Comparative Analysis on the Effects of Diesel Particulate Filter and Selective Catalytic Reduction Systems on a Wide Spectrum of Chemical Species Emissions

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Two methods, diesel particulate filter (DPF) and selective catalytic reduction (SCR) systems, for controlling diesel emissions have become widely used, either independently or together, for meeting increasingly stringent emissions regulations worldwide. Each of these systems is designed for the reduction of primary pollutant emissions including particulate matter (PM) for DPF and nitrogen oxides (NOx) for SCR. However, there have been growing concerns regarding the secondary reactions that these aftertreatment systems may promote, involving unregulated species emissions. This study was performed to gain an understanding of the effects that these aftertreatment systems may have on the emission levels of a wide spectrum of chemical species found in diesel engine exhaust. Samples were extracted using a source dilution sampling system designed to collect exhaust samples representative of real-world emissions. Testing was conducted on a heavy-duty diesel engine with no aftertreatment devices to establish a baseline measurement and also on the same engine equipped first with a DPF system and then a SCR system. Each of the samples was analyzed for a wide variety of chemical species, including elemental and organic carbon, metals, ions, n-alkanes, aldehydes, and polycyclic aromatic hydrocarbons, in addition to the primary pollutants, due to the potential risks they pose to the environment and public health. The results show that the DPF and SCR systems were capable of substantially reducing PM and NOx emissions, respectively. Further, each of the systems significantly reduced the emission levels of the unregulated chemical species, while the notable formation of new chemical species was not observed. It is expected that a combination of the two systems in some future engine applications would reduce both primary and secondary emissions significantly.

Introduction

Advances in diesel engine and aftertreatment technologies have led to a significant reduction in the emission levels of particulate matter (PM) and nitrogen oxides (NOx). Recently, however, increasingly stringent regulations have been set forth in the United States, Europe, and other locations around the world. In the United States, the common air pollutants regulated by the Environmental Protection Agency (EPA) include PM, NOx, carbon monoxide (CO), hydrocarbons (HC), ozone (O3), sulfur dioxide (SO2), and lead (Pb) (1). Of these emissions, the most difficult to control in diesel engine applications are those of PM and NOx. Consequently, these two emissions are of the utmost concern in current diesel emission research.

In addition to the common air pollutants, the EPA maintains a list of compounds identified as mobile source air toxics (MSATs) (1). These compounds are identified as being known to or suspected of causing serious health and environmental effects. The compounds listed as MSATs include volatile organics, metals, PM, and diesel exhaust organic gases. Some of the harmful compounds identified include polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (n-PAHs). PAHs and n-PAHs are considered to be among the greatest threats to human health; many are known to cause cancer, DNA damage, and genetic mutations (2). There are over 100 PAH compounds that have been found present in particulate matter (3). Currently, they are not specifically regulated; however, these compounds from engine emissions have recently raised concerns, which has led to more studies into the emission rates of these species and their epidemiological effects (4).

One attractive option in aftertreatment technology is the diesel particulate filter (DPF), which has been shown to substantially decrease concentrations of PM from diesel engine emissions (5–7). The DPF is currently being used widely in the United States as a primary means of reducing diesel engine PM emissions when combined with combustion processes optimized for low NOx emission levels. DPFs are typically produced with alternating flow channels, which are plugged at the ends to force the exhaust flow to pass through the wall of the filtration media. The filtration efficiency of the DPF generally improves with increasing filter loading. However, due to the induced pressure drop across the filter, it becomes necessary to periodically perform filter regeneration in which the loaded diesel PM is oxidized at elevated exhaust temperatures. The regeneration process introduces the potential for thermal dealkylation, a secondary reaction which may produce methyl- and dimethyl-substituted PAHs which would otherwise not be found in the exhaust stream (8, 9). Another option in exhaust aftertreatment is the selective catalytic reduction (SCR) system, which has become well-established in Europe as a means of controlling diesel engine NOx emissions when combined with combustion processes optimized for low PM mass emission levels. SCR systems usually operate using ammonia derived from a urea solution to initiate chemical reactions with the NOx content of the exhaust, causing conversion to form nitrogen and water. However, the use of certain catalyst materials introduces concerns about secondary emissions, such as dioxins and furans as well as byproducts of C10 to C25 aliphatic hydrocarbons (8, 10).

