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Emission Measurements from a Crude Oil Tanker at Sea

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This work presents an all-inclusive set of regulated and nonregulated emission factors for the main propulsion engine (ME), auxiliary engine (AE) and an auxiliary boiler on a Suezmax class tanker while operating at sea. The data include criteria pollutants (carbon monoxide, nitrogen oxides, sulfur oxides, and particulate matter), a greenhouse gas (carbon dioxide), the principal speciated hydrocarbons needed for human health risk assessments, and a detailed analysis of the PM into its primary constituents (ions, elements, organic, and elemental carbon). Measurements followed ISO 8178-1 methods with modifications described in the paper. The vessel burned two fuels: a heavy fuel oil in the ME and boiler and a distillate fuel in the AE. The weighted NO_x emissions for the ME and AE are 19.87 ± 0.95 and 13.57 ± 0.31 g/kWh, respectively. The weighted PM mass emissions factor is 1.60 ± 0.08 g/kWh for the ME and 0.141 ± 0.005 g/kWh for the AE, with the sulfate content of the PM being the root cause for the difference. For the ME, sulfate with associated water is about 75% of total PM mass, and the organic carbon ranges from 15 to 25% of the PM mass. A deeper analysis showed that the conversion of fuel sulfur to sulfate in the ME ranged from 1.4 to 5%. This article also provides emission factors for selected polycyclic aromatic hydrocarbons, heavy alkanes, carbonyls, light hydrocarbon species, metals, and ions for the ME, AE, and the boiler.

Introduction

Emissions from diesel engines are of concern to the health communities, and many investigators have reported the emissions of regulated and other compounds from diesel engines (1–4). Ocean-going vessels (OGVs) are a significant and growing source of diesel emissions to the local and global environments (5–10), yet emission factors from operating vessels are scarce, and limited progress has been made toward reducing these emissions (11, 12). In the past 15–20 years, air pollution from other transportation sources has reduced significantly across the world (5, 13). For example, the use of advanced engine and emission control technologies has resulted in the exhaust from new vehicles being 90% cleaner than they were 10–20 years ago (14). However, emission

reductions from OGVs lag behind other transportation sources, resulting in OGVs as one of the largest anthropogenic sources of air pollution in many areas of the world (5–7).

Concerns have been raised about the levels of sulfur dioxide (SO₂), nitrogen oxides (NO_x), and PM emissions released into the atmosphere from slow- and medium-speed marine diesel engines. Recent estimates indicate OGVs represent approximately 9% of global SO_x emissions and 18–30% of the world's NO_x pollution (15). Sulfur from the fuel is oxidized in the combustion chamber to SO₂ and SO₃, typically in a ratio of 15:1 (11). Nitrogen oxides (NO_x) are formed when fuel nitrogen and nitrogen in air react with oxygen at high temperatures in the burning fuel spray. A first-order approximation shows a 100 °C increase in combustion temperatures may increase NO_x emissions by a factor of 3 (11). Particulate emissions in the exhaust gas originate from agglomeration of very small particles of partly burned fuel, partly burned lube oil, the ash content of fuel oil and cylinder lube oil, sulfates, and water (16).

Currently, the U.S. 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 for assessing the impact of ports on regional and global air quality (17). Various studies (17–31) have focused on developing emission inventories from OGVs. Recently, Petzold et al. (26) measured microphysical and chemical properties in the exhaust gas of a four-stroke marine diesel engine under various load conditions. Kasper et al. (20) presented results for emissions of particulate matter from a turbocharged common rail two-stroke marine diesel engine. Corbett and Koehler (15) published gaseous emissions from marine engines. Cooper et al. (8, 21–23) carried out emission measurements from main engines of ferries and various auxiliary engines and reported emissions data for speciated hydrocarbons. Lloyd's Register of Shipping has performed testing of multiple engines to determine emission factors for the principal marine diesel engine exhaust emission species (29–31). Measured emissions from ship plumes reported by researchers (27, 28) provide insight into particle number and gaseous emission factors. In addition to the regulated emissions, there is a widespread interest in hydrocarbons species because these compounds are often included in the human health risk assessment for people living near the ports.

Many of the emission studies (20, 24–26, 29–31) for slow- and medium-speed marine diesel engines were carried out with the engine on test rigs. In this research, the data were gathered at sea while the tanker was operating at the certification load points and during typical operation. Typical operation included maneuvering and sailing at 12 knots in and out of the harbor as a part of a voluntary vessel speed reduction program (32). Testing and emissions measurements took place over a 3-day period.

Experimental Methods

Engine Description. The sampling was conducted on a Suezmax class vessel equipped with one main propulsion engine, three auxiliary engines, and an auxiliary boiler with three burners. Table 1 provides information about the test engines. The boiler type was ADM-707, weighing 70.2 tons. The maximum evaporation rate was 70 000 kg/h, and the working pressure and temperature were 16 kg/cm² and 203.4 °C, respectively.

