

Effect of Selective Catalytic Reduction Unit on Emissions from an Auxiliary Engine on an Ocean-Going Vessel

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Executive Summary

A major cargo shipping company and the University of California, Riverside (UCR) worked together under a contract with the California Air Resources Board (CARB) to demonstrate the effectiveness of a selective catalytic reduction (SCR) unit in removing criteria pollutants from a typical marine auxiliary engine. Testing was conducted aboard a post-Panamax vessel. The auxiliary engine equipped with the SCR control was tested using a Heavy Fuel Oil (HFO) as well as a Marine Distillate Oil (MDO). The test cycle used to evaluate the emissions approximated as closely as possible the ISO 8178-D2 marine engine certification cycle.

The sampling was conducted in two campaigns July 2005 and December 2005 each of which lasted two days. Real-time gaseous emissions data (CO₂, NO_x and CO) were logged before and after the SCR unit. Filter samples were collected and analyzed to determine the total particulate matter (PM_{2.5}) emission factor and speciated PM_{2.5} emission factors that include elemental carbon (EC), organic carbon (OC), hydrated sulfate (H₂SO₄.6.5H₂O). The inorganic (ash) PM_{2.5} emission factor was estimated by assuming that the ash content of the fuel was all converted to PM_{2.5}.

The SCR unit was unstable and not operating within its specifications during the July 2005 test. After significant review, re-engineering and re-commissioning of the system, it was tested in December 2005. The gaseous emission factors for the, MAN B&W 7L32-40, before and after the SCR are shown in Table ES-1.

**Table ES-1 Effect of SCR on Gaseous Emission Factors
MAN B&W 7L32-40 Auxiliary Engine**

Fuel	Target Load ISO	Actual Load		CO ₂ (g/kW-hr)		CO (g/kW-hr)		NO _x (g/kW-hr)	
		Before SCR	After SCR	Before SCR	After SCR	Before SCR	After SCR	Before SCR	After SCR
December 2005									
HFO 3.8%S	25%	30%	35%	814	809	1.61	2.45	17.3	1.7
	50%	52%	50%	708	743	0.94	1.70	16.4	1.6
	75%	67%	67%	684	700	0.75	1.19	16.0	1.4
MDO 0.16%S	25%	22%	21%	955	930	1.99	3.80	14.7	2.4
	50%	52%	53%	697	682	0.98	1.73	11.3	1.8
	75%	69%	65%	676	689	0.64	1.29	8.9	1.6

Note: kW-hr denotes generated power. %S denotes fuel sulfur content in wt/wt % basis.
Testing was conducted using a three meter heated transfer line in the sampling train.

The SCR reduced the NO_x emission factor by 90-91% in the case of the HFO fuel and 82-84% in the case of the MDO. The CO emissions increased by a factor of 1.4 to 2.0, due to the potential oxidation of the organic carbon in the gas phase.

Total and speciated PM emission factors determined before and after the SCR are reported in Table ES-2. These emission factors are biased low due to the use of 3m long heated raw gas transfer lines while sampling. Though the certification method allows a transfer line up to 5m in length, we subsequently learned that there can be a PM loss as high as 40% while testing high sulfur fuels (Jayaram et al., 2009). Though absolute values of these emissions factors are not accurate, we believe these PM emission factors provide a reasonably good indication of the effects of the SCR.

**Table ES-2 Effect of SCR on Total and Speciated PM Emission Factors, December 2005
MAN B&W 7L32-40 Auxiliary Engine**

Fuel	Target Load ISO	PM Mass (g/kW-hr)		EC (g/kW-hr)		OC (g/kW-hr)		H ₂ SO ₄ ·6.5H ₂ O (g/kW-hr)	
		Before SCR	After SCR	Before SCR	After SCR	Before SCR	After SCR	Before SCR	After SCR
HFO 3.8%S	25%	0.675	1.192	0.035	0.013	0.276	0.033	0.382	1.198
	50%	0.479	1.438	0.009	0.006	0.175	0.031	0.347	1.517
	75%	0.293	1.090	0.006	0.005	0.134	0.031	0.178	1.379
MDO 0.16%S	25%	0.702	0.297	0.060	0.050	0.438	0.038	0.027	0.245
	50%	0.297	0.440	0.010	0.004	0.195	0.024	0.038	0.511
	75%	0.192	0.552	0.006	0.004	0.130	0.029	0.049	0.601

Note: kW-hr denotes generated power. %S denotes fuel sulfur content in wt/wt % basis.
Testing was conducted using a three meter heated transfer line in the sampling train.

PM_{2.5} emissions, increase downstream of the SCR, especially for the high sulfur HFO fuel. This can be attributed to a significant increase in sulfate species due to the conversion of sulfur dioxide to sulfate in the SCR. The vanadium catalyst used in the SCR is known to oxidize the sulfur dioxide to sulfur trioxide thereby enhancing the formation of the sulfate species (Svachula et al., 1993). The EC and OC fractions of the PM, decrease downstream of the SCR due to the oxidizing nature of the SCR catalyst.

1. Introduction

Ocean going vessels (OGVs) contribute significantly to global anthropogenic emissions. Recent estimates indicate that they represent approximately 9% of global SO_x emissions and 18-30% of the world's NO_x pollution (Corbett et al., 2003). A comparison of emissions from OGVs and aviation shows that OGVs emit about 9.2 times more nitrogen oxide (NO_x) emissions and 1200 times more particulate matter than aviation (Eyring et al., 2005a). With the increasing international trade and lack of stringent emission standards, emissions from OGVs are growing relative to other sources.

The principal sources of emissions aboard ships are the main and auxiliary engines. The main propulsion engines are 2-stroke, low speed diesel engines. Auxiliary engines on the other hand are 4-stroke high to medium speed marine diesel engines with power outputs in the range of 30-3000kW (Cooper et al., 2003). The main engines are usually used while at sea, while the auxiliary engines can operate in all modes of ship operation during transiting, maneuvering and hotelling. Hence, emissions from auxiliary engines can have considerable effects on both local and regional air quality.

Currently the International Maritime Organization (IMO) regulates the sulfur content of fuels (Table 1-1) and the NO_x emissions for marine engines (Table 1-2). These standards are more stringent in areas designated as “emission control areas” (ECA). The NO_x emissions standards are a function of the engine speed (International Maritime Organization., 1998).

Table 1-1 IMO Fuel Sulfur Limits

Date	Sulfur Limit in Fuel (%m/m)	
	SO _x ECA	Global
2000	1.5%	4.5%
2010.07	1.0%	
2012		3.5%
2015	0.1%	
2020 [†]		0.5%

[†] alternative date is 2025, to be decided by a review in 2018

Table 1-2 IMO NO_x Emission Standards

Tier	Year	NO _x Limit (g/kW-hr)		
		n < 130	130 ≤ n < 2000	N ≥ 2000
Tier I	2000	17.0	45*n ^{-0.2}	9.8
Tier II	2011	14.4	44*n ^{-0.23}	7.7
Tier III	2016 [†]	3.4	9*n ^{-0.2}	1.96

[†] In NO_x Emission Control Areas (ECA). Tier II standards apply outside ECA

‘n’ engine speed in rpm

Two promising NO_x reduction technologies for marine vessels are water emulsification and selective catalytic reduction (SCR), with SCR offering greater NO_x control (Corbett et al. 2002, Eyring et al. 2005b, MAN B&W Diesel).

Since very little in-use data are available on the use of the SCR technology on auxiliary marine diesel engines CARB, a major cargo shipping company and UCR collaborated on a project to test the effect of the SCR on the criteria pollutants and greenhouse gases.

1.1. Project Objective

The objective of this project was to measure the effect of an SCR system on the emissions from a typical marine auxiliary engine. To serve this purpose an auxiliary engine was fitted with an SCR unit aboard a post-Panamax container vessel (capacity 8000 TEUs). In-use emissions of a greenhouse gas (CO₂), and criteria pollutants that include oxides of nitrogen (NO_x), carbon monoxide (CO) and particulate matter (PM_{2.5}) were measured both upstream and downstream of a SCR unit following the engine certification cycle. The engine was tested while operating on two different fuels marine distillate oil (MDO) and heavy fuel oil (HFO).

2. Test Plan

2.1. Overview

Normally, the emissions from diesel engines are measured while the engine is in a test cell and mounted on an engine dynamometer. These conditions are necessary for the purpose of certification. For this project, emissions testing was performed on an operating engine fitted with an SCR on a vessel following the load points in the ISO 8178 D2 cycle. This approach added complexity to the project.

A plan was developed to measure the in-use emissions before and after the SCR. This involved moving a suite of equipment on board the container vessel, finding sampling ports, setting up the laboratory, calibrating the instruments and then testing the emissions all within the limited time period that the ship was on berth at the port. The ISO test protocol was therefore modified where necessary to accommodate safety and operational considerations of the vessel.

A pre-test inspection was conducted aboard the vessel during which UCR worked with the ship's engineering crew to install sample ports and locate utilities necessary for operating the sampling systems. Further, a detailed plan and schedule for testing was developed and finalized along with the Chief Engineer.

This section provides: (a) information on the test engine, SCR, test fuels, test cycle and test schedule; (b) a brief description of the emissions testing procedures. Additional details on the testing procedures can be found in Appendix A.

2.2. Test Engine

One of the five auxiliary engines aboard a post-Panamax container vessel was used for the test program. Details of the same are provided in Table 2-1.



Figure 2-1: MAN B&W 7L32-40

Table 2-1 Test Engine Specifications

Manufacturer /Model	MAN B&W /7L32-40
Manufacture Year	1999
Technology	4-Stroke
Max. Power Rating	3500 kW
Max. Generated Power	3125 kW
Rated Speed	720 rpm
# of Cylinders	7
Displacement	225.2 lit

2.3. Selective Catalytic Reduction Unit

The test engine was retrofitted with a custom designed SCR for NO_x control. A hole was cut out in the side of the vessel and the silencer in the exhaust system of the engine was replaced by the SCR. Since the SCR was installed on an existing vessel, there were space limitations; as a consequence no diesel oxidation catalyst (DOC) was installed downstream of the unit. Pictures of the SCR and the control system for the urea injection on site are shown in Figures 2-2 and 2-3.

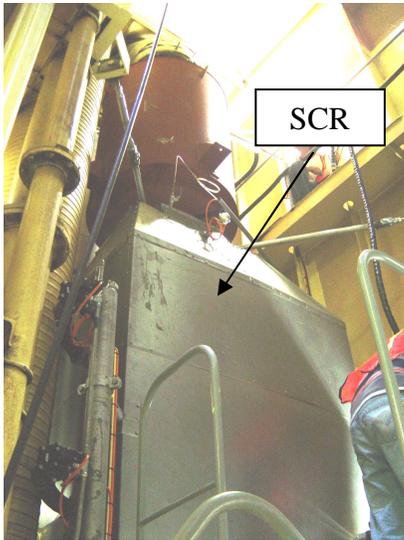


Figure 2-2: SCR

The SCR control system adjusts the urea injection rate based on the concentration of NO_x downstream of the unit. Details of the temperature of operation and urea injection rate at the time of testing are presented in the Section 3.2.



Figure 2-3: SCR Control System

The SCR unit uses the SINO_x urea-SCR technology. The catalytic converter consists of vanadium pent oxide catalyst embedded on a titanium oxide bed. The principle of operation is briefly described below (Amon et al., 2001a; Fritz et al., 1999).

