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### **Authors**

Gysel, Nicholas R Russell, Robert L Welch, William A et al.

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# Impact of Aftertreatment Technologies on the In-Use Gaseous and Particulate Matter Emissions from a Tugboat

Nicholas R. Gysel, †,‡ Robert L. Russell,\*,†,‡ William A. Welch,†,‡ and David R. Cocker, III<sup>†,‡</sup>

ABSTRACT: In-use gaseous and particulate matter (PM) emissions were characterized aboard a tugboat fueled with a California Air Resources Board (CARB)-based ultralow-sulfur diesel (ULSD) before and after selective catalytic reduction (SCR)-diesel particulate filter (DPF) control technologies. Emissions of measured individual gaseous pollutants include nitrogen oxides  $(NO_x)$ , carbon monoxide (CO), carbon dioxide  $(CO_2)$ , and ammonia  $(NH_3)$  slip, while PM emission measurements include PM<sub>2.5</sub> mass, elemental carbon (EC), and organic carbon (OC). Measurements were conducted according to the ISO 8178 measurement and sampling protocol, while emissions were weighted according to the ISO 8178-4-E3 steady-state test cycle for main engine marine applications. Overall weighted emission factors showed that the SCR reduced NO, by ~92%, while the DPF reduced PM<sub>2.5</sub> emissions by  $\sim$ 96%. The lowest reductions in NO<sub>x</sub> and highest NH<sub>3</sub> slip were observed at the 27% load point, where the exhaust temperature was below the light-off temperature of the SCR catalyst. Reductions in PM<sub>2.5</sub> were consistent throughout all load points ranging from 92 to 97%, respectively. PM<sub>2.5</sub> was composed mainly of OC with OC/total carbon (TC) ratios ranging from 0.85 to 0.97 before the catalyst and from 0.98 to 1.0 after the catalyst. The increasing emissions from a forced DPF regeneration were also captured in real time and are reported herein.

### **■ INTRODUCTION**

Emissions from marine vessels and harbor craft near ports and port communities contribute significantly to local air pollution and cause adverse health effects. 2-8 Pope et al. 9,10 reported that prolonged exposure to PM<sub>2.5</sub> emissions can cause respiratoryrelated diseases and death, while Corbett et al.<sup>3</sup> estimated that shipping-related particulate matter (PM) contributes to approximately 60 000 cardiopulmonary and lung cancer deaths annually. Moreover, marine vessels and harbor crafts are significant contributors of nitrogen oxide (NO<sub>x</sub>) emissions, which are key precursors to atmospheric photochemical ozone (O<sub>3</sub>) formation. Corbett and Fischbeck<sup>11</sup> determined that approximately 65% of all NO<sub>x</sub> emissions in the United States are contributed from marine vessels in inland waterways.

The relative contribution of NO<sub>x</sub> from marine vessels and harbor craft to local and nationwide inventories is expected to increase as a result of improvements in fuels, aftertreatment controls, and cleaner engine technologies in the transportation sector. 12 Various studies have investigated biofuels and other novel fuels and their effects on NOx and PM emissions from marine vessels; however, few studies have explored the effects of aftertreatment controls on these emissions. The limiting factor in using catalysts, such as selective catalytic reduction (SCR) and diesel particulate filter (DPF), for marine applications is the high sulfur levels in the fuels that significantly shorten catalyst lifetimes. 13 Regulations imposed by MARPOL Annex VI have greatly reduced fuel sulfur levels from 1.5 to 0.10% and from 4.5 to 0.50% (2020) for marine vessels operated in emission control areas (ECAs) and in non-ECAs, respectively, allowing for technologies once solely used for heavy-duty diesel applications in the transportation sector to be considered for marine vessels and harbor craft.

