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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\textsuperscript{-1} h\textsuperscript{-1}) of PM and NO\textsubscript{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\textsubscript{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\textsubscript{x}) and nitrogen oxides (NO\textsubscript{x}) emissions in many areas of the world (Corbett and Fischbeck, 1997). The high levels of PM and SO\textsubscript{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\textsubscript{2} and SO\textsubscript{3}, typically in ratio of 15:1 (MAN B&W, 2004). NO\textsubscript{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; Lyrynan et al., 1999; Chen et al., 2002; Sinha et al., 2003; Petzold et al.,...
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%

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
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\textsubscript{2} or NO\textsubscript{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\textsubscript{2} and NO\textsubscript{x} concentrations, agreed within 5%, well within the 10% specified in the reference method (ISO 8178-1, 1996).

Emission measurements of different gases, PM\textsubscript{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\textsubscript{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\textsubscript{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

Table 2

<table>
<thead>
<tr>
<th>Load (%)</th>
<th>8%</th>
<th>27%</th>
<th>52%</th>
<th>63%</th>
<th>70%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (kW)</td>
<td>4013</td>
<td>13,545</td>
<td>26,088</td>
<td>31,607</td>
<td>35,119</td>
</tr>
<tr>
<td>Speed (rpm)</td>
<td>49.2</td>
<td>73.0</td>
<td>91.0</td>
<td>98.1</td>
<td>101.8</td>
</tr>
</tbody>
</table>

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°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 cm² 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: CO₂, CO, SO₂ and NOₓ. Emissions of CO were low as expected for diesel engines. The results of gaseous emissions factors for CO₂, CO, NOₓ and SO₂ (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 NOₓ could be achieved. The emission factors developed for the vessel studied show that the NOₓ 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.

3.2. Particulate matter (PM2.5) 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>
<thead>
<tr>
<th>Load (%)</th>
<th>PM</th>
<th>EC</th>
<th>OC</th>
<th>H₂SO₄·6.5H₂O</th>
<th>Ash</th>
</tr>
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<tr>
<td>8</td>
<td>1.699</td>
<td>0.029</td>
<td>0.498</td>
<td>1.071</td>
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<tr>
<td>27</td>
<td>1.091</td>
<td>0.016</td>
<td>0.286</td>
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<tr>
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<td>0.281</td>
<td>1.257</td>
<td>0.123</td>
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<td>1.660</td>
<td>0.020</td>
<td>0.254</td>
<td>1.370</td>
<td>0.123</td>
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<td>1.757</td>
<td>0.017</td>
<td>0.259</td>
<td>1.495</td>
<td>0.123</td>
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</table>

<table>
<thead>
<tr>
<th>Load (%)</th>
<th>CO₂ (g kW⁻¹ h⁻¹)</th>
<th>SO₂ (g kW⁻¹ h⁻¹)</th>
<th>CO (g kW⁻¹ h⁻¹)</th>
<th>NOₓ (g kW⁻¹ h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 (VSR)</td>
<td>660</td>
<td>8.60</td>
<td>7.78</td>
<td>20.96</td>
</tr>
<tr>
<td>27</td>
<td>588</td>
<td>7.66</td>
<td>1.81</td>
<td>15.84</td>
</tr>
<tr>
<td>52</td>
<td>613</td>
<td>7.99</td>
<td>0.87</td>
<td>16.40</td>
</tr>
<tr>
<td>63</td>
<td>643</td>
<td>8.37</td>
<td>0.81</td>
<td>17.85</td>
</tr>
<tr>
<td>70</td>
<td>658</td>
<td>8.57</td>
<td>0.77</td>
<td>18.89</td>
</tr>
</tbody>
</table>
Table 5
Emissions (g kW⁻¹ h⁻¹) of various elements as a function of engine load

