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Jason Carter Evans  
*West Virginia University*

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**Influence Of Fuel Sulfur Content On Emissions From  
Diesel Engines Equipped With Oxidation Catalysts**

**Jason Carter Evans**

**Thesis submitted to the  
College of Engineering and Mineral Resources  
at West Virginia University  
in partial fulfillment of the requirements  
for the degree of**

**Master of Science  
in  
Mechanical Engineering**

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**Morgantown, WV  
2000**

**Keywords: Diesel Oxidation Catalysts, Emissions, Fuel Sulfur**

## **ABSTRACT**

### **Influence Of Fuel Sulfur Content On Emissions From Diesel Engines Equipped With Oxidation Catalysts**

**Jason C. Evans**

Diesel oxidation catalysts (DOCs) are a viable exhaust aftertreatment alternative for alleviating regulated exhaust emissions of hydrocarbon (HC), carbon monoxide (CO), and particulate matter (PM) from diesel-fueled heavy-duty engines. This study was a part of the Diesel Emissions Control-Sulfur Effects (DECSE) program that was aimed at determining the impact of diesel fuel sulfur levels on diesel oxidation catalysts that were designed to lower brake-specific PM, HC, and CO emissions from on-highway trucks and buses in the 2002-2004 model years. The research focused on high-temperature DOCs installed on a Cummins ISM370 ESP engine, and low-temperature DOCs installed on a Navistar T444E engine to determine how the DOCs affect the various emissions, how fuel sulfur affects emissions, and how fuel sulfur poisons the catalysts over time.

The DOCs were found to affect the brake-specific PM, HC, and CO emissions. The PM emissions were not significantly affected by the DOCs when lower sulfur fuels (3 ppm and 30 ppm) were used. Brake-specific PM emissions were dramatically increased with the higher sulfur fuel (350 ppm) due to the formation of sulfates and the associated sulfate bound water. Hence, fuel sulfur affected the brake-specific PM, HC, and CO emissions from DOC equipped heavy-duty diesel engines.

Brake-specific HC emissions were eliminated by nearly 100% by the use of the DOCs. The DOCs had various reduction efficiencies ranging from 90% to 100% for CO emissions from the Navistar engine and 24% to 79% for the Cummins engine.

The DOCs were only evaluated for only 250 aging hours, which is a relatively short duration. Over this short amount of time, there was no significant evidence of the fuel sulfur poisoning the diesel oxidation catalysts.

## ACKNOWLEDGEMENTS

After six years of college education, a part of my life has finally ended. However, there is another part about to begin. Through the past two years of graduate school I have encountered some rough times, but it seemed that the better always won. As I look back on these past two years, I know I could not have accomplished everything on my own. I would like to take this time to express my thanks to the ones that helped see me through this challenging and rewarding time.

The first and foremost who needs to be recognized is God. I would never be here if were not for Him. Even though He is unseen, I know His presence is always with me. He needs to be recognized due to the fact that too often He does go unacknowledged.

Now to my parents, where I believe there is not enough time and words to show my appreciation and gratitude. Mom and Dad, without your love, encouragement, understanding, and support, I know none of this could have been possible. You have been there for me all the way, and I know you will always be there for me in the future. I can't express how much I love the two of you for this. You need to be recognized for one huge accomplishment, financially supporting three boys through engineering school. Dad, I know it was a lot of hard work for you, and Mom, thanks for the clean clothes, the food you sent back with me, and always being there, it was very important. I love you.

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## TABLE OF CONTENTS

	<u>Page</u>
<b>ABSTRACT</b> .....	<b>II</b>
<b>ACKNOWLEDGEMENTS</b> .....	<b>III</b>
<b>TABLE OF CONTENTS</b> .....	<b>V</b>
<b>LIST OF TABLES</b> .....	<b>VII</b>
<b>LIST OF FIGURES</b> .....	<b>VIII</b>
<b>LIST OF ACRONYMS</b> .....	<b>XII</b>
<b>CHAPTER 1 ~ INTRODUCTION</b> .....	<b>1</b>
<b>CHAPTER 2 ~ LITERATURE REVIEW</b> .....	<b>5</b>
2.1 INTRODUCTION .....	5
2.2 DIESEL ENGINE TECHNOLOGY .....	8
2.2.1 <i>Improved Fuel Injection</i> .....	9
2.2.1.1 Hydraulic Electronic Unit Injection.....	9
2.2.1.2 Improved Injector Nozzles.....	10
2.2.1.3 Rate Shaping and Multiple Injections.....	11
2.2.2 <i>Combustion Chamber Modifications</i> .....	11
2.2.2.1 Increasing Compression Ratio .....	12
2.2.2.2 Reduced Oil Consumption.....	12
2.2.3 <i>Turbocharger Improvements</i> .....	13
2.3 AFTERTREATMENT TECHNOLOGY.....	13
2.3.1 <i>Diesel Oxidation Catalysts</i> .....	14
2.3.2 <i>Lean NO<sub>x</sub> Catalysts</i> .....	16
2.3.3 <i>Selective Catalyst Reduction Using Urea</i> .....	18
2.4 FUEL SULFUR.....	19
<b>CHAPTER 3 ~ EXPERIMENTAL SET-UP</b> .....	<b>21</b>
3.1 EXPERIMENTAL EQUIPMENT .....	21
3.1.1 <i>Engines</i> .....	21
3.1.2 <i>Fuel Specifications</i> .....	25
3.1.3 <i>Dilution Tunnel</i> .....	27
3.1.4 <i>Secondary Dilution Tunnel</i> .....	28
3.1.5 <i>Particulate Sampling</i> .....	29
3.1.6 <i>Bypass System</i> .....	32
3.1.7 <i>Gaseous Emissions Sampling</i> .....	33
3.1.7.1 Hydrocarbon Analyzer.....	34
3.1.7.2 Oxides of Nitrogen (NO <sub>x</sub> ) Analyzer .....	35

3.1.7.3 Carbon Monoxide / Carbon Dioxide Analyzers .....	36
3.1.8 Bag Sampling .....	37
3.2 EXPERIMENTAL PROCEDURES .....	38
3.2.1 Catalyst Degreening.....	38
3.2.2 Steady State Test Cycles.....	39
3.2.3 Transient Test Cycles .....	41
3.2.4 Split-Exhaust System.....	42
<b>CHAPTER 4 ~ RESULTS AND DISCUSSION.....</b>	<b>52</b>
4.1 PM EMISSION ANALYSIS .....	52
4.2 HC EMISSION ANALYSIS .....	64
4.3 CO EMISSION ANALYSIS .....	68
4.4 NO <sub>x</sub> EMISSION ANALYSIS.....	77
4.5 RESULTS AND 2004 EMISSION STANDARDS .....	79
<b>CHAPTER 5 ~ CONCLUSIONS.....</b>	<b>81</b>
<b>REFERENCES.....</b>	<b>83</b>
<b>APPENDICES .....</b>	<b>85</b>
<b>APPENDIX A: NAVISTAR PM EMISSION RESULTS.....</b>	<b>86</b>
<b>APPENDIX B: CUMMINS PM EMISSION RESULTS.....</b>	<b>94</b>
<b>APPENDIX C: NAVISTAR HC EMISSION RESULTS.....</b>	<b>102</b>
<b>APPENDIX D: CUMMINS HC EMISSION RESULTS.....</b>	<b>110</b>
<b>APPENDIX E: NAVISTAR CO EMISSION RESULTS.....</b>	<b>118</b>
<b>APPENDIX F: CUMMINS CO EMISSION RESULTS .....</b>	<b>125</b>
<b>APPENDIX G: TEST MATRIX.....</b>	<b>132</b>
<b>APPENDIX H: CERTIFICATES OF FUEL ANALYSIS .....</b>	<b>134</b>

## LIST OF TABLES

<u>Table</u>	<u>Page</u>
Table 2.1 Heavy-Duty Diesel Engines Emissions Standards.....	6
Table 2.2 Effect of the DOC on Gaseous and PM Emissions (Patalzy et al. 1994).....	16
Table 2.3 Urea – SCR OICA* Emissions Results (Miller et al. 2000).....	19
Table 3.1 Navistar T444E Engine Specifications .....	23
Table 3.2 Comparing Nominal Fuel Sulfur Levels to Actual Fuel Sulfur Levels .....	25
Table 3.3 Average Test Results From Fuel Chemical Analysis .....	26
Table 3.4 Steady State Mode Description for Navistar T444E Test Engine.....	40
Table 3.5 Steady State Mode Description for Cummins ISM370ESP Test Engine .....	40
Table 3.6 Navistar T444E Engine Evaluation Conditions .....	41
Table 3.7 Cummins ISM370 Engine Evaluation Conditions.....	41
Table 4.1 Average Catalyst Temperature of the Modes in Steady State Tests .....	60
Table 4.2 Year 2004 Emission Standards Compared to WVU DOC Emissions .....	80
Table G.1 DECSE DOC Navistar and Cummins Test Matrix .....	133



## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
Figure 3.1 Schematic of Test Cell Layout.....	22
Figure 3.2 Navistar T444E Test Cell Engine .....	23
Figure 3.3 Navistar T444E Torque Curve.....	24
Figure 3.4 Cummins ISM370ESP Torque Curve.....	24
Figure 3.5 Secondary Dilution Tunnel Outlet and Filter Holder .....	30
Figure 3.6 Bypass System for Steady State Tests .....	33
Figure 3.7 Background and Dilute Bag Sampling System Schematic .....	38
Figure 3.8 FTP Comparison of Full Flow to Split Flow Engine-Out Exhaust .....	45
Figure 3.9 OICA* Comparison of Full Flow to Split Flow Engine-Out Exhaust.....	45
Figure 3.10 FTP-75 Comparison of Full Flow to the Split Flow Engine-Out Exhaust ....	46
Figure 3.11 Nav-9* Comparison of Full Flow to Split Flow Engine-Out Exhaust .....	46
Figure 3.12 Cummins CO <sub>2</sub> Comparison of Full Flow to Split Flow DOC Exhaust .....	47
Figure 3.13 Navistar CO <sub>2</sub> Comparison of Full Flow to Split Flow DOC .....	47
Figure 3.14 Orifice Flow Rate Comparison in the Two Exhaust Legs .....	49
Figure 3.15 CO <sub>2</sub> Split Ratio Comparison in Full Flow and DOC Exhaust.....	49
Figure 3.16 Bad Orifice Flow Data on an OICA* Test .....	50
Figure 3.17 CO <sub>2</sub> Split Comparison of an OICA* with Split Ratio .....	51
Figure 4.1 Navistar Steady-State (Nav-9*) Comparing PM Emissions and Fuel Sulfur..	53
Figure 4.2 Navistar Steady State Nav-9* Sulfate Emissions at 250 Hours.....	55
Figure 4.3 Navistar Nav-9* PM Emission Reduction Efficiency at 250 Hours .....	55
Figure 4.4 Cummins Steady-State (OICA*) Comparing PM Emissions and Fuel Sulfur	56
Figure 4.5 Cummins Sulfate Emissions for an OICA* at 250 Hours .....	57
Figure 4.6 Cummins OICA* PM Reduction Efficiency at 250 Hours.....	57
Figure 4.7 Navistar FTP-75 Comparing PM Emissions and Fuel Sulfur.....	58
Figure 4.8 Navistar FTP-75 PM Reduction Efficiency.....	59
Figure 4.9 Cummins FTP Comparing PM Emissions and Fuel Sulfur.....	59
Figure 4.10 Cummins FTP PM Emission Reduction Efficiency .....	60
Figure 4.11 PM Emissions on the Cummins FTP with 3 ppm Fuel .....	61
Figure 4.12 PM Emissions on the Cummins FTP with 350 ppm Fuel .....	62

Figure 4.13 Navistar FTP-75 Tests Comparing PM Emissions, Fuel, and Aging Time...	63
Figure 4.14 Cummins FTP Tests Comparing PM Emissions, Fuel, and Aging Time .....	63
Figure 4.15 Navistar Nav-9* HC Emissions .....	64
Figure 4.16 Navistar Nav-9* Tests Comparing HC Emissions, Aging Hour, and Fuel ...	65
Figure 4.17 Navistar Nav-9* HC Emission Reduction Efficiency at 250 Hours.....	65
Figure 4.18 Cummins OICA* HC Emissions .....	66
Figure 4.19 Cummins OICA* Tests Comparing HC Emissions, Aging Hour, and Fuel..	67
Figure 4.20 Cummins OICA* HC Emission Reduction Efficiency.....	67
Figure 4.21 Navistar Nav-9* CO Emissions .....	68
Figure 4.22 Navistar Nav-9* CO Emission Reduction Efficiency at 150 Hours.....	69
Figure 4.23 Navistar Nav-9* Tests Comparing CO Emissions, Aging Hours, and Fuel..	70
Figure 4.24 Navistar FTP-75 CO Emissions.....	71
Figure 4.25 Navistar FTP-75 CO Emissions Reduction Efficiency.....	71
Figure 4.26 Navistar FTP-75 Tests Comparing CO Emissions, Aging Hours, and Fuel..	72
Figure 4.27 Cummins OICA* CO Emissions .....	73
Figure 4.28 Cummins OICA* CO Emissions Reduction Efficiency .....	73
Figure 4.29 Cummins OICA* Test Comparing CO Emissions, Aging Hours, and Fuel..	74
Figure 4.30 Cummins FTP CO Emissions at 250 Hours .....	75
Figure 4.31 Cummins FTP CO Emissions Reduction Efficiency .....	76
Figure 4.32 Cummins FTP Tests Comparing CO Emissions, Aging Hour, and Fuel .....	76
Figure 4.33 Navistar FTP-75 NO <sub>x</sub> Emissions at 250 Hours .....	77
Figure 4.34 Navistar Nav-9* NO <sub>x</sub> Emissions at 250 Hours.....	78
Figure 4.35 Cummins FTP NO <sub>x</sub> Emissions at 250 Hours.....	78
Figure 4.36 Cummins OICA* NO <sub>x</sub> Emissions at 250 Hours.....	79
Figure A.1 Navistar Transient FTP-75 PM Emissions with 3 ppm Fuel .....	87
Figure A.2 Navistar Nav-9* PM Emissions with 3 ppm Fuel .....	87
Figure A.3 Navistar FTP-75 PM Emissions at 0 Hours.....	88
Figure A.4 Navistar FTP-75 PM Emissions at 150 Hours.....	88
Figure A.5 Navistar FTP-75 PM Emissions at 250 Hours.....	89
Figure A.6 Navistar Nav-9* PM Emissions for 0 Hours .....	89
Figure A.7 Navistar Nav-9* PM Emissions for 150 Hours .....	90
Figure A.8 Navistar Nav-9* PM Emissions for 250 Hours .....	90
Figure A.9 Navistar FTP-75 PM Emissions with 30 ppm Fuel .....	91

Figure A.10 Navistar Nav-9* PM Emissions with 30 ppm Fuel .....	91
Figure A.11 Navistar FTP-75 PM Emissions with 350 ppm Fuel .....	92
Figure A.12 Navistar Nav-9* PM Emissions with 350 ppm Fuel .....	92
Figure A.13 Navistar FTP-75 PM Emission Reduction Efficiency at 0 Hours .....	93
Figure A.14 Navistar FTP-75 PM Emissions Reduction Efficiency at 150 Hours.....	93
Figure B.1 Cummins FTP PM Emissions with 3 ppm Fuel.....	95
Figure B.2 Cummins OICA* PM Emissions with 3 ppm Fuel.....	95
Figure B.3 Cummins FTP PM Emissions at 150 Hours .....	96
Figure B.4 Cummins FTP PM Emissions at 250 Hours .....	96
Figure B.5 Cummins OICA* PM Emissions at 0 Hours.....	97
Figure B.6 Cummins OICA* PM Emissions at 150 Hours.....	97
Figure B.7 Cummins OICA* PM Emissions 250 Hours .....	98
Figure B.8 Cummins FTP PM Emissions with 30 ppm Fuel.....	98
Figure B.9 Cummins OICA* PM Emissions with 30 ppm Fuel.....	99
Figure B.10 Cummins FTP PM Emissions with 350 ppm Fuel.....	99
Figure B.11 Cummins OICA* PM Emissions with 350 ppm Fuel.....	100
Figure B.12 Cummins FTP PM Emission Reduction Efficiency at 150 Hours.....	100
Figure B.13 Cummins FTP PM Emission Reduction Efficiency at 250 Hours.....	101
Figure C.1 Navistar Nav-9* HC Emissions at 0 hours .....	103
Figure C.2 Navistar Nav-9* HC Emissions at 150 Hours.....	104
Figure C.3 Navistar Nav-9* HC Emissions at 250 Hours.....	104
Figure C.4 Navistar Nav-9* HC Emission Reduction Efficiency at 0 Hours .....	105
Figure C.5 Navistar Nav-9* HC Emission Reduction Efficiency at 150 Hours .....	105
Figure C.6 Navistar FTP-75 HC Emissions at 0 Hours .....	106
Figure C.7 Navistar FTP-75 HC Emissions at 150 Hours .....	106
Figure C.8 Navistar FTP-75 HC Emissions at 250 Hours .....	107
Figure C.9 Navistar FTP-75 HC Emission Reduction Efficiency at 0 Aging Hours.....	108
Figure C.10 Navistar FTP-75 HC Emission Reduction Efficiency at 150 Aging Hours	108
Figure C.11 Navistar FTP-75 HC Emission Reduction Efficiency at 250 Aging Hours	109
Figure D.1 Cummins OICA* HC Emissions at 0 Hours.....	111
Figure D.2 Cummins OICA* HC Emissions at 150 Hours.....	112
Figure D.3 Cummins OICA* HC Emissions at 250 Hours.....	112
Figure D.4 Cummins OICA* HC Emission Reduction Efficiency at 0 Hours .....	113

Figure D.5 Cummins OICA* HC Emission Reduction Efficiency at 150 Hours .....	113
Figure D.6 Cummins OICA* HC Emission Reduction Efficiency at 250 Hours .....	114
Figure D.7 Cummins FTP HC Emissions at 0 Hours .....	114
Figure D.8 Cummins FTP HC Emissions at 150 Hours .....	115
Figure D.9 Cummins FTP HC Emissions at 250 Hours .....	115
Figure D.10 Cummins FTP HC Emission Reduction Efficiency at 0 Hours .....	116
Figure D.11 Cummins FTP HC Emission Reduction Efficiency at 150 Hours .....	116
Figure D.12 Cummins FTP HC Emission Reduction Efficiency at 250 Hours .....	117
Figure E.1 Navistar FTP-75 CO Emissions at 0 Hours .....	119
Figure E.2 Navistar FTP-75 CO Emissions at 150 Hours .....	119
Figure E.3 Navistar FTP-75 CO Emissions at 250 Hours .....	120
Figure E.4 Navistar FTP-75 CO Emissions Reduction Efficiency at 0 Hours .....	120
Figure E.5 Navistar FTP-75 CO Emissions Reduction Efficiency at 150 Hours .....	121
Figure E.6 Navistar FTP-75 CO Emissions Reduction Efficiency at 250 Hours .....	121
Figure E.7 Navistar Nav-9* CO Emissions at 0 Hours .....	122
Figure E.8 Navistar Nav-9* CO Emissions at 150 Hours .....	122
Figure E.9 Navistar Nav-9* CO Emissions at 250 Hours .....	123
Figure E.10 Navistar Nav-9* CO Emissions Reduction Efficiency at 0 Hours .....	123
Figure E.11 Navistar Nav-9* CO Emissions Reduction Efficiency at 150 Hours .....	124
Figure E.12 Navistar Nav-9* CO Emissions Reduction Efficiency at 250 Hours .....	124
Figure F.1 Cummins FTP CO Emissions at 0 Hours .....	126
Figure F.2 Cummins FTP CO Emissions at 150 Hours .....	126
Figure F.3 Cummins FTP CO Emissions at 250 Hours .....	127
Figure F.4 Cummins FTP CO Emissions Reduction Efficiency at 0 Hours .....	127
Figure F.5 Cummins FTP CO Emissions Reduction Efficiency at 150 Hours .....	128
Figure F.6 Cummins FTP CO Emissions Reduction Efficiency at 250 Hours .....	128
Figure F.7 Cummins OICA* CO Emissions at 0 Hours .....	129
Figure F.8 Cummins OICA* CO Emissions at 150 Hours .....	129
Figure F.9 Cummins OICA* CO Emissions at 250 Hours .....	130
Figure F.10 Cummins OICA* CO Emissions Reduction Efficiency at 0 Hours .....	130
Figure F.11 Cummins OICA* CO Emissions Reduction Efficiency at 150 Hours .....	131
Figure F.12 Cummins OICA* CO Emissions Reduction Efficiency at 250 Hours .....	131

## LIST OF ACRONYMS

CFR – Code of Federal Regulation  
CFV – critical flow venturi  
CI – compression ignition  
CO – carbon monoxide  
CO<sub>2</sub> – carbon dioxide  
CVS – constant volume sampler  
DECSE – Diesel Emission Control – Sulfur Effects  
DOC(s) – diesel oxidation catalyst(s)  
DOE – U.S. Department of Energy  
EERL – Engine and Emission Research Laboratory  
EMA – Engine Manufacturers Association  
EPA – Environmental Protection Agency  
EUI – electronic unit injection  
FF EO – full flow engine-out (no catalysts)  
FTP – Federal Test Procedure  
FTP-75 – Simulation of chassis dynamometer FTP-75  
HC – hydrocarbon(s)  
HDDE – heavy-duty diesel engine  
HEUI – hydraulic electronic unit injector  
HFID – heated flame ionization detector  
MECA – Manufacturers of Emission Controls Association  
MY – model year  
Nav-9 – steady state test of Ford Motor Company  
Nav-9\* – modified version of the Nav-9\*  
NDIR – non-dispersive infrared  
NO – nitric oxide  
NO<sub>x</sub> – oxides of nitrogen  
NO<sub>2</sub> – nitrogen dioxide  
NREL – National Renewable Energy Laboratory  
OICA – Organisation Internationale des Constructeurs d'Automobiles  
OICA\* -- modified version of the OICA  
ORNL – Oak Ridge National Laboratory  
PM – particulate matter  
ppm – parts per million  
SCR – selective catalyst reduction  
SI – spark ignition  
SOF – soluble organic fraction  
SP EO – split flow engine-out (no catalyst)  
STP – standard temperature and pressure  
TPM – total particulate matter  
WVU – West Virginia University

## CHAPTER 1 ~ INTRODUCTION

The popularity of diesel or compression ignition (CI) engines is derived primarily from their fuel efficiency and longer life relative to the gasoline spark-ignited (SI) engine. Diesel engines operate very lean. The lean overall mixture provides ample oxygen to promote complete combustion of the fuel in the cylinder. The extra air tends to lower the overall combustion temperature thereby reducing the formation of oxides of nitrogen ( $\text{NO}_x$ ). The lower temperatures reduce wear on cylinder and exhaust system components.

Diesel engines do not incorporate a throttle, pumping losses associated with moving air through the diesel engine are much less than a throttled spark ignition engine. Diesel engine compression ratios, ranging from 15:1 to 20:1, are much higher than the 8:1 to 10:1 compression ratios typical of SI engines. The lack of a throttle, the lean-burn characteristics, and high compression ratio increase the efficiency of a diesel engine. Higher engine efficiency translates into a better fuel economy.

Emissions from a diesel engine are composed of three phases: solid, semi-volatile solids (insolubles) along with the adsorbed organics (the soluble organic fraction, SOF) are the constituents of the total particulate matter (TPM), and gases. TPM consists of a carbonaceous core (elemental carbon), wear metal, inorganic oxides (primarily sulfates and the SOF that is primarily partially burnt lubricating oil and fuel. Semi-volatiles consists of partially burnt or unburnt lubricating oil and fuel. Semi-volatile organic compounds are defined as compounds having vapor pressure approximately between  $10^{-4}$  to  $10^{-11}$  atm at ambient temperatures. Hsieh et al. (1993) stated that semi-volatile compounds have a vapor pressure and boiling point between those of volatile and non-volatile compounds. When diesel fuel is burned, a portion of the sulfur is oxidized to

SO<sub>3</sub> that upon reaction with the moisture in the exhaust becomes H<sub>2</sub>SO<sub>4</sub>. Gaseous hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), and sulfur dioxide (SO<sub>2</sub>) are the constituents of the third phase. Exhaust emissions from leaner burning diesel engines are more complex than those of gasoline engines. Hence, any attempts to reduce the diesel emissions with exhaust aftertreatment systems force severe challenges.

In previous years, engine manufacturers could meet emission standards primarily through improvements and modifications to the diesel engine. Due to the tighter emission standards mandated by the Environmental Protection Agency (EPA) for the years 2002-2004, diesel engine manufacturers will have to begin using aftertreatment technology in the form of oxidation catalytic converters and PM traps, catalyzed or uncatalyzed. The particulate traps consist of filters (ceramic monoliths, foams, metal mesh, silicon carbide, and low temperature paper) that collect the soot in the exhaust stream and invoke further burning in order to eliminate the particulates.

It is certain that in the very near future, diesel engines will require exhaust aftertreatment in order to meet the stringent 2007 EPA emission standards. Attention needs to be directed towards the fuel sulfur content in diesel fuel due to the possible use of aftertreatment technology such as oxidation catalytic converters. The sulfur in diesel fuel can significantly affect the performance and durability of diesel aftertreatment devices.

This research study was conducted as part of the Diesel Emission Control – Sulfur Effects (DECSE) program with support from the U.S. Department of Energy, Office of Transportation Technologies. The DECSE program was a joint effort of the federal government, industry (engine manufacturers and catalysts manufacturers), universities,

and national laboratories. Specifically, the participants were the United States Department of Energy (DOE), the National Renewable Energy Laboratory (NREL), Oak Ridge National Laboratory (ORNL), the Engine Manufacturers Association (EMA), the Manufactures of Exhaust Catalysts Association (MECA), West Virginia University (WVU), and Engine Tests Services (ETS and FEV). The objective of the research undertaken at WVU was to determine the impact of diesel fuel sulfur levels on diesel oxidation catalyst technologies that could be implemented to lower emissions of HC, CO, and particulate matter (PM) from on-highway trucks in the 2002-2004 timeframe. Fuel sulfur is known to adversely affect the operation of diesel exhaust emission control systems. The fuel sulfur levels being used in the DECSE research were 3 ppm, 30 ppm, 150 ppm and 350 ppm. This document investigated only three of the four fuel sulfurs, 3 ppm, 30 ppm, and 350 ppm fuel. Measurements were recorded at each sulfur level up to 250 hours of engine operation.

Research data was collected on two diesel engines, a medium-duty diesel engine and a heavy-duty diesel engine. Companion medium-duty and heavy-duty engines were used at WVU to carry out the catalysts aging process. The aging engines were only used to age the catalysts after they were evaluated in the emissions measurement facility. The medium-duty test engine was a V-8 Navistar T444E 7.3-liter engine. The heavy-duty test engine was an in-line 6 cylinder Cummins ISM 370ESP 10.8-Liter engine. Both engines were tested with and without diesel oxidation catalysts. While brake-specific gaseous emissions were collected, particular emphasis was focused on the PM emissions. Engines and the exhaust aftertreatment devices were tested over steady state schedules and transient modes of operation.



The objectives of this study were to determine how fuel sulfur levels affected brake-specific PM, HC, and CO emissions from DOC equipped heavy-duty diesel engines operated over a range of speed-load conditions. Investigation was also focused on determining if there was any evidence of fuel sulfur poisoning to the DOCs over the 250 hour evaluation.

Published literature associated with the research will be discussed in Chapter 2. Chapter 3 pertains to the experimental setup. This chapter includes sections on the test engine and aging engine setup, split exhaust, analyzers, the testing procedures, and testing cycles. Chapter 4 includes the results and discussion of the research performed. Finally, Chapter 5 examines the conclusions and recommendations.

## CHAPTER 2 ~ LITERATURE REVIEW

### 2.1 Introduction

Motor vehicles received little attention as air pollution sources until the 1950's. Previously, uncontrolled air pollution emissions from industry, and the emissions from coal combustion were the primary contributors to air pollution in most U.S. cities. As these sources were controlled and as natural gas replaced coal as the principal urban heating fuel in the United States, a new type of air pollution was discovered in Los Angeles. There, the principal home and industrial heating fuel was natural gas, and there were few "smokestack" industries. However, a type of eye and nose-irritating air pollutant, later named smog, occurred there mostly in the summer. Professor A.J. Haagen-Smit (1952) demonstrated that the eye-irritating materials were largely formed from emissions from automobiles.

California began regulating auto emissions in 1963. In the Clean Air Act of 1970 Congress began federal regulations of automobiles, requiring fairly strict rules for any states that already had state rules (only California), but also requiring fairly strict rules for the rest of the country. In 1975, the Environmental Protection Agency (EPA) established a Federal Test Procedure (FTP) simulating the average driving conditions in the United States in which CO, HC, and NO<sub>x</sub> would be measured. The FTP cycle was conducted on an engine dynamometer and included measurements from the automobile during three conditions: (1) cold start, after the engine was idle (non-operational) for eight hours (2) hot start, and (3) a combination of urban and highway driving conditions. The actual development of the 1975 FTP using a vehicle on a chassis dynamometer began in the

1950 time period. It evolved through the 1960s and was adopted by the EPA as the 1975 FTP. It is basically a driving cycle through Los Angeles, and California.

In the early 1970's the automotive emission regulations issued by EPA were intentionally *technology forcing*, i.e., they could not be met using existing technology (De Nevers, 1995). The EPA regulations have become increasingly stringent in recent years. Some of the heavy-duty diesel engine emission regulations can be seen in Table 2.1.

Table 2.1 Heavy-Duty Diesel Engines Emissions Standards

Year	HC	NO <sub>x</sub>	CO	PM
1990	1.3	6.0	15.5	0.60
1991-93	1.3	5.0	15.5	0.25
1994-97	1.3	5.0	15.5	0.10
1998+	1.3	4.0	15.5	0.10
2004+	1.3	2.5	15.5	0.10

All emissions levels stated in (g/bhp-hr).

The most obvious emission from a diesel engine is the characteristic smoke trail produced when the vehicle operates under load. This smoke is comprised of solid particles and liquid droplets generated by poor combustion of the fuel. Smoke from diesel engines can be blue, white, or gray-black in color. Blue smoke is typically caused by excessive lubricating oil in the combustion chamber due to poor piston ring sealing or valve guide wear. Blue smoke can be minimized or eliminated by proper maintenance. White smoke, generated when the combustion temperature in the cylinder during fuel injection is too low, can be produced during transient operation during starting, especially during cold weather. White smoke can also be produced when the fuel injection is initiated too late during the engine cycle or when the compression ratio is too low.

Gray-black smoke is typically generated when the engine is operating at or near full load and too much fuel is injected or when the air intake is partially obstructed (dirty air filter). Heavy smoke from a diesel engine usually indicates a loss in thermal efficiency, power output, and fuel economy. Gray-black smoke results from poor maintenance of air filters and fuel injectors or from improper adjustment of the fuel injection pump. It should be noted that it is essentially impossible to completely eliminate smoke produced by diesel engines; thus, some carbon particles will always be present in the exhaust of diesel fueled engines (Maxwell, 1995).

Unlike those of gasoline engines, diesel gaseous HC and CO emissions are relatively low, and their reduction was not necessary to meet the 1994 U.S. truck standards. The problem is reducing the particulates. In order to meet the increasingly stringent emission regulations, engine manufacturers are focusing in areas such as valves, fuel pumps, pistons, and combustion chambers (Ferguson, 1993). Another approach to meet emission requirements is the oxidation of the SOF (which may represent up to approximately 65 percent of the particulate) with the usage of a catalyst, thereby greatly reducing the total particulates emitted. Some manufacturers focus on the use of aftertreatment technology including catalytic converters and/or particulate traps.

Diesel particulate emissions continue to challenge researchers and scientists in the industrialized world. In spite of many design improvements in recent years, diesel engines are still emitting particulate emissions which are uncomfortably close to the mandated level. In order to meet the future emission standards, engineers are not only investigating new diesel engine technology, but they also have been working on solutions involving exhaust aftertreatment.

On May 17, 2000, the EPA announced proposed emission standards for model year 2007 and later heavy-duty highway engines. The proposed rule includes two components: diesel fuel regulation and emission standards. The proposed fuel regulation limits the sulfur contents in on-highway diesel fuel to 15 ppm, down from the previous 500 ppm. The fuel provisions would go into effect in June 2006. The proposal discusses various phase-in approaches for the diesel fuel industry (dieselnet.com, 2000).

The second part of the proposal introduces new emission standards. The EPA proposes a particulate matter (PM) emission standard of 0.01 g/bhp-hr, to take full effect in the 2007 heavy-duty engine model year. The proposed standards for NO<sub>x</sub> and HC are 0.20 g/bhp-hr and 0.14 g/bhp-hr, respectively. These NO<sub>x</sub> and HC standards would be phased in for diesel engines between 2007 and 2010. The phase-in would be on a percent-of-scale basis: 25% in 2007, 50% 2008, 75% in 2009, and 100% in 2010 (dieselnet.com, 2000).

## **2.2 Diesel Engine Technology**

Simultaneously achieving low NO<sub>x</sub> and PM emissions present the diesel engine manufacturer with a major challenge. Some of the more effective strategies to reduce NO<sub>x</sub> emissions tend to increase PM emissions and vice-versa. While manufacturers will try technologies that have a “flatter” NO<sub>x</sub> versus PM curve, reaching low NO<sub>x</sub> emissions while keeping PM emission low will require a combination of technologies. Some of the useful engine technologies discussed on the next few pages includes improved fuel injection, combustion chamber modifications, and turbocharger improvements.

### **2.2.1 Improved Fuel Injection**

Fuel injection parameters have a dramatic impact on the nature of combustion in diesel engines. Consequently, engine manufacturers will continue to focus on fuel injection in an effort to reduce emissions and improve engine performance. Among the more recent advances in fuel injection technology are the development of the hydraulic electronic unit injection, improved injector nozzles, and the use of rate shaping or multiple injections.

#### **2.2.1.1 Hydraulic Electronic Unit Injection**

Hydraulic electronic unit injection (HEUI) offers benefits over even advanced pump-line-nozzle fuel injection systems due to the ability to achieve high injection pressures (1400 to 1900 bar) and to specify parameters such as start of injection and injection duration at different engine loads and speeds. The high injection pressure is beneficial because it aids in fuel atomization in the combustion chamber and reduces PM emissions. It is expected that HEUI will be widespread in most heavy-duty diesel engines by 2004 (Browning, 1997).

The HEUI consists of three main components: control valve, intensifier plunger and barrel, and a nozzle. The control valve initiates and terminates the injection process. It is comprised of a poppet valve, armature, and solenoid. To begin injection, the solenoid is energized moving the poppet valve from the lower to the upper seat. Injection continues until the solenoid is de-energized and the poppet moves from the upper to lower seat (Glassey et al. 1993).

The middle segment of the injector consists of the hydraulic intensifier piston, the plunger and barrel, and the plunger spring. As the piston and plunger move downward, the pressure of the fuel below the plunger rises. The piston continues to move downward

until the solenoid is de-energized causing the poppet to return to the lower seat, blocking oil flow. The plunger return spring returns the piston and plunger to their initial positions. As the plunger returns, it draws replenishing fuel into the plunger chamber across a ball check valve.

The nozzle is typical of other diesel fuel system nozzles. Fuel is supplied to the nozzle through internal passages. As fuel pressure increases, the nozzle needle lifts from the lower seat allowing injection to occur. As pressure decreases at the end of injection, the spring returns the needle to its lower seat (Glassey et al. 1993).

#### **2.2.1.2 Improved Injector Nozzles**

The injector nozzle itself significantly affects the delivery of fuel into the combustion chamber and can have a major impact on air-fuel mixing and thus emissions. There are a couple of ways to improve the injector nozzles. Improving the injector nozzle improves the fuel atomization.

One way for improving the atomization is to consider Sauter Mean Diameter. The Sauter Mean Diameter consists of the function of the spray hole diameter and fuel flow velocity at the spray hole. The formula is as shown:  $D_{32} = f\left(\frac{d}{V}\right)$ , where  $D_{32}$  is the Sauter Mean Diameter,  $d$  is the spray hole diameter, and  $V$  is the fuel flow velocity. In other words, an effective way for better atomization is to reduce the spray hole diameter thus increasing the fuel flow velocity. Through experiments, enlarging the chamfer at the spray hole inlet proved to be the most effective and suitable method for establishing high flow velocity injection nozzles (Yoda & Tsuda, 1997).

Nozzle hole diameters must be optimized to provide the proper spray and amount of fuel atomization. The number of nozzle holes should be matched with the fuel

injection pressure and combustion chamber geometry to provide the best air utilization. Other optimization parameters would include nozzle position and spray cone angle.

### **2.2.1.3 Rate Shaping and Multiple Injections**

Injection rate shaping is a complex factor to quantify. Today, most fuel injection-rate shaping systems provide an injection rate that has a lower slope at the beginning of injection such that less fuel is injected early in the combustion. As a result, less premixed combustion occurs thus less  $\text{NO}_x$  is formed. This shape is typical for high speed or high load conditions. At idle, low speed and low load, the injection rate often becomes discontinuous with two “humps” separated by an interval with no injection (first hump injected - no injection - second hump injected), (Ghaffarpour & Baranescu, 1996).

For 2004, it is envisioned that technological advancements will allow full electronic control of rate shaping or multiple injections with parameters being fully controlled with the engines electronic control module.

### **2.2.2 Combustion Chamber Modifications**

Combustion chamber designs have already gone through a significant evolution; however, further incremental improvements still can be made. Today, engine designers have at their disposal more powerful computers and better computer models to assist them in a design process which involves extensive testing, computer modeling, model validation, extension of predictions, and further testing. Some of the combustion chamber modifications include increasing the compression ratio and reduced oil consumption.



### **2.2.2.1 Increasing Compression Ratio**

Increasing the compression ratio in a diesel engine reduces the ignition delay period, thereby reducing the amount of fuel burned in the premixed region and allowing more injection timing retard to control NO<sub>x</sub> emissions (Browning, 1997). Since raising the compression ratio also increases the combustion temperature, cold start PM emissions and white smoke are reduced. High compression ratios offer the most emissions reductions at high speed, light load conditions when ignition delay is the longest, and under cold operating conditions (Browning, 1997). In both cases, major reductions in HC emissions are achieved.

### **2.2.2.2 Reduced Oil Consumption**

Engine oil left in the cylinder during the expansion stroke, or oil otherwise introduced into the combustion chamber can contribute significantly to engine-out PM emissions. For instance soluble oil can account for about thirty-five percent of diesel engine PM emissions (Heck, 1995). Several methods have been utilized to lower oil consumption in diesel engines. Precise bore honing and enhance ring pack design have been shown to reduce PM emissions. Improvements to other mechanical components such as valve guides and valve guide seals can also play an important role in the reduction of PM emissions (Richards and Sibley, 1988). Engine designers must balance the need to control oil consumption with the need to avoid engine wear from too little oil remaining on cylinder walls.

Sulfur from the lubricating oil can contribute to overall engine-out sulfur emissions. There is some sulfur in the lubricating oil base stock. However, much of this sulfur content is associated with detergents and anti-wear additives in the additive packages of commercial lubricating oils. Specifically, the anti-wear additives typically

contain sulfur and phosphorus in the form of zinc dithiophosphates. The net effect is that commercial diesel engine lubricating oils contain from 4000 to 10000 ppm sulfur (DECSE Interim Report, 1999).

### **2.2.3 Turbocharger Improvements**

As engine manufacturers face the oncoming emission standards, it is important to reduce emissions without losing engine power and fuel economy. Increasing the air intake charge has received much attention. Improved turbochargers can provide significant improvements in fuel consumption and emissions. Turbochargers are expected to be an important component for heavy-duty diesel engines meeting 2004 emissions standards.

Variable geometry turbochargers provide leaner air/fuel ratios under full load conditions, thereby reducing emissions and also improving transient response at lower loads and speeds. The variable geometry turbocharger controls the turbine power by changing the nozzle angle and varying the throat area. Through this, sufficient boost pressure can be achieved in low flow regions, and a wide operating range that extends to high flow rates and high speed ranges can be realized (Anada, et al. 1997).

## **2.3 Aftertreatment Technology**

Even though there is progress being made on diesel engine technology, more and more attention is focused on the aftertreatment technology. In order for the engine manufacturers to meet the upcoming stringent 2007 EPA emission standards, especially the NO<sub>x</sub> and PM standards, aftertreatment will be mandatory. Some of the aftertreatment devices include diesel oxidation catalyst (DOC), lean NO<sub>x</sub> catalyst, urea selective catalytic reduction (SCR), and particulate traps. The use of catalysts to remove the major

air pollutants, carbon monoxide, unburned hydrocarbons, and oxides of nitrogen from vehicle exhaust is becoming an almost worldwide requirement. The control of CO and HC in diesel exhaust is relatively straightforward with standard platinum group metal-based oxidation catalysts, but NO<sub>x</sub> control is difficult because of the highly oxidizing nature of the exhaust.

### **2.3.1 Diesel Oxidation Catalysts**

Diesel oxidation catalysts are very effective in reducing HC, CO, SOF emissions from diesel exhaust. The largest problem is controlling sulfate formation resulting from sulfur in the diesel fuel. Ideally, the design of these catalysts promotes the oxidation of the SOF borne by the particulate with minimal sulfate production from SO<sub>2</sub> oxidation (Fredholm, 1993). The removal of the SOF produces a reduction in the mass of particulate in proportion to its organic content. The production of sulfate through the oxidation of SO<sub>2</sub> increases the mass of the particulate in proportion to the fuel sulfur level. The trade-off between the SOF and SO<sub>2</sub> oxidation over the operating temperature range of a given test cycle determines whether or not a diesel oxidation catalyst will be effective in reducing particulate emissions over that test cycle. Oxidation catalysts also store sulfuric acid formed from sulfates and water vapor under low to moderate temperature conditions and release sulfates during a higher temperature condition. This storage and release of sulfates can result in bursts of particulate matter during speed and load changes and adversely affect the durability of the catalyst (Fredholm, 1993).

The operating condition of the engine requires that the catalyst first adsorb and retain the SOF at low temperatures (that is, at idle), followed by its combustion as the

exhaust temperature reaches light off (that is, at 200-250°C), according to the following reaction:  $\text{SOF} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ .

There have been several studies on the use of diesel oxidation catalysts for the control of the exhaust emissions. These studies have generally focused on the use of platinum group oxidation catalysts for control of HC, CO, and SOF (Wyatt et al. 1993). Catalysts based on the platinum group metals, usually either platinum (Pt) and/or palladium (Pd), which are precious metals, are generally required due to the low exhaust temperatures encountered in diesel exhaust (Heck, 1995). However, the platinum group metals also catalyze the oxidation of  $\text{SO}_2$  to sulfur trioxide particularly by Pt, in the  $\text{SO}_2$ -rich exhaust of the typical diesel engine. The sulfate trioxide produced reacts with water in the exhaust to form sulfuric acid; this tends to either condense on, or react with the catalyst or adsorbs onto the particulate present in the exhaust. Thus, active oxidation catalysts often increase the mass emission rate of particulate matter, especially around 300°C, even when the amount of SOF present is significantly reduced. Good particulate control requires a catalyst that is capable of oxidizing HC, CO, and SOF with minimal oxidation of  $\text{SO}_2$  (Wyatt et al. 1993).