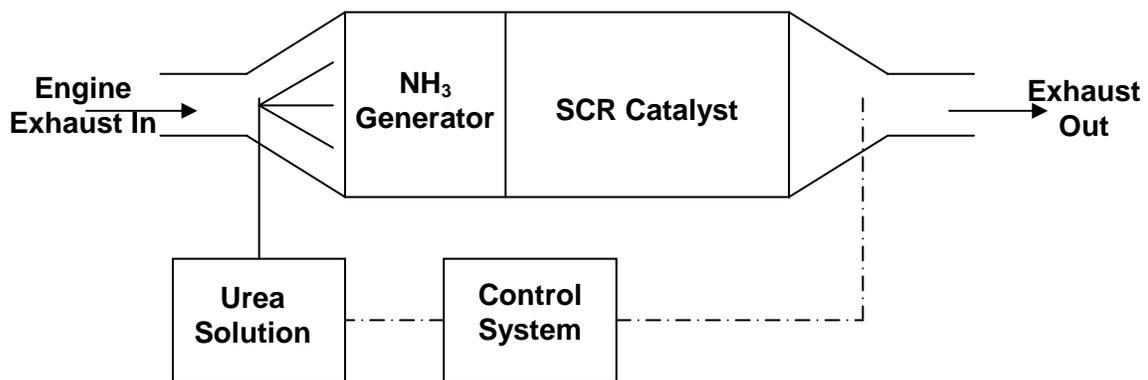
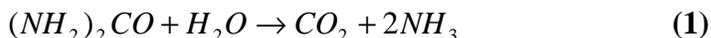
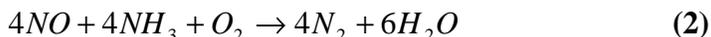


Figure 2-4: Schematic of the SCR

An aqueous solution of urea is injected into the exhaust upstream of the catalyst. Hydrolysis reaction occurs at a temperature of 180°C or above converting the urea to ammonia.



Ammonia reacts with the nitrogen oxides in the exhaust converting them into nitrogen and water in the presence of the catalyst.



2.4. Test Fuels

The auxiliary engine was tested on two fuels HFO and MDO.

HFO commonly known as bunker fuel or residual oil is the residual fraction of crude refining. It has very high viscosity and sulfur content.

MDO is a refined fraction of the crude which has lower sulfur content; however it is almost twice as expensive as HFO.



Figure 2-5: HFO



Figure 2-6: MDO

Both fuels used during the test were typical of normal supply. Properties of the test fuels are discussed in Section 3.1.

2.5. Test Cycle and Operating Conditions

The emissions were measured following the ISO certification cycle both upstream and downstream of the SCR. Table 7-1 in Appendix A details the load points and protocol specified by ISO for certification of auxiliary engines. The protocol requires the following:

- Allowing the gaseous emissions to stabilize before measurement.
- Measuring gaseous and PM concentrations for a time period long enough to get measurable filter mass
- Recording engine RPM, displacement, boost pressure and intake manifold temperature in order to calculate the mass flow rate of the exhaust.

Due to practical considerations, the actual engine load could differ by a factor of $\pm 5\%$ from the ISO target load; also not all load points specified in the ISO cycle could be tested. For example, the auxiliary engine was never operated at loads higher than 75% because a safety feature onboard the vessel would automatically turn on another auxiliary engine to distribute the load whenever the load on the engine increased beyond that point.

2.6. Test Schedule

The SCR system on the MAN B&W 7L32/40 engine was tested during a total of two test campaigns July 2005 and December 2005.

During the July 2005 campaign, the auxiliary engine was operating in a Low NO_x mode. Also, the SCR unit was quite unstable and not operating within its specifications. As a result a second campaign was undertaken in December of 2005.

Each of these campaigns lasted a period of two days. Details of test schedule are provided in Table 2-2.

Table 2-2 Test Schedule

Test Expedition	Date	Fuel	Sample Location	Test
July 2005 Low NO _x Mode	07/24/2005	HFO	Before SCR	RT & ISO; 75%,50%,25% MOUDI; 50%
		HFO	After SCR	RT & ISO; 75%,50%,25% MOUDI; 50%
	07/25/2005	MDO	Before SCR	RT & ISO; 50%,25% MOUDI; 50%
		MDO	After SCR	RT & ISO & MOUDI; 50%
December 2005	12/23/2005	MDO	After SCR	RT & ISO; 75%, 50%, 25%
		MDO	Before SCR	RT & ISO; 75%, 50%, 25%
		HFO	After SCR	RT & ISO; 75%, 50%, 25%
	12/24/2005	HFO	Before SCR	RT & ISO; 75%, 50%, 25%

RT: Real Time Monitoring and Recording of Emission Gaseous Samples

ISO: Filter Samples taken in accordance with ISO 8178-4 D2

MOUDI: Size Segregated PM Data

2.7. Emissions Testing Procedure

The emissions testing of the auxiliary engine was performed using a partial dilution system that was developed based on the ISO-8178 protocol. This section gives a brief description of this testing procedure. Refer to Appendix A for further details.

2.7.1. Sampling Ports

Sample probe access into the exhaust stream was gained by using sampling ports installed during pre-test inspection. A schematic of the sampling port locations is shown in Figure 2-7.

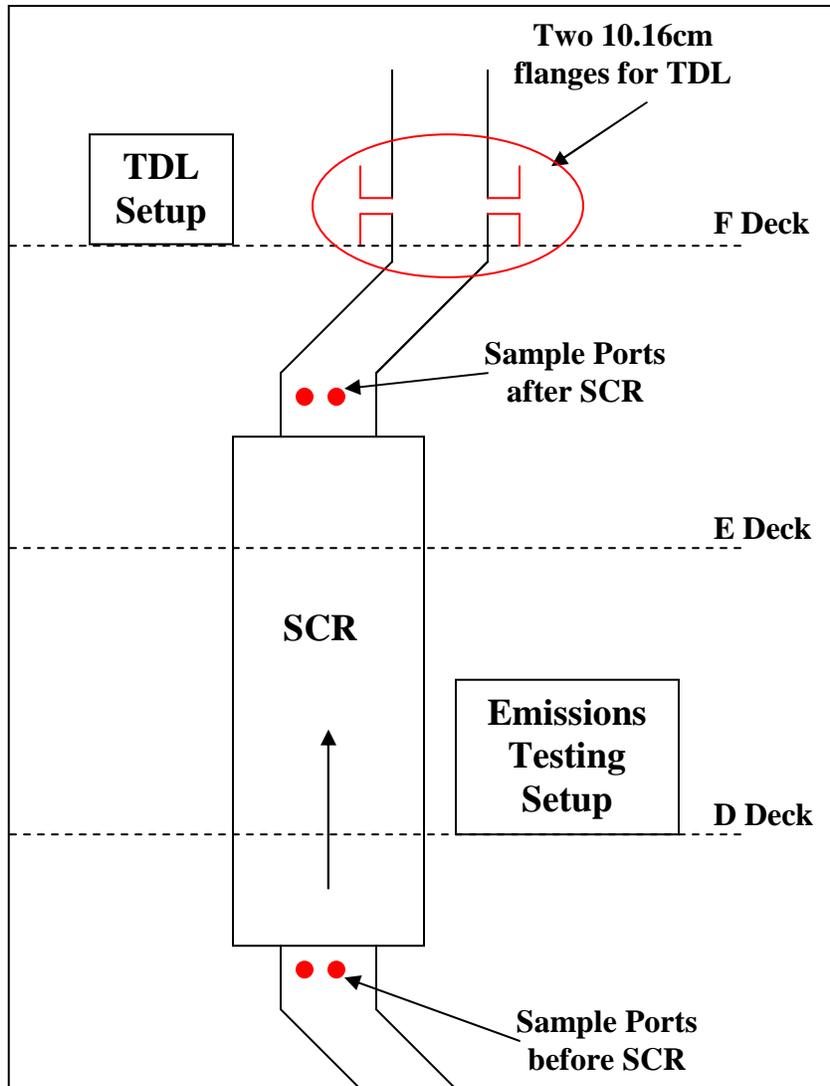


Figure 2-7 Location of Sampling Ports

There are two sampling ports (one for raw exhaust and other for dilution tunnel) at each location (before and after the SCR). The sample probes, ¼" diameter schedule 40 stainless steel tubes, extended about 6" into the raw exhaust stack (18" diameter). This distance is sufficiently away from any conditions found near the stack wall boundary.

Besides this two 10.6cm flanges were installed directly opposite each other within 1° for the tunable diode laser (TDL) system that measures NH₃ after the SCR. A close-up of the TDL setup is shown in Figure 2-8.

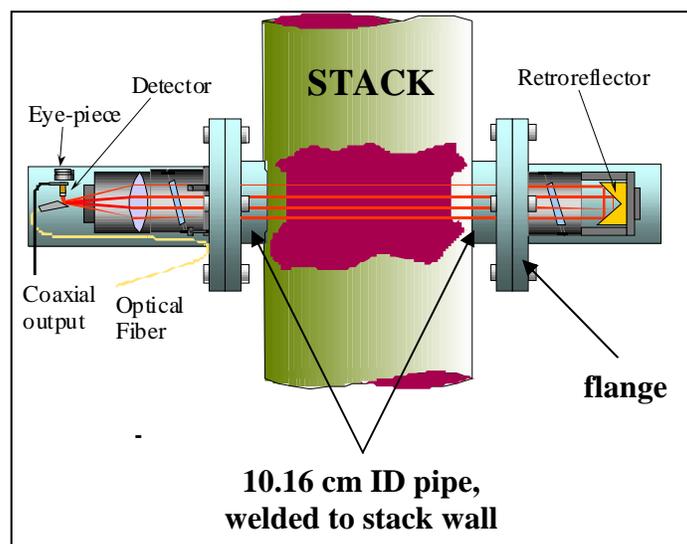


Figure 2-8 TDL Installation

2.7.2. Transfer Line

A 3m long heated transfer line was used to connect the sampling probe to the dilution tunnel. The ISO-8178 protocol is effective for testing fuels with sulfur content less than 0.8% sulfur; the fuels we tested had fuel sulfur contents in the range of 0.16 to 3.8% sulfur (Table 3-1). The protocol allows the use of a heated transfer line not more than 5m in length. Further it states that “If the tube is longer than 1 m, it shall be insulated and heated to a minimum wall temperature of 523 K (250 °C)”. The transfer line we used was unable to achieve this temperature; it was maintained at a temperature >120 °C. Subsequent testing showed this transfer line resulted in significant losses of PM_{2.5} (Jayaram et al, 2009). Though the PM_{2.5} emission factors from the test are not accurate they give a reasonable indication of the effects of the SCR on PM_{2.5} emissions.

2.7.3. Measuring Gases and PM_{2.5} emissions

The concentrations of carbon dioxide (CO₂), nitrogen oxide (NO_x) and carbon monoxide (CO) were measured both in the raw exhaust and the dilution tunnel with a Horiba PG-250 portable multi-gas analyzer (Appendix A, Section 7.2.1). During the July 2005 campaign, the concentration of ammonia (NH₃) downstream of the SCR was measured using a tunable diode laser (Appendix A, Section 7.2.2).

Particulate matter (PM_{2.5}) was sampled from the dilution tunnel on Teflo® and Quartz filters. These filters were analyzed to determine the total and speciated PM_{2.5} mass emissions (Appendix A, Section 7.2.3).

2.7.4. Calculating Exhaust Flow Rates from Intake Air

An accurate calculation of the exhaust gas flow rate is essential for calculating emission factors. For this project the exhaust gas flow rate was calculated as equal to the flow of

intake air. This method is widely used for calculating exhaust flow rates in diesel engines similar to marine auxiliary engines. This method assumes the engine is an air pump, so the flow of air into the engine will be equal to the exhaust flow out of the engine. The flow rate of intake air is determined from the cylinder volume, recorded rpm, and the temperature and pressure of the inlet air. The method works best for four stroke engines or for two-stroke engines where there the scavenger air flow is much smaller than the combustion air. The auxiliary engine we tested was a 4-stroke engine.

2.7.5. Calculation of Emission Factors

The emission factor at each mode is calculated from the measured gaseous and PM_{2.5} concentration, the reported engine load in kilowatts (kW) and the calculated mass flow in the exhaust.

An overall single emission factor representing the engine is determined by weighting the modal data according to the ISO 8178 D2 requirements and summing them. The equation used for the overall emission factor is as follows:

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

Where:

A_{WM} = Weighted mass emission level (HC, CO, CO₂, PM_{2.5}, or NO_x) in g/kW-hr

g_i = Mass flow in grams per hour,

P_i = Power measured during each mode, including auxiliary loads, and

WF_i = Effective weighing factor.