For these reasons, it is important to understand the effects that engine and aftertreatment technologies may have on the reduction or formation of the full spectrum of chemical
species. In order to compare the effects that the DPF and SCR aftertreatment systems have upon unregulated emissions, each of these systems was analyzed as a part of the present study. Samples were collected from three testing configurations using a source dilution sampling system as described in the literature (11). In order to gauge the effects of each system individually, samples were first collected from a heavy-duty diesel engine with no aftertreatment system to establish baseline values for comparison. The engine was then subjected to two additional test cycles, one with the DPF aftertreatment system and another with the SCR system. The samples from these three test cycles were then analyzed for chemical content, and comparisons were made in order to gauge the overall effectiveness of each of the two popular aftertreatment technologies.

Experimental Methods

Test Configurations. The engine used for the present study was a 2001 model year, 10.8 L, heavy-duty diesel engine with no exhaust gas recirculation system. The engine speed and load were simulated by a direct-current dynamometer, which was capable of performing the majority of the U.S. and European steady-state and transient cycles for engines up to 525 kW (700 hp). For this study, the same engine and fuel were used throughout the testing matrix, only as sources of pollutants which would be commonly found in diesel engine exhaust under normal operation. The test fuel was determined to have a cetane number of 47, a sulfur content of 308.5 ppm, a particulate matter content of 0.1 mg/liter, and a composition of 29.5% aromatics.

To determine the effects of two common diesel aftertreatment devices, the test engine was operated first with a DPF system placed in the exhaust flow and then with a SCR system. The DPF system that was used in the present study consisted of two stages. The exhaust gas first passed through a diesel oxidation catalyst (DOC). The DOC, which measured 26.7 cm in diameter and 10.2 cm in length and was coated with precious metals, is primarily designed to convert NO to NO₂, which in turn may be used to assist with filter regeneration. The precious metal coating found on the surface of the filtration media may also aid in the gaseous oxidation of organic species emissions in addition to assisting filter regeneration (12). It has been reasoned that the soluble organic fraction (SOF) in the diesel exhaust would condense in the pore structure of the washcoat at low exhaust temperatures. As the exhaust temperature increased, the SOF would volatize, and the active catalyst would then initiate its oxidation (13). During operation, pressure sensors on either side of the DPF system were used to monitor the pressure drop to ensure proper operation throughout the duration of the test.

The other aftertreatment device analyzed as part of the present study was a SCR aftertreatment system, which utilized a zeolite-based catalyst and urea injection to control NOₓ present in diesel engine exhaust. The end products of the SCR reactions most often include N₂ and H₂O, though the production of undesirable N₂O and NH₄NO₃ may also occur if the urea dosing rate and exhaust gas temperature range are not optimized. The analysis of N₂O and NH₄NO₃ was outside the scope of this study. The SCR system used for this study also contained a downstream DOC to reduce ammonia slip. During testing with the SCR system in place, upstream and downstream NOₓ sensors were used to provide feedback to the control system which regulated the injection rate of urea solution.

Testing Procedure. Tailpipe emissions were piped through a constant-volume system—critical-flow venturi (CVS-CFV) primary dilution tunnel prior to entering the source dilution sampling (SDS) system, as shown in Figure 1. At the entrance to the tunnel, the dilution air was purified using pre, activated carbon, and high-efficiency particulate air filters in order to reduce background contamination. The SDS system utilized
a secondary microdiluter as well as a residence time chamber (RTC) to age the exhaust samples to ambient conditions (14, 15).

Stemming from the RTC, an array of seven sampling trains was used to allow for the simultaneous, isokinetic collection of multiple samples. Six of the trains used a flow rate of 16.7 L per minute (lpm), which was regulated by critical flow orifices in series with a rotary vacuum pump located downstream of the filters, and each of the sampling trains was used for the collection of a different variety of species. The seventh sampling train used a flow rate of 90 lpm so that the ultralow emission levels of some of the gaseous samples collected would be quantifiable. Further, additional gaseous samples were collected using thermal desorption (TD) tubes and dinitritylhydrazine (DNPH) cartridges for the analysis of PAHs, n-alkanes, and aldehydes.

The test engine was operated under the transient Federal Test Procedure (FTP) heavy-duty cycle, which consists of four phases in series and runs for a total time of 1200 s. Each phase is designed to simulate different driving situations that would be commonly encountered during the on-road operation of an average heavy-duty diesel engine. At least three separate samples were collected for each test configuration to allow for the determination of sample mean and variation. Throughout the testing, a strict quality assurance and quality control procedure was followed, which included the use of background, handling, dilution, dynamic, and transportation blanks for contamination correction.