A previous study (Pataky et al. 1994) investigated the effects of a diesel oxidation catalyst on a 1991 Cummins L10-310 diesel engine fueled with a 0.01 weight percent sulfur fuel. The DOC effects were determined by measuring and comparing exhaust emissions with and without the platinum-based DOC installed in the exhaust system. The engine operated at three steady-state modes. Prior to the testing, the DOCs were conditioned for approximately 50 hours with engine exhaust at temperatures around 400°C or greater. The tests were performed with three modified EPA steady state modes.

The three modes chosen were modes 9, 10, and 11, which are defined as 75, 50 and 25 percent load, respectively, at rated engine speed of 1800 RPM. The corresponding loads for modes 9, 10, and 11 were 920, 614, and 307 N-m, respectively. These modes were chosen to provide a range of exhaust temperatures as well as a range of emission characteristics. A sample of the results obtained in the experiment can be seen in Table 2.2.

Table 2.2 Effect of the DOC on Gaseous and PM Emissions (Patalzy et al. 1994)

<b>Emission</b>	<b>Mode 9</b>	<b>Mode 9</b>	<b>Mode 10</b>	<b>Mode 10</b>	<b>Mode 11</b>	<b>Mode 11</b>
	<i>Baseline</i>	DOC	<i>Baseline</i>	<i>DOC</i>	<i>Baseline</i>	<i>DOC</i>
NO <sub>x</sub> (ppm)	531	539	365	362	213	210
NO (ppm)	506	511	344	345	196	205
HC (ppm)	72	28	96	34	177	53
TPM (mg/m <sup>3</sup> )	8.1	5.9	8.7	5.7	15.4	7.0
SOF (mg/m <sup>3</sup> )	5.1	2.4	5.2	2.1	11.6	3.4

It was found that the DOC had no significant effect on (NO<sub>x</sub>) and nitric oxide (NO) at any mode. The DOC reduced the (HC) emissions by 60 to 70 percent in all three modes. The DOC reduced TPM levels by 27 to 54 percent, primarily resulting from 53 to 71 percent reductions of the soluble organic fraction. It can be seen in Table 2.2 how vital the aftertreatment DOCs were on the emissions and how their performance was proven with a high degree of success.

### 2.3.2 Lean NO<sub>x</sub> Catalysts

Lean NO<sub>x</sub> catalysts provide a catalytic reduction of NO<sub>x</sub> emissions in a fuel-lean environment. It is envisioned that lean NO<sub>x</sub> catalysts will not be incorporated as part of

the aftertreatment by the year 2004 (Litorell, 1995). However, research continues on this technology and some manufacturers are holding out hope that this can prove viable in the near future. Previous work with copper zeolites (Cu-ZSM-5) showed feasibility of reducing NO<sub>x</sub> emissions by using hydrocarbons in the diesel engine exhaust at higher temperatures of 425 °C to 555 °C (Arakawa, et al. 1998). The problem was that it required a significant amount of hydrocarbons to reduce the NO<sub>x</sub> (approximately 4 to 1) and that the systems were very sensitive to poisoning by SO<sub>2</sub>, and inhibition by water (Browning, 1997). Platinum-based catalysts are quite active in reducing NO<sub>x</sub> emissions in the 200°C to 300°C range and need lower amounts of HC to reduce NO<sub>x</sub> (2 to 1). However, platinum produces sulfates from the fuel sulfur, which increase particulate emissions.

The most significant problem with lean NO<sub>x</sub> catalysts is the need for a large amount of a reductant (hydrocarbons). Current lean NO<sub>x</sub> catalysts also prefer lower molecular weight hydrocarbons such as propane (Litorell, 1995). However, it is clear for such a system to be realistic on diesel engines, it must use diesel fuel as the source of hydrocarbons.

Three approaches have been suggested to provide the addition of hydrocarbons using diesel fuel. The first approach places an additional fuel injector in the exhaust pipe to inject diesel fuel into the exhaust system upstream of the catalyst. Such a system could encourage tampering since removal of this injector would not result in any performance loss and would actually result in fuel savings. The second method injects more fuel mixture into the cylinder during the injection process to create additional hydrocarbons. While this method is less liable to be tampered with, larger fuel penalties and higher HC

emissions could result. The third method injects additional fuel during the exhaust stroke. This method is the most feasible to date (Browning, 1997). It is estimated that fuel consumption will increase approximately 5 percent to provide enough hydrocarbons for efficient NO<sub>x</sub> reduction. However, since these catalysts would replace other methods of NO<sub>x</sub> control which are also associated with a fuel economy penalty, some of the increased fuel consumption attributed to these catalysts would be counteracted.

### **2.3.3 Selective Catalyst Reduction Using Urea**

Urea selective catalytic reduction (SCR) has been widely used since the 1980's to reduce NO<sub>x</sub> emissions from exhaust gas in stationary applications (utility boilers, gas turbines, waste incineration, and diesel engines used for power generation). More recently the technology has been applied to mobile diesel engine applications such as ships, locomotives, and prototype on-road heavy-duty vehicles. Since 1990, urea has been increasingly used to replace anhydrous ammonia and aqueous ammonia as the reducing agent for reasons of safety in handling and storage (Miller et al. 2000). The SCR method using urea as the reducing agent is estimated as the most powerful technology allowing compliance with future heavy-duty NO<sub>x</sub> standards.

Miller et al. (2000) recently measured emissions in a transient test cell with a DC dynamometer and partial dilution tunnel using the urea-SCR technology. NO<sub>x</sub>, CO, CO<sub>2</sub>, HC, and PM were measured using accepted analyzers and procedures. Standard diesel fuel with 400 – 500 ppm sulfur content was utilized for all tests. The SCR reducing agent was a urea solution containing 32.5% urea by weight and de-mineralized water. The test was performed on a 12-liter inline six cylinder heavy-duty diesel engine (HDDE).

Results from an OICA steady state test using the urea technology can be seen in Table 2.3 (Miller et al. 2000).

Table 2.3 Urea – SCR OICA Emissions Results (Miller et al. 2000)

<b>Exhaust Emission (g/bhp-hr)</b>	<b>Baseline (engine-out)</b>	<b>Urea-SCR (catalyst-out)</b>
NO <sub>x</sub>	4.86	0.70 (-85.6%)
HC	0.01	0.00 (-100%)
PM	0.04	0.04 (equal)
NH <sub>3</sub>	0.00	0.24
CO	0.29	0.29 (equal)
CO <sub>2</sub>	506	515 (+1.8%)

It is clearly evident that significant NO<sub>x</sub> reduction was achieved during the OICA test cycles, while HC emissions were eliminated all together. One possible reason for the reduction may be due to the steady state nature of the test and high catalyst temperatures achieved. Overall, urea-SCR may be a key component of technology to meet future emissions standards.

## 2.4 Fuel Sulfur

Due to the upcoming EPA 2007 stringent emission standards, one must take into consideration the contribution of fuel sulfur to particulate emissions. In the past years, the influence of diesel fuel sulfur upon particulate emissions has become a topic of active engineering research.

There are a number of issues associated with the contribution of diesel fuel sulfur to the atmospheric particulate concentration. Perhaps the most obvious is the effect of fuel sulfur on directly emitted particulate which is measured in EPA emissions tests. The presence of sulfur compounds in the exhaust also precludes the use of some attractive



emission control technologies employing aftertreatment catalysts for hydrocarbon and particulate reduction, due to the excessive sulfate formation (Wall, 1987).

Sulfur is in the form of sulfates and bound water. It is a component of the total particulate matter collected during heavy-duty transient and steady state tests. Most of the fuel sulfur is oxidized to sulfur dioxide during combustion and emitted in the atmosphere where it forms sulfates (Baranescu, 1988). Sulfates in return contribute to acid rain. Sulfur in diesel fuel also affects the operation and the durability of the catalytic aftertreatment systems.

Sulfur, a natural constituent of crude oil, can be removed during the refining operations by special hydrotreating procedures. The degree of removal depends upon existing fuel specifications. The existing ASTM standards limit the maximum level of sulfur in diesel fuel at 0.5% by weight (Baranescu, 1988). However, states have the authority to set their own limits of sulfur in diesel fuels sold within their boundary.

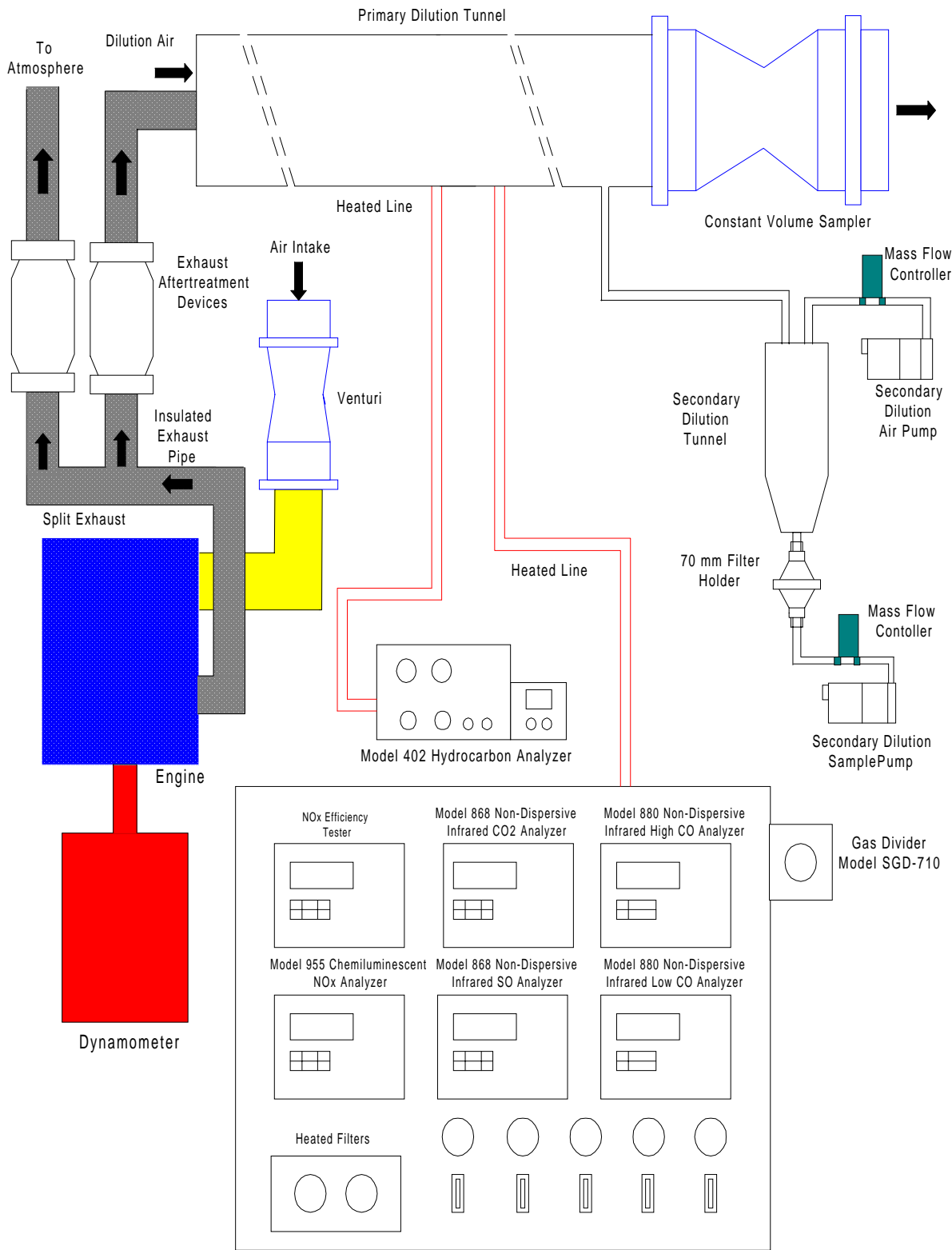
## CHAPTER 3 ~ EXPERIMENTAL SET-UP

### 3.1 Experimental Equipment

The emissions testing was performed in WVU's heavy-duty engines FTP emissions measurement facility while the aging of the catalysts was carried out on test beds in a separate adjoining area. A schematic of the emissions testing facility is shown in Figure 3.1. This chapter discusses major components of the experimental equipment used and the procedures that were followed to operate the equipment and carry out the evaluations.

#### 3.1.1 Engines

Throughout the DECSE project, two Navistar T444E (7.3L, 99 MY) engines and two Cummins ISM370 ESP (10.8L, 99 MY) engines were used for aging and evaluating the catalysts. The Navistar V-8 turbocharged engines were rated at 210 hp at 2300 rpm. The Cummins in-line 6 cylinder engines were turbocharged and rated at 370 hp at 1800 rpm. Table 3.1 lists the specifications of the Navistar T444E engines and the Cummins ISM370 ESP engines. One Navistar engine and one Cummins engine were used for catalyst aging, while the other two engines were used for catalyst evaluation in the test cell. The engine torque curves of the Navistar engine and the Cummins engine can be seen in Figure 3.3 and Figure 3.4, respectively. Both, Navistar and Cummins provided the electronic control box, engine calibration software, and test cell accessories. All four engines were conditioned for 50 hours, according to the recommendations of the engine manufacturers.



Note: The sampling probes are located 10 tunnel diameters downstream of the exhaust inlet to the primary dilution tunnel.

Figure 3.1 Schematic of Test Cell Layout

Table 3.1 Navistar T444E Engine Specifications

	<b>Cummins ISM30</b>	<b>Navistar T444E</b>
IGNITION	COMPRESSION	COMPRESSION
INJECTION	DIRECT	DIRECT
NO. OF CYLINDERS	IN-LINE 6	V-8
BORE	5.92	4.11 in.
STROKE	5.79	4.18 in.
DISPLACEMENT	10.8 L	7.3 L
COMPRESSION RATIO	16.3 : 1	17.5 : 1
PEAK TORQUE	1350 ft-lb	516 ft-lb
RATED POWER	370 hp	210 hp

Figure 3.2 shows the medium-duty Navistar T444E diesel engine connected to the GE 550 hp direct current engine dynamometer located in the West Virginia University Engine and Emission Research Laboratory (WVU EERL).

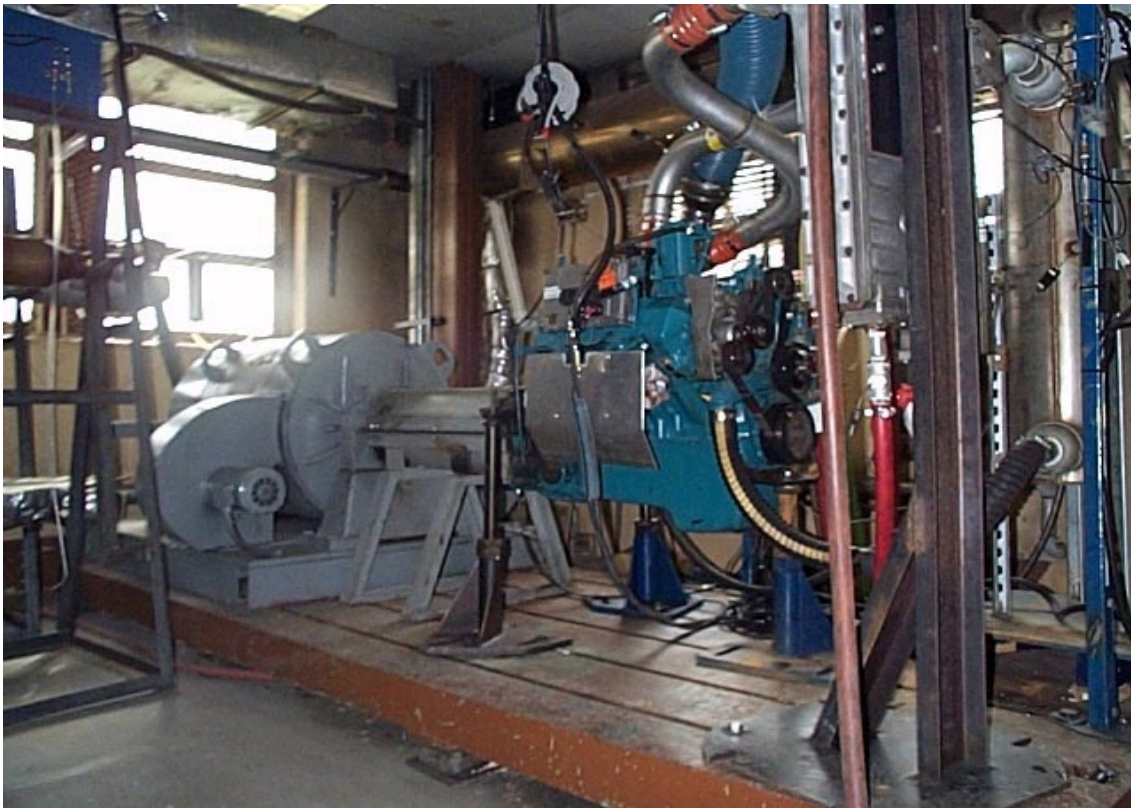


Figure 3.2 Navistar T444E Test Cell Engine

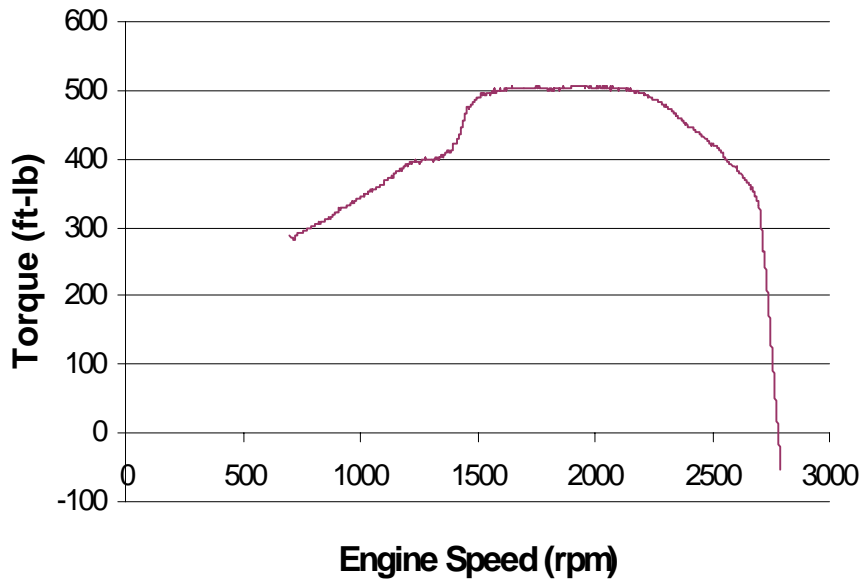


Figure 3.3 Navistar T444E Torque Curve

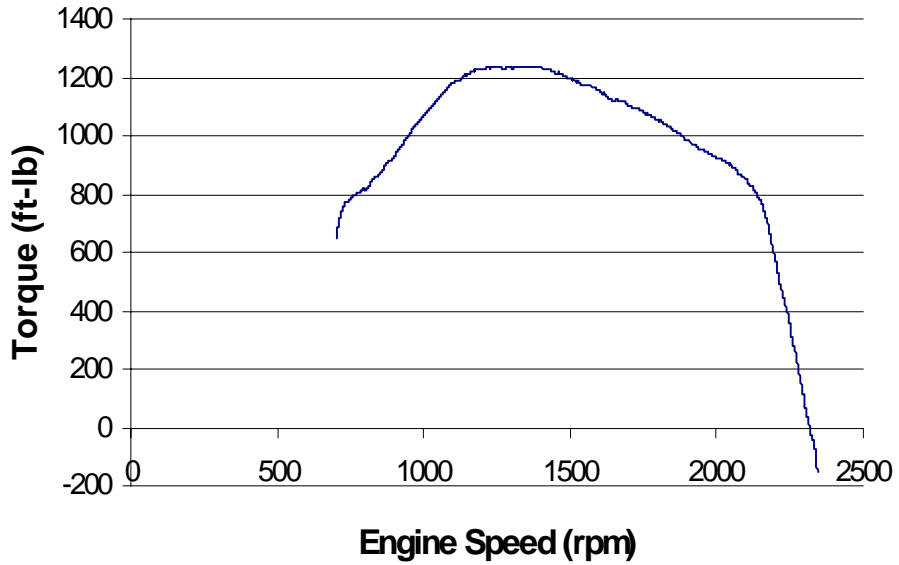


Figure 3.4 Cummins ISM370ESP Torque Curve

### 3.1.2 Fuel Specifications

The diesel fuel used throughout the research was supplied by Phillips Petroleum Company (Phillips 66). Phillips 66 used the same base fuel and then used an additive to increase the fuel sulfur level per WVU's request. Table 3.2 shows the comparison between the nominal fuel sulfur levels to the actual fuel sulfur levels received in the fuel from Phillips 66. Table 3.3 shows the average results and the standard deviation from the fuel chemical analyses that were performed on the fuel batches supplied to WVU. Phillips Chemical Company performed the chemical analysis of the fuel and provided the certificates of analysis. Upon examining the test results in Table 3.3, it should be noted that all of the chemical properties of the fuel were approximately the same. The only difference in the various fuels was the sulfur content. The Certificates of Analysis for the fuels can be seen in Appendix H.

Table 3.2 Comparing Nominal Fuel Sulfur Levels to Actual Fuel Sulfur Levels

	<b>3 ppm Fuel Sulfur</b>	<b>30 ppm Fuel Sulfur</b>	<b>350 ppm Fuel Sulfur</b>
Actual Fuel Sulfur Added to Tanker #1	3.3	29 ppm	361
Actual Fuel Sulfur Added to Tanker #2	1.3	25 ppm	335

Table 3.3 Average Test Results From Fuel Chemical Analysis

<u>TESTS</u>	<u>AVERAGE RESULTS</u>	<u>STANDARD DEVIATION</u>	<u>METHOD</u>
Specific Gravity, 60/60	0.8263	0.0004	ASTM D-4052
API Gravity	39.71	0.0522	ASTM D-1298
Sulfur, ppm	****	****	ASTM D-4294
Flash Point (°F)	152.7	0.2582	ASTM D-93
Pour Point (°F)	-5.0	0.000	ASTM D-97
Cloud Point (°F)	-5.0	0.000	ASTM D-2500
Viscosity, cs 40C	2.5	0.0408	ASTM D-445
Carbon, wt%	86.4	0.2000	ASTM D-5291
Hydrogen, wt%	13.6	0.2000	ASTM D-5291
Net Heat of Combustion BTU/LB	18552.4	23.02	ASTM D-3343
Cetane Index	53.5	0.0665	ASTM D-976
Cetane Number	44.0	0.7014	ASTM D-613
<b><u>DISTILLATION, (°F)</u></b>			ASTM D-86
IBP	360.4	5.455	
5%	387.7	2.455	
10%	402.6	1.074	
20%	430.3	2.497	
30%	459.8	1.878	
40%	482.8	0.9223	
50%	497.4	0.6998	
60%	509.4	0.6795	
70%	523.5	0.8892	
80%	546.7	1.068	
90%	597.6	2.104	
EP	663.4	2.591	
Loss	0.5	0.2639	
Residue	1.1	0.0894	
<b><u>HYDROCARBON TYPE, VOL%</u></b>			ASTM D-1319
Aromatics	26.5	0.3445	
Olefins	2.5	0.3286	
Saturates	73.0	2.800	

### **3.1.3 Dilution Tunnel**

The dilution tunnel is the most widely used technique for the sampling of diesel exhaust particulate and has been adopted by the EPA as the standard method (Williams, 1988). The primary purpose of the dilution tunnel is to mix the raw diesel exhaust emissions with a larger volume of air in an effort to reduce the dew point temperature, and try to mimic the atmospheric dilution of exhaust. Upon mixing, the diluted exhaust temperature is lowered to 125°F at the PM sampling filter face. The dilution process can consist of mixing all or a portion of the engine exhaust. Details on dilution tunnels are discussed by Smith (1993) and Miller (1997). In the DESCE research program, engine-out tests were performed with the full exhaust flow directed into the dilution tunnel. Catalyst-out emissions tests were conducted by splitting the flow so that approximately fifty percent of the exhaust was directed into the dilution tunnel. Splitting the exhaust is a diversion from the EPA certification procedures. In order to age the DOC and lean NO<sub>x</sub> catalysts simultaneously and economically they were sized for one half of the total exhaust flow. During the aging process, a split exhaust system directed approximately half of the total exhaust flow rate through each catalyst. Consequently, exhaust splitting was also required during catalyst evaluation.

The Code of Federal Regulations (CFR) 40, Part 86, Subpart N, states that diesel exhaust must be connected to a critical flow venturi constant volume sampler (CFV-CVS) or a positive displacement pump-constant volume sampler (PDP-CVS) in order to sample particulate emissions. When operating the Navistar engine, CFV-CVS flow rate was set at 1400 scfm for total flow exhaust dilution and 1000 scfm for split-flow exhaust dilution. When the Cummins ISM was running on the dynamometer, the CFV was set on



2400 scfm for the full flow exhaust dilution, and 1400 scfm for the split flow exhaust dilution. The mixing of the diesel exhaust and ambient air not only simulated the effect of exhaust emissions in real world applications, but it also aids in the emissions sampling process.

Diluting the raw diesel exhaust with the ambient air, which is drawn into the tunnel by the CVS, lowers the dew point temperature, which in return prevents water condensation. If water condensation were to occur, certain gaseous components would be lost which would alter the emissions measurement results. Additionally, the non-dispersive infrared analyzers would be affected by the water condensation.

#### **3.1.4 Secondary Dilution Tunnel**

There are two types of dilution systems used in the measuring of particulate matter, single-dilution and double-dilution. West Virginia University uses the double-dilution method in their engine test cell. In the single dilution method, the flow capacity of the CVS must be sufficient to maintain the diluted exhaust stream at a temperature of 125°F (51.7°C) or less at the sampling zone in the primary dilution tunnel. Condensation at any point in the dilution tunnel must also be prevented. If these requirements are met, then direct sampling of the particulate matter may be taken.

In the double-dilution system, the flow capacity must be sufficient to maintain the diluted exhaust stream in the primary dilution tunnel at a temperature of 375°F (191°C) or less at the sampling zone and prevent condensation at any point in the dilution tunnel. More importantly, the filter face temperature should be less than 125°F. It is essential to have the dilute exhaust mixture thoroughly mixed at the sampling zone. For this to occur, the sample zone is located 10 pipe diameters or approximately fifteen feet

downstream from where the exhaust enters the tunnel. Gaseous emission samples may then be taken directly from this sample zone. An exhaust sample must then be taken at this point and diluted for a second time for use in determining particulate emissions. The secondary dilution system must provide sufficient secondary dilution air to maintain the double-diluted exhaust stream at a temperature of 125°F (51.7°C) or less immediately before the primary particulate filter.

### **3.1.5 Particulate Sampling**

The process of measuring PM emissions of particulate matter from diesel engines consists essentially of conveying the exhaust to a dilution tunnel (single or double) in which it is diluted with air and cooled to a temperature not exceeding 125°F (51.7°C). A representative sample of the particulate matter in the dilute sample is obtained by filtration, and the mass collected on the filter or filters is determined gravimetrically. As stated earlier, the WVU laboratory uses the double-dilution method for particulate matter sampling by drawing a proportional sample of diluted exhaust from the primary tunnel and diluting it further in the secondary dilution tunnel before it passes through two Pallflex 70-mm fluorocarbon coated fiberglass filters which collect the particulate matter. The high efficiency filters are over 99% efficient on 0.5 µm particles. Figure 3.5 is a schematic of the WVU's secondary dilution tunnel and filter holder.

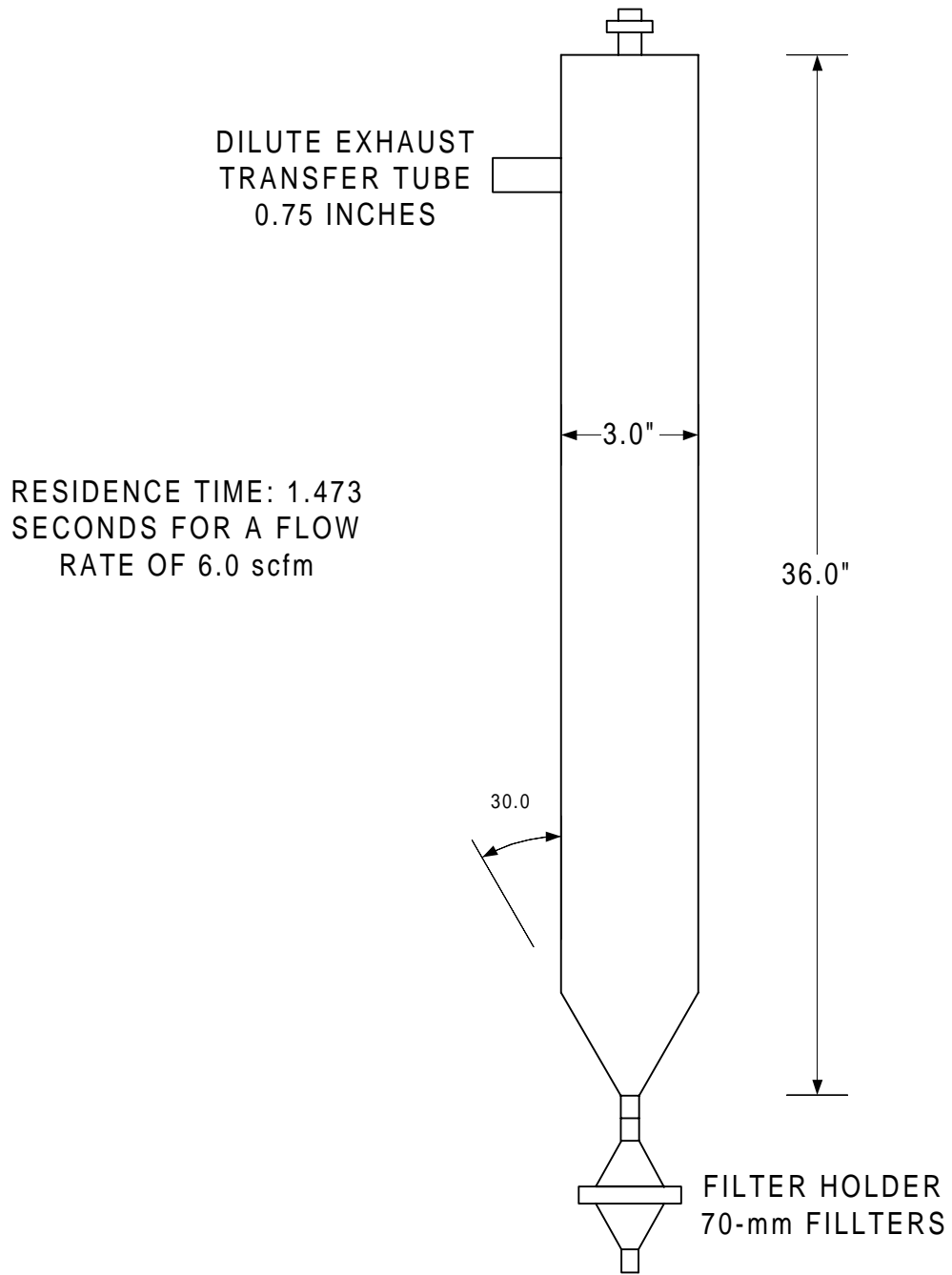


Figure 3.5 Secondary Dilution Tunnel Outlet and Filter Holder

Total flow and secondary dilution air flow through the secondary tunnel were controlled by two Sierra 740 series mass flow controllers and two Gast Model series rotary vane pumps. A Roots positive displacement pump provided an additional check on the total flow rate through the PM filters. The secondary dilution air flow rates ranged from 0-3 scfm. During testing, flow through the secondary dilution tunnel varied proportionally to the flow rate through the primary dilution tunnel.

The secondary dilution tunnel is 3.0 inches in diameter and 36 inches long. The size of the secondary dilution tunnel provided sufficient residence time for the exhaust sample to be mixed with the dilution air and to reach a temperature of 125°F (51.7°C). A filter holder is located at the end of the secondary dilution tunnel during testing to house the primary and secondary filters. The filter holder is constructed of stainless steel to prevent reactions with the corrosive exhaust sample. The design of the filter holder allowed easy access to both the primary and secondary filters.

Throughout the DECSE project, the filters were weighed at Oak Ridge National Laboratory located in Tennessee and also at the West Virginia University EERL. First, the 70-mm filters were sent from WVU to ORNL to be pre-weighed before usage. Upon re-arrival from ORNL, WVU also weighed the filters before using them. Before weighing, the filters were equilibrated for 12 hours at a 50% relative humidity and 70°F in an Environtronics model SH8 environmental chamber.

Once WVU collected PM on the primary and secondary filters from a steady state or transient test, the filters were again equilibrated in the environmental chamber and re-weighed. After WVU re-weighed the filters, they were packaged and sent back to ORNL

for chemical characterization of PM. ORNL performed the breakdown analysis of the PM for sulfates, nitrates, and SOF.

The particulate filters were stored in glass petri dishes while conditioning in the environmental chamber. All of the petri dishes were covered but not sealed to prevent dust and other particles from settling on the samples while allowing the humidity to exchange.

Since the primary and secondary dilution air was not filtered, background particulate samples were taken. The total particulate mass was determined from weighing the filters before and after the test, after the conditioning process. A Cahn 32 microbalance was used for weighing the filters. The microbalance was placed on a vibration isolation table. The balance has a 3.5 gram weighing capacity with three weighing ranges and a sensitivity of 0.01  $\mu\text{g}$ .

### **3.1.6 Bypass System**

A bypass system was built for use during steady state tests (OICA\* and Nav-9\*). The bypass system allows the exhaust to bypass the PM filter so that the PM sampling could be taken for a specified time at the end of each steady state mode. This allowed the catalysts temperatures and the catalysts out emissions to stabilize during the long steady state modes prior to emissions sampling. During the stabilization period, the diesel exhaust would exit the secondary dilution tunnel, and bypass the PM filter travelling through a Balston stainless steel filter housing with a Parker Filtration filter. This filtered out the PM to protect the mass flow controllers. A three-way solenoid EVASCO valve controlled the direction of exhaust flow. After passing through the three-way elliptical valve, the exhaust flowed to, and through the mass flow controller. When PM sampling

began, the three-way valve switched positions, and allowed the exhaust to travel through the PM filter. Figure 3.6 shows a schematic of the bypass system.

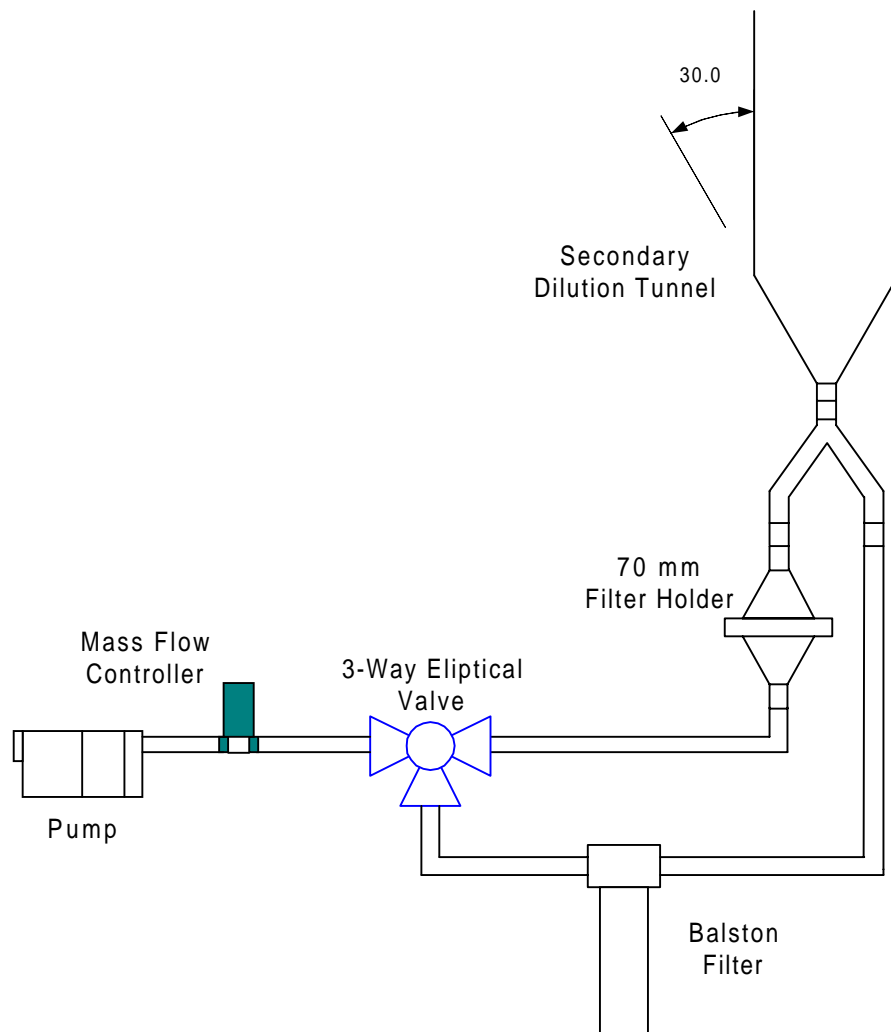


Figure 3.6 Bypass System for Steady State Tests

### 3.1.7 Gaseous Emissions Sampling

A gas analysis bench was used to measure the concentration of gaseous components in a diluted exhaust gas stream. The gaseous samples were withdrawn 10 diameters (diameter of the primary dilution tunnel was 18 inches) downstream of the mixing zone to allow for complete mixing in the primary dilution tunnel. Three separate

probes were used to sample the gaseous emissions, one each for the HC and NO<sub>x</sub>. The CO and CO<sub>2</sub> analyzers share a probe. These three heated stainless steel probes were connected to heated lines that transfer the emissions to the analyzers.

The gaseous emissions were sampled for the entire length of the transient tests. When the steady state tests were conducted, gaseous emissions samples were only taken for a specified duration at the end of each mode. In the steady state tests, the engines' oil and coolant temperatures were allowed to stabilize prior to the start of sampling.

### **3.1.7.1 Hydrocarbon Analyzer**

The total hydrocarbon measurements were made with a Rosemount Model 402 heated flame ionization detector (HFID). This model was designed to measure the total HC content of exhaust emissions from gasoline, diesel, turbine, and jet engines. The analyses were based on flame ionization, a highly sensitive detection method. The hydrocarbon sensor was a burner where a regulated flow of sample gas passes through a flame sustained by regulated flows of a fuel and hydrocarbon free air. The analyzer uses a premixed fuel gas consisting of 40% hydrogen and 60% helium. Within the flame of the HFID, the hydrocarbon components of the sample stream undergo a complex ionization that produces electrons and positive ions. Polarized electrodes collect these ions, causing current to flow through measuring circuitry located in the electronics unit. The ionization current was proportional to the rate at which carbon atoms enter the burner, and was therefore a measure of the concentration of hydrocarbons in the original sample (Rosemount, 1991). The 402 HFID was capable of measuring hydrocarbon concentrations from 50 to 250,000 parts per million (ppm) and produces a full-scale linear output of 0 – 1 volt.

The continuous THC sampling system was maintained at a temperature of 375° +/- 10°F (190° +/-5°C).

### **3.1.7.2 Oxides of Nitrogen (NO<sub>x</sub>) Analyzer**

The NO/NO<sub>x</sub> analyzer used in WVU Engine and Emission Research Laboratory was a Rosemount Model 955 Chemiluminescent Analyzer. The heated sample probe, line, and temperature controllers were identical to those used for the THC sampling analysis, except that the NO<sub>x</sub> sampling system was maintained at a temperature of 250° +/- 10°F (121° +/- 5°C) to avoid water condensation. The analyzer can determine the concentration of either: (1) nitric oxide (NO) or (2) NO and nitrogen dioxide (NO<sub>2</sub>) which together is called NO<sub>x</sub>.

The analyzer utilizes the chemiluminescent method of detection. In the nitric oxide determination, sample NO was quantitatively converted into NO<sub>2</sub> by gas-phase oxidation with molecular ozone produced within the analyzer, from air or oxygen supplied by an external supply. A characteristic of this reaction was the elevation of approximately 10% of the NO<sub>2</sub> molecules to an electronically excited state, followed by immediate reversion to the non-excited state accompanied by emission of photons. These impinge on a photomultiplier detector, generating a low-level DC current that was then amplified to drive a front-panel meter (Rosemount, 1992).

Analyzer operation for the NO<sub>x</sub> determination was identical to that described above for the NO determination except that, before entry into the reaction chamber, the sample was routed through a converter where the NO<sub>2</sub> component was reduced to form NO. Instrument response was proportional to total NO in the converted sample, that was, the sum of the NO present in the original sample plus the NO produced by dissociation of



NO<sub>2</sub>. In addition to the Model 955, included in the setup was a Rosemount Model 958 NO<sub>x</sub> Efficiency Tester which, when operated, allowed for the calculation of how efficiently the converter was converting NO<sub>2</sub> to NO. The conversion efficiency was typically 98%+.

### **3.1.7.3 Carbon Monoxide / Carbon Dioxide Analyzers**

The carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) analyzers were Rosemount Model 868 and Model 880 Non-Dispersive Infrared (NDIR) analyzers. There are two CO analyzers, a high CO and a low CO. Throughout the DECSE project, only the low CO was considered. Whenever CO is mentioned here throughout, it is referring to low CO. The CO and CO<sub>2</sub> sampling systems were similar to that of the NO<sub>x</sub>. Both carbon monoxide and carbon dioxide samples were taken through the same probe and line, although two separate analyzers were used to determine the concentrations of the two gases. Diluted exhaust samples were drawn from the primary dilution tunnel through the heated sample probe and line and a heated filter to remove solid particulate matter. To prevent water vapor from condensing within the system, not only are the sampling lines heated, a Hankinson single stream refrigerator/dryer was placed in-line to remove any water that may be mixed with the sample. Water interference checks were made periodically to insure that the refrigerator/dryer was working properly.

The low CO analyzer had ranges of 0-1000 and 0-5000 ppm. The CO<sub>2</sub> analyzer had ranges of 0-1 and 0-6 percent. The NDIR used the exhaust gas species being measured to detect itself by the principle of selective absorption, which means that the infrared energy of a particular wavelength, specific to a certain gas, would be absorbed by that gas (Atkinson, 2000). Infrared energy of other wavelengths would be transmitted by that gas, just as the absorbed wavelength would be transmitted by other gases. By this

method, certain gases would correspond with certain wavelengths in the infrared energy band. For CO<sub>2</sub> the absorption wavelength was between 4 and 4.5 microns and for the CO the range was 4.5 to 5 microns. Within the analyzer, two equal energy infrared beams were produced. The two beams pass through two parallel optical cells; one containing a continuous flowing sample and the other, a sealed reference cell that had been tuned for the wavelength of the desired component, CO or CO<sub>2</sub>. The difference between the two readings was a measure of the concentration of the component being measured (Rosemount, 1991).