3. Results and Discussions

3.1. Fuel Properties

During each campaign the auxiliary engine was tested on two fuels HFO and MDO. Both fuels were typical of the normal supply. Selected properties of the fuels are shown below.

Table 3-1 Selected Fuel Properties

Test Expedition	Fuel	Density @ 15°C (kg/m ³)	Viscosity @ 50°C mm ² /s	Sulfur Content (%m/m)	Ash Content (%m/m)
July 2005	HFO	983.6	376	3.4	0.04
	MDO	847.4	n/a	0.16	n/a
Dec 2005	HFO	989.5	389	3.8	0.02
	MDO	846.9	n/a	0.160	n/a

n/a: Not Available

3.2. Operating Conditions of the SCR

The average urea injection rates and average temperatures before and after the SCR during the test runs are presented in Tables 3-2 and 3-3.

During the July 2005 campaign we found unusually high PM_{2.5} emission numbers while sampling before the SCR. Since the sampling port before the SCR was located after the point of urea injection we suspected that the PM_{2.5} mass was contaminated with urea. As a result during the December 2005 campaign the urea injection was turned off while sampling before the SCR.

Table 3-2 SCR Operating Conditions (July 2005)

Fuel	Sampling Location	ISO Target Load	Actual Load	Urea Injection Rate lit/hr	Temperature (°C)	
					Before SCR	After SCR
July 2005 – Low NO_x Mode						
HFO	Before SCR	-	40%	16.0	357	371
		50%	54%	25.0	370	385
		75%	68%	28.8	365	377
	After SCR	-	40%	16.0	357	371
		50%	54%	25.0	370	385
		75%	68%	28.8	365	377
MDO	Before SCR	50%	52%	28.5	359	372
	After SCR	50%	52%	28.5	359	372

Table 3-3 SCR Operating Conditions (December 2005)

Fuel	Sampling Location	ISO Target Load	Actual Load	Urea Injection Rate lit/hr	Temperature (°C)	
					Before SCR	After SCR
December 2005						
HFO	Before SCR	25%	30%	0.0	349	356
		50%	52%	0.0	362	364
		75%	67%	0.0	359	362
	After SCR	25%	35%	18.4	349	368
		50%	50%	27.0	361	379
		75%	67%	38.3	352	371
MDO	Before SCR	25%	22%	0.0	349	356
		50%	52%	0.0	362	367
		75%	69%	0.0	354	357
	After SCR	25%	21%	9.2	328	343
		50%	53%	19.9	357	371
		75%	65%	20.0	351	360

3.3. Primary Gaseous Emissions

The major gaseous emissions of interest in the exhaust gas were: carbon dioxide (CO₂), carbon monoxide (CO), sulfur dioxide (SO₂) and nitrogen oxides (NO_x). All of the gaseous emissions were measured using ISO instruments, except for SO₂.

The ISO 8178-1 section 7.4.3.7 states “The SO₂ concentration shall be calculated from the sulfur content of the fuel used, since experience has shown that using the direct measurement method for SO₂, does not give more precise results.” Due to practical considerations we were unable to measure the fuel consumption during the testing procedure. Hence, the fuel flow rate was estimated based on the assumption that 100% of the fuel C (fuel C content: 86% wt/wt for HFO; 87% wt/wt for MDO) is converted to CO₂. This in turn was used along with the sulfur (S) content of the fuel to calculate the SO₂ emissions. Since 2 to 4% of the fuel sulfur gets converted to PM, the SO₂ emissions are biased low. This bias is within our experimental error of 5%.

A detailed list of the gaseous emission factors upstream and downstream of the SCR is provided in Table 3-4 for both fuel types HFO and MDO. Triplicate measurements were made at each load and an average of these is shown in Table 3-4. The error bars in Figures 3-3, 3-4 and 3-5 represent the confidence limits of the analyzed data.

**Table 3-4 Gaseous Emission Factors and Ammonia Slip
MAN B&W 7L32-40 Auxiliary Engine**

Target Load ISO	Actual Load		CO ₂ (g/kW-hr)		CO (g/kW-hr)		NO _x (g/kW-hr)		SO ₂ EPA Calculated (g/kW-hr)	NH ₃ Slip (ppmV)
	Before SCR	After SCR	Before SCR	After SCR	Before SCR	After SCR	Before SCR	After SCR	Before SCR	After SCR
July 2005 Low NO_x Mode: Heavy Fuel Oil (3.6%S)										
-	40%	40%	655	702	1.98	2.72	11.16	1.02	7.06	0.89
50%	54%	54%	632	632	1.33	2.02	11.16	1.19	6.82	1.77
75%	68%	68%	618	614	0.67	1.31	9.66	0.98	6.67	0.66
July 2005 Low NO_x Mode: Marine Distillate Oil (0.16%S)										
50%	52%	52%	649	647	1.60	2.52	8.31	0.00	0.20	36.8
December 2005: Heavy Fuel Oil (3.8%S)										
25%	30%	35%	814	809	1.61	2.45	17.3	1.7	9.81	n/a
50%	52%	50%	708	743	0.94	1.70	16.4	1.6	8.53	n/a
75%	67%	67%	684	700	0.75	1.19	16.0	1.4	8.24	n/a
December 2005: Marine Distillate Oil (0.16%S)										
25%	21%	20%	955	930	1.99	3.80	14.7	2.4	0.48	n/a
50%	48%	49%	697	682	0.98	1.73	11.3	1.8	0.35	n/a
75%	64%	65%	676	689	0.64	1.29	8.9	1.6	0.34	n/a

Note: kW-hr denotes generated power. n/a: not available as it wasn't sampled. %S denotes fuel sulfur content in wt/wt % basis. Tests were conducted with a three meter heated transfer line in the sampling train.

As mentioned earlier, the engine was operating in the low NO_x mode during the July 2005 test. Also the SCR operation was unstable and not meeting the manufacturer's specifications during this test. There was a significant drift in both the urea injection rates and NO_x concentrations after the SCR at a particular engine load point during testing, an example of which is shown in Figure 3-1.

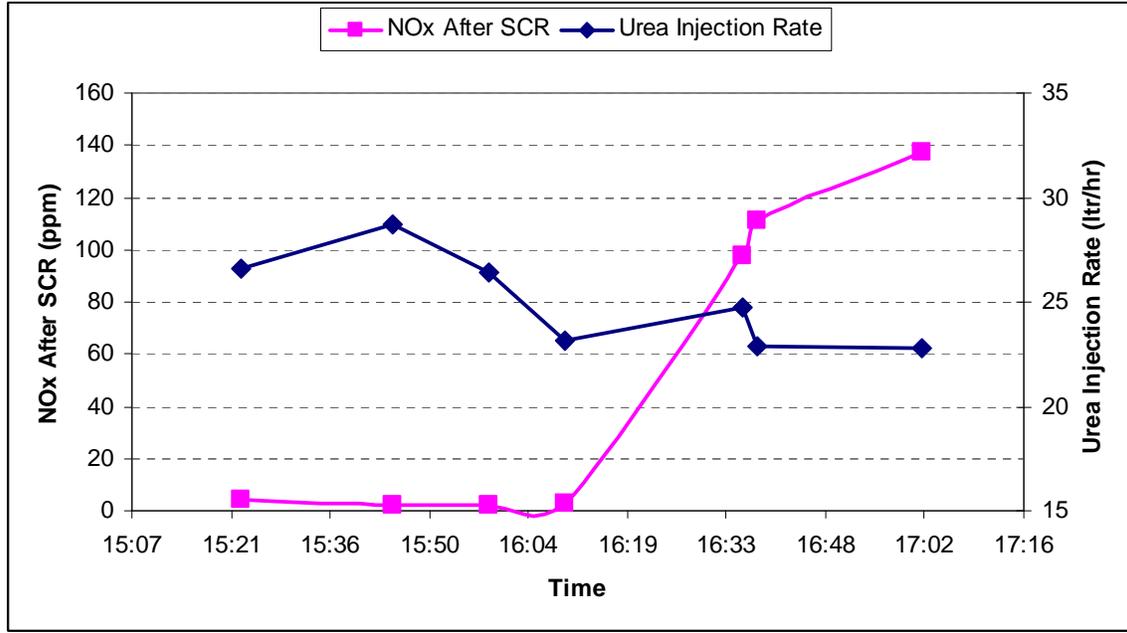


Figure 3-1 Urea Injection Rate and Downstream NO_x @50% Engine Load with HFO July 2005

This issue with the SCR unit was corrected after extensive review and reengineering of the system. The SCR was then tested after in December of 2005.

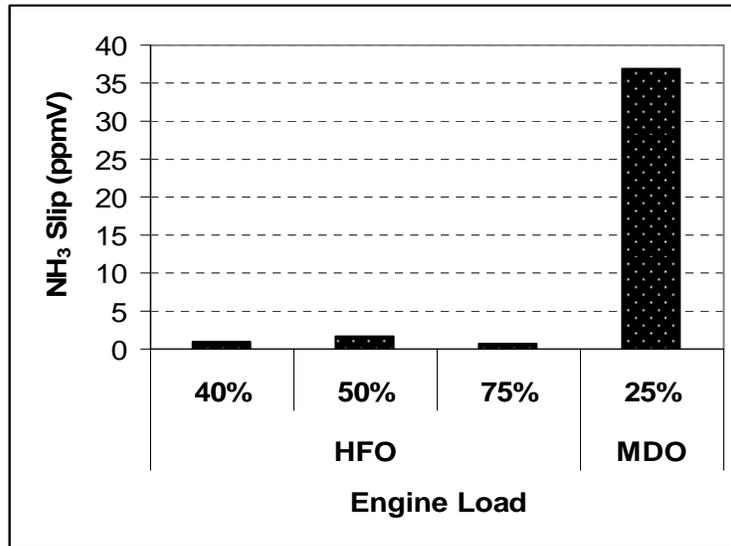
3.3.1. NH₃ Gas Emissions

Ammonia was measured with a TDL. Huai et al, 2003 compares two systems for measurement of NH₃: the more commonly used fourier transform infrared system and the TDL. They further show that TDL has greater sensitivity and a smaller response time than FTIR, hence is better suited for NH₃ measurements.

The common control level for NH₃ is <10ppm. For most of the July 2005 campaign the NH₃ slip measured downstream of the SCR met this control level. However, during the final stages of the campaign, the NH₃ slip increased to as high as 76ppmV and the test had to be abandoned. Average values of the NH₃ slip measured at each test mode during the July 2005 test are shown below (Figure 3-2).

Most SCRs are equipped with a DOC that helps to oxidize any NH₃ downstream of the catalyst to NO_x. As mentioned earlier, due to space constraints this system did not have a DOC. Due to unstable operation of the SCR unit during the July 2005 campaign as well as unusually high NH₃ slip during the final stages the system had to be shut down. Extensive review and reengineering of the system had to be done before it could be tested again in December of 2005.

