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Technical note

In-use gaseous and particulate matter emissions from a modern ocean going container vessel

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Abstract

Ocean going vessels are one of the largest uncontrolled sources of pollutants and the emissions data from these sources are scarce. This paper provides the emission measurements of gases, particulate matter (PM), metals, ions, elemental and organic carbon, conducted from the main engine of an ocean going PanaMax class container vessel, at certification cycle and at vessel speed reduction mode, during actual operation at sea. The weighted emission factor ($g\,kW^{-1}\,h^{-1}$) of PM and NO_x were 1.64 and 18.2, respectively, for the main engine operating on a 2.05 wt% sulfur heavy fuel oil (HFO). The NO_x emissions at the vessel speed reduction mode (8% of full load) are 30% higher than at 52% engine power, the normal cruise speed. The composition of PM, from main engine is dominated by sulfate and water bound with sulfate (about 80% of total PM) and organic carbon constitutes about 15% of the PM. Sulfur, vanadium and nickel are the significant elements in the exhaust from the engine running on the HFO. At the point of sampling 3.7–5.0% of the fuel sulfur was converted to sulfate.

Keywords: Ship; Emissions; Main engine; Particulate matter; Elemental carbon; Organic carbon; Sulfate; Ocean going vessel; Heavy fuel oil; Vessel speed reduction

1. Introduction

Ships are a significant source of particulate matter (PM), sulfur oxides (SO_x) and nitrogen oxides (NO_x) emissions in many areas of the world (Corbett and Fischbeck, 1997). The high levels of PM and SO_x emissions from slow-speed marine diesel engines are primarily associated with high levels of sulfur in the heavy fuel oil (HFO), used in these engines. The fuel sulfur, during combustion, is oxidized into different oxides of sulfur, mainly SO_2 and SO_3, typically in ratio of 15:1 (MAN B&W, 2004). NO_x are formed when fuel nitrogen and nitrogen in air react with oxygen at high temperatures in the burning fuel spray (MAN B&W, 2004). Particulate emissions in the exhaust originate from a number of sources like agglomeration of very small particles of partly burned fuel, partly burned lubricating oil, ash content of fuel oil and cylinder lubricating oil, sulfates and water (Heywood, 1988).

A few studies in past have focused on developing emission inventories from the low-speed marine diesel engines (ENTEC, 2002; Lyyranen et al., 1999; Chen et al., 2002; Sinha et al., 2003; Petzold et al.,

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2004, 2007; Kasper et al., 2007). Recently, Petzold et al. (2007) measured microphysical and chemical properties in the exhaust gas of a four-stroke marine diesel engine under various load conditions. Kasper et al. (2007) have presented results from tail pipe emissions of PM from a two-stroke marine diesel engine from a test rig study. Corbett and Koehler (2003) published a comprehensive study on emissions from marine engines focusing on gaseous emissions. ENTEC (2002) presents a comparison of various services data for main engine marine emission factors. Measurement of emissions from ship plume studies by researchers in past (Chen et al., 2002; Sinha et al., 2003) provides additional insight into particle number and gaseous emission factors from diesel powered ships.

Currently, the US Environmental Protection Agency (EPA) offers only limited guidance regarding the development of port emission inventories. Many current emission inventories suffer from poor quantification of port activity and use of outdated emission factors to assess the impact of ports on regional and global air qualities (USEPA, 2006).

Few engine studies which have contributed to emissions data from slow-speed marine diesel engines have been performed either on engine test rigs or are plume measurement studies. While the emissions data presented in these studies give insight into the emissions profile of low-speed marine diesel engines, the current study focuses on developing emission factors for in-use marine diesel engine, during its actual operation at sea.