### **3.1.8 Bag Sampling**

The West Virginia University Engine and Emission Research Laboratory collects bag samples of dilute exhaust and background air. For the transient tests, the dilute and background bags were collected for the entire test. For the steady state tests, bag samples and emissions were collected simultaneously during the last 100 to 360 seconds. The gaseous sampling time will be discussed later on in the document. The background bag measured an integrated value of ambient gaseous constituents in the dilution air to the primary tunnel. This background bag was then used to correct the dilute exhaust bag sample and the gaseous sample readings.

These samples were collected in separate 30 x 30 inch tedlar bags. The sampling system of the dilute bag and the background are the same, and a schematic of the sampling system can be seen in Figure 3.7. Once the tests are completed, the bag samples were connected to the gas analyzers and their respective concentrations were measured. The bags were then evacuated with a pump.

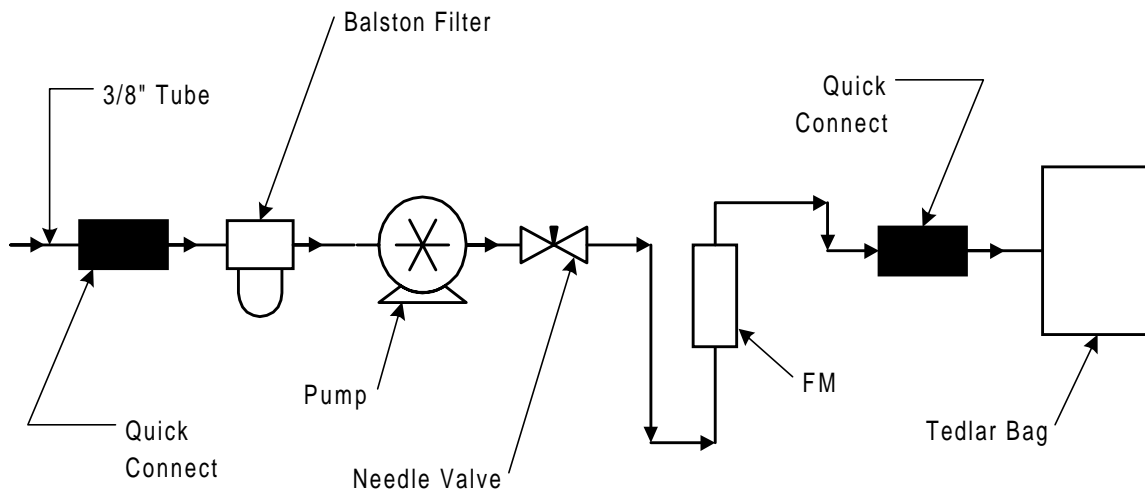


Figure 3.7 Background and Dilute Bag Sampling System Schematic

## 3.2 Experimental Procedures

In order to strive for the goal of achieving the most accurate results, it was necessary to perform all of the experimental work and procedures consistently and accurately. A strict set of procedures and guidelines were developed in order to meet the goal of accurate results. The procedures followed are comprised of the test cycles, the split exhaust, setting of the backpressure on the engine, weighing and usage of the PM filters, and the taking of the gaseous emissions data.

### 3.2.1 Catalyst Degreening

The diesel oxidation catalyst break-in or degreening was performed on each catalyst prior to the start of testing. The degreening process consisted of 10 hours of catalyst aging. A test fuel of 3 ppm was used during this break-in process. All DOCs were tested from 0 hours to 250 hours on the three fuels: 3ppm, 30 ppm and 350ppm. A summary of the catalyst aging and evaluation on the three fuels can be found in a test matrix in the Appendix G.

### 3.2.2 Steady State Test Cycles

For steady state testing cycles on the Cummins ISM 370, four selected modes from the 13-mode OICA test cycle were used. The steady state test cycles were developed with the input of technical representatives of the DECSE steering committee that oversaw the testing. To evaluate the high temperature catalyst with the Cummins ISM engine, modes 2, 10, 3, and 11 were selected from the European Stationary Cycle (OICA). Similarly, modes 2, 3, 7, and 9 were chosen from the Nav-9 test cycle for evaluating the low temperature catalysts using the Navistar 7.3L engine. The Nav-9, which is similar to the OICA, is a steady state test that was developed by Ford Motor Company specifically for testing the Navistar 7.3L diesel engine. Weighting factors of the Nav-9 cycle are proprietary and were not used. WVU determined the weighting factors for the DECSE test with the help of a Navistar representative. Throughout the document, it must be noted that original 13-mode OICA and Nav-9 steady state tests were not used. *When the author refers to the OICA and Nav-9 cycles, they are the modified four mode cycles, and will be referred to as OICA\* and Nav-9\* in this document.*

For accuracy, a pre-stabilization time was assigned to a given test mode before the emissions data were collected. To reduce this pre-stabilization time, the mode sequence was designed to run from the lowest temperature mode to the highest temperature mode; for the OICA\* (11 → 3 → 10 → 2) and for the Nav-9\* (2 → 3 → 7 → 9). The total mode time was fixed at 20 minutes for each selected test mode, OICA\* and Nav-9\* steady state tests. For both steady state tests, there was a short warm-up mode of 3 minutes, and a short motoring cool-down mode of 5 minutes. With the short idling and motoring modes, the test consisted of a total of 6 modes. There was no gaseous emissions and PM

sampling in the first and last mode. Sampling time was assigned to each test mode according to the mode-weighting factor. The sampling times were determined such that ample PM mass was collected on the PM filters while the relative weights specified in the official cycle procedures were maintained. A description of the various modes can be seen in Table 3.4 and Table 3.5. The specific steady state modes for both engines can be seen in Table 3.6 and Table 3.7.

Table 3.4 Steady State Mode Description for Navistar T444E Test Engine

<b>Nav-9* Mode</b>	<b>Description</b>	<b>Weighting Factor (percent)</b>
Begin	Idle	0
9	High rpm, high torque, high temperature	40
7	High rpm, low torque, low temperature	20
3	Low rpm, high torque, low temperature	20
2	Low rpm, low torque, low temperature	20
End	Motoring	0

Table 3.5 Steady State Mode Description for Cummins ISM370ESP Test Engine

<b>OICA* Mode</b>	<b>Description</b>	<b>Weighting Factor (percent)</b>
Begin	Idle	0
2	High torque, high temperature	40
10	Rated condition	40
3	Road load	10
11	Low temperature operation	10
End	Motoring	0

Table 3.6 Navistar T444E Engine Evaluation Conditions

Nav-9* Mode #	Engine Speed (rpm)	Engine Torque (ft-lb)	Catalyst Inlet Temp. (°C)	Mode Time (seconds)	Sampling Time (seconds)
Idle	700	0	----	180	0
2	1000	81	135	1200	170
3	1250	122	207	1200	280
7	2000	122	247	1200	190
9	2200	406	405	1200	360
Cool down	1200	-100	----	300	0

Table 3.7 Cummins ISM370 Engine Evaluation Conditions

OICA* Mode #	Engine Speed (rpm)	Engine Torque (ft-lb)	Catalyst Inlet Temp. (°C)	Mode Time (seconds)	Sampling Time (seconds)
Idle	700	0	----	180	0
11	1883	246	273	1200	100
3	1569	582	380	1200	200
10	1883	982	448	1200	160
2	1254	1229	528	1200	160
Cool down	1200	-100	----	300	0

### 3.2.3 Transient Test Cycles

West Virginia University Engine and Emission Research Laboratory is equipped to perform heavy-duty FTP transient cycles. When operating the Federal Test Procedure on a full flow engine-out test, on either engine, the test complied with all the CFR 40 regulations. One important note is that the FTP *did not* comply with the CFR 40 when the tests were performed with a split flow exhaust system. NO<sub>x</sub>, total hydrocarbons (THC), CO, CO<sub>2</sub>, and PM emissions were recorded for the transient test cycles as well as the steady state cycles.

While heavy-duty diesel emissions testing is primarily conducted on an engine dynamometer, light-duty engine certification is done on a chassis dynamometer. For evaluation of the aftertreatment devices on the Navistar T444E engine with the usage of an engine dynamometer, WVU simulated the FTP-75 chassis schedule for engine dynamometer applications. WVU engineer, Richard Atkinson, constructed the FTP-75 simulation. The engine speed versus time was determined from the speed versus time requirements taken from the CFR 40 Part 86, Subpart B, Appendix 1. The gear ratios in a Ford F-250 transmission were used to convert the road speed versus time to engine speed versus time. Torque versus time was determined by simulating vehicle inertia, wind drag, and acceleration.

#### **3.2.4 Split-Exhaust System**

West Virginia University conducted evaluations of both DOC and lean NO<sub>x</sub> catalysts. In order to age the DOC and lean NO<sub>x</sub> simultaneously and economically, the catalysts were sized for half of the engine exhaust. The engine-out exhaust was split into two streams. At the EERL, WVU set up the split-exhaust systems for both the catalyst aging and catalyst evaluations. As a result, both fuel usage and experimental time could be saved. In order to measure catalyst out emissions it was necessary to split the exhaust into two streams in the test cell in order to insure that the space velocity of the exhaust passing through the catalysts did not exceed the design parameters. A “dummy catalyst” was installed in the bypass leg of the split exhaust to balance the restriction of the active catalyst being evaluated in the monitored exhaust leg.

The exhaust flows were balanced using CO<sub>2</sub> measurements and were also monitored using an orifice meter in each leg of the split system. To balance the spit-flow

exhaust with the CO<sub>2</sub> analyzer, first the CO<sub>2</sub> had to be measured during the 4-mode steady state testing sequence with the full exhaust flow introduced into the dilution tunnel. Once the CO<sub>2</sub> emissions were determined for full flow engine-out exhaust, the measured CO<sub>2</sub> concentration for the split exhaust was adjusted to approximately half of the full flow concentration. Approximately half of the exhaust was then passed through the active catalysts being evaluated and directed into the primary dilution tunnel. The remaining exhaust passed through a muffler and was vented from the building. A correction factor was then calculated based on CO<sub>2</sub> concentrations measured during full flow and split flow tests. The correction factor was the ratio of the measured full flow CO<sub>2</sub> over measured split flow CO<sub>2</sub>. This correction factor was applied to CO, NO<sub>x</sub>, HC, and CO<sub>2</sub> measurements to correct the split flow emissions back to full flow conditions. Equation one (1) through equation four (4) shows the split flow correction factor equations for CO<sub>2</sub>, HC, CO, and NO<sub>x</sub>, respectively.

$$\text{Equation (1) } CO_{2(\text{Full Flow})} = \frac{CO_{2(\text{Full-Flow})}}{CO_{2(\text{Split-Flow})}} \cdot CO_{2(\text{Split-Flow})}$$

$$\text{Equation (2) } HC_{(\text{Full Flow})} = \frac{CO_{2(\text{Full-Flow})}}{CO_{2(\text{Split-Flow})}} \cdot HC_{(\text{Split-Flow})}$$

$$\text{Equation (3) } CO_{(\text{Full Flow})} = \frac{CO_{2(\text{Full-Flow})}}{CO_{2(\text{Split-Flow})}} \cdot CO_{(\text{Split-Flow})}$$

$$\text{Equation (4) } NO_{x(\text{Full Flow})} = \frac{CO_{2(\text{Full-Flow})}}{CO_{2(\text{Split-Flow})}} \cdot NO_{x(\text{Split-Flow})}$$

The flow balance and exhaust back pressure were set using butterfly valves located in each branch down stream of the catalyst. The butterfly valves were adjusted so that the CO<sub>2</sub> concentrations measured in the split exhaust was roughly half of that



measured previously in the full exhaust from the engine while maintaining the specified back pressure. The adjustments were made with the engine operating at one of the steady state modes selected from the test cycle. The backpressure range on the Navistar T444E engine had to be maintained within the range of 30-32 inches of water, while the Cummins had the range of 40-42 inches of water.

A comparison of the full flow gaseous CO<sub>2</sub> emissions and the split flow engine-out CO<sub>2</sub> gaseous emissions, for an FTP and OICA\* test on the Cummins ISM370 heavy-duty diesel engine, can be seen in Figure 3.8 and Figure 3.9, respectively. A similar comparison is made with an FTP-75 and a Nav-9\* test, in Figure 3.10 and Figure 3.11, respectively. It can be clearly seen that in Figure 3.8, Figure 3.9, Figure 3.10, and Figure 3.11 the CO<sub>2</sub> exhaust emissions in the split flow engine-out is nearly one half of the CO<sub>2</sub> emissions in the full flow exhaust. Upon viewing this, it can be stated that the split exhaust system worked quite well in dividing the exhaust system into two different flow paths. Figure 3.8 through Figure 3.11 are comparisons where no catalysts were involved.

Figure 3.12 and Figure 3.13 show a comparison of CO<sub>2</sub> mass emission rates (g/sec) between full flow engine-out exhaust and split flow exhaust with diesel oxidation catalysts (DOCs). The CO<sub>2</sub> split ratio can also be seen in these figures. It can be seen that the split factor in both tests was approximately 0.5. Also, one can tell that the DOCs *did not* affect the splitting of the exhaust flow rate.

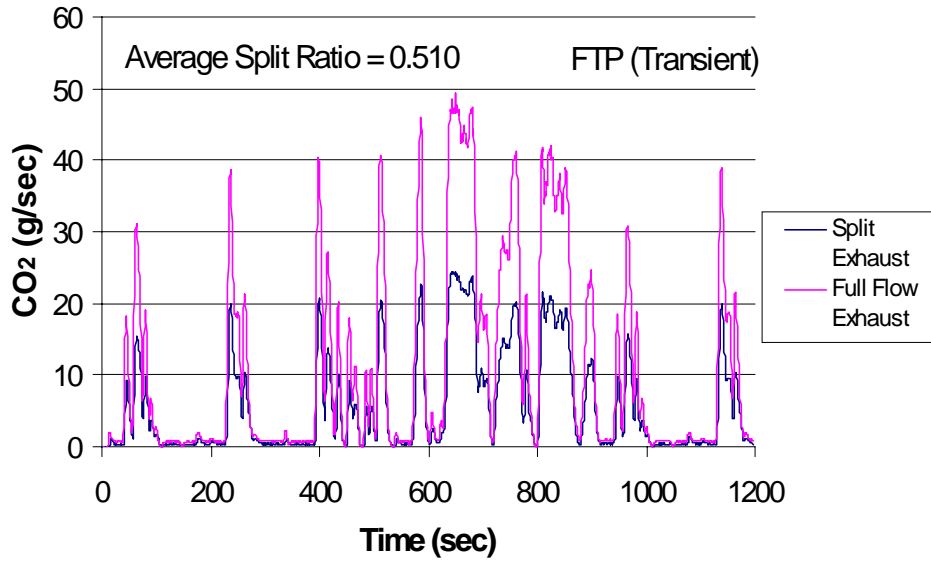


Figure 3.8 FTP Comparison of Full Flow to Split Flow Engine-Out Exhaust

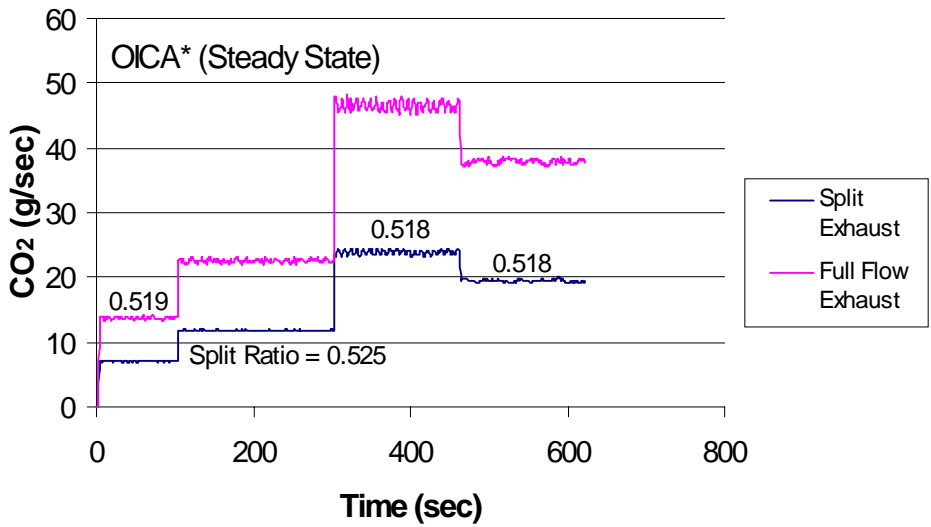


Figure 3.9 OICA\* Comparison of Full Flow to Split Flow Engine-Out Exhaust

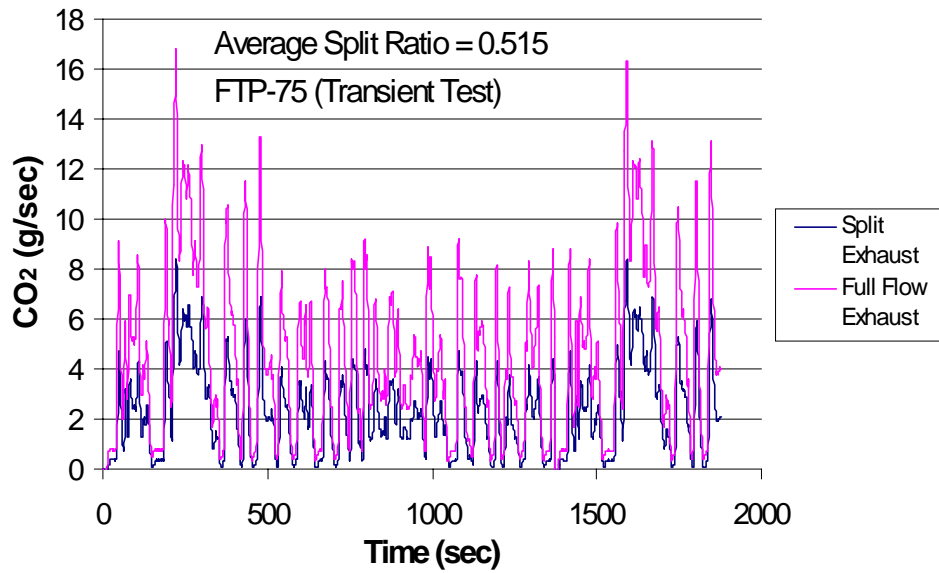


Figure 3.10 FTP-75 Comparison of Full Flow to the Split Flow Engine-Out Exhaust

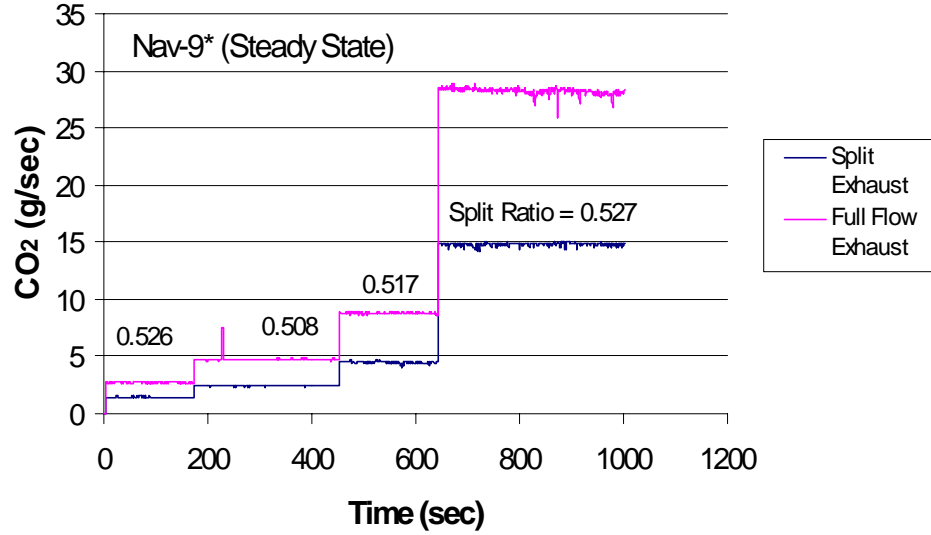


Figure 3.11 Nav-9\* Comparison of Full Flow to Split Flow Engine-Out Exhaust

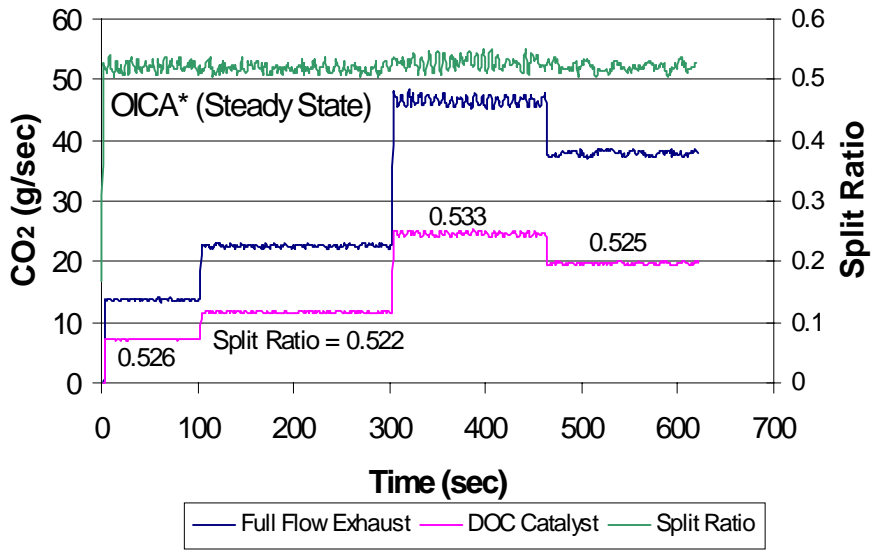


Figure 3.12 Cummins CO<sub>2</sub> Comparison of Full Flow to Split Flow DOC Exhaust

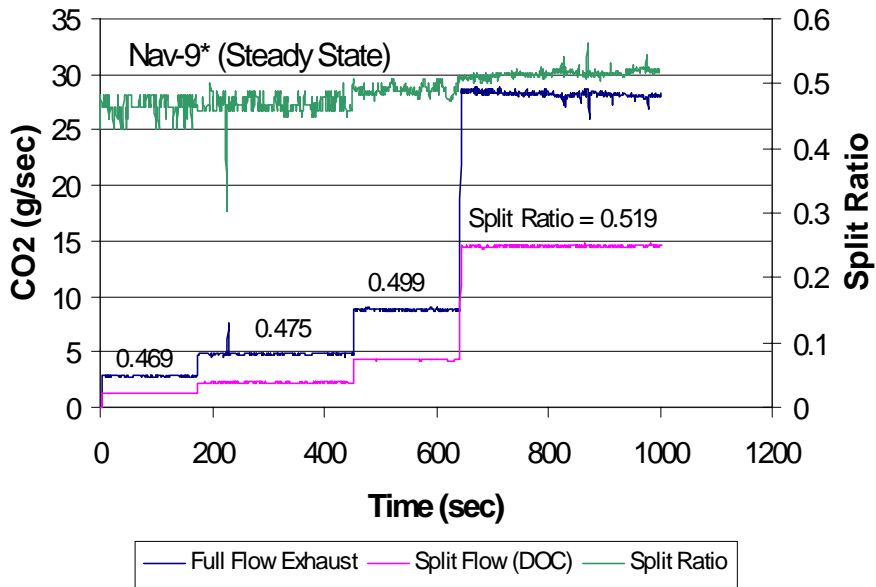


Figure 3.13 Navistar CO<sub>2</sub> Comparison of Full Flow to Split Flow DOC

Figure 3.12 shows that the split ratio is slightly higher than 0.5. In this test the cause of the slightly higher ratio was operator error. The operator of this particular test did not adjust the butterfly valves precisely in the split exhaust legs. The exhaust leg,

which was monitored and directed toward the primary dilution tunnel, had a higher flow rate than the leg directed towards the atmosphere.

Figure 3.13 shows that the split ratio was drifting during the test. The probable reason for the drift was that the butterfly valve was not tightened down properly before testing. Hence, the valve constantly vibrated during the test.

Figure 3.14 and Figure 3.15, a comparison is made between the two methods of monitoring exhaust flow rates. In both of these figures, the data was taken from the same test, a steady state OICA\* test at 150 hours on 3 ppm fuel with the diesel oxidation catalysts. This test was run on the Cummins ISM370. In Figure 3.14, it can be seen that the exhaust flow rate was split nearly in half because the exhaust flows rates through orifice meter are in fairly good agreement with each other, indicating that the exhaust flow rates were the same.

In Figure 3.15, the second exhaust method, the splitting of CO<sub>2</sub>, is shown to work extremely well. The blue line represents a full flow exhaust measured when running the OICA\* test with 150 hrs and 3ppm fuel. The pink line represents the same split flow DOC test as in Figure 3.14. Inspection of the graph shows that this exhaust splitting method based on CO<sub>2</sub> worked well.

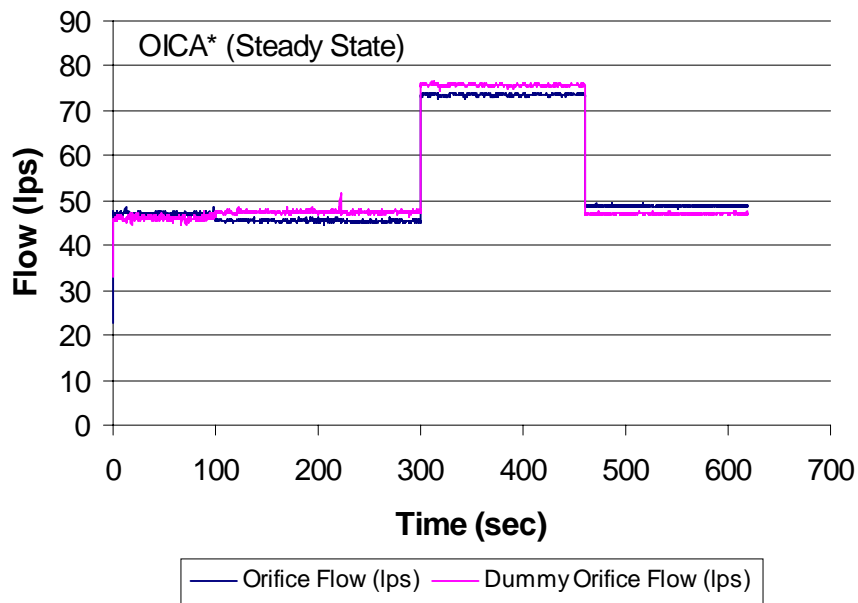


Figure 3.14 Orifice Flow Rate Comparison in the Two Exhaust Legs

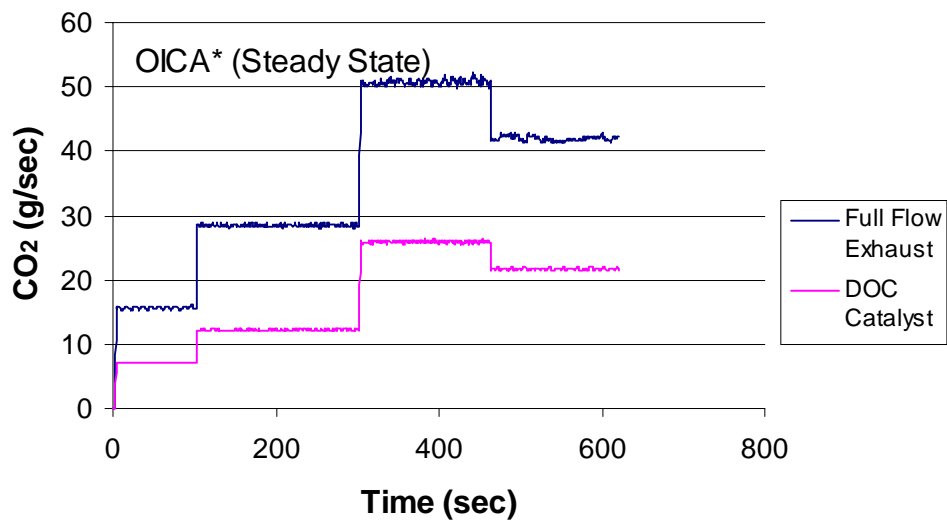


Figure 3.15 CO<sub>2</sub> Split Ratio Comparison in Full Flow and DOC Exhaust

Throughout the testing period, the recorded orifice data would show excursions every now and then. Through this occurrence, the CO<sub>2</sub> split ratio always seemed to hold steady. An example of this can be seen in Figure 3.16. In this figure, the flow rates between the two exhaust legs are not in agreement. Thereby, implying that the exhaust

flows were not split evenly. However, Figure 3.17, the CO<sub>2</sub> comparison shows that in fact, the exhaust flow was split very evenly on the exact same test. The test used in both figures came from the data recorded from an OICA\* at 250 hours on 30 ppm fuel. In Figure 3.17, the CO<sub>2</sub> split ratio shows that the exhaust was evenly distributed between the two exhaust legs. Through most of the OICA\* tests the exhaust was almost split evenly. The method of using CO<sub>2</sub> comparison seemed to be more reliable than the method of monitoring orifice flow rates.

Various problems with the orifice monitoring could have contributed to the poor orifice flow rate results. Some of these problems with monitoring exhaust flow rates splitting using orifice meters include: (1) exhaust temperature effects on the differential transducers, (2) incorrect correction of flow rates for standard temperature and pressure (STP) in the reduction program, (3) the orifices reversed in the split exhaust, not giving the correct calibration coefficients in the reduction program.

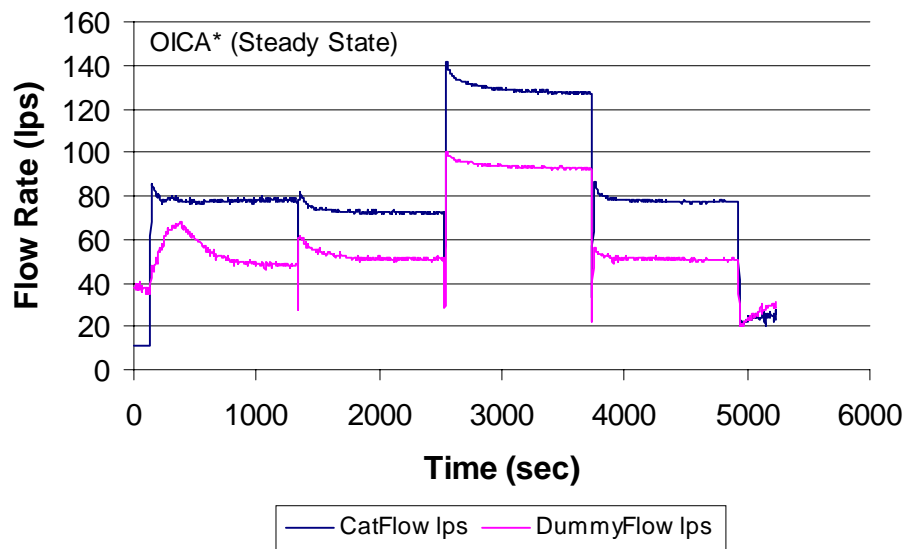


Figure 3.16 Bad Orifice Flow Data on an OICA\* Test

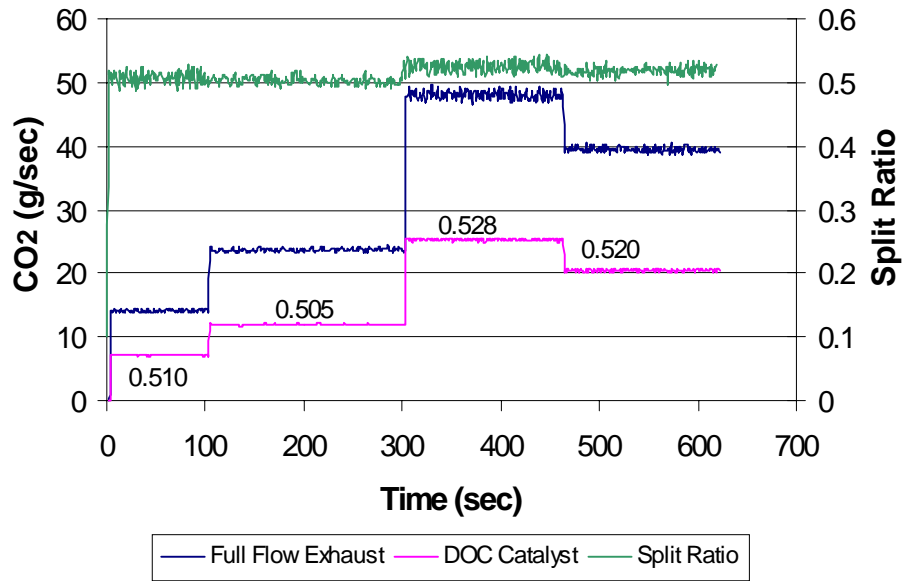


Figure 3.17 CO<sub>2</sub> Split Comparison of an OICA\* with Split Ratio



## CHAPTER 4 ~ RESULTS AND DISCUSSION

Diesel oxidation catalysts reduce HC, CO, and PM emission levels in engine exhaust by oxidation over precious metal catalysts. PM is lowered by oxidation of the soluble organic fraction (SOF) of the diesel particulate.

### 4.1 PM Emission Analysis

Diesel particulate emissions continue to challenge researchers and scientists in the industrialized world. Part of the overall DECSE research focused on determining the effect of fuel sulfur levels on brake-specific PM emissions from DOC and lean NO<sub>x</sub> equipped heavy-duty diesel engines. The PM was collected for both transient and steady state tests. Sulfur effects were evident in the TPM, SOF, and in the sulfate (SO<sub>4</sub>) brake-specific emissions. Brake-specific PM emission values were collected and reported in g/bhp-hr were an average over a complete cycle, whether it was a Nav-9\*, OICA\*, or a transient test, and were determined with a single filter method. It should be noted that the effects of any one particular steady state mode could not be identified. Hence, the reported values will reflect the input of both high and low-temperature modes. Throughout the report, “low-temperature DOC” implies that the oxidation catalysts was evaluated on the Navistar T444E engine, and “high temperature DOC” implies that the oxidation catalysts was evaluated on the Cummins ISM370. The effect of sulfur on catalyst-out PM emissions during steady state operation is small at fuel sulfur levels of 3 ppm and 30 ppm. The PM emissions are even lower in the transient tests than those in the steady state tests. Figure 4.1 and Figure 4.4 show the total PM emissions that were collected in steady state tests evaluated at 250 hours, while Figure 4.7 and Figure 4.9 show the PM emissions collected in the transient tests. In Figure 4.1 and Figure 4.4, it is

seen that there is very little difference in brake-specific PM emissions between the two lower sulfur fuels (3ppm and 30ppm). Figure 4.1, shows that for the higher sulfur fuel (350ppm) test on the Navistar T444E engine, full flow engine-out PM emissions increased 21.86% from full flow engine-out PM emissions of the 3ppm fuel. When evaluating the full flow tests for the Cummins engine as seen in Figure 4.4, there was a 48.89% increase in the PM emissions for the 350ppm fuel, when compared to the 30ppm evaluations. The difference in the brake-specific emissions between full flow engine-out and split flow engine-out implies that the manual exhaust splitting with the butterfly valve was not exactly set at fifty percent with the CO<sub>2</sub> ratio.

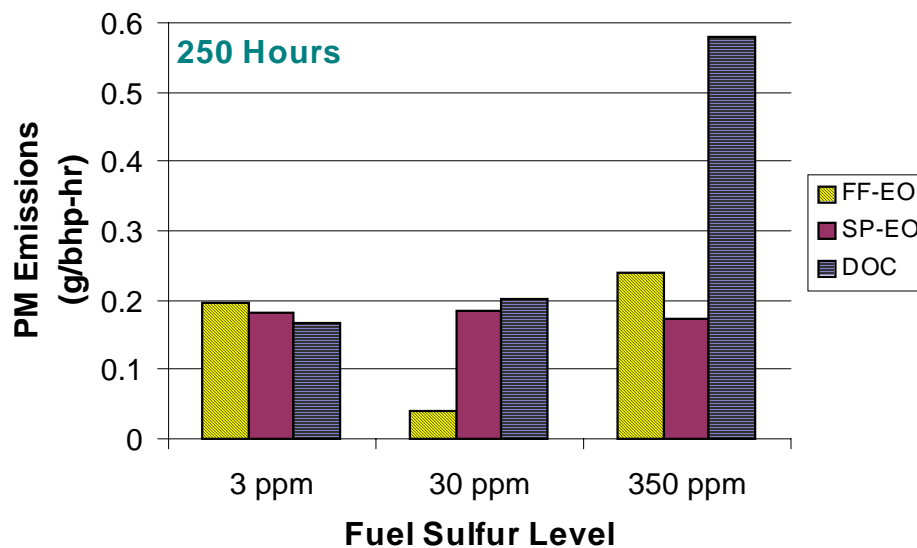


Figure 4.1 Navistar Steady-State (Nav-9\*) Comparing PM Emissions and Fuel Sulfur

In Figure 4.1, there was a large discrepancy in data regarding the full flow engine-out (FF EO) with the 30ppm fuel. In this figure, the PM emissions for the full flow 30 ppm fuel was found to be 0.039 g/bhp-hr and the 3 ppm fuel had brake-specific PM emissions of 0.196 g/bhp-hr. The full flow engine-out data at 30 ppm fuel appeared to be

an anomalous result. Reasons for the anomalous results could be from human error or even from filter defects such as holes in the filter allowing the PM to pass through.

Figure 4.1 shows a 187% increase in PM emissions when the results from the evaluation of DOC on 30ppm fuel are compared to the evaluation of the DOC on 350 ppm fuel. While this was an unusually large increase in the PM emissions, the jump in the PM emissions can be attributed to the formation of sulfates, which are a by-product of the catalytic reaction in the presence of sulfur. It must be noted that the increase in the brake-specific PM emissions reflects an increase not only due to the sulfates, but also due to sulfate-bound water. Each gram of  $\text{SO}_4$  in the PM has 1.3 grams of bound water (at 50% relative humidity) associated with it (Baranescu, 1988). Engine-out brake-specific PM emissions, without a catalytic converter, were shown (Baranescu, 1988) to increase by 0.025 g/bhp-hr for each 0.1% by weight increase in fuel sulfur. Hence, the extremely large increase of PM for the DOC equipped Navistar T444E engine operating on 350 ppm sulfur fuel may be attributed solely to the sulfate formation occurrence in the DOC. Positive evidence of a large increase in sulfates can be seen in Figure 4.2, with an 827% increase in sulfates from 30 ppm fuel to 350 ppm fuel. Figure 4.3 shows the PM reduction efficiency of the DOC equipped Navistar T444E relative to the full flow engine-out (without a DOC) PM emissions. In the reduction efficiency figure, it is evident that the 30 ppm fuel result is anomalous. This result corresponds to the 30 ppm in Figure 4.1. Then with the 350 ppm fuel, it is apparent that the sulfates were formed and caused the PM emissions from a DOC equipped engine to be greater than the PM emission of engine-out tests. The negative reduction efficiencies in Figure 4.3 imply that the DOCs brake-specific PM emissions were greater than the engine-out PM emissions.

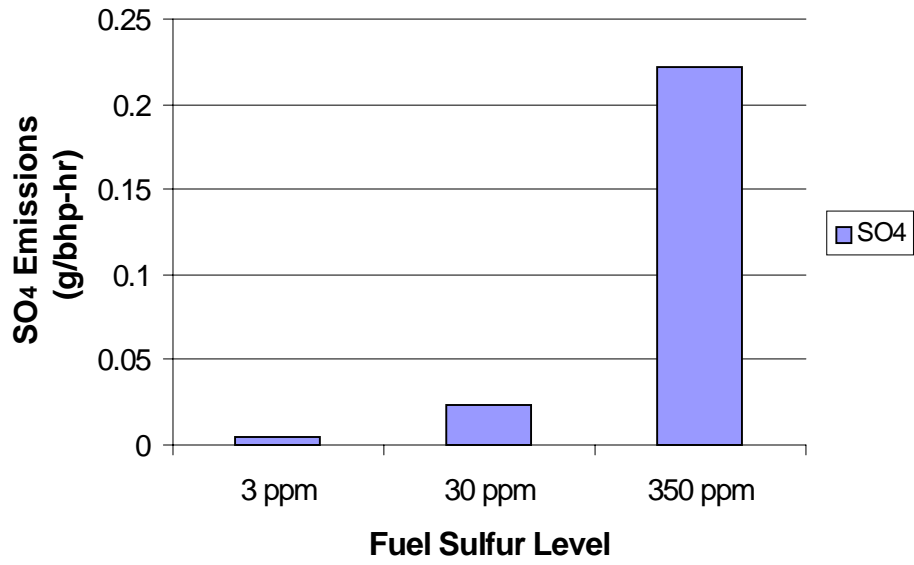


Figure 4.2 Navistar Steady State Nav-9\* Sulfate Emissions at 250 Hours

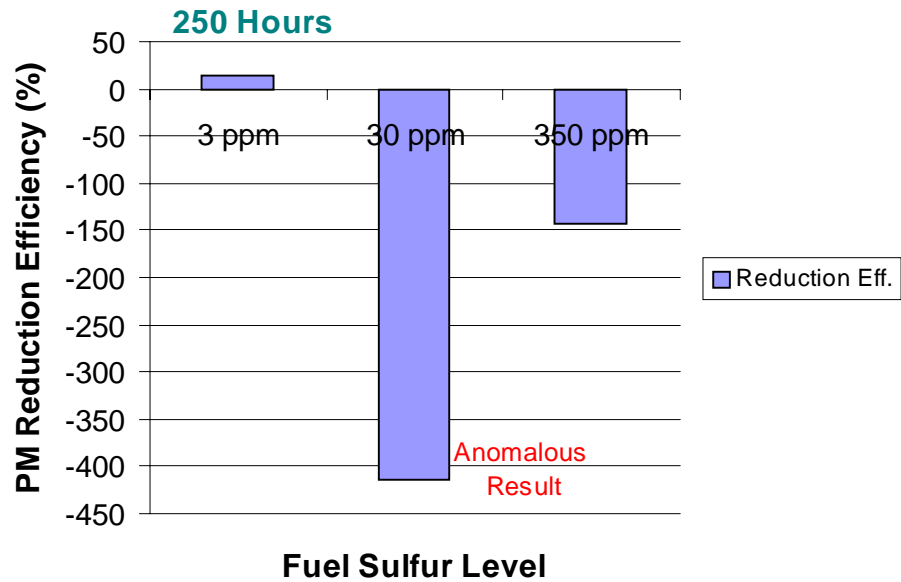


Figure 4.3 Navistar Nav-9\* PM Emission Reduction Efficiency at 250 Hours

Figure 4.4 show that there is a similar trend with the DOC data as found in Figure 4.1 with the Navistar engine. In Figure 4.4, the Cummins ISM370 DOC PM emissions showed a 46% increase from the 30 ppm fuel to the 350 ppm fuel.