Fuel Properties. Two fuels were used during the testing. The main engine and the boiler burned heavy fuel oil (HFO)

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TABLE 1. Properties of Test Engines

source	manufacturer/model	serial no.	power, kW	technology	maximum RPM
main engine	Sulzer 6RTA72	MS08.799/800	15 750	2-stroke	90
auxiliary engine no. 3	Wartsila Vasa 6R22/26 spec. no. 17327	5759	900	4-stroke	1200
auxiliary boiler	IHI, 2-drum-type steam generator with heating surface of 679 m ²				

with 2.85 wt % sulfur and 0.04 wt % ash content, and the auxiliary engine burned marine gas oil with 0.06 wt % sulfur and 0.01 wt % ash content. One-liter samples were drawn from the main engine and auxiliary engine final filter drains, immediately upstream of the injector rail, for subsequent analysis. Both fuels met DNV specifications, (33) and detailed fuel analyses are reported in the Supporting Information.

Test Cycles. Emissions from a diesel engine strongly depend on the load and RPM of the engine. Therefore, two sets of operating conditions were used. The first approach measured emissions while the engine followed the steady-state certification load points, as outlined in ISO 8178 (34). These data allowed the engine manufacturer to verify the engine was operating near design. This provided credibility that the nonregulated values were also representative of a normal engine. For the main engine, testing followed the ISO 8178-E3 four-mode test cycle, except that testing was not carried out at the 100% power due to practical limitations.

Additional mode points were acquired at 85% load, the maximum practical steady power, and 13% load, since the vessel spent a considerable percentage of time at this load point. Measurements for the auxiliary engine were made as per the ISO 8178-D2 cycle, except for the 100% power. The test cycles and test schedules are provided in the Supporting Information.

The second set of operating conditions measured gaseous and PM emissions in real time and continuously while the engines followed typical operating conditions. The current state of knowledge concerning the transient nature and magnitude of marine “real world” emission data is scarce, so exploratory measurements were conducted during startup, sailing from the harbor following the vessel speed reduction (32) at 12 knots, maneuvering and operating at various speeds at sea. In addition to testing the diesel engines, emissions were measured from the boiler with all three burners

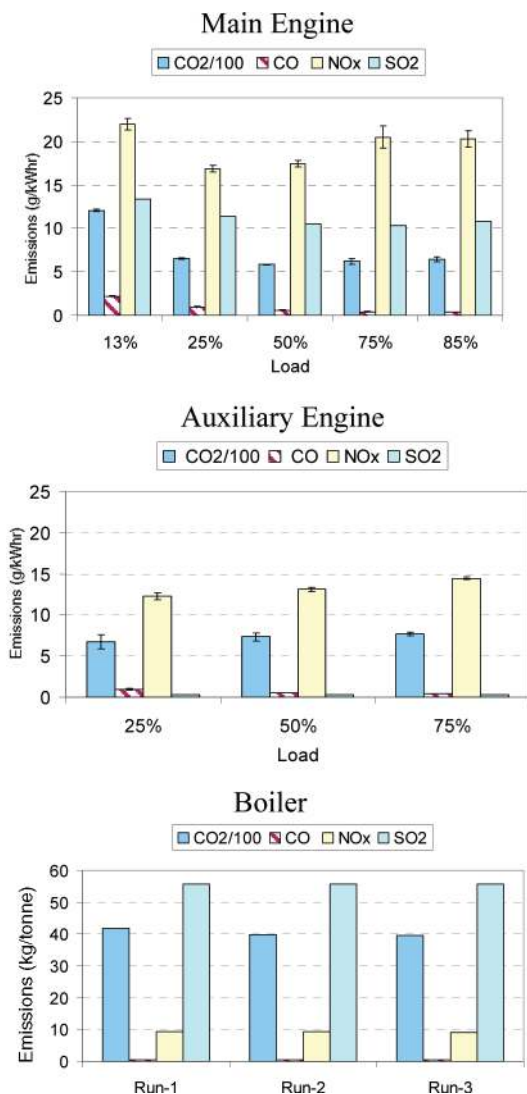


FIGURE 1. Emission factors of different gases for the main engine, the auxiliary engine, and the boiler.