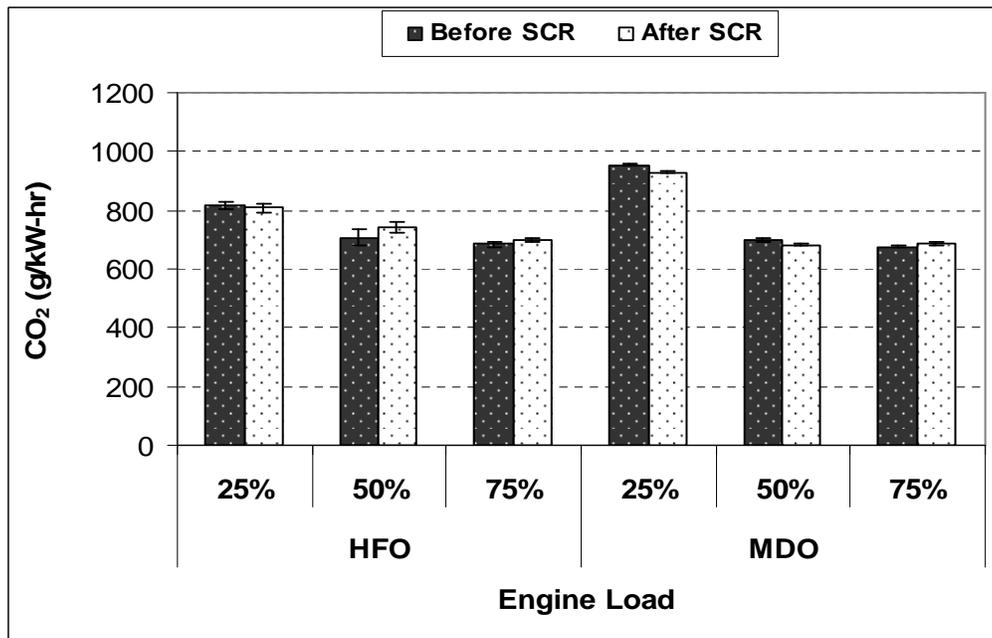
Figure 3-2 NH₃ Slip, July 2005



3.3.2. CO₂ Emission Factors

A comparison of the CO₂ emission factors in g/kW-hr across loads and fuel types before and after the SCR is presented in Figure 3-3. As expected there was no significant change in the CO₂ emission factor after the SCR. The small error bars in the figure, representing the standard deviations of the triplicate measurements taken at each test mode, show good repeatability in the test cycle.

**Figure 3-3 Effect of SCR on CO₂ Emissions
MAN B&W 7L32-40 Auxiliary Engine**

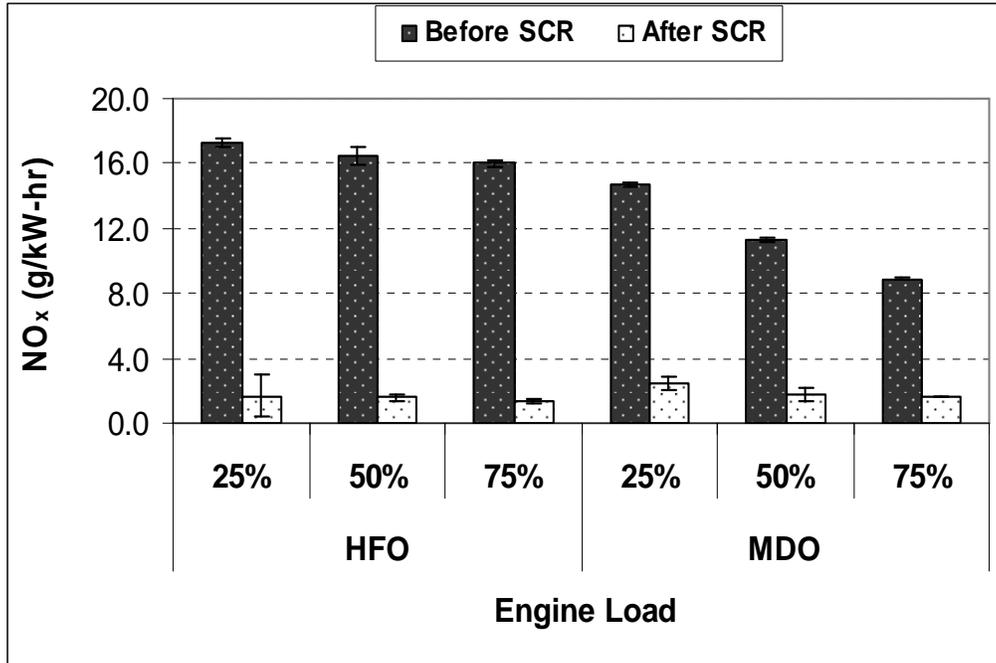


Note: kW-hr denotes generated power

3.3.3. NO_x Emission Factors

The SCR reduced the NO_x emissions from the auxiliary engine by 90-91% in the case of the HFO fuel and 82-84% in the case of the MDO fuel (Figure 3-4).

**Figure 3-4 Effect of SCR on NO_x Emissions
MAN B&W 7L32-40 Auxiliary Engine**



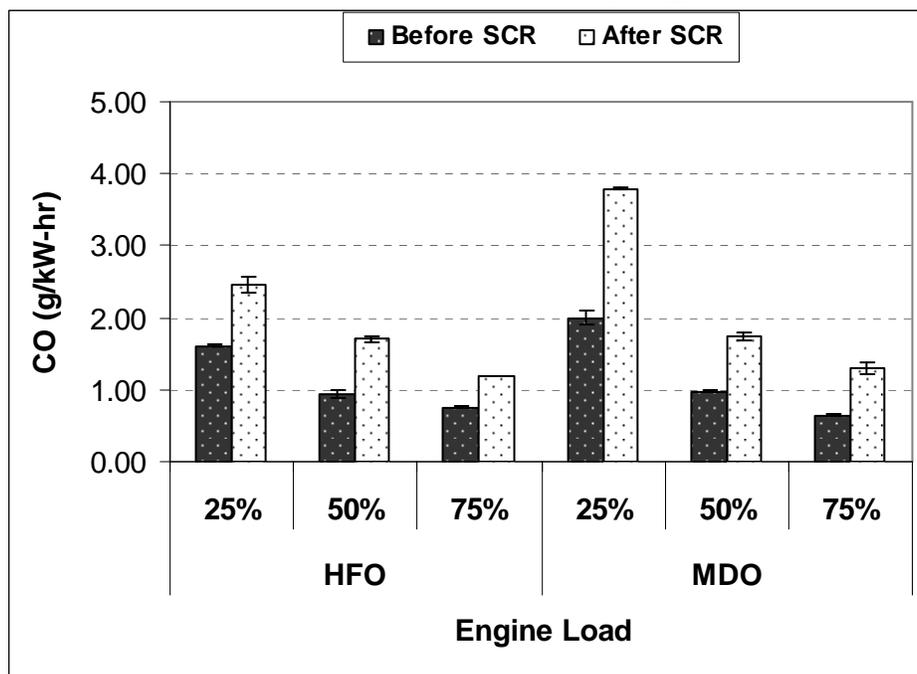
Note: kW-hr denotes generated power

Comparison of the upstream values for HFO and MDO reveal that switching to MDO from HFO results in a NO_x reduction of about 15-45% with the reduction increasing as the engine load is increased. The NO_x emission factor shows a downward trend with the increase in engine load which is typical of this engine model (Jayaram et al., 2009).

3.3.4. CO Emission Factors

Since marine diesel engines are highly efficient, the CO emission factor is expected to be very low. This is demonstrated by the emission factors measured on the post-Panamax vessel shown in Figure 3-3. Note here that the CO emissions increased by a factor of 1.4 to 2.0 downstream of the SCR. This is contrary to the results presented on the SCR tests performed on the Staten Island Ferry where a reduction in CO emissions was observed (M.J. Bradley & Associates, 2006). This difference in findings is expected since the SCR system does not have a DOC like the Staten Island Ferry; hence CO emissions did not reduce.

Figure 3-5 Effect of SCR on CO Emissions
MAN B&W 7L32-40 Auxiliary Engine



Note: kW-hr denotes generated power

The vanadium in the SCR catalyst is known to partial oxidize hydrocarbons and carbonaceous PM matter (Amon et al., 2001a, Amon et al., 2001b). In this project also we noticed a reduction of the elemental and organic carbon associated with the PM (Sections 3.5.1 and 3.5.2). Hence, the increase in CO emission factor may be attributed to partial oxidation of hydrocarbons and carbonaceous PM matter occurring in the selective catalytic reduction unit.

3.4. Particulate Matter Emissions

In addition to the gaseous emissions, this project measured the Particulate Matter (PM) mass emission factors. Particulate emissions mainly originate due to the incomplete combustion of fuel and lubricating oil and from the condensation of sulfuric acid and hydrocarbon aerosols. Secondary sources of PM include the elements in the fuel and lubricating oil; for example, vanadium in bunker fuel and calcium on the lube oil.

As described earlier, the PM mass was sampled from the main stream with a partial dilution method and collected on filter media. Subsequent analyses allowed us to report the total PM_{2.5} mass and the speciated PM_{2.5} mass fractions such as hydrated sulfate, Organic Carbon (OC) and Elemental Carbon (EC).

3.4.1. PM_{2.5} Emissions, July 2005

During the July 2005 campaign besides the total and speciated PM_{2.5} emission factors size-segregated PM emissions were measured using a Micro Orifice Uniform Deposit Impactor (MOUDI). Unfortunately there were a couple of issues encountered during this

campaign. Firstly, the operation of the SCR system during this campaign was unstable (Section 3.3). So the PM samples taken downstream of the SCR are suspect.

Next, the sampling port before the SCR was installed downstream of the point of urea injection. During a subsequent campaign in October of 2005 conducted to determine baseline emissions upstream of the SCR, we found unusually high PM mass numbers (results reported in Jayaram et al., 2009). The October 2009 filters tested positive for urea using reflective Fourier Transform Infra Red (FTIR) spectrometry technique.

PM numbers measured in July 2005 campaign were higher than the December 2005 campaign but not as high as the October 2005 campaign. However, the engine was operating on Low NO_x mode during the July 2005 campaign and so the PM numbers from his campaign are not directly comparable to the other two campaigns. Since the urea injection was on during the July 2005 campaign we suspect that the filters collected before the SCR were contaminated. Unfortunately, these filters had been destroyed by further analysis on them and were unavailable to test for urea by reflective FTIR.

As a result the total and speciated PM_{2.5} mass numbers from the July 2005 campaign both before and after the SCR are suspect. They are presented in Appendix B.

3.4.2. PM_{2.5} Emissions Factors, December 2005

During the December 2005 campaign the operation of the SCR was stable and special care was taken to turn off the urea injection while sampling upstream of the SCR to avoid issues of urea contamination of the filters. Total PM_{2.5} mass emission factors obtained during the December 2005 test are reported in Table 3-5 and Figure 3-6. Triplicate measurements were made at each test mode; the error bars in the figure are presented as an indication of the confidence limits.

These emission factors have to be used with caution as they are believed to be underreported due to the use of a long raw gas transfer line. The certification method currently allows a for a transfer line up to 3m in length. Recent testing at UCR, however, indicates that PM transfer losses in a 3m line can be as high as 40% when using high sulfur fuels (Jayaram et al., 2009). Though the absolute value of these emissions factors are not accurate, they can however be used to determine the effect of the SCR.