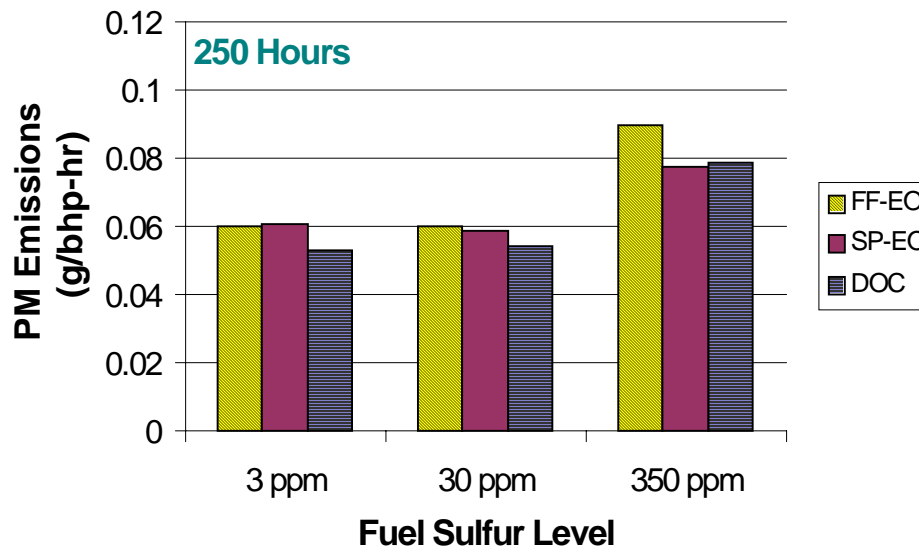


Figure 4.4 Cummins Steady-State (OICA\*) Comparing PM Emissions and Fuel Sulfur

Figure 4.5 shows that there is a tremendous increase in the sulfate production from the 30 ppm fuel to the 350 ppm fuel. Brake-specific sulfate emissions show an enormous increase of 1173% from 30 ppm to 350 ppm fuel. This was an unusually large increase in sulfate emissions. One would expect an increase of 0.008 g/bhp-hr from the 30 ppm fuel to the 350 ppm fuel, hence the approximate value of the sulfate emissions should be 0.01 g/bhp-hr. These values are based upon the research from Baranescu performed in the SAE paper, “Influence of Fuel Sulfur Content on Diesel Particulate Emissions.”

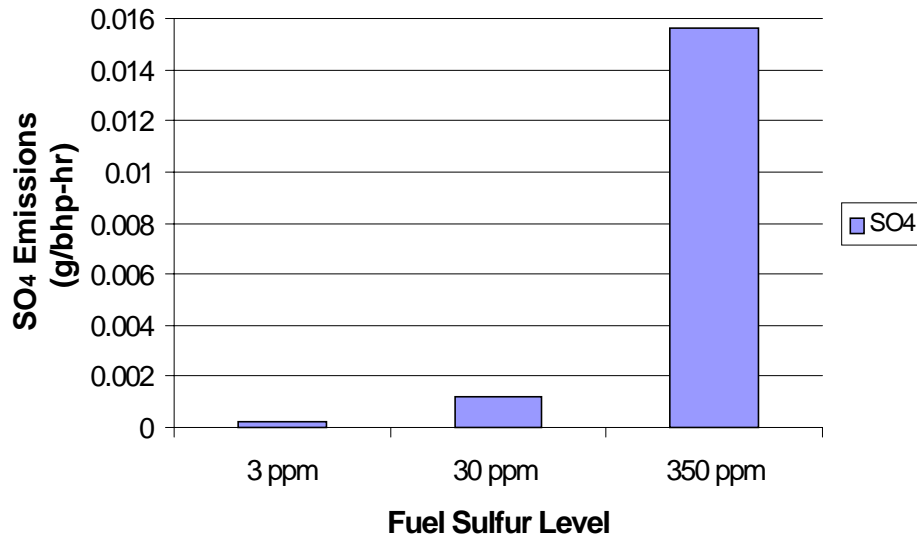


Figure 4.5 Cummins Sulfate Emissions for an OICA\* at 250 Hours

Figure 4.6 shows the PM reduction efficiencies for the steady state Nav-9\* tests at 250 hours. The reduction efficiency compares the full flow engine-out (no catalysts) to the DOC-out emissions. The reduction efficiencies were found to be 11.5%, 10.4%, and 12.0% for the 3 ppm, 30 ppm, and 350 ppm, respectively.

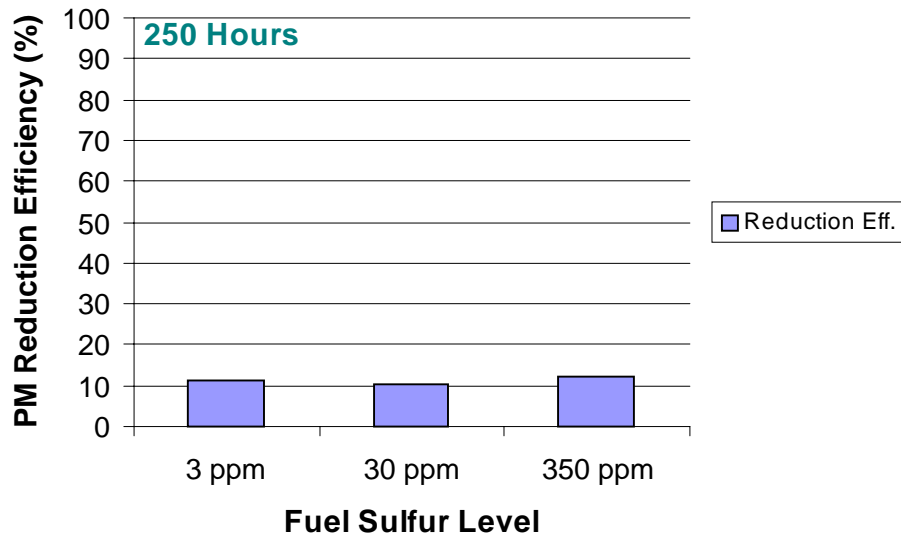


Figure 4.6 Cummins OICA\* PM Reduction Efficiency at 250 Hours

Now, investigation of the transient tests for both engines can be seen in Figure 4.7 and Figure 4.9 for the 250 hour evaluation. In Figure 4.7, there was a 44.5% reduction in the PM emissions for the 350 ppm fuel, while there was a 47.8% and a 48.3% reduction for the 30 ppm and 3 ppm fuel, respectively. All PM emission reduction comparisons were with full flow engine-out and DOC. Next, the inspection of the reduction efficiency of the PM emissions was performed. For the Navistar engine, seen in Figure 4.8, the reduction efficiencies of the PM emissions were approximately 45% - 50% and very uniform over the different fuel types.

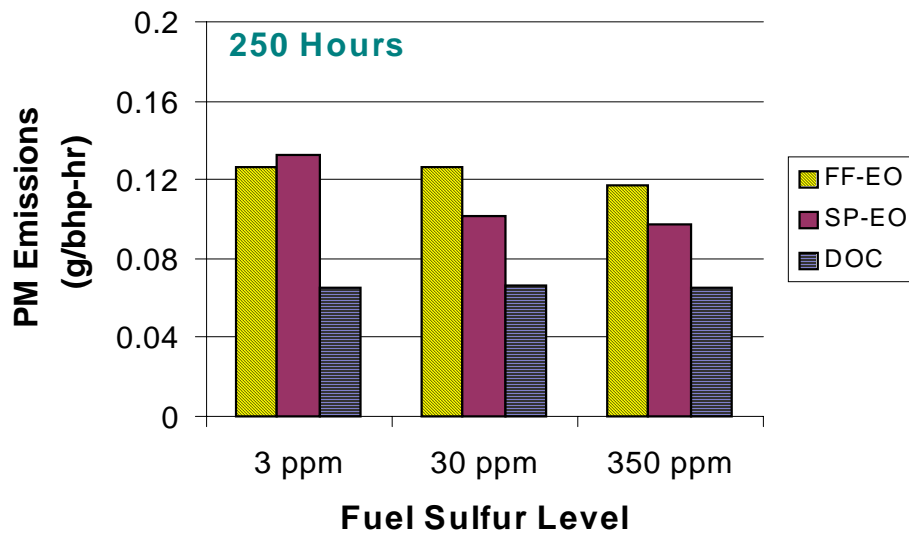


Figure 4.7 Navistar FTP-75 Comparing PM Emissions and Fuel Sulfur

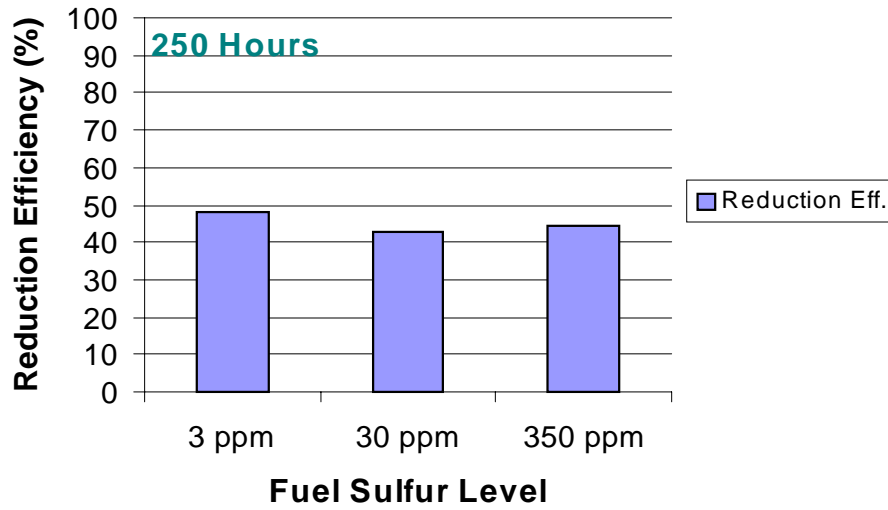


Figure 4.8 Navistar FTP-75 PM Reduction Efficiency

Figure 4.9 shows that for the Cummins ISM370 a 31.6% reduction in the brake-specific PM emissions was obtained for the 350 ppm fuel and a 15.7% and 3.6% reduction for the 30 ppm and 3 ppm fuel, respectively. Figure 4.10 corresponds to these reduction efficiencies for the different fuel types.

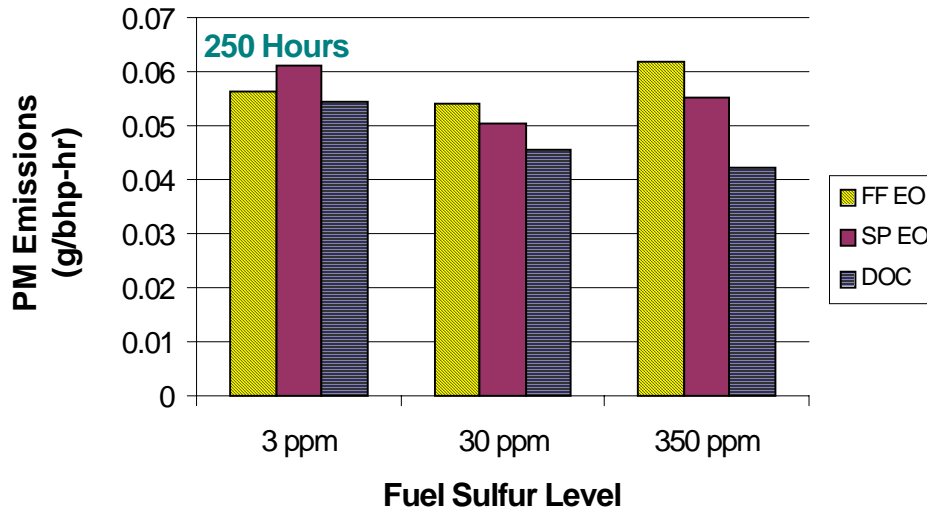


Figure 4.9 Cummins FTP Comparing PM Emissions and Fuel Sulfur



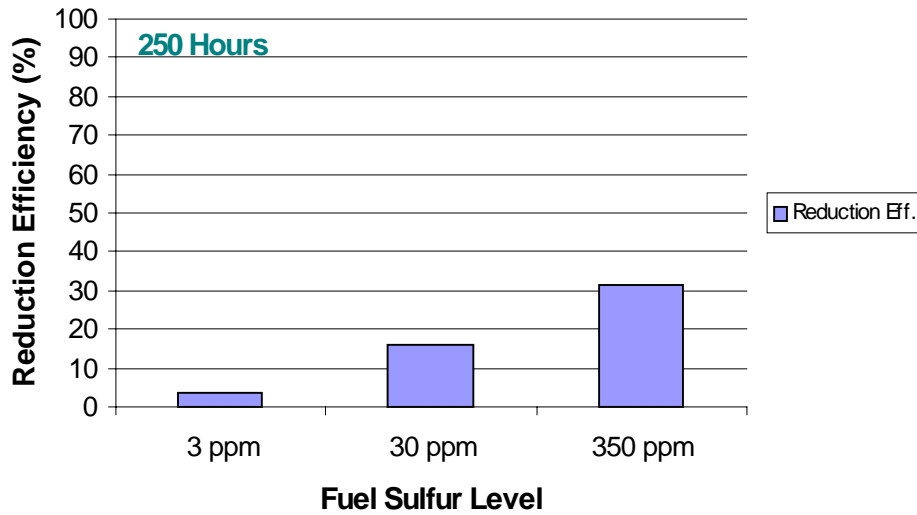


Figure 4.10 Cummins FTP PM Emission Reduction Efficiency

The differences in the PM emissions between the transient and steady state tests can very well be from the temperatures of engine operation. The average temperature for the transient tests for the Navistar engine was 172.1°C while the steady state Nav-9\* tests average temperature was found to be 256.8°C. The average temperature for the transient tests for the Cummins ISM370 engine was found to be 236.33°C while the average temperature of the OICA\* test was determined to be 394.6°C. The temperatures for each mode for the steady state OICA\* and Nav-9\* tests are shown in Table 4.1.

Table 4.1 Average Catalyst Temperature of the Modes in Steady State Tests

Navistar T444E Steady State Nav-9*		Cummins ISM370 Steady State OICA*	
Mode Number	Temperature (°C)	Mode Number	Temperature (°C)
2	149.8	11	264.6
3	198.7	3	364.1
7	250.0	10	440.0
9	428.7	2	509.7

In Figure 4.11 and Figure 4.12, the aging effects on the Cummins DOC steady state (OICA\*) results were investigated. The DOC performance of the Cummins evaluations for 3ppm fuel, which is found in Figure 4.11, shows a decrease in PM emissions as the catalysts were aged. When evaluating the steady state results with the DOC on the Cummins with 3ppm fuel, there was an 8% decrease in PM from 50 hours to 250 hours. Considering that there was very little fuel sulfur to form sulfates in 3ppm fuel, the DOC still managed a reduction in PM emissions. For the Cummins engine, as the aging hours increased, the performance of the DOC increased. The DOC results show a trend with decreasing PM emissions as the aging hours increase. Figure 4.12 shows the trend with the DOC with the 350 ppm fuel. The DOC performance increased with time. In Figure 4.11 and Figure 4.12 some of the data at 0 hours and 50 hours was not presented, this to due to the fact that in early evaluations the full flow and split flow engine-out tests were not always ran.

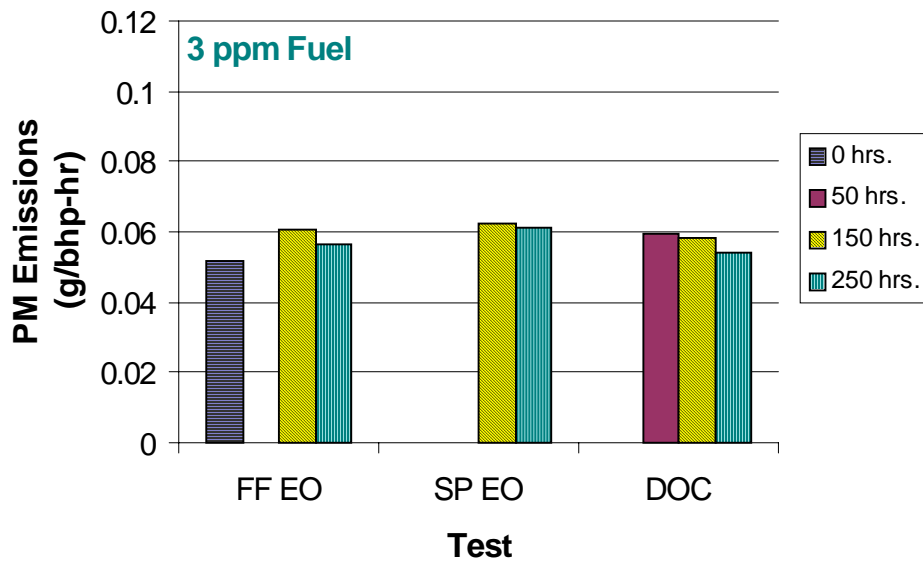


Figure 4.11 PM Emissions on the Cummins FTP with 3 ppm Fuel

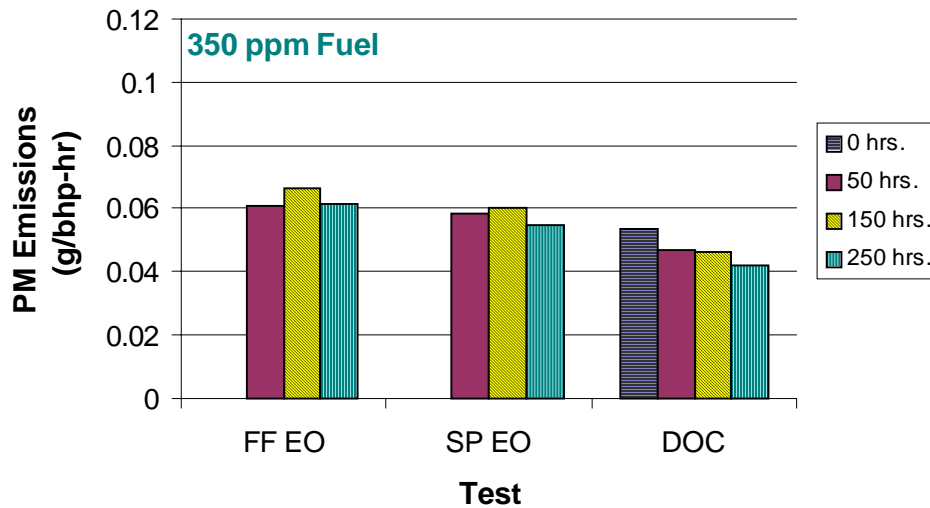


Figure 4.12 PM Emissions on the Cummins FTP with 350 ppm Fuel

Next, the PM emissions are compared with the aging time and the diesel fuel sulfur used. Examples of this can be seen in Figure 4.13 and Figure 4.14. By this comparison a few things can be seen and understood. The first and most obvious is that the DOCs reduced all of the PM emissions in each and every FTP-75 test evaluated. Next, the DOCs overall performance continued to improve with time or as the aging hours increase. Some of the tests were not performed for every aging stage, such as that of the DOC for 30 ppm fuel at zero hours for the DOC. With the data taken, it can be seen that the DOC worked very well with the three fuels once again. There is a noticeable difference in the DOC results for the 30ppm and 350 ppm fuel compared to that of the 3 ppm fuel. But with the low sulfur fuel (3ppm) there is so little sulfur added that would contribute to the formation of the sulfates. There is no evidence of fuel sulfur poisoning of the DOCs over the short 250 hour catalyst evaluation. Graphs of similar comparisons for the steady state tests for both engines can be seen in Appendix A and Appendix B.

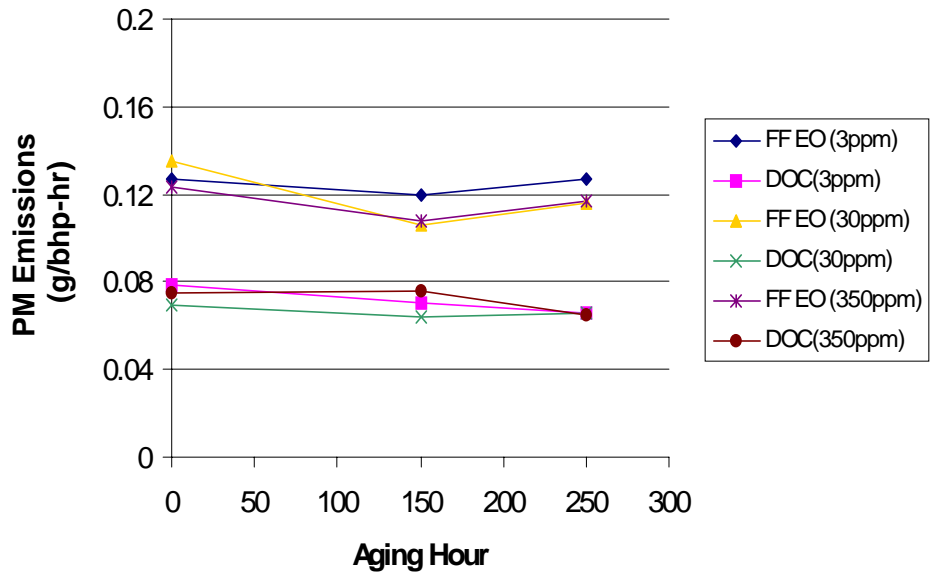


Figure 4.13 Navistar FTP-75 Tests Comparing PM Emissions, Fuel, and Aging Time

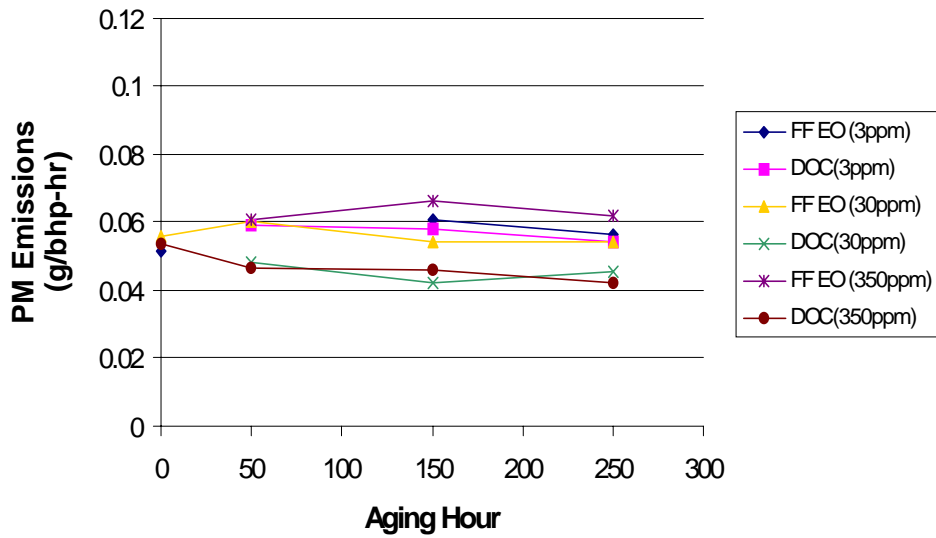


Figure 4.14 Cummins FTP Tests Comparing PM Emissions, Fuel, and Aging Time

## 4.2 HC Emission Analysis

Next, attention is directed towards the hydrocarbon (HC) emissions. Upon looking at both engines, the Navistar and Cummins, the HC were reduced dramatically when the DOCs were used for the aftertreatment.

Figure 4.15 shows the HC emissions from the steady state test at 250 aging hours. The negative values can be deceiving if they are not appropriately examined. The DOC HC emission values do not imply that engine is producing negative HCs, but instead, the background HC emissions were greater than catalyst-out emissions. When comparing the full flow engine-out to the DOC out emissions for the lower sulfur fuels (3ppm and 30ppm), the HC reduction was 100%. For the 350 ppm fuel, the HC emission reduction was 90.3%.

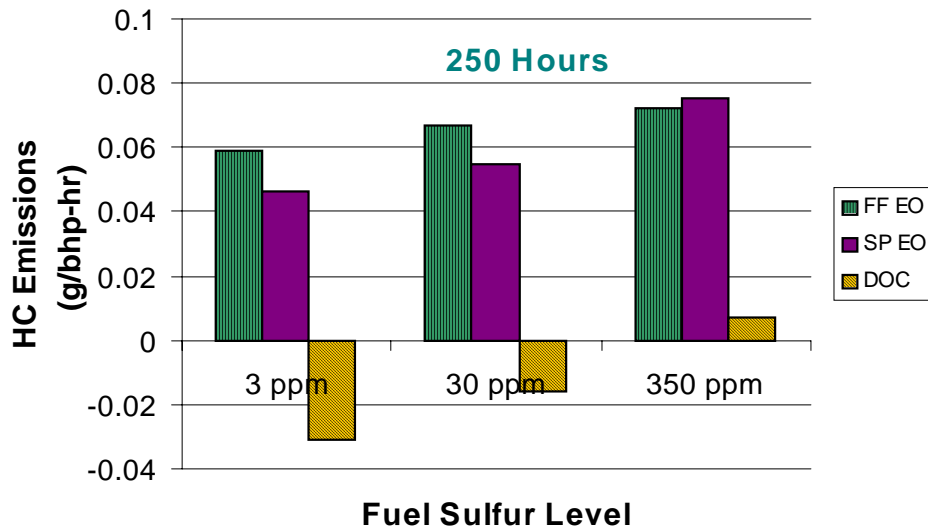


Figure 4.15 Navistar Nav-9\* HC Emissions

In Figure 4.16, it is very noticeable that the HC emissions were greatly reduced over time with all of the Nav-9\* tests. The DOC performed very well with HC reduction

with the Navistar engine. Other HC emission reduction graphs can be seen in Appendix C. Appendix C also includes the Navistar transient (FTP-75) HC emission results.

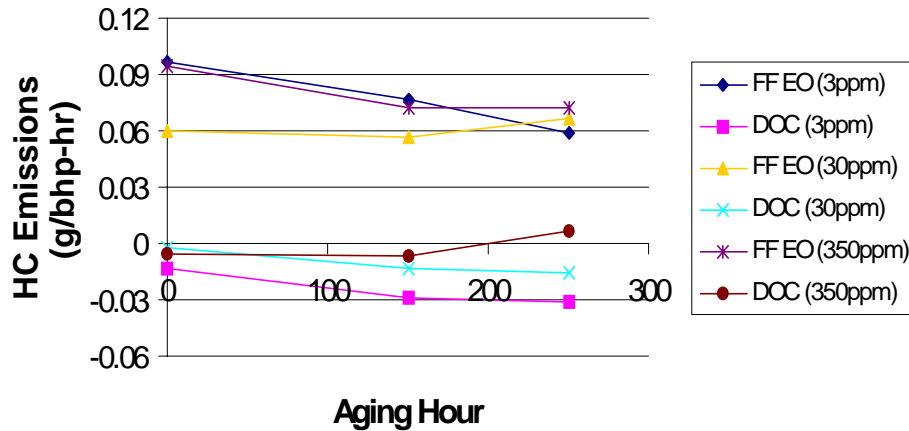


Figure 4.16 Navistar Nav-9\* Tests Comparing HC Emissions, Aging Hour, and Fuel

In Figure 4.17, the HC emission reduction efficiency is shown. Any efficiency above 100% implies that the background HC emissions were greater than those HC emissions in the monitored exhaust.

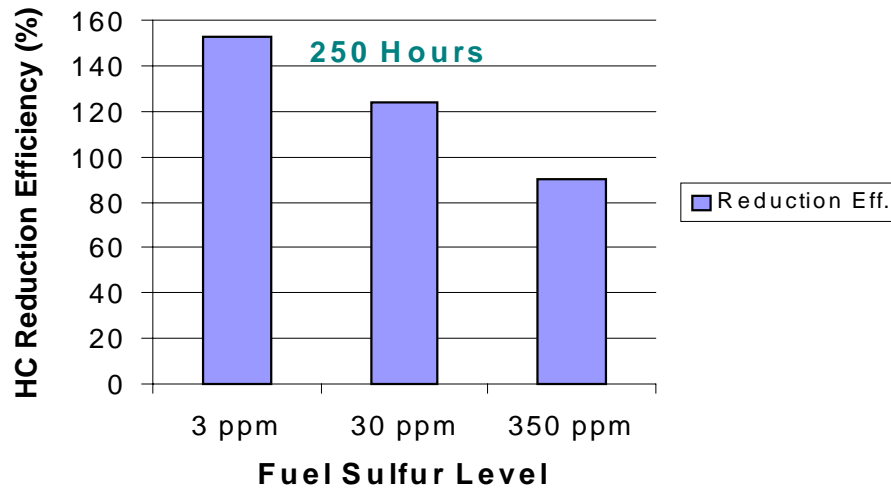


Figure 4.17 Navistar Nav-9\* HC Emission Reduction Efficiency at 250 Hours

In Figure 4.18, it can be easily detected that the DOCs for the Cummins engine worked extremely well. For the 3 ppm fuel, between the full flow engine-out and DOC, the HC emissions were reduced 82.5%. For the 30 ppm fuel, there was an 82.2% reduction between the full flow engine-out and the DOC. Then finally for the 350 ppm fuel, there was an 89.5% decrease in the HC emissions between the full flow exhaust and the DOC. The fuel sulfur levels did not affect the HC emissions and the HC emission reductions. The DOCs HC emissions reduction was approximately the same for the three fuels. Other HC emission results of the Cummins engine can be seen in Appendix D.

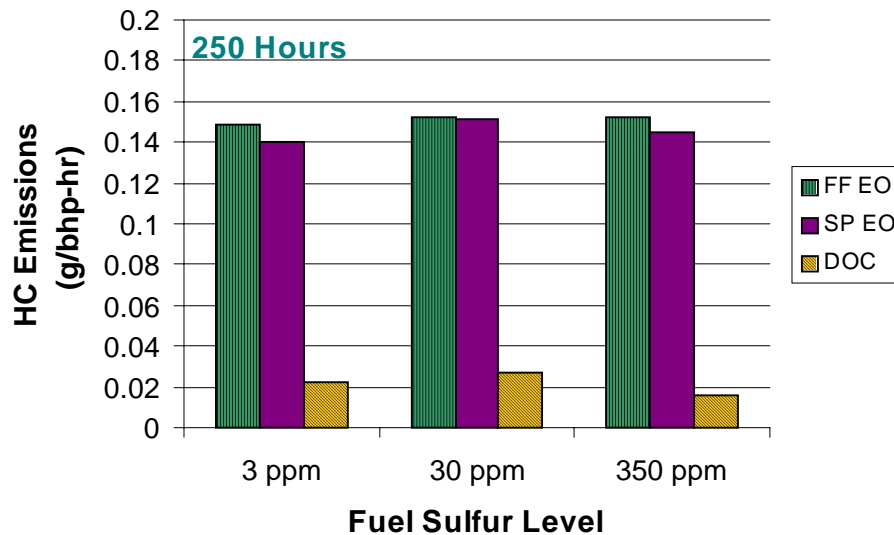


Figure 4.18 Cummins OICA\* HC Emissions

In Figure 4.19, a comparison is made between the HC emissions, the aging hour, and the fuel. The DOCs greatly reduced the HC emissions from the full flow engine-out emissions. It can be concluded that the fuel sulfur does not affect the HC emissions produced from the engines, and the DOCs worked on all fuel sulfur levels and aging hours.

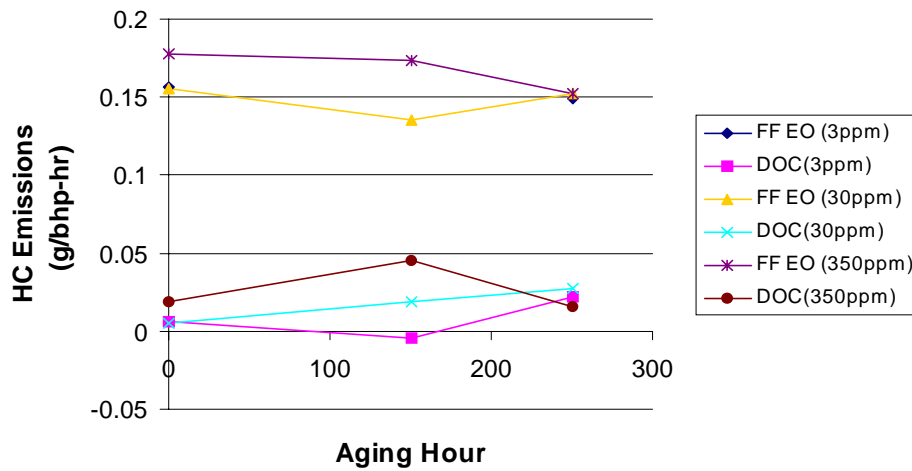


Figure 4.19 Cummins OICA\* Tests Comparing HC Emissions, Aging Hour, and Fuel

In Figure 4.20, the HC emission reduction efficiency is shown from the Cummins OICA\* testing. The DOC did greatly reduce these HC emissions compared to the full flow engine-out HC emissions.

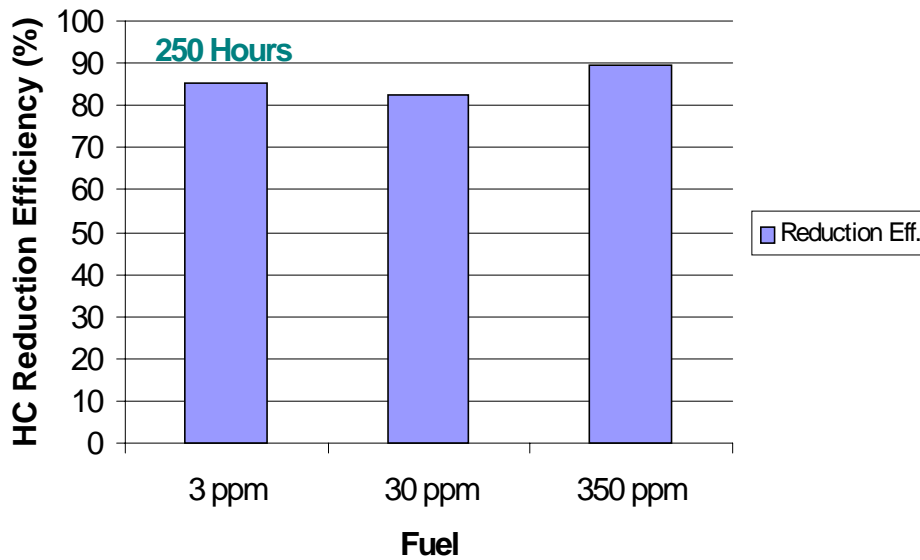


Figure 4.20 Cummins OICA\* HC Emission Reduction Efficiency



### 4.3 CO Emission Analysis

Now, attention is brought to the carbon monoxide (CO) emissions to see how effective the DOCs are at reducing CO and how fuel sulfur affects CO reduction efficiency. CO emission results are seen in this section of text and also in Appendix E and Appendix F.

Figure 4.21 shows the steady state CO emission at 150 hours. With the 3 ppm fuel, there is a 91% reduction in the CO emissions compared to the full flow engine-out levels. The 30 ppm fuel shows a 95.2% reduction in the CO emissions. Finally, the 350 ppm fuel has an 88.4% reduction. The average CO emission reduction for all three fuels is 91.5%. It is evident that the various fuel sulfur levels do not affect the CO emissions. The CO emissions are relatively the same throughout the three different fuel sulfurs used.

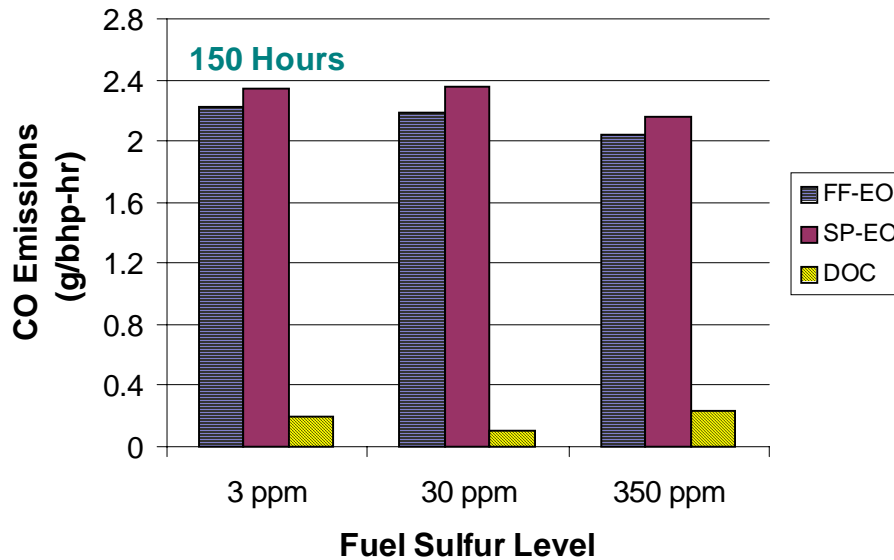


Figure 4.21 Navistar Nav-9\* CO Emissions

Figure 4.22 shows the reduction efficiencies of the CO emissions that were tabulated for the Navistar Nav-9\* test for the three different fuel sulfur levels. The efficiencies are calculated between the full flow engine-out and the DOC-out.

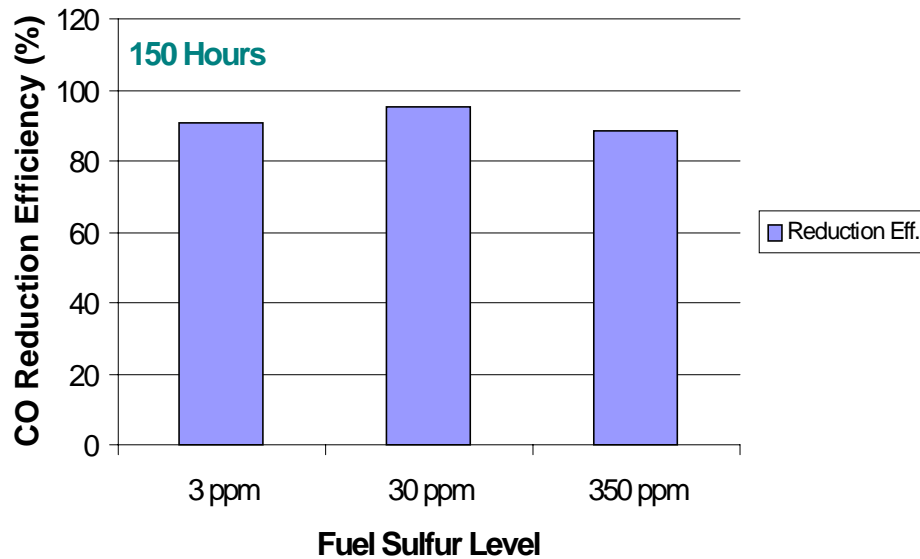


Figure 4.22 Navistar Nav-9\* CO Emission Reduction Efficiency at 150 Hours

Figure 4.23 shows the graph is of Navistar steady state tests (Nav-9\*). The graph compares the CO emissions, the aging hour, and the fuel being used. By inspection of this figure, one can conclude that the fuel sulfur did not affect the CO emissions. All CO emissions were lowered to nearly zero with all three fuels evaluated on the DOCs. It is evident in Figure 4.21, Figure 4.22, and Figure 4.23 that the DOCs did perform properly at reducing the CO emissions.

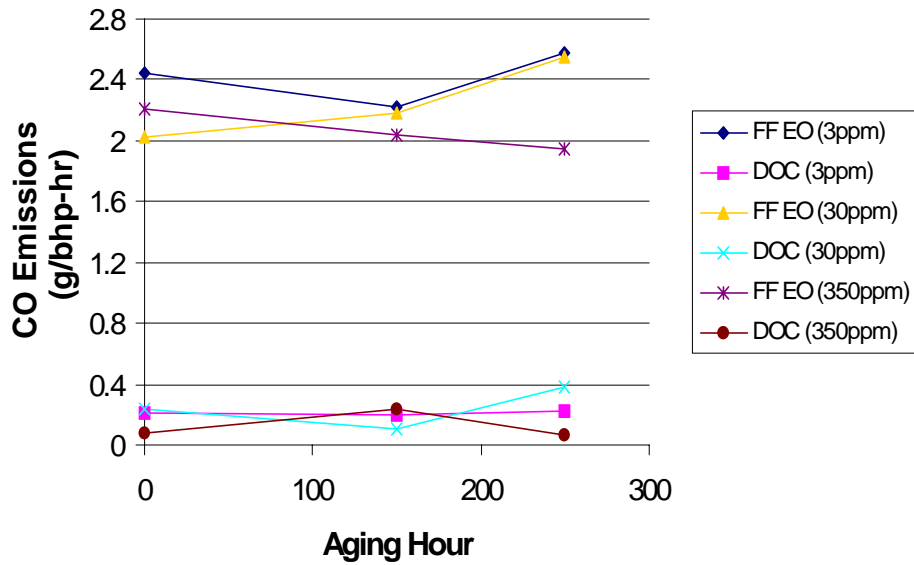


Figure 4.23 Navistar Nav-9\* Tests Comparing CO Emissions, Aging Hours, and Fuel

Figure 4.24 shows the CO emissions for the FTP-75 tests. Once again, the performance of the DOC proved to be very successful. On 3 ppm fuel, the CO emissions were reduced 91% from full flow engine-out to DOC evaluation. For the 30 ppm fuel, the CO emission reduction was 95.2%. The CO emission reduction was 88.4% for the 350 ppm fuel evaluations. The average CO emission reduction over all of the FTP-75 tests was found to be 92.0%. It can easily be stated that the DOC performed well in reducing CO emissions. Figure 4.25 presents the CO emission reduction efficiencies for the various fuel ran on the FTP-75 cycle at the 150 hour aging stage.