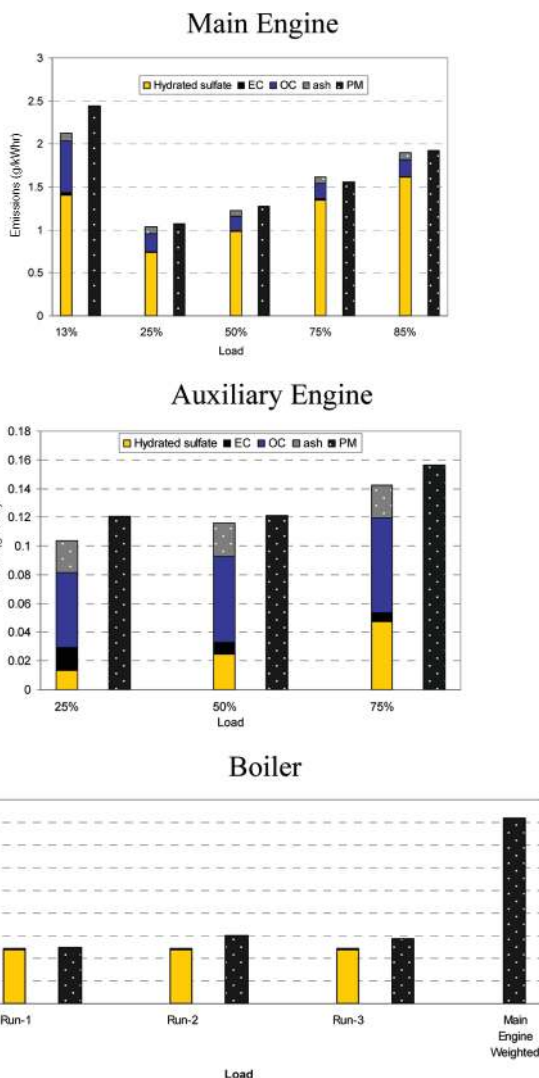


FIGURE 2. Emission factors of PM, EC, OC, ash, and hydrated sulfate (H₂SO₄·6.5H₂O) for the main engine, auxiliary engine, and the boiler.

operating at the maximum firing rate and reflective of when the vessel is discharging crude oil from the tanker.

Sampling and Analysis. The methods for sampling and analysis of the gases and particulate matter (PM) conformed to the requirements of ISO 8178-1 (34). The approach involved the use of a partial flow dilution system with single venturi (Figure S1 of the Supporting Information). Although ISO 8178-1 allows a transfer line of 5 m, no transfer line was used in this research. The concentrations of CO₂ or NO_x were measured in the raw exhaust gas and diluted gas streams using an exhaust gas analyzer. The dilution ratio was determined from both the CO₂ and NO_x raw and dilute concentrations, and the dilution ratios agreed within 5%, as specified in the reference method (34).

Nonregulated emission measurements for different gases; PM_{2.5} mass; metals; ions; elemental and organic carbon; and selected hydrocarbon species, including PAHs, carbonyls, and *n*-alkanes were performed following methods that are described in detail in the Supporting Information. The real time PM measurements with a Dekati mass monitor (35) were performed during actual tanker activity.

Results

Emission results for the main and auxiliary engines during the modal tests are reported as grams per kilowatt-hour (g/kWh) using the concentration of the measured species, the recorded engine load, and the calculated flow rate. The calculated flow rate assumed the engine operated as an air pump and used recorded values for RPM and scavenger air pressure and temperature. The load points, corresponding RPM values and scavenger properties, are provided in the Supporting Information. Emission factors for the gases and PM were sent to the engine manufacturer, who verified the values were representative for an engine running near design.

Emissions rates for the auxiliary boiler at full power and the exploratory continuous measurements of gases and PM from the main engine can only be reported on a fuel-specific basis (grams per gram or kilogram of fuel or carbon dioxide) since flow or load information was not available. The real time traces of PM, NO_x, and CO₂ concentrations during transient operations in leaving the harbor, including maneuvering, are presented in the Supporting Information.

In addition to the modal emission factor, an overall emission factor is calculated using the methodology and weighting factors specified in ISO 8178 E3 for the main engine and ISO 8178 D2 for the auxiliary engine.

Gaseous Emissions. In this study, the concentration of carbon dioxide (CO₂), carbon monoxide (CO), and nitrogen oxides (NO_x) were measured, and the concentration of sulfur dioxide (SO₂) was calculated from the sulfur in the fuel as per ISO 8178-4. Modal data for the engines and for the boiler at full power are presented in Figure 1. The results show gaseous emissions dominated by CO₂ and NO_x with emissions of CO low, as expected. Since triplicate measurements were made at each point, the error bars indicate the confidence limits.

Of particular interest was the modal emission rate at 12 knots. In May 2001, a Memorandum of Understanding between the Ports of Los Angeles and Long Beach (POLA/POLB) and others (32) was signed requesting OGVs to voluntarily reduce their speed to 12 knots at a distance of 20 nautical miles from POLA/POLB to reduce the overall NO_x emissions. For this vessel, the 12 knots speed corresponded to 50% engine load, which is an efficient operating zone for the diesel engine. However, these values should not be used for container ships. Modern container ships often have ME about 60 MW engines for which the 12 knot speed corresponds to an 8–13% engine load. Emission rates of NO_x and PM per kWh on the container ship would be much higher than the values measured at 50% power (38) in this study.

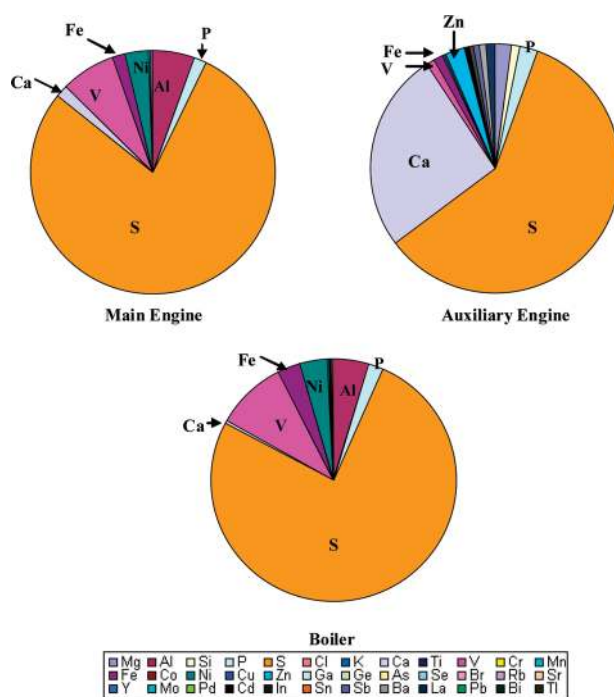


FIGURE 3. Relative weighted emission factors of various trace elements.