This study presents the emission factors of various gases and speciated PM from the main engine (low-speed, two-stroke marine diesel engines) of an ocean going container vessel. Measurements were made while the main engine operations approximated the modes in the ISO 8178 E-3 (ISO 8178-1, 1996) certification test cycles and while the vessel followed the voluntary vessel speed reduction (VSR) program implemented by the California Air Resources Board (CARB) (CARB, 2001). Emission factors from this study should be helpful in developing emission models and inventory calculations.

2. Experimental methods

2.1. Engine description

The sampling was conducted on a PanaMax class container ship equipped with one main engine: a MAN B&W Model 11K90MC-C. This is a large two-stroke, slow-speed engine of the MC generation. The engine was manufactured in 1995 and is rated at 50,270 kW and 104 rpm.

2.2. Fuel properties

The main engine burned HFO meeting ISO 8217 specifications (ISO 8217, 2005). Fuel was typical of normal supply. A fuel sample was obtained during the course of the emissions testing. A 1 liter fuel sample was drawn from the main engine final filter drain, immediately upstream of the injector rail. This sample was subsequently analyzed for a number of fuel properties. Selected data from the analysis of fuel are presented in Table 1.

2.3. Test cycle

The "in-use" emission testing in this study was carried out with the engine operating on a vessel during an actual sea voyage. The emissions were measured while following the modes for the ISO certification cycle (ISO 8178-4, 1996). These emissions data would verify that the engine was operating at design and values from these tests could be compared with certification data from similar sources. Testing for the main engine followed the EPA guidance and the ISO 8178-E3 four-mode test cycle, except that testing was not carried out at the 100% power due to practical limitations. The actual achievable load points were determined at the time of testing which depends on several factors; including operational constraints, sea current, wave pattern, wind speed/direction, and cargo load. Efforts were made to conduct the emissions measurements at loads as close as possible to those specified in ISO 8178-E3. The testing was conducted at the 8%, 27%, 52%, 63% and 70% of the full engine load. The engine load in this study is determined from the engine computer. The 8%

Table 1
Selected fuel properties

Fuel type	HFO
Density ($kg\,m^{-3}$) at 15 °C	990.8
Viscosity ($mm^2\,s^{-1}$) at 50 °C	296.8
Micro-carbon residue ($\%m\,m^{-1}$)	14.5
Sulfur ($\%m\,m^{-1}$)	2.05
Ash ($\%m\,m^{-1}$)	0.072
Vanadium ($mg\,kg^{-1}$)	259
Nickel ($mg\,kg^{-1}$)	26

engine load corresponds to VSR (CARB, 2001). Engine operating conditions are presented in Table 2.

2.4. Sampling and analysis

The methods for sampling and analysis of the gases and PM conformed to the requirements of ISO 8178-1 1996. The approach involved the use of a partial flow dilution system with single venturi as shown in Fig. 1. In the present study no transfer tube was used for the sampling. The sampling train was flushed with exhaust air for 2 min before each run. The concentrations of CO_2 or NO_x were measured in the raw exhaust gas and the diluted gas in the dilution tunnel using the exhaust gas analyzer (EGA), to determine the dilution ratio. The dilution ratio determined from CO_2 and NO_x concentrations, agreed within 5%, well within the 10% specified in the reference method (ISO 8178-1, 1996).

Table 2
Engine operating conditions

Load (%)	8%	27%	52%	63%	70%
Load (kW)	4013	13,545	26,088	31,607	35,119
Speed (rpm)	49.2	73.0	91.0	98.1	101.8

Emission measurements of different gases, $PM_{2.5}$ mass, metals, ions, elemental and organic carbon were performed.

2.5. Measurement of gases

The concentrations of gases in the raw exhaust and the dilution tunnel were measured with a Horiba PG-250 portable multi-gas analyzer. For quality control, analyzer checks with calibration gases both before and after each test were made to check for drift. The SO_2 gas data provided in this paper are calculated from the sulfur level in the fuel as suggested by the certification method in ISO 8178.

