Effects of a Zeolite-Selective Catalytic Reduction System on Comprehensive Emissions from a Heavy-Duty Diesel Engine

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ABSTRACT
The effects of a zeolite urea-selective catalytic reduction (SCR) aftertreatment system on a comprehensive spectrum of chemical species from diesel engine emissions were investigated in this study. Representative samples were collected with a newly developed source dilution sampling system after an aging process designed to simulate atmospheric dilution and cooling conditions. Samples were analyzed with established procedures and compared between the measurements taken from a baseline heavy-duty diesel engine and also from the same engine equipped with the exhaust aftertreatment system. The results have shown significant reductions for nitrogen oxides (NOx), carbon monoxide, total hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and organic carbon (OC) emissions. Additionally, less significant yet notable reductions were observed for particulate matter mass and metals emissions. Furthermore, the production of new species was not observed with the addition of the zeolite urea-SCR system joined with a downstream oxidation catalyst.

INTRODUCTION
Diesel engines are often celebrated for their higher fuel efficiency when compared with gasoline powered engines, which corresponds with decreased energy consumption and reduced carbon dioxide (CO2) emissions, a primary contributor to global warming. However, emissions from diesel engines can have less desirable effects on human health and the environment.1,2 The response to diesel engine emissions has been increasingly stringent regulations set forth worldwide. Often, diesel engine research emphasizes nitrogen oxides (NOx) and particulate matter (PM) because of their importance as criteria air pollutants and the difficulty faced in controlling their emissions. PM and NOx have been shown to have detrimental effects on air quality and health ailments for humans. Specifically, NOx is capable of reacting with other elements in the atmosphere thus contributing to acid rain, forming ozone, inhibiting plant growth, irritating the lungs, causing bronchitis and pneumonia, and lowering resistance to respiratory infections.2–4

There are various aftertreatment technologies for controlling NOx emissions from lean-combustion diesel engines, including exhaust gas recirculation, lean NOx catalysis, selective catalytic reduction (SCR), and NOx adsorption. SCR systems have demonstrated high efficiencies for reducing NOx emissions under steady-state conditions and have been used for years on stationary emission sources. Additionally, SCR systems are tolerant to higher sulfur content and have recently been adapted by several engine manufacturers for use in mobile emission sources to meet stringent NOx regulations.2

A variety of SCR catalysts are available, including precious metal catalysts such as platinum (Pt), base metal catalysts such as vanadium oxide(V2O5)/titanium dioxide (TiO2), and zeolite catalysts. In general, urea-SCR systems use ammonia (NH3), generated through the evaporation, pyrolysis, and hydrolysis of urea solution, to react selectively with NOx, producing elemental nitrogen (N2) and water (H2O) in excess amounts of oxygen according to the reactions described in eqs 1 and 2.5

\[
4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1)
\]

\[
4\text{NH}_3 + 2\text{NO}_2 + \text{O}_2 \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O} \quad (2)
\]

There are undesirable reactions that have been known to occur during SCR processes. For example, eq 3 shows the production of nitrous oxide (N2O), a greenhouse gas, and eq 4 shows the reaction of NH3 with nitrogen dioxide (NO2) to produce the explosive gas ammonium nitrate (NH4NO3).

\[
2\text{NH}_3 + \text{O}_2 \rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O} \quad (3)
\]

\[
2\text{NH}_3 + 2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{NO}_3 + \text{NH}_4\text{NO}_2 \quad (4)
\]
However, both of these reactions can be minimized by optimizing the urea dosing rate and exhaust gas temperature range.\textsuperscript{5}

Despite SCRs popularity, little is known about its effects on the emissions of non-criteria species such as those produced during engine wear and in-cylinder combustion. Diesel fuel has been shown to contain aliphatic hydrocarbons that consist of 10–25 carbon atoms. Additionally, these compounds and their byproducts have been found in diesel engine emissions.\textsuperscript{6} Another potential source of contaminants is heavy molecular \textit{n}-alkanes, which may be produced through the thermal breakdown of \textit{n}-alkyl hydrocarbons from refined lubrication oil.\textsuperscript{7}

To fully examine the viability of implementing SCR exhaust aftertreatment systems for mobile applications, an analysis of the SCR systems’ effects upon the full spectrum of diesel engine emissions is necessary. Some of the non-criteria species found in the emissions from diesel engines are included on the U.S. Environmental Protection Agency’s (EPA) list of mobile source air toxics (MSATs), along with several polycyclic aromatic species identified as polycyclic organic matter (POM).\textsuperscript{8,9} Listed MSATs include volatile organic compounds, metals, PM, and diesel exhaust organic gases (DEOGs). Included within these compounds are polycyclic aromatic hydrocarbons (PAHs) that have been shown to cause cancer, DNA damage, and genetic mutations, which can result in serious disease or even death.\textsuperscript{2,8} These compounds have seldom been accounted for in diesel engines that utilize SCR exhaust aftertreatment systems.