It is important to characterize emissions from marine vessels and harbor craft and develop strategies for reducing them, yet in-use emission data remain scarce. This study characterizes the in-use emission benefits of aftertreatment technologies on a tugboat. The control devices include a SCR for NO, removal and a DPF for PM removal. Although various studies on heavy-duty diesel vehicles have shown that the addition of a DPF-SCR control system significantly reduces NO, and PM emissions from on-road heavy-duty diesel vehicles, we are not aware of any peer-reviewed studies on the effectiveness of combined SCR-DPF on marine vessels or harbor craft. Gaseous and PM emissions of NOx, carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), ammonia (NH<sub>3</sub>), and PM<sub>2.5</sub> were measured according to ISO 8178 and MARPOL Annex VI<sup>14</sup> guidelines.

# ■ EXPERIMENTAL SECTION

Test Vessel, Engine Specifications, and Fuel. This tugboat is equipped with two Detroit Diesel 12-V71 two-stroke, GMC 127, MY 1973 engines upgraded to Tier 2 emission levels with Clean Cam Technology Systems (CCTS) in the summer of 2011. The CCTS works by modifying the camshaft, cylinder liner, and piston as well as changing fuel injection timing and the oxygen ratio for improved engine out emissions. 15 A Nauticlean S system was installed to control engine out emissions in addition to the CCTS technology. This system consists of a DPF for PM removal and a SCR for NO<sub>x</sub> removal. The DPF substrate is a ceramic honeycomb structure made of mullite, a non-metal silicate-based mineral. It has 100 cells per square inch, which are coated with Na<sub>2</sub>CO<sub>3</sub> (6 g/L) and Na<sub>2</sub>SiO<sub>3</sub> (50 g/L). The DPF retains particles up to a size of 20–300 nm. <sup>16</sup> The SCR substrate

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Department of Chemical and Environmental Engineering, University of California, Riverside, Riverside, California 92521, United States <sup>‡</sup>Center for Environmental Research & Technology, College of Engineering, University of California, Riverside, Riverside, California 92507, United States

is a ceramic product consisting of TiO<sub>2</sub> (75%), WO<sub>3</sub> (8%), V<sub>2</sub>O<sub>5</sub> (1–3%), and others (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and MgO) (approximately 15%) in the form of glass fibers and clay. The precious metal loading is vanadium pentoxide (15 g/ft<sup>3</sup>).  $^{16}$ 

The test fuel used in this study is a California Air Resources Board (CARB) ultralow-sulfur diesel (ULSD) fuel, which is the typical fuel that these engines run.

**Test Matrix.** Emission measurements were conducted following the ISO 8178-4-E3<sup>17</sup> test cycle for marine applications. The target ISO load points and actual load points for both test conditions are shown in Table 1. Load points differed slightly from the target ISO 8178 load points as a result of the ocean current.

Table 1. ISO 8178 and Achieved Load Points

condition	ISO 8178-E3	mode 1	mode 2	mode 3	mode 4
before catalyst	ISO load	100	75	50	25
	%	100	71	42	27
after catalyst	kW	188	133	78	52
	%	100	71	41	27
	kW	189	135	79	51

Sampling and Analysis. Measurements are conducted following the ISO 8178-2<sup>18</sup> sampling protocol. Both gaseous and PM emissions are sampled from a partial flow venturi dilution system with a sample probe at >10 diameters downstream of the venturi. Real-time gaseous pollutants of NO<sub>x</sub>, CO, and CO<sub>2</sub> are measured with a HORIBA portable gas analyzer (PG-250). PG-250 uses common analysis principles, which include chemiluminescence for NOx and non-dispersive infrared absorption (NDIR) for CO and CO2. The dilution ratios are determined at each load by measuring NOx and CO2 concentrations at raw and dilute sampling locations with PG-250. A tunable diode laser (TDL) is used to measure ammonia (NH<sub>3</sub>) slip from the SCR. The NH<sub>3</sub> slip is measured directly from the stack with a 1 m heated sample cell heated to the exhaust gas temperature to minimize thermal perturbations of the sample. The sample lines are also heated between the stack and the quartz line sample line. The TDL sample cell optics is configured for dual-pass operation.