**Analysis Procedures.** The samples collected from the source dilution sampling system were subjected to an in-depth chemical analysis using established methods. NOx, CO, and THC emissions were each evaluated using a gas analyzer bench with chemiluminescent, infrared, and flame ionization detection analyzers, respectively. Primary particulate emissions were analyzed by filter weighing for total particulate mass emissions in an environmentally controlled room with robotic mechanisms to minimize weighing procedure errors. Once the particulate sample filters were weighed, the composition of the particulate matter emissions was determined through a detailed chemical speciation. The particulate samples were analyzed for elemental and organic carbon, inorganic ions, trace metals, and particulate organics.

The particulate samples collected on baked quartz and polytetrafluoroethylene (PTFE) filters were analyzed for elemental carbon (EC) and organic carbon (OC) composition using a method based on the thermal-optical method described in the literature (16). In order to evolve the OC present in the sample, the filters were first heated under a helium atmosphere. The evolved OC was then oxidized to form CO2 before being reduced to CH4 and read by a flame ionization detection analyzer. The sample was then reheated under helium and oxygen, and the EC within the sample was quantified. The total amount of OC within the sample was calculated as the sum of the evolved OC and any pyrolyzed carbon that may have been formed during the initial stages of the analysis. The OC measurement was corrected for nonadsorbed gaseous OC by using a series of two filters and subtracting the second filter measurement from the first (17). Additionally, the OC mass measurement was converted to total organic mass (OM) by multiplying by a factor of 1.2 to account for the oxygen, hydrogen, and nitrogen components of the OC emissions (18).

Additional sets of PTFE filters were analyzed for inorganic ion and trace metallic emissions. The filter pair to be analyzed for inorganic ions was extracted in water, and the ionic composition was determined using ion chromatography as described by Schauer et al. (19). A second filter pair was analyzed for trace metallic content by high-resolution inductively coupled plasma mass spectrometry after the filters were extracted in an aggressive acidic solution of hydrochloric, nitric, and hydrofluoric acids (19). This analysis procedure allowed for the quantification of 37 unique trace metallic compounds found within the emissions from the heavy-duty diesel engine.

The remaining particulate samples were analyzed for particulate organic species emissions. The samples for organic speciation were collected on baked quartz and polyurethane foam (PUF) substrates and were analyzed for PAHs, PAH derivatives, aromatics, and hopanes and steranes. Prior to sample collection, the filters were baked at 550 °C to remove any organic compounds which may have been present on the filters already. After sample collection, the particle-phase organics were quantified using gas chromatography–mass spectrometry (GC/MS), which allowed the emissions levels to be determined for a large number of organic species (8).

An analysis of gaseous organic emissions was also performed as part of the present study. The samples for gaseous organic speciation were collected on PUF cartridges, TD tubes, and DNPH cartridges, which were each analyzed for PAHs, n-alkanes, and aldehydes using standard methods.

**Results and Discussion**

**Gaseous Criteria Pollutants.** Each of the gaseous criteria pollutants, NOx, CO, and HC, were reduced through the use of exhaust aftertreatment technology. The gaseous NOx emissions displayed a reduction of 50.6 ± 11.1% through the use of the SCR system, while the reduction across the SCR catalyst has typically been reported closer to 70–90% efficient when using steady-state operating conditions (22). The lower conversion of NOx over the SCR system may be due to nonoptimized urea dosing algorithms used in this study during the highly variable sections of the transient FTP cycle. Additionally, the NOx reduction across the DPF system was insignificant, similar to what has been observed in the past (5, 6).

The emissions of CO were observed to reduce by 93.8 ± 3.4% and 81.4 ± 7.6% with the use of the DPF and SCR systems, respectively. In each case, it is presumed that the CO emissions were converted, through oxidation, to CO2 and H2O with the aid of the catalyst material found in each of the aftertreatment systems (12, 23, 24).

Lastly, the gaseous HC emissions were found to be reduced by 77.7 ± 3.7% and 86.5 ± 2.4% due to the DPF and SCR systems, respectively. The higher HC reduction efficiency displayed by the SCR system may be attributed to the tendency for zeolites to be particularly receptive to hydrocarbon storage possibly caused by van der Waal’s forces between the hydrocarbon species and the porous walls of the zeolite catalyst (24). The emission levels of each of the criteria gaseous pollutants can be found in Figure 2, which compares the emissions levels for each pollutant for each of the test configurations analyzed in the present study. Error bars for all charts represent the standard error of the mean, which is a measure of the variation of the sample mean.