Particulate Matter (PM_{2.5}) Emissions. Understanding the mass and composition of PM from marine engines and boilers was a critical goal for this research, since data are scarce. Results in Figure 2 provide emission factors for particulate matter mass and the mass speciated into elemental and organic carbon (EC/OC), ash, and hydrated sulfate (H₂SO₄·6.5H₂O). Results from the main engine's burning the high-sulfur fuel show the PM mass is primarily hydrated sulfate, a moderate amount of organic carbon (OC), and small amounts of elemental carbon and ash. The auxiliary engine emissions are about 10% of those of the main engine, largely due to the use of a lower-sulfur distillate fuel. Emissions from the boiler are predominately sulfate and lower than the weighted main engine value when reported on the same basis. In these charts, the OC positive artifact was assumed to offset hydrogen and oxygen content of the organic mass, on the basis of previous research (36).

An important quality element designed into the analysis was a check of whether the total PM mass was conserved. Specifically, the total mass collected on the Teflon filter was compared with the sum of the masses independently measured as sulfate, organic and elemental carbon, and calculated water bound with sulfate. Ash emissions were calculated from the ash content in the fuel. The data presented in Figure 2 show a favorable comparison of the two independent approaches to determining the PM_{2.5} mass.

Emissions of Metals and Other Elements. Both modal and overall weighted emission factors were figured on the basis of the elemental analysis. Relative weighted emission factors for the main engine, the auxiliary engine, and the boiler are presented in Figure 3. The main engine and boiler show the expected predominance of sulfur, followed by vanadium and nickel and the metals from the crude oil. For the auxiliary engine, sulfur is followed by calcium, a constituent of the lube oil used with sulfurous fuels. Also found were zinc and phosphorus, the antiwear elements in the lube oil. The emission factors for different elements as a function of load are presented in the Supporting Information.

Emissions of Carbonyls and Selected C₄–C₈ Hydrocarbons. The concentration of 13 different carbonyls and

TABLE 2. Emission Factors of Different Carbonyls and Selected C4–C8 Hydrocarbons for Main Engine, Auxiliary Engine, and the Boiler

	main engine emission factor (mg/kWh)			auxiliary engine emission factor (mg/kWh)			boiler emission factor (g/ton)
	percent load			percent load			
	25%	50%	75%	25%	50%	75%	
formaldehyde	13%	10.6 ± 0.4	4.95 ± 0.41	5.5 ± 0.23	11.2 ± 1.9	7.87 ± 6.8	0.79 ± 0.16
acetaldehyde	14.2 ± 0.4	4.21 ± 0.09	1.54 ± 0.18	1.94 ± 0.37	2.66 ± 1.6	7.87 ± 6.8	3.27 ± 0.06
acetone	7.82 ± 0.33	2.62 ± 0.17	0.17 ± 0.08	0.33 ± 0.37	0.7 ± 0.5	0.65 ± 0.26	2.81 ± 0.92
acrolein	0.81 ± 0.24	0.36 ± 0.12	0.05 ± 0.04	0.15 ± 0.12	0.53 ± 0.27	0.43 ± 0.37	BDL
propionaldehyde	3.15 ± 0.30	1.02 ± 0.61	0.67 ± 0.07	0.52 ± 0.06	0.40 ± 0.22	0.34 ± 0.29	0.20 ± 0.02
crotonaldehyde	0.22 ± 0.20	0.08 ± 0.03	N/A	0.002 ± 0.003	0.12 ± 0.09	0.07 ± 0.06	BDL
methacrolein	0.89 ± 0.14	0.79 ± 0.93	0.03 ± 0.01	0.04 ± 0.01	0.07 ± 0.07	0.07 ± 0.03	0.26 ± 0.30
methyl ethyl ketone	0.09 ± 0.17	0.08 ± 0.02	N/A	N/A	0.07 ± 0.06	0.07 ± 0.06	0.09 ± 0.15
butyraldehyde	6.12 ± 0.40	1.52 ± 0.01	0.35 ± 0.01	0.42 ± 0.03	1.05 ± 0.75	0.72 ± 0.61	0.11 ± 0.11
benzaldehyde	0.24 ± 0.42	0.18 ± 0.05	0.21 ± 0.05	0.22 ± 0.01	0.29 ± 0.07	0.16 ± 0.14	BDL
valeraldehyde	1.08 ± 0.94	0.27 ± 0.03	0.17 ± 0.02	0.19 ± 0.01	0.13 ± 0.05	0.10 ± 0.08	BDL
tolualdehyde	N/A	0.11 ± 0.06	0.02 ± 0.04	0.06 ± 0.01	0.14 ± 0.07	0.06 ± 0.05	BDL
hexaldehyde	0.67 ± 0.27	0.25 ± 0.06	0.13 ± 0.03	0.11 ± 0.01	0.29 ± 0.38	0.11 ± 0.07	BDL
1,3 butadiene ^a	1.15	0.37	0.20	0.19	0.20	0.20	1.25
benzene ^a	3.41	1.15	0.65	0.56	1.22	0.61	0.75
toluene ^a	1.55	0.56	0.30	0.33	0.82	0.28	3.86
m- and p-xylene ^a	2.69	0.74	0.25	0.33	0.46	0.12	1.39
ethyl benzene ^a	0.49	0.15	0.07	0.07	0.19	0.04	0.39
o-xylene ^a	0.97	0.28	0.10	0.13	0.13	0.04	0.26