This study analyzes the effects of a zeolite-SCR system with a downstream oxidation catalyst on diesel emissions using samples collected with a source dilution sampling (SDS) system as described by Liu et al.\textsuperscript{10} Representative samples were collected after the exhaust gas had undergone an aging process designed to simulate atmospheric dilution and cooling conditions. An established laboratory using well-defined procedures analyzed the samples. A comparison between the emissions of a baseline heavy-duty diesel engine with the emissions of the same engine equipped with a zeolite urea-SCR aftertreatment system will be made to evaluate the effects of the SCR system upon the emissions of a comprehensive spectrum of chemical species.

**EXPERIMENTAL METHODS**

**Fuel, Lubrication Oil, and Test Engine**

A 10.8-L diesel engine (2001 model year) with an inline-six cylinder configuration was used for testing. The engine was capable of producing a maximum torque of 1967 Nm (1450 ft-lb) at 1200 rpm and a maximum power of 325 kW (435 hp) at 1600 rpm with the speed and load being simulated by a direct-current dynamometer. The test engine was operated both with and without the addition of a zeolite-SCR system.

The lubrication oil used for this study was Shell Rotella T 15W-40 and the fuel was Chevron Phillips Low Sulfur Certified No. 2 Diesel. Chemical analysis of the test fuel revealed a cetane number of 47, a sulfur content of 308.5 ppm, a PM content of 0.1 mg/L, and a composition of 29.5% aromatics. Although the sulfur content of the test fuel was higher than is typically seen in diesel fuel sold in the United States, diesel fuels with higher sulfur contents are being used in many countries where SCR technology may be implemented. Therefore, this study was conducted with constant sulfur content and the fuel was viewed only as a source of energy and pollutants.

**Zeolite-SCR Catalyst**

A zeolite urea-SCR system was used in this study to analyze the effects of a SCR system on the emissions from a heavy-duty diesel engine. There are several benefits to using a zeolite-based catalyst. For example, zeolite-SCR systems are capable of operating up to 600 °C, a temperature commonly seen during diesel particulate filter regeneration, whereas Pt and \textit{V}_2\text{O}_5 catalysts have maximum operating temperatures of 250 °C and 450 °C, respectively.\textsuperscript{5} Additionally, because of their selectivity, the conversion efficiencies of zeolite-catalysts increase with increasing temperature, unlike precious-metal-based catalysts, which often have a narrow range of operating temperatures.\textsuperscript{5} A further concern for the use of \textit{V}_2\text{O}_5 catalysts is the issues associated with their disposal. The dust from vanadium catalysts can act as an irritant, causing problems with respiration.\textsuperscript{11}

The NO\textsubscript{x} emission levels were mapped from previous engine data on the basis of the engine load, speed, and air-to-fuel ratio. The data were fed to an electronic control unit (ECU) that was then used to regulate the urea dosing rate via a control valve. A NO\textsubscript{x} sensor downstream of the SCR system was installed to monitor NO\textsubscript{x} emission levels. It should be noted that the dosing response time was not well optimized in this test setup to counter the rapid changes in engine speed and load during transient operation, which may have led to lower NO\textsubscript{x} reduction efficiencies.