Table 3-5 Effect of SCR on PM Emission Factors, December 2005
MAN B&W 7L32-40 Auxiliary Engine

Target Load ISO	PM Mass (g/kW-hr)			
	HFO		MDO	
	Before SCR	After SCR	Before SCR	After SCR
25%	0.675	1.192	0.702	0.297
50%	0.479	1.438	0.297	0.440
75%	0.293	1.090	0.192	0.552

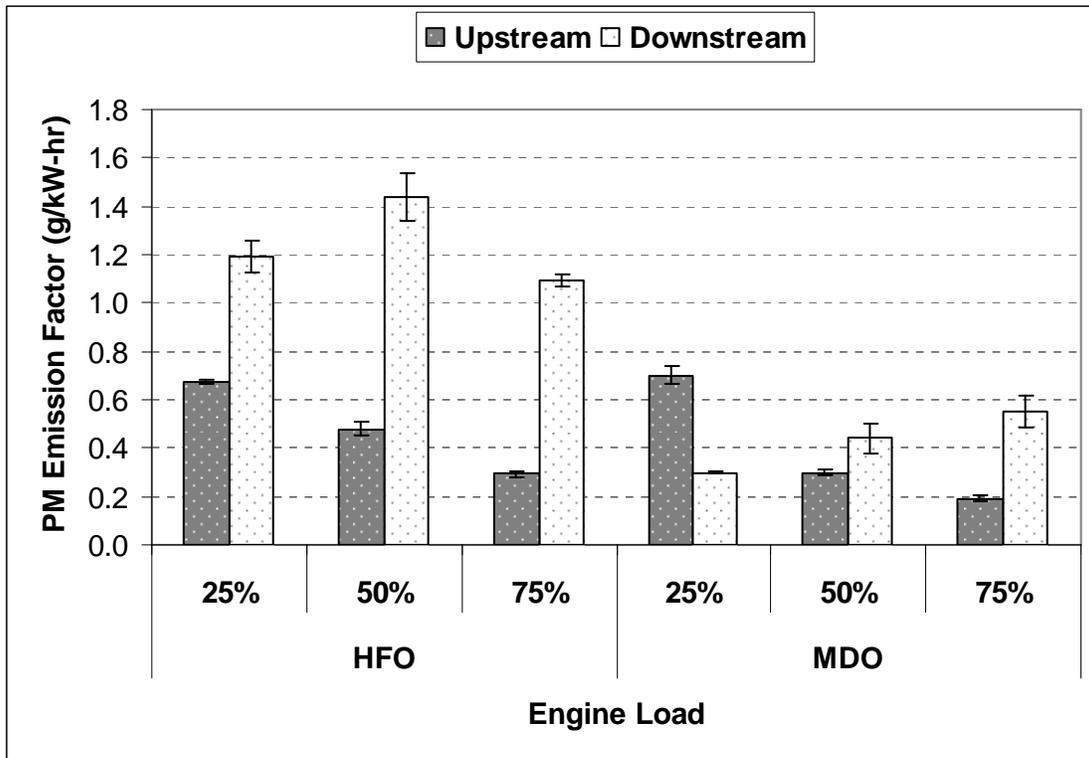
Note: kW-hr denotes generated power. Fuel sulfur content: HFO 3.8%, MDO 0.16%. Tests conducted with 3m transfer line in sampling train

PM mass was measured during the July 2005 test as well. There were two issues with the PM sampling in July 1) the SCR system was unstable b) we suspect that the PM measured upstream of the catalyst during this test could have been contaminated with urea. Details of this are provided in Section 8.1

The PM emission increases by a factor of 1.7 to 3.7 downstream of the SCR for HFO. It also increases in the case of MDO at higher loads. Other tests using this SCR technology on a ferry and trucks have reported reduction in PM mass (M.J. Bradley & Associates 2006, Amon et al., 2001a, Amon et.al, 2001b, Klaus et al., 2003). However all of these engines used fuels with much lower sulfur content. Coal fired power plants that use high sulfur coals have reported an increase in PM emissions downstream of SCR (Morita et al., 2005).

In this study we see a reduction in elemental and organic carbon fractions of the PM and a substantial increase in the sulfate fraction of PM (Section 3.5). Since the fuels here are high sulfur fuels the increase in the sulfate fraction clearly off-sets the decrease in the carbonaceous PM mass hence leading to an overall increase in PM mass. Also HFO having the higher sulfur content shows a greater increase in the PM mass across the SCR as compared to MDO.

Figure 3-6 Effect of SCR on PM Emission Factor, December 2005
MAN B&W 7L32-40 Auxiliary Engine



Note: kW-hr denotes generated power. Fuel sulfur content: HFO 3.8%, MDO 0.16%. Tests conducted with 3m transfer line in sampling train.

Note that for the MDO test at 25% mode there is actually a reduction in PM mass, this is because there was a very high concentration of OC in the PM upstream of the SCR and the reduction in OC was much larger than the increase in hydrated sulfate across the SCR.

3.5. Speciated Particulate Matter Emissions, December 2005

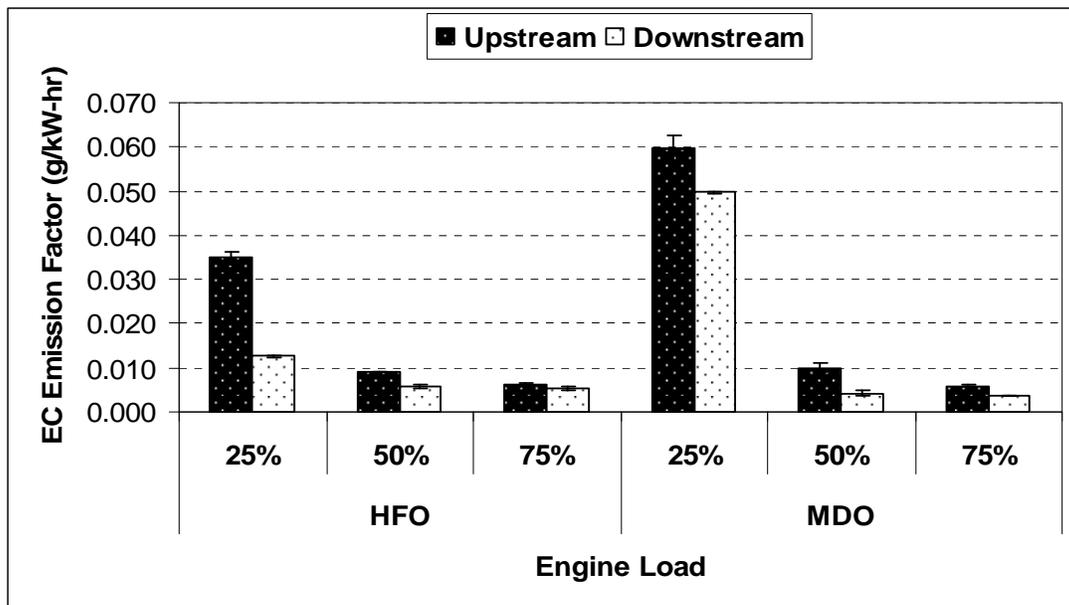
There is very little in-use data of speciated PM from marine diesel engines available in literature. The chief constituents of PM from marine diesel engines are sulfate for bunker fuel followed by organic carbon and elemental carbon. The emission factors of these three species measured during the December 2005 expeditions are compared before and after the SCR in the following sections. As in the case of PM mass, triplicate measurements were made at each load and the error bars in the Figures 3-6, 3-7 and 3-8 give an idea of the confidence limits for the test. Details of the analysis are provided in Section 7.2.3.

Note that the emission factors reported below are underestimated due to the losses that occur with the use of a transfer line (Jayaram et al., 2009) however they can be used for a comparison across the SCR as relative losses will be the same.

3.5.1. Elemental Carbon (EC)

The elemental carbon fraction of the PM accounts for less than 8% of the total PM mass. It was found that this fraction reduces by an average of 35% downstream of the SCR (Figure 3-7). Klaus et al., 2003 have also reported a reduction of elemental carbon downstream of the SCR catalyst.

**Figure 3-7 Effect of SCR on Elemental Carbon fraction of PM, December 2005
MAN B&W 7L32-40 Auxiliary Engine**

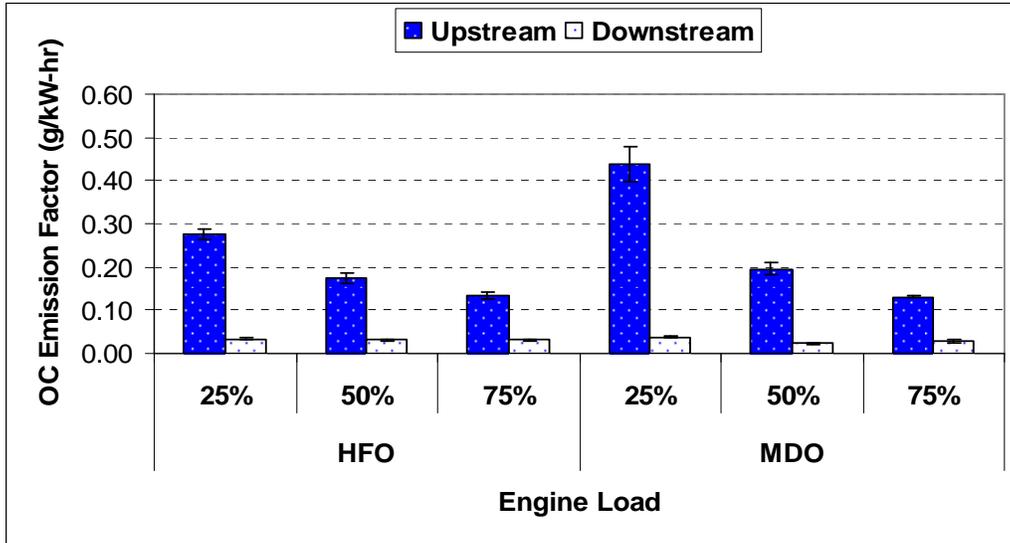


Note: kW-hr denotes generated power. Fuel sulfur content: HFO 3.8%, MDO 0.16%. Tests conducted with 3m transfer line in sampling train.

3.5.2. Organic Carbon (OC)

The ratio of organic carbon to elemental carbon in the PM mass is about 8 to 22 upstream of the SCR. As we go downstream, the OC emission factor reduces by 77% -91% (Figure 3-8). Other studies on trucks have reported a reduction in the organic carbon fraction of the PM mass (Amon et al., 2001b, Klaus et al., 2003). The ratio of OC to EC becomes lower (1to 8) downstream of the SCR because the reduction in OC is much greater than EC.

**Figure 3-8 Effect of SCR on Organic Carbon fraction of PM, December 2005
MAN B&W 7L32-40 Auxiliary Engine**



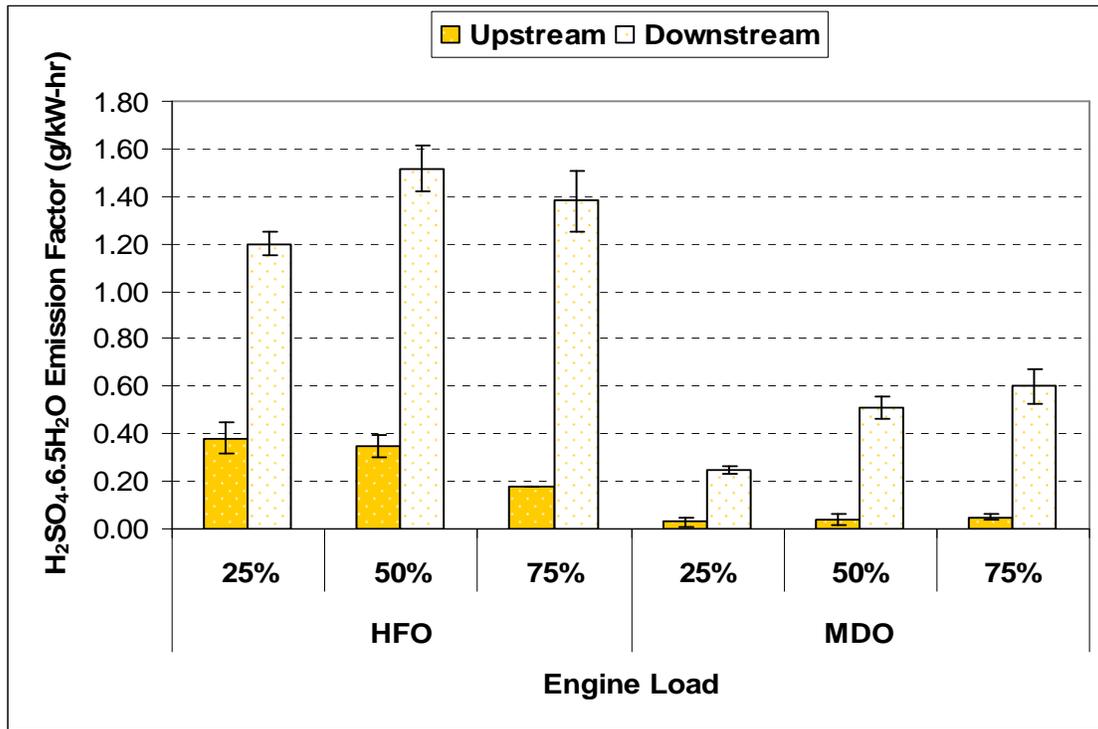
Note: kW-hr denotes generated power. Fuel sulfur content: HFO 3.8%, MDO 0.16%. Tests conducted with 3m transfer line in sampling train.

