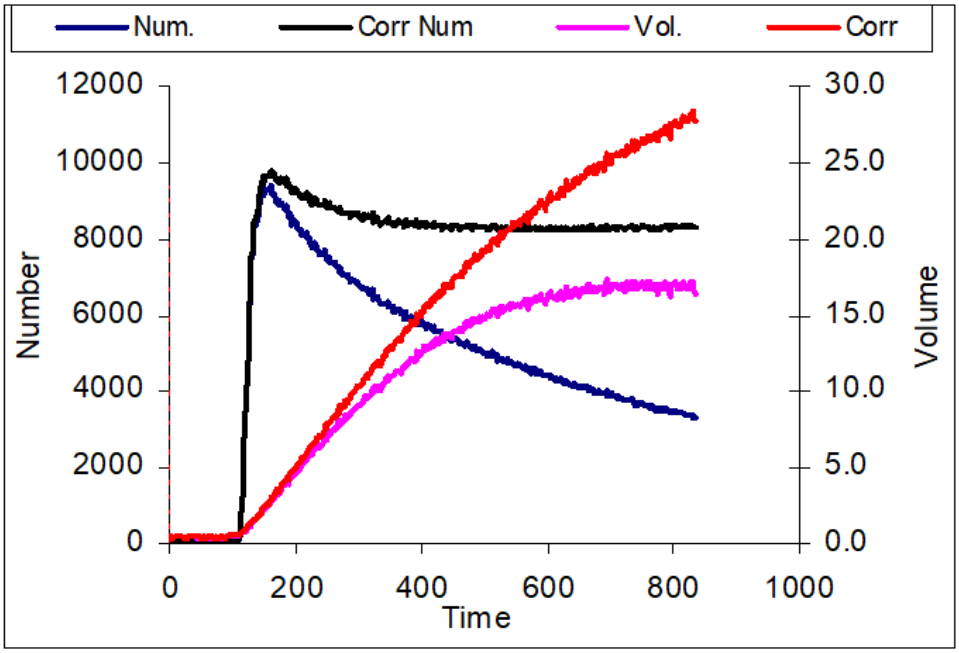

Figure 8. EPA 2620: New Chamber; M-Xylene 47 ppb + 1ppm H_2O_2; with X-Ray

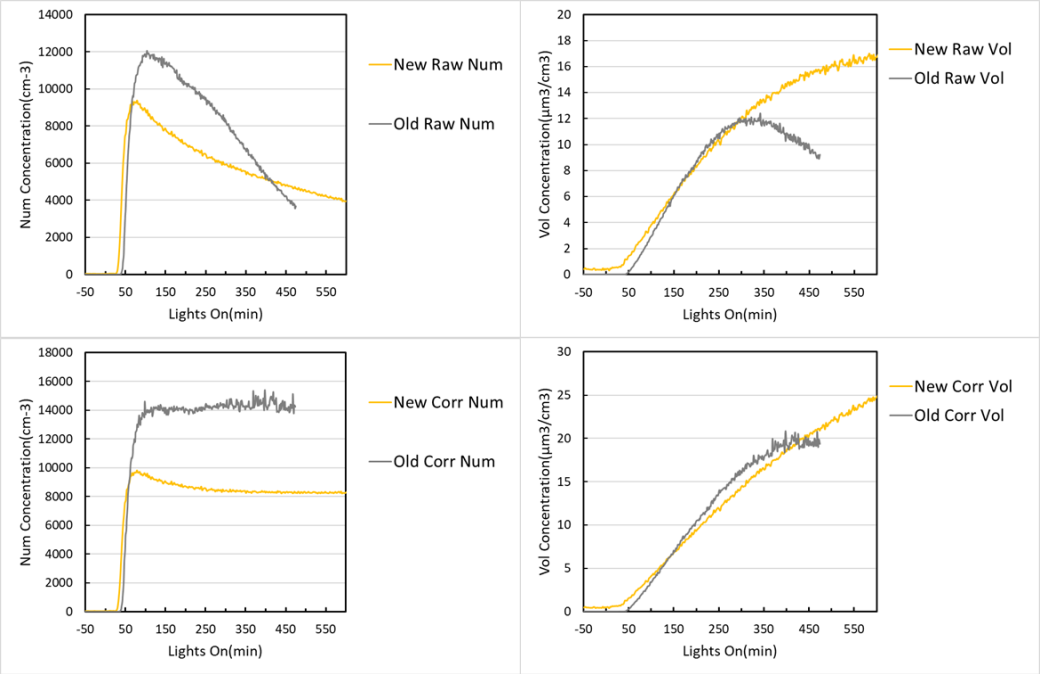

Figure 9. Comparison Between EPA 2620 and EPA 2534

The key takeaways from the two comparative runs are the differences in decay rate and volume concentration percentage correction. The decay rate in the new system is nearly three times less, and the correction for the SOA yield is less by a factor of ten. Due to the automated nature of the new exhaust system, the new reactor reaches the same benchmark for "clean" background in roughly 12 hours.

Since this work was done, Le et al. (2023) have done a thorough analysis on the effects of coagulation, and have found the true particle decay rate to be even lower. The results of the analysis on coagulation effects, shown in Figure 10 below, that "the particle decay rate decreased from ~6 day^{-1} (old collapsible chamber, without coagulation correction, ~3 day^{-1} with coagulation correction) to ~0.3 day^{-1} (new fixed-volume chamber with coagulation correction and dilution correction)" (ARB 2023).

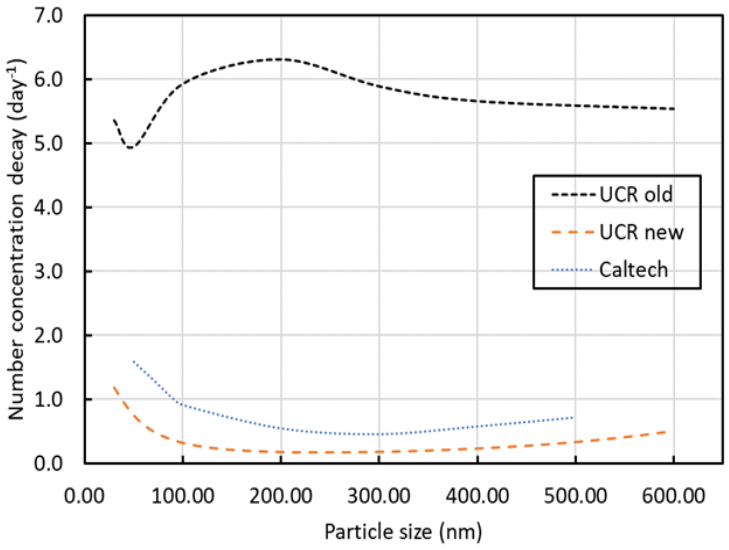

Figure 10. Particle number concentration decay rate of UCR old collapsible chamber, UCR new fixed-volume chamber and Caltech chamber. Note the data are coagulation corrected except for UCR old chamber data. (Le et al., 2023).

2.5 Future Work

The first task with the new chamber is to characterize the wall losses in the new insulated system, and determine if a new data treatment model needs to get constructed. The next steps to maximize the benefits from the new generation of environmental chamber at UCR CE-CERT are to investigate effects previously impossible to observe. In order to fully understand the total mass losses in the SOA yield data, vapor wall loss would be a logical next step. Given the minimized particle wall losses, coagulation can also be verified experimentally and corrected in the code used to treat data. The final immediate benefit of this type of chamber is the extended duration of experiments due to the increased volume. The next experiments that could capitalize on this feature are longer runs to investigate reversible vs. irreversible thermodynamics on particle growth.

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3. EVALUATING EMISSIONS FROM A DUAL BOILER, STEAM TURBINE DRIVEN OCEAN-GOING VESSEL WHILE AT SEA

ABSTRACT

Ocean-going vessels, while necessary to connect resources with manufacturing and distribution around the world, are the one of the primary contributors to poor air quality in regions near ports and harbors. Furthermore, as land-based transport continues moving towards electrification, emissions from ocean-going vessels stand to comprise an ever-increasing portion of mobile source inventories in the not-so-distant future. Thus, it is increasingly more important to develop data from a wide variety of marine propulsion systems, including engines that predate emission standards. OGVs have an operational lifespan of 20 to 30 years. The first emissions standards that apply directly to OGV engines published by the International Maritime Organization (IMO) took effect in the year 2000[1]. Therefore, any vessel produced before 2000 will not have prioritized engine emissions in the engineering plan, yet those vessels are at least 5 years from being out of operation. In extreme cases, vessels can exceed their operational lifetime by 10 years or more.

This study measured the emissions of a container ship built in 1979, that is an active part of a commercial fleet. The vessel is powered by two type “D” foster wheeler boilers

and a steam turbine, and the test fuel was ultra-low sulfur marine distillate (ULSFO) approved by the California Air Resources Board[2]. The following emission factors were measured at full sea travel speed: 6.52 g/kW-hr NO_x, 1540 g/kW-hr CO_2, and 0.0178 g/kW-hr of PM. The NO_x emission factors are low enough to be in compliance with the Tier II NO_x standards for modern compression ignition (CI) engines, the CO_2 is reasonable based on the fuel consumption, and the PM levels are low relative to other modern build OGVs with compression ignition (CI) engines.

3.1 Background

While necessary to connect goods to different parts of the world, ocean-going vessels (OGVs) are the one of the primary contributors to poor air quality in ports and surrounding regions. At present, the commercial maritime industry also accounts for 4% of the global fuel consumption[3]. With the continued electrification of land-based transport, emissions from ocean-going vessels stand to comprise an ever-increasing portion of pollutants from fossil fuel combustion in the atmosphere. Thus, minimizing and understanding the emissions from OGVs remains a priority for air quality regulatory and compliance agencies around the world.

Typically, emissions reduction is achieved through the following means: regulating engines directly based on build year[1], limiting vessel speeds in select zones[4,5,6,7,8], and restricting sulfur concentration in marine fuels used in Emissions Control Areas (ECAs)[9,10]. Even though new engine standards are published in tandem with the availability of new control technology, those emission standards only apply to vessels built after the year of publication[11]. Due to the high cost of OGVs, up to hundreds of millions of dollars for a single vessel commission, vessels are kept in operation for 20 to 30 years. That being said, it is important for emission inventory models to have accurate data on older engines using modern fuels.

While boiler fed steam turbines used to be a common method of marine propulsion, compression ignition (CI) engines dominated the commercial maritime industry by the time the first emissions standards for OGV engine emissions were published in the year 2004.

Since then, there are so few boilers in use for propulsion, that no emissions standards exist for marine boilers. Furthermore, due to the availability of sampling opportunities, only two published sets of "in-use" marine boiler data are published[12,13]. Furthermore, they are both used as auxiliary gensets, so the available data is limited to single operational load points.

3.2 Research Goals

In order to address the lack of information mentioned in the previous section, this work covers the measurement and analysis of main boiler emissions from a large, steam turbine driven, merchant container ship while using California regulated ULSFO. The specific research goals are as follows: 1) measure particulate matter (PM) and gaseous emissions from main boiler at 5 different engine load points, 2) collect fuel sample for independent analysis, 3) conduct load specific analysis of emissions factors and fuel consumption.

3.3 Research Plan

3.3.1 Ship Specifications

The test vessel is a container ship built in 1979, sailing under the flag of the United States of America, with a carrying capacity of 2,325 twenty-foot equivalent units (TEUs). Her current draught is reported to be 9 meters, length overall (LOA) is 247.9 meters, and her width is 27.43 meters. Her gross tonnage is 28219 and her summer deadweight tonnage is 31439.

3.3.2 Boiler Specifications

The boiler used on the ship was made by Foster Wheeler. There are two (2) "D" type steam generators located in the machinery space of this vessel to provide steam required for propulsion and auxiliary services. One generator is on the left-hand (starboard side) and the other, right-hand (port side). A left-hand boiler is the boiler with the furnace on the left side of the steam drum when facing the burner front.

According to the Foster Wheeler brochure, each steam generator consists of the boiler section (steam drum, water drum, headers, tubes, casings, refractories), superheater and accessories (oil burners, rotary regenerative air heater, soot blowers, safety valves, water level indicators, smoke indicators and miscellaneous valves). The boiler includes the upper (steam) drum, the lower (water) drum and an inclined bank of tubes consisting of two (2) rows of screen tubes, one (1) row of superheater support tubes and the main bank of tubes. The screen tubes protect the superheater from the radiant heat of the furnace. Specifications for a boiler is shown in Appendix 1: Boiler Specifications.

