



## **Characterization of Fuel and Aftertreatment Device Effects on Diesel Emissions**

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**Includes the Commentary of the Institute's  
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# **HEI** HEALTH EFFECTS INSTITUTE

The Health Effects Institute, established in 1980, is an independent and unbiased source of information on the health effects of motor vehicle emissions. HEI studies all major pollutants, including regulated pollutants (such as carbon monoxide, ozone, nitrogen dioxide, and particulate matter), and unregulated pollutants (such as diesel engine exhaust, methanol, and aldehydes). To date, HEI has supported more than 150 projects at institutions in North America and Europe.

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# HEI Statement

## Synopsis of Research Report Number 76

### Effects of Fuel Modification and Emission Control Devices on Heavy-Duty Diesel Engine Emissions

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#### BACKGROUND

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Diesel engine exhaust contains small carbonaceous particles and a large number of chemicals that are adsorbed onto these particles or present as vapors. Diesel exhaust is a public health concern because (1) the particles are an important component of air pollution, (2) the particles are small enough to be inhaled deeply into the lungs where they may persist, and (3) the vapors and particles include mutagens, carcinogens, lung irritants, and contributors to ozone formation. Epidemiologic studies of workers in certain occupations suggest a weak association between exposure to diesel exhaust and lung cancer. Other studies have found that daily increases in mortality from heart and lung diseases are correlated with increases in particulate air pollution. The Clean Air Act of 1970 mandates decreased particle emissions from vehicles with diesel engines. Although engine manufacturers have reduced emissions substantially by improving engine designs, fuel composition may need to be modified and emission control devices may need to be added to achieve further reductions in the future. Because the Clean Air Act requires that such devices contribute no new risks, the Health Effects Institute sponsored this study to help evaluate whether using low-sulfur fuel with emission control devices might alter diesel emissions in ways that could affect human health.

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#### APPROACH

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Dr. Susan Bagley and colleagues conducted a laboratory study to characterize the physical and chemical composition and the mutagenicity of emissions from a heavy-duty 1988 diesel engine equipped with a ceramic particle trap. This engine was operated with low-sulfur fuel at a constant speed under two different load conditions. The investigators compared their results to those obtained in an earlier study (HEI Research Report Number 56) in which they had used the same engine and a conventional, high-sulfur fuel. They also studied the effects of an oxidation catalytic converter on emissions from a heavy-duty 1991 diesel engine using a low-sulfur fuel. A unique aspect of this study was that the investigators determined the number and size of particles within the two typical classes of diesel particulate matter: the small, primary particles (nuclei mode) and the larger particle agglomerates (accumulation mode).

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#### RESULTS AND IMPLICATIONS

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The ceramic particle trap substantially decreased the weight and number of particles emitted, and as a result, lowered the levels of organic chemicals associated with particles and the mutagenicity of diesel exhaust. Use of the trap caused an increase in the amount of one chemical (fluoranthene) in the emission vapors, but no statistically significant changes were noted in the amounts or types of other vapor-phase chemicals. Regenerating the particle-loaded trap by heating it to combust the particles produced negligible increases in emission constituents and mutagenicity. Compared with results from conventional, high-sulfur fuel in the earlier study, low-sulfur fuel decreased sulfate emissions and the number of small sulfate particles, but had little effect on the weight of total particulate matter. The oxidation catalytic converter on the other hand had no effect on the number of particles, but decreased the amount of organic chemicals in the vapors and adsorbed onto the particles. Because most of the chemicals adsorbed onto the particles were removed, the weight of the total particulate matter decreased. These results indicate that the use of low-sulfur fuel in combination with emission control devices reduces selected pollutants in heavy-duty diesel engine exhaust without significantly increasing emissions of other pollutants. Preliminary results show that, despite a substantial reduction in the weight of total particulate matter, the total number of particles in emissions from the more advanced 1991-model engine was 15 to 35 times greater than the number of particles from the 1988 engine when both engines were operated without emission control devices. This unexpected finding was due to a 30- to 60-fold increase in the number of small, primary particles. These data are of concern because the smaller particles in emissions are more likely to be trapped and retained in human lungs. However, these findings need to be validated because only one engine of each type was tested and the main objective of this study was not to compare different engines. Further inquiry, including studies with new diesel engine designs, is needed to clarify this potentially important result.

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This Statement, prepared by the Health Effects Institute and approved by its Board of Directors, is a summary of a research project sponsored by HEI from 1989 to 1993. This study was conducted by Dr. Susan T. Bagley and colleagues of the Michigan Technological University, Houghton, MI. The following Research Report contains both the detailed Investigators' Report and a Commentary on the study prepared by the Institute's Health Review Committee.

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This Statement, prepared by the HEI and approved by the Board of Directors, is a nontechnical summary of the Investigators' Report and the Health Review Committee's Commentary.

#### II. INVESTIGATORS' REPORT . . . . . 1

When an HEI-funded study is completed, the investigators submit a final report. The Investigators' Report is first examined by three outside technical reviewers and a biostatistician. The Report and the reviewers' comments are then evaluated by members of the HEI Health Review Committee, who had no role in the selection or management of the project. During the review process, the investigators have an opportunity to exchange comments with the Review Committee and, if necessary, revise the report.

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## Characterization of Fuel and Aftertreatment Device Effects on Diesel Emissions

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### ABSTRACT

Heavy-duty diesel engines operated with a low-sulfur (LS)\* fuel and either a particle trap or an oxidation catalytic converter (OCC) have been studied during steady-state operation (and during regeneration of the particle trap) to determine the effects of these devices on regulated and unregulated emissions, including the chemical and biological character of the exhaust. This study consisted of two phases, both of which were designed to determine the effects of fuel, particle control system, and engine type on (1) levels of regulated emissions such as oxides of nitrogen ( $\text{NO}_x$ ), total hydrocarbons (HC), and total particulate matter (TPM); (2) levels of unregulated emissions such as particle-associated soluble organic fraction (SOF), sulfate ( $\text{SO}_4$ ), solids (SOL), and the vapor-phase organic fraction collected on XAD-2 resin (XOC); (3) levels of selected mutagenic and carcinogenic polynuclear aromatic hydrocarbons (PAHs) in the particle-associated and vapor-phase organic fractions; (4) mutagenic activity associated with the same organic fractions; and (5) exhaust particle size distributions. Phase I involved a 1988 Cummins Engine Co. LTA 10-300 (L10) engine equipped with a ceramic particle trap having built-in regeneration controls. Phase II involved a 1991 prototype Cummins Engine Co. LTA 10-310 (LTA) engine equipped with an OCC. The 1991 LTA engine also contained a higher pressure fuel-injection system than the 1988 L10 engine and used an intake charge air-to-air aftercooling system, instead of the intake air-intercooler system on the 1988 engine.

Phase I was designed to complement an earlier study (Bagley et al. 1993) that used the same engine and a similar trap with an electrical regeneration system. The previous study used a conventional, high-sulfur (CS) fuel (0.32% sulfur by weight), and the current study primarily used an LS fuel (0.01% sulfur by weight). The Phase I study was originally designed to indicate how the L10 engine and particle trap would respond to the reductions in fuel sulfur levels under controlled operating and sampling conditions, where TPM levels should be lower due to less  $\text{SO}_4$  production with the LS fuel. Samples were collected at U.S. Environmental Protection Agency (EPA) steady-state, rated speed modes 9 and 11 (75% and 25% load, respectively) for both baseline (no particle trap) and trap (trap in place) conditions. In addition, engine particle and vapor-phase emissions were measured during electrically assisted particle trap regeneration.

After the CS and LS fuel data had been analyzed, some of the results could not be explained by fuel sulfur difference alone. As the CS and LS fuels differed in more than sulfur content, a limited, additional study was conducted after doping the LS fuel with di-*tert*-butyl disulfide to 0.29% sulfur by weight (termed doped-sulfur or DS fuel).