3.5.3. Hydrated Sulfate

The sulfate on the filter is represented in the hydrated form $H_2SO_4 \cdot 6.5H_2O$. The emission factors of hydrated sulfate at different loads upstream and downstream of the SCR are reported in Figure 3-9.

The PM emitted by HFO fuel has a much higher sulfate fraction than that of MDO basically because HFO has higher fuel sulfur content. There is a 68% to 87% increase in the hydrated sulfate fraction of PM for HFO and an 89% to 92% increase for MDO downstream of the SCR. The vanadium catalyst in the SCR is known to help in the oxidation of SO_2 to SO_3 which in turn will enhance the formation of sulfate (Svachula et al., 1993). Other studies have also shown an increase in the sulfate fraction of the PM mass downstream of the SCR (M.J. Bradley & Associates 2006, Morita et al., 2005)

**Figure 3-9 Effect of SCR on hydrated Sulfate fraction of PM, December 2005
MAN B&W 7L32-40 Auxiliary Engine**



Note: kW-hr denotes generated power. Fuel sulfur content: HFO 3.8%, MDO 0.16%. Tests conducted with 3m transfer line in sampling train.

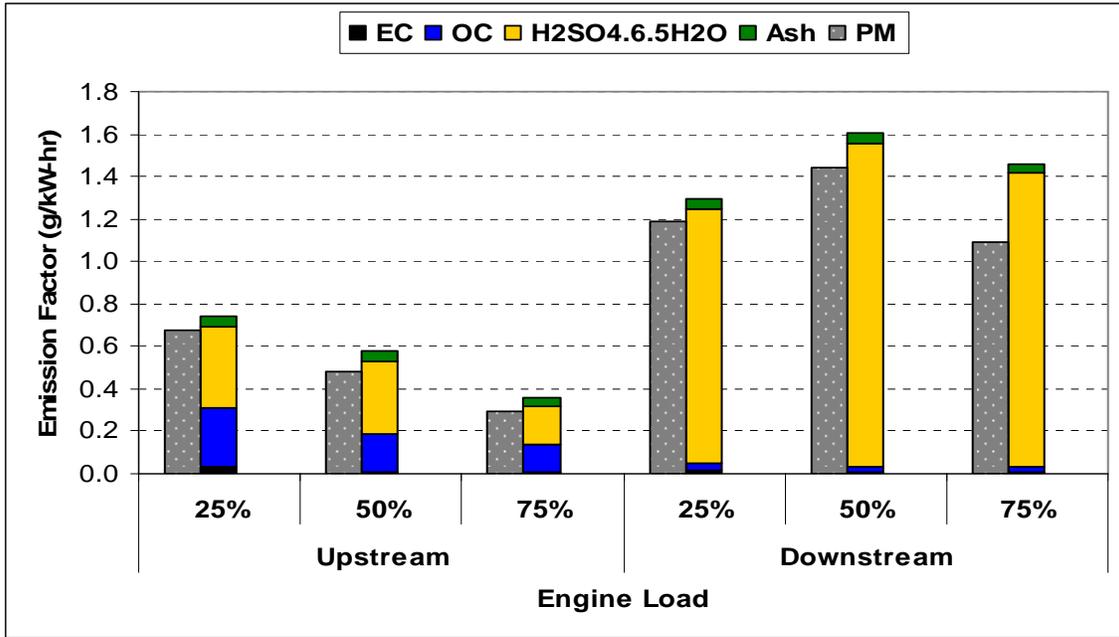
The PM emitted by HFO fuel has a much higher sulfate fraction than that of MDO basically because HFO has higher fuel sulfur content. There is a 68% to 87% increase in the hydrated sulfate fraction of PM for HFO and an 89% to 92% increase for MDO downstream of the SCR. The vanadium catalyst in the SCR is known to help in the oxidation of SO₂ to SO₃ which in turn will enhance the formation of sulfate (Svachula et al., 1993). Other studies have also shown an increase in the sulfate fraction of the PM mass downstream of the SCR (M.J. Bradley & Associates 2006, Morita et al., 2005)

3.5.4. Internal Quality Check: Conservation of Mass Emissions

An important element in UCR's analysis approach is the QA/QC check that total mass is conserved for the various PM methods. Specifically, we compare the total mass collected on the Teflon filter with the sum of the masses independently measured as sulfate, organic, elemental carbon and ash (calculated).

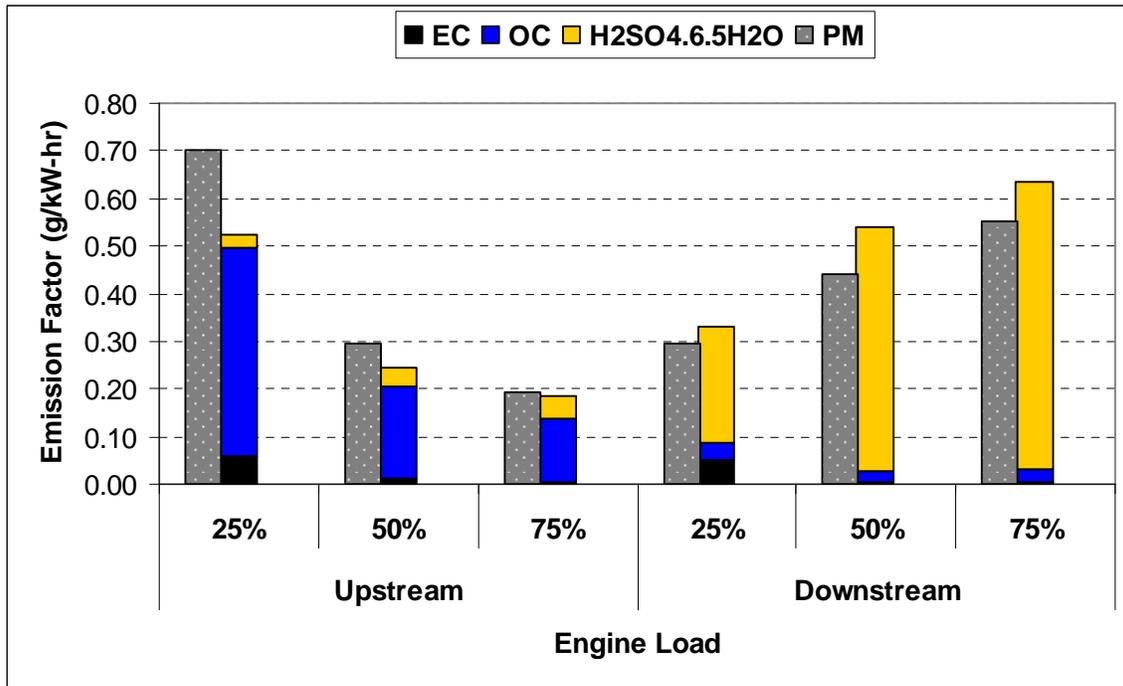
The ash content of the PM is calculated based on the assumption that all of the ash in the fuel goes to PM. We do not have the actual rate of fuel consumption so it is estimated from the CO₂ emission factor, as done for the calculation of SO₂. The fuel ash content was not available for MDO; hence it is not shown in the Figure 3-10. Figures 3-9 and 3-10 show reasonably good balance between the speciated PM and total PM Mass for HFO and MDO fuels respectively.

Figure 3-10 Speciated PM Emission Factors for HFO, December 2005
 MAN B&W 7L32-40 Auxiliary Engine



Note: kW-hr denotes generated power. Fuel sulfur content: HFO 3.8%, MDO 0.16%. Tests conducted with 3m transfer line in sampling train.

Figure 3-11 Speciated PM Emission Factors for MDO, December 2005
 MAN B&W 7L32-40 Auxiliary Engine



Note: kW-hr denotes generated power. Fuel sulfur content: HFO 3.8%, MDO 0.16%. Tests conducted with 3m transfer line in sampling train.

4. Summary and Recommendations

UCR, CARB and a major shipping company collaborated on the measurement of criteria and greenhouse gas (CO₂) emissions both upstream and downstream of a SCR installed on an auxiliary engine of a post-Panamax container ship. The auxiliary engine was tested on two fuels HFO and MDO and the test cycle approximated the ISO 8178-D2 marine engine certification test cycle. Detailed emissions factors for CO₂, CO, NO_x, PM mass and speciated PM (EC, OC and hydrated sulfate) were determined.

The testing project was successful. Identified below are areas for further investigation.

- Though the SCR is effective in reducing the NO_x emission it increases the emissions of PM mass especially for the high sulfur fuel. The operating conditions of the SCR should be further investigated to determine if operation of the SCR at different temperatures and/or urea injection rates can produce less PM mass while still providing a considerable reduction in NO_x emission factors.
- The organic and elemental carbon fraction of the PM mass were reduced considerably downstream of the SCR. This may indicate that gaseous hydrocarbons are also reduced in the SCR. Sampling speciated hydrocarbons such as carbonyls and polyaromatic hydrocarbons upstream and downstream of the SCR could provide more insight into this.

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6. Glossary of Symbols and Abbreviations

Al	Aluminum
°C	degree centigrade
C	Carbon
CA	California
CARB	California Air Resources Board
CFO	Critical Flow Orifice
CFR	Code of Federal Regulation
CO	Carbon monoxide
CO ₂	Carbon dioxide
DAF	Dilution Air Filter
DNPH	2,4Dinitrophenylhydrazine
DT	Dilution Tunnel
EC	Elemental Carbon
EGA	Exhaust Gas Analyzer
EP	Exhaust Pipe
EPA	Environmental Protection Agency
Ft	feet
FTIR	Fourier Transform Infra-Red
F.S./day	full scale per day
g/kW-hr	grams per kilowatt-hour
HFO	Heavy Fuel Oil
Hz	Hertz
HCLD	heated chemiluminescence detector
HEPA	High Efficiency Particulate Air
H ₂ O	Water
H ₂ SO ₄ .6.5H ₂ O	hydrated sulfate or hydrated sulfuric acid
IMO	International Maritime Organization
ISO	International Organization for Standardization
kg/m ³	kilograms per cubic-meter
kW	kilowatt
lit	liters
lit/hr	liters per hour
m	meter
MDO	Marine Distillate Oil
MI	Michigan
min	minutes
MOUDI	Micro-Orifice Uniform Deposit Impactor
mm ² /s	square-millimeter per second
m/m	mass by mass
NDIR	Non-dispersive infra red
(NH ₂) ₂ CO	Urea
NH ₃	Ammonia
NIOSH	National Institute of Occupations Safety and Health

NO	Nitrogen monoxide
NO _x	Oxides of Nitrogen
NO ₂	Nitrogen dioxide
N ₂	Nitrogen
OC	Organic Carbon
PM	Particulate Matter
PTFE	Polytetrafluoroethylene or Teflon Filter
ppm	parts per million
ppmV	parts per million by volume
psig	pound-force per square-inch gauge
PUF	Poly Urethane Foam/XAD
QC/QA	Quality Control/Quality Assurance
RH	Relative Humidity
RPM	revolutions per minute
SCR	Selective Catalytic Reduction
SO ₂	Sulfur dioxide
SO ₃	Sulfur trioxide
SP	Sampling Probe
T	Temperature
TDL	Tunable Diode Laser
TDS	Thermal Desorption System
TT	Transfer Tube
UCR	University of California, Riverside
U.S.	United States
V	Volts
VN	Venturi
vol%	volume %
wt/wt%	weight by weight %
WI	Wisconsin

7. Appendix A

7.1. Certification Emission Test Protocol for Marine Auxiliary Engines

In general, the operating conditions during a certification test for internal combustion engines follows a prescribed sequence that is specified in the ISO 8178-Part 4, *Test cycles for different engine applications*. The ISO 8178 D-2 test cycle is used for engines operating at constant speed with intermittent load, such as backup generators or auxiliary engines. The standard test protocol consists of a series of preconditioning cycles to warm and stabilize the engine at full load followed by a sequence of stabilization and testing at the five specified modes, each with a defined speed, load and minimum test duration as shown in The weighting factors used in the determination of the emission factor are listed as well.