**PM Mass Emissions.** The emissions of PM mass are also important to consider due to their inclusion on the EPA’s regulated common air pollutants and MSAT lists. The emissions of PM mass were found to reduce by 18.9 ± 6.8% and 98.2 ± 6.1% after the inclusion of the SCR and DPF
The emissions of sulfate from the engine with DPF and the emissions of hopenes and steranes for each aftertreatment system were below the detection limits. As can be seen in Figure 3, the reduction of PM mass emissions over the DPF system was caused by significant reductions of each of the major contributing particulate species, with the exception of ammonium.

The largest contributors to the total PM mass included elemental carbon, organic matter, inorganic ions, and trace metals, as seen in Figure 3. Elemental carbon and organic matter made up greater than 99% of the total PM mass emissions from the baseline engine, and therefore, we would expect the species in these two categories to have the greatest influence over the total particulate emissions. The elemental carbon emissions were found to be reduced by 99.7 ± 6.7% with the DPF system, while the OM emissions were reduced by greater than 93%. Each of these reductions was most likely due to particulate filtration since EC is in the particle-phase and OM emissions often adsorb onto the primary EC particles. With the use of the SCR aftertreatment system, a reduction of 64 ± 7.2% was found for OM emissions. Because EC is in the particle-phase, we would not expect the SCR system to have much of an effect on its emission level. However, the reductions observed for OM may be due to a removal of gaseous organic emissions before they have been adsorbed by the primary EC particles.

The emissions of the inorganic ionic species from the engine used in the present study consisted primarily of the sulfate and ammonium ions. The ammonium ion emissions were found to be undetectable and have large uncertainty for the baseline and SCR system cases, while the ammonium emissions for the DPF case were detectable but were found to have a low emission rate, which was not significantly different from the emissions for either of the other test aftertreatment systems, respectively. As can be seen in Figure 3, the reduction of PM mass emissions over the DPF system was caused by significant reductions of each of the major contributing particulate species, with the exception of ammonium.

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significant reductions for the majority of the MSAT species analyzed as part of the present study. To a lesser extent, the SCR system also produced reductions in several of the MSAT species, with a primary focus on the lower-molecular-weight hydrocarbons which were more likely to be present in the gaseous phase at typical diesel exhaust gas temperatures. Both the DPF and the SCR systems were found capable of reducing many of the \( n \)-alkane species emissions by greater than 85%. Also, it was observed that the SCR significantly reduced emission levels of the aromatic species such as xylene, toluene, and ethylbenzene. This was most likely due to the low molecular weight of the aromatic species and the high gaseous oxidation efficiency of the SCR catalyst (28).

Other species that also displayed high emission rates from the baseline engine included the aldehydes, formaldehyde and acetaldehyde. Each of these compounds was reduced below the analysis detection limits by the DPF system, while the SCR system reduced the emission levels of each by greater than 60%. Finally, a few high-molecular-weight hopanes and steranes, which have been used in the past as tracers for engine emissions in the atmosphere (8, 29), were found in the emissions from the baseline heavy-duty diesel engine. In the case of these compounds, both the DPF and SCR systems reduced the emission levels significantly, most likely through particle filtration for the DPF and possible scavenging for the SCR system.

Figure 6 shows the overall reduction rates for each of the main categories of organic species analyzed in this study, including \( n \)-alkanes, branched alkanes, aromatics, and PAHs. As presented, it is apparent that both of the exhaust afttreatment systems produced significant reductions in the organic species emissions from each category of compounds. The DPF system produced greater reductions for the PAH species, while the SCR system reduced the emission levels of many other organic species by a greater portion, especially for the overall emissions of the aromatic compounds.

As the data have shown, each afttreatment system has unique strengths. For example, the DPF system performed better on emissions of PM and PAHs, while the SCR system performed better for \( NO_x \) and many lower-molecular-weight organic emissions. If used in conjunction with one another, the combined system as a whole would most likely have the ability to greatly reduce the total emissions of particulate, gaseous, semivolatile, and volatile species. Therefore, it is expected that a combination of the two systems in some future engine applications would reduce both regulated and unregulated emissions significantly.

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