2.6. Measurement of particulate matter (PM) mass, metals and ions

The mass concentrations of $PM_{2.5}$, metals and ions were acquired by analysis of particulates collected on 47-mm diameter 2 μm 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

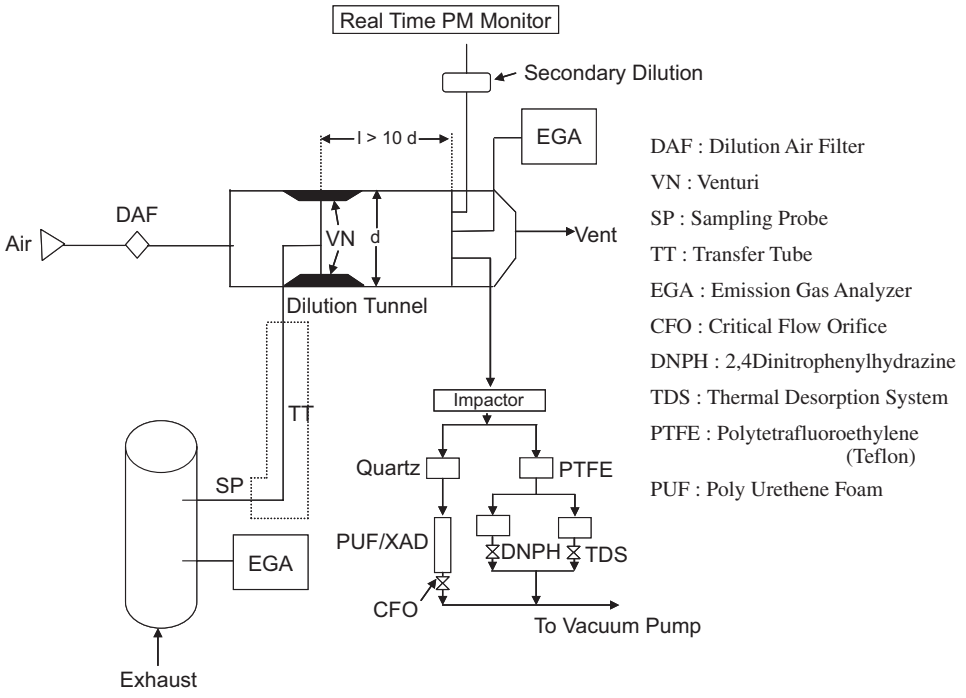

Fig. 1. Flow diagram of the sampling system.

procedure guidelines of the Code of Federal Regulations (CFR). Before and after collection, the filters were conditioned for 24 h in an environmentally controlled room (RH = 40%, $T = 25\,^{\circ}C$) and weighed daily until two consecutive weight measurements were within 3 μg.

The Teflo filters were subsequently analyzed for metals using XRF method as per EPA IO-3 at an outside laboratory. Finally, the filters were extracted with HPLC grade water and isopropyl alcohol and analyzed for the sulfate ions using a Dionex DX-120 ion chromatograph.

2.7. 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 (1996) reference method.

3. Results and discussion

Measurements were conducted in triplicate, consecutively, and the results are presented in following section. Typical dilution ratio achieved range from five to six. The emission factors presented in this study are corrected for temperature and humidity.

3.1. Gaseous emissions

The major gaseous emissions of interest in the exhaust were: CO_2, CO, SO_2 and NO_x. Emissions of CO were low as expected for diesel engines. The results of gaseous emissions factors for CO_2, CO, NO_x and SO_2 (calculated based on fuel sulfur content) in terms of $g\,kW^{-1}\,h^{-1}$ are presented (Table 3). The coefficient of variation for the gases was typically 3%.

In May 2001, a Memorandum of Understanding (MOU) between the Ports of Los Angeles and Long Beach (POLA/POLB) and various other agencies was signed requesting OGVs to voluntarily reduce their speed to 12 knots at a distance of 20 nautical miles from POLA/POLB. It was expected that in doing so, significant reduction in NO_x could be achieved. The emission factors developed for the vessel studied show that the NO_x emissions when the vessel is running at VSR mode are around 30% higher than the emissions at 52% of full load, because these engines are running less efficiently at low loads.