Table 7-1 Five Mode Test Cycle for Constant Speed Engines (ISO-8178-D-2 test cycle)

Mode number	Engine Speed ¹	Observed Torque ²	Minimum time in mode, min.	Weighting factors
1	Rated	100	5.0	0.05
2	Rated	75	5.0	0.25
3	Rated	50	5.0	0.30
4	Rated	25	5.0	0.30
5	Rated	10	5.0	0.10

During this time the gases and particulate matter in the exhaust are sampled and analyzed according to the previously described procedures. Additionally, the engine conditions, such as charge air pressure and temperature, and the engine operating parameters used to determine the mass flow rate were measured and recorded at each test mode. The test procedure was designed to determine the brake-specific emissions of criteria emissions: carbon monoxide, oxides of nitrogen, and particulate matter.

7.2. Protocol for Measuring Actual In-Use Emissions from Auxiliary Engines

UCR has considerable experience in making real time measurements of emissions from various pieces of operating equipment. Methods for sampling and analysis of the gases

¹ Engine Speed: $\pm 2\%$ of point

² Torque: Throttle fully open at 100% point. Other points $\pm 2\%$

and particulate matter (PM) from actual in-use auxiliary engines were selected in conformance to the requirements of ISO 8178-1³.

The approach involved the use of a partial flow dilution system with single venturi as shown in Figure 7-1. Raw exhaust gas was transferred from the exhaust pipe (EP) to the dilution tunnel (DT) through the sampling probe (SP) and the transfer tube (TT) due to the negative pressure created by the venturi (VN) in DT. The transfer line is heated to prevent condensation of exhaust components (including water and sulfuric acid) at any point in the sampling and analytical systems.

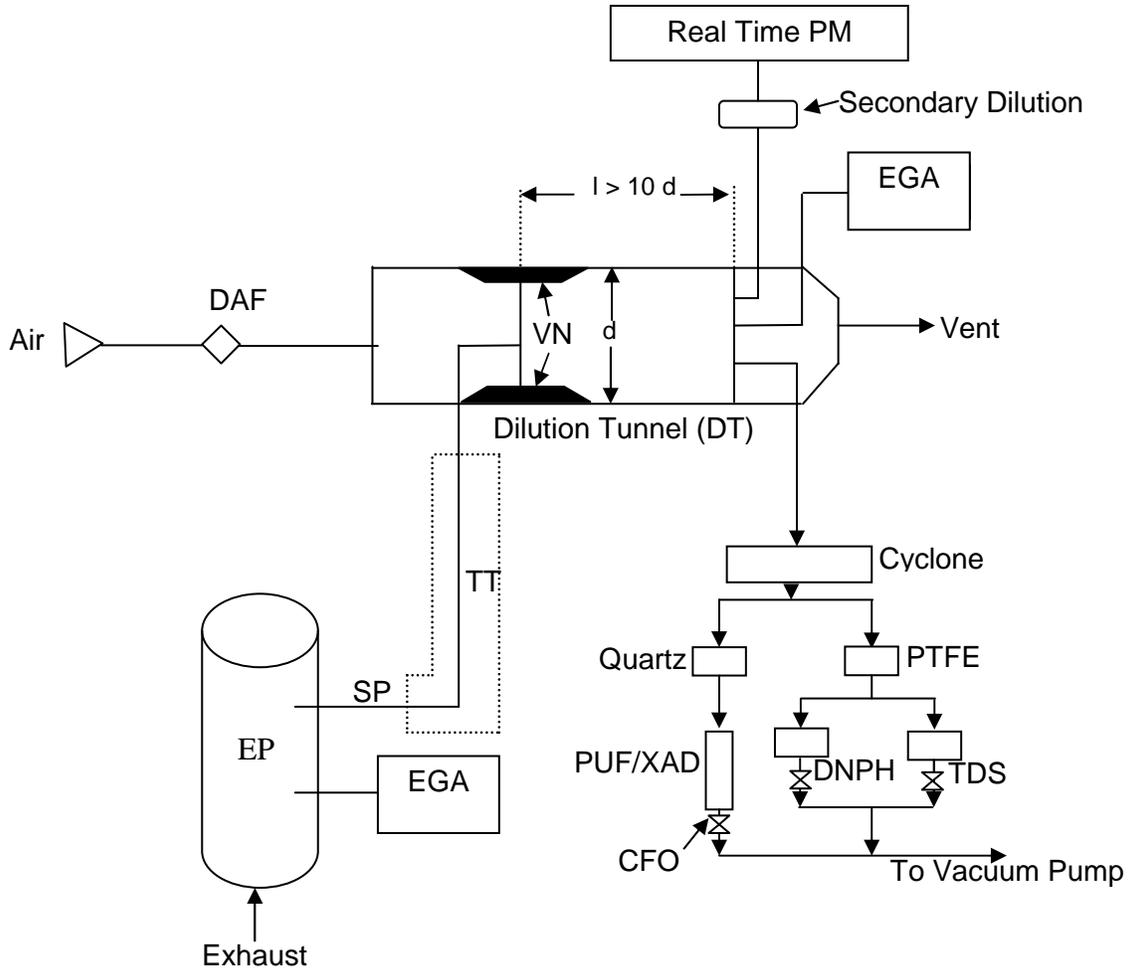


Figure 7-1 Partial Flow Dilution System with Single Venturi, Concentration Measurement and Fractional Sampling

The gas flow rate through TT depends on the momentum exchange at the venturi zone and is therefore affected by the absolute temperature of the gas at the exit of TT. Consequently, the exhaust split for a given tunnel flow rate is not constant, and the

³ 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*

dilution ratio at low load is slightly lower than at high load. The tracer gas concentrations (CO_2 or NO_x) are measured in the raw exhaust gas, the diluted exhaust gas and the dilution air using the exhaust gas analyzer (EGA), and the dilution ratio is calculated from the measured values.

In order to apply the ISO approach in the field, UCR designed a portable set of equipment that is field deployable. The equipment fits into several metal cases with an interior of foam molding to allow sensitive equipment, like computers, to be easily transported or even be lifted and dropped into cargo areas on a vessel without harm to the contents. For practical purposes, the design includes pieces of equipment that allow the use of a range of common electrical (120/240V, 50/60Hz) and supply air utilities. For example, while UCR tries to obtain instrument grade pressurized air for dilution air, we further process any supply air through a field processing unit to assure the quality of the dilution air. The processing air takes the supply air through a number of steps including reducing the pressure to about 30psig as that allows a dilution ratio of about 5/1 in the geometry of our system. The next stages, in sequence, for conditioning the supply air included: liquid knock-out vessel, desiccant to remove moisture with silica gel containing an indicator, hydrocarbon removal with activated charcoal and a HEPA filter for the fine aerosols that might be present in the supply air. The silica gel and activated carbon are changed for each field campaign. Figure 6-2 below shows the unit for processing the dilution air.



Figure 7-2 Field Processing Unit for Purifying Dilution Air in Carrying Case

7.2.1. Measuring Criteria Gaseous Emissions

The concentrations of gases in the raw exhaust and the dilution tunnel were measured with a Horiba PG-250 portable multi-gas analyzer. The PG-250 can simultaneously measure up to five separate gas components using the measurement methods recommended by the EPA. The signal output of the instrument was interfaced directly

with a laptop computer through an RS-232C interface to record measured values continuously. Major features include a built-in sample conditioning system with sample pump, filters, and a thermoelectric cooler. The performance of the PG-250 was tested and verified under the U.S. EPA ETV program.



Figure 7-3 In-Field Illustration of Continuous Gas Analyzer and Computer for Data Logging

Details of the gases and the ranges for the Horiba instrument are shown in Table 7-2. Note that the Horiba instrument measured sulfur oxides (SO_2); however, the ISO reference³ reports: “The SO_2 , concentration shall be calculated from the sulfur content of the fuel used, since experience has shown that using the direct measurement method for SO_2 , does not give more precise results.”

For quality control, UCR carried out analyzer checks with calibration gases both before and after each test to check for drift. Because the instrument measures the concentration of five gases, the calibration gases are a blend of several gases (super-blend) made to within 1% specifications by Praxair (Los Angeles, CA). Drift was determined to be within manufacturer specifications of $\pm 1\%$ full scale per day, except for SO_2 set at $\pm 2\%$ F.S./day. Other specifications of the instruments are provided in Table 7-3.

Table 7-2 Detector Method and Concentration Ranges for Monitor

Component	Detector	Ranges
Nitrogen Oxides (NO _x)	Heated Chemiluminescence Detector (HCLD)	0-25, 50, 100, 250, 500, 1000, & 2500 ppmv
Carbon Monoxide (CO)	Non dispersive Infrared Absorption (NDIR)	0-200, 500, 1000, 2000, & 5000 ppmv
Carbon Dioxide (CO ₂)	Non dispersive Infrared Absorption (NDIR)	0-5, 10, & 20 vol%
Sulfur Dioxide (SO ₂)	Non dispersive Infrared Absorption (NDIR)	0-200, 500, 1000, & 3000 ppmv
Oxygen	Zirconium oxide sensor	0-5, 10, & 25 vol%

Table 7-3 Quality Specifications for the Horiba PG-250

Repeatability	±0.5% F.S. (NO _x : ≤100ppm range CO: ≤1000ppm range) ±1.0% F.S.
Linearity	±2.0% F.S.
Drift	±1.0% F.S./day(SO ₂ : ±2.0%F.S./day)

7.2.2. Measuring Ammonia Emissions

Ammonia emissions in the engine exhaust were measured using a portable Tunable Diode Laser (TDL) system. This system is used to measure NH₃ concentration over an open path based on an EPA approved method. It consists of an integrated transmitter/receiver (transceiver) unit and a remote, passive retro reflector. These two components have to be installed on either side of the path in which the ammonia has to be measured. The infield setup in the exhaust of the auxiliary engine shown in Figure 7-4.



Figure 7-4 In Field Illustration of TDL

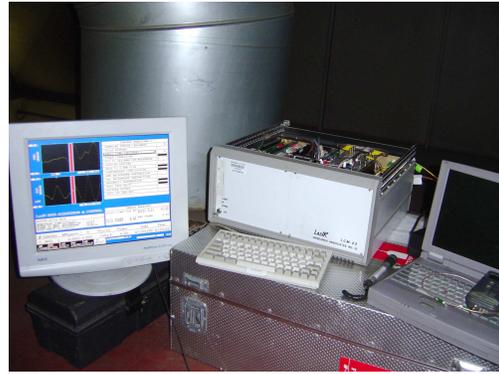


Figure 7-5 Data Logging for TDL

The transceiver unit houses a laser diode source, drive electronics, a photodiode detector module and microcomputer subsystems. The laser emitted from this unit propagates through the exhaust to the retro reflector and returns to the source where it is focused onto the detector. Also a portion of the laser is passed through a reference cell to provide a continuous calibration update. The signal from the detector is logged continuously on a computer (Figure 7-5).

7.2.3. Measuring the Particulate Matter (PM) Emissions

A raw particulate sampling probe was fitted close to and upstream of the raw gaseous sample probe in the exhaust. In order to measure PM, a sampling probe was inserted into the end of the dilution tunnel (>10 diameters downstream) and directed to a PM sample splitter that allowed up to three samples to be collected.

For this test, we used one of the PM lines and directed it to a cyclone separator, sized to remove particles >2.5 μm . From the separator, we added two lines with 47 Gelman filter holders, one for collecting PM on a TefloTM filter and the other for collecting PM on a Quartz filter. Thus the flow in the dilution tunnel was split into two fractions, a smaller flow for measuring PM mass and PM properties and a much larger flow that was vented outside the vessel. Note, with the partial dilution approach for measuring gases and PM, it is critical for the dilution ratio be determined very accurately.

UCR collected simultaneous TefloTM and Quartz filters at each operating mode and analyzed them according to standard procedures. The simultaneous collection of Quartz and TefloTM filters allows an internal quality check of the PM mass. TefloTM filters used to acquire PM mass were weighted following the procedure of the Code of Federal Regulations (CFR) (40 CFR Part 86). Briefly, total PM were collected on Pall Gelman (Ann Arbor, MI) 47 mm TefloTM filters and weighed using a Cahn (Madison, WI) C-35 microbalance. Before and after collection, the filters were conditioned for 24 hours in an environmentally controlled room (RH = 40%, $T = 25^\circ\text{C}$) and weighed daily until two consecutive weight measurements were within 3 μg .