Phase II was conducted with the LTA engine with and without the OCC using the same batch of LS fuel. The engine operating protocols and the emissions measured were the same as for Phase I, with the addition of EPA mode 10 (50% load at rated speed). The data from both studies were analyzed primarily using analysis of variance (ANOVA) techniques.

Comparing the Phase I emissions data with data from the earlier study (Bagley et al. 1993) demonstrates some direct evidence of the effects of fuel sulfur levels, and indicates that other fuel components also may affect some of the regulated and unregulated emissions. Although  $\text{SO}_4$  levels decreased to below detection limits, a significant difference in TPM levels between the CS and LS fuels was found only at mode 9 baseline. For mode 11 and mode 9 trap, there was little difference in TPM levels even when the  $\text{SO}_4$  component decreased. The XOC and HC levels also were generally higher with the LS fuel, whereas SOL levels were generally lower. In contrast, TPM emission levels were significantly

\* A list of abbreviations appears at the end of the Investigators' Report.

This Investigators' Report is one part of Health Effects Institute Research Report Number 76, which also includes a Commentary by the Health Review Committee, and an HEI Statement about the research project. Correspondence concerning the Investigators' Report may be addressed to Dr. Susan T. Bagley, Department of Biological Sciences, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931-1295.

Although this document was produced with partial funding by the United States Environmental Protection Agency under Assistance Agreement 816285 to the Health Effects Institute, it has not been subjected to the Agency's peer and administrative review and, therefore, may not necessarily reflect the views of the Agency, and no official endorsement by it should be inferred. The contents of this document also have not been reviewed by private party institutions, including those that support the Health Effects Institute; therefore, it may not reflect the views or policies of these parties, and no endorsement by them should be inferred.

lower with the LS fuel than with the DS fuel. Bimodal particle size distributions indicated that the nuclei-mode particles consisted mainly of SO<sub>4</sub> particles for the 1988 L10 engine. The accumulation-mode particles were found to be mainly formed in the engine and the nuclei-mode particles were formed during the dilution process. When using the 1988 L10 engine with either CS or DS fuel, the majority of the nuclei-mode particles were formed in the dilution tunnel by heteromolecular nucleation of the H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> vapors. In general, all analyzed PAHs except for fluoranthene were present at higher levels in emissions with the LS fuel than with either the DS or CS fuel. Mutagenic activity increased with the LS fuel emissions, particularly in the XOC. Emissions produced with the trap were typically lower than without it. Emissions produced during trap regeneration contributed negligibly to overall emissions with the trap, provided a second trap was used to treat the by-pass exhaust.

The results from the Phase II studies showed that the OCC primarily affected the organic component of the exhaust. In general, all emission components containing hydrocarbons (HC, SOF, and XOC) were decreased with the OCC; reductions in TPM concentrations therefore occurred at all modes due to the SOF reductions. Concentrations of most of the measured PAHs were decreased by the OCC in both the particle and vapor phases of the exhaust. Although the mutagenic activity associated with the particle- and vapor-phase organic extracts typically increased on a collected mass basis with the OCC (particularly at modes 9 and 10), the activity on an exhaust concentration basis typically decreased due to the large reductions in SOF and XOC emissions. The OCC produced increases in SO<sub>4</sub> emissions at the higher temperature modes (9 and 10); however sulfates still composed less than 6% of the TPM due to the low levels of sulfur in the fuels. There were no effects on NO<sub>x</sub> or SOL concentrations or particle size distributions at any mode. The majority of the particles in the nuclei-mode from the LTA engine, when operated with LS fuel, were considered to be individual carbon spheres with adsorbed hydrocarbons.

Compared with emissions from the L10 engine with CS fuel and no particle control system, using the 1991 LTA engine and this OCC (with LS fuel) produced similar reductions in TPM but greater reductions in hydrocarbon-type emissions (HC, SOF, and XOC) than did using the LS fuel and an uncatalyzed trap with the 1988 L10 engine. However, using the L10 engine, particle trap, and LS fuel resulted in SOL emissions equivalent to those found when the LTA engine was used with the OCC (and LS fuel). The

LTA engine produced 30 to 60 times more particles in the nuclei mode than the L10 engine when both engines used LS fuel under baseline conditions. A definite shift toward more nuclei-mode particles and less accumulation-mode particles was noted when using the LS fuel for the 1991 engine compared with the 1988 engine; this increase was attributed to the increase in solid nuclei-mode particles.

## INTRODUCTION

Particles, vapors, and gaseous emissions from diesel engines continue to be considered to have adverse effects on human health and the environment and have been the focus of many studies, including the one described in this report. Numerous studies have been carried out since interest in health and the environment developed in the early 1970s. These studies have resulted in having whole diesel exhaust considered a potential occupational carcinogen by the National Institute for Occupational Safety and Health (1988) and a probable human carcinogen by the International Agency for Research on Cancer (1989). A recent evaluation conducted by the Health Effects Institute (1995) of the emissions, exposure, and health effects data indicates the potential importance of diesel emissions, particularly the relationship of the particles to human lung cancer, as well as the potential for direct and indirect effects of exhaust components on other human health effects. In the past, these studies have centered around the identification of potentially harmful fractions of diesel exhaust or specific exhaust compounds and the quantification of these species collected from diesel exhaust produced under controlled conditions. More recently, the impacts of parameters such as engine type, engine operating conditions, fuel-injection pressure, fuel type, fuel additives, and aftertreatment devices such as catalytic converters and uncatalyzed particle traps have been described in the literature and have turned into a major focus for study.

Environmental concerns over national air quality and the increase in diesel engine usage prompted the federal government to promulgate emission standards for light- and heavy-duty diesel engines. When passed, the standards were considered "technology forcing", implying that these goals could not be met without technology development. At one time it was thought that such strict standards would be difficult to enforce and too costly to meet. Engine manufacturers have met the challenge and the health and environmental concerns have directed the development of the modern diesel engine that can meet the emission standards for bus and heavy-duty diesel truck engines. The 1994 EPA

on-highway heavy-duty diesel standards specify an NO<sub>x</sub> standard of 5 g/brake horsepower-hour (bhp-hr), a HC standard of 1.3 g/bhp-hr, and a particulate standard of 0.1 g/bhp-hr for on-highway trucks and 0.07 g/bhp-hr for urban buses (Walsh 1993). The 1996 urban bus particulate standard is 0.05 g/bhp-hr and the 1998 heavy-duty truck NO<sub>x</sub> standard is 4 g/bhp-hr (Sawyer and Johnson 1995).

The requirement to control diesel emissions has resulted in an increased understanding of their formation and composition and the interaction among various emissions. For example, the amount of TPM can be increased by adsorbed hydrocarbons (often termed soluble organic fraction or SOF) and sulfates (Baranescu 1988). The impetus for diesel emission control has resulted in numerous control approaches. Typically these can be classified into three areas: fuel composition changes, engine modifications, and exhaust aftertreatment devices. In practice, various combinations of all three approaches have been employed.

More recently, interest has shifted toward determining the impact of specific components of the fuel on emissions, primarily aromatic content and sulfur levels (Wall et al. 1987; Baranescu 1988; Ullman et al. 1990a,b). In addition, there has been an increased interest in the ceramic particle trap and the OCC as aftertreatment devices. In the studies described in this report, the effects of a low-sulfur fuel in combination with a particle trap or an OCC will be presented.

## FUEL COMPOSITION

Previously, it has been proposed that the type of engine and mode of operation were the most important factors in determining emission characteristics. This may be valid when looking at gross characteristics of emissions such as TPM and SOF. More recently, researchers are establishing the effects that specific types of chemical species in fuels may have on the compounds of biological interest such as PAHs and nitro-PAHs in diesel exhaust.