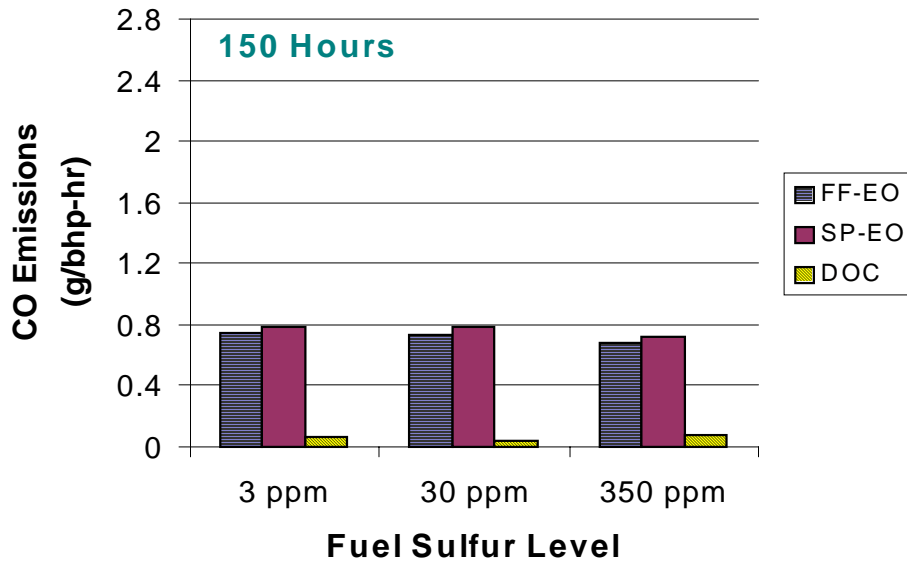


Figure 4.24 Navistar FTP-75 CO Emissions

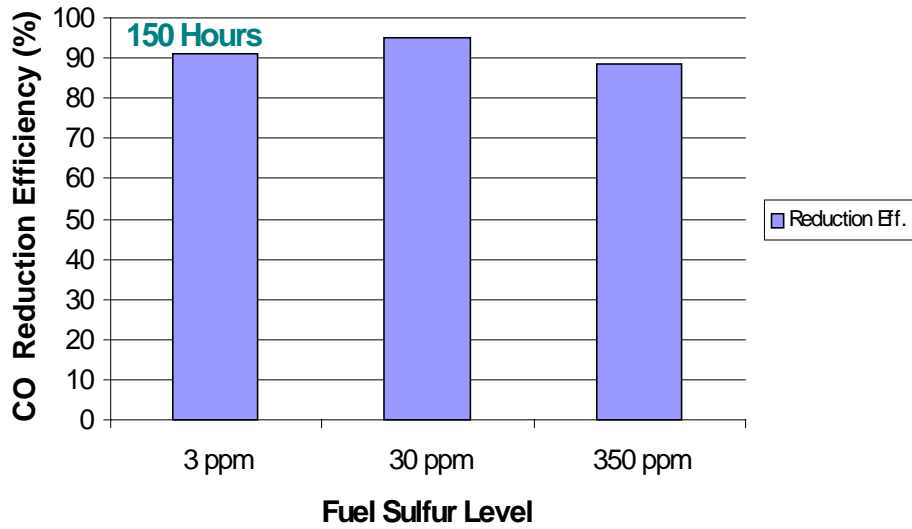


Figure 4.25 Navistar FTP-75 CO Emissions Reduction Efficiency

Figure 4.26 shows the FTP-75 cycle CO emissions as a function of the aging hours and the fuel type used. Once again, all the CO emissions were nearly reduce by 100%.

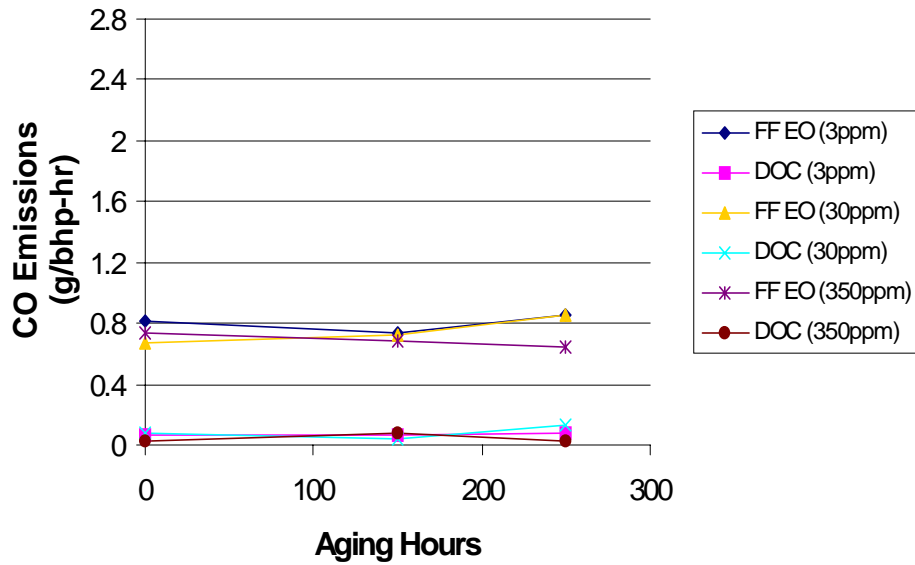


Figure 4.26 Navistar FTP-75 Tests Comparing CO Emissions, Aging Hours, and Fuel

Figure 4.27 shows the CO emissions for the Cummins steady state (OICA\*) tests at 250 hours. The emission reductions from full flow engine-out to DOC-out evaluations were not as good as of those from the Navistar engine. The CO reduction was found to be 65.4% for the 3 ppm fuel. For the 30 ppm fuel, there was a 59% CO reduction. Then finally for the 350 ppm fuel, there was a 73.3% CO emission reduction.

By inspection of Figure 4.27, it is apparent that the CO emissions were not effected by the sulfur in the fuel. This is known because the CO emissions at full flow engine-out are all the same for the various fuel types.

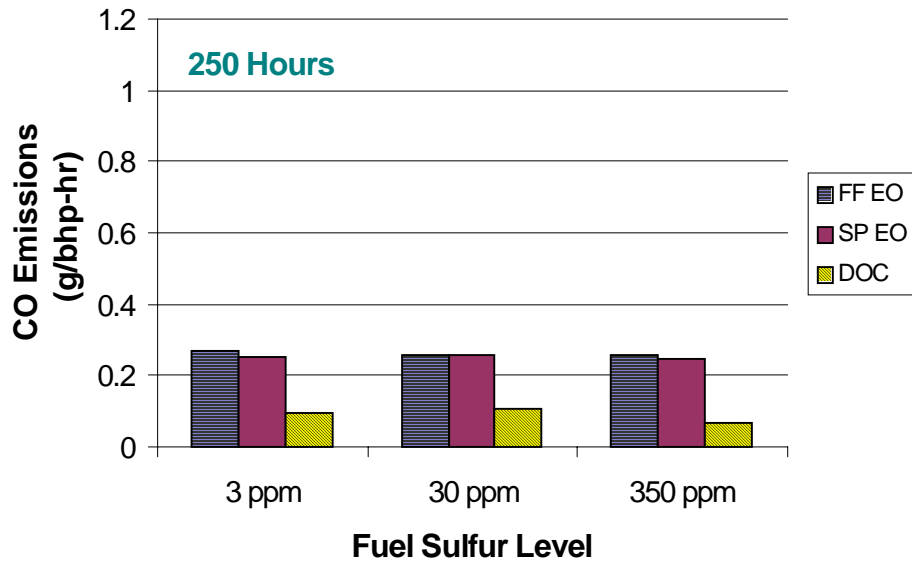


Figure 4.27 Cummins OICA\* CO Emissions

In Figure 4.28, the CO emission reduction efficiencies from the OICA\* tests evaluated at 250 hours can be seen. The high temperature DOCs for the Cummins engine did not reduce the CO emissions nearly as well as the low temperature DOCs used on the Navistar engine.

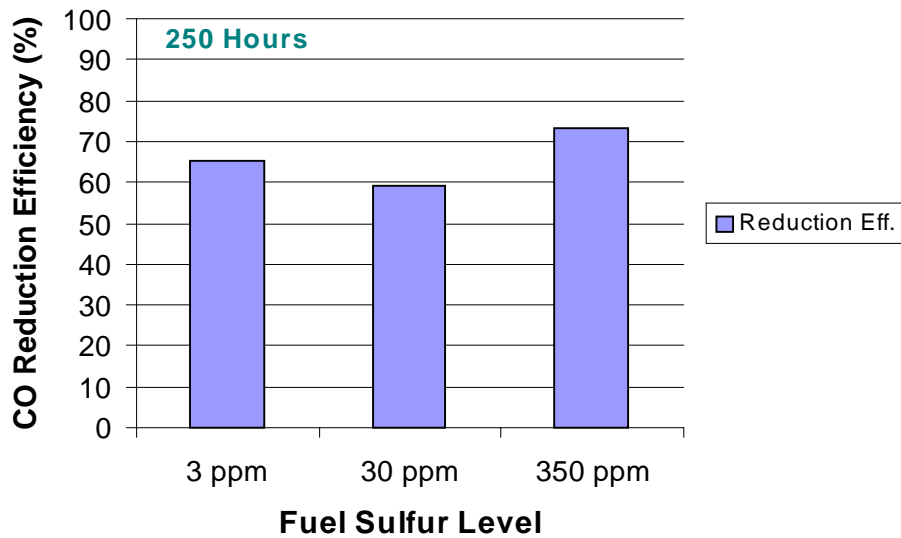


Figure 4.28 Cummins OICA\* CO Emissions Reduction Efficiency

Figure 4.29 shows the comparisons of the CO emissions with the aging hours and the fuel sulfur. All CO emissions were reduced from the full flow engine-out to DOC-out evaluations.

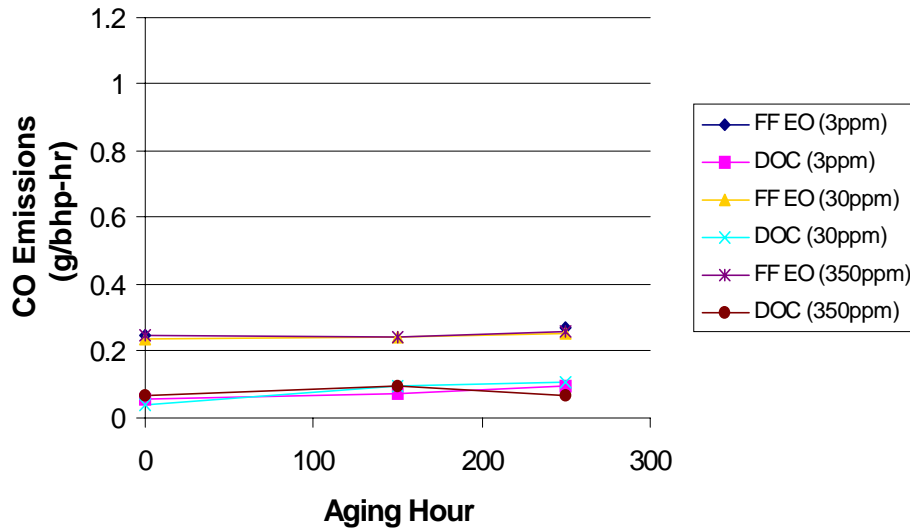


Figure 4.29 Cummins OICA\* Test Comparing CO Emissions, Aging Hours, and Fuel

In Figure 4.30, the CO emissions can be seen from the FTP tests evaluated with the various fuels at 250 hours. The DOCs did reduce the CO emissions in the FTP tests, but not as well as in the steady state tests. The CO emission reduction efficiencies are calculated for each fuel. The reduction is calculated from the CO emissions at full flow engine-out and DOC-out emissions. With the 3 ppm fuel, there was only a 24.4% reduction in the CO emissions. With the 30 ppm fuel the CO emission reduction was found to be 24%. Then finally, the 350 ppm CO reduction with the DOC was 24.9%. Figure 4.30 shows that the sulfur levels in the fuel did not effect the CO emissions. The CO emissions at 3 ppm, 30 ppm and 350 ppm are all approximately the same at full flow engine-out.

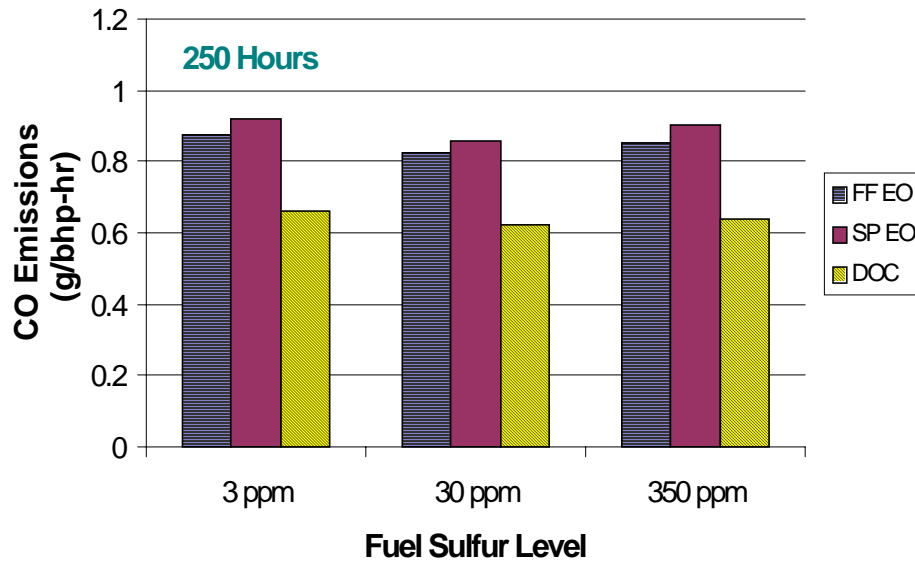


Figure 4.30 Cummins FTP CO Emissions at 250 Hours

Figure 4.31 shows the reduction efficiencies for the FTP of the Cummins engine at 250 hours. The reduction efficiencies for the FTP were much less than those of the OICA\* test. The reduction efficiencies were around 25%. The efficiencies were approximately the same at 0 hours and 150 hours. These values can be seen in Appendix F.

In Figure 4.32, the graph shows the Cummins FTP tests and comparing the aging hour, fuel sulfur, and the CO emissions. The CO emissions were reduced from the DOCs in the FTP tests shown in Figure 4.32.



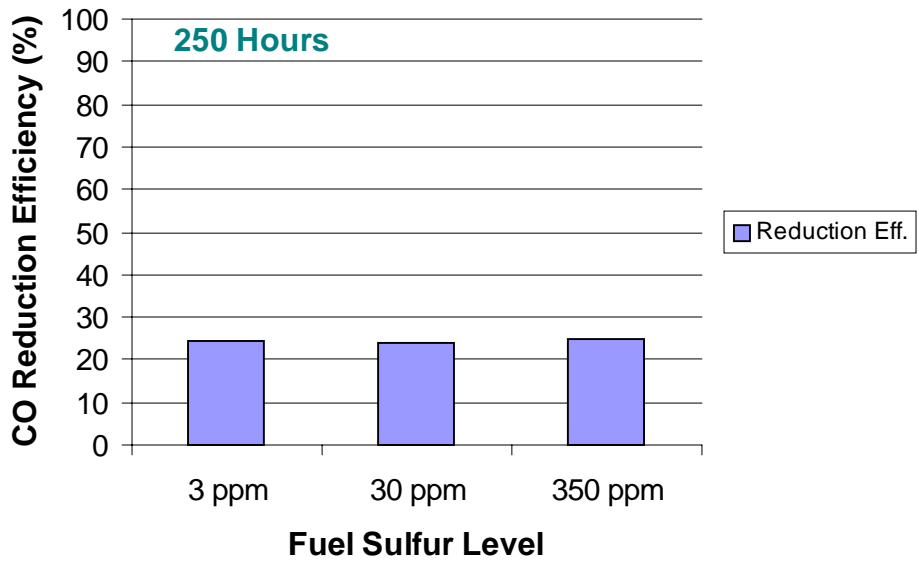


Figure 4.31 Cummins FTP CO Emissions Reduction Efficiency

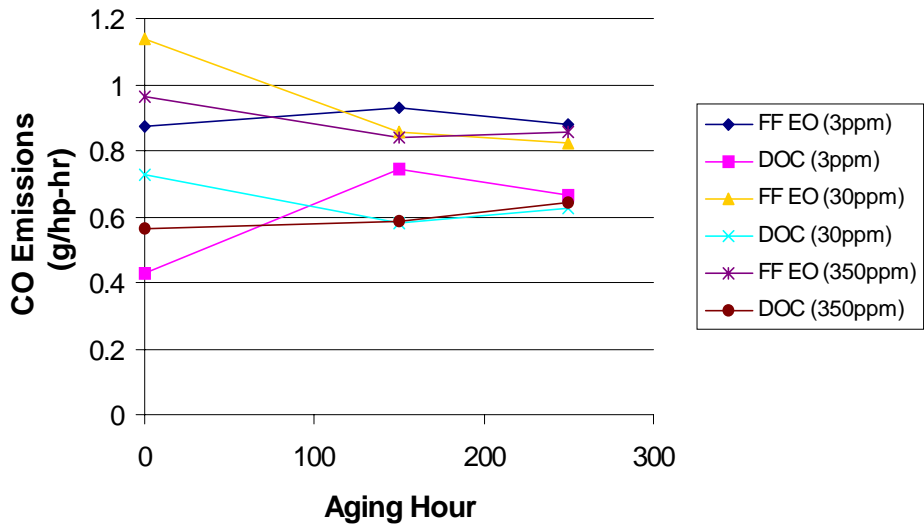


Figure 4.32 Cummins FTP Tests Comparing CO Emissions, Aging Hour, and Fuel

#### 4.4 NO<sub>x</sub> Emission Analysis

Finally, inspection of the NO<sub>x</sub> emissions will be examined. The DOC catalysts are not designed to reduce the NO<sub>x</sub> emissions. So this short section will only double check the NO<sub>x</sub> emission to see if they stay the same from full flow engine-out to DOC evaluation.

Figure 4.33, Figure 4.34, Figure 4.35, and Figure 4.36, all show that the fuel sulfur did not have any affect on the NO<sub>x</sub> emissions. Also it is apparent that the DOCs do not have any chemical reactions with their washcoats to reduce the NO<sub>x</sub> emissions. The last four figures all refer to transient and steady state tests for the Navistar and Cummins engine evaluations at 250 hours.

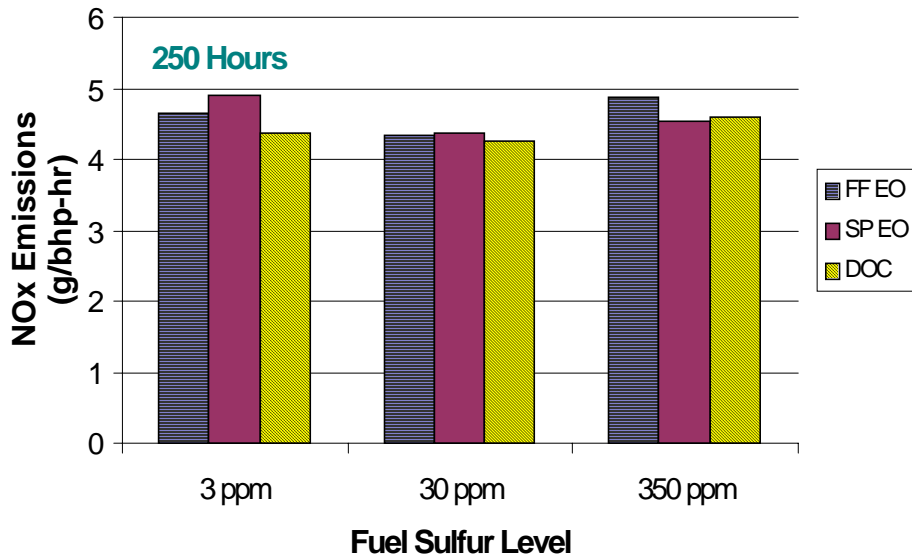


Figure 4.33 Navistar FTP-75 NO<sub>x</sub> Emissions at 250 Hours

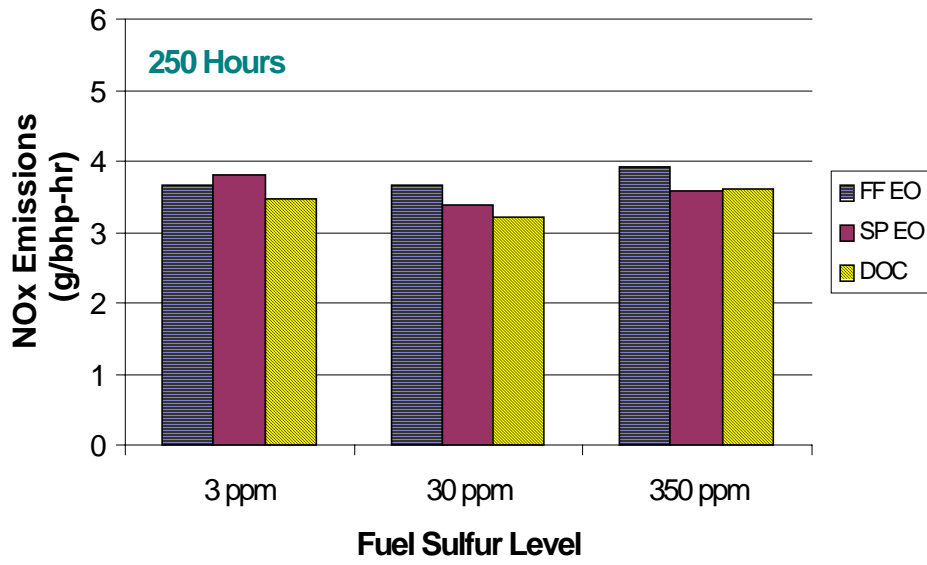


Figure 4.34 Navistar Nav-9\* NO<sub>x</sub> Emissions at 250 Hours

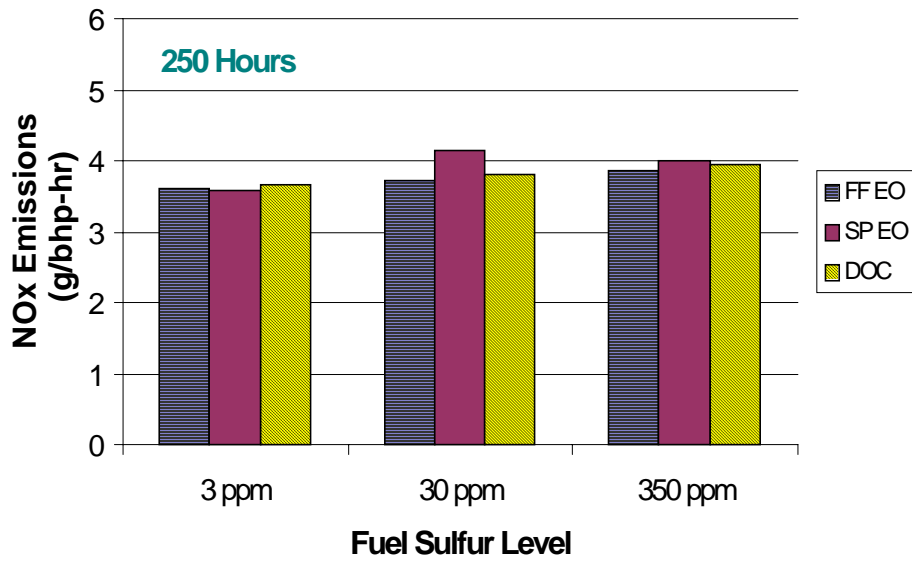


Figure 4.35 Cummins FTP NO<sub>x</sub> Emissions at 250 Hours

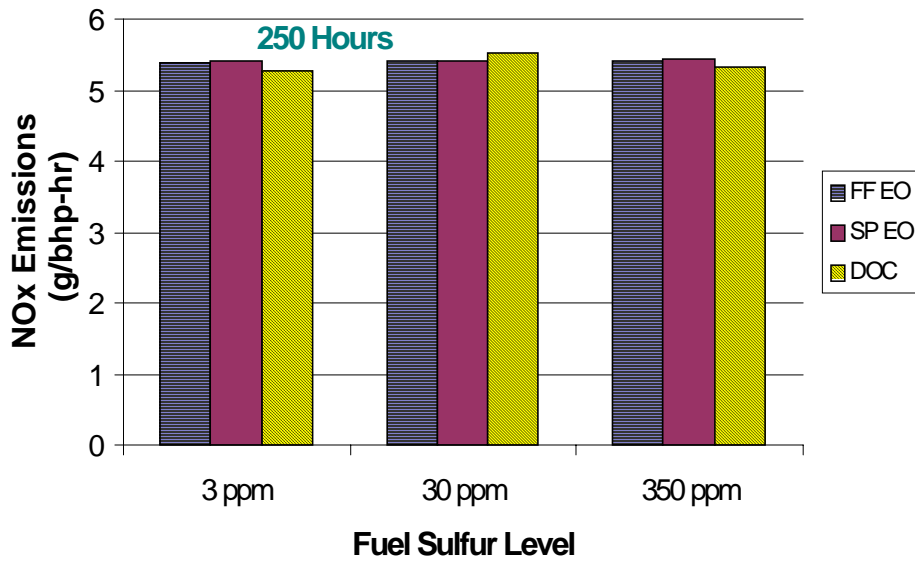


Figure 4.36 Cummins OICA\* NO<sub>x</sub> Emissions at 250 Hours

#### 4.5 Results and 2004 Emission Standards

Table 4.2 shows the year 2004 brake-specific emission standards listed with actual brake-specific emissions results measured in the DECSE research conducted at WVU with the Navistar T444E and Cummins ISM370 ESP engine. It was evident that the fuel sulfur level did effect the brake-specific emissions. The Cummins engine would meet the 2004 brake-specific emission standards with the 3 ppm sulfur level fuel with the usage of the DOC, however, it would not meet the emission standards on the 350 ppm sulfur level. The DOC equipped Navistar T444E would not meet the 2004 brake-specific emission standards on the 3 ppm fuel nor the 350 ppm fuel

Table 4.2 Year 2004 Emission Standards Compared to WVU DOC Emissions

Year 2004+	Fuel Sulfur Level	EPA Standards	Navistar T444E With DOCs		Cummins ISM370 With DOCs	
			FTP-75	Nav-9*	FTP	OICA*
HC	3 ppm	1.3	0	0	0.02	0.02
HC	30 ppm	1.3	0.0173	0	0.045	0.027
HC	350 ppm	1.3	0.02166	0.007	0.018	0.016
CO	3 ppm	15.5	0.0743	0.044	0.66	0.093
CO	30 ppm	15.5	0.125	0.082	0.625	0.105
CO	350 ppm	15.5	0.02066	0.003	0.64	0.069
NO <sub>x</sub>	3 ppm	2.5	4.4	3.5	3.7	5.3
NO <sub>x</sub>	30 ppm	2.5	4.3	3.2	3.8	5.5
NO <sub>x</sub>	350 ppm	2.5	4.6	3.6	3.9	5.3
PM	3 ppm	0.10	0.0655	0.16	0.05	0.05
PM	30 ppm	0.10	0.0662	0.20	0.045	0.054
PM	350 ppm	0.10	0.065	0.57	0.042	0.08

## CHAPTER 5 ~ CONCLUSIONS

In order to meet the 2002-2004 EPA emission standards along with the upcoming 2007 standards, aftertreatment devices and the fuel sulfur levels need very close attention. This part of the DECSE research was focused on three major issues related to the effect of fuel sulfur on DOCs and subsequently on the brake-specific emissions. The major topics included how the catalysts effected the brake-specific emissions, how the fuel sulfur levels effected the brake-specific emissions, and if there was any evidence of sulfur poisoning of the DOCs.

The catalysts had no significant effects on PM emissions with the low sulfur fuels (3 ppm and 30 ppm). With the higher sulfur level (350 ppm), the catalytic oxidation of sulfur caused a large increase in sulfates, hence an increase in brake-specific PM emissions. This was found to be true for both, the Navistar, and the Cummins engine.

The catalysts were found to greatly affect the HC emissions for both engines. For the Cummins DOC-out brake-specific HC emissions, the reduction efficiency was found to range from 80% to 90%. The Navistar engine produced DOC-out HC emissions that had reduction efficiencies of nearly 100%. It was evident in the analysis that the HC brake-specific emissions did increase as the fuel sulfur level increased from 3 ppm to 350 ppm fuel.

The catalysts also affected the CO emissions. The reduction efficiency of the DOC-out CO emissions for the Navistar engine was found to be between 90%-100%. The approximate reduction efficiency for the DOC-out of the CO emissions for the Cummins engine was found to be between 59%-74%.

It was concluded that the Cummins engine, running on any of the three fuels tested, equipped with DOCs can meet the EPA 2004 emission standards except for the brake-specific NO<sub>x</sub> emissions. A conclusion could not be made for the Navistar T444E due the testing was done with the FTP-75. The EPA emission standards are conducted and concluded with the FTP, not the FTP-75.

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## **APPENDICES**

**APPENDIX A: NAVISTAR PM EMISSION RESULTS**

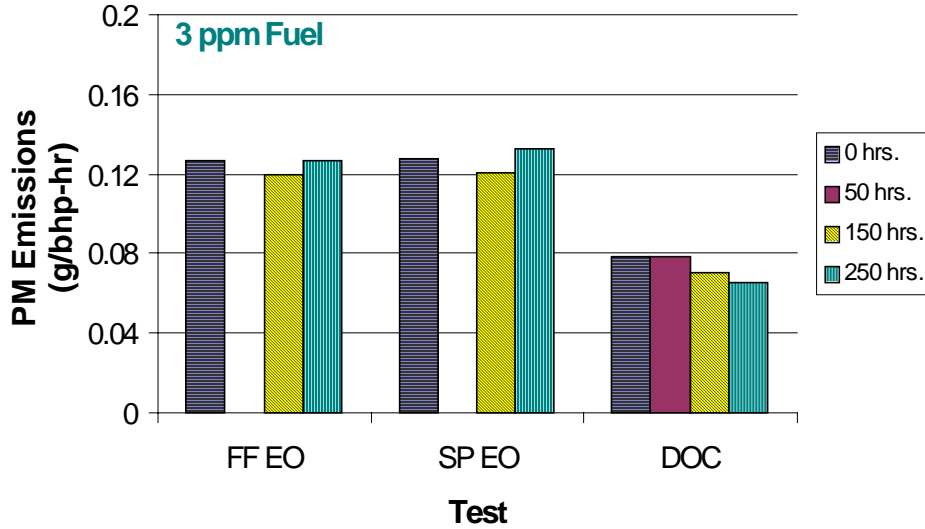


Figure A.1 Navistar Transient FTP-75 PM Emissions with 3 ppm Fuel

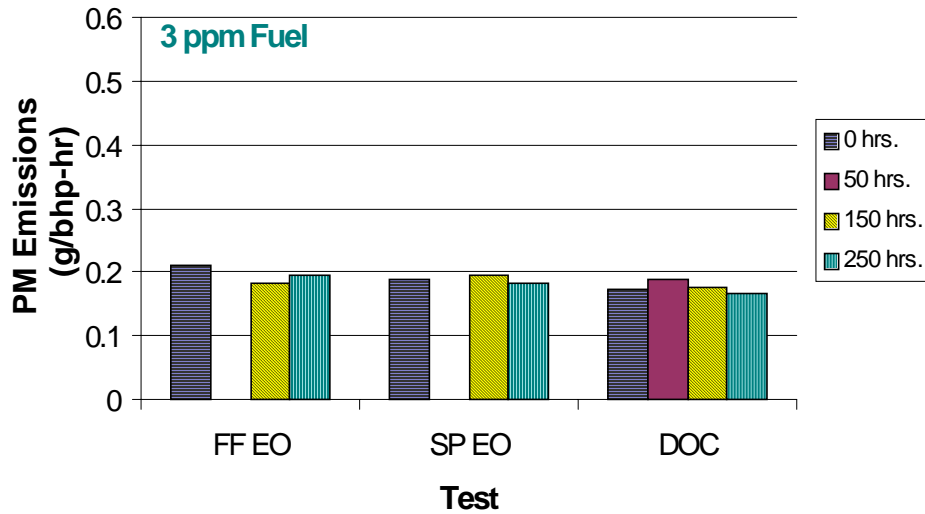


Figure A.2 Navistar Nav-9\* PM Emissions with 3 ppm Fuel

The two figures above are comparing the PM emissions with the type of exhaust at the various aging hours. The tests were performed on 3ppm fuel. While the graphs on the following page are showing the PM emissions on the transient FTP-75 test for the Navistar engine. The following graphs are comparing PM emissions with the type of

exhaust and the type of diesel fuel sulfur used. One can see that the DOC did in fact reduce the PM emissions as the aging hours increased.

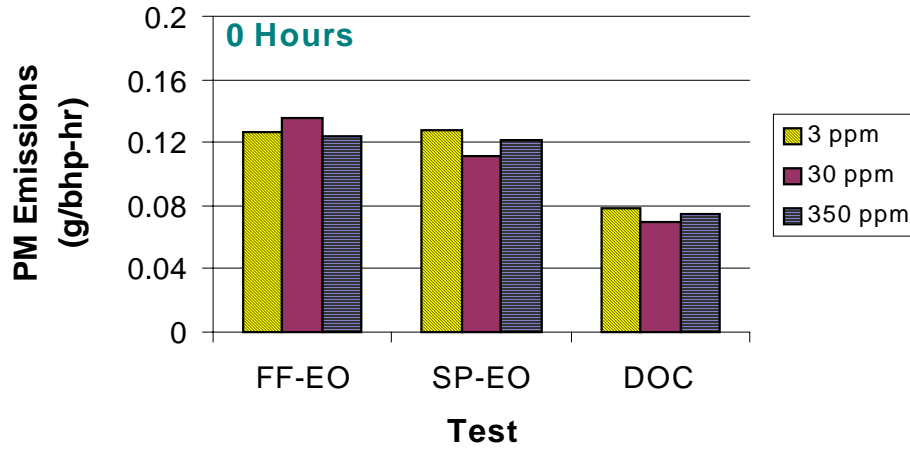


Figure A.3 Navistar FTP-75 PM Emissions at 0 Hours

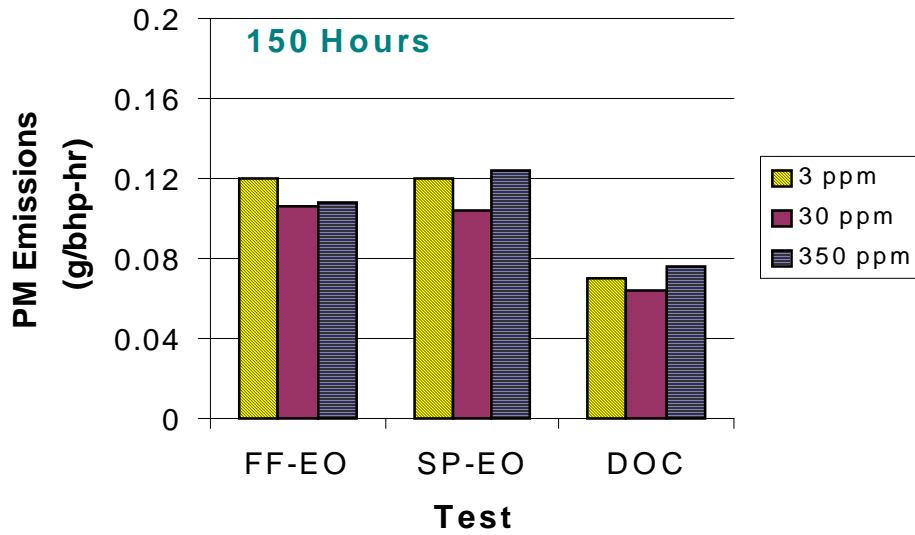


Figure A.4 Navistar FTP-75 PM Emissions at 150 Hours

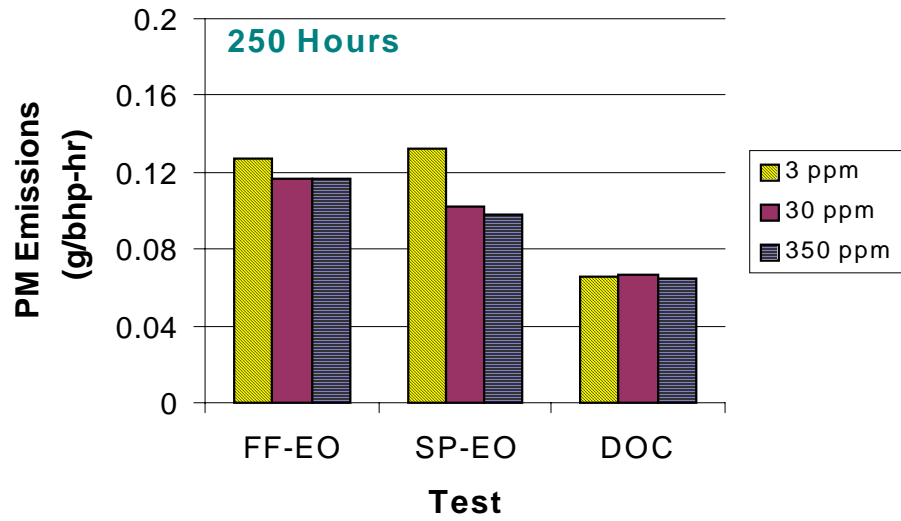


Figure A.5 Navistar FTP-75 PM Emissions at 250 Hours

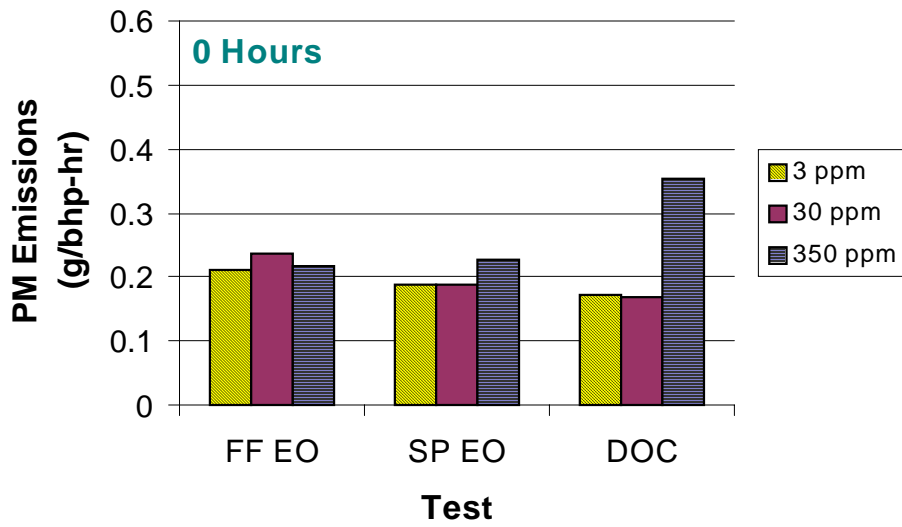


Figure A.6 Navistar Nav-9\* PM Emissions for 0 Hours

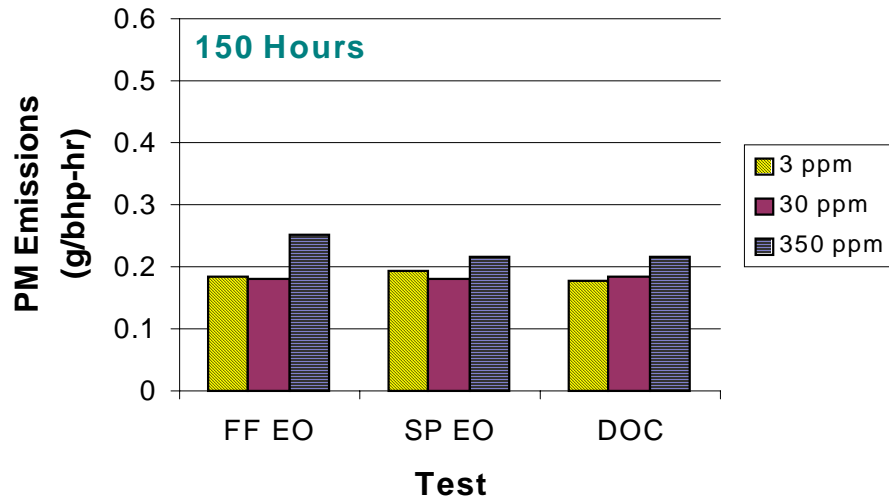


Figure A.7 Navistar Nav-9\* PM Emissions for 150 Hours

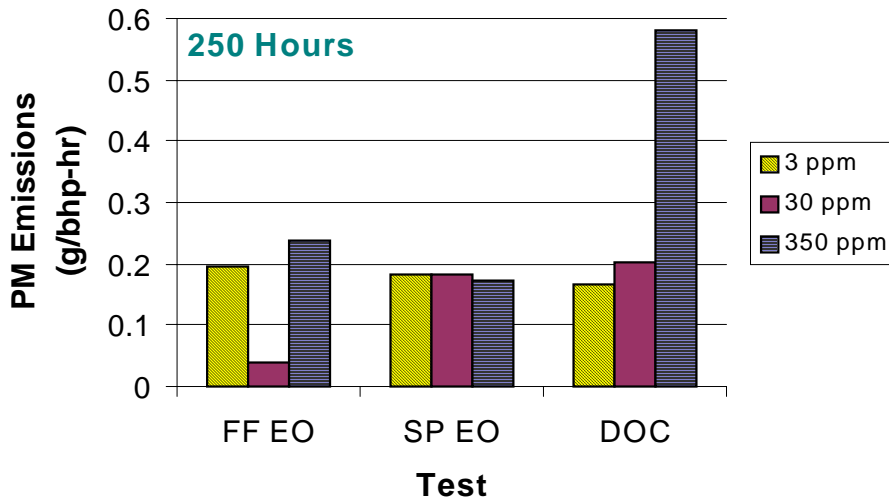


Figure A.8 Navistar Nav-9\* PM Emissions for 250 Hours

The three figures on the previous pages investigate the steady state tests ran with the Navistar engine. On the steady state tests, the DOC maintained a stable PM emission with 3 and 30 ppm fuels. But with the higher sulfur fuel (350 ppm), the excess sulfur contributed to an increase in PM emission along with the increase in aging hours.

The figures below indicate the PM emissions collected for 30 ppm fuel over the various aging hours. By inspection one can tell that the DOC worked very well while evaluating the FTP-75 tests. In the Nav-9\* test, the PM emissions for the full flow engine-out at 250 hours are very low. One very possible reason for this low number is from human error. More than likely the PM filter for that test was weighed incorrectly.