Table 3
Emission factor of different gases for main engine

Load (%)	CO_2 ($g\,kW^{-1}\,h^{-1}$)	SO_2 ($g\,kW^{-1}\,h^{-1}$)	CO ($g\,kW^{-1}\,h^{-1}$)	NO_x ($g\,kW^{-1}\,h^{-1}$)
8 (VSR)	660	8.60	1.78	20.96
27	588	7.66	1.81	15.84
52	613	7.99	0.87	16.40
63	643	8.37	0.81	17.85
70	658	8.57	0.77	18.89

Table 4
Emission factor ($g\,kW^{-1}\,h^{-1}$) of PM and speciated PM for main engine

Load (%)	PM	EC	OC	$H_2SO_4 \cdot 6.5H_2O$	Ash
8	1.699	0.029	0.498	1.071	0.123
27	1.091	0.016	0.286	0.946	0.123
52	1.386	0.017	0.281	1.257	0.123
63	1.660	0.020	0.254	1.370	0.123
70	1.757	0.017	0.259	1.495	0.123

3.2. Particulate matter ($PM_{2.5}$) emissions

About 80% of the PM is primarily composed of sulfate and water bound with sulfate and the reminder is organic carbon, elemental carbon and the trace chemical elements in the fuel and lubricating oil. The emission factor of PM is presented (Table 4) as a function of the engine load. The PM emissions from these low-speed marine diesel engines vary less with the engine load.

3.3. Speciated PM emissions

There are few data from low-speed marine diesel engines where the PM mass is fractioned into its major constituent groups: sulfate, organic carbon, elemental carbon and ash. The HFO (2.05 wt% S) is associated with the large sulfate emissions from these engines. The results show that 3.7–5% of the fuel sulfur was converted to sulfate for the main engine at the point of sampling. The remaining PM is composed of organic carbon, elemental carbon and ash. The organic carbon levels are greater than ten times of the elemental carbon emissions for the

Table 5
Emissions ($g\,kW^{-1}\,h^{-1}$) of various elements as a function of engine load