^a Typically repeats ± 15%. BDL = below detection limit.

TABLE 3. Weighted Emission Factors of PAHs and Alkanes^a

	main engine	auxiliary engine	boiler
	g/kWhr	g/kWhr	kg/ton
naphthalene	8.12×10^{-3}	7.20×10^{-3}	1.54×10^{-2}
acenaphthylene	1.17×10^{-4}	2.71×10^{-5}	8.14×10^{-5}
acenaphthene	2.48×10^{-4}	1.17×10^{-5}	2.59×10^{-4}
fluorene	1.16×10^{-4}	4.81×10^{-5}	6.71×10^{-5}
phenanthrene	5.85×10^{-4}	4.69×10^{-4}	7.85×10^{-4}
anthracene	8.26×10^{-5}	1.48×10^{-4}	3.05×10^{-4}
fluoranthene	3.16×10^{-5}	2.45×10^{-5}	2.32×10^{-5}
pyrene	1.70×10^{-4}	3.37×10^{-5}	4.07×10^{-4}
benzo(a)anthracene	2.02×10^{-5}	1.72×10^{-6}	4.96×10^{-5}
chrysene	3.49×10^{-5}	2.80×10^{-6}	4.96×10^{-5}
benzo(b)fluoranthene	1.25×10^{-5}	7.80×10^{-7}	3.27×10^{-5}
benzo(k)fluoranthene	1.37×10^{-5}	1.46×10^{-6}	3.43×10^{-5}
benzo(a)pyrene	3.58×10^{-4}	1.46×10^{-6}	9.31×10^{-4}
indeno[1,2,3-cd]pyrene	5.90×10^{-5}	5.90×10^{-6}	1.74×10^{-4}
dibenz[a,h]anthracene	5.68×10^{-5}	1.22×10^{-6}	9.08×10^{-5}
benzo[ghi]perylene	2.30×10^{-5}	2.40×10^{-5}	4.68×10^{-5}
dodecane	8.24×10^{-4}	4.84×10^{-3}	4.88×10^{-2}
tetradecane	1.18×10^{-3}	5.58×10^{-3}	1.75×10^{-2}
hexadecane	7.97×10^{-4}	4.38×10^{-3}	1.70×10^{-2}
octadecane	9.96×10^{-4}	3.85×10^{-3}	8.30×10^{-3}
nonadecane	7.08×10^{-4}	2.23×10^{-3}	2.84×10^{-3}
eicosane	1.60×10^{-3}	3.26×10^{-4}	6.90×10^{-4}
docosane	2.25×10^{-3}	1.19×10^{-4}	2.29×10^{-4}
tetracosane	5.49×10^{-4}	8.10×10^{-5}	3.18×10^{-4}
hexacosane	3.26×10^{-4}	5.35×10^{-5}	3.92×10^{-4}
octacosane	9.13×10^{-4}	8.02×10^{-5}	1.21×10^{-4}
triacontane	1.15×10^{-3}	1.44×10^{-4}	7.20×10^{-4}

^a Note: Typically repeats ± 15%.

selected hydrocarbons (1,3 butadiene; benzene; toluene; m-plus p-xylene; ethylbenzene and o-xylene) were measured in triplicate for the exhaust of the main and auxiliary engines and the boiler. The emission factors for these hydrocarbons are presented in Table 2.

Polycyclic Aromatic Hydrocarbons (PAHs) and C10+ Alkanes. The concentrations of 11 different alkanes and 16 different PAHs were measured, and weighted emission factors are presented in Table 3. The emission factors for different PAHs and alkanes as a function of engine load for the main engine and the auxiliary engine are provided in the Supporting Information.

Methane and Total Gaseous Non-Methane Organics (TGNMO) as Methane. The concentrations of methane and TGNMO as methane in the diluted exhaust were low and near ambient levels. Data are provided in the Supporting Information. This measurement was an exploratory probe, and samples collected from future measurements for this analysis will be collected from raw exhaust to avoid near detection limit concentrations in the SUMMA canisters.