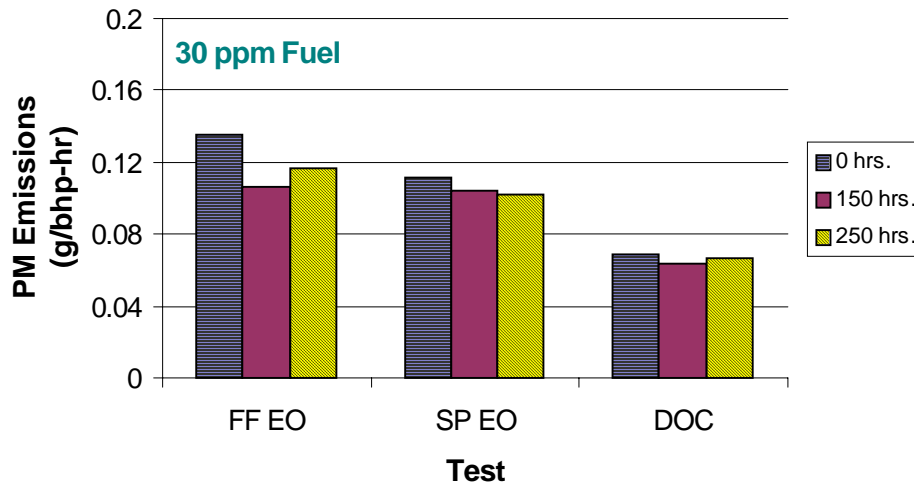


Figure A.9 Navistar FTP-75 PM Emissions with 30 ppm Fuel

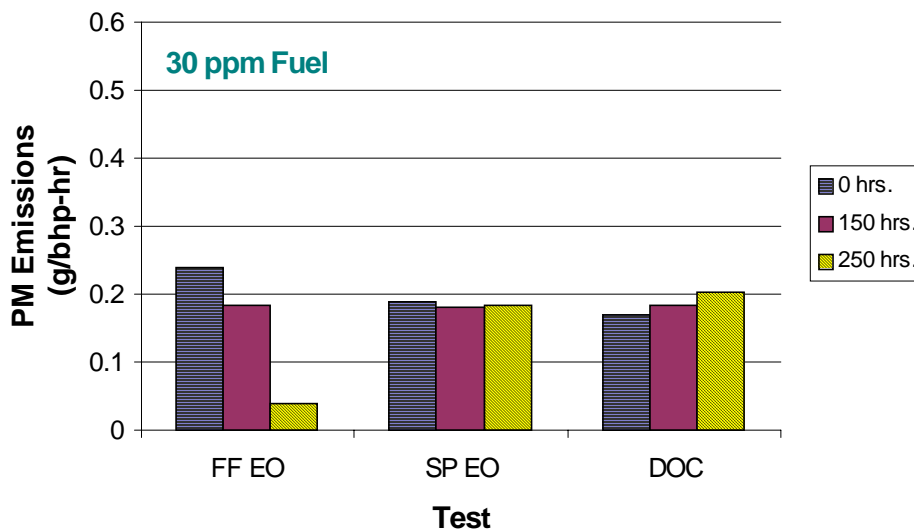


Figure A.10 Navistar Nav-9\* PM Emissions with 30 ppm Fuel



The following figures show the PM emissions gathered on 350 ppm fuel at the various aging hours. The FTP-75 PM emissions on 350 ppm fuel show that the DOC reduced the emissions quite well. On the steady state tests, the DOC catalyst evaluated with the 350 ppm fuel became poisoned, and did not reduce the emissions with time, but instead it became worse with the aging hours.

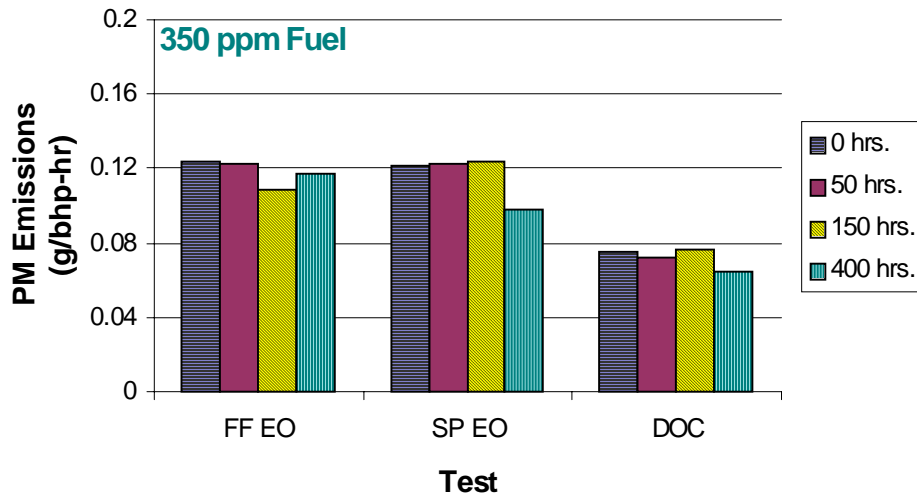


Figure A.11 Navistar FTP-75 PM Emissions with 350 ppm Fuel

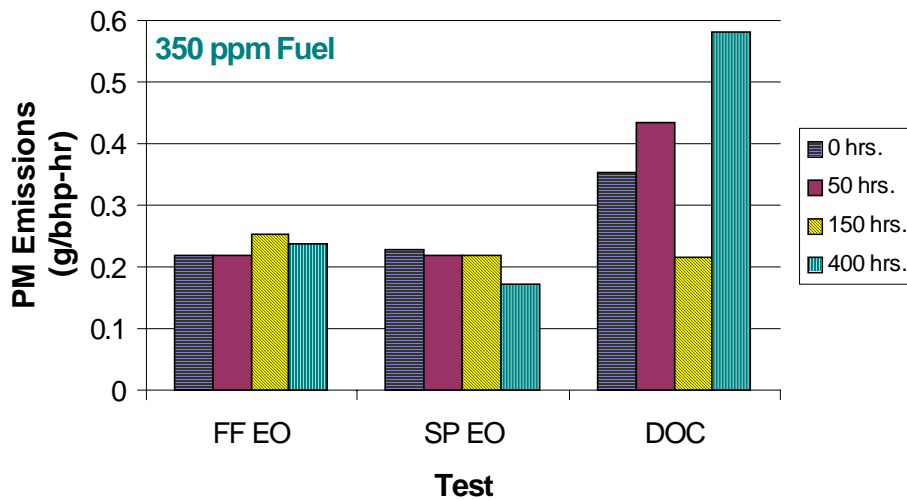


Figure A.12 Navistar Nav-9\* PM Emissions with 350 ppm Fuel

The following two figures indicate the PM emission reduction efficiencies at 0 hours and 150 hours when operating with transient tests. From using the DOC, there was a significant reduction in the PM emissions.

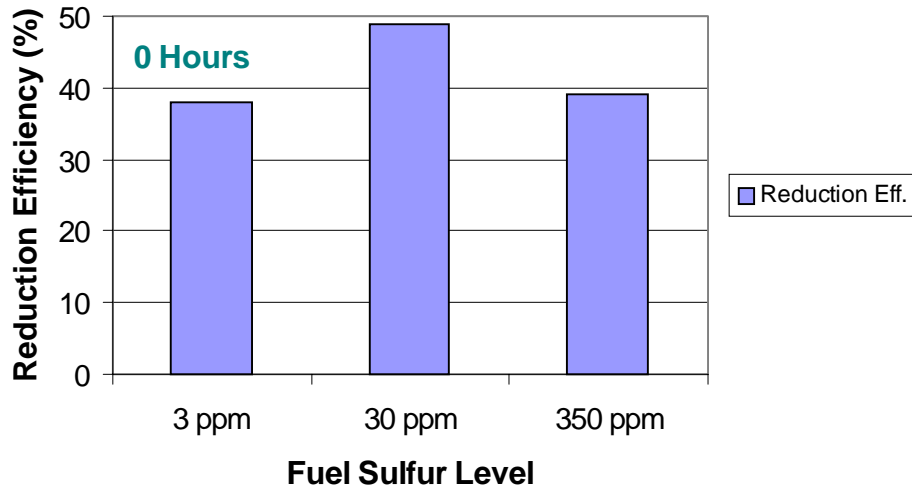


Figure A.13 Navistar FTP-75 PM Emission Reduction Efficiency at 0 Hours

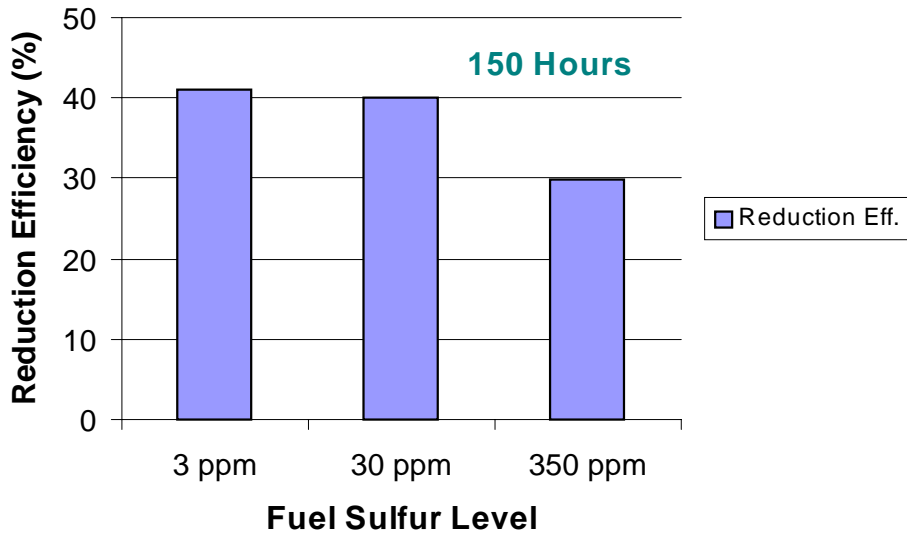


Figure A.14 Navistar FTP-75 PM Emissions Reduction Efficiency at 150 Hours

**APPENDIX B: CUMMINS PM EMISSION RESULTS**

The following two graphs are of the Cummins transient (FTP) and steady state (OICA\*) tests. By inspecting the graphs, one can tell that the DOC performed fairly well by reducing the PM emissions. As the evaluation of the aging hours grew, the performance of the DOC increased. This can be seen in both of the figures.

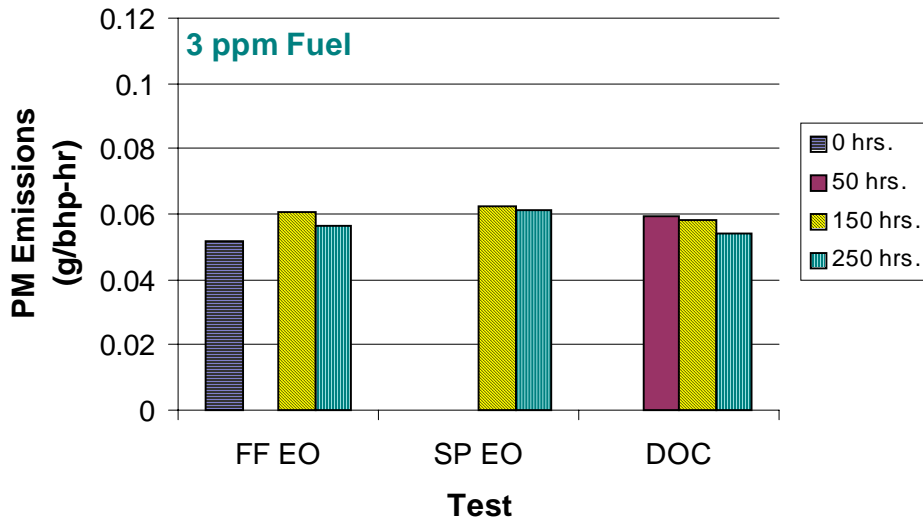


Figure B.1 Cummins FTP PM Emissions with 3 ppm Fuel

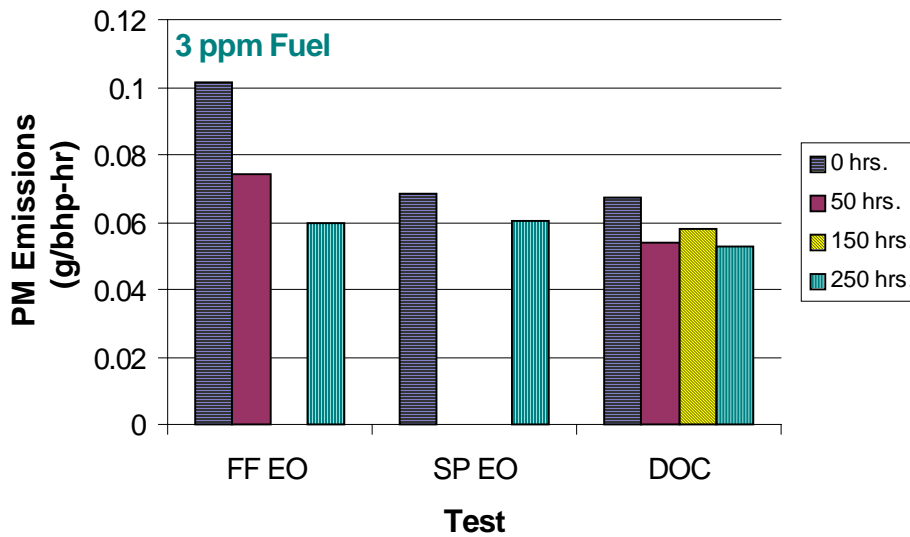


Figure B.2 Cummins OICA\* PM Emissions with 3 ppm Fuel

The following two graphs are for transient FTP tests ran on the Cummins test cell engine. For these transient tests, the DOCs reduced the PM emissions for each type of diesel fuel used.

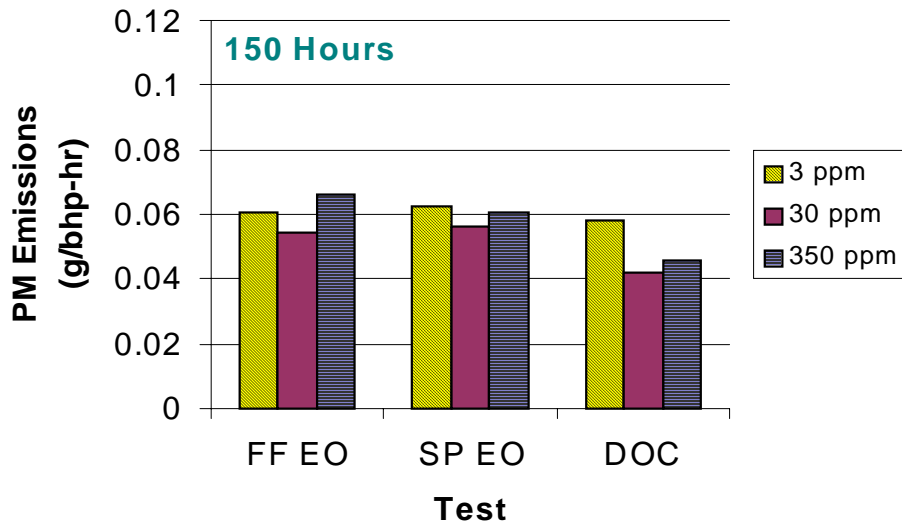


Figure B.3 Cummins FTP PM Emissions at 150 Hours

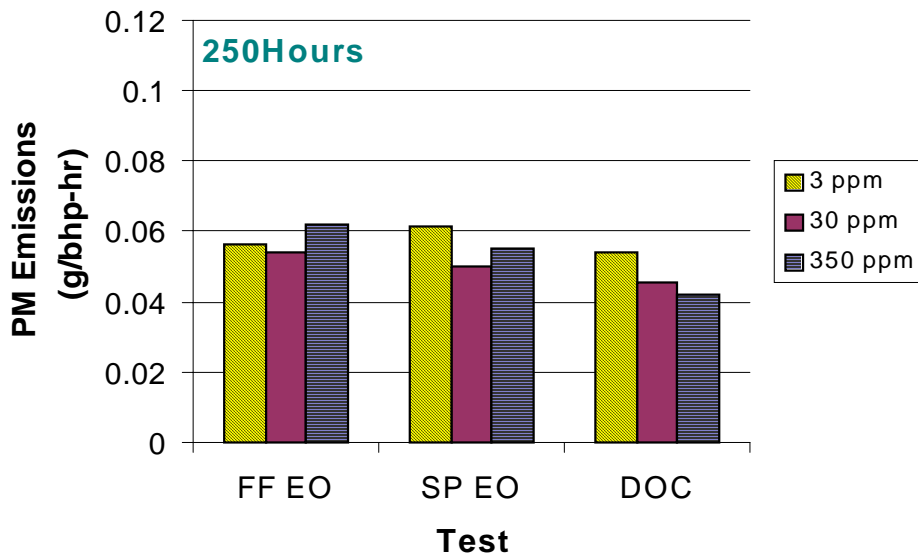


Figure B.4 Cummins FTP PM Emissions at 250 Hours

The following three graphs show the PM emissions obtained from the OICA\* tests at the various aging hours.

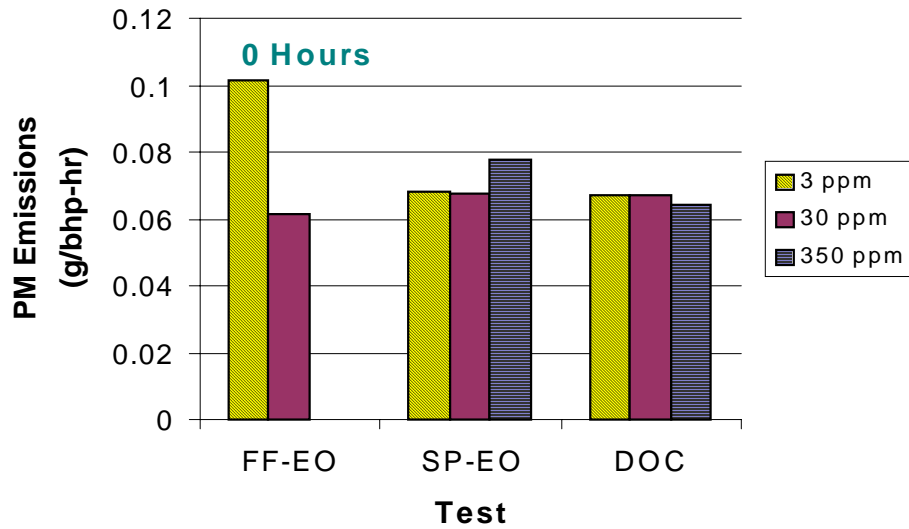


Figure B.5 Cummins OICA\* PM Emissions at 0 Hours

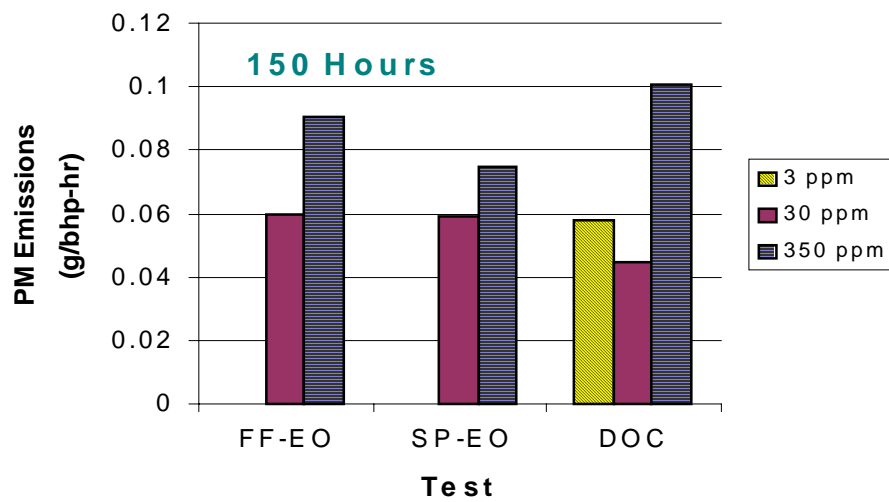


Figure B.6 Cummins OICA\* PM Emissions at 150 Hours

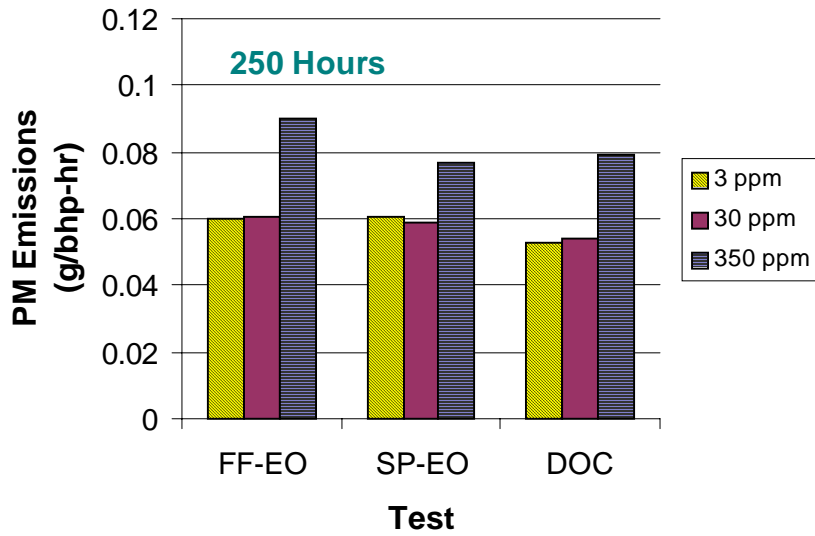


Figure B.7 Cummins OICA\* PM Emissions 250 Hours

The following two graphs show the transient (FTP) and steady state (OICA\*) PM emission results from the Cummins Engine. For the transient test, the DOCs reduced the PM emissions for every hour of evaluation. The DOCs reduced the PM emissions also when evaluation occurred with the steady state tests.

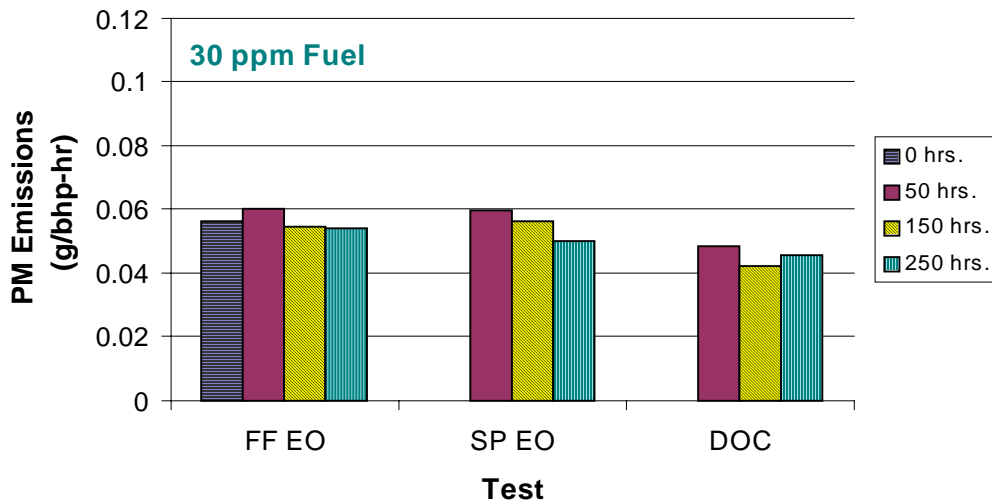


Figure B.8 Cummins FTP PM Emissions with 30 ppm Fuel

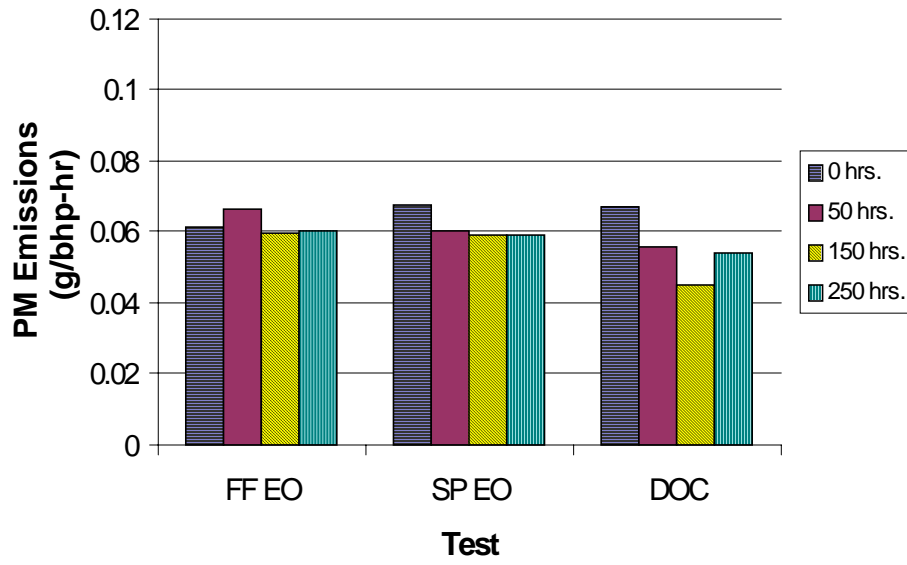


Figure B.9 Cummins OICA\* PM Emissions with 30 ppm Fuel

The following two graphs evaluate the DOCs with 350 ppm fuel on transient and steady state tests. In the transient test evaluations, it is very noticeable that the DOCs performed very well with reducing the PM emissions.

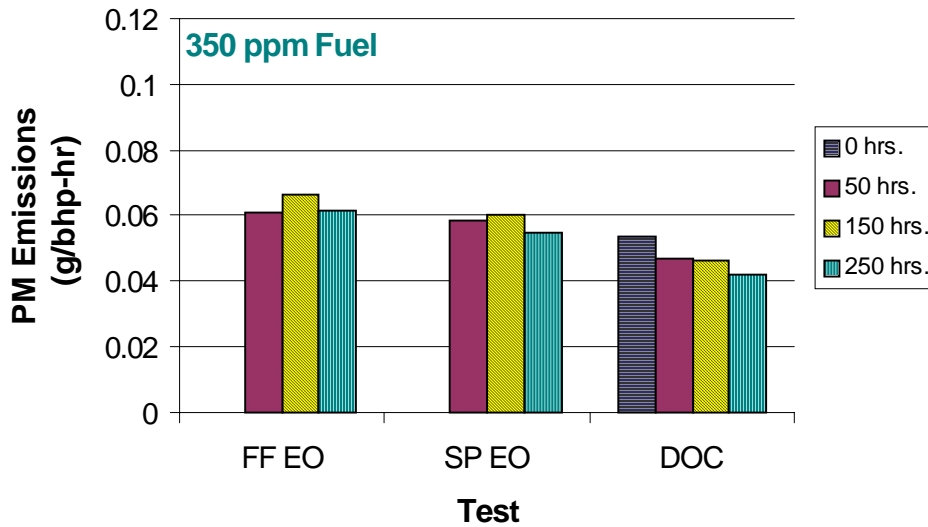


Figure B.10 Cummins FTP PM Emissions with 350 ppm Fuel



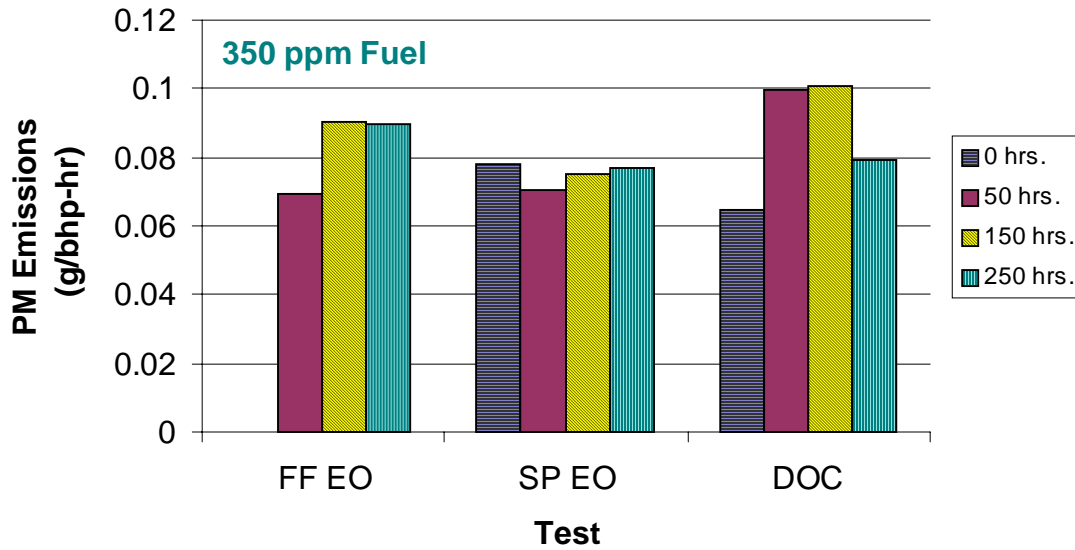


Figure B.11 Cummins OICA\* PM Emissions with 350 ppm Fuel

Finally, a look is at the PM emission reduction efficiency for the Cummins test cell engine. There is a reduction efficiency for each of fuels at the 150 and 250 aging hours. There was not enough data for 0 hour evaluation.

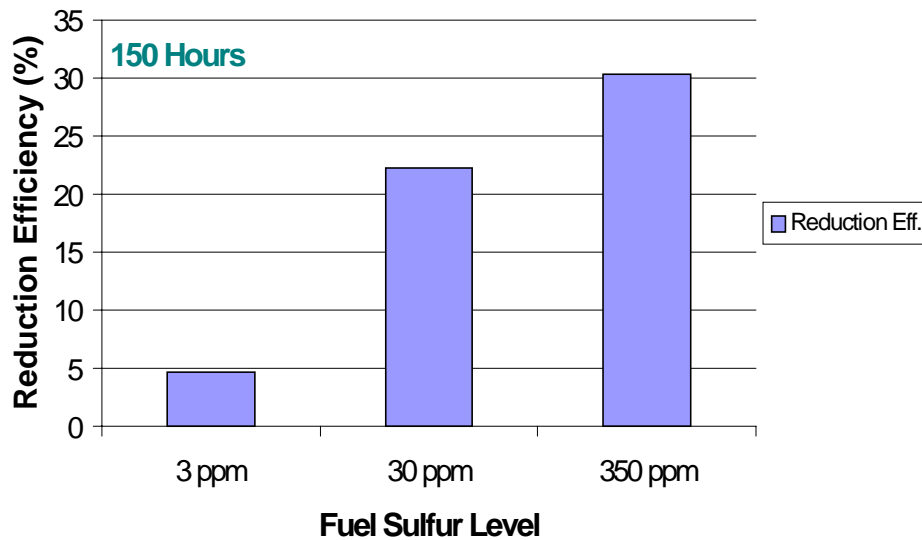


Figure B.12 Cummins FTP PM Emission Reduction Efficiency at 150 Hours

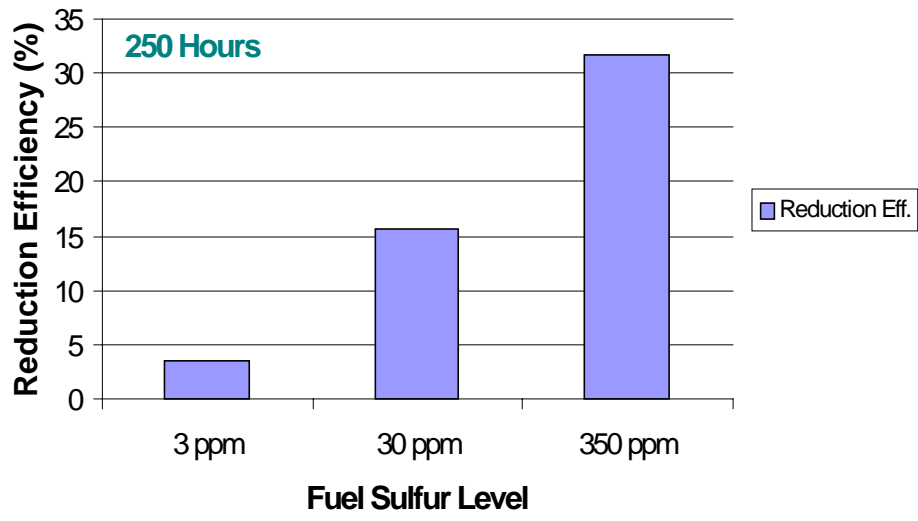


Figure B.13 Cummins FTP PM Emission Reduction Efficiency at 250 Hours

## **APPENDIX C: NAVISTAR HC EMISSION RESULTS**

In Figure C.2, Figure C.2, and Figure C.3 the HC emissions results are given for the Navistar steady state (Nav-9\*) tests, at 0 hours, 150 hours, and 250 hours of catalyst evaluation. HC reduction was found to be 100% in almost all of these tests. The negative brake-specific HC values for the DOCs imply that the ambient background brake-specific HC emissions were greater than the HC emissions produced from the engine. Hence, periodically when subtracting the DOC HC emissions from the background HC emission, a negative emission value would be obtained. The background emissions were subtracted from the engine emissions due to the ambient air drawn into the dilution tunnel.

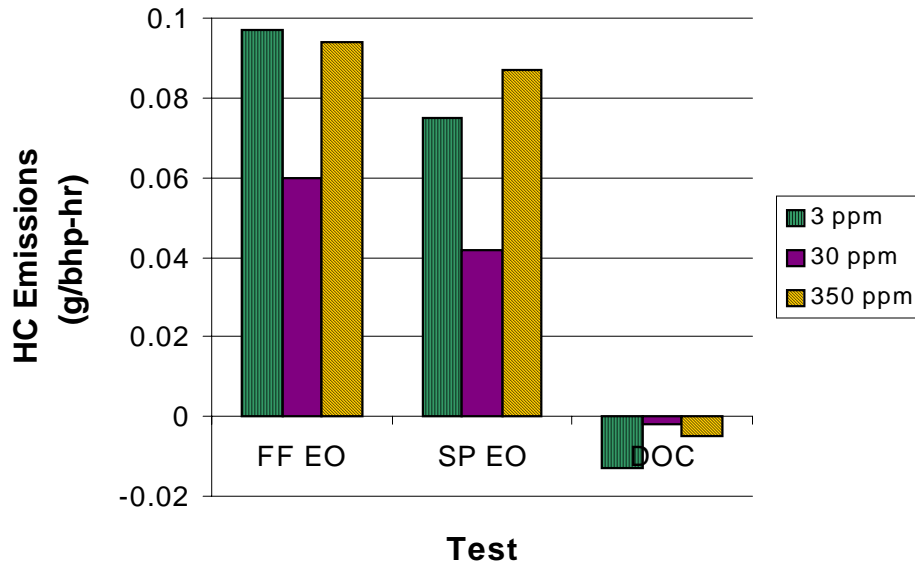


Figure C.1 Navistar Nav-9\* HC Emissions at 0 hours

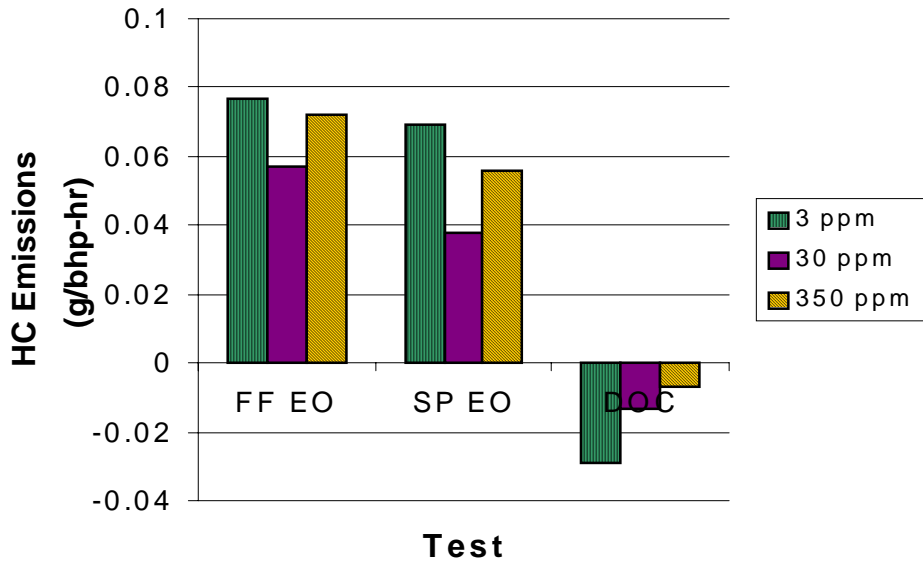


Figure C.2 Navistar Nav-9\* HC Emissions at 150 Hours

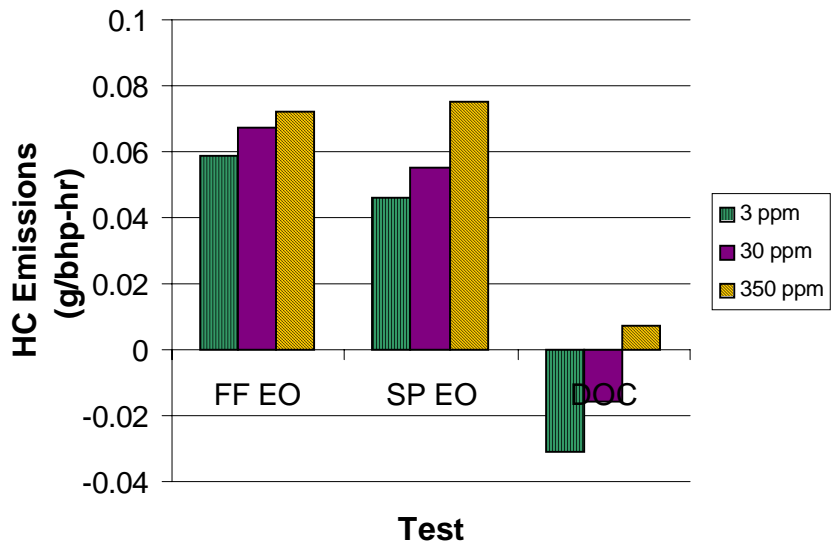


Figure C.3 Navistar Nav-9\* HC Emissions at 250 Hours

In Figure C.4 and Figure C.5, the reduction efficiency of the HC emissions can be seen. These tests were performed on the steady state cycle (Nav-9\*). The emissions were reduced 100%. The excess of 100% implies that the background HC were greater than those of the engine emissions.

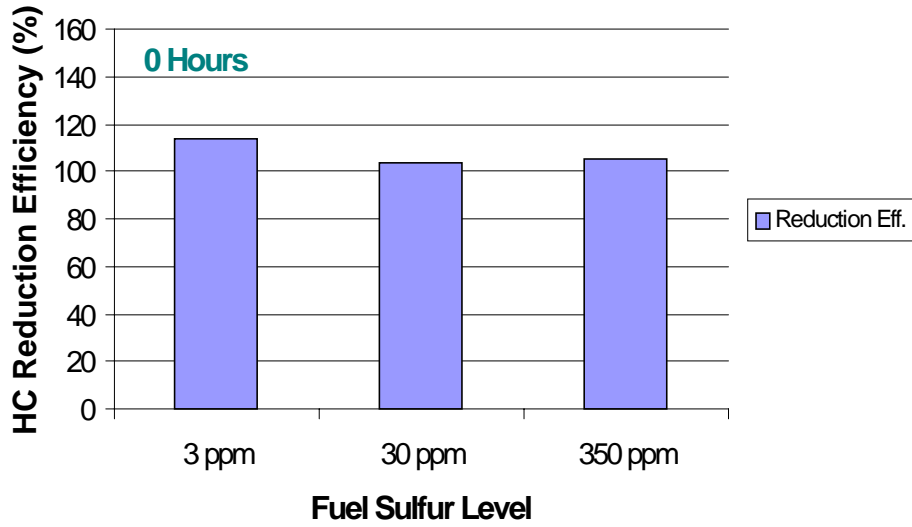


Figure C.4 Navistar Nav-9\* HC Emission Reduction Efficiency at 0 Hours

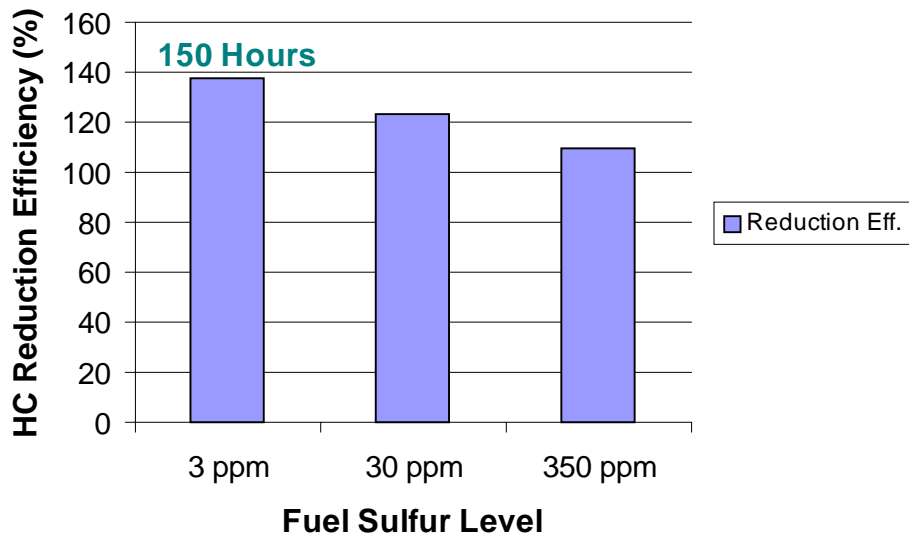


Figure C.5 Navistar Nav-9\* HC Emission Reduction Efficiency at 150 Hours

In Figure C.6, Figure C.7, and Figure C.8, the HC emissions are shown for the transient (FTP-75) tests. All of the HC emissions were nearly cut by 100% again.