A variety of studies on the effects of fuel on heavy-duty diesel emissions have been carried out (Wall et al. 1987; Baranescu 1988; Ullman et al. 1990a,b; Lange 1991; Fukuda et al. 1992; McCarthy et al. 1992). Baranescu (1988), Lange (1991), and Wall and colleagues (1987) investigated the impact of fuel sulfur on emissions; all of these studies concluded that sulfur must be removed from diesel fuel for effective particle emission control. Ullman and associates (1990a,b) showed that, as particulate levels became increasingly lower, sulfates, which originate mainly from the sulfur in the fuel, became more significant. In a study on the impact of cetane number and aromatic content of the fuel on emissions, Ullman and associates 1990a,b also found

that, as cetane number increased, both gaseous and particle emissions decreased, while aromatic content reductions produced varied results on the emissions. (Cetane number is a fuel property related to the ignition delay or time between fuel injection into the cylinder and its ignition; it is determined in a single-cylinder engine using blends by volume of two pure reference fuels to achieve the same ignition delay as the actual fuel. The reference fuels are  $\alpha$ -methyl naphthalene, which is designated as 0 cetane number, and hexadecane, which is designated as 100 cetane number.) In a related study, Rasmussen (1990) reported some significant correlations between SOF mutagenic activity (without S9) and fuel sulfur and aromatic contents. Weight-specific activity (revertants/ $\mu$ g SOF) decreased with increasing fuel sulfur content, and work-specific activity (revertants/bhp-hr) increased with increasing content of aromatic compounds. McCarthy and associates (1992) studied fuel property effects on emissions using a heavy-duty diesel engine meeting the 1994 emission standards and found similar fuel sulfur effects to those reported by Ullman and colleagues (1990a,b). The emissions of PAH compounds were not included in these studies.

In a literature review on the effects of fuel properties on diesel engine emissions, van Beckhoven (1991) concluded that reductions in fuel sulfur from approximately 0.30 wt % to 0.05 wt % yielded a reduction in particulate emissions by 15 to 30%. Additionally, other properties, such as fuel volatility and the cetane quality were found to affect hydrocarbon and particulate emissions of diesel engines. In an effort to assist engine manufacturers in meeting future particulate matter standards, the EPA has specified a maximum sulfur level in diesel fuel of 0.05 wt % and a minimum cetane index specification of 40 (or a maximum aromatic content of 35 vol %) as of October 1, 1993 (Federal Register 1990). Fuels such as methanol, ethanol, and vegetable oils have also been suggested as viable alternatives for standard diesel formulations (Walsh 1993).

## ENGINE MODIFICATIONS

Modifications to engine hardware have shown that substantial reductions to meet the 1991 emissions standards can be obtained. The more stringent 1994 standards, however, require a low-sulfur (0.05 wt %) fuel and some engines will require exhaust aftertreatment devices. Engine design practices that have resulted in low emissions for heavy-duty direct-injection diesel engines include turbocharging, intercooling, combustion system optimization by high-pressure fuel injection with electronics, injection timing control as a function of load and speed, improved combustion bowl designs, and low lubrication oil consumption

(Zelenka et al. 1990a; Needham et al. 1989). Most heavy-duty truck engines did not require aftertreatment devices to meet the 1994 0.1 g/bhp-hr particulate standard, although some medium-duty truck engines use catalysts. However, heavy-duty urban bus engines will probably require catalysts to meet the lower 0.07 and 0.05 g/bhp-hr standards.

## AFTERTREATMENT DEVICES

The standards considered most challenging to meet for diesel engines are those for NO<sub>x</sub> and TPM. Generally, modifications to reduce TPM require higher temperatures to promote combustion of TPM; however, the higher temperatures lead to the formation of NO<sub>x</sub> (Gill 1988). Since NO<sub>x</sub> is more difficult to treat in diesel exhaust than particulate matter, NO<sub>x</sub> is controlled by engine parameters such as injection timing and exhaust gas recirculation. If required, particulate matter can be controlled by exhaust aftertreatment devices.

Because of its high particle filtration efficiency, the particle trap has been the object of considerable research for over a decade. In its most common form, the trap consists of a porous ceramic material of cellular configuration that is extruded to form a matrix of parallel channels. At the inlet end, every other cell is plugged with nonporous ceramic material with the adjacent cells being plugged similarly at the outlet. Consequently, the particle-laden exhaust is forced through the ceramic wall of the channel, where the particles are filtered and collected. The mechanism and mathematical modeling of this process are discussed by Konstandopoulos and Johnson (1989). A variety of studies have characterized emissions from engines equipped with ceramic traps (Baumgard and Kittleson 1985; Mogan et al. 1986b; Dorie et al. 1987; Draper et al. 1987; Konstandopoulos et al. 1988; Bagley et al. 1993; Kojetin et al. 1993). Control efficiencies for TPM of over 90% have typically been reported. Reductions in HC, mutagenic activity, and PAHs have typically not been as great, but NO<sub>x</sub> levels were unaffected. Reductions were found in the number of larger accumulation-mode particles and increases in the number of smaller nuclei-mode particles were often observed (Bagley et al. 1993).

Unfortunately, after a relatively short period of time, the particles collected within the trap caused excessive back-pressure on the engine, reducing fuel economy and engine performance. The trap must then be regenerated by burning the collected particulate matter (Howitt and Montierth 1981; Laymac et al. 1991; Kojetin et al. 1993). The trap's main drawbacks include cost, complexity of the regeneration process, and questionable durability (Ball and Stack 1990).

The other exhaust aftertreatment device often studied is the OCC, which is similar in configuration to a typical automotive catalytic converter. The OCC is used to oxidize hydrocarbons in the exhaust that would otherwise be adsorbed to the TPM, thus resulting in a reduction of the total particle mass. The OCC also promotes the oxidation of carbon monoxide (CO) and gaseous hydrocarbons to carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O).

Platinum and palladium are most commonly used as catalysts in OCCs (Heywood 1988; Farrauto and Mooney 1992). Noble metals are preferred over base metal oxides because they are more resistant to sulfur deactivation, exhibit higher specific activity for the oxidation of hydrocarbons, and are superior in thermal resistance to the degradation of low temperature activity (Kummer 1981).

Exhaust composition can affect the degree of oxidation, with molecules possessing high polarity being more strongly adsorbed to the catalyst. If such molecules are present in high enough concentrations, they may inhibit reactions of less polar molecules by covering catalyst sites (Church et al. 1989). Solid catalysts often require high temperatures for chemisorption and catalytic reactions to occur. Consequently, the effectiveness of the OCC can be greatly limited at low temperatures. At sufficiently high steady-state operating temperatures, a fresh OCC can remove over 90% of the mass of HC and CO (Heywood 1988). Others have reported similar results (McClure et al. 1988; Horiuchi et al. 1990; Zelenka et al. 1990b; Horiuchi et al. 1991; Porter et al. 1991). Oxidation catalytic converters have also been found to reduce diesel exhaust odor (Marshall 1975; Sercombe 1975). Consequently, OCCs have been used for a number of years on diesel-powered equipment used in underground mining applications (Rehnberg 1981; Mogan and Dainty 1986; McClure et al. 1988; Farrauto et al. 1992).

Numerous studies have described the effectiveness of the OCC for oxidizing hydrocarbons that comprise the SOF component of the TPM in the cooled exhaust (Horiuchi et al. 1990), substantiating that OCCs can be effectively used as particle control devices. It is proposed that the OCC works by oxidizing some of the exhaust hydrocarbons that could be adsorbed to the particles, resulting in a decrease in TPM emissions. The extent of OCC effects on emissions depends upon OCC design, placement in the exhaust system, engine characteristics, engine operating cycle, and fuel composition (Barris 1992; Gulati 1992).