<table>
<thead>
<tr>
<th>Load (%)</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
</tr>
</thead>
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<tr>
<td>8</td>
<td>2.09E-03</td>
<td>1.15E-02</td>
<td>&lt;1.61E-03</td>
<td>2.19E-03</td>
<td>1.87E-01</td>
<td>&lt;9.39E-05</td>
<td>&lt;2.68E-05</td>
<td>4.96E-03</td>
<td>1.30E-04</td>
<td>5.36E-02</td>
<td>&lt;2.68E-05</td>
</tr>
<tr>
<td>27</td>
<td>&lt;1.18E-03</td>
<td>8.76E-03</td>
<td>&lt;1.18E-03</td>
<td>1.63E-03</td>
<td>1.35E-01</td>
<td>&lt;6.90E-05</td>
<td>&lt;1.97E-05</td>
<td>4.01E-03</td>
<td>1.74E-04</td>
<td>4.41E-02</td>
<td>&lt;1.97E-05</td>
</tr>
<tr>
<td>52</td>
<td>&lt;9.65E-04</td>
<td>1.07E-02</td>
<td>&lt;9.65E-04</td>
<td>4.09E-03</td>
<td>1.62E-01</td>
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<td>8.74E-05</td>
<td>4.65E-02</td>
<td>&lt;1.61E-05</td>
</tr>
<tr>
<td>63</td>
<td>&lt;1.10E-03</td>
<td>1.34E-02</td>
<td>&lt;1.10E-03</td>
<td>2.85E-03</td>
<td>2.07E-01</td>
<td>&lt;6.44E-05</td>
<td>&lt;1.84E-05</td>
<td>4.75E-03</td>
<td>1.15E-04</td>
<td>5.26E-02</td>
<td>&lt;1.84E-05</td>
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<tr>
<td>70</td>
<td>&lt;1.12E-03</td>
<td>1.72E-02</td>
<td>&lt;1.12E-03</td>
<td>6.56E-03</td>
<td>2.52E-01</td>
<td>&lt;6.52E-05</td>
<td>8.94E-05</td>
<td>5.11E-03</td>
<td>1.49E-04</td>
<td>5.60E-02</td>
<td>&lt;1.86E-05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Load (%)</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Ga</th>
<th>Ge</th>
<th>As</th>
<th>Se</th>
<th>Rb</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>&lt;1.34E-05</td>
<td>2.84E-03</td>
<td>1.46E-04</td>
<td>1.20E-02</td>
<td>9.66E-05</td>
<td>1.29E-04</td>
<td>3.25E-04</td>
<td>&lt; 2.68E-05</td>
<td>&lt; 6.71E-06</td>
<td>&lt; 2.68E-05</td>
<td>&lt; 1.34E-05</td>
</tr>
<tr>
<td>27</td>
<td>&lt;9.85E-06</td>
<td>2.58E-03</td>
<td>1.20E-04</td>
<td>9.65E-03</td>
<td>6.11E-05</td>
<td>1.02E-04</td>
<td>&lt;4.19E-04</td>
<td>7.09E-05</td>
<td>&lt; 4.02E-06</td>
<td>&lt; 1.97E-05</td>
<td>&lt; 9.85E-06</td>
</tr>
<tr>
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<td>2.15E-03</td>
<td>1.36E-04</td>
<td>1.04E-02</td>
<td>4.89E-05</td>
<td>9.23E-05</td>
<td>1.06E-04</td>
<td>&lt;1.61E-05</td>
<td>&lt; 4.60E-06</td>
<td>&lt; 1.61E-05</td>
<td>&lt; 8.04E-06</td>
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<tr>
<td>63</td>
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<td>3.48E-03</td>
<td>1.70E-04</td>
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<td>5.52E-05</td>
<td>9.85E-05</td>
<td>1.77E-04</td>
<td>&lt;1.84E-05</td>
<td>&lt; 4.66E-06</td>
<td>&lt; 1.84E-05</td>
<td>&lt; 9.20E-06</td>
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<tr>
<td>70</td>
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<td>3.89E-03</td>
<td>1.76E-04</td>
<td>1.27E-02</td>
<td>1.01E-04</td>
<td>1.43E-04</td>
<td>&lt;3.96E-04</td>
<td>&lt;1.86E-05</td>
<td>&lt; 4.02E-06</td>
<td>&lt; 1.86E-05</td>
<td>&lt; 9.31E-06</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Load (%)</th>
<th>Sr</th>
<th>Y</th>
<th>Mo</th>
<th>Pd</th>
<th>Cd</th>
<th>In</th>
<th>Sn</th>
<th>Sb</th>
<th>Ba</th>
<th>La</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>6.44E-05</td>
<td>&lt; 6.71E-06</td>
<td>1.86E-04</td>
<td>&lt;4.82E-05</td>
<td>8.90E-05</td>
<td>1.45E-04</td>
<td>1.13E-04</td>
<td>4.02E-04</td>
<td>3.07E-04</td>
<td>1.61E-04</td>
<td>&lt; 6.71E-05</td>
</tr>
<tr>
<td>27</td>
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<td>&lt; 4.02E-06</td>
<td>1.14E-04</td>
<td>&lt;2.96E-05</td>
<td>&lt;1.97E-05</td>
<td>2.09E-04</td>
<td>&lt;2.96E-05</td>
<td>2.28E-04</td>
<td>2.93E-04</td>
<td>4.18E-04</td>
<td>&lt; 4.02E-05</td>
</tr>
<tr>
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<td>1.48E-04</td>
<td>&lt;2.76E-05</td>
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<td>1.53E-04</td>
<td>&lt; 4.66E-05</td>
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<tr>
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<td>&lt; 4.02E-06</td>
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<td>2.48E-04</td>
<td>4.04E-04</td>
<td>2.50E-04</td>
<td>&lt; 4.02E-05</td>
</tr>
</tbody>
</table>
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 (H₂SO₄ · 6.5H₂O), 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
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.

### Acknowledgments

This study would have not been possible without the support of the funding agency, California Air Resources Board (CARB), the analytical support from Ms. Kathy Cocker, Ms. Varalakshmi Jayaram and Dr. Abhilash Nigam and a helping hand in the field from the shipping company crew. We would like to thank undergraduate students Ms. Cristina Hall and Ms. Mary Sheppy for helping in chemical analyses.

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