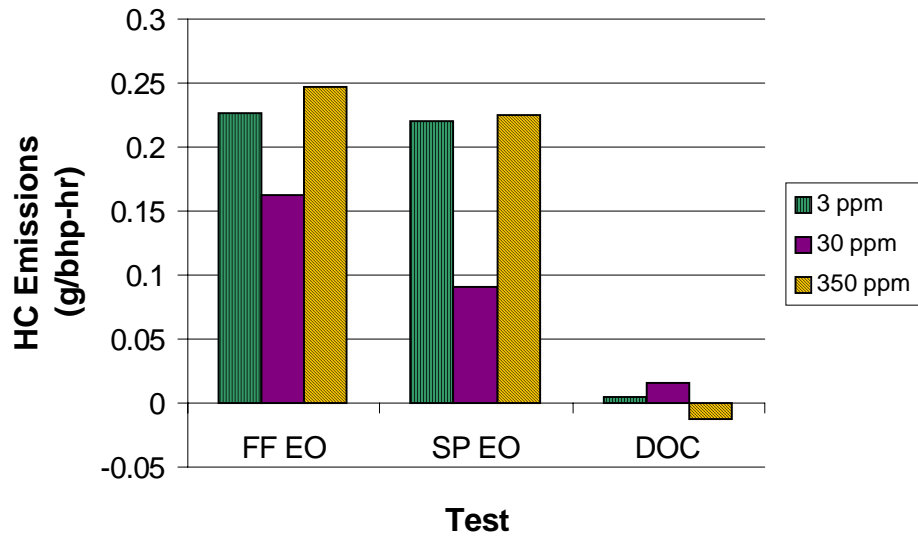


Figure C.6 Navistar FTP-75 HC Emissions at 0 Hours

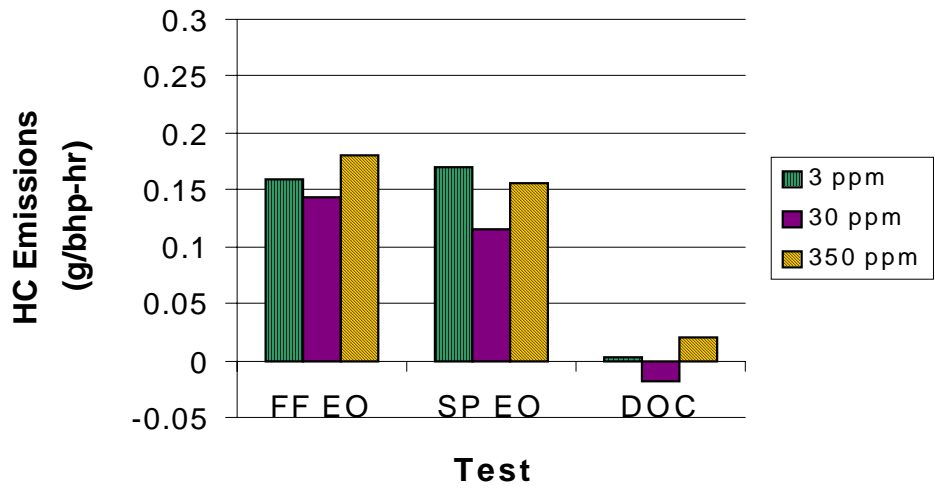


Figure C.7 Navistar FTP-75 HC Emissions at 150 Hours

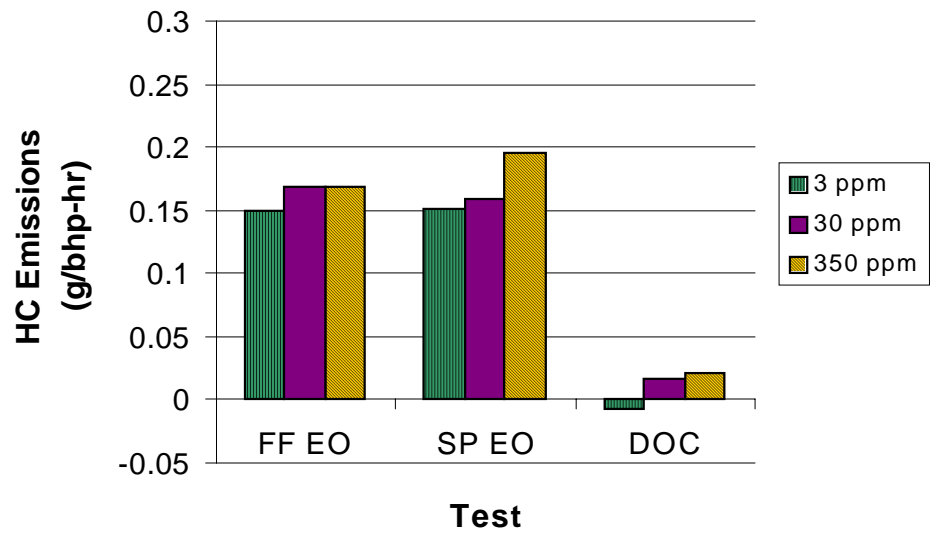


Figure C.8 Navistar FTP-75 HC Emissions at 250 Hours



The FTP-75 HC emission reduction efficiencies are shown in Figure C.9, Figure C.10, and Figure C.11. In this three graphs, the reduction efficiency ranges from 87% to 100%. This reduction efficiency inspects how well the DOCs reduce the HC emissions compared to those of the full flow engine-out. And it is seen that the DOCs have a great affect on the HC emission reduction.

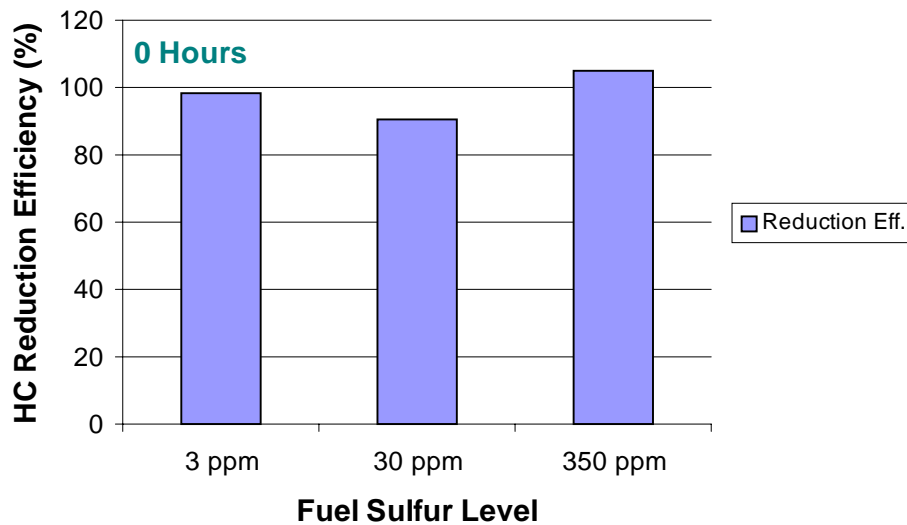


Figure C.9 Navistar FTP-75 HC Emission Reduction Efficiency at 0 Aging Hours

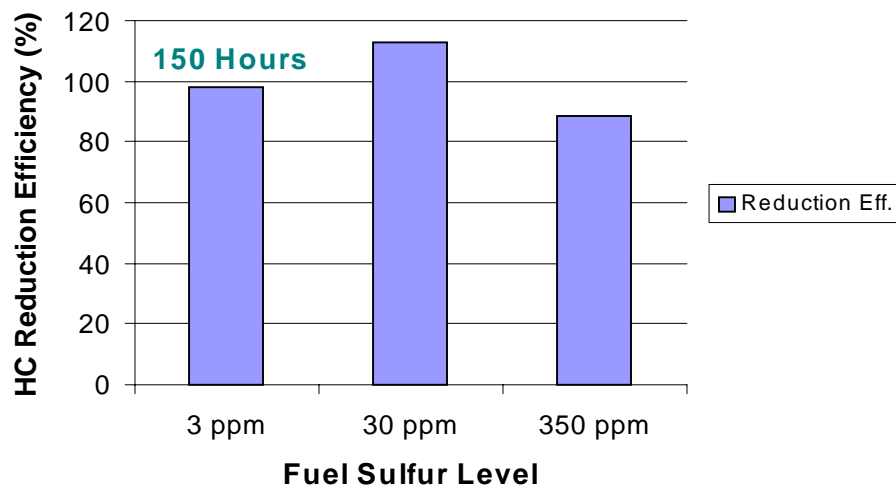


Figure C.10 Navistar FTP-75 HC Emission Reduction Efficiency at 150 Aging Hours

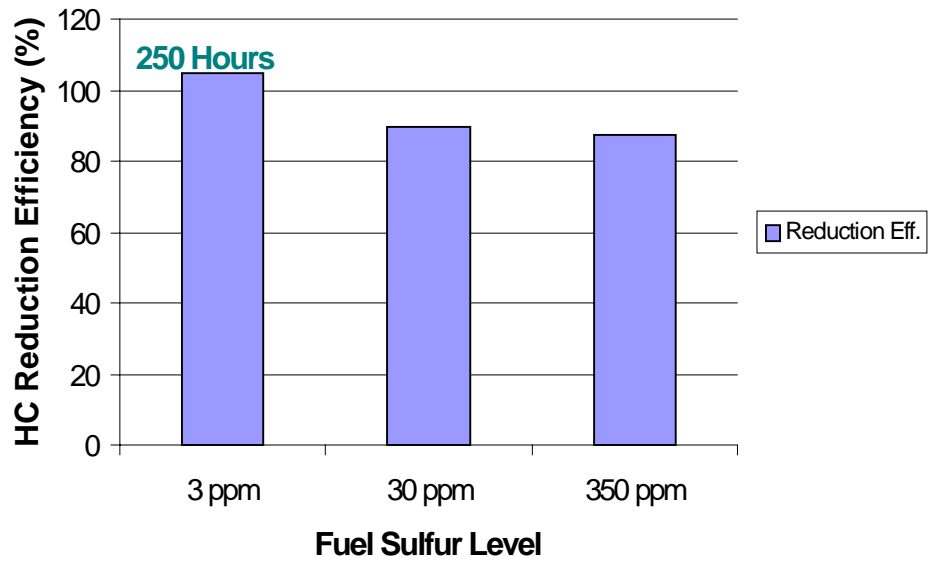


Figure C.11 Navistar FTP-75 HC Emission Reduction Efficiency at 250 Aging Hours

**APPENDIX D: CUMMINS HC EMISSION RESULTS**

In Figure D.1, Figure D.2, and Figure D.3 the HC emissions for the steady state (OICA\*) tests are shown. The DOC reduced the HCs extremely well such as that of the Navistar. The 3ppm HC reduction from full flow to DOC was 96.2%. The 30 ppm HC reduction from full flow emissions to DOC emissions was found to be 96.8%. The 350 ppm fuel HC emission reduction from full flow to DOC was found to be 89.3%. The calculations are for the OICA\* tests at 0 aging hours. The calculations are very similar for the 150 and 250 aging hours. So once again it is seen that the DOC catalyst did have a positive affect on the HC emissions.

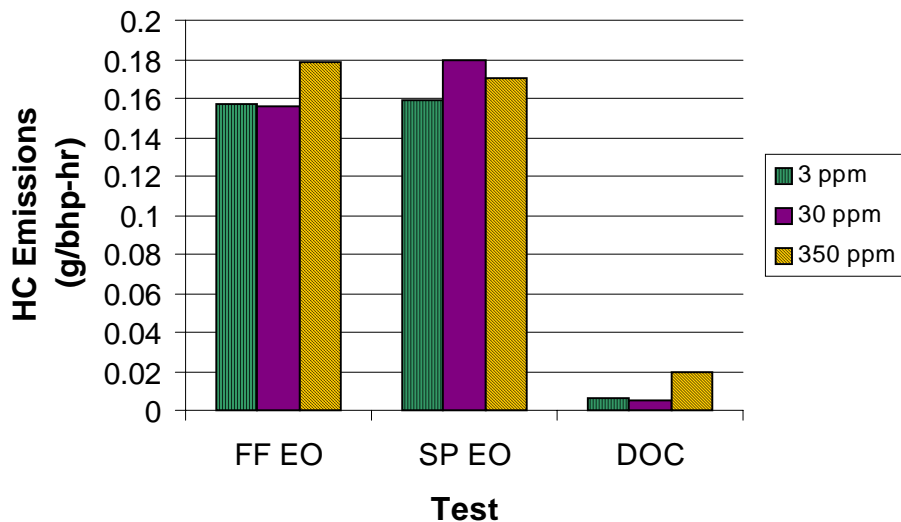


Figure D.1 Cummins OICA\* HC Emissions at 0 Hours

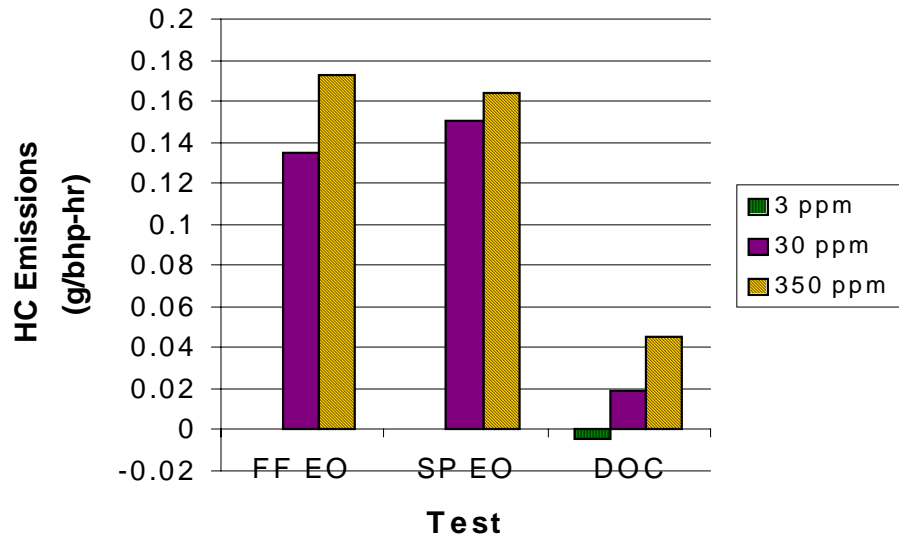


Figure D.2 Cummins OICA\* HC Emissions at 150 Hours

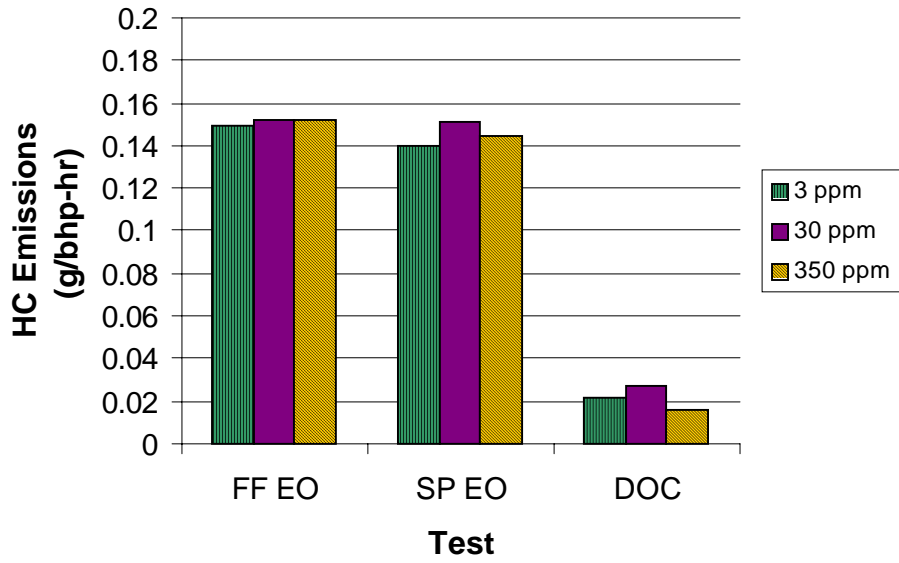


Figure D.3 Cummins OICA\* HC Emissions at 250 Hours

Now, the HC reduction efficiency is given for the OICA\* tests at the various aging hours. The HC reduction efficiency varied from 74% to 96.8%.

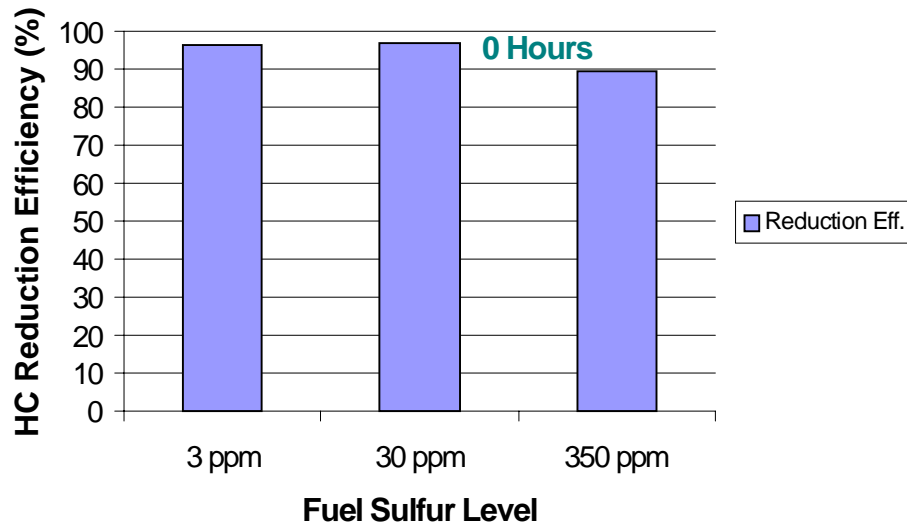


Figure D.4 Cummins OICA\* HC Emission Reduction Efficiency at 0 Hours

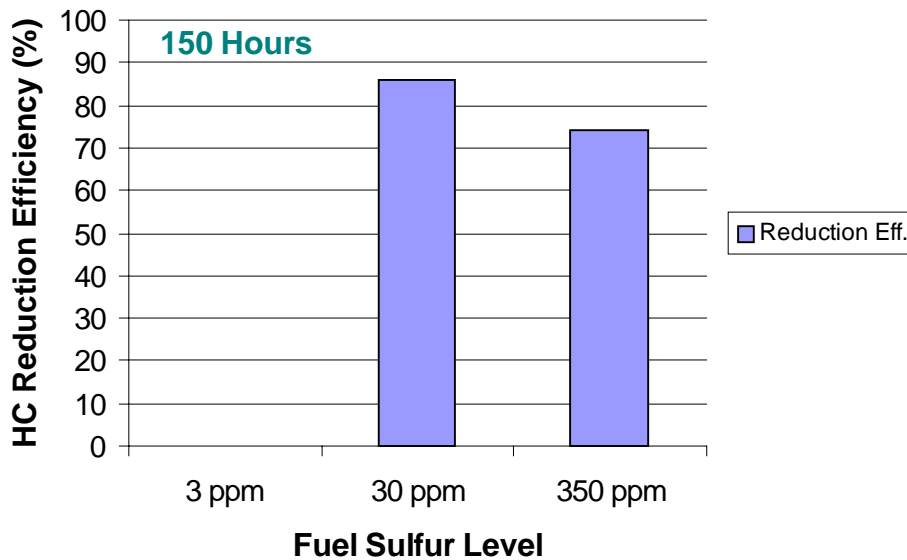


Figure D.5 Cummins OICA\* HC Emission Reduction Efficiency at 150 Hours

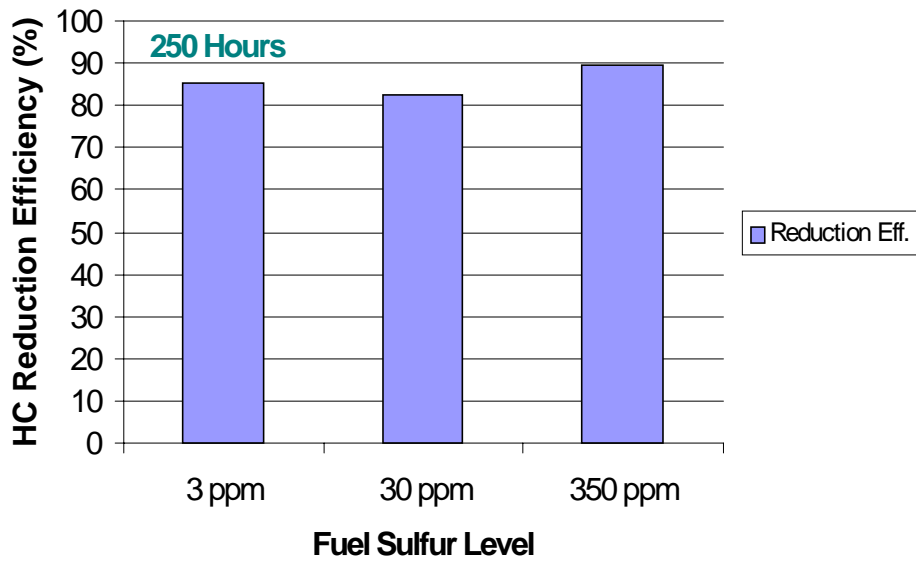


Figure D.6 Cummins OICA\* HC Emission Reduction Efficiency at 250 Hours

Now in Figure D.7, Figure D.8, and Figure D.9, the HC emissions are shown for the transient FTP tests ran on the Cummins engine. By inspection again, the HCs were greatly reduced by the DOCs from their original values found in the full flow engine-out.

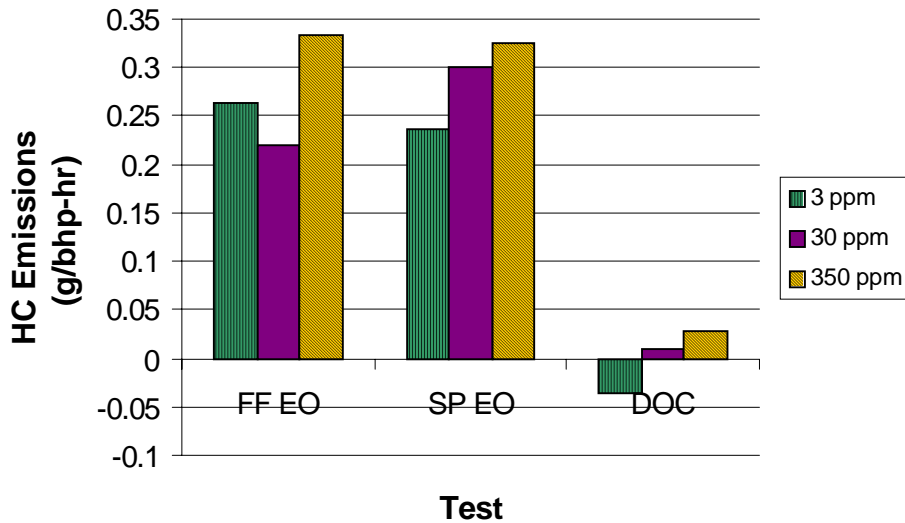


Figure D.7 Cummins FTP HC Emissions at 0 Hours

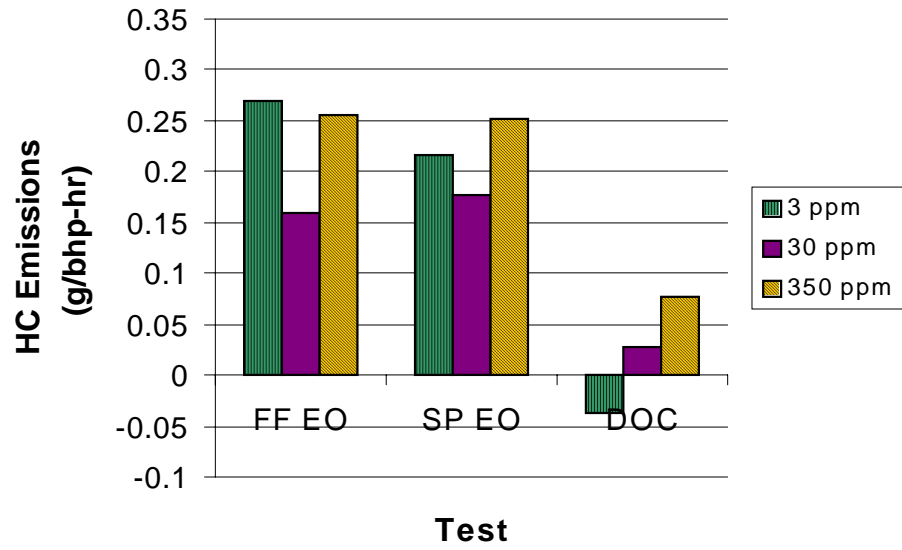


Figure D.8 Cummins FTP HC Emissions at 150 Hours

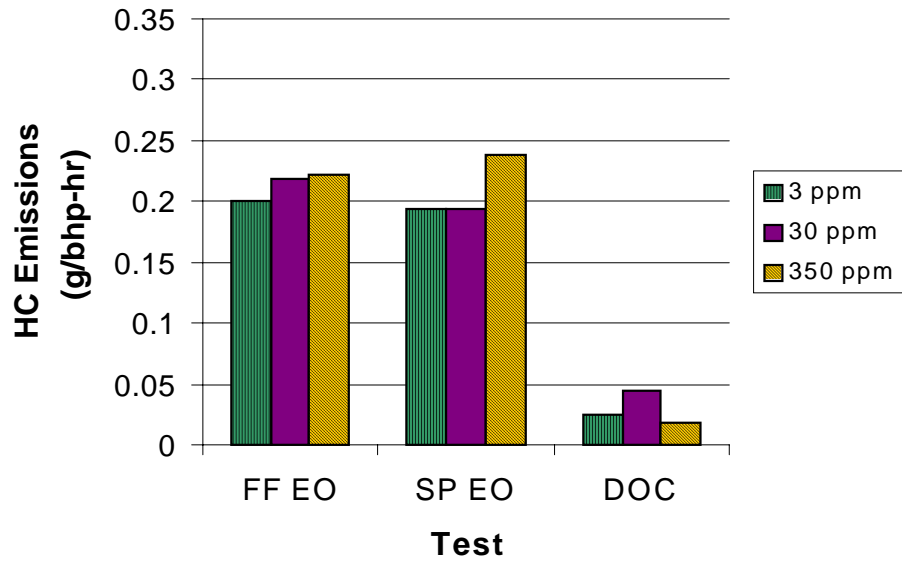


Figure D.9 Cummins FTP HC Emissions at 250 Hours



The following figures show the HC reduction efficiencies.

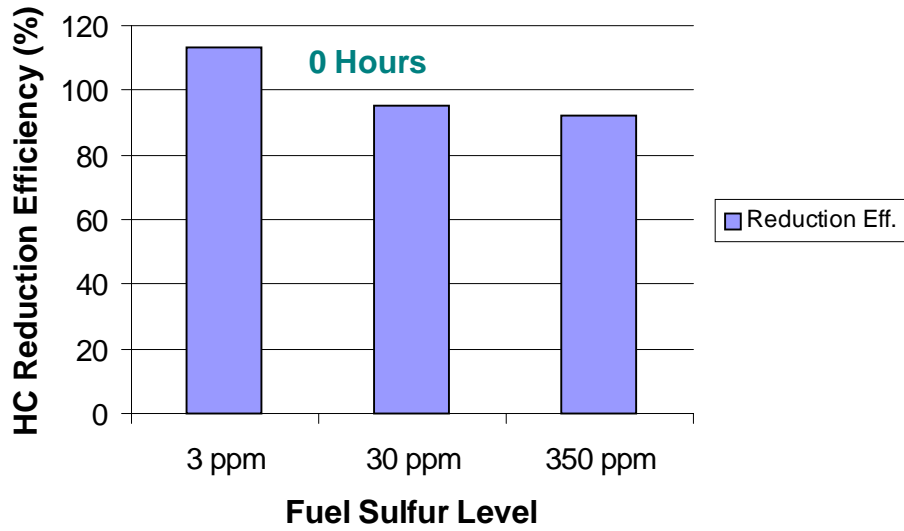


Figure D.10 Cummins FTP HC Emission Reduction Efficiency at 0 Hours

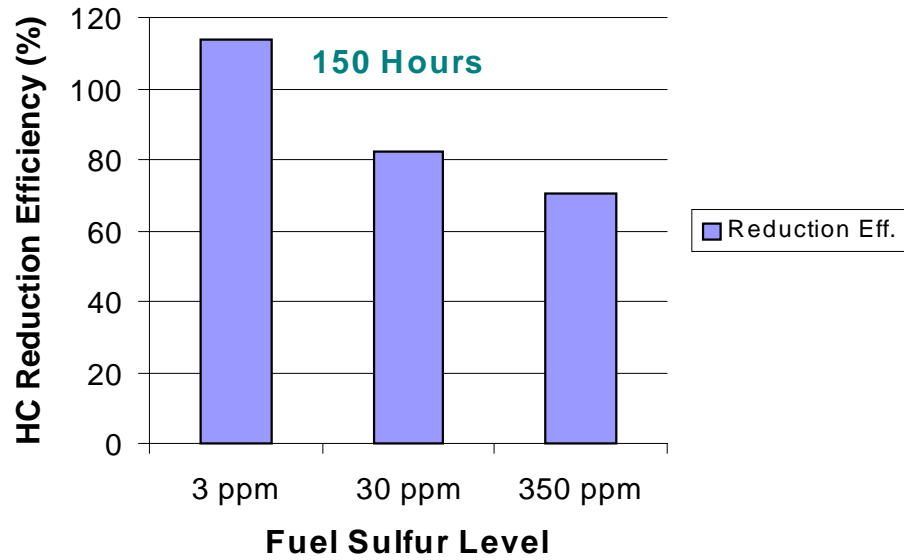


Figure D.11 Cummins FTP HC Emission Reduction Efficiency at 150 Hours

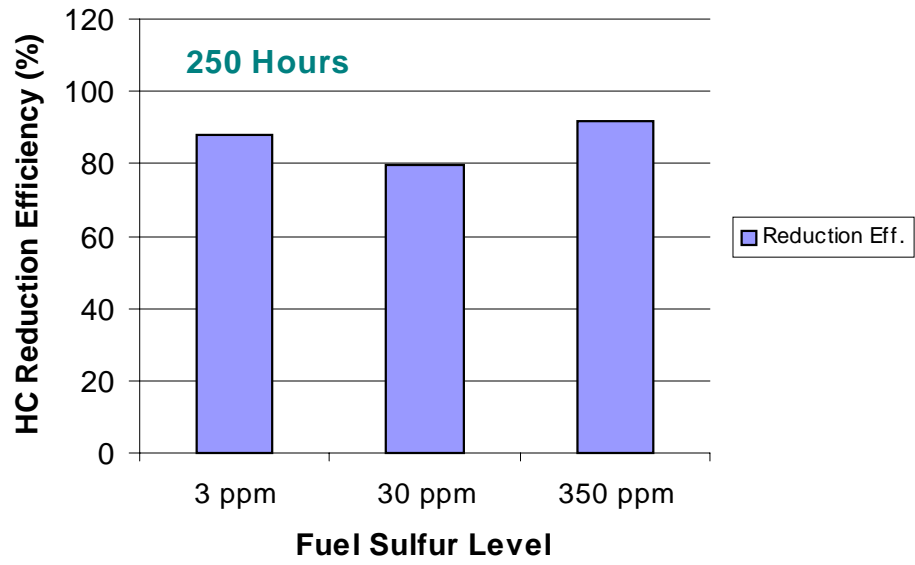


Figure D.12 Cummins FTP HC Emission Reduction Efficiency at 250 Hours

**APPENDIX E: NAVISTAR CO EMISSION RESULTS**

In the following three figures the CO emissions for each test on the various fuel sulfurs are given. By inspection, one can easily see that the DOC performed very well at reducing the CO emissions.

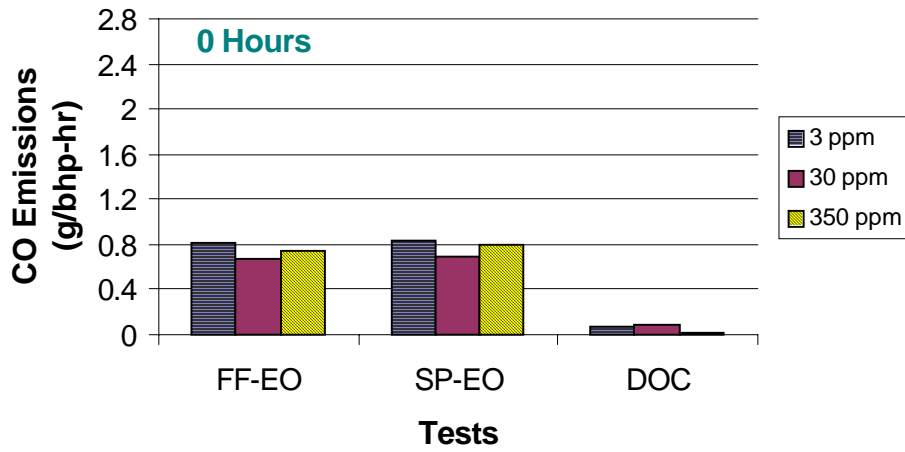


Figure E.1 Navistar FTP-75 CO Emissions at 0 Hours

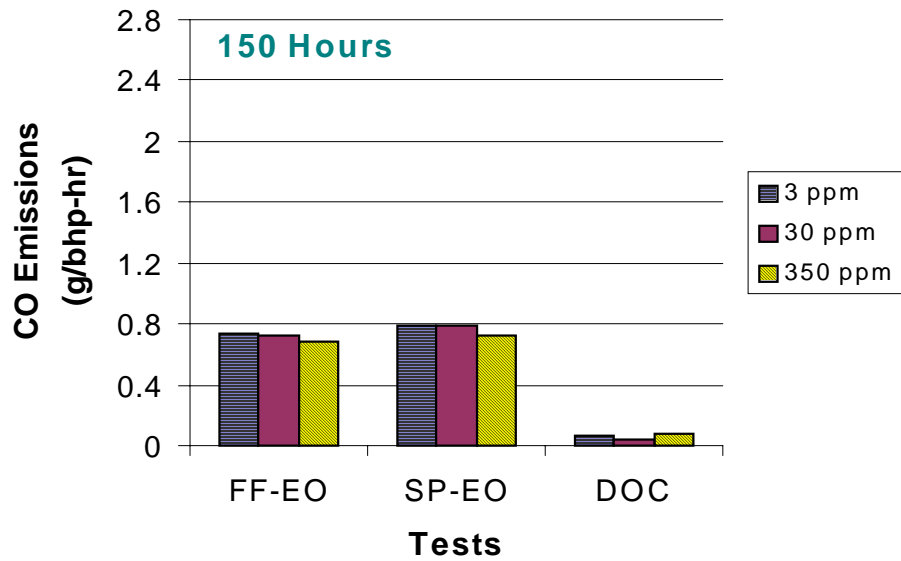


Figure E.2 Navistar FTP-75 CO Emissions at 150 Hours

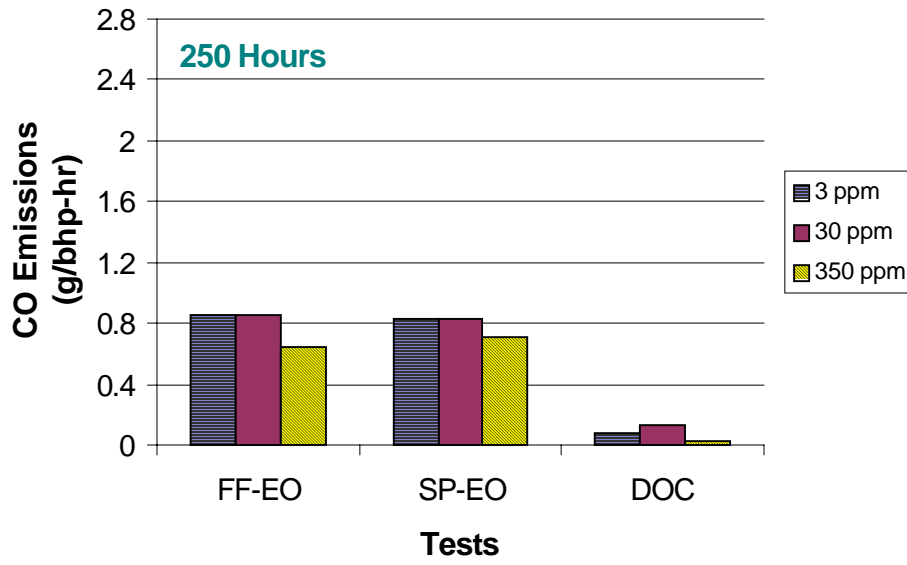


Figure E.3 Navistar FTP-75 CO Emissions at 250 Hours

The following three figures, Figure E.4, Figure E.5, and Figure E.6 show the reduction efficiencies at 0 hours, 150 hours, and 250 hours, with 3 ppm, 30 ppm, and 350 ppm fuel. All CO emission reduction efficiencies for the FTP-75 tests were between approximately 85%-100%.

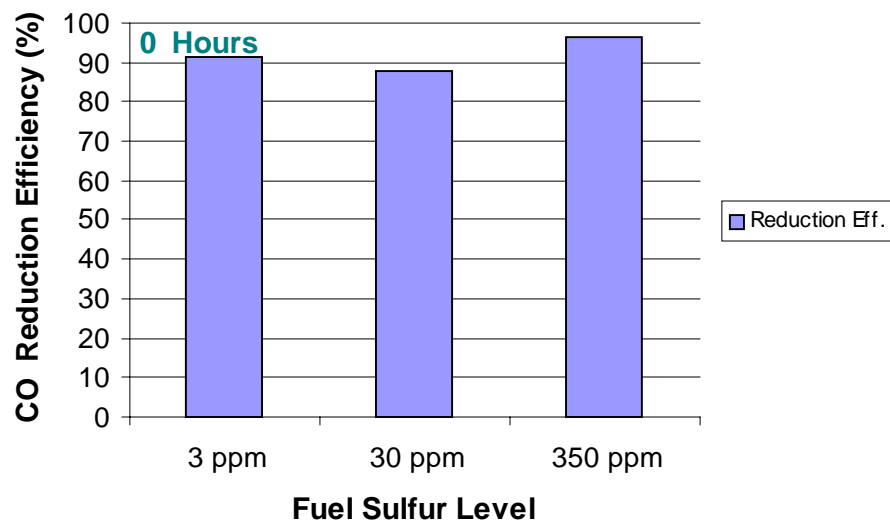


Figure E.4 Navistar FTP-75 CO Emissions Reduction Efficiency at 0 Hours

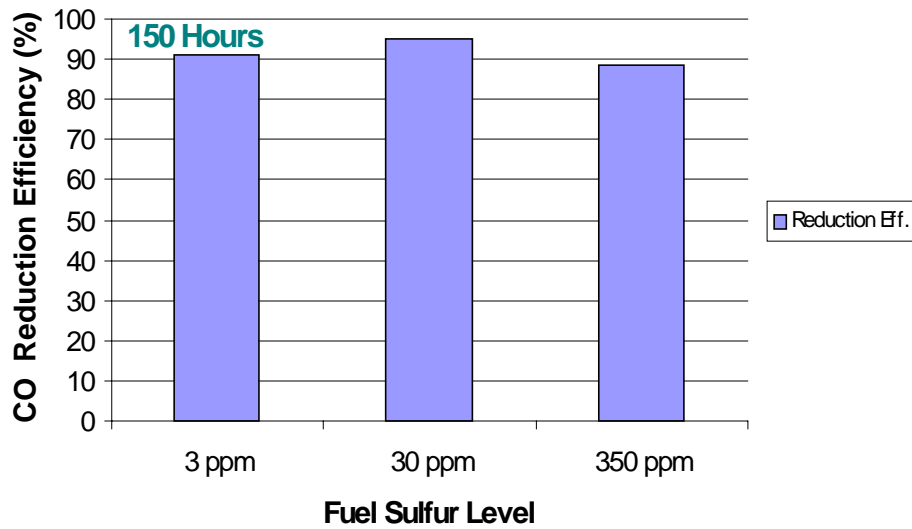


Figure E.5 Navistar FTP-75 CO Emissions Reduction Efficiency at 150 Hours

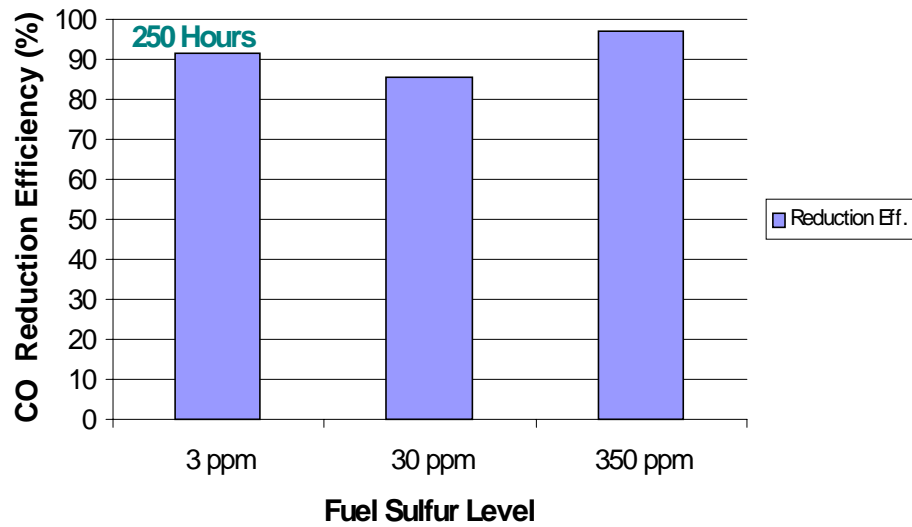


Figure E.6 Navistar FTP-75 CO Emissions Reduction Efficiency at 250 Hours

Figure E.7, Figure E.8, and Figure E.9 show the brake-specific CO emissions from the Navistar T444E engine operated on the steady state Nav-9\* tests. The CO emissions reduction efficiencies ranged from 85% to 97% for the three aging stages.

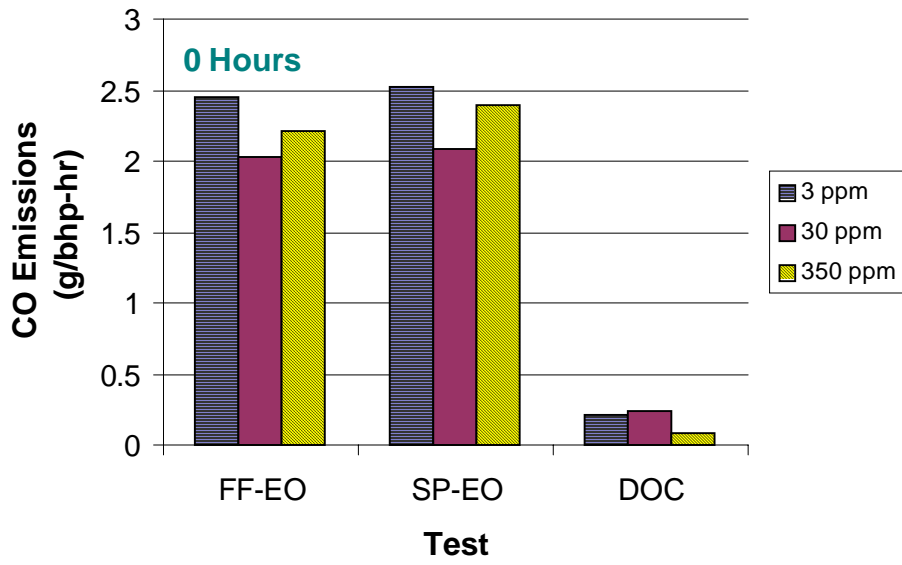


Figure E.7 Navistar Nav-9\* CO Emissions at 0 Hours

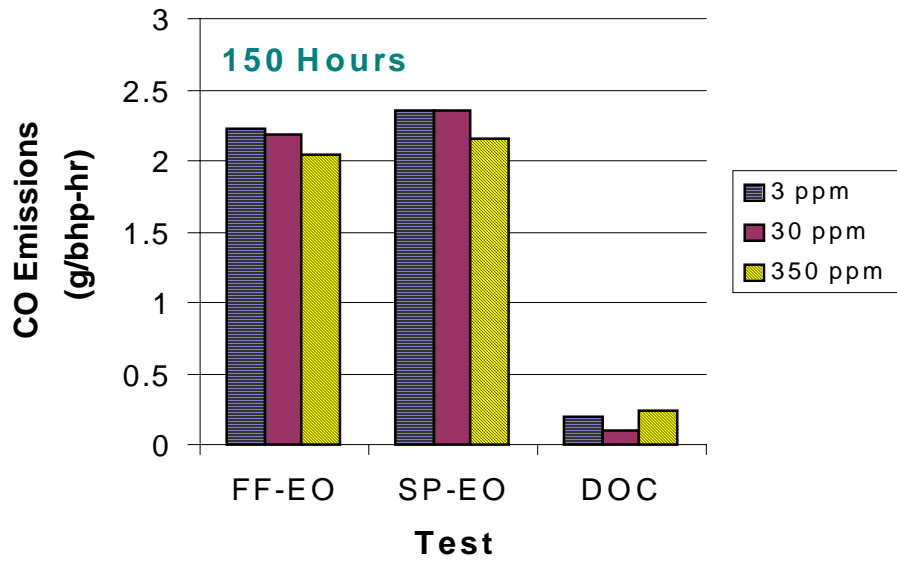


Figure E.8 Navistar Nav-9\* CO Emissions at 150 Hours

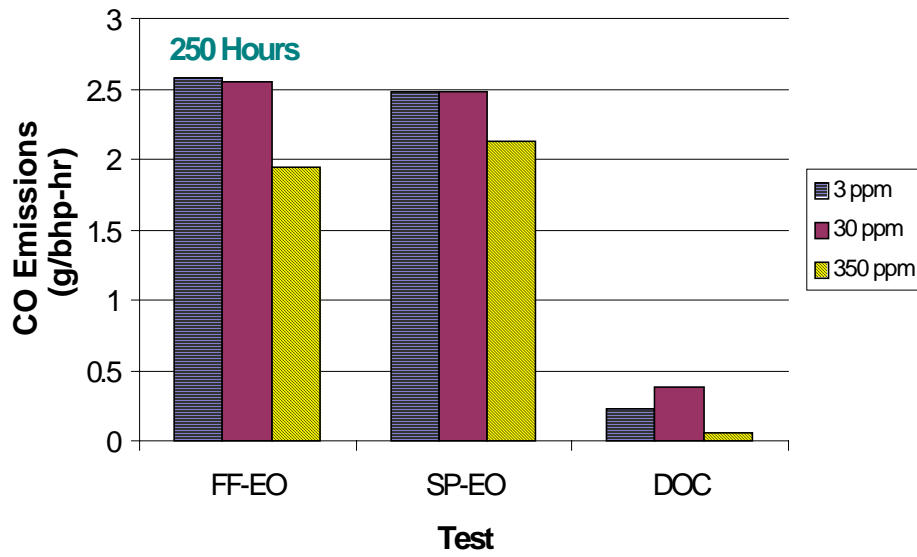


Figure E.9 Navistar Nav-9\* CO Emissions at 250 Hours

Figure E.10, Figure E.11, Figure E.12, shows the reduction efficiencies for the CO emissions from the Navistar T444E engine. The following three figures are for the steady state Nav-9\* tests.