**Source Sampling System**

The samples required for chemical speciation were collected via the SDS system utilizing a full-partial-full source sampling method to achieve representative sampling under transient operating conditions as described in the literature (see Figure 1).\textsuperscript{10} The components of the system included a constant volume system-critical flow venturi (CVS-CFV) primary full-dilution tunnel, a secondary microdiluter, a residence time chamber (RTC), and an assortment of sampling trains that were utilized for the collection of PM, volatile and semi-volatile organic, and gas-phase samples. Dilution air entering the tunnel was purified using pre-, activated carbon, and high-efficiency particulate air (HEPA) filters before being mixed thoroughly by turbulent conditions with the full engine exhaust gas flow. A sample of the diluted exhaust was isokinetically extracted from the CVS-CFV tunnel and was piped through the secondary microdiluter to add further dilution air to the exhaust sample and lower their collective temperature to ambient levels. The full gas sample was then directed to the RTC to be collected onto substrates by isokinetic sampling.\textsuperscript{10}

For collection of the other species of interest, a RTC was used as described in the literature and was calibrated for a residence time of 30 sec to age the samples and to allow them to be homogeneously mixed and distributed.\textsuperscript{10} Eight individual sampling trains were located in the sampling section of the RTC and were spaced at even intervals to ensure uniform and simultaneous sample collection.
from multiple ports. The sampling train probes were oriented to provide isokinetic sampling and the edges were sharpened.10 Samples were collected using baked quartz filters (47-mm diameter, Pall Corp.), polytetrafluoroethylene (PTFE) membrane filters (47-mm diameter, Pall Corp.), polyurethane foam (PUF) cartridges (51-mm diameter by 75-mm length, SKC Inc.), thermal desorption (TD) tubes (CDS Analytical), and dinitrophenylhydrazine (DNPH) cartridges (Waters Corporation) as described by Liu et al.10 All PM samples were preclassified through fine PM (PM2.5) cyclones. Additionally, fractional samples of the flow from the engine tailpipe and from the RTC were piped to a Horiba gas analyzer bench for analysis of NOx, carbon monoxide (CO), total hydrocarbon (THC), oxygen (O2), and CO2 concentrations. The raw and diluted concentrations of NOx and CO2 were used to calibrate the total dilution ratios of the SDS system.

Test Procedure
Before testing, the engine underwent 2 hr of warm-up by running at ISO mode 8 (50% load and 1313 rpm).12 The engine was then turned off and blank samples were collected to analyze the possibility for contamination from handling and dilution air. During testing, the engine was operated under the transient Federal Test Procedure (FTP) heavy-duty cycles.8 The FTP cycle runs for 1200 sec and consists of four segments in series designed to simulate real-world traffic conditions commonly seen in New York and Los Angeles. At least three sets of samples were collected for each test configuration, with and without the SCR system, to determine the sample variation. Sensors were installed to monitor pressure, temperature, and humidity to ensure the stability of the measurement conditions.10 After each test cycle, handling and dilution air blanks were once again collected. Additionally, background blanks were placed in the testing room for the entire test duration each day to check for background contamination. Upon completing the testing, samples were immediately placed into a temperature-controlled freezer for preservation. After all samples were collected, they were packaged with blue-ice in an insulated box and transported to the Wisconsin State Laboratory of Hygiene (WSLH) for analysis. At this time, transportation blanks were included with the samples to test for contamination during the transportation process.

RESULTS AND DISCUSSION
Probable Emission Sources
There are several potential sources for the chemical species found in diesel engine emissions including fuel or lubrication oil content, engine wear, incomplete combustion, catalytic reactions, or formation during the combustion process. Fuel sulfur content is known to have dramatic effects on the emissions of sulfur dioxide (SO2), sulfate ion, and sulfur particles and can also affect the combustion process within the engine, which is known to have a significant effect upon other chemical species emissions.2,13 Additionally, diesel fuel contains aliphatic hydrocarbons with 10–25 carbon atoms that have been found in diesel emissions in the past.6 Trace metal emissions have been shown to derive from their presence in the engine lubrication oil as well as a possible contribution from engine wear.13–15

Incomplete combustion within the engine also contributes a significant number of compounds to engine emissions.15 Hydrocarbons present in diesel emissions, such as PAHs and other organic compounds, are known to exist partially because of incomplete combustion of fuel hydrocarbons or formation during the combustion process.2,15,16 Additionally, some of these compounds such as heavy molecular n-alkanes may be attributed to the thermal alteration of n-alkyl hydrocarbons at combustion temperatures of greater than 250 °C.7 The fact that these species are dependent upon the combustion process means that their emission levels can also be affected by fuel composition or engine operating conditions as described by Kweon et al.17 Furthermore, catalytic reactions in the aftertreatment system may have an effect upon the emissions of chemical species.
Criteria Air Pollutant Emissions