Load (%)	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr
8	2.09E−03	1.15E−02	<1.61E−03	2.19E−03	1.87E−01	<9.39E−05	<2.68E−05	4.96E−03	1.30E−04	5.36E−02	<2.68E−05
27	<1.18E−03	8.76E−03	<1.18E−03	1.63E−03	1.35E−01	<6.90E−05	<1.97E−05	4.01E−03	1.74E−04	4.41E−02	<1.97E−05
52	<9.65E−04	1.07E−02	<9.65E−04	4.09E−03	1.62E−01	< 5.63E−05	<1.61E−05	4.76E−03	8.74E−05	4.65E−02	<1.61E−05
63	<1.10E−03	1.34E−02	<1.10E−03	2.85E−03	2.07E−01	< 6.44E−05	<1.84E−05	4.75E−03	1.15E−04	5.26E−02	<1.84E−05
70	<1.12E−03	1.72E−02	<1.12E−03	6.56E−03	2.52E−01	< 6.52E−05	8.94E−05	5.11E−03	1.49E−04	5.60E−02	<1.86E−05
Load (%)	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Rb
8	<1.34E−05	2.84E−03	1.46E−04	1.20E−02	9.66E−05	1.29E−04	3.25E−04	< 2.68E−05	< 6.71E−06	<2.68E−05	<1.34E−05
27	<9.85E−06	2.58E−03	1.20E−04	9.65E−03	6.11E−05	1.02E−04	<4.19E−04	7.09E−05	< 4.02E−06	<1.97E−05	<9.85E−06
52	<8.04E−06	2.15E−03	1.36E−04	1.04E−02	4.89E−05	9.23E−05	1.06E−04	< 1.61E−05	< 4.60E−06	<1.61E−05	<8.04E−06
63	<9.20E−06	3.48E−03	1.70E−04	1.16E−02	5.52E−05	9.85E−05	1.77E−04	< 1.84E−05	< 4.66E−06	<1.84E−05	<9.20E−06
70	<9.31E−06	3.89E−03	1.76E−04	1.27E−02	1.01E−04	1.43E−04	<3.96E−04	< 1.86E−05	< 4.02E−06	<1.86E−05	<9.31E−06
Load (%)	Sr	Y	Mo	Pd	Cd	In	Sn	Sb	Ba	La	Pb
8	6.44E−05	<6.71E−06	1.86E−04	<4.02E−05	8.90E−05	1.45E−04	1.13E−04	4.02E−04	3.07E−04	1.61E−04	<6.71E−05
27	<1.97E−05	<4.02E−06	1.14E−04	<2.96E−05	<1.97E−05	2.09E−04	<2.96E−05	2.28E−04	2.93E−04	4.18E−04	<4.02E−05
52	2.94E−05	<4.60E−06	1.22E−04	<2.41E−05	<1.61E−05	1.31E−04	<2.41E−05	1.75E−04	3.02E−04	2.80E−04	<4.60E−05
63	<1.84E−05	<4.66E−06	1.48E−04	<2.76E−05	7.65E−05	9.89E−05	8.68E−05	2.24E−04	1.74E−04	1.53E−04	<4.66E−05
70	4.47E−05	<4.02E−06	1.60E−04	5.59E−05	5.59E−05	1.88E−04	1.10E−04	2.48E−04	4.04E−04	2.50E−04	<4.02E−05

low-speed marine diesel engine. The OC and EC emission factors presented (Table 4) can be used for source apportionment research. The ash component was calculated from the ash content in the fuel and the brake-specific fuel consumption was assumed constant (171 g kW^{-1} h^{-1}) as a function of engine load.

The emission factors of different elements analyzed are presented (Table 5). Sulfur is the most dominant element in the exhaust, followed by vanadium and nickel (Fig. 2), which are associated with the HFO.

An important element in this analysis is the QA/QC that checks that total mass is conserved for the various PM methods. Specifically, the total mass collected on Teflon filter is compared with the sum of the masses independently measured as hydrated sulfate ($H_2SO_4 \cdot 6.5H_2O$), EC, OC and calculated ash (Fig. 3).

3.4. Comparison of the measured data

The measured emission factors were weighted according to the specification in ISO 8178 test cycles. USEPA (2006) and CARB estimate the emission factors of PM based on brake-specific fuel consumption. The weighted emission factors measured in this study are comparable to Lloyds