3.3.3 Fuel Specifications

While operating within 24 nautical miles of the California Coastline, all Ocean-Going Vessels (OGV) must follow the CARB marine fuel regulations[9], first proposed on July 24, 2008 and later amended it in 2011. This regulation requires the use of distillate grade marine fuels, marine gas oil (DMA/DMX) or marine diesel oil (DMB), with a maximum sulfur level of 0.1% while operating main engines, diesel-electric engines, auxiliary engines, and boilers and provides significant health and air quality benefits.

3.3.4 Proposed Test Plan

As allowed by the vessel's operating schedule, exhaust emissions measurements were to be taken in triplicate at five firing rates from a steam boiler on a container ship between the Port of Oakland, CA (OAK) and the Port of Long Beach, CA (POLB). Emission data collected during this voyage is intended to advance the state of understanding of emissions for steam turbine ships operating on ULSFO distillate fuel at various load points.

3.4 Methods

3.4.1 Sampling Exhaust

3.4.1.1 Dekati Dilution System

The heart of the sampling system was incorporation of a Dekati® eDiluter™ Pro, a newly introduced commercial product that allows easy sample conditioning for a wide range of particle measurement applications. The operating principle is based on two-stage dilution. The first stage is heated while the second dilution stage operates at room temperature where the aerosol sample is also cooled in a controlled manner. Both dilution stages consist of an ejector diluter with additional sheath air flow. The use of a large ejector nozzle and sheath air reduces the need for cleaning, and also minimizes particle losses within the system. Built-in sensors constantly monitor the dilution process parameters and an integrated control unit actively compensates for any fluctuations in the sample inlet pressure ensuring that the selected dilution factor is kept constant under all conditions. Although the structure was compact, the design allowed dilution ratio to be adjusted from 1:25 to 1:225.

In the field, the QA/QC procedure was to measure raw NO_x (ppm) from an access port in the transfer line between the diluter and the stack and compare concentration to NO_x (ppm) measured after first stage dilution. If the dilution value was more than 10% above the set point, then corrective action was to shut down the diluter and the injectors associated with the first and second stages.

3.4.1.2 Dilution Air System

High-purity dilution air is critical for the Dekati system to dilute the extracted exhaust gas without changing the properties. Although instrument-grade air is available on the ships, we added a purification unit with four clean-up steps in series to ensure the dilution air met our specifications. These units were: 1) a 10µ oil, water, and particulate matter (PM) filter, a 1µm coalescing hydrocarbon and PM filter; 2) a desiccant column with silica gel; 3) a column filled with Purafil™ and charcoal in 2 even layers and 4) a HEPA-filter to remove particulates >1µm. We followed the manufacturer quality assurance program for each element.

3.4.1.3 Sample Splitter

In the third element of the design, samples from the Dekati unit were split into multiple branches and distributed for simultaneous independent gaseous and particulate analysis. Sample flow rate from each line leaving the splitter was measured using critical flow orifices (CFOs) with continuous monitoring of the temperature and pressure drop across the CFO. QA/QC for flow elements on branches was done by comparing monitored values with known nominal flow data at critical pressure. Design was in accordance with 40 CFR 1065[14-19], as well as ISO sampling standards[20] for gaseous and particulate species.

A schematic of the overall control sampling system is shown in Figure 11. A full list of the species the sample system is capable of measuring is located in Appendix 2.

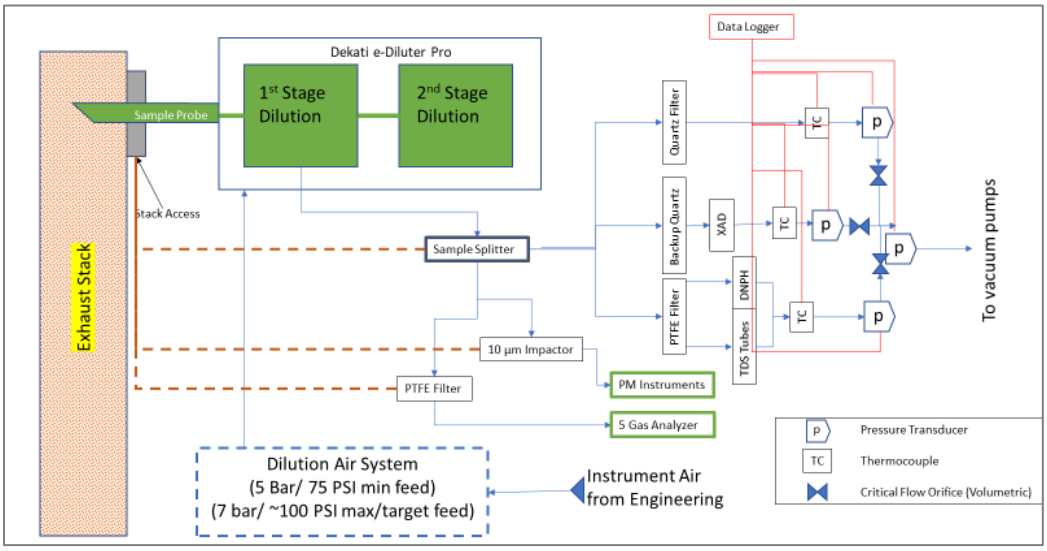

Figure 11. Schematic of Sample Collection Train

3.4.2 Measuring the Concentrations of Gases

The concentrations of nitric oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), sulfur oxides (SO_2) and oxygen in the raw exhaust and the diluted samples were measured continuously with a Horiba PG-350 portable five-gas analyzer. The details of the gases and the ranges for the Horiba instrument are given in the supplement. For quality control, analyzer checks with calibration gases both before and after each test were made to check for drift. Certified Grade N_2 gas was used for the Zero-point and an EPA certified four-gas mixture consisting of NO_x, CO, CO_2, and SO_2 was used for the span. The SO_2 gas concentrations in this report were calculated from the sulfur level in the fuel as advised by ISO-8178-1[20].

3.4.3 Measuring the Concentrations of Particles

3.4.3.1 Measurements of Particulate Matter (PM) Mass and Ions

The mass concentrations of $PM_{2.5}$, metals and ions were acquired by analysis of particulates collected on 47mm diameter 2µm pore Teflo filters (Pall Gelman, Ann Arbor, MI). The filters were measured for net gains using a Cahn C-35 (Madison, WI) microbalance following the weighing procedure guidelines of the Code of Federal Regulations (CFR)[21]. Before and after collection, the filters were conditioned for 24 hours in an environmentally controlled room (RH = 40%, T = 25 C) and weighed daily until two consecutive weight measurements were within 3µg.

3.4.3.2 Real-Time Particulate Measurements

Since particulate mass collected over a period of time on a filter do not indicate any disruptions or transient behavior, we used a Dust Trak II to continuously measure PM mass. The Dust Trak II is a desktop battery-operated, data-logging, single-channel, light-scattering laser photometer that gives real-time aerosol mass readings. It has a 10µm impactor and the QA/QC procedure is to zero the instrument using an OEM particulate filter supplied with the instrument. Output from this Dust Trak II are compared to values from the reference federal mass measurement method to provide real-time mass measurements.

3.4.4 Calculations

3.4.4.1 Calculating the Exhaust Flow

An accurate measurement of the exhaust gas flow rate is essential for calculating accurate emission factors. One method, the so-called carbon balance method[22], calculates the exhaust flow rate by comparing the concentration of CO_2 in the exhaust with the mass flow of carbon in the fuel. Since most carbon in the exhaust is found as carbon dioxide, the dilution provides the mass of exhaust flow. In this report, we used measured values for the percentage of carbon in the fuel and the instrument panel reading for fuel rate as the crew reported the fuel flow meters had been recently calibrated. The following formula is used to calculate exhaust flow rate using diesel as the fuel:

$$Q = \frac{\dot{F} \times w_c}{Mw_C} \times \frac{1}{C_{CO2}} \times \frac{R \times T_{atm}}{P_{atm}} \quad (1)$$

where:

- Q is volumetric stack flow (m^3/hr)
- $\dot{F}$ is fuel flow (g/hr)
- w_c is weight fraction of carbon in fuel (unitless)
- Mw_C is the molar weight of carbon (g/mol)
- C_{CO2} is the volume % of CO_2 in the exhaust, taken to be equivalent to mole fraction (unitless)
- T_{atm} is atmospheric temperature (K)
- P_{atm} is atmospheric pressure (Pa)
- R is the universal gas constant (J/mol K)

3.4.4.2 Calculating the Specific Fuel Consumption (SFC)

The SFC of a vessel is the fuel consumption rate at a specified shaft power. This is a critical figure for contextualizing the emissions factor results into total vessel emissions. Equation 2 is used to calculate the SFC

$$S_j = \dot{F}_j \div P_j \quad (2)$$

where:

- S_j is SFC at time "j" (g/kW-hr)
- $\dot{F}$ is fuel flow at time "j" (g/hr)
- P_j is the shaft power at time "j" (kW)

3.4.4.3 Calculating the Modal Emission Factor

3.4.4.3.1 *Modal Emission Rates (grams/hour)*

Using measured concentrations and calculated exhaust flow rate, Emission Rates in g/hr can be determined by the following calculation:

$$Er_i = Q \times C_i \quad (3)$$

where:

- Er_i is the emission rate of compound "i" (g/hr)
- Q is the exhaust flow rate calculated above (m^3/hr)
- C_i is the concentration of compound "i" (g/m^3)

3.4.4.3.2 *Modal Emission Factors (g/kW-hr)*

Modal emissions factors are calculated using the modal emission rate and the recorded shaft power in kW from the instrument panel at the time of sampling as shown in the following equation:

$$Ef_i = Er_i \div P_i \quad (4)$$

where:

- Ef_i is the emission factor of compound "i" (g/kW-hr)
- Er_i is the emission rate of compound "i" calculated above (g/hr)
- P_i is the shaft power at the time of sampling (kW)

3.5 Results

3.5.1 Actual Test Sequence

The proposal was to measure the emissions at five firing rates or as many as could be realized in a voyage between Oakland and the Port of Long Beach. A tight operating schedule and the very low PM levels severely limited the collection of multiple samples at each mode. Results for a single determination are presented in Table 4.

Table 4. Specific Fuel Consumption/ Brake Specific Fuel Consumption

Speed	Load % of NCR	Turbine Load (kW)	Fuel Mass Flow (g/hr)	SFC (g/kW-hr)
Idle	12.9	1.25.E+03	9.49.E+02	757
Dead Slow	18.1	1.75.E+03	1.18.E+03	671
Slow Ahead	28.2	2.73.E+03	1.61.E+03	590
Half Ahead	31.5	3.06.E+03	1.75.E+03	574
Full Sea	102	9.85.E+03	4.78.E+03	486

The trends shown below in Figure 2 are typical for fuel consumption and efficiency curves seen in marine engine data.

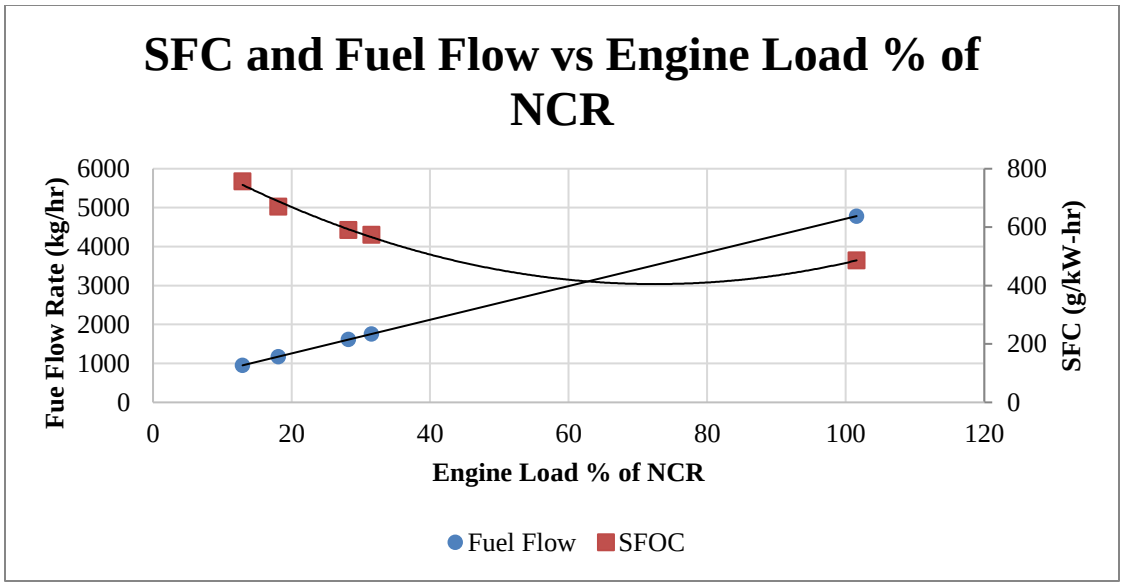

Figure 12. SFC and Fuel Flow Rate Data vs Load % of NCR

3.5.2 Fuel Analysis

Samples taken during the voyage were sent to Southwest Research Institute for analysis as they are a recognized laboratory for fuel analysis. An abbreviated report of the fuel analysis for the first vessel is located in Table 5 below, and these results are representative of both fuel analyses. The results confirm that the fuel met the California standards for sulfur and that the fuel was free of metals as expected for a distillate fuel. The carbon percentage was used in the carbon balance method when determining exhaust flow.