PM samples were preclassified using PM$_{2.5}$ cyclones before being collected by filtering a volume of diluted exhaust gas. The PM mass was quantified by the WSLH, where PTFE membrane filters were conditioned and weighed in a climate-controlled room that utilized a filter-handling robot and an electrostatic free environment to achieve the most accurate measurements possible. The exposed filter measurement was compared with the weight of the filter before sample collection to determine the net mass of PM emissions. PM mass measurements showed a reduction of approximately 25% of PM emissions from a SCR-equipped engine relative to a baseline measurement from the same engine equipped with no exhaust aftertreatment system. The majority of the PM mass reduction can be attributed to the reduction of organic matter (OM), specifically organic carbon (OC), which would normally adsorb onto the particle-phase compounds present within the exhaust gas. Detailed discussion of these OM compounds will be made in the next section.

NO$_x$, CO, and THC emissions were each analyzed on-site using a Horiba gas bench with chemiluminescent, infrared, and flame ionization detection analyzers, respectively. The raw and diluted exhaust samples were extracted with and without the SCR system to calculate the total emission levels and the reduction rates according to the methods specified within the regulations. NO$_x$, CO, and THC emissions saw a significant reduction with the addition of the SCR system to the exhaust flow from the engine. With the use of the zeolite urea-SCR exhaust aftertreatment system, a reduction of approximately 50, 81, and 86% was seen relative to the baseline engine for NO$_x$, CO, and THC emissions, respectively. The observed NO$_x$ reduction is lower than the typical reduction of approximately 70–90% while using steady-state operating conditions. This reduced NO$_x$ conversion efficiency is most likely attributed to the nonoptimized control system used in this study to achieve the precise urea dosing rate for many of the cycle set points. Hydrocarbon emissions are known to be particularly receptive to storage by zeolite catalysts during engine cold-start. As exhaust temperatures increase, these hydrocarbon species are released, aiding in the NO$_x$ reduction process. In this study, the benefits of hydrocarbon storage and release on NO$_x$ reduction were not observed and may have been overshadowed by the effects of inadequate urea dosing response time. Additionally, the emission rate of CO is typically increased over a zeolite-catalyst when the partial oxidation occurs during hydrocarbon release under certain temperature ranges. The downstream oxidation catalyst was capable of controlling both the THC and CO emissions by oxidation to form CO$_2$ and H$_2$O. Figure 2 shows a comparison of the emission levels of the criteria air pollutants for a baseline heavy-duty diesel engine both with and without a SCR aftertreatment system. The error bars for all charts represent the standard error of the mean, which is a measure of the variation of the sample mean, an important statistical quantity that gives an indication of the sampling error.

Comprehensive Speciation

A more comprehensive analysis of the diesel engine emissions is necessary to gain a better understanding of the effects that the SCR system produces. Species analyzed in this study included elemental carbon (EC), OM, inorganic ions, trace metals, PAHs, and other organic compounds.

To understand the detailed effects of the SCR system on PM emissions, it is important to look at the emissions of OM as well as another major contributor to total PM mass, EC. The OM mass was calculated by multiplying the mass measurement for OC by a factor of 1.2 to account for...
the aerosol mass of the other elements present within the organic compounds such as O\textsubscript{2}, hydrogen, and N\textsubscript{2}. The EC and OC samples were captured using two 47-mm quartz filters in series. Before testing, the filters were baked at 550 °C for 15 hr to remove pre-existing organics. EC and OC in the PM samples were measured using a method based upon the thermal-optical method described by Birch and Cary. The analysis utilized a 1.45-cm\textsuperscript{2} section of the particle-laden filter that was precisely removed with a punch specifically fabricated for the EC/OC analysis. The punch was heated under a helium atmosphere to evolve OC, which was measured by a flame-ionization detector (FID) after oxidizing the evolved carbon to CO\textsubscript{2} and subsequent reduction to methane. The sample was then cooled and reheated in a helium-plus-O\textsubscript{2} atmosphere to remove all carbon from the filter. The evolved carbon was corrected for pyrolysis carbon formed during the initial analysis stage using a laser that monitors the filter absorbance throughout the analysis to quantify the EC in the sample. OC is reported as the sum of the carbon evolved during the initial stage of the analysis plus the pyrolysis carbon. The final particle-phase OC mass was
then adjusted by subtracting the second filter measurement in the series from the first. This was done to correct for gaseous OC that was absorbed onto the first filter, which is assumed to be equivalent to the gaseous OC absorbed onto the second filter, as described by Kolodziej et al.\textsuperscript{23} The results show a reduction of approximately 64% of the organic mass emissions with the addition of the SCR system and downstream oxidation catalyst. Originally, the OM comprised 52.8% of the total PM mass emitted, whereas after the SCR system was added to the exhaust flow, the OM only contributed 23.4% of the total PM mass emissions. It should be noted that the correction factor of 1.2 for OM has not been validated for use with SCR-system-equipped diesel engines. A negligible reduction of approximately 3.5% of EC mass emissions was observed, potentially because of soot impaction on the catalyst surfaces or coagulation with the urea spray droplets leading to dropout. Additionally, EC emissions went from comprising 45.6% of the PM mass emissions to 54.3%. Similar results have been seen in the past and it is assumed that the oxidation catalyst removes some of the gas-phase organics before they have had a chance to adsorb onto the particle-phase EC because only weak interactions exist between the catalysts and the compounds of the insoluble fraction.\textsuperscript{14,19} It should be noted that recent publications suggest that the dynamic phase partitioning of organic material can be dependent on dilution and temperature conditions of the sampling systems.\textsuperscript{24,25}