Unfortunately, OCCs also oxidize sulfur dioxide (SO<sub>2</sub>) to sulfur trioxide (SO<sub>3</sub>) with the potential for producing sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (McClure et al. 1988; Ball and Stack 1990; Horiuchi et al. 1990; Zelenka et al. 1990b; Cooper and Roth 1991; Porter et al. 1991; Brear et al. 1992; Harayama et

al. 1992; Henk et al. 1992). In addition to oxidation of SO<sub>2</sub>, OCCs have been shown to oxidize nitric oxide (NO) to nitrogen dioxide (NO<sub>2</sub>) with the reaction being favored at high exhaust temperatures (Rehnberg 1981; Mogan and Dainty 1986; McClure et al. 1988).

Due to the effectiveness of OCCs for oxidizing hydrocarbons, it was suspected that the OCC would be effective for oxidizing PAHs and therefore decreasing the mass of PAHs in the exhaust of diesel engines. McClure and colleagues (1992), Arai (1992), Zelenka and colleagues (1990a,b), and Andrews and colleagues (1987) have observed decreases of certain PAHs in their studies. In spite of the decrease of PAHs by OCCs, the mutagenic activity per mass of particle extract has been shown in some cases to increase over baseline levels (Hunter et al. 1981a,b; Mogan et al. 1986a,b; McClure et al. 1992). There are strong indications that these increases in mutagenic activity are caused by higher levels of nitro-PAH compounds in the extracts. The nitro-PAH compounds are recognized mutagens and can be formed by the nitration of PAHs by NO<sub>2</sub> in an acidic environment (Pitts et al. 1979; Mogan and Dainty 1986), as well as by other reactions (Ross et al. 1987). It is thought that the residence time of the particles in the OCC is sufficient for the nitration reactions to occur.

The advantages of the OCC for reducing CO, HC, and diesel exhaust odor provide reasons to continue the study of the OCC as a means for controlling gaseous emissions, in spite of the disadvantages of producing NO<sub>2</sub>, SO<sub>3</sub>, and nitro-PAHs. Recently, the OCC has also been considered as a feasible means for decreasing particle emissions to meet the 1994 and later standards. Various authors (Gill 1988; Richards and Sibley 1988; Porter et al. 1991; Ozturk et al. 1994; Voss et al. 1994) have suggested using the OCC as an aftertreatment device along with a low-sulfur fuel in order to control particle emissions in the 1990s.

## SPECIFIC AIMS

This project was designed to obtain some of the data necessary for evaluating the toxicological impact of LS (< 0.05 wt %) fuel and particle control devices on emissions from late-model heavy-duty diesel engines. Studies were conducted with two engines and control devices: (1) a 1988 Cummins Engine Co. LTA10-300 heavy-duty diesel engine meeting the California 1988 particle standards equipped with a ceramic particle trap having built-in regeneration controls (Phase I); and (2) a 1991 Cummins Engine Co. LTA10-310 heavy-duty diesel engine meeting the EPA 1991 particle standards equipped with an OCC (Phase II). The 1991 LTA engine also contained a high pressure fuel-injection system than the 1988 L10 engine and used an intake-

charge-air-to-air aftercooling system, compared to an intake air intercooler system on the 1988 engine. This plus other engine modifications in the 1991 engine were also implicit in the emissions comparisons between engines and control systems for the Phase I and II studies.

For both phases of this project, the specific objectives were to determine the effects of the fuels and particle control systems on:

1. levels of regulated and unregulated emissions such as NO<sub>x</sub>, HC, TPM, SOF, SO<sub>4</sub>, SOL and XOC;
2. levels of selected mutagenic and carcinogenic PAHs in the SOF and XOC organic fractions;
3. mutagenic activity associated with the SOF and XOC fractions; and
4. exhaust particle size distributions, particularly for those size fractions most likely to be inspired.

The major tasks conducted during each phase are presented in Figure 1. An additional comparison was made on the effects of engine type (L10 versus LTA) on these emissions.

SOF and XOC samples for all engine, fuel and control device combinations were analyzed for nitro-PAHs. However, questions about the accuracy of the nitro-PAH measurements arose because the chromatographic separation procedures used for these analyses did not completely resolve the individual nitro-PAH peaks, and a second separation and measurement technique was not available to confirm the data. Therefore, the nitro-PAH data are not included in this report.

The Phase I study was specifically designed to complement an earlier HEI-funded study (Bagley et al. 1993) with a commercially available CS (0.32 wt %) fuel using the same L10 engine and type of control device; testing was conducted at the same engine operating conditions and samples were analyzed using similar techniques. The data from Phase I of this study were to be used to indicate how such an engine, without any further modifications, would respond to reductions in fuel sulfur levels under controlled operating and sampling conditions. As no low-sulfur fuels were commercially available at the time this study was initiated, arrangements were made to obtain a batch of low-sulfur fuel directly from a refinery. The two fuels (LS and CS), therefore, necessarily differed in properties other than just fuel sulfur content. An additional objective for Phase I was to measure the engine particle and semivolatile vapor-phase organic emissions (including associated mutagenicity and particle size distributions) during trap regeneration.

After the CS and LS fuel comparisons of Phase I were completed, the HEI Research Committee requested addi-