Table 5. Selected Fuel Analysis

Method	Compound/Metric	Units	Measurement
D1298	Specific Gravity	kg/m^3	0.8636
D445 40c	Viscosity	cSt	2.943
D4294	Sulfur	Mass %	0.011
	ppm	ppm	107
D5291 CH	Carbon	wt%	86.40
	Hydrogen	wt%	12.68
D5762	Nitrogen	microg/g	447.5
D5185	Al, Sb, Ba, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, P, Si, Ag, Na, Sn, Zn, K, Sr, V, Ti, Cd	ppm	<1

3.5.3 Gaseous Emission Results

Using the loads and exhaust flow calculated earlier, the concentrations of various pollutants are expressed as grams per kW-hr in Table 6 below. While it is common practice to express OGV main engine emission factors with shaft power as the contextual unit, boiler emissions are often expressed in g/kg-fuel, those emission factors can be found in Appendix 3 at the end of this chapter. It is worth noting that while sampling gaseous species from the main exhaust, the measured O_2 level was found to be different than the reported O_2 level from the vessel metrics. Depending on how they use the reported O_2, this could indicate a problem with the vessel air to fuel ratio for the port side boiler.

Table 6. Gaseous Species Emission Factors by Load (g/kW-hr)

Load % of NCR	NO_x (g/kW-hr)	SO_2 (g/kW-hr)	CO (g/kW-hr)	CO_2 (g/kW-hr)
12.9	7.21	0.166	0.262	2.40E+03
18.1	6.19	0.147	0.843	2.12E+03
28.2	5.37	0.130	1.59	1.87E+03
31.5	5.62	0.126	0.944	1.82E+03
102	6.52	0.107	0.426	1.54E+03

While no weighting scheme exists for this manner of OGV propulsion, the high load NO_x emission factor is 6.52 g/kW-hr with an unweighted average of 6.18 g/kW-hr. For reporting purposes, the high load emission factors should be taken as the general emission factor for the genset as it is closest to the normal operating load point.

3.5.4 Particulate Emissions Results

Similarly, the particulate emissions gathered from filter samples are reported below in Table 7.

Table 7. PM_{10} Emission Factors by Load (g/kW-hr)

	By Filter Mass	By Real-time Instrument
Load % of NCR	**PM_{10} Emission Factor (g/kW-hr)**	**PM_{10} Emission Factor (g/kW-hr)**
12.9	7.04E-03	7.01E-03
18.1	1.18E-01	3.44E-02
28.2	6.70E-03	3.04E-03
31.5	2.31E-03	1.52E-03
102	1.78E-02	4.73E-02

For the purposes of reporting emission factors, the filter weights are far more accurate, and are the federal reference method. The data from the dustrak™ can be used to evaluate trends, but the method by which the instrument zero's itself while operating malfunctioned during the campaign. The following figure is a selected sample of real time PM_{10} stack concentration data from the port side boiler stack departing Oakland. The signal on the far left and right are steady state idle and constant acceleration respectively. This

sampling was chosen to display the temporary nature of the transient concentration increase in PM due to igniting burners from cold start during the departure.

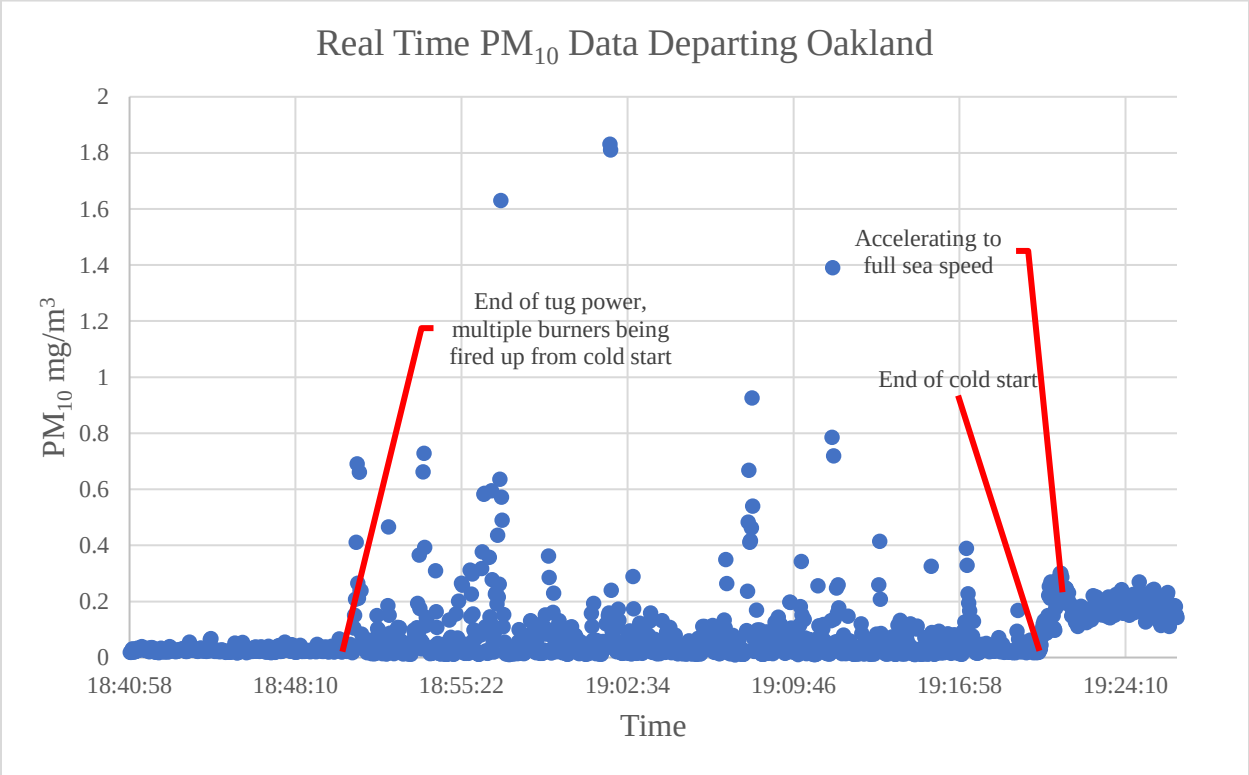

Figure 13. Real time PM_{10} Data Showing Temporary Nature of High PM Concentrations when Igniting Cold Burners

3.6 Discussion

Results for the emissions of criteria pollutants were measured over a number of load points while traveling from Oakland to Long Beach. One of the more interesting features of the campaign was the low PM emission factors. Most OGV engines are CI diesel, and adequate PM mass (>100µg) is collected in 15. However, the boiler system was producing so little PM that even after one hour of continuous sampling, the amount of PM mass collected was <50µg per sample. This data is similar to the emissions the author sampled from a modern tanker using a boiler to generate steam for a turbine in order to discharge the on-board crude[23]. Boilers in both projects used a fuel meeting the CARB standard.

The NO_x emission factors are another notable aspect of this vessel. With an average NO_x emission factor of 6.18 g/kW-hr, this is 3 times higher than the published estimates at 2.1 g/kW-hr in marine inventories from both CARB[24] and EPA[25]. This contradiction evidences the need for more robust data regarding marine gensets.

The SFC on this boiler system is nearly 5 times higher than the SFC on modern OGVs using CI engines that have a similar max load[20]. That notwithstanding, given the cost of OGVs and OGV engines, vessels of this type will likely continue to operate in the commercial maritime industry for the foreseeable future.

3.7 References

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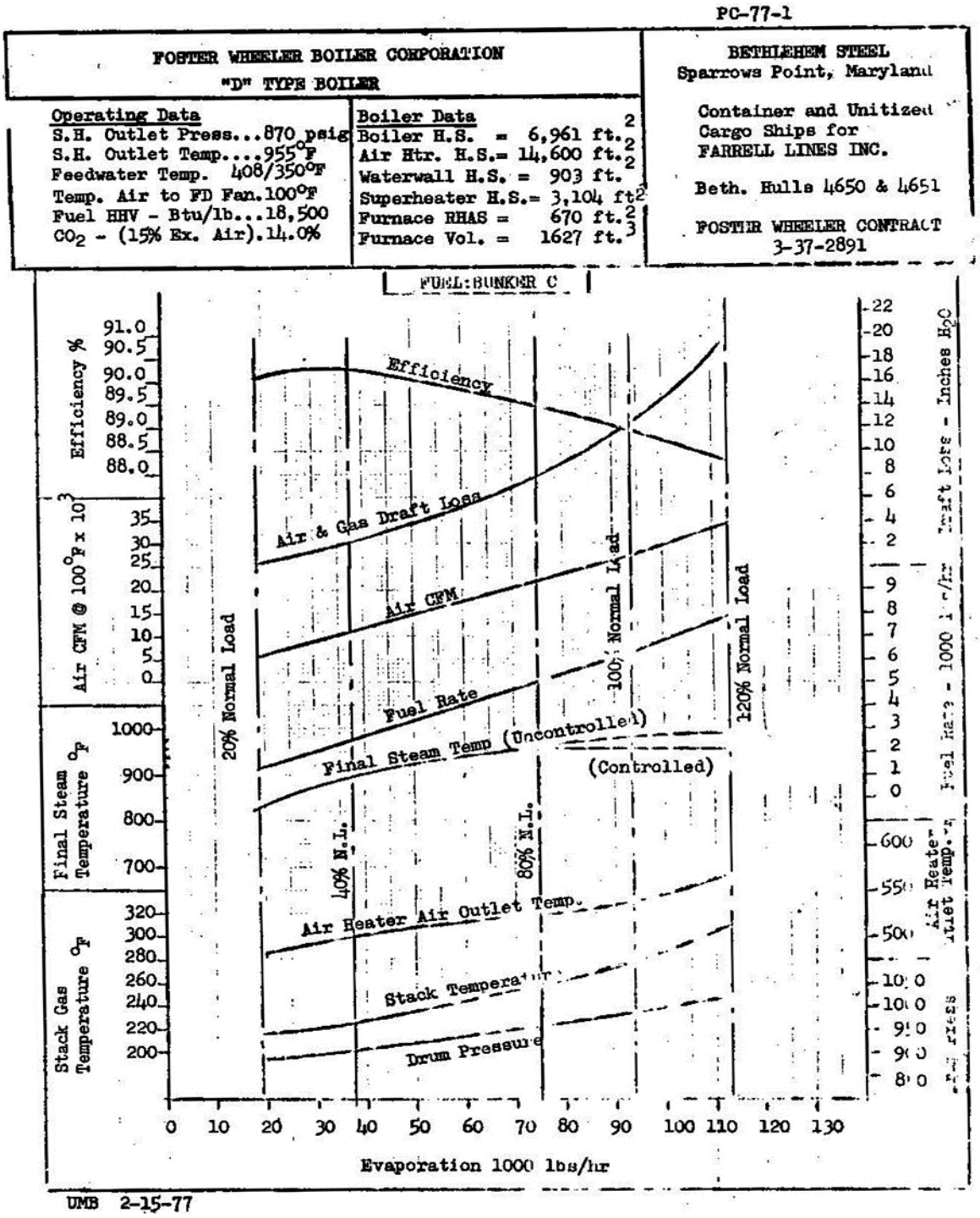
3.8 Appendix 1: Boiler Specifications