Inorganic ionic species were collected from the RTC sampling section via the isokinetic sampling probes on two 47-mm PTFE membrane filters (see Figure 1). Analysis for ions was conducted following the Occupational Safety and Health Administration (OSHA) ID 113 method.\textsuperscript{26} The filters were extracted in H\textsubscript{2}O and analyzed by ion chromatography. A notable result was the increase of nitrate ion emissions, which were found in the emissions from the engine equipped with the SCR system at an average level of 2.41 ± 1.41 mg/bhp · hr. One possible explanation for this is that

### Table 1. Emission levels in the exhaust from a baseline diesel engine and the same engine equipped with SCR aftertreatment system by group.

<table>
<thead>
<tr>
<th>Name</th>
<th>FTP</th>
<th>FTP with SCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM mass</td>
<td>5.02 × 10\textsuperscript{-2} ± 8.26 × 10\textsuperscript{-3}</td>
<td>4.07 × 10\textsuperscript{-2} ± 1.42 × 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>6.74 ± 1.35</td>
<td>3.33 ± 7.60 × 10\textsuperscript{-1}</td>
</tr>
<tr>
<td>CO</td>
<td>7.49 × 10\textsuperscript{-1} ± 5.04 × 10\textsuperscript{-2}</td>
<td>1.39 × 10\textsuperscript{-1} ± 1.11 × 10\textsuperscript{-1}</td>
</tr>
<tr>
<td>THC</td>
<td>4.5 × 10\textsuperscript{-1} ± 1.92 × 10\textsuperscript{-2}</td>
<td>6.14 × 10\textsuperscript{-2} ± 1.15 × 10\textsuperscript{-2}</td>
</tr>
<tr>
<td>Total inorganic ion species</td>
<td>6.61 × 10\textsuperscript{-5} ± 6.81 × 10\textsuperscript{-6}</td>
<td>2.71 × 10\textsuperscript{-3} ± 5.00 × 10\textsuperscript{-4}</td>
</tr>
<tr>
<td>Total metals and elements</td>
<td>6.04 × 10\textsuperscript{-5} ± 5.55 × 10\textsuperscript{-5}</td>
<td>4.56 × 10\textsuperscript{-4} ± 4.66 × 10\textsuperscript{-5}</td>
</tr>
<tr>
<td>Total elemental carbon</td>
<td>2.29 × 10\textsuperscript{-2} ± 4.26 × 10\textsuperscript{-3}</td>
<td>2.21 × 10\textsuperscript{-2} ± 6.25 × 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Total OC</td>
<td>2.21 × 10\textsuperscript{-2} ± 4.35 × 10\textsuperscript{-3}</td>
<td>7.94 × 10\textsuperscript{-3} ± 1.04 × 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Total PAHs</td>
<td>1.85 × 10\textsuperscript{-5} ± 1.13 × 10\textsuperscript{-6}</td>
<td>7.62 × 10\textsuperscript{-7} ± 4.33 × 10\textsuperscript{-8}</td>
</tr>
</tbody>
</table>

Notes: All given values have units of g/bhp · hr; all uncertainty values are reported in 2 \(\sigma\).