The PM mass on the Teflo™ filter was then extracted in double distilled water after wetting the filter surface with a few drops of isopropyl alcohol. This solution was then filtered and analyzed in a Dionex ICS 1000 using Ion Chromatography to determine the mass of sulfate on the filter.

PM samples were collected in parallel on a 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 reference method (NIOSH 1996). All PM filters were sealed in containers immediately after sampling, and kept chilled until analyzed.

7.2.4. Measuring Size Segregated PM Emissions

In order to measure the size segregated PM emissions (aerodynamic diameter) the sample probe is inserted into the dilution tunnel (>10 diameters downstream of) and directed to the Micro Orifice Uniform Deposition Impactor (MOUDI). The MOUDI is a precision high performance cascade impactor that provides a high sampling flow rate, low inter-stage wall loss and sharp cut-point characteristics. The 10 stage non-rotating MOUDI Model 110 provides cut point diameters of 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1, and 0.056 μm.



Figure 7-6 Micro Orifice Uniform Deposit Impactor

47mm Al filter substrates are used for collecting the sample. These are weighed before and after collection using a Cahn (Madison, WI) C-35 microbalance. Before each weighing, the filters were conditioned for at least 24 hours in an environmentally controlled room (RH = 40%, $T = 25^{\circ}\text{C}$). Also they were weighed daily until two consecutive weight measurements were within 3 μg.

7.3. Quality Control/Quality Assurance (QC/QA)

Each of the laboratory methods for PM mass and chemical analysis has a standard operating procedure including the frequency of running the standards and the repeatability that is expected when the standard is run. Additionally the data for the standards are plotted to ensure that the values fall within the upper and lower control limits for the method and that there is no obvious trends or bias in the results for the reference materials. As an additional quality check, results from independent methods are compared and values from this work are compared with previously published values, like the manufacturer data base.

- For the ISO cycles, run the engine at rated speed and the highest power possible to warm the engine and stabilize emissions for about 30 minutes.
- Determine a plot or map of the peak power at each engine RPM, starting with rated speed. UCR suspected the 100% load point at rated speed was unattainable with propeller torque so Mode 1 would represent the highest attainable RPM/load.
- Emissions were measured while the engine operates according to the requirements of ISO-8178-D2. For the auxiliary engine the highest power mode was run first and the then each mode was run in sequence. The minimum time for auxiliary engine samples was 5 minutes and if necessary, the time was extended to collect sufficient particulate sample mass or to achieve stabilization with large engines.
- The gaseous exhaust emission concentration values were measured and recorded for the last 3 min of the mode.
- Engine speed, displacement, boost pressure, and intake manifold temperature were measured in order to calculate the gaseous flow rate.
- Emissions factors are calculated in terms of grams per kilowatt hour for each of the operating modes and fuels tested, allowing for emissions comparisons of each blend relative to the baseline fuel.

8. Appendix B

8.1. PM Emissions for the July 2005 Test

Three tests were performed on this auxiliary engine – July 2005, October 2005 and December 2005. The October 2005 test reported in Jayaram et al., 2009 was conducted to determine baseline emissions upstream of the SCR. During this test we found that the filters were white in color and the PM mass numbers were extremely large. Analysis of the filters by reflective Fourier Transform Infra Red (FTIR) spectrometry confirmed that they were contaminated with urea. Hence during the December 2005 test special care was taken to turn off the urea injection while sampling upstream of the SCR.

However during the July 2005 test which was our first expedition testing the SCR, the urea injection was on while sampling before the catalyst. The PM mass numbers measured were higher than that in December 2005 test, though not as high as the October 2005 test. Note here that during this test the engine was probably running on the Low NO_x mode so these PM numbers are not directly comparable to that from the October or the December tests. Unfortunately, the filters had been destroyed by further analysis on them and were unavailable to test for urea by reflective FTIR.

Another difference is that a heated Teflon transfer line was used here while a heated stainless steel transfer line was used for subsequent tests. The ISO method requires use of a heated stainless steel line. Tests conducted at CE-CERT on a back up generator running on ULSD show that there is no significant difference in PM mass by changing the transfer line from stainless steel to Teflon, though the error bars are higher for the Teflon line (Welch, 2006). Later tests on auxiliary engines showed that there is a loss of PM mass as high as 40% with the used of the stainless steel transfer line (Jayaram et al., 2009). We have not quantified this number for the Teflon transfer line.

Table 8-1 PM Emissions Factors for July 2005 Test

Fuel	Actual Load	PM Mass (g/kW-hr)		EC (g/kW-hr)		OC (g/kW-hr)		H ₂ SO ₄ .6.5H ₂ O (g/kW-hr)	
		Before SCR	After SCR	Before SCR	After SCR	Before SCR	After SCR	Before SCR	After SCR
HFO	40%	0.703	0.858	0.033	0.008	0.226	0.030	0.297	0.787
	54%	0.789	0.769	0.009	0.006	0.279	0.036	0.282	0.582
	68%	0.841	0.820	0.004	0.004	0.225	0.039	0.388	0.439
MDO	52%	0.616	0.148	0.022	0.022	0.200	0.022	0.027	0.093

Considering all the variables involved and the possibility that the filters were indeed contaminated with urea this data is to be used with extreme caution. Note here that, urea would be detected OC, hence the OC numbers may be larger than they actually are. The EC and hydrated Sulfate fractions of the PM mass however would not be affected by the

urea injection. A detailed list of the emission factors is provided in Table 8-1. It is interesting to observe that as in the December 2005 test the OC and EC decrease downstream of the SCR and the hydrated sulfate fraction increases.

8.2. Size Segregated PM Emissions for July 2005 Test

This was our first experience in testing size segregated PM emissions from an in-use marine auxiliary engine. The chief aim of this was to set up the protocol and gain experience in sampling on the Micro-Orifice Uniform Deposit Impactor (MOUDI). The PM mass numbers obtained here are not reliable for three reasons.

- The pump used was unable to handle the pressure drop across the MOUDI and the flow through the MOUDI was only 18lit/min instead of 30lit/min hence cut size of each stage will be very different from that of the instrument. We were unable to correct for this as the flow was too far from the target value to make a reasonable correction.
- We suspect that there was urea contamination of the filters while sampling upstream of the SCR. Refer 8.1 to Section for more details.
- The use of a transfer line causes significant loss of PM mass (Jayaram et al., 2009).

Hence the data presented below should be used with extreme caution. No definite conclusions can be made from these.

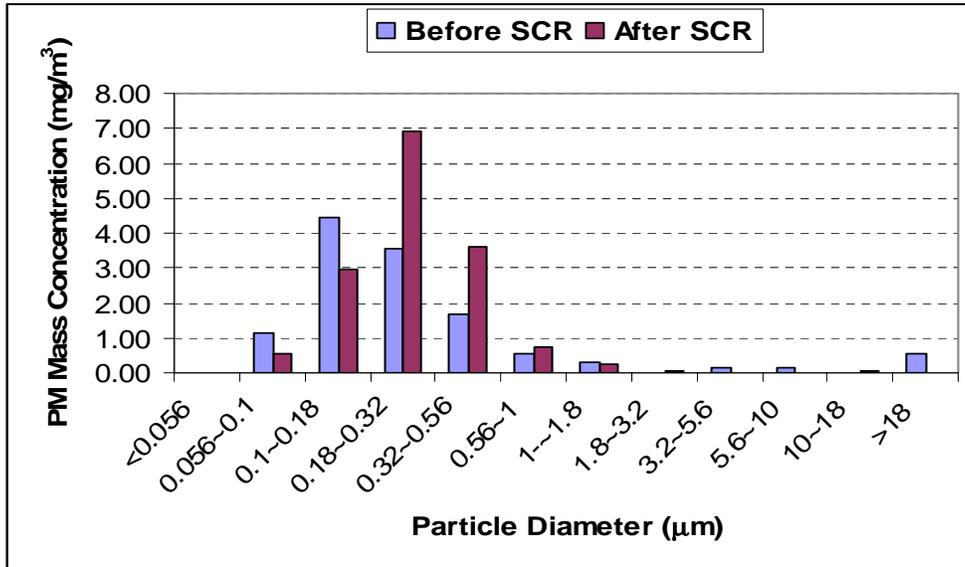
Table 8-2 Size Segregated PM Emissions

Size Range of Particle ¹ µg	Concentration in Exhaust mg/m ³			
	HFO, 50% Load		MDO, 50% Load	
	Before SCR	After SCR	Before SCR	After SCR
<0.056	n/a	n/a	n/a	n/a
0.056-0.1	5.03	n/a	1.14	0.54
0.1-0.18	0.11	4.19	4.45	2.99
0.18-0.32	0.05	0.66	3.57	6.89
0.32-0.56	0.13	24.97	1.69	3.58
0.56-1	0.32	0.00	0.53	0.74
1-1.8	0.21	0.00	0.28	0.24
1.8-3.2	0.28	8.15	0.00	0.07
3.2-5.6	0.15	1.67	0.15	0.00
5.6-10	0.32	0.00	0.13	0.00
10-18	0.32	7.35	0.00	0.07
>18	0.18	7.14	0.53	0.00

¹Actual Particle Size will be higher because the flow through the MOUDI was lower
n/a: not available

Note here that this experience showed us that the MOUDI needs to be sampled for a much longer time of about one hour to get sufficient mass on the different stages. During this test no after filter was used. Subsequent tests showed that a significant amount of mass was collected on the after filter. Understandably, the total mass collected on the MOUDI was much lower than that collected on the Teflo filter.

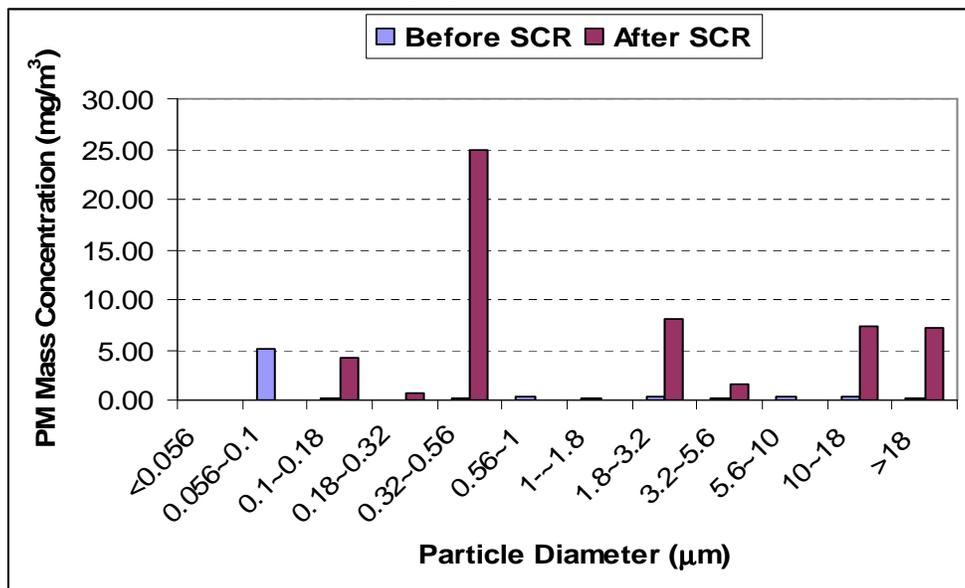
Figure 8-1 Size Segregated PM Emission for MDO



Actual particle diameter will be higher because the flow through the MOUDI was lower

Interesting to note here that in the case of MDO there is a shift in the particle diameter downstream of the SCR which is similar to a shift reported by Klaus et al., 2003.

Figure 8-2 Size Segregated PM Emission for HFO



Actual particle diameter will be higher because the flow through the MOUDI was lower