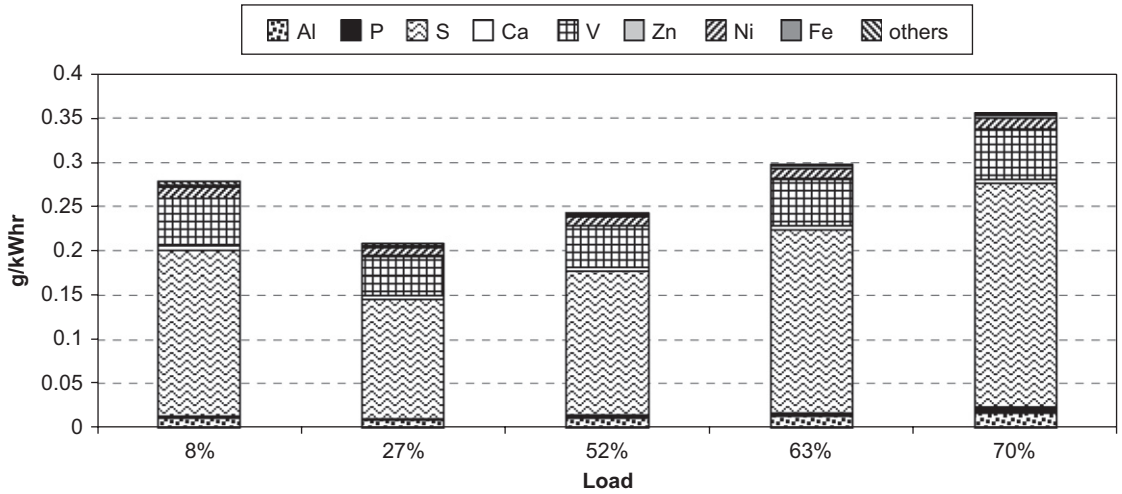

Fig. 2. Emission factors of different elements as a function of engine load.

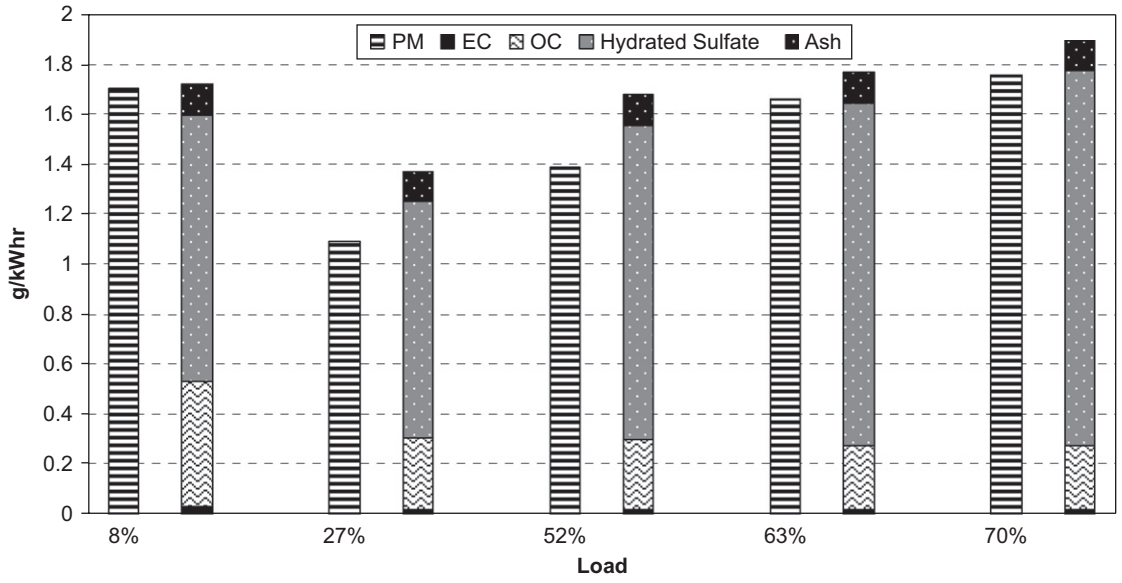

Fig. 3. PM speciation.

Table 6
Comparison of the measured emission factors with the literature and estimates by regulatory agencies

	Units	Measured (weighted)	Llyods services data	USEPA Efs	CARB Efs
NO_x	$g\,kW^{-1}\,h^{-1}$	18.21	18.7	18.1	18.1
PM	$g\,kW^{-1}\,h^{-1}$	1.64	1.23	1.08	1.5
SO_2	$g\,kW^{-1}\,h^{-1}$	8.39	–	10.3	10.5

services data (ENTEC, 2002) and the emission factor estimates by USEPA and CARB (Table 6). The chemical composition in % PM of EC, OM, sulfate and water bound with sulfate, in this study compares well with Petzold et al. (2007).