 $PM_{2.5}$  gravimetric measurement is performed on 2  $\mu$ m, 47 mm diameter Teflo filters (Pall Gelman, Ann Arbor, MI) weighed with a Mettler Toledo UMX2 microbalance. All weighing procedures follow the Code of Federal Regulations. Pall Real-time quantitative PM mass concentrations are measured with a TSI DustTrak model 8520. Speciated  $PM_{2.5}$  samples for speciation are collected on 47 mm diameter 2500 QAT-UP Tissuquartz (Pall Gelman, Ann Arbor, MI) filters, which are preconditioned at 600 °C for 5 h. A 1.5 cm² is analyzed according to the NIOSH 5040 reference method<sup>20</sup> with a Sunset Laboratory (Forest Grove, OR) thermal/optical carbon analyzer.  $PM_{2.5}$  emissions reported herein in grams per kilowatt hour (g/kWh) are based on the gravimetric filter measurements.

**Overall Weighted Emission Factors.** The overall weighted emission factors for the gaseous and PM pollutants for the steady-state ISO 8178-4-E3 test cycle are calculated in g/kWh as

$$EF_{x} = \frac{\sum_{i=1}^{i=n} m_{i} WF_{i}}{\sum_{i=1}^{i=n} p_{i} WF_{i}}$$
(1)

where  $\mathrm{EF}_x$  is the weighted mass emission level in  $\mathrm{g/kWh}$  of each pollutant and  $m_i$  ( $\mathrm{g/h}$ ),  $\mathrm{WF}_p$  and  $p_i$  are the mass emission rate, weighting factor, and engine load, respectively, for the ith operating mode.

#### RESULTS

Triplicate samples are collected at each load point. Exhaust flow is calculated using the ISO 8178-2 carbon balance method assuming that all carbon is converted to  $\mathrm{CO}_2$  during the combustion process.

A forced regeneration event was run at the conclusion of the triplicate load point testing.

**Gaseous Emissions.** Modal and weighted NO<sub>x</sub>, CO, and CO<sub>2</sub> emission factors are summarized in Table 2. Error bars represent the standard deviation of the three test runs conducted at each load point. Statistical significance is determined by a two-tailed, paired t test, where  $p \le 0.05$ . NO<sub>x</sub> emissions before the catalyst are highest at the 71% (7.65  $\pm$  0.21 g/kWh) and 100% (10.8  $\pm$  1.3 g/kWh) load points, respectively. Weighted NO<sub>x</sub> emissions are reduced by 92% by the SCR. The highest NO<sub>x</sub> emissions after the SCR are observed at the 27% load point (4.48  $\pm$  0.26 g/kWh) as a result of the reduced removal efficiencies at the lower exhaust temperatures. CO emission factors ranged from 0.42  $\pm$  0.01 to 0.95  $\pm$  0.01 g/kWh before the oxidation catalyst and from 0.13  $\pm$  0.01 to 0.20  $\pm$  0.01 g/kWh after the catalyst.

CO reductions are statistically significant at all load points ranging from 63 to 79%. CO<sub>2</sub> emission factors show a decreasing trend as engine load increases from 27 to 100%. No statistically significant differences in CO<sub>2</sub> are observed before and after the DPF–SCR system; this is expected because the engine is doing the same amount of work during the pre- and post-DPF–SCR measurements.

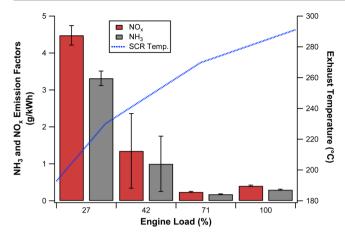
NH<sub>3</sub> measurements are made post-catalyst (Figure 1) and correlate very well with NO<sub>x</sub> as a function of the load point ( $R^2 = 1$ ). Ammonia slip emissions are highest at the 27% load point (1.66  $\pm$  0.10 g/kWh), where the highest NO<sub>x</sub> emissions (4.48  $\pm$  0.26 g/kWh) are observed, and lowest at the 71% load point (0.089  $\pm$  0.006 g/kWh), where the lowest NO<sub>x</sub> emissions (0.24  $\pm$  0.01 g/kWh) are observed.