## Phase I Specific Tasks - Cummins 1988 L10 Engine and Donaldson Trap System

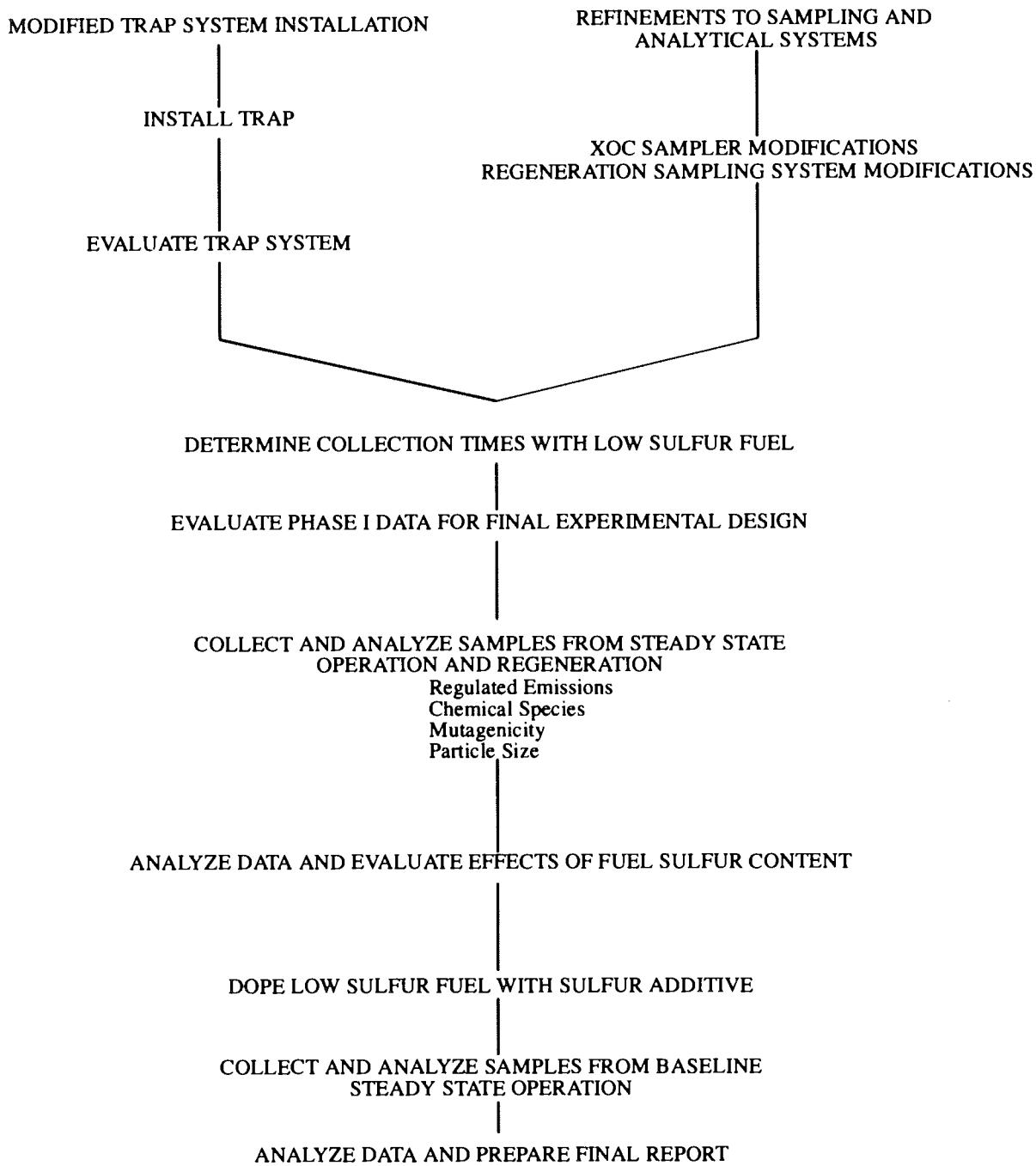


Figure 1A. Specific tasks conducted during the project, Phase I: Cummins 1988 L10 engine and ceramic trap system.

## Phase II Specific Tasks - Cummins 1991 LTA Engine and Oxidation Catalytic Converter

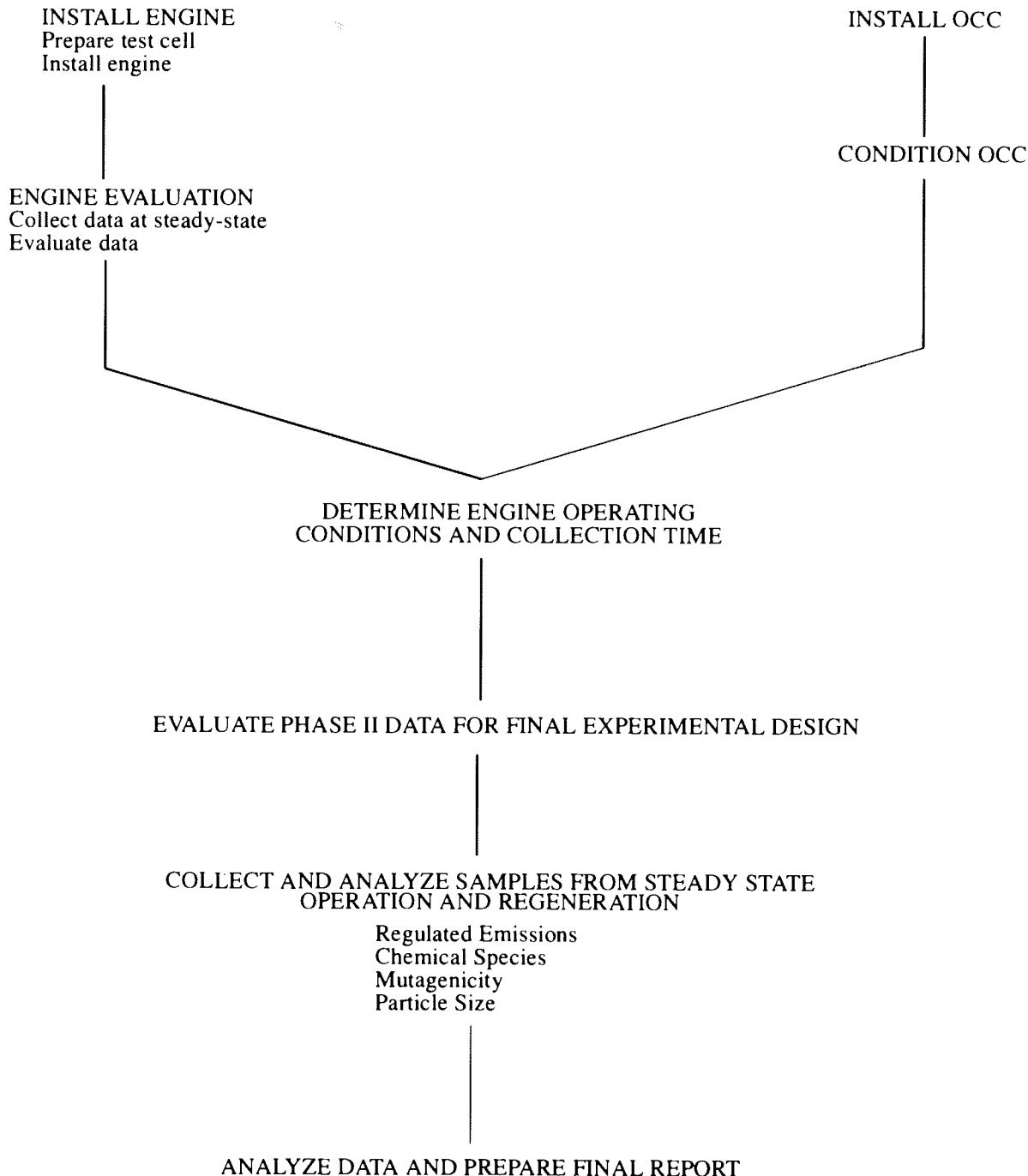


Figure 1B. Specific tasks conducted during the project. Phase II: Cummins 1991 LTA engine and OCC.

tional experiments using a DS fuel, in which a sulfur-containing fuel additive was mixed with the remaining batch of LS fuel to increase its sulfur content to approximately that of the CS fuel. This study, actually conducted after the Phase II engine tests were completed, was performed with the 1988 engine without the particle trap. Data from these limited sets of samples were compared to the LS fuel data to assess the effects on emissions for changes related only to fuel sulfur content.

#### PHASE I. EMISSIONS FROM A CUMMINS 1988 LTA10-300 ENGINE AND A CERAMIC PARTICLE TRAP USING A LOW-SULFUR FUEL

#### METHODS AND STUDY DESIGN

##### Engine, Fuel, and Ceramic Trap

The same engine was used in this study as for Phase II of the previous HEI study (Bagley et al. 1993). This 1988 L10 engine (Cummins Engine Co., Columbus, IN) was rated at 224 kW at 1900 revolutions per minute (rpm). The six-cylinder engine was direct-injected, turbocharged, and after-cooled with a water-to-air heat exchanger. The fuel used for the majority of the project was a Chevron LS fuel purchased from the Poma Distributing Company (Bloomington, CA). Some initial tests used the same Chevron CS fuel used in the 1993 study, and some later tests were performed using the LS fuel doped with di-*tert*-butyl disulfide to obtain sulfur levels near the CS fuel level. The fuel specifications for all of these fuels in Phases I and II can be compared in Table 1.

The ceramic trap system used in this study was provided by the Donaldson Company (Minneapolis, MN) and is shown in Figure 2. The trap system was designed to be used in the horizontal position and includes the inlet diffuser, ceramic foam disk, electric heating element, ceramic substrate, and exit outlet section. The diffuser, ceramic disk, and heating element serve to achieve uniform flow and particulate matter deposition in the ceramic substrate. The ceramic substrate (EX 54 material; Corning, Corning, NY) was a single extrusion that differed from the four piece "quad" substrate of the trap system used during Phase II of the previous study (Bagley et al. 1993). The quad substrate consisted of four pie-shaped ceramic pieces cemented together to form a cylinder. Because the cement acted as a heat sink, emission measurements were complicated by the four individual combustion wave fronts that traveled through the trap during regeneration (Laymac et al. 1991). For both HEI studies, regeneration or oxidation of the collected particles was accomplished by diverting the exhaust before it entered the trap and using a 4000-W electric heater

to heat 280 L of air/minute to 500°C. This hot air then passed through the trap and burned the collected particles. During testing, all pertinent temperatures, pressures, speeds, and flows were recorded.