### Table 2. Detection limits and percent reductions observed for organic compounds displaying significant reductions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Detection Limit (g/bhp · hr)</th>
<th>FTP\textsuperscript{a}</th>
<th>FTP with SCR\textsuperscript{a}</th>
<th>Percent Reduction\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo[a]anthracene</td>
<td>1.68 × 10\textsuperscript{-7}</td>
<td>9.87 × 10\textsuperscript{-7}</td>
<td>0.00</td>
<td>83.0</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>3.36 × 10\textsuperscript{-7}</td>
<td>3.92 × 10\textsuperscript{-6}</td>
<td>1.02 × 10\textsuperscript{-7}</td>
<td>91.4</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>3.36 × 10\textsuperscript{-7}</td>
<td>7.25 × 10\textsuperscript{-7}</td>
<td>0.00</td>
<td>53.7</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>1.68 × 10\textsuperscript{-7}</td>
<td>6.09 × 10\textsuperscript{-7}</td>
<td>0.00</td>
<td>72.4</td>
</tr>
<tr>
<td>Benzo[g,h,i]fluoranthene</td>
<td>1.68 × 10\textsuperscript{-7}</td>
<td>1.59 × 10\textsuperscript{-6}</td>
<td>0.00</td>
<td>89.4</td>
</tr>
<tr>
<td>Pyrene</td>
<td>1.68 × 10\textsuperscript{-7}</td>
<td>4.85 × 10\textsuperscript{-6}</td>
<td>6.60 × 10\textsuperscript{-7}</td>
<td>96.4</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>1.68 × 10\textsuperscript{-7}</td>
<td>9.13 × 10\textsuperscript{-7}</td>
<td>0.00</td>
<td>81.6</td>
</tr>
<tr>
<td>Cyclopenta[c,d]pyrene</td>
<td>1.68 × 10\textsuperscript{-7}</td>
<td>1.10 × 10\textsuperscript{-6}</td>
<td>0.00</td>
<td>84.8</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>1.68 × 10\textsuperscript{-7}</td>
<td>5.94 × 10\textsuperscript{-7}</td>
<td>0.00</td>
<td>71.7</td>
</tr>
<tr>
<td>Benzo[e]pyrene</td>
<td>1.68 × 10\textsuperscript{-7}</td>
<td>6.53 × 10\textsuperscript{-7}</td>
<td>0.00</td>
<td>74.3</td>
</tr>
<tr>
<td>Chrysene</td>
<td>1.68 × 10\textsuperscript{-7}</td>
<td>1.21 × 10\textsuperscript{-6}</td>
<td>0.00</td>
<td>86.1</td>
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<tr>
<td>Acephenanthrylene</td>
<td>1.68 × 10\textsuperscript{-7}</td>
<td>1.36 × 10\textsuperscript{-6}</td>
<td>0.00</td>
<td>87.7</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>4.86 × 10\textsuperscript{-5}</td>
<td>5.67 × 10\textsuperscript{-3}</td>
<td>0.00</td>
<td>99.1</td>
</tr>
<tr>
<td>Benzene</td>
<td>4.86 × 10\textsuperscript{-5}</td>
<td>5.09 × 10\textsuperscript{-3}</td>
<td>1.63 × 10\textsuperscript{-3}</td>
<td>68.0</td>
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<tr>
<td>Xylene</td>
<td>4.86 × 10\textsuperscript{-5}</td>
<td>8.57 × 10\textsuperscript{-3}</td>
<td>1.08 × 10\textsuperscript{-9}</td>
<td>99.4</td>
</tr>
<tr>
<td>Styrene</td>
<td>4.86 × 10\textsuperscript{-5}</td>
<td>1.05 × 10\textsuperscript{-3}</td>
<td>9.68 × 10\textsuperscript{-5}</td>
<td>90.8</td>
</tr>
<tr>
<td>Toluene</td>
<td>4.86 × 10\textsuperscript{-5}</td>
<td>1.52 × 10\textsuperscript{-3}</td>
<td>1.25 × 10\textsuperscript{-10}</td>
<td>96.8</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>4.86 × 10\textsuperscript{-5}</td>
<td>3.17 × 10\textsuperscript{-3}</td>
<td>5.84 × 10\textsuperscript{-9}</td>
<td>98.5</td>
</tr>
</tbody>
</table>