Discussion of Regulated Emissions

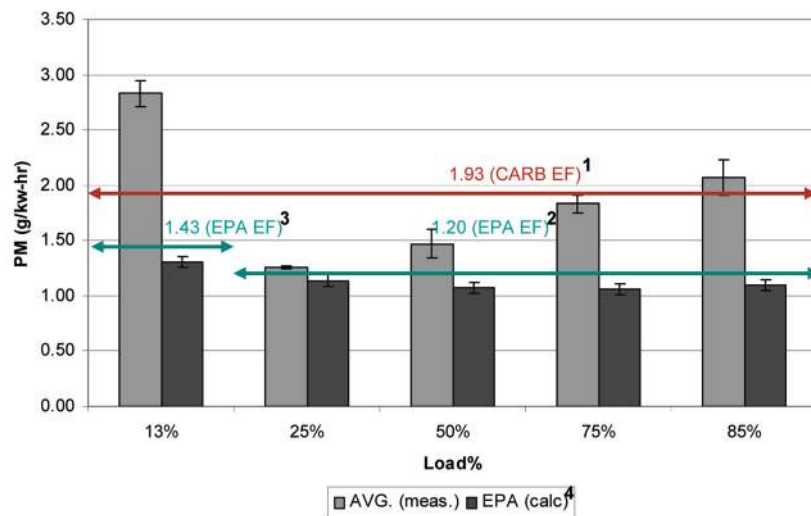
Tankers are around 10% of the total number of ocean going vessels worldwide (14, 15), and yet, there are very little data available from tankers during actual operation at sea. Table 4 compares the measured weighted emission factors (EFs) of NO_x, PM, and calculated weighted EFs for SO₂ from this study with literature data and those used by regulatory agencies. The NO_x emission factors for the main and auxiliary engines from this study are comparable to those in Lloyd's and the regulatory agencies. Although the SO₂ levels show differences, they should be similar if calculated from the ISO protocol and measured sulfur levels in the fuel.

Key elements of the research were to measure the PM mass and to dissect the PM mass into its major constituents, since it is classified as a toxic air contaminant in California. This study shows PM mass levels are 30% higher than Lloyd, 48% higher than EPA, and close to ARB's number. A deeper analysis of the PM mass from main engine running on HFO

TABLE 4. Comparison of measured emission factors with literature data

	units	measured (weighted)	Lloyds Services data (12)	Cooper et al. (8)	US EPA EFs (17)	CARB EFs (40)
Auxiliary Engines						
NO _x	g/kWh	13.57 ± 0.31	13.9	17.5–17.9	13.9	13.9
PM	g/kWh	0.141 ± 0.005	0.3	0.26	0.42	0.25
SO ₂ ^a	g/kWh	0.28	1.1	0.14–0.16	0.66 ^b	0.4
Main Engine						
NO _x	g/kWh	19.87 ± 0.95	18.7		18.1	18.1
PM	g/kWh	1.60 ± 0.08	1.23		1.08	1.5
SO ₂ ^a	g/kWh	10.5			10.3	10.5
Boiler						
NO _x	kg/ton	9.24 ± 0.09			12.3	
PM	kg/ton	2.78 ± 0.26			1.04	
SO ₂ ^a	kg/ton	55.7			54	

^a SO₂ values reported are calculated from sulfur in the fuel. ^b Corrected for sulfur in the fuel used.



¹ from CARB “Emissions Estimation Methodology for Ocean-Going Vessels,” October, 2005 (transit/maneuvering modes, corr. from 2.5 wt. % to 2.85 wt.% S fuel)
² from US EPA “Current Methodologies and Best Practices in Preparing Port Emission Inventories,” January, 2006 (corr. from 2.7 wt.% to 2.85 wt.% S fuel)
³ from reference (2), corr. to 13% load
⁴ from Environ/EPA calculation based on brake-specific fuel consumption and 2.85 wt. % S fuel

FIGURE 4. Comparison of measured emission factors in this study and estimated EFs of PM for main engine.

shows the PM is dominated by hydrated sulfate (about 75% of total PM). Organic carbon constitutes about 15–25% of the PM, and the remainder is EC and ash. For the auxiliary engine running on marine gas oil, the PM is dominated by organic carbon, which constitutes about 45% of total PM. The EC/OC ratio for the main engine varies from 0.03 to 0.05 and from 0.1 to 0.4 for auxiliary engines, and these ratios are significantly different from the on-road diesel engine range of 1–4 (37). This finding may be useful for researchers doing source apportionment projects.

A deeper investigation of the fuel sulfur to sulfate formation revealed that for the auxiliary engine running on marine gas oil, the conversion of fuel sulfur to sulfate increased from 1.4 to 5% as engine load increased from 25 to 75%. For the main engine running on heavy fuel oil, the conversion of sulfur from fuel to sulfate increased from 1.9 to 3.9% as engine load increased from 25 to 85%. Kasper et al., (20) report a conversion ratio of 1.4% at 100% engine load for a 2-stroke marine diesel engine running on marine diesel oil. The data gathered by the present study shows a higher conversion of fuel sulfur to sulfate than earlier investigators but does not provide the relationship between conversion, engine, fuel, and combustion conditions.