**Particulate Emissions.** Modal and weighted PM<sub>2.5</sub>, elemental carbon (EC), and organic carbon (OC) emission factors (g/kWh) are presented in Figure 2. The highest PM<sub>2.5</sub> emission factors are observed at the 100% load point for both before pre-catalyst (0.31  $\pm$  0.06 g/kWh) and post-catalyst (0.010  $\pm$  0.003 g/kWh).

OC/total carbon (TC) ratios ranged from 0.85 to 0.97 precatalyst and from 0.97 to 1.0 post-catalyst. The average OC/TC ratios are lowest ( $\sim$ 0.87 and  $\sim$ 0.85) at the lower load points (27 and 42%) and highest ( $\sim$ 0.97 and  $\sim$ 0.89) for the higher load points (100 and 71%). Overall, PM<sub>2.5</sub> and EC emissions are reduced by 96 and  $\sim$ 99%, respectively, by the DPF.

Table 2. Gaseous Emission Factors (g/kWh)

	test mode	before catalyst			after catalyst			reduction		
Ī	load (%)	$NO_x$ (g/kWh)	CO (g/kWh)	CO <sub>2</sub> (g/kWh)	$NO_x$ (g/kWh)	CO (g/kWh)	CO <sub>2</sub> (g/kWh)	NO <sub>x</sub> (%)	CO (%)	CO <sub>2</sub> (%)
	27	$6.2 \pm 0.1$	$0.9 \pm 0.01$	$921.9 \pm 0.2$	$4.5 \pm 0.3$	$0.2 \pm 0.01$	$922.2 \pm 0.6$	28	79	-0.04
	42	$5.9 \pm 0.2$	$0.5 \pm 0.02$	$880.5 \pm 0.1$	$1.4 \pm 1.01$	$0.1 \pm 0.05$	$881.8 \pm 0.4$	77	73	-0.1
	71	$7.6 \pm 0.2$	$0.4 \pm 0.01$	$812.4 \pm 0.2$	$0.2 \pm 0.01$	$0.2 \pm 0.01$	$810.5 \pm 0.2$	97	63	0.2
	100	$10.8 \pm 1.3$	$0.5 \pm 0.07$	$791.8 \pm 0.5$	$0.4 \pm 0.02$	$0.1 \pm 0.01$	$791.1 \pm 0.2$	96	74	0.1
	weight average	$8.4 \pm 0.5$	$0.5 \pm 0.03$	$819.5 \pm 0.06$	$0.7 \pm 0.1$	$0.2 \pm 0.01$	$818.2 \pm 0.2$	92	69	0.2



**Figure 1.**  $NO_x$  and  $NH_3$  emissions versus exhaust temperature (°C) post-catalyst.

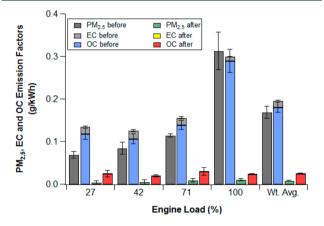


Figure 2. PM<sub>2.5</sub>, EC, and OC emission factors (g/kWh) (EC emission factors contribute a small percentage of total PM<sub>2.5</sub> at this scale).

 $PM_{2.5}~(\sim\!97\%)$  and OC  $(\sim\!92\%)$  emission factor reduction is greatest at the 100% load.