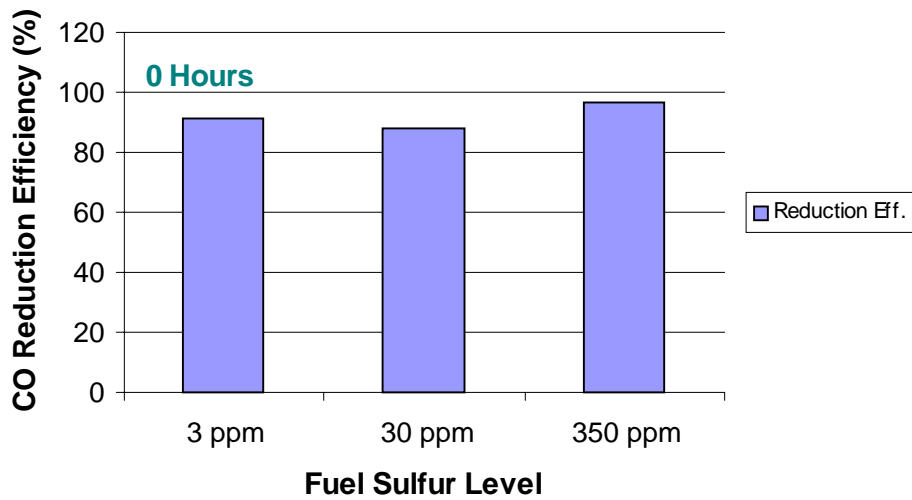


Figure E.10 Navistar Nav-9\* CO Emissions Reduction Efficiency at 0 Hours



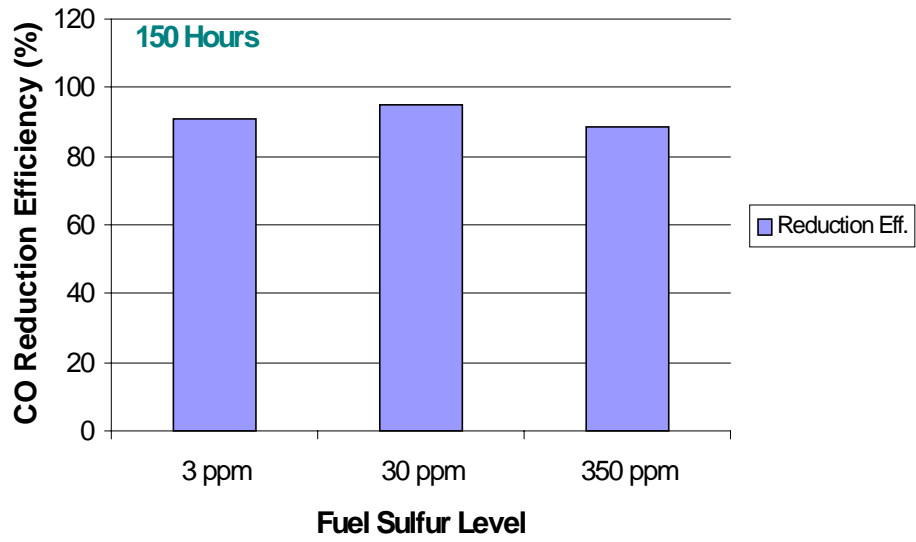


Figure E.11 Navistar Nav-9\* CO Emissions Reduction Efficiency at 150 Hours

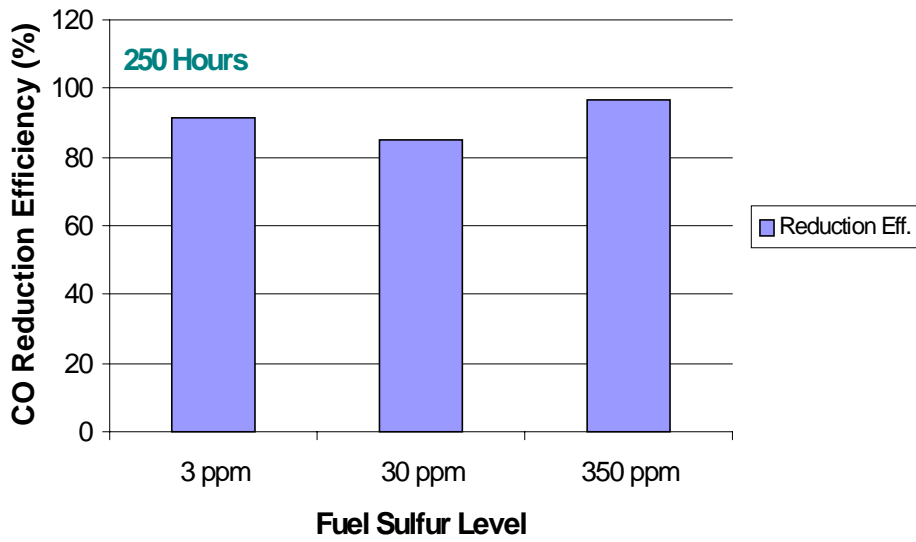


Figure E.12 Navistar Nav-9\* CO Emissions Reduction Efficiency at 250 Hours

**APPENDIX F: CUMMINS CO EMISSION RESULTS**

Figure F.1, Figure F.2, Figure F.3 all show Cummins FTP test results of CO emissions at the various aging stages.

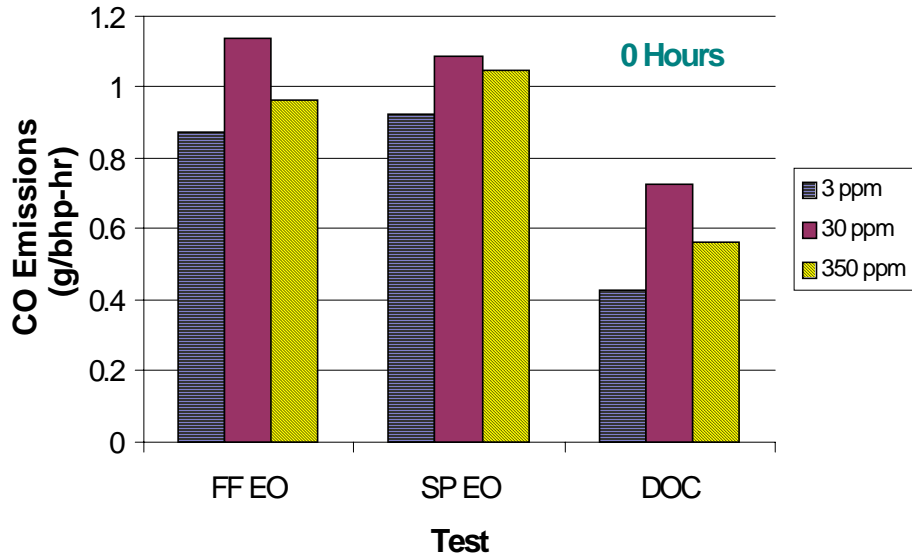


Figure F.1 Cummins FTP CO Emissions at 0 Hours

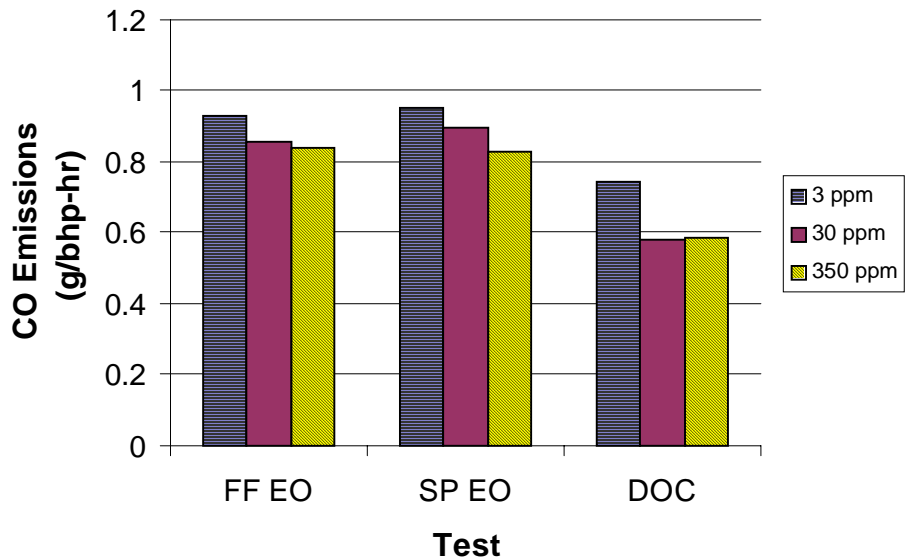


Figure F.2 Cummins FTP CO Emissions at 150 Hours

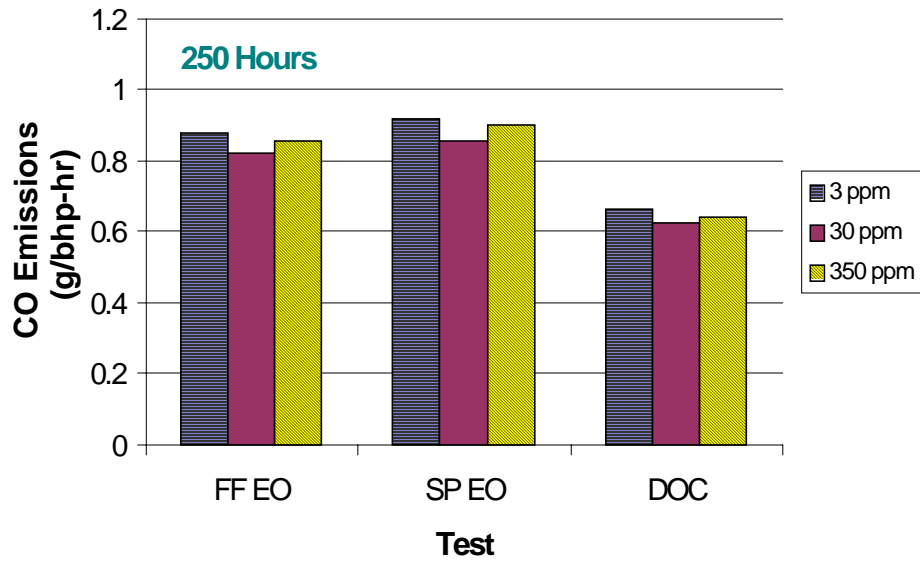


Figure F.3 Cummins FTP CO Emissions at 250 Hours

Figure F.4, Figure F.5, and Figure F.6 show the reduction efficiencies of the CO emissions from the Cummins transient FTP tests.

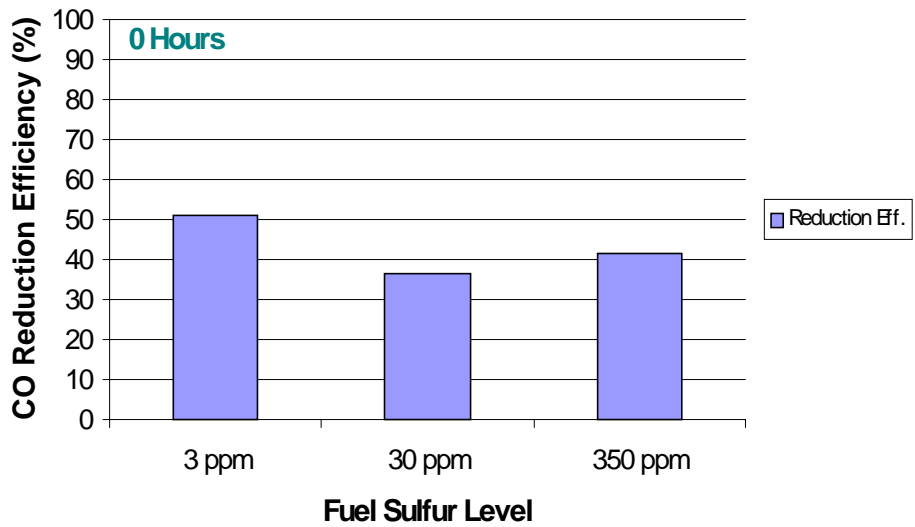


Figure F.4 Cummins FTP CO Emissions Reduction Efficiency at 0 Hours

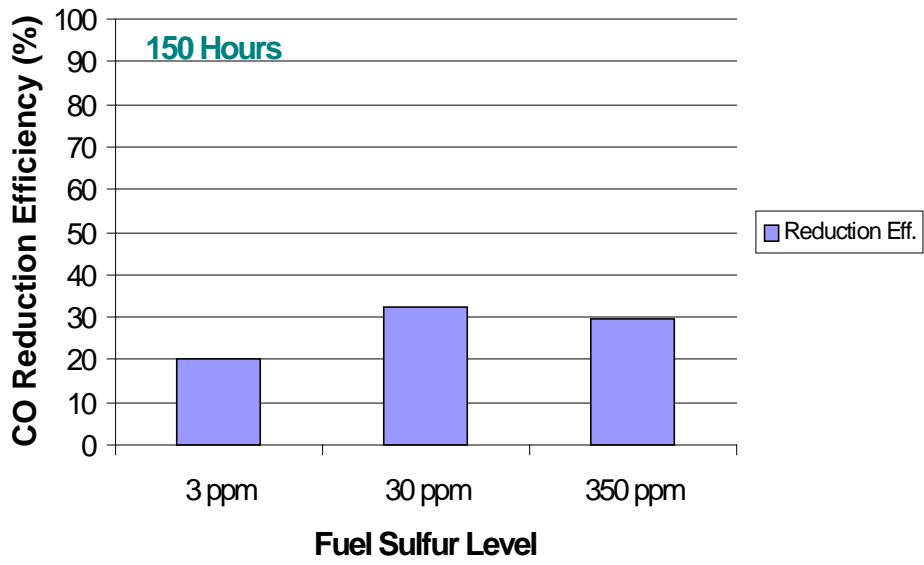


Figure F.5 Cummins FTP CO Emissions Reduction Efficiency at 150 Hours

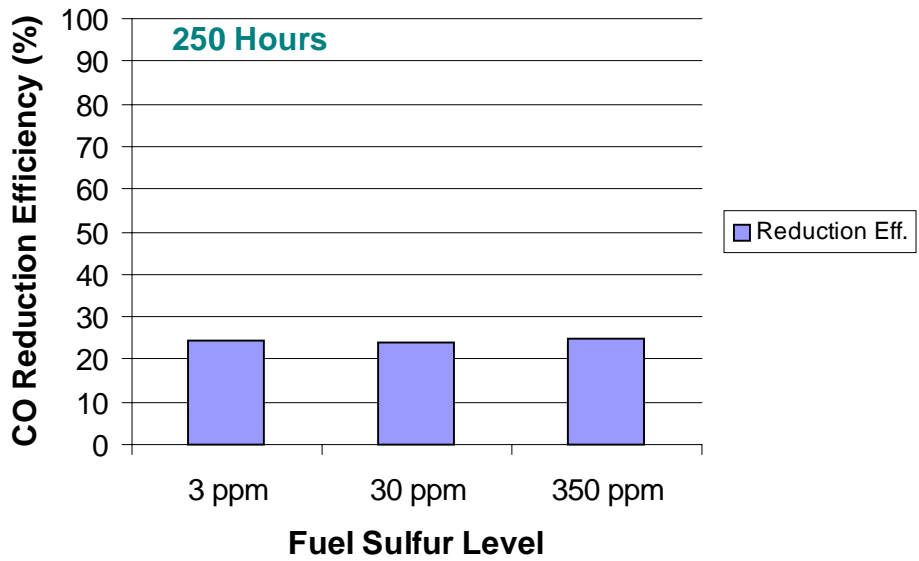


Figure F.6 Cummins FTP CO Emissions Reduction Efficiency at 250 Hours

The following three graphs, Figure F.7, Figure F.8, Figure F.9, show the CO emissions results of the Cummins steady state OICA\* tests at the 3 aging stages.

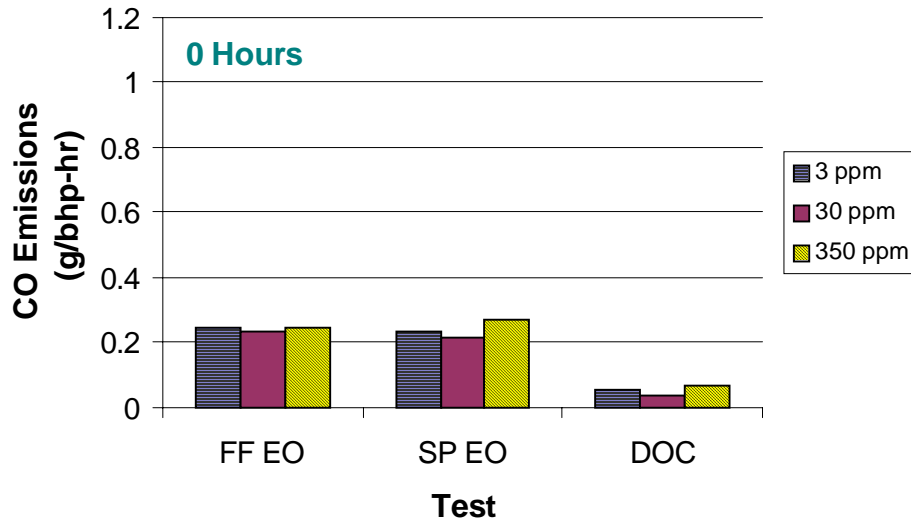


Figure F.7 Cummins OICA\* CO Emissions at 0 Hours

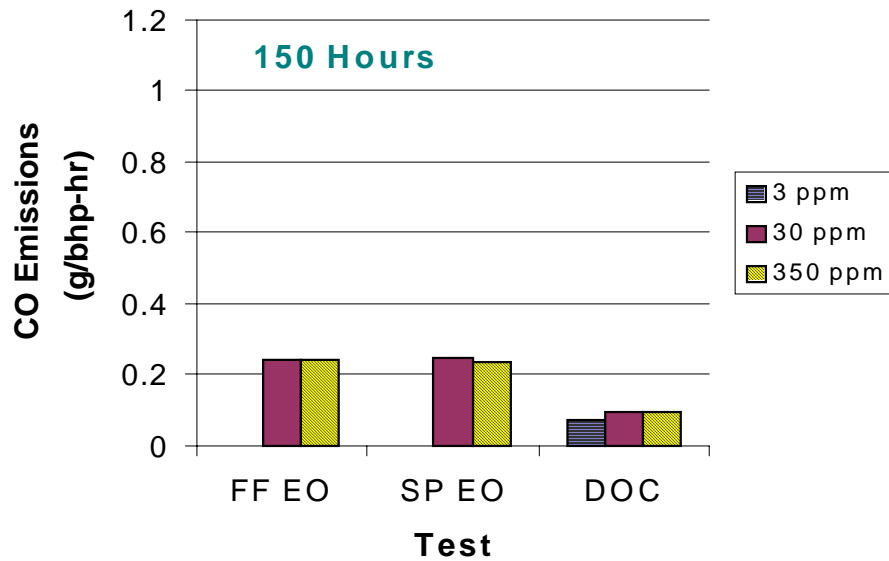


Figure F.8 Cummins OICA\* CO Emissions at 150 Hours

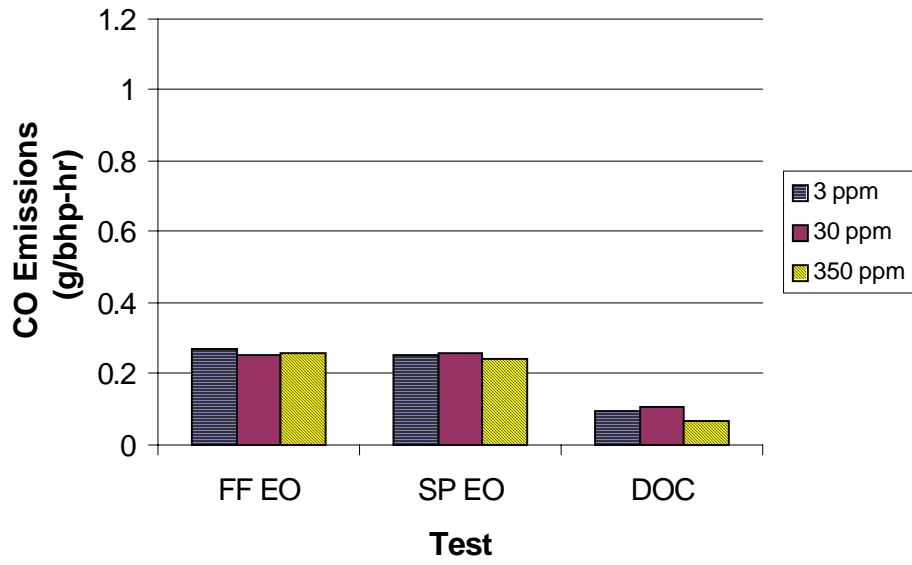


Figure F.9 Cummins OICA\* CO Emissions at 250 Hours

Figure F.10, Figure F.11, and Figure F.12, show the CO emission reduction efficiencies of the OICA\* tests with the Cummins ISM370 engine.

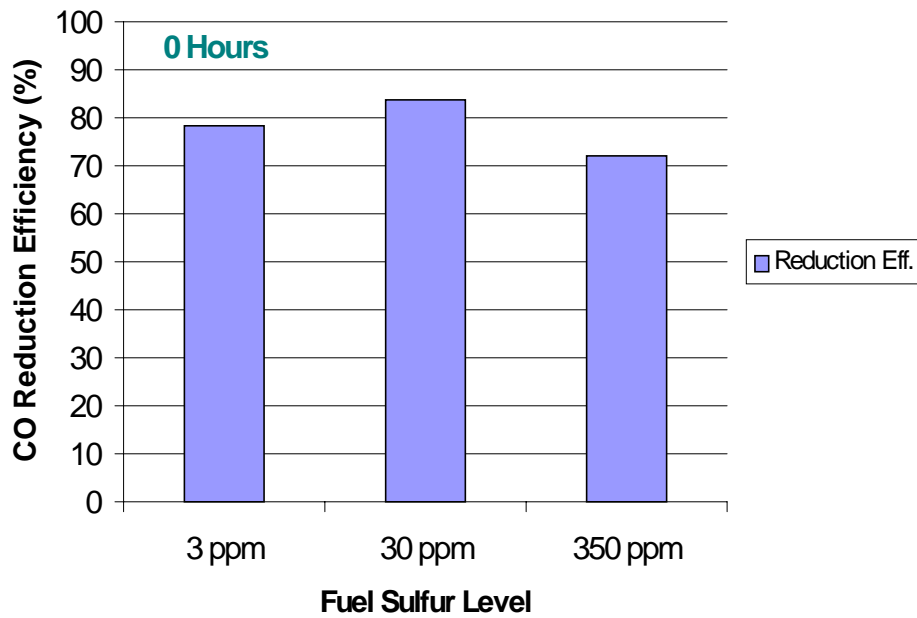


Figure F.10 Cummins OICA\* CO Emissions Reduction Efficiency at 0 Hours

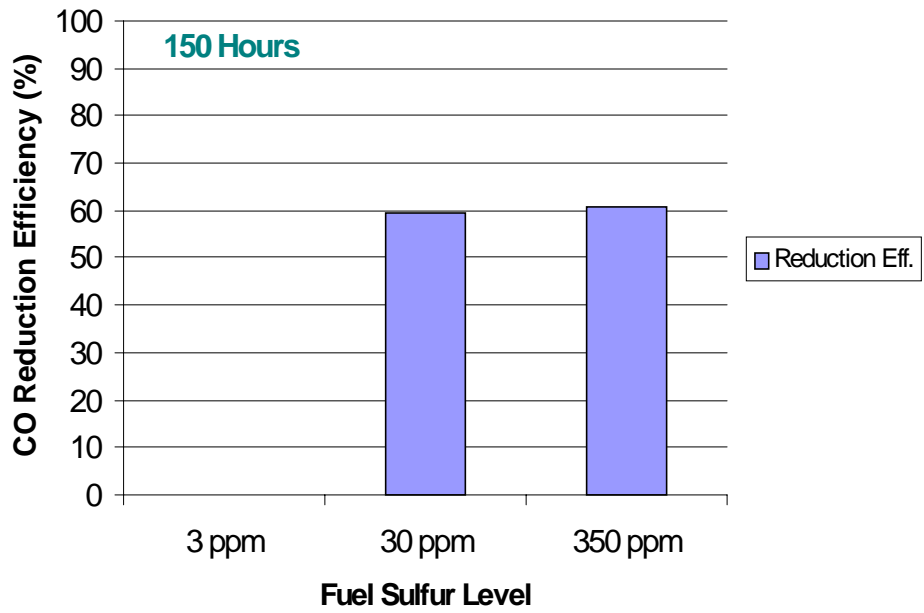


Figure F.11 Cummins OICA\* CO Emissions Reduction Efficiency at 150 Hours

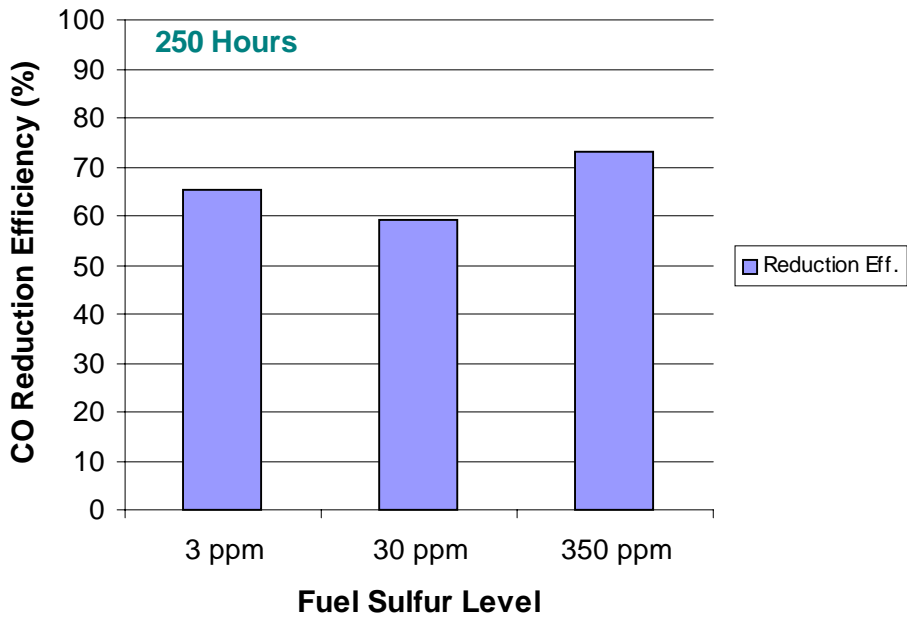


Figure F.12 Cummins OICA\* CO Emissions Reduction Efficiency at 250 Hours



## **APPENDIX G: TEST MATRIX**

Table G.1 DECSE DOC Navistar and Cummins Test Matrix

Aging Hours	Fuel Sulfur Level (ppm)				
	<10	30	350	30	150
0	EO A1 A1	EO A2	EO A4 A4	EO A4	EO A3 A3
	eo a1 a1	eo a2 a2	eo a4	eo a4 a4	eo a3 a3
50	A1	A2	A4	A4	A3
	a1 a1	a2 a2	a4 a4	a4 a4	a3 a3
150	A1	A2	A4 A4	A4	A3
	a1 a1	a2 a2	a4 a4	a4 a4	a3 a3
250	A1 A1 EO	A2 A1 EO	A4 A4 A1 EO	A4 A4 EO	A3 A3 A1 EO
	a1 a1 eo	a2 a2 a1 a1 eo	a4 a4 a1 eo	a4 a4 a1 a1 eo	a3 a3 a1 a1 eo

EO = OICA\*-13 test – engine out (total tests = 5 + 5 reps = 10)

Ai = OICA\*-13 test – post catalyst Ai (total tests = 24 + 7 reps = 31)

eo = FTP test – engine out (total tests = 5 + 5 reps = 10)

ai = FTP test – post catalyst Ai (total tests = 24 + 24 reps = 48)

**APPENDIX H: CERTIFICATES OF FUEL ANALYSIS**



# Certificate of Analysis

**PHILLIPS CHEMICAL COMPANY**  
A DIVISION OF PHILLIPS PETROLEUM COMPANY

SPECIALTY CHEMICALS  
P.O. BOX 968  
BORGER, TX 79008-0968

DATE OF SHIPMENT  
04-15-99

CUSTOMER ORDER NO.  
DE-AC36-98-GO10337

INV./REQN. NO.  
2443353

CONTAINER NO.  
TRLR #368

MFG. DATE: 03/99

0.05 DIESEL UL SULFUR TYPE 2  
9CP05L01

TESTS	RESULTS	SPECIFICATIONS	METHOD
Specific Gravity, 60/60	.8264	0.82 - 0.85	ASTM D-4052
API Gravity	39.7	35.0 - 41.0	ASTM D-1298
Sulfur, PPM	1.3	<10	ASTM D-4294
Flash Point, °F, PM	157	>125	ASTM D-93
Viscosity, cs 40C	2.5	>2.0	ASTM D-445
Cetane Index	53.5	Report	ASTM D-876
Cetane Number	45.6	42-48	ASTM D-613
<u>DISTILLATION, °F</u>			<u>ASTM D-86</u>
IBP	362.0	340-360	
5%	392.8		
10%	404.4	410-440	
20%	430.4		
30%	450.4		
40%	482.8		
50%	498.5	490-520	
60%	510.5		
70%	525.3		
80%	549.0		
90%	599.3	590-610	
95%	642.6		
EP	668.5	620-680	
Loss	0.6		
Residue	1.0		
<u>HYDROCARBON TYPE, VOL%</u>			<u>ASTM D-1319</u>
Aromatics	26.4	25 - 32	
Olefins	3.2	1 - 3	
Saturates	70.4	55 - 70	
Polynuclear Aromatics, wt%	10.5	3 - 10	
Molecular Weight	TBR	Report	Phillips
Net Heat of Combustion, btu/lb	TBR	Report	ASTM D-240
Carbon, wt%	TBR	Report	ASTM D-5291
Hydrogen, wt%	TBR	Report	ASTM D-5291
Nitrogen, wt%	TBR	Report	ASTM D-5291

RSR:jam  
04/15/99  
1024297



# Certificate of Analysis

PHILLIPS CHEMICAL COMPANY  
A DIVISION OF PHILLIPS PETROLEUM COMPANY

SPECIALTY CHEMICALS  
P.O. BOX 968  
BORDER, TX 79009-0968

DATE OF SHIPMENT  
08-13-99

CUSTOMER ORDER NO.  
JCO-9-29921-01

INV./REQN. NO.  
3110941

CONTAINER NO.  
TLR #360

MFG. DATE: 0499

## DIESEL UL SULFUR TYPE 2 9DPO5L01

<u>TESTS</u>	<u>RESULTS</u>	<u>SPECIFICATIONS</u>	<u>METHOD</u>
Specific Gravity, 60/60	826	0.82 - 0.85	ASTM D-4052
API Gravity	39.8	35.0 - 41.0	ASTM D-1298
Sulfur, PPM	3.3	<10	ASTM D-4294
Flash Point, °F, PM	157.5	>125	ASTM D-93
Pour Point, °F	-5	Report	ASTM D-97
Cloud Point, °F	-5	Report	ASTM D-2500
Viscosity, cs 40C	2.5	>2.0	ASTM D-445
Hydrogen, wt%	13.4	Report	Phillips
Carbon, wt%	86.6	Report	Phillips
Molecular weight	to be reported	Report	ASTM D-524
Net Heat of Combustion, btu/lb	18593	Report	ASTM D-3338
Gross Heat of Combustion, btu/lb	19838		
Cetane Index	53.5	Report	ASTM D-976
Cetane Number	44.4	42-48	ASTM D-813
<u>DISTILLATION, °F</u>			ASTM D-86
IBP	364.5		
5%	387.1		
10%	402.9		
15%	413.0		
20%	430.6		
30%	460.0		
40%	483.0		
50%	497.6		
60%	509.9		
70%	524.0		
80%	547.4		
90%	598.5		
95%	643.3		
EP	661.7		
Loss	0.45		
Residue	1.2		
<u>HYDROCARBON TYPE, VOL%</u>			ASTM D-1319
Aromatics	26.9	25 - 32	
Diolefins	2.3	1 - 3	
Saturates	70.8	55 - 70	
Polynuclear Aromatics, wt%	9.8	3 - 10	

DGO:jam  
08/13/99  
1024297



# Certificate of Analysis

**PHILLIPS CHEMICAL COMPANY**  
A DIVISION OF PHILLIPS PETROLEUM COMPANY

SPECIALTY CHEMICALS  
P.O. BOX 968  
BORGER, TX 79008-0968

DATE OF SHIPMENT  
11-13-99

CUSTOMER ORDER NO.  
JCO-9-29021-01

INV. REQ. NO.  
3648897

CONTAINER NO.  
TRLR #380

MFG. DATE: 11/99

**DIESEL UL SULFUR TYPE 2 (30 PPM)**  
**9KP05L01**

TESTS	RESULTS	SPECIFICATIONS	METHOD
Specific Gravity, 60/60	.8256	Report	ASTM D-4052
API Gravity	39.68	40 Max	ASTM D-1298
Sulfur, PPM	25	Report	ASTM D-4045
Flash Point, °F, PM	157	Report	ASTM D-93
Pour Point, °F	-5	Report	ASTM D-97
Cloud Point, °F	-5	Report	ASTM D-2500
Viscosity, cs @40C	2.50	Report	ASTM D-445
Carbon, wt%	86.2	Report	Phillips
Hydrogen, wt%	13.8	Report	Phillips
Net Heat of Combustion BTU/LB	18540	Report	ASTM D-3338
Cetane Index	53.4	Report	ASTM D-976
Cetane Number	43.8	40 Min	ASTM D-613
<b>DISTILLATION, °F</b>			<b>ASTM D-86</b>
IBP	351.6		
5%	389.2		
10%	401.7		
20%	427.8		
30%	457.9		
40%	481.9		
50%	496.8		
60%	508.8		
70%	522.9		
80%	546.3		
90%	598.0		
95%	641.8		
EP	684.0		
Loss	0.8		
Residue	1.1		
<b>HYDROCARBON TYPE, VOL%</b>			
Aromatics	26.2	Report	ASTM D-1319
Olefins	2.6		
Saturates	76.2		
Aromatics, wt%	29.8		
Polynuclear Aromatics, wt%	10.2		

OGD:teh  
11/13/99  
1024309



# Certificate of Analysis

**PHILLIPS CHEMICAL COMPANY**  
A DIVISION OF PHILLIPS PETROLEUM COMPANY

SPECIALTY CHEMICALS  
P.O. BOX 968  
BORGER, TX 79008-0968

DATE OF SHIPMENT  
09-28-99

CUSTOMER ORDER NO.  
JC0-9-29021-01

INV./REQN. NO.  
3375082

CONTAINER NO.  
TRLR #366

MFG. DATE: 05/99

**DIESEL UL SULFUR TYPE 2**  
**9/PP6L91**

TESTS	RESULTS	SPECIFICATIONS	METHOD
Specific Gravity, 60/60	.8258	0.82 - 0.85	ASTM D-4062
Sulfur, PPM	29	27 - 33	ASTM D-4294
Flash Point, °F, PM	157	>125	ASTM D-93
Pour Point, °F	-5	Report	ASTM D-97
Cloud Point, °F	-5	Report	ASTM D-2500
Viscosity, cs 40C	2.5	>2.0	ASTM D-445
Cetane Index	53.4	Report	ASTM D-976
Cetane Number	43.8	42-48	ASTM D-813
Net Heat of Combustion, btu/lb.	18540	Report	ASTM D-3343
Carbon, wt%	86.4	Report	ASTM D-5291
Hydrogen, wt%	13.6	Report	ASTM D-5291
Nitrogen, wt%	<0.15	Report	ASTM D-5291
<b>DISTILLATION, °F</b>			<b>ASTM D-88</b>
IBP	349.9	340-360	
5%	385.9		
10%	403.7	410-440	
20%	434.6		
30%	463.0		
40%	484.4		
50%	498.2	490-520	
60%	509.8		
70%	523.9		
80%	546.3		
90%	593.6	590-610	
95%	635.4		
EP	665.8	620-680	
Loss	0.1		
Residue	1.0		
<b>HYDROCARBON TYPE, VOL%</b>			<b>ASTM D-1319</b>
Aromatics	26.2	25 - 32	
Olefins	2.6	1 - 3	
Saturates	71.2	55 - 70	
Polynuclear Aromatics, wt%	10.2	3 - 10	ASTM D-5186

DGD:jam  
09/28/99  
1024297



# Certificate of Analysis

**PHILLIPS CHEMICAL COMPANY**  
A DIVISION OF PHILLIPS PETROLEUM COMPANY

SPECIALTY CHEMICALS  
P.O. BOX 988  
BORGER, TX 79008-0988

DATE OF SHIPMENT  
01-07-2000

CUSTOMER ORDER NO.  
JCO-9-29021-01

INV./REQN. NO.  
3840835

CONTAINER NO.  
TRLR #59-83006

**0.05 SULFUR DIESEL FUEL TYPE 2**  
**9LP05202**

<u>TESTS</u>	<u>RESULTS</u>	<u>SPECIFICATIONS</u>	<u>METHOD</u>
Specific Gravity, 60/60	.8286	Report	ASTM D-4052
API Gravity	39.68	40 Max.	ASTM D-1298
Sulfur, ppm	335	320 - 380	HOUSTON ATLAS
Flash Point, °F, PM	157.5	>125	ASTM D-93
Pour Point, °F	-5	Report	ASTM D-2500
Cloud Point, °F	-5	0 Max.	ASTM D-2500
Viscosity, cs 40C	2.6	>2	ASTM D-445
Carbon, wt%	86.6	Report	
Hydrogen, wt%	13.4	Report	ASTM D-3338
Net Heat of Combustion, BTU/lb.	18549	Report	ASTM D-976
Cetane Index	53.55	Report	ASTM D-613
Cetane Number	44.4	42 - 48	
<b><u>DISTILLATION, °F</u></b>			<b>ASTM D-86</b>
IBP	354.5		
5%	387.1		
10%	402.9		
20%	430.6		
30%	450.0		
40%	483.0		
50%	487.6		
60%	509.9		
70%	524.0		
80%	547.4		
90%	598.5		
96%	643.3		
EP	681.7		
Loss	0.45		
Residue	1.2		
<b><u>HYDROCARBON TYPE, VOL%</u></b>			<b>ASTM D-1319</b>
Aromatics	26.9	Report	
Olefins	2.3		
Saturates	70.8		
Polynuclear Aromatics, wt%	9.8		ASTM D-5186-96

BJS:jam  
01/07/00  
1024295





# Certificate of Analysis

**PHILLIPS CHEMICAL COMPANY**  
A DIVISION OF PHILLIPS PETROLEUM COMPANY

SPECIALTY CHEMICALS  
P. O. BOX 969  
BORGER, TX 79008-0968

DATE OF SHIPMENT  
11-13-89

CUSTOMER ORDER NO.  
JCO-9-25021-01

INV/REQN. NO.  
3548897

CONTAINER NO.  
TRLR #380

MFG. DATE: 11/89

**DIESEL UL SULFUR TYPE 2 (350 PPM)**  
**9KP36L02**

<u>TESTS</u>	<u>RESULTS</u>	<u>SPECIFICATIONS</u>	<u>METHOD</u>
Specific Gravity, 60/60	8266	Report	ASTM D-4052
API Gravity	39.68	40 Max	ASTM D-1298
Sulfur, PPM	361	Report	ASTM D-4045
Flash Point, °F, PM	157	Report	ASTM D-63
Pour Point, °F	-5	Report	ASTM D-67
Cloud Point, °F	-5	Report	ASTM D-2500
Viscosity, cs-40C	2.50	Report	ASTM D-445
Carbon, wt%	86.2	Report	Phillips
Hydrogen, wt%	13.8	Report	Phillips
Net Heat of Combustion BTU/LB	18540	Report	ASTM D-3338
Cetane Index	53.4	Report	ASTM D-876
Cetane Number	43.8	40 Min	ASTM D-613
			ASTM D-86
<b><u>DISTILLATION, °F</u></b>			
IBP	351.6		
5%	389.2		
10%	401.7		
20%	427.8		
30%	457.9		
40%	481.9		
50%	496.8		
60%	508.8		
70%	522.9		
80%	546.3		
90%	568.6		
95%	641.6		
EP	664.0		
Loss	0.8		
Residue	1.1		
<b><u>HYDROCARBON TYPE, VOL%</u></b>			
Aromatics	26.2	Report	ASTM D-1319
Olefins	2.6		
Saturates	76.2		
<b><u>HYDROCARBON TYPE, WT%</u></b>			
Aromatics, wt%	29.8		
Polynuclear Aromatics, wt%	10.2		

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