Various regulatory agencies estimate PM mass emission factors from the brake specific fuel consumption and the

sulfur level in the fuel (39, 40). The U.S. EPA considers emission factors to be constant, down to about 20% load. Below 20% load, diesel engines are less efficient, and the fuel consumed per unit work will increase, so EPA has an adjustment factor (39). Thus, although mass emissions (grams per hour) decrease with low loads, the emission factor will increase as the load decreases (40), which is consistent with the measured emission factors in this study. Figure 4 compares the emission factor of PM mass from the main engine measured in this study with emission factors estimated by regulatory agencies.

Discussion of Nonregulated Emissions

As expected, the concentration of methane and total gaseous non-methane organics as methane were low and near ambient levels. An important objective of this research was to report emissions of speciated hydrocarbons, especially hazardous air pollutants, since they were nonexistent for the main engine and boiler of ocean going tankers. The deeper analysis of the total hydrocarbons showed that formaldehyde emissions were significant and were over 50% of the total aldehydes for the main and auxiliary engine. For the boiler, acetaldehyde was the primary aldehyde. Details are provided on the emissions of other HAPs and indicate, for example, that benzene emissions were about 10% of the formaldehyde values.

Cooper et al. (21) provided emission factors of PAH and C₆–C₁₂ hydrocarbon emissions from auxiliary engines (medium speed marine diesel engines), emphasizing that PAH emissions from marine diesel engines are most probably a significant PAH source. The emission factors of PAHs presented in this study for the auxiliary engine are in general agreement with Cooper.

Auxiliary boilers on tankers are significantly larger than auxiliary boilers on container vessels because a lot of steam is needed to pump the large volume of crude oil. The fuel-specific emissions show that PM emissions from the boiler were about 34% of the weighted emissions from the main engine, and NO_x emissions were 9% of the weighted emissions from the main engine.

The weighted emission factors for all the different hydrocarbon species are provided in the Supporting Information.

Acknowledgments

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Supporting Information Available

A detailed description of the sampling and analysis performed in this study is provided in the Supporting Information. The weighted emission factors for all the species analyzed in this study for different engines tested are compiled in a table. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Hildemann, L. M.; Markowski, G. R.; Cass, G. R. Chemical composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* **1991**, *25*, 744–759.
- Gartzianda, E. L.; Tetry, V.; Carlier, P. Sampling and analysis of organic compounds in diesel particulate matter. *Environ. Monit. Assess.* **2000**, *65*, 155–163.
- Saxe, H.; Larsen, T. Air pollution from ships in three Danish ports. *Atmos. Environ.* **2004**, *38* (24), 4057–4067.
- Cocker, D. R.; Shah, S. D.; Johnson, K. C.; Zhu, X.; Miller, J. W.; Norbeck, J. M. Development and application of a mobile laboratory for measuring emissions from diesel engines. 2. Sampling for toxics and particulate matter. *Environ. Sci. Technol.* **2004**, *38*, 6809–6816.
- Corbett, J. J.; Fischbeck, P. S. Emissions from Ships. *Science* **1997**, *278* (5339), 823–824.
- California Air Resources Board. Goods movement action plan: Phase I. Available at <http://www.arb.ca.gov/gmp/docs/finalgmpplan090205.pdf>
- Corbett, J. J.; Winebrake, J. J.; Green, E. H.; Kasibhatla, P.; Eyring, V.; Lauer, A. Mortality from ship emissions: A global assessment. *Environ. Sci. Technol.* **2007**, *41*, 8512–8518.
- Cooper, D. A. Exhaust emissions from ships at berth. *Atmos. Environ.* **2003**, *37*, 3817–3830.
- Capaldo, K.; Corbett, J. J.; Kasibhatla, P.; Fischbeck, P. S.; Pandis, S. N. Effects of ship emissions on sulfur cycling and radiative climate forcing over the ocean. *Nature* **1999**, *400*, 743–746.
- Lawrence, M. G.; Crutzen, P. J. Influence of NO_x emissions from ships on tropospheric photochemistry and climate. *Nature* **1999**, *402*, 167–170.
- MAN B&W Diesel. Emission control: MAN B&W two-stroke diesel engines. Copenhagen, 2004. www.manbw.com
- Entec UK Limited. Quantification of emissions from ships associated with ship movements between ports in the European Community/European Commission, July 2002.
- International Maritime Organization Sub-Committee on Bulk Liquids and Gases. Review of MARPOL annex VI and the NO_x technical note, development of standards for NO_x, PM and SO_x. Available at www.arb.ca.gov/research/seca/imo07b.pdf
- Eyring, V.; Kohler, H. W.; van Aardenne, J.; Lauer, A. Emissions from international shipping: 1. The last 50 years. *J. Geophys. Res.* **2005**, *110*, 17305.
- Corbett, J. J.; Koehler, H. Updated emissions from ocean shipping. *J. Geophys. Res.* **2003**, *108*, 4650.