Notes: \textsuperscript{a}Reported values have units of g/bhp · hr and are the average of the test cycles; \textsuperscript{b}The percent reduction was conservatively determined using the detection limit if the reported value was below detection.
the oxidation catalyst converted some of the gas-phase nitric oxide(NO)/NO2 to form nitric acid, which would be present as the nitrate ion in the particle phase. Additionally, sulfate ion emissions increased most likely through the oxidation of SO2 to form sulfur trioxide (SO3) and then particulate sulfates over the oxidation catalyst; this has been noted in the past with sulfate emissions known to increase as much as 10 times over the oxidation catalyst.14,15

Using the same sample collection methods as were used for the ions, trace metals and elemental species were analyzed using a slightly different procedure as described by Schauer et al.26 The sample filters were digested into an aggressive acid solution consisting of hydrofluoric, nitric, and hydrochloric acids. The trace metals and elements were then quantified using high-resolution inductively coupled plasma mass spectroscopy (ICP-MS), which allowed for the quantification of 37 unique elements. Results showed a notable reduction of approximately 24.5% for trace metallic compounds possibly resulting from impaction with the front face of the catalysts and coagulation with the urea droplets.

The above results are displayed in Figure 3 and show that for baseline emissions, more than 99% of the total PM mass emissions could be attributed to EC, OM, trace metals, and ions, whereas for the engine equipped with the SCR system, only 85% of the total PM mass emission could be attributed to these same compounds. The remaining 15% of the PM mass emissions were most likely due to the factor of 1.2 used to account for organic mass being a poor approximation for SCR-system-equipped diesel engines in which the PM may be more oxygenated.

Organic compounds, especially PAHs, are important species to consider because these two groups have come under scrutiny for their acknowledged links to cancer, DNA damage, and genetic mutations.14 The distribution of these PAHs and substituted PAHs, along with n-alkanes, hopanes, and steranes can be used to probe the mechanisms in the engine that lead to the formation of PM emissions from diesel engines. PAHs, n-alkanes, hopanes, and steranes were all analyzed following the method described by Schauer et al.6 Before testing, 47-mm quartz filters were baked at 550 °C for 12 hr and PUF cartridges were cleaned using solvent extraction. After testing, both the filters and the PUF cartridges were analyzed by gas chromatography-mass spectrometry (GC/MS) on a Hewlett-Packard GC/MSD.6 The data from this study show that the majority of the compounds identified as PAHs were reduced to levels below the detection limits. This corresponded to a conservative total polyaromatic hydrocarbon (PAH) reduction rate of at least approximately 85% when the detection limits were used as the minimum emission levels for nondetectable species. From Figure 4, it can be seen that fluoranthene and pyrene were the primary PAH emissions, and significant reductions were seen for fluoranthene, pyrene, and other PAHs with the addition of the SCR system as evident in Tables 1 and 2. The reduction of these compounds can most likely be attributed to the downstream oxidation catalyst or to adsorption of the soluble organic fraction (SOF) by the SCR catalyst at low exhaust temperatures and then combustion of the SOF to form CO2 and H2O as exhaust temperatures increase.5,14 Additionally, past studies have observed the ability of zeolite catalysts to break heavy hydrocarbons into smaller molecules.27

Further samples of gaseous organic compounds were captured using both TD tubes and DNPH cartridges and were analyzed following modified versions of the National Institute for Occupational Safety and Health method 254928 and EPA method T0-11A,29 respectively. The TD tubes were conditioned to room temperature, placed into a thermal desorber, and organics were then quantified by GC/MS. The DNPH cartridges were desorbed with acetonitrile and analyzed using high-performance liquid chromatography (HPLC) with a NOVA-PAK C18 column and ultraviolet detection. Organic compounds such as formaldehyde, acetaldehyde, hexane, benzene,
styrene, toluene, and xylene are important to consider because of their presence on EPA’s MSAT list. Summarized in Table 2 and Figure 5, the results for species found on EPA’s MSAT list show that the SCR system reduced the production of new species over the catalysts and oxides of nitrogen. The species such as xylene, toluene, and ethylbenzene were always found to be below the detection limits for the measurement methods when the SCR system was used.

The addition of the zeolite urea-SCR system and oxidation catalyst to the exhaust path of a heavy-duty diesel engine reduced the emissions of a wide variety of chemical compounds under the testing conditions used in the present study. Significant reductions were seen for NOx, CO, THC, PAHs, and OC. There were notable reductions for PM mass and trace metallic compounds as well. Additionally, the production of new species over the catalysts was not observed in this study.

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