##### Emission Sampling

Gaseous HC measurements were obtained during baseline and trap sampling using a Beckman Instruments Model 402 Hydrocarbon Analyzer (Rosemount Analytical, Lom-

**Table 1.** Properties of the Fuels Used in This Project

Fuel Property	Conventional Sulfur		Low Sulfur	
	AM 1988 <sup>a</sup>	AM 1990 <sup>b</sup>	Chev 1990 <sup>c</sup>	Chev 1992 <sup>d</sup> DS <sup>e</sup>
API gravity <sup>f</sup> (at 16°C)	38.4	NA <sup>g</sup>	34.5	NA
Distillation profile (°C)				
Initial-boiling point	162	157	183	186
10%	195	201	224	226
50%	254	258	269	269
90%	307	311	318	318
95%	318	NA	331	333
End-boiling point	327	333	352	352
Elemental analysis (wt %)				
Carbon	85.6	86.0	NA	86.9
Hydrogen	13.3	13.5	NA	13.1
Sulfur	0.317	0.314	0.01	0.29
Nitrogen (ppm)	40	47	26.9	NA
Hydrocarbon analysis (vol %)				
Paraffins/naphthenes	73.0	78.0	71.0	70.3
Olefins	3.5	1.5	0.0	0.0
Aromatics (FIAM <sup>h</sup> )	23.5	20.5	29.9	29.7
Cetane number	NA	52.8	42.4	NA
Cetane index	48.6	51.0	NA	54.1

<sup>a</sup> Test performed by AMOCO, Naperville, OH, in 1988.

<sup>b</sup> Test performed by AMOCO in 1990.

<sup>c</sup> Test performed by Chevron Research and Technology Co., Richmond, CA, in 1990.

<sup>d</sup> Test performed by Chevron Research and Technology Co. in 1992.

<sup>e</sup> Low-sulfur fuel doped with di-*tert*-butyl disulfide.

<sup>f</sup> The American Petroleum Institute hydrometer scale for measuring the specific gravity of liquids.

<sup>g</sup> NA = no data available.

<sup>h</sup> FIAM = fluorescence indicator adsorption method.

bard, IL). The NO<sub>x</sub> measurements were also made during baseline and trap sampling in the raw and diluted exhaust using a Beckman Instruments Model 955 NO/NO<sub>x</sub> Analyzer. The raw exhaust samples for both instruments were drawn through heated Teflon sample lines as per the Society of Automotive Engineers (SAE) recommended practices (SAE Handbook 1990). The instruments were calibrated using Scott Specialty Acublend Master Gases (Troy, MI).

Carbon monoxide emissions were measured only during regeneration sampling, using an Ecolizer 2600 Analyzer (National Drager, Inc., Pittsburgh, PA). This instrument was designed to operate at near-ambient air levels of CO and therefore the sample was diluted with a calibrated dilution system prior to measurement. The concentration after the trap was then determined by multiplying the measured value by the dilution ratio.

All TPM and XOC samples collected under baseline, trap, and regeneration conditions were mixed in the dilution tunnel with filtered ambient air before collection. Figure 3 shows the baseline sampling configuration in Michigan Technological University's (MTU) test cell. In the trap configuration, the baseline transfer pipe was removed and a separate pipe was used to transfer a fraction of the raw exhaust after the trap to the dilution tunnel. In the dilution tunnel, the exhaust-air mixture was turbulently

mixed as it passed through the 4.6-m dilution tunnel to the sampling location. In the sampling section, diluted NO<sub>x</sub> was measured so that the exhaust dilution ratio could be determined.

A fraction of the diluted exhaust was then drawn through a filter and XAD-2 resin to collect TPM and XOC, respectively, using the ultra-high-volume sampler (UHVS). The filtered exhaust was then returned to the constant volume sampler. Particulate material was collected on 508- × 508-

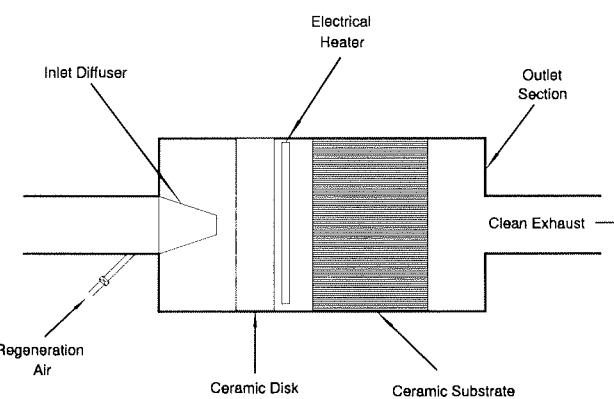


Figure 2. Schematic of the ceramic trap system.

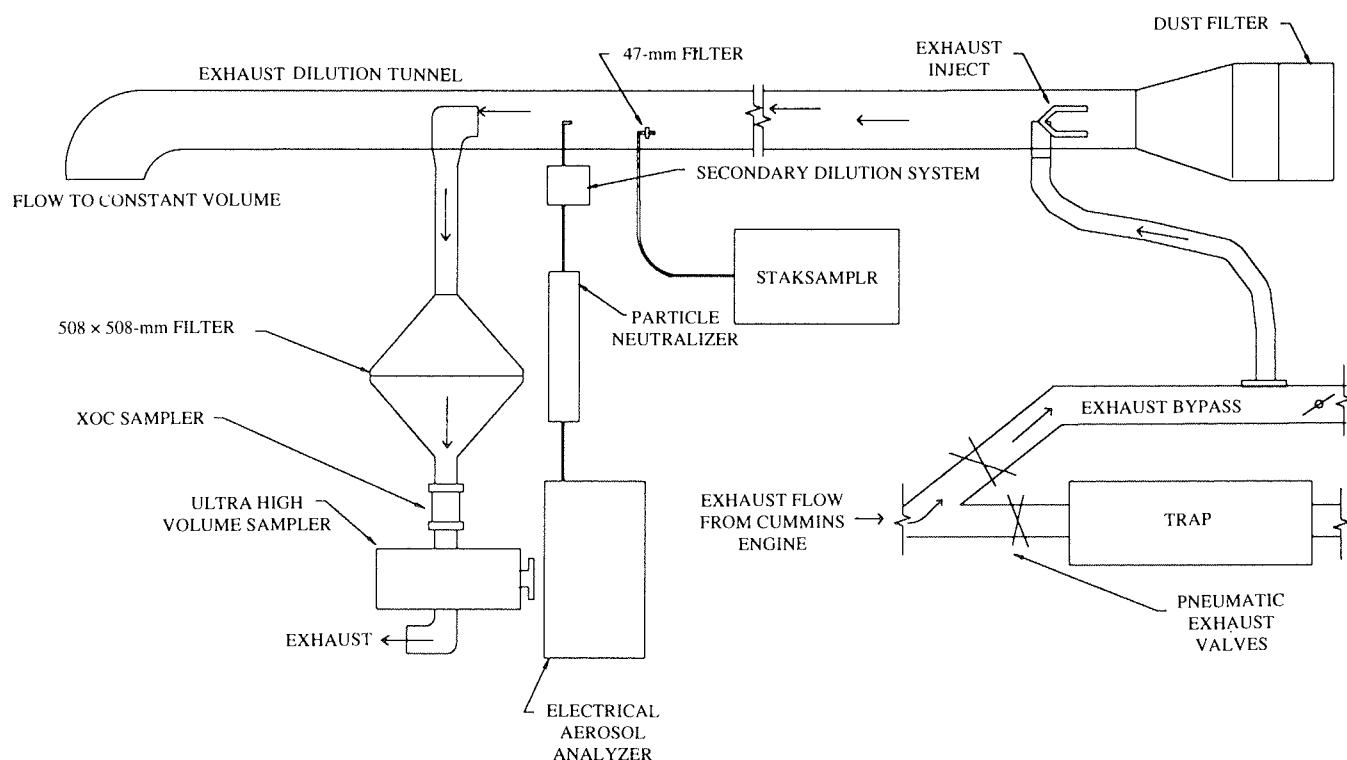


Figure 3. Schematic of the dilution tunnel for baseline sampling with the 1988 Cummins L10 engine.

mm woven glass fiber, Teflon-coated filters (Pallflex TX40HI20-WW, Pallflex Corp., Putnam, CT). The filter face temperature was maintained at  $45^\circ \pm 1^\circ\text{C}$  by varying the dilution ratio. As a consequence, the dilution ratio varied from 10:1 to 16:1 depending on the engine condition. The mass of material collected on the filter was analyzed for TPM, SOF, and SO<sub>4</sub>. In the preliminary stages of this study, particulate matter was also collected on 47-mm filters consisting of the same material as the 508- × 508-mm filters.