4. Conclusions

Exhaust sampling at sea was successfully conducted for the main engine of a PanaMax class container vessel running on HFO. Emission factors for different gases, $PM_{2.5}$ mass, metals, ions, elemental and organic carbon are presented in this study. The measured emission factors in this study compares well with the emission estimates by various regulatory agencies. The speciated PM data provided in this study is useful for source apportionment studies. There exists very few emission measurements data from in-use Ocean going vessels (Emissions Estimation Methodology for Ocean-Going Vessels, 2005), and more studies like as-presented can improve the emissions inventory and aid in understanding the profile of emissions.

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References

California Air Resources Board (CARB), 2001. Vessel Speed Reduction (VSR) for Ocean Going Vessels, ⟨http://www.arb.ca.gov/ports/marinevess/vsr/vsr.htm⟩.

Chen, G., Huey, G., Trainer, M., et al., 2002. An investigation of the chemistry of ship emission plumes during ITCT. Journal of Geophysical Research 110, D10S90.

Code of Federal Regulations. Protection of the Environment, 40 CFR 86.

Corbett, J.J., Fischbeck, P.S., 1997. Emissions from ships. Science 278 (5339), 823–824.

Corbett, J.J., Koehler, H., 2003. Updated emissions from ocean shipping. Journal of Geophysical Research 108, 4650.

Emissions Estimation Methodology for Ocean-Going Vessels, 2005. California Air Resources Board. ⟨http://www.arb.ca.gov/regact/marine2005/appd.pdf⟩.

Entec UK Limited, 2002. Quantification of Emissions From Ships Associated with Ship Movements Between Ports in the European Community. European Commission, July 2002.

Heywood, J.B., 1988. Internal Combustion Engine Fundamentals. McGraw-Hill, New York.

International Standards Organization, ISO 8178-1, Reciprocating Internal Combustion Engines—Exhaust Emission Measurement—Part 1: Test-bed Measurement of Gaseous Particulate Exhaust Emissions, first ed., 1996-08-15.

International Organization for Standardization. 1996. first ed. ISO 8178-4.

ISO 8217, 2005. Petroleum Products–Fuels (classF)–Specifications of Marine Fuels. ISO 8217:2005(E).

Kasper, A., Aufdenblatten, S., Forss, A., Mohr, M., Burtscher, H., 2007. Particulate emissions from a low-speed marine diesel engine. Aerosol Science and Technology 41, 24–32.

Lyyranen, J., Jokiniemi, J., Kauppinen, E.I., Joutsensaari, J., 1999. Aerosol characterisation in medium-speed diesel engines operating with heavy fuel oils. Journal of Aerosol Science 30, 771–784.

MAN B&W Diesel. 2004. Emission Control: MAN B&W Two-Stroke Diesel Engines. Copenhagen, 2004. ⟨www.manbw.com⟩.

NIOSH, 1996. NIOSH Manual of Analytical Methods. National Institute of Occupational Safety and Health, Cincinnati, OH.

Petzold, A., Feldpausch, Ph., Fritzsche, L., Minikin, A., Lauer, P., Kurok, C., Bauer, H., 2004. Particle emissions from ship engines. Journal of Aerosol Science, Abstracts of the European Aerosol Conference, S1095–S1096.

Petzold, A., Hasselbach, J., Lauer, P., Baumann, R., Franke, K., Gurk, C., Schlager, H., Weingartner, E., 2007. Experimental studies on particle emissions from cruising ship, their characteristic properties, transformation and atmospheric lifetime in the marine boundary layer. Atmospheric Chemistry and Physics Discussion 7, 15105–15154.

Sinha, P., Hobbs, P.V., Yokelson, R.J., Christian, T.J., Kirchstetter, T.W., Bruintjes, R., 2003. Emission of trace gases and particles from two ships in the southern Atlantic Ocean. Atmospheric Environment 37, 2139–2148.

USEPA 2006, Current Methodologies and Best Practices in Preparing Port Emission Inventories—Final Report, vol. 5 ⟨http://www.epa.gov/sectors/ports/bp_portemissionsfinal.pdf⟩.