- Heywood, J. B. *Internal Combustion Engine Fundamentals*; McGraw-Hill: New York, 1988.
- U.S. Environmental Protection Agency. Current methodologies and best practices in preparing port emission inventories: final report; January 5, 2006; http://www.epa.gov/sectors/ports/bp_portemissionsfinal.pdf
- Endresen, Ø.; Sørsgard, E.; Sundet, J. K.; Dalsøren, S. B.; Isaksen, I. S. A.; Berglen, T. F.; Gravir, G. Emission from international sea transportation and environmental impact. *Journal of Geophysical Research* **2003**, *108* (D17), 4560.
- Skjølsvik, K. O.; Andersen, A. B.; Corbett, J. J.; Skjelvik, J. M. MT Report: MT00 A23-038; Trondheim, Norway, March 2000.
- Kasper, A.; Aufdenblatten, S.; Forss, A.; Mohr, M.; Burtscher, H. Particulate emissions from a low-speed marine diesel engine. *Aerosol Sci. Technol.* **2007**, *41*, 24–32.
- Cooper, D. A.; Peterson, K. Hydrocarbon, PAH and PCB Emissions from Ferries: A case study in the Skagerak-Kattegat-Oresund region. *Atmos. Environ.* **1996**, *30* (14), 2463–2473.
- Cooper, D. A.; Andreasson, K. Predictive NO_x emission monitoring on board a passenger ferry. *Atmos. Environ.* **1999**, *33* (28), 4637.
- Cooper, D. A. Exhaust emissions from high speed passenger ferries. *Atmos. Environ.* **2001**, *35* (24), 4189–4200.
- Lyrranen, J.; Jokiniemi, J.; Kauppinen, E. I.; Joutsensaari, J. Aerosol characterisation in medium-speed diesel engines operating with heavy fuel oils. *J. Aerosol Sci.* **1999**, *30*, 771–784.
- Petzold, A.; Feldpausch, Ph.; Fritzsche, L.; Minikin, A.; Lauer, P.; Kurok, C.; Bauer, H. Particle emissions from ship engines. *J. Aerosol Sci.* **2004**, S1095–S1096 Abstracts of the European Aerosol Conference.
- Petzold, A.; Hasselbach, J.; Lauer, P.; Baumann, R.; Franke, K.; Gurk, C.; Schlager, H.; Weingartner, E. Experimental studies on particle emissions from cruising ship, their characteristic properties, transformation and atmospheric lifetime in the marine boundary layer. *Atmos. Chem. Phys. Discuss.* **2007**, *7*, 15105–15154.
- Sinha, P.; Hobbs, P. V.; Yokelson, R. J.; Christian, T. J.; Kirchstetter, T. W.; Bruintjes, R. Emission of trace gases and particles from two ships in the southern Atlantic Ocean. *Atmos. Environ.* **2003**, *37*, 2139–2148.
- Chen, G.; Huey, G.; Trainer, M. An investigation of the chemistry of ship emission plumes during ITCT 2002. *J. Geophys. Res.* **2005**, *110*, D10S90, doi:10.1029/2004JD005236.
- Lloyd's Register. Marine Exhaust Emissions Research Programme: Steady State Operation (including Slow Speed Addendum); Lloyd's Register of Shipping: London 1990.
- Lloyd's Register. Marine Exhaust Emissions Research Programme: Transient Emissions and Air Quality Impact Evaluation; Industry Research Report. Lloyd's Register of Shipping: London, 1993.
- Wright, A. Marine Diesel Engine Particulate Emissions. *Trans IMarE* **1997**, *109*, 345–364.
- Vessel Speed Reduction (VSR) for ocean going vessels. <http://www.arb.ca.gov/ports/marinevess/vsr/vsr.htm>
- International Standards Organization. ISO 8217. *Petroleum products: Fuels (class F), Specifications of marine fuels*. ISO 8217: 2005(E), 2005.
- International Standards Organization. ISO 8178-1, Reciprocating internal combustion engines: Exhaust emission measurement. Part 1: Test-bed measurement of gaseous particulate exhaust emissions, First edition 1996-08-15.
- Dekati Mass Monitor (DMM). <http://www.dekati.com/cms/dmm>
- Shah, S. D.; Temitope, A.; Ogunyoku, J.; Miller, W.; Cocker, D. R., III. On-road emission rates of PAH and *n*-alkane compounds from heavy-duty diesel vehicles. *Environ. Sci. Technol.* **2004**, *39* (14), 5276–5284.
- Shah, S. D.; Cocker, D. R.; Miller, J. W.; Norbeck, J. M. Emission rates of particulate matter and elemental and organic carbon from in-use diesel engines. *Environ. Sci. Technol.* **2004**, *38*, 2544–2550.
- Agrawal H.; Malloy Q.; Welch W. A.; Miller J. W.; Cocker, D. R. In-use gaseous and particulate matter emissions from a modern ocean going container vessel. *Atmos. Environ.* **2008**, *42*, 5504–5510.
- Energy and Environmental Analysis Inc. Analysis of Commercial Marine Vessels Emissions and Fuel Consumption Data; EPA420-R-00-002, February 2000.
- California Air Resources Board. Emissions Estimation Methodology for Ocean-Going Vessels. October 2005 <http://www.arb.ca.gov/regact/marine2005/appd.pdf>.

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