The CARB ULSD fuel has very little sulfur, ash, and metals limiting their contribution to non-carbon PM<sub>2.5</sub>. The EC plus the organic material (OM) downstream provide an important quality check of the PM emissions (Figure 3) between two

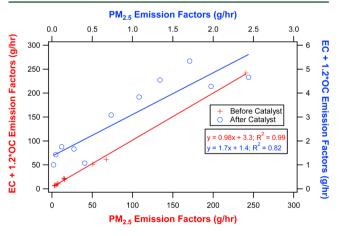


Figure 3. Comparison of total PM mass on quartz and Teflo filters.

independent methods. The OM is estimated in this work by multiplying the OC by a factor of 1.2<sup>1</sup> to account for hydrogen

and oxygen bound to carbon. The linear regression shows extremely good agreement pre-catalyst ( $R^2 = 0.998$ ), while post-catalyst, the agreement is reasonable ( $R^2 = 0.824$ ). Post-catalyst PM<sub>2.5</sub> and TC emissions are extremely low, leading to higher variability compared to the pre-catalyst measurements.

**Fuel Consumption.** A comparison of fuel consumption pre- and post-catalyst calculated by the carbon balance method provides an important quality check of the emission data (Figure 4). No statistically significant differences between the

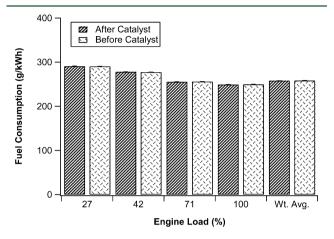


Figure 4. Modal and weighted fuel consumption before and after the catalyst.

test conditions are observed as a function of the modal and weighted average. The engine is observed to be more efficient at the 100 and 71% load points compared to the 27 and 42% load points, with an average reduction in fuel consumption of  $\sim$ 11% for the lower engine loads.

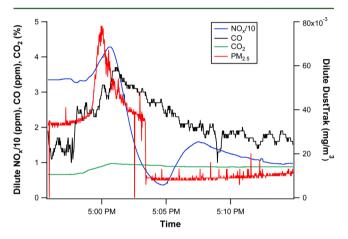
### DISCUSSION

Few studies have been conducted on marine vessels with DPF-SCR. One such study by Nuszkowski et al.<sup>21</sup> characterized the emission benefits of a SCR on a passenger ferry (~94% during cruise mode). The vast majority of existing literature on DPF-SCR controls is obtained from heavy-duty diesel vehicles tested on chassis dynamometers. 22-29 The engine in this study with the CCTS is rated at a Tier 2 emission level before the addition of the DPF-SCR aftertreatment technologies. Weighted NO<sub>x</sub> emissions pre-DPF-SCR (Table 2) are  $\sim$ 14% higher (8.35  $\pm$  0.54 g/kWh) compared to the Tier 2 standard (7.2 g/kWh). The United States Environmental Protection Agency (U.S. EPA) allows for a 20% allowance for in-use measurements, which would increase the Tier 2 in-use measured limit to  $\sim$ 8.6 g/kWh. The addition of the DPF-SCR aftertreatment technology reduces  $NO_x$  emissions by ~92%. The highest NO<sub>x</sub> emissions are observed at the lower load points (27 and 42%), where exhaust temperatures entering the SCR are below 250 °C. At temperatures above 250 °C (Figure 1) for the 71% (0.24  $\pm$  0.01 g/kWh) and 100% (0.40  $\pm$ 0.02 g/kWh) load points, NO<sub>x</sub> emissions begin to stabilize. These results are consistent with those found in the literature for SCR-equipped heavy-duty diesel vehicles, which have optimal SCR operating temperatures ranging from 250 to 427 °C. 30 NH<sub>3</sub> slip emissions are highest during highest NO<sub>x</sub> emissions (27 and 42% load points), attributable to the ammonia injection system responding to the higher NO<sub>x</sub> concentrations in the SCR because the temperature in the SCR is below 250 °C for these load points.