The XOC was collected on XAD-2 resin beads (40 g, 20 by 40 mesh, preextracted with dichloromethane (DCM), Supelco, Inc., Bellefonte, PA) located downstream of the 508- × 508-mm filter in the XOC sampler. Details of the sampler have been presented by Waldenmaier and colleagues (1990). The XOC sampler was modified from the previous project (Bagley et al. 1993) by incorporating rubber boots on both the inlet and outlet ends, which eliminated the leakage problem that was identified during the previous HEI study. The XAD-2 resin, a copolymer of styrene and divinylbenzene, collected intermediate-molecular-weight, semivolatile hydrocarbons.

Particle size distributions were determined during both baseline and trap sampling using a Thermo Systems, St. Paul, MN Model 3030 electrical aerosol analyzer (EAA). The EAA measured the size distributions according to the electrical mobility equivalent diameter, which is defined as the diameter of a spherical particle that, when charged under the same conditions, has the same electrical mobility as the particle under study (Hinds 1982). Because the instrument operated on the electrical mobility principle, the incoming aerosol was neutralized by passing through a particle neutralizer to bring the particles to the Boltzmann's equilibrium. In the EAA, the particles passed through a charging chamber, where the particles were positively charged. The number of charges acquired per particle was dependent upon the particle's size, with the larger particles acquiring more charges. After the particles were charged, they entered a mobility chamber that consisted of two concentric cylinders separated by an air space through which the charged particles passed. An electric field was created in the radial direction by applying a voltage between the two cylinders. The particle-laden stream was introduced as an annular flow just inside the outer cylinder and separated from the inner cylinder by a flowing stream of particle-free sheath air. The particles were classified by increasing the voltage gradient in a series of nine steps. At the low voltages, only the small particles with high electrical mobility had a high enough radial drift velocity to cross the sheath air and be collected on the inner collecting rod. This allowed only particles larger than a certain size to pass through and be collected on the collecting plate, where the

particles relinquished their charge and the current was measured. From the nine electrometer currents corresponding to each of the nine size ranges, using the calibration data for the instruments, a size distribution between 0.0075 and 1.0  $\mu\text{m}$  could be obtained.

The EAA was designed to operate at ambient concentrations and, therefore, a secondary dilution system was required (Baumgard and Kittelson 1985). This system consisted of supplying filtered compressed air to two air ejectors in series; the system used in the previous study used only one air ejector. The dilution ratio was then changed by replacing the inlet orifices on the air ejectors. Depending on the engine/trap condition, the dilution ratio varied from 200:1 to 2000:1.

A separate sampling system, shown in Figure 4, was designed as part of the previous HEI study for collection of emissions during regeneration (Laymac et al. 1991). The use of two sampling systems (one for baseline and trap and the other for regeneration) eliminated the potential for contamination from the relatively high particle concentrations found in the baseline and trap sampling systems as compared to the regeneration sampling system. During regeneration sampling, pneumatic valves in the exhaust system were activated, which diverted the exhaust around the trap. The electric heater was then turned on and auxiliary air was supplied to the trap. The valve arrangement allowed for the entire effluent from the trap to be injected into the 150 mm diameter dilution tunnel. Because of the high levels of variability in the regeneration emissions measured during the previous HEI study, several changes were made to the sampling system. In order to minimize particle losses to the walls due to thermophoretic forces (Friedlander 1977), the transfer pipe from the trap to the dilution tunnel was wrapped with heating tape and the wall temperature was maintained at essentially the same temperature as the gas stream. The filter holder was reduced in size from 200 × 254 mm to 130 × 170 mm to increase the mass collected per filter area and reduce weighing errors. The filters were of the same type as those used with the UHVS. Collection filter face temperatures were controlled by heating the dilution tunnel inlet air to maintain an approximately  $45^\circ\text{C}$  filter face temperature. As with the baseline and trap sampling system, the XOC sampler was placed directly downstream of the filter. The regeneration collection time was 30 minutes, which was based on the observed time required for complete regeneration to occur.

During regeneration, the EAA was used as a real-time particle indicator. This was accomplished by setting the EAA on channel 3 and recording the total current output from the instrument. The current was an indirect measurement of the total number of particles.

## Chemical Characterization

### Determination of TPM, SOF, $\text{SO}_4$ , SOL, XOC, and Aldehydes

All filters used to collect particulate matter were equilibrated in a constant relative humidity chamber ( $42 \pm 3\%$  relative humidity and  $25^\circ \pm 1^\circ\text{C}$ ) and weighed prior to exposure. After exposure, the filters were ammoniated for one hour in a covered Plexiglas chamber containing an open Petri dish of ammonium hydroxide. The filters were then reequilibrated in the constant relative humidity chamber and reweighed to obtain the mass of TPM.

After reweighing, the exposed filters were extracted for 24 hours with DCM in a Soxhlet apparatus to obtain the SOF. The mass of SOF was determined gravimetrically on a small (100- $\mu\text{L}$ ) aliquot of the total extract, which was brought to dryness. The DCM-extractable organic compounds from the XAD-2 resin samples (XOC) were obtained and treated in an identical manner to the SOF. All extracts (SOF and XOC) were stored frozen ( $-16^\circ \pm 4^\circ\text{C}$ ) until they were divided into aliquots for Ames assay and PAH quantification. Unexposed filters and XAD-2 resin were also extracted (one sample each per test day) and the masses of extractable material were used to correct the exposed samples for background contributions on a mass basis.

The filters were extracted with sonication in distilled, deionized water (after SOF extraction) to obtain the  $\text{SO}_4$  fraction. Sulfate concentrations were determined on these extracts using ion chromatography with a conductance detector by comparison to an aqueous standard curve consisting of solutions having known concentrations of potassium sulfate.

The SOL emissions were defined as the mass left on the filter after extractions with DCM and deionized water. The SOL levels were, therefore, determined by the difference in TPM, SOF, and  $\text{SO}_4$  masses as:  $\text{SOL} (\text{mg}) = \text{TPM} (\text{mg}) - \text{SOF} (\text{mg}) - \text{SO}_4 (\text{mg})$ .

Considerable effort was also expended in attempting to collect and quantify low-molecular-weight aldehydes from the dilute exhaust stream. As detailed in Appendix A, a system was devised that showed good precision and about 90% recovery of standard samples in laboratory bench-top experiments. However, when sampling of the exhaust gas from the dilution tunnel was carried out, poor precision in the measurements resulted. This was most likely due to the relatively high background of aldehydes that existed on the 2,4-dinitrophenylhydrazine (DNPH) sampling cartridges (prepared at MTU) compared to the amount of aldehydes

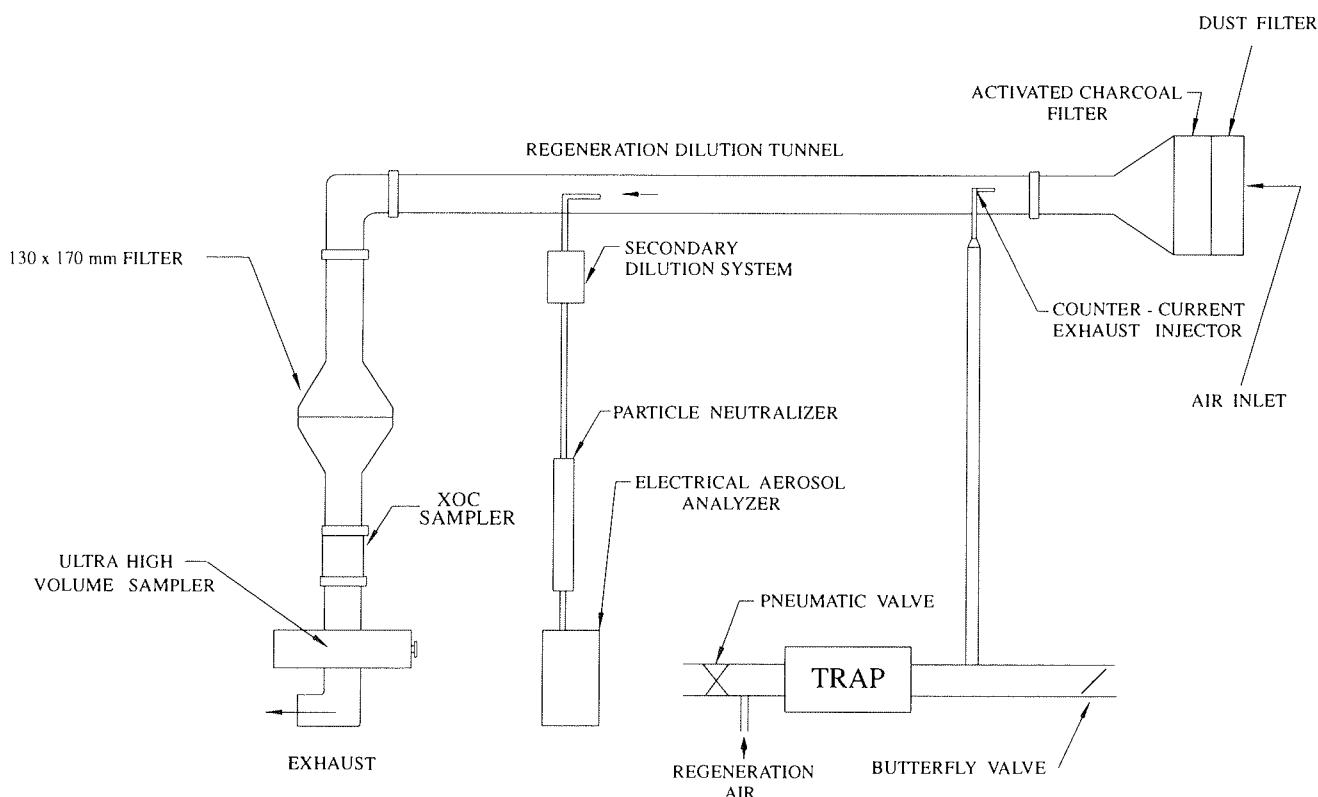


Figure 4. Schematic of the regeneration dilution tunnel.

collected from the diluted exhaust. Compounds containing the carbonyl functional group, such as acetone, are ubiquitous in laboratory environments and tend to be contaminants in the preparation of the DNPH sampling cartridges. Low levels of aldehydes could also have been present in the air entering the dilution tunnel. The end result was that these MTU-prepared cartridges could not be used effectively for low-level aldehyde measurements. Consequently, the measurement of aldehydes in the diluted exhaust was discontinued as part of this project as there was not sufficient time to develop modified procedures allowing for preparation of uncontaminated sampling cartridges. (Commercially prepared cartridges were not yet available at the time this initial work was being conducted.)

**Quantification of PAHs for Low-Sulfur Fuel Study** The PAH compounds chosen for quantification were the same as those used in the previous HEI study (Bagley et al. 1993), that is, fluoranthene (FLU), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), and benzo[a]pyrene (BaP). These compounds were of interest due to their health effects (Barfknecht et al. 1982; Amin et al. 1986; LaVoie et al. 1987; Cavalieri et al. 1988; Solt et al. 1988) or because of their potential to be converted to compounds with known or suspected health effects (for example, PYR).

The SOF and XOC samples were first separated into four fractions (aliphatic compounds, PAHs, nitro-PAHs, and a polar fraction) using a two-column procedure (Figure 5). The PAH fraction was then analyzed via high-performance liquid chromatography (HPLC) with fluorescence detection. A standard reference material (SRM 1647) from the National Institute for Standards and Technology (NIST, Gaithersburg, MD) containing certified levels of the PAHs of interest was used as an HPLC calibration standard (diluted 1:250). NIST SRM 1650, certified diesel particulate matter, was used as a control sample and was subjected to Soxhlet extraction and column separation procedures prior to analysis by HPLC.

The HPLC column used was a Vydac 54TP201 with octadecylsilane bonded to silica particles (nominally 5 µm in diameter) in a 4.6- × 250-mm stainless-steel column (P. J. Cobert Assoc., St. Louis, MO), using a Hewlett Packard (HP; Avondale, PA) model 1084 instrument and a Schoeffel FS970 fluorescence detector. A mobile-phase gradient was used (methanol and water) and the seven PAH compounds of interest were eluted in about one hour. The method details were previously published (Gratz et al. 1991) and have been summarized in Table 2. Example chromatograms

are given in Figure B.1 in Appendix B. Recovery data for the PAHs of interest in SRM 1650 are presented in Table B.1.

**Quantification of PAHs for Doped-Sulfur Fuel Study** The HPLC method for quantification of PAHs used for the LS fuel study (and the previous CS fuel study) was adapted for use with an HP 1090 HPLC instrument and an HP 1046AX fluorescence detector. This instrument provided enhanced sensitivity and selectivity due to the capability of the HPLC to pump reproducible gradients at microbore flowrates and also due to the programmable fluorescence detector, which enabled the optimization of both excitation and emission wavelengths during a chromatographic run. Therefore, the selectivity and sensitivity could be enhanced compared to the instrumentation used previously. Typically, minimum detection limits (MDLs) were reduced by an order of magnitude with the use of this system. Although BaA and CHR eluted rather closely together, they had different wavelengths of maximum absorption and emission; it was necessary to make two separate HPLC runs for each sample: one for BaA quantification and the other for all the remaining PAHs. The method details are summarized in Table 3. Example chromatograms are provided in Figure B.2 in Appendix B.

**Analysis of Fuel Samples for PAHs** The fuel samples (500 µL) were analyzed for the same PAH compounds as for the SOF and XOC samples. The method of analysis was slightly modified, however, in that a different column procedure was used prior to HPLC quantification. Samples were separated on alumina (10 g), where the first fraction (hexane, 20 mL), presumably containing mostly aliphatic compounds, was followed by elution of an aromatic fraction (toluene, 40 mL). The PAH fraction was then analyzed using the HPLC-fluorescence method described for the SOF and XOC samples in the DS fuel study with one modification; that is, phenanthrene and anthracene were added to the list of PAHs quantified.

**Mutagenicity Assays** Mutagenic activity of the SOF and XOC samples was determined using a version of the microsuspension (micropreincubation) modification of the *Salmonella typhimurium*/microsome mutagenicity bioassay or Ames test (Kado et al. 1983; Maron and Ames 1983; Bagley et al. 1993). This modified Ames test resulted in increased sensitivity, lower sample mass requirements, and lower media and supply requirements than the standard plate incorporation Ames test.

Tester strain TA98 was provided by Dr. Bruce Ames (University of California, Berkeley) and tester strains