3.9 Appendix 2: Test Methods

Table 8. Reference methods for emission sampling

Compound/ Target Data	Method	Sample Type	Proposed Load %
Stack exhaust flow rate	EPA Method 1	Universal Mol Balance	10, 25, 50, 75, 100
Fuel Sample	40 CFR 1065.701-790	Single Sample from Engineering	10, 25, 50, 75, 100
NO_x	40 CFR 1065.270	Real Time	10, 25, 50, 75, 100
SO_2	ISO 8178	Calculation and Real Time (Chemiluminescence)	10, 25, 50, 75, 100
CO_2	40 CFR 1065.250	Real Time (NDIR)	10, 25, 50, 75, 100
O_2	40 CFR 1065.250	Real Time (NDIR)	10, 25, 50, 75, 100
PM_{10} Total	40 CFR 1065.290, EPA-IO3	Gravimetric Sample on PTFE and Real Time	10, 25, 50, 75, 100

3.10 Appendix 3: Additional Tables

Table 9. Engine Data and Calculations at Operating Loads

Speed	Fuel Mass Flow (kg/min)	Fuel Carbon Mass Flow (kg/min)	Fuel Carbon Molar Flow (mol/min)	Exhaust Flow Rate (m^3/hr)
Idle	1.581E+01	1.366E+01	1.137E+03	1.036E+05
Dead Slow	1.961E+01	1.695E+01	1.411E+03	1.459E+05
Slow Ahead	2.690E+01	2.324E+01	1.935E+03	2.400E+05
Half Ahead	2.923E+01	2.525E+01	2.103E+03	2.557E+05
Full Sea	7.973E+01	6.889E+01	5.735E+03	4.296E+05

Table 10. Gaseous Species Emission Factors by Fuel Mass (kg/ton of fuel)

Load % of NCR	**NO_x (kg/ton of fuel)**	**SO_2 (kg/ton of fuel)**	**CO (kg/ton of fuel)**	**CO_2 (kg/ton of fuel)**
12.9	9.53	0.220	0.346	3.17E+03
18.1	9.22	0.220	1.26	3.17E+03
28.2	9.09	0.220	2.69	3.17E+03
31.5	9.80	0.220	1.65	3.17E+03
102	13.4	0.220	0.877	3.17E+03

Table 11. PM_{10} Emission Rates and Emission Factors by Load (g/kW-hr)

	By Filter Mass		By Real-time Instrument	
Load % of NCR	**PM_{10} Emission Rate (g/hr)**	**PM_{10} Emission Factor (g/kW-hr)**	**PM_{10} Emission Rate (g/hr)**	**PM_{10} Emission Factor (g/kW-hr)**
12.9	8.82	7.04E-03	8.78	7.01E-03
18.1	208	1.18E-01	60.4	3.44E-02
28.2	18.3	6.70E-03	8.30	3.04E-03
31.5	7.07	2.31E-03	4.65	1.52E-03
102	175	1.78E-02	465	4.73E-02

4. TIER III NO_X STANDARDS FOR OCEAN GOING VESSELS REDUCE DEEP-SEA EMISSIONS BUT ARE NOT PROTECTING PORT AIR QUALITY

ABSTRACT

Emissions of nitrogen oxides (NO_x) from ocean-going vessels (OGVs) are a significant contribution to port inventories, often resulting in nearby cities failing to meet clean air standards. To mitigate these effects, the International Maritime Organization (IMO)[1] has various policies to reduce maritime NO_x emissions, which have since been adopted and added to by the US Environmental Protection Agency (EPA)[2] and the California Air Resources Board (CARB). The methods by which OGV NO_x is controlled are: NO_x emission standards for OGV engines[1,2], emissions control areas[3], and vessel speed reduction (VSR) zones near ports and ecological areas[4,5,6,7,8]. Emission standards are prescribed by vessel build year, the most recent of which are the Tier III standards, having been implemented in 2016[2]. Emission standards are a certified weighted average of modal NO_x emission factors at specific load points between 25% - 100% of the engine's full power, or maximum continuous rating (MCR)[9]. While in operation, OGV NO_x emissions are not to exceed 1.5 times the weighted emission standard at any load above 25%. ECA and VSR regulations are meant to minimize NO_x emissions by reducing vessel speed, thereby reducing fuel consumption and emissions in specific zones.

This project measured the emissions of NO_x, and various other gaseous and particulate species, from the main engines on two Tier III Con-Ro OGVs while operating at sea under normal conditions. Both engines were equipped with exhaust gas recirculation (EGR) as a Tier III NO_x control strategy, and followed identical voyage routes in and out of Emission Controlled Areas (ECA). The weighted NO_x emission factors for the test vessels were 2.88 g/kW-hr and 3.14 g/kW-hr, well within the limits of the published Tier III NO_x emission standard of 3.4 g/kW-hr. While operating within the range of certified load points between 25% and 100% MCR, both vessels were found to have their in-use emissions at or below 1.5 times the Tier III standard[2].

In VSR zones, both vessels were found to have their engine load drop below 25%, or "off-cycle", where NO_x emissions are not factored into the weighted emission factors. While traveling near ports, coastal communities, and other protected zones, the NO_x emission factors for both vessels were as high as 25.0 g/kW-hr, or 7.3 times the Tier III standard. Even more alarming is that these emissions are 1.7 times higher than the previous Tier II standard. The findings in this research have demonstrated that vessel engines using Tier III NO_x controls can be certified for use, yet fail compliance while in operation. Furthermore, the largest emission signals from these vessels are experienced primarily in regions with the most human exposure, and worst pre-existing air quality.

4.1 Background

Ocean going vessels (OGVs) are defined as ships that cross the open ocean while taking part in foreign commerce transporting freight or passengers. OGVs are the primary means of connecting the raw materials, manufacturing and distribution centers of finished goods to the world, and today, about 80% of the goods move over the oceans. The transition from local to efficient global manufacturing sites is only possible with the efficiencies offered by the network of ocean-going vessels. However, those vessels are contributing an ever-increasing percentage of the total global and regional emissions of criteria, hazardous and greenhouse air pollutants. Pollutants, like NO_x and particulate matter (PM), are harmful to people and the environment and pose a serious threat. Notwithstanding the ever-increasing fraction of air pollution from OGVs, there was steady progress in reducing emissions of particulate matter, sulfur oxides and nitric oxides. These reductions were the result of agreements reached within International Maritime Organization (IMO)'s Maritime Environmental Protection Committee (MEPC)[1]. These new regulations controlled the sulfur content of fuels, and sulfur and nitric oxides released to the air. There were also new regulations that created Emission Control Areas (ECAs)[3]. Following the implementation of new standards for sulfur and nitric oxides, the MEPC focused on climate change and new requirements became effective on January 1, 2023. With these new regulations, ship owners are now responsible for reporting their Energy Efficiency Existing Ship Index (EEXI), and their annual operational Carbon Intensity Indicator (CII) rating.

The purpose of this paper is to investigate gaseous and particulate emissions from OGVs meeting the Tier III requirements, with a focus on NO_x. The control of diesel engine NO_x emissions is achieved through the survey and certification requirements leading to the issuance of an Engine International Air Pollution Prevention (EIAPP) Certificate and the subsequent demonstration of in-service compliance in accordance with IMO regulations 13.8 and 5.3.2 respectively and the NO_x Technical Code 2008[1,10].

Table 12. Nitric Oxide (NO_x) Emission Limits[1]

Tier	Ship construction date on or after	Total weighted cycle emission limit (g/kWh) n = engine's rated speed (rpm)		
		n < 130	n = 130 - 1999	n ≥ 2000
I	1 January 2000	17.0	45·n(-0.2) e.g., 720 rpm – 12.1	9.8
II	1 January 2011	14.4	44·n(-0.23) e.g., 720 rpm – 9.7	7.7
III	1 January 2016	3.4	9·n(-0.2) e.g., 720 rpm – 2.4	2.0

Table 12 above lists the different standards for NO_x emission limits for Tiers I-III. The Tier III controls apply only to specified ships built after January 2016, and while operating within the ECA. Outside ECA, the OGVs meet Tier II emission standards and limits. Furthermore, a marine diesel engine that is installed on a ship constructed on or after the following dates and operating in the following ECAs shall comply with the Tier III NO_x standard:

1. 1 January 2016 and operating in the North American ECA and the United States Caribbean Sea ECA; or
2. 1 January 2021 and operating in the Baltic Sea ECA or the North Sea ECA.

4.1.1 Emission Control Technologies

A number of technology options are available for achieving the Tier III NO_x limits when combustion uses a petroleum -based fuel. However, the Selective Catalytic Reduction (SCR) and Exhaust Gas Recirculation (EGR) processes dominate the installed units. One study showed that the SCR process was installed with 75% of the new engines. The SCR process is well proven for on-land applications and relies on mixing urea, or possibly ammonia, as reducing agents with the exhaust stream. Next, the mixture is passed through a unique catalyst where over 90% of the NO_x can be converted to nitrogen. The catalyst temperature is controlled within a specific window for desired catalyst efficiency. A temperature too high will burn ammonia and a temperature too low will not reach the desired NO_x conversion. Care is taken during design to limit the ammonia slip to the atmosphere.

The second NO_x control technology, EGR, recirculates 30–40% of the exhaust gas into the inlet air, thus lowering the concentration of oxygen for the inlet air reaching the combustion zone[11]. Lowering the oxygen concentration will reduce the peak flame temperature and thereby reduce the formation of thermal NO_x. However, the lower oxygen concentration may slightly increase in the amount of soot produced and reduce the efficiency of fuel usage. Hanson[11] reports that if the EGR process is not properly managed, the reduced concentration of oxygen in the combustion zone will lead to adverse effects.

Other NO_x control approaches to achieve Tier III limits include use of the new dual-fueled engines with natural gas, and methanol-water fueled engines; neither approach requiring added exhaust control units.

4.1.2 Certifying Marine Engines

Marine engines are certified following the standards in the IMO's Annex VI; Appendix II - Test cycles and weighting factors (Regulation 13)[1]. These test cycles are also listed in ISO-8178-4[12]. For example, most main propulsion engines (ME) follow ISO 8178-E3 Cycle or the "propeller curve". Occasionally, there are MEs certified to the ISO 8178-E2 cycle but for this paper, the focus is the E-3 Cycle[12].

Table 13. Propeller Test Cycle (ISO 8178-4 E3)

Type E3, Mode #	**1**	**2**	**3**	**4**
Power, %	100	75	50	25
Speed, %	100	91	80	63
Weighting factor	0.2	0.5	0.15	0.15

The ISO E3 Test Cycle requires measuring emissions at the four loads specified in Table 13 and calculating the overall emission factor using the listed weighting factors. These weighting factors are intended to represent the percentage of time that the engine operates at that power. For Tier III, the IMO NO_x Technical Code paragraph 3.1.4[1] further limits the measured increase at each load: "In the case of an engine to be certified in accordance with paragraph 5.1.1 of Regulation 13, the specific emission at each individual

mode point shall not exceed the applicable NO_x emission limit value by more than 50%."[1] The "Not to Exceed Limit" is particularly applicable to emissions at the lowest power level where emissions tend to be higher.

4.1.3 Focus of this Research

During the development of the MARPOL Annex VI, NO_x Technical Code in 2007, the United States (US) raised several issues. For example, the US pointed to reduced ship speed and power levels near ports, leading to engine operating at <25% power and proposed lowering the 25% power in the existing standard to 15% power. Another issue was the US wanted the exhaust equipped with a continuous emissions NO_x monitor (CEM) within ECA to assure that the emissions and personal exposure were reduced. The US opined that emission reductions near ports were paramount and needed in order to limit exposure of workers and people living near the ports and harm to their health. The US agreed with others to establish ECA zones and to limit in-use emissions to 1.5 times the cycle weighted standard for all power settings.

The final NO_x Technical Code did not include either certification at 15% power or CEMS. As a consequence, we do not know the power setting where the control technology for NO_x is turned off and we do not have records of measured NO_x emissions for <25% power to assure that the intended reduction in personal exposure is realized. Interestingly, in 2023, the massive SKIPPER Project concluded that NO_x emission standards are needed down to 10% power and that the ships should have NO_x CEMS installed to ensure that the intended emission reductions were realized.

The current investigation had a number of primary objectives. First within ECA, we wanted to: 1) measure the emissions factors at various power settings within the certification power values to compare with published standards; 2) confirm emissions between the certification points were similar; 3) learn at what power setting the NO_x control technology was discontinued; and 4) measure the emissions factor below 25% power to learn if the intended reduction in personal exposure to ship emissions was realized. The secondary objective was to measure the emissions factors outside ECA with a global fuel.

4.2 Research Plan and Methods

The project plan was to measure the emissions of a modern vessel with engines meeting Tier III NO_x standards. The emissions were measured at available certification loads and other modes, as available.

4.2.1 Specifications of the Vessel and the Engines

The platform for the project were 2 identical ConRo vessels launched in 2019 with MAN *6G90ME-C10.5-GI, 2-stroke* engines for the main propulsion. Maximum continuous power rating for the main engine is 31.9 kW at 82 RPM. Tier-III NO_x standards are met using EGR on the main engines. The beam on the vessel is 34.9m, length is 265.0m and gross tonnage is 59,522 tons.

Each vessel also had four auxiliary engines (AEs), 2 identical sets, based on the same engine block, operated as a medium speed engine at mmm RPM while following a four-stroke cycle. All 4 AEs are of the Hyundai engine family: *JYYDN18.HD27*. 2 AEs are 6-cylinder engines rated at 1,620kW and the other 2 are 7 cylinder engines rated at 2,430kW. The AEs met Tier III NO_x standards using SCR to control the exhaust levels. The auxiliary and boiler genset emissions were tested, but are not reported in this paper.

4.2.2 Test Fuels

The vessel operated on two fuels. One fuel was ultra-low sulfur marine distillate (ULSFO), a distillate fuel meeting the California Air Resources marine fuel standard in Title13, California Code of Regulations (CCR) §2299.2[13] and Title 17, CCR §93118.2[14],

as required for all ocean-going vessels within 24 nautical miles of the California Coastline. This fuel also meets the IMO standard for vessels operating within 200nm of North America ECA[3]. The second test fuel a was very-low sulfur marine distillate (VLSFO), a marine fuel meeting the ISO-8217 standard once the vessel passed the ECA boundary. Fuel samples were taken while measuring emissions and results from an independent lab were compared with the Certificate of Analysis (COA) issued at the time of refueling, or bunkering. The selected properties the fuels were analyzed for are listed in Table 14. Note that the carbon content is measured to enable the exhaust flow to be calculated by the carbon balance method.

Table 14. Selected Fuel Analyses

Property Measured	**ASTM Method**
Kinematic Viscosity @ 40 Cº	D445
Relative Density or API Gravity	D1298
Determination of Carbon and Hydrogen	D5291
Elemental Analysis by ICP	D5185
Sulfur by X-ray Fluorescence	D2662-07
Nitrogen by Chemiluminescence	D5762

4.2.3 Main Engine Operation While Measuring Emissions

Emissions from the main engine can only be measured when the vessel was at sea. While it is desirable to measure emissions at all the certification test modes specified in ISO 8178-4 E3, *Test Modes and Weighting Factors for a Heavy-duty Marine Engine*

Following the Propeller Curve[12]*;* shown in Table 13, the actual load points where emissions are measured are dictated by the schedule of the vessel. During this project, we were able to get many points near the E3-loads used for certification and some between the specified modes to confirm that emissions did not increase. Also, important data was collected at the 10-knots vessel speed limit when operating in the Santa Barbara Channel during the whale migration season, and at ~12 knots, when entering the harbor. When sailing at 10 and 12 knots, the engine was operating below 25% power, a focus for the desired research data.

4.2.4 Auxiliary Engine and Boiler Operation While Measuring Emissions

During emission measurements, the AEs were operated at ~50% power, which was the in-use shaft power at the time of sampling. Time was allowed for the NO_x control technology to turn-on and for emissions to reach a steady value.

A challenging issue with testing boilers in normal use on a container ship is that steam demand is low, and allowable peak pressure in the boiler is reached in a short time, causing the fuel supply to abruptly shut off. As fuel supply turns on and off, the emissions values fluctuated thereby making it difficult to collect an exhaust sample with a steady value. Thus, boiler sampling was done at the maximum achievable power at berth. This was achieved by opening the steam system to ambient pressure.

4.3 Methods

4.3.1 Sampling the Raw Exhaust

The sampling platform consisted of purified dilution air, a state-of-the-art dilution unit and a specialty designed sample distribution system. High-purity air is critical for any system to dilute the extracted raw exhaust without changing the properties. Although instrument-grade air is available on ships, we added a purification unit with four clean-up steps in series to ensure the dilution air met our specifications. These four units were: 1) a 10µm oil, water, and PM filter; 2) a desiccant drying column with silica gel; 3) a column filled with Purafil™ charcoal in two even layers and 4) a HEPA-filter to remove particulates >1µm.

The second key component of the sampling system is a state-of-the-art Dekati® eDiluter™ Pro. This commercial product allowed two-stage sample conditioning. The first stage dilution ratio was 5:1 and the final dilution ratio could be adjusted from 1:25 to 1:225. The first stage is heated while the second dilution stage operates at room temperature where the aerosol sample is cooled in a controlled manner. Built-in sensors constantly monitor the dilution process parameters and an integrated control unit actively compensates for any fluctuations in the sample inlet pressure ensuring that the selected dilution factor is kept constant under all conditions. In the field, the QA/QC procedure for the dilution ratio was to measure raw and dilute NO_x concentrations and compare with the set value. Corrective action is required if the measured value is >10 % above the set point.

In the third element of the design, samples from the Dekati unit were split into multiple branches and distributed for simultaneous independent gaseous and particulate analysis. Sample flow rate from each line leaving the splitter was measured using critical flow orifices (CFOs) with continuous monitoring of the temperature and pressure drop across the CFO. QA/QC for flow elements on branches was done by comparing monitored values with known nominal flow data at critical pressure. Design was in accordance with 40 CFR 1065[15-20], as well as ISO sampling standards[21] for gaseous and particulate species. A schematic of the overall control sampling system is shown in Figure 11.

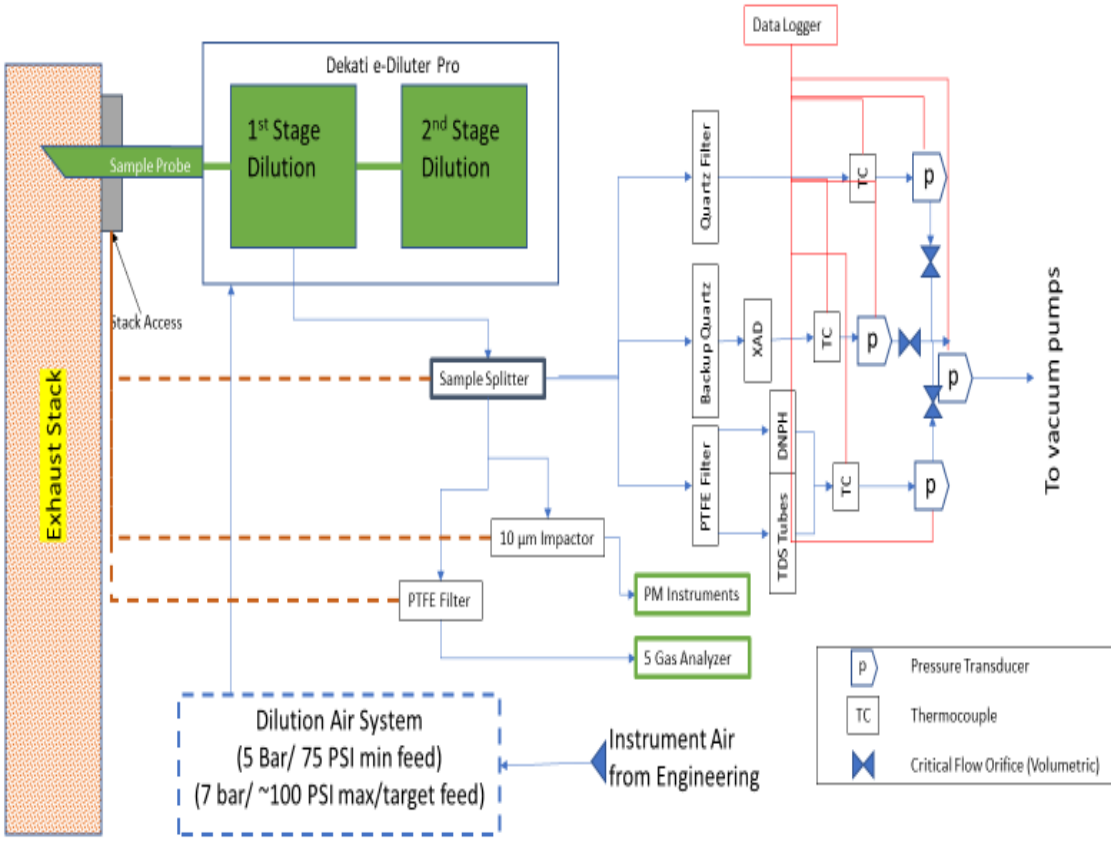


Figure 14. Schematic of Samples Collected from First Stage Dilution

4.3.2 Measuring concentrations of gases and particulate matter

4.3.2.1 Measurement of regulated gases

The concentrations of nitric oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), sulfur oxides (SO_2) and oxygen in the raw exhaust and the diluted samples were measured continuously with a Horiba PG-350 portable five-gas analyzer. For quality control, analyzer checks with calibration gases both before and after each test were made to check for drift. Certified Grade N_2 was used for the zero-point and an EPA Protocol Gas, consisting of a mixture of NO_x, CO, CO_2, and SO_2, was used for the span. The SO_2 gas concentrations in this paper were calculated from the sulfur level in the fuel as directed by ISO 8178 -1[21].

4.3.2.2 Measurement of Particulate Matter (PM) mass

The mass concentrations of $PM_{2.5}$, metals and ions were acquired by analysis of particulates collected on 47mm diameter 2µm pore Teflo filters (Pall Gelman, Ann Arbor, MI). The filters were measured for net gains using a Cahn C-35 (Madison, WI) microbalance following the weighing procedure guidelines of the Code of Federal Regulations (CFR)[22]. Before and after collection, the filters were conditioned for 24 hours in an environmentally controlled room (RH = 40%, T = 25 C) and weighed daily until two consecutive weight measurements were within 3µg.

4.3.2.3 Measurement of Elemental and Organic Carbon (EC-OC)

OC/EC analysis was performed on samples collected on 2500 QAT-UP Tissuquartz Pall (Ann Arbor, MI) 47 mm filters that were preconditioned at 600°C for 5 h. A 1.5 cm^2 punch is cut out from the quartz filter and analyzed with a Sunset Laboratory (Forest Grove, OR) Thermal/Optical Carbon Aerosol Analyzer according to the NIOSH 5040 reference method[23].

4.3.2.4 Real-time particulate measurements

Real-time PM mass measurements were monitored by a Dust Trak II, a single channel, data logger using a light-scattering laser photometer. The Dust Trak provides real-time qualitative aerosol mass readings to ensure the PM concentration was near constant while flowing to the filter. The QA/QC procedure is to zero the instrument using an OEM particulate filter supplied with the instrument. Output from the Dust Trak are calibrated to values from the reference federal mass measurement method to provide real-time mass measurements.

4.3.3 Calculations

4.3.3.1 Calculating the Exhaust Flow Rate

An accurate measurement of the exhaust gas flow rate is essential for calculating accurate emission factors. EPA Method 1[24], or the carbon balance method, calculates the exhaust flow rate by comparing the concentration of CO_2 in the exhaust with the mass flow of carbon in the fuel. Since most carbon is found as carbon dioxide in the exhaust, the dilution provides the mass of exhaust flow. Carbon weight percentage is determined from

the fuel analysis, and fuel flow rate is part of the data package gathered on vessel metrics. Equation 1 is used to calculate exhaust flow rate:

$$Q = \frac{\dot{F} \times w_c}{Mw_C} \times \frac{1}{C_{CO2}} \times \frac{R \times T_{atm}}{P_{atm}} \quad (1)$$

where:

- Q is volumetric stack flow (m^3/hr)
- $\dot{F}$ is fuel flow (g/hr)
- w_c is weight fraction of carbon in fuel (unitless)
- Mw_C is the molar weight of carbon (g/mol)
- C_{CO2} is the volume % of CO_2 in the exhaust, taken to be equivalent to mole fraction (unitless)
- T_{atm} is atmospheric temperature (K)
- P_{atm} is atmospheric pressure (Pa)
- R is the universal gas constant (J/mol K)

4.3.3.2 Calculating Specific Fuel Consumption (SFC)

The SFC of a vessel is the fuel consumption rate at a specified shaft power. This is a critical figure for contextualizing the emissions factor results into total vessel emissions. Equation 2 is used to calculate the SFC

$$S_j = \dot{F}_j \div P_j \quad (2)$$

where:

- S_j is SFC at time "j" (g/kW-hr)
- $\dot{F}$ is fuel flow at time "j" (g/hr)
- P_j is the shaft power at time "j" (kW)

4.3.3.3 Calculating emissions factors

4.3.3.3.1 Modal data: Emissions in grams/hour

Using measured concentrations and calculated exhaust flow rate, Emission Rates in g/hr can be determined by Equation 3:

$$Er_{ij} = Q \times C_{ij} \quad (3)$$

where:

- Er_{ij} is the emission rate of compound "i" at time "j" (g/hr)
- Q is the exhaust flow rate calculated above (m^3/hr)
- C_{ij} is the concentration of compound "i" at time "j" (g/m^3)

4.3.3.3.2 Modal data: Emission Factors in g/kW-hr

Modal emissions factors are calculated using the modal emission rate and the recorded shaft power in kW from the instrument panel at the time of sampling as shown in Equation 4:

$$Ef_{ij} = Er_{ij} \div P_j \quad (4)$$

where:

- Ef_{ij} is the emission factor of compound "i" (g/kW-hr)
- Er_{ij} is the emission rate of compound "i" at time "j" calculated above (g/hr)
- P_j is the shaft power at the time "j" (kW)

The overall emission factor would be calculated using the weighting factors in Table 13.

4.3.3.4 Calculating Total Emissions of Specific Species at Fixed Engine Load

Total emissions at various load points allow for a simplified quantification of the potential impact on air quality an OGV in use contributes. In this paper, the total emissions will be paired with the geographical locations of those emission signals to shed light on discrepancies between the Tier III emission standards, the ISO 8178-E3 weighting cycle, and the real-world operation of OGVs in California shipping lanes. Those total emissions can be calculated using Equation 5

$$Et_{ij} = Ef_{ij} \times P_j \times t \div 1000 \quad (5)$$

where:

- Et_{ij} is the total emissions of compound "i" at time "j" (kg)
- Ef_{ij} is the emission factor of compound "i" at time "j" (g/kW-hr)
- P_j is the shaft power at the time "j" (kW)
- t is the duration spent at shaft power P_j (hr)

4.3.4 Determining Ship Activity and Human Exposure

The analysis of emission measurements has traditionally focused on whether the vessel met the IMO certification standards while operating at sea. Modal emission factors were weighted by values provided in ISO 8178-E3. However, more investigators today are measuring the actual activity and developing a more accurate set of weighing factors to use when calculating the overall emission factor. In either case, these overall emissions are subsequently used for calculating the contribution to inventory and in subsequent air quality models.

This approach; however, leaves out the answer to an important question: Do people living and working in ports have reduced exposure as a consequence of the lower OGV emission standards? This important and complex question was asked during the development of the Tier III standard and requires additional data and a deeper analysis. Specifically, emissions rates and ship speed (velocity) are needed at each vessel location, especially as the vessel moves closer to where people are located.

The most direct approach is to overlay our emission data with ship speed data from SCADA or AIS, but we did not have that option. Accordingly, we added two commercial Garmin GPS units and specified collection rates. The Garmin units were placed on the flybridge, just above the bridge/navigation level, and alongside the vessel's positioning and communication equipment in order to ensure GPS resolution <5 m. One of the Garmin units recorded vessel GPS parameters in 5-minute intervals, and the second unit recorded

distance (km) based intervals. The resolution was set at single-km intervals during open sea travel. A higher resolution (sub-km) was used during port and near-coast activity.

The second approach to monitor ship speed used three mobile iOS apps: Navionics, iNavX, and Aqua Map GPX. The iOS devices were placed two decks below the bridge/navigation level and run continuously and concurrently, recording position, course (heading), and speed (knots) at sub-minute resolution with .GPX and .KML file outputs. These formats are easily readable as plain text or .CSV.

Taken together, the emissions rate and ship location, will allow a dispersion modeler to predict whether people in the ports have reduced exposure as a consequence of the new IMO Tier III standards within ECA.

4.4 Results

A number of testing and measurement campaigns were necessary for each vessel as there were multiple combustion sources that needed emission measurements. Those schedules and test results are summarized and discussed in this section.

4.4.1 Testing

Emissions from the main engine were measured while sailing from the Port of Oakland to the Port of Long Beach, and from the Port of Long Beach to Honolulu. These routes include operation within the Tier II and Tier III zones. A timeline for the first vessel is shown in Table 15 and is representative of the schedule for the second vessel.

Table 15. **Sample Test Schedule for the Main Engine**

Dates	**Fuel**	**NO_x Tier**	**Vessel Activity**
12-May 2022	CA-ECA	Tier III	Disembark Oakland for Long Beach
12-13 May 2022	CA-ECA	Tier III	At sea, from Oakland to Long Beach
13-14 May 2022		Tier III	At berth in Long Beach,
14-18 May 2022	CA-ECA & Global	Tier III/Tier II	At sea, coastal and international waters, from Long Beach to Honolulu
18-20 May-2022	Global & ECA	Tier III	At berth in Honolulu, sampling offload

The details of the voyage routes and general travel speed are detailed below in Figures 15 and 16. Throughout the route in Figure 15, the vessel was operating in Tier III mode with the EGR engaged. Full speed travel zones are highlighted green, transitional speed and VSR zones are highlighted in yellow, and the Channel Islands VSR zone is highlighted in red.

Figure 15. **Voyage route from Port of Oakland to Port of Long Beach**

As seen in Figure 16, the vessels disengage the EGR at the 200 nautical mile coastal boundary enroute to the Port of Honolulu, and finish the voyage operating in Tier II mode. The total distance from port to port is roughly 2300 nautical miles. The vessel is traveling at full speed for this leg of the voyage with little to no variability in engine load.

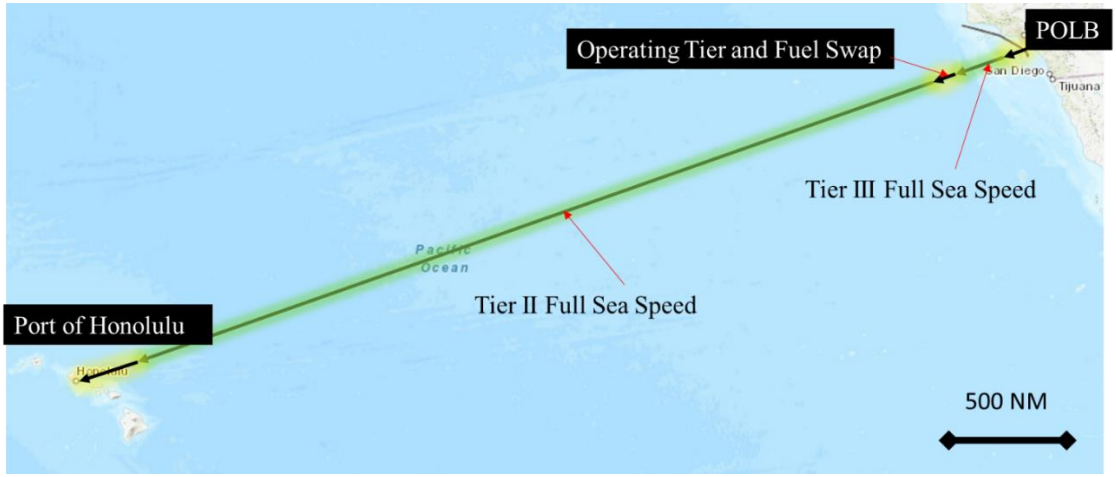


Figure 16. Vessel route from Port of Long Beach to Port of Honolulu

Testing of the auxiliary engines (AEs) and boilers took place at the Port of Long Beach during sampling events separate from main engine testing. Engine and boiler testing was conducted at the conditions described in the previous section.

4.4.2 Engine Metrics

Using the on-board Command and Control/Central Alarm Management System (CoCo/CAMS), hourly data on the following engine metrics were gathered on all testing days: fuel flow rate (mass and volume), fuel density, fuel viscosity, scavenger air pressure, scavenger air pressure, engine shaft power, and engine load % of normal continuous rating (NCR) (Figure 17). Calculated exhaust flows are at standard atmospheric conditions to be representative of the environmental conditions the exhaust stream will be exposed to once out of the exhaust stack.

Figure 17. **Sample CoCo/CAMS data from vessel 1**

Modal SFC, featured below in Figure 18, was calculated using this data and Equation 2. The Tier III data shows a negative relationship between SFC and load %, Tier 2 data is inconclusive due to lack of data at different loads. The trend in the Tier III data suggests increasing fuel efficiency as load increases.

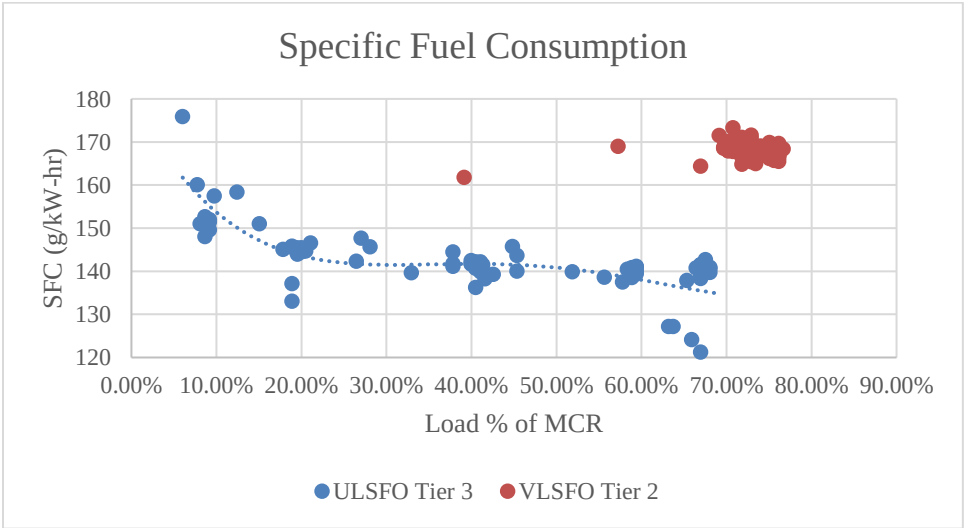


Figure 18. **Graphical SFC data**

4.4.3 Fuel Analysis Results

Separate fuel samples were obtained from the fuel system during each testing event and analyzed by an outside lab. Samples were drawn from the vessel fuel system just upstream of the engine while in operation. This guaranteed a truly representative component analysis of the fuels used inside and outside the ECA zones for both vessels. Listed in the table below are the condensed results of the fuel samples taken from the main engines. It is important to note that the ULSFO and VLSFO samples had sulfur concentrations below 0.1% and 0.5%, respectively. This means that all four fuels used during testing were in compliance with the applicable CARB and IMO regulations.

Table 16. Key Properties of Test Fuels

Method	**Compound/Metric**	**Units**	**Vessel 1 ULSFO**	**Vessel 2 ULSFO**	**Vessel 1 VLSFO**	**Vessel 2 VLSFO**
D1298	Specific Gravity	kg/m^3	0.8502	0.8361	0.9670	0.9687
D445 40c	Viscosity	cSt	3.169	2.878	283.642	111.282
D4294	Sulfur	Mass %	0.026	0.008	0.393	0.417
D5291 CH	Carbon	wt%	85.72	86.19	86.12	88.84
	Hydrogen	wt%	12.90	13.45	10.26	10.33
D5762	Nitrogen	microg/g	382.2	77.5	5277.3	1377.2
D5185	Al, Sb, Ba, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, P, Si, Ag, Na, Sn, Zn, K, Sr, V, Ti, Cd	ppm	<25	<35	<150	<50

4.4.4 Weighted Emission Factors for the Main Engines Inside ECA

While operating inside the ECA zones and coastal shipping lanes regulated by CARB, Tier III controls, emission standards, and fuels are in use. Weighted emission factors for the main engines show that the NO_x emissions of vessel 1 and 2 are 2.88 g/kW-hr and 3.14 g/kW-hr respectively. These emission factors both meet the Tier III NO_x emission standard of 3.4 g/kW-hr ± 50% while in operation at all loads greater than 25%. The emission factors for all species on both vessels are summarized below in Table 17.

Table 17. Weighted Tier III Emission Factors

Operating Mode	Tier III	
Fuel	ULSFO	
(g/kW-hr)	Vessel 1	Vessel 2
PM	0.104	0.0517
NO_x	2.88	3.14
CO	0.470	0.413
CO_2	436	450
SO_2	0.0723	0.0228

4.4.5 Weighted Emission Factors for the Main Engines Outside ECA

As soon as the vessel exited the ECA Zone, both the use of the California marine fuel and the EGR were discontinued. Given that the vessels were traveling at fixed speeds, the ocean conditions were calm, and the engines were at steady state, weighting factors were not used for Tier II. The NO_x emission factors for vessel 1 and 2 were 11.13 g/kW-hr and 15.79 g/kW-hr respectively. This places the emission from both vessels in

compliance with the Tier II NO_x standard of 14.4 g/kW-hr ± 50% while in operation at all loads greater than 25%. The emission factors for all species on both vessels are summarized below in Table 18.

Table 18. Weighted Tier II Emission Factors

Operating Mode	Tier II	
Fuel	VLSFO	
(g/kW-hr)	Vessel 1	Vessel 2
PM	0.152	0.172
NO_x	11.1	15.8
CO	0.494	0.438
CO_2	510	547
SO_2	1.27	1.40

4.4.6 Modal Emission Factors for the Main Engines

This finding has covered the weighted emission factors based on data gathered at the modal power values used for engine certification by CARB, the EPA, and IMO; however, the modal data provides a clearer picture that can be better applied to activity and dispersion models. Figures 19 through 21 show the data points for PM, CO_2, and NO_x corresponding to gravimetric PM filter samples gathered during emissions testing. For the following figures, the vessels are in Tier III mode for all ULSFO data points, and Tier II mode for all VLSFO data points.

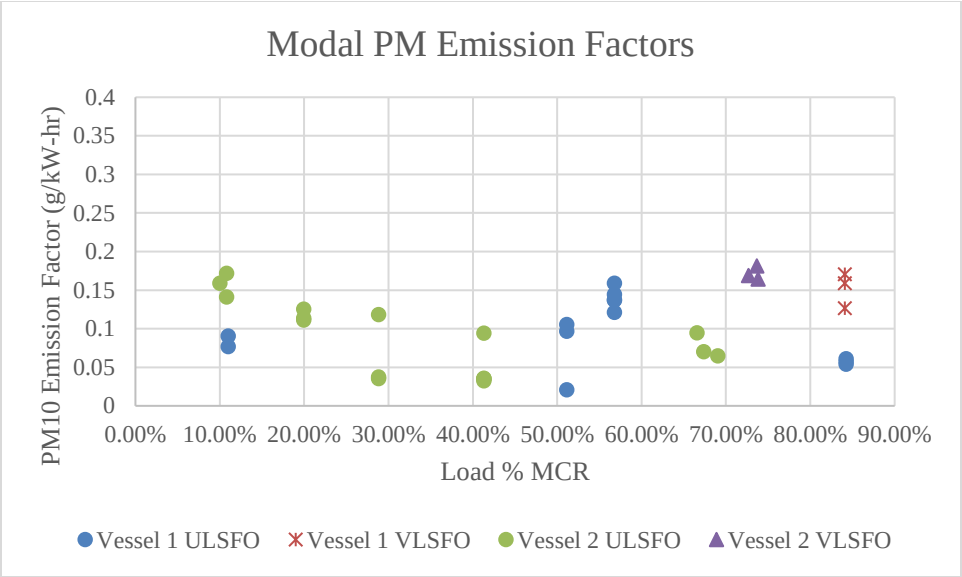


Figure 19. PM emission factors determined via ISO 8178 compliant batch samples at different loads from both vessels and fuel types

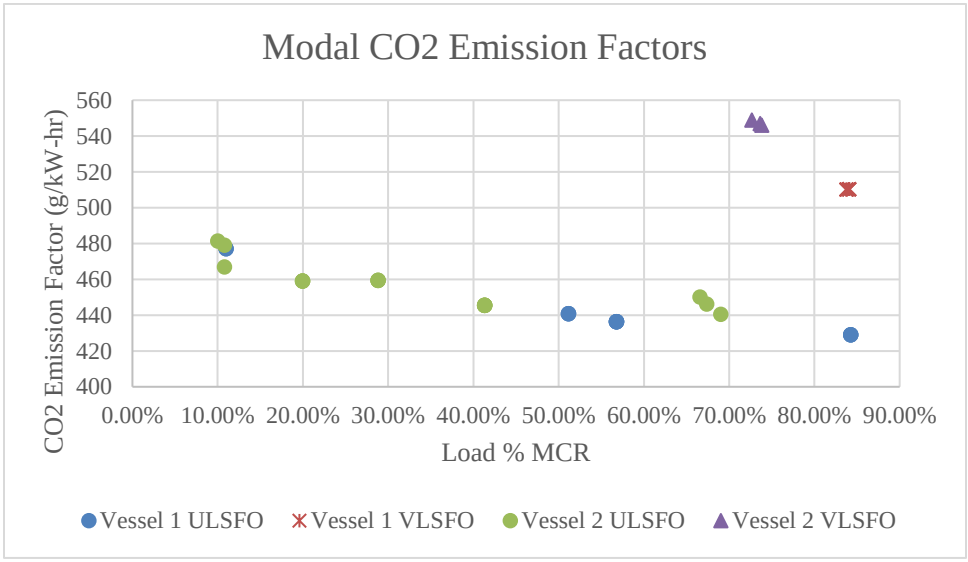


Figure 20. CO_2 emission factors corresponding to ISO 8178 compliant PM samples at different loads from both vessels and fuel types

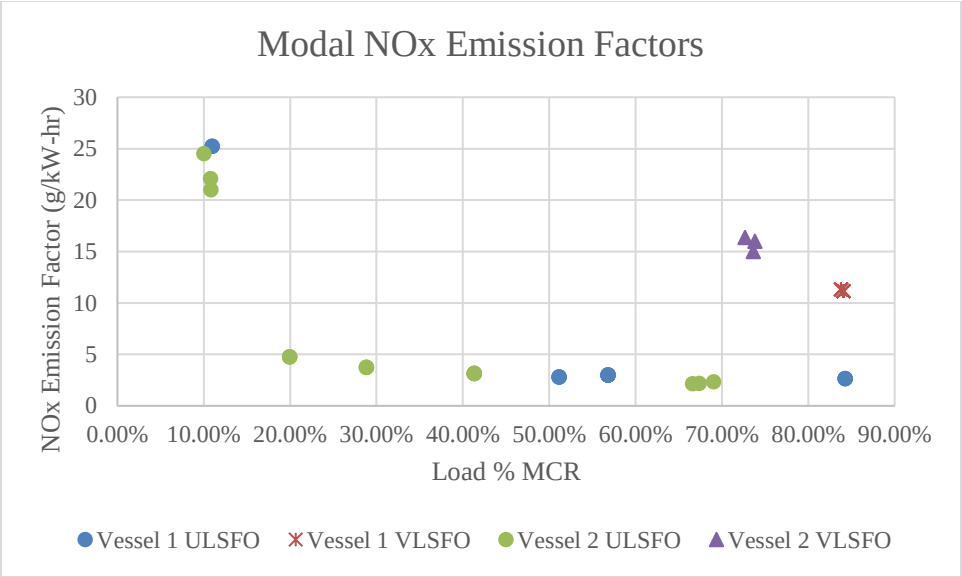


Figure 21. NO_x emission factors corresponding to ISO 8178 compliant PM samples at different loads from both vessels and fuel types

The emission factors for PM, CO_2, and NO_x decrease with increasing engine load, which is to be expected given increase in fuel efficiency seen in Figure 18. However, the Tier III NO_x emission factors below 25% load increase drastically, whereas CO_2 and PM do not. To further investigate these findings, NO_x emission factors were calculated for every load point available on vessel 2 and graphed below in Figure 22.

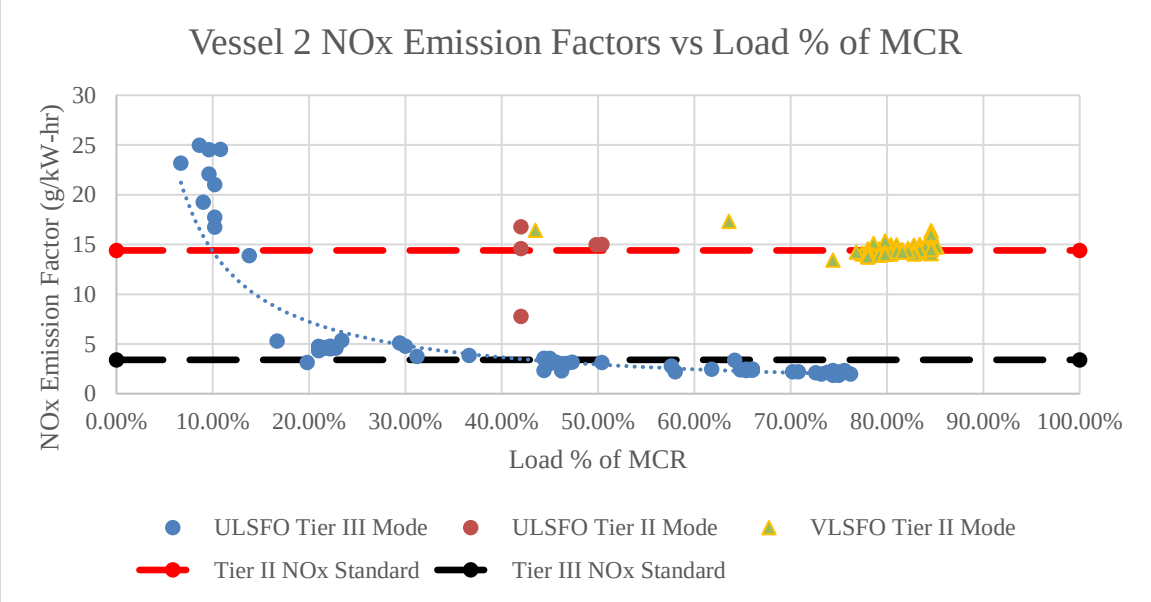


Figure 22. NO_x emission factors corresponding to all vessel load data for vessel 2

Below 20% engine load, NO_x emission factors in Tier III mode exceed the Tier III emission standard by a factor of up to 7.34. Those emission factors are also in exceedance of the Tier II standards by a factor of up to 1.73. the NO_x data shows a sharp increase at load points below 25%. To get a better understanding of the NO_x emissions in the transitional region near 25% load, NO_x emission factors for all real time engine data points from vessel 2 were calculated and graphed in Figure 22 above.

From this data, it can be inferred that the EGR ceases functioning at ~20% MCR. The ISO 8178-4 E3 certification cycle does not require weighting or reporting for loads below 25% MCR. This combination necessitated a closer look at the load points and NO_x emissions on the vessels while in operation. Data gathered between Oakland and Long Beach was used to highlight these impacts.

4.4.7 NO_x Emitted by Vessels Travelling Between Oakland and Long Beach

In order to assess the impact of <25% NO_x emissions, several aspects of the vessel operation must be considered. The primary feature is the amount of time the vessels operate above and below 25% MCR. This is dictated by the vessel schedules and the amount of cargo on-board during operation. Vessel 1 had a full cargo load when emission sampling was completed, but vessel 2 was operating with ballast plates only, no commercial cargo. This is reflected in the amount of time each vessel's main engine spent at different loads. Figures 8 below show the vessel with full cargo ran the main engine at higher loads for much longer, whereas the vessel with no cargo operated at lower loads to achieve the same distance in roughly the same amount of time.

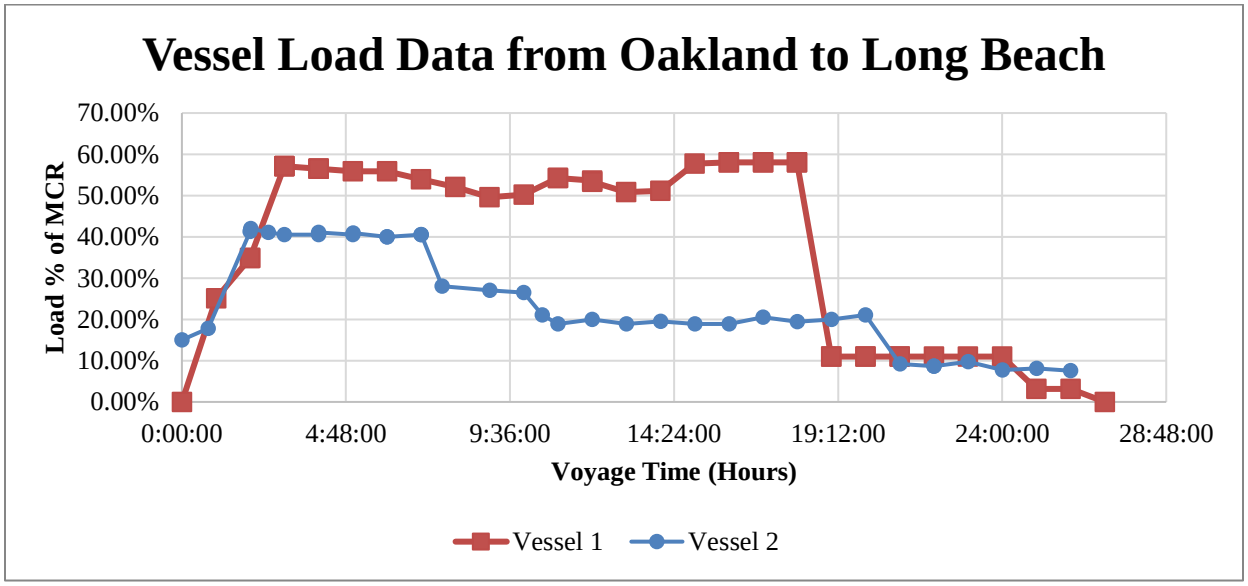


Figure 23. Real time vessel load data for both vessels while enroute from Oakland to Long Beach using absolute voyage time in hours on the x-axis

To quantify the significance of the off-cycle emissions, the total NO_x emitted above and below 25% MCR was calculated and compared for both vessels. Given that the test vessels have identical engines and build plans, and traveled the same route, the only differences between the data sets are a result of the amount of cargo. Thus, two data points for total emissions represent both extremes of the spectrum for NO_x emissions in Tier III OGVs using EGR as a NO_x control strategy. The results were calculated with Equation 5, from the previous section, and are summarized below in Table 19.

Table 19. Total NO_x Emissions Above and Below 25%

	Total Time Over 25% Load (hrs)	Total Time Under 25% Load (hrs)	Total NO_x Over 25% Load (kg)	Total NO_x Under 25% Load (kg)
Vessel 1	17	10	818	795
Vessel 2	8	18	381	860

The data clearly shows the significance of "off-cycle" emissions. For these voyages, the "off-cycle" emissions account for 49.3% of total NO_x for a vessel with cargo, and 69.2% of total NO_x without cargo. The impacts from these load points are currently unrepresented in the ISO 8178-4 E3 marine engine certification cycle.

4.5 Discussion

4.5.1 Discussion of emissions values at high load and at low loads

Although a certification process is intended to measure emissions that are representative of the operating cycle of an OGV, the vessel actually operates in two regimes: the open sea and the harbor. Most miles and emissions occur at sea and the percentage of time at various loads in the certification cycle is set accordingly when determining the overall emission factor. However, most of the personnel exposure is when vessels operate near the ports, and as explained earlier, when OGVs operate at <25% load, so called "off-cycle," where there are no data.

"Off-cycle" emissions have been a problem area for land-based vehicles, allowing some engine manufacturers to circumvent meeting emission standards below that operating point [25,26,27]. Instead, the vehicle engines are designed such that emissions meet certification criteria for loads in the test cycle, and operate with increased fuel efficiency and higher NO_x on the "off-cycle" points. Even in cases where there is no intent to defeat the certification process, there are still issues with using data from certification testing for inventory purposes rather than measuring the real world and actual emissions with CEMS. In at least two recent reports with properly certified engines, higher NO_x emissions were measured during real world operations:

- Dixit[28] et al. investigated the differences in emissions between urban driving and certification. The authors found a significant difference in NO_x emissions between engine manufacturers at low load and one certified design was found to be 10-times

higher NO_x than a certified engine from another manufacturer. Neither engine had a SCR installed so the difference was in the ECM design. They concluded: “These results have implications for scientists who build inventories using certification values instead of real-world emission values.”

- Tam[27] et al. monitored NO_x emissions from seventy-two heavy-duty diesel vehicles with a selective catalytic reduction (SCR) emissions control unit. Results showed that there were large differences between in-use and certification NO_x emissions, with twelve HDDVS emitting more than three times the standard. Another data set pointing to the need for real-world emission factors.

4.5.2 “Off-Cycle” Marine Data

It appears that a key issue in using certification data to develop inventories is that without actual real-world data, the estimates may have a larger degree of uncertainty than desired. One key problem with emissions from ships is estimating the emissions below 25% load. From experience with internal combustion engines, we know the engines are designed to operate with fuel efficiency where they are operated most of the time. Also, in that operating zone of the engine map, the engines meet emission standards. However, at low loads, experience has shown that efficiency is much lower and emissions per kW-hr are higher.

4.5.3 Unregulated or "Off-Cycle" Emissions

An important understanding of the certification process is to recognize that when OGVs operate below 25% power, the emissions of all pollutants are unregulated and without limits. Emissions from operation at <25% are often referred to as the "off-cycle" emissions and are known to exceed limits within the regulated/certified area. Furthermore, vessels must operate at low power when entering "go slow" zones or harbors where people are working and living. Earlier studies show that the emissions at low-power and below the 25% load are significantly higher than the standard as indicated in Figure 22. Similar findings were observed in on-road studies of heavy-duty trucks[25,26].

Table 20. Selected Data Showing NO_x Increase in EMFAC below 25% Load

Engine Size, kW	Reg standard	Cruise or ~ 25%	VSR	% increase
68,530	Tier I	16.8	26.4	157
36 740	Tier 0	19	25.2	133
15,750	Tier 0	~17	~22	129
1,902	Tier II	8.5	17.5	205
1,342	Tier II	7.7	11.0	143

4.6 Implications

The results of this study have exposed a great gap in understanding between policy makers, available technology, and real-world conditions. The existing policy and emissions standards succeed in minimizing the total emissions of OGVs, but fails to reduce human health impacts. Moreover, the technology enabling compression ignition (CI) engines to meet Tier III standards, does not stay engaged at low loads. When the Tier III aftertreatment is disengaged, the "off-cycle" NO_x emission factors are up to 7.3 times the Tier III standard and 1.7 times the Tier II standard. Worse yet, engine technology that poses a large risk factor to human health is being incentivized by the regulatory agencies. If the situation is left unchecked, OGV contributions to ports and harbors air pollution will resemble the contributions during or before the implementation of the Tier I emissions standards. This demands a paradigm shift in maritime emissions policy. Accounting for "off-cycle" emissions in the E-3 engine certification cycle, or developing a separate set of emissions standards in ports and harbors for loads lower than 25% MCR are the two most likely solutions.

Given that Tier III exhaust aftertreatment technology functions separately of the engine, there is some debate regarding the nature of disengaging the EGR at 20% load. Vessel engineering crews have reported to the author of this paper that the engines burn too inefficiently at lower loads with the EGR on, therefore it is turned off to prevent engine damage. Contrary to this, EGRs in light duty on-road vehicles are tuned to continue to functioning at engine idle. Regardless of where the responsibility lies for this, the certainty

of this situation is that there is no method to enforce vessel adherence to emission standards while in-use. The only way vessel emissions are directly measured from the exhaust stack are as part of campaigns or projects like the project described in this chapter. Given the logistics and collaboration necessary to accomplish a campaign of this type, it is unrealistic to discover that a vessel is intentionally operating in violation of the standards. This could be addressed by installing CEMS devices on OGV, including software to log CEMS data, and vessels digitally sharing voyage CEMS data periodically with the relevant compliance agencies either in their country of origin, or at port of call.

There are also regional implications of this work that are applicable to CARB. Given that the VSR zone near the Channel Islands extends the durations of "off-cycle" emissions to nearly 16 hours, and that Tier III engines have such a high "off-cycle" NO_x signal, regional air quality issues may become exacerbated in southern California coastal communities, pushing more areas out of attainment.

4.7 Future work

Following this, the real time NO_x and PM activity data gathered during sampling will be analyzed, and used to quantify the impacts of "off-cycle" emissions on human health at port, harbor, and coastal communities. The data from speciated VOC and PM samples, in conjunction with the data in this paper, will be used to construct a universal mole balance on the test engines. This will be the start of a Tier III OGV emissions inventory. Finally, the data from the auxiliary engines and boilers will be used in conjunction with the data in this paper to construct a holistic view of the emissions profile of newer build OGVs. This would differ from current practices in the field as the vessel will be treated as one system, as opposed to individual engines.

4.8 References

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5. Conclusions

There is a lot to be gleaned from the studies conducted in the process of this doctorate. Regarding indoor atmospheric chambers, efforts to minimize the wall losses and particle decay can be applied to other chambers in the field. The loss effects for the previous UCR reactor were far greater than other chambers of its type, and now the loss effects are far lower than any other chamber in the world. While many of the steps to mitigate surface charge were subjective, there are at least 3 aspects of that design strategy that could be broadly applied. The most versatile design element is the implementation of the soft x-ray. The device has no special requirements, and delivers x-rays at an intensity so low, that the reactor enclosure needed no special adaptations for installation or use. Taking extra steps to electronically insulate the chamber frame and infrastructure should also be a primary concern with any chamber design. While charge sources vary from chamber to chamber, the task of identifying possible sources and proceeding to isolate your system remain the same iterative process.

The conclusions that can be drawn about the marine emission field are far more involved and have a much higher level of accountability beyond the publications that work can generate. The most straightforward conclusions that can be drawn from that work are that more data needs to be gathered on OGV engines. The outright lack of deep-sea emissions data is indicative of a tremendous shortcoming for policymakers in an industry that accounts for 5% of the global fuel consumption, and nearly 25% of global NO_x. Moreover, a re-evaluation of the emission certification cycle for category 3 OGV

engines needs to be conducted. New emission factors that apply only the engine load points less than 25% need to be configured in order to minimize negative impacts to human health in coastal regions and regions adjacent to ports.

To ensure the integrity of vessel emissions standards is maintained by owners and operators, novel methods for emissions compliance enforcement must be devised. A larger study, perhaps in partnership with SCIPPER, needs to be conducted on the potential for CEMS units as a method for compliance enforcement. In that, there should be a cost benefit analysis of the cost of CEMS units weighted against the potential air quality benefits (including human health), as well as fines remitted to regional compliance enforcement agencies.

The final conclusion that can be drawn from the marine work is a reevaluation of the vessels eligible to take advantage of financially incentivized VSR zones. While VSR may still serve its original purpose for Tier 0, Tier I, and Tier II vessel, in Tier III diesel driven vessels, this practice does more harm in the NO_x contributions to regional air quality than good to the total production of CO_2.

6. Publications

Indoor Environmental Chamber Re-Design

1. "Next-Generation UCR 120- m^3Fixed-Volume Chamber – Experimental Characterization of Particle Wall-loss Using Monodisperse Seed Injections," (in preparation, expected to be published in 2023), Le et al. (2^{nd} author)
2. "A Novel Design for the UCR 120- m^3 Fixed-Volume Chamber," (in preparation, expected to be published in 2024), Eckel et al.

Vehicle Study

3. "Comparing SOA from E-10 and E-15 Blended Fuels ULEV and SULEV Vehicles," (in preparation, expected to be published in 2024), Eckel et al.
4. "Comparing POA from E-10 and E-15 Blended Fuels ULEV and SULEV Vehicles," (in preparation, expected to be published in 2023), Tang et al. (2^{nd} author)

OGV Primary Emissions

5. "Tier III NO_x Standards for Ocean Going Vessels: Reducing At-Sea Emissions While Failing to Protect Port Air Quality," (in preparation, expected to be published in 2023), Eckel et al.

6. “Full Spectrum Emissions Profiles for New Build Tier 3 Commercial Marine Vessels,” (in preparation, expected to be published in 2024), Eckel et al.
7. “Comparing Tier 3 and Tier 2 Commercial Marine Vessel Emissions Profiles: Benefits of a New Technology Class,” (in preparation, expected to be published in 2024), Eckel et al.
8. “Analysis of the Current Regulatory Compliance Models Utilized by CARB, EPA, and MARPOL to Determine Overall Emission Factors for Marine Emissions,” (in preparation, expected to be published in 2024), Eckel et. al.
9. “Applying Real-Time On-Board Emissions Measurements and GIS Data to Evaluate the Applicability of AIS-based Emissions Inventory Estimates of Ocean-Going Vessels,” (in preparation, expected to be published in 2023), Drover et. al. (2nd Author)
10. “Evaluating “In-Use” Emissions from a Dual Boiler, Steam Turbine Driven Ocean-Going Vessel,” (in preparation, expected to be published in 2023), Eckel et. al.
11. “Holistic emissions profile of a Category 3 Container Ship While At-Sea”