CO emissions from compression-ignition marine vessels are very low, as seen with previous studies. 31–36 Both modal and weighted and pre-SCR–DPF CO are well below the Tier 2 standard for CO emissions (5 g/kWh). Herner et al. 23 and Liu et al. 29 observed CO reductions of ~94 and ~84%, respectively, for DPF–SCR equipped systems compared to the 69% reduction observed in CO for the current study. Reductions in CO by the DPF–SCR system reflect the ability of the catalyst to efficiently oxidize CO to CO<sub>2</sub>. Catalyst "light-off" specified by the manufacturer states that CO conversion to CO<sub>2</sub> increases rapidly above 200 °C, and the majority of exhaust temperatures exceeded 200 °C for the load points tested.

Previous studies<sup>37</sup> of DPF-equipped heavy-duty diesel vehicles observe PM mass emission reductions of >90%. PM reduction post-DPF–SCR of  $\sim$ 92% is consistent with earlier studies of DPF effectiveness. Overall, PM<sub>2.5</sub> emissions pre-DPF–SCR were well below the Tier 2 emissions (0.30 g/kWh).

Real-time NO<sub>x</sub>, CO, CO<sub>2</sub>, and DustTrak concentrations during a forced regeneration event are shown (Figure 5). This



**Figure 5.** Gaseous and PM emissions from forced regeneration at 25% load point.

regeneration event was triggered at the end of the study.  $NO_x$  and PM concentrations exceeded 200 ppm and  $\sim$ 0.4 mg/m<sup>3</sup>, respectively. The manufacturer of the SCR-DPF system states

that, in normal operations, regenerations occur after every 20 h of engine operation and the regenerations are complete within 20 min. This implies that, for 98.3% of the engine operating time, there are no regenerations. Using the foregoing statement as a guide, inclusion of the regeneration emissions decreases the  $NO_x$  percent reduction by ~1% and the PM percent reduction by ~3.5%.

#### CONCLUSION

The effect of a SCR-DPF aftertreatment system on in-use emissions of a tugboat is characterized in this study. Overall, NO<sub>x</sub> and PM emissions are reduced by ~92 and ~96%, respectively. Pre- and post-DPF-SCR PM<sub>2.5</sub> mass emissions contained mainly OC, with very little EC present. Aftertreatment technologies, such as SCR, have the potential to significantly reduce NO<sub>x</sub> emissions in ports and nearby port communities because nearly 65% of all NO<sub>x</sub> emissions from marine vessels occur in inland waterways. 11 The addition of a catalyzed DPF can help significantly reduce PM emissions and, therefore, reduce adverse health effects to those living in nearby port communities. Previously, these technologies were only available for heavy-duty diesel vehicles in the transportation sector because high sulfur content in the fuels used in marine applications rapidly degrade catalyst performance. The additions of such technologies are now possible in the marine sector because MARPOL Annex VI has regulated the sulfur levels in marine fuels.

#### APPENDIX

The measurement setup is shown in Figure A1.

#### AUTHOR INFORMATION

### **Corresponding Author**

\*E-mail: rrussell@engr.ucr.edu.

#### Notes

The authors declare no competing financial interest.

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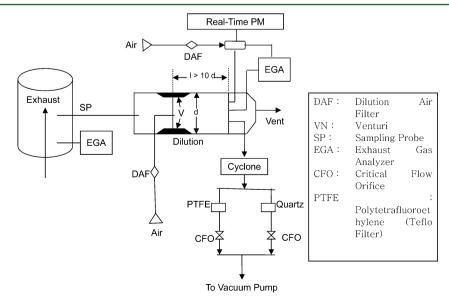


Figure A1. Measurement setup.

support, Sause Brothers for operating their vessel according to the prescribed test conditions, and all personnel who assisted in making any necessary modifications. Appreciation is extended to the crew members for their support and cooperative efforts during the emission testing. The authors also thank Kurt Bumiller for help with the test preparation and Chia-Li Chen, Jinyu Xu, and the rest of the staff in the Analytical Laboratory at Center for Environmental Research & Technology (CE-CERT) for their help and support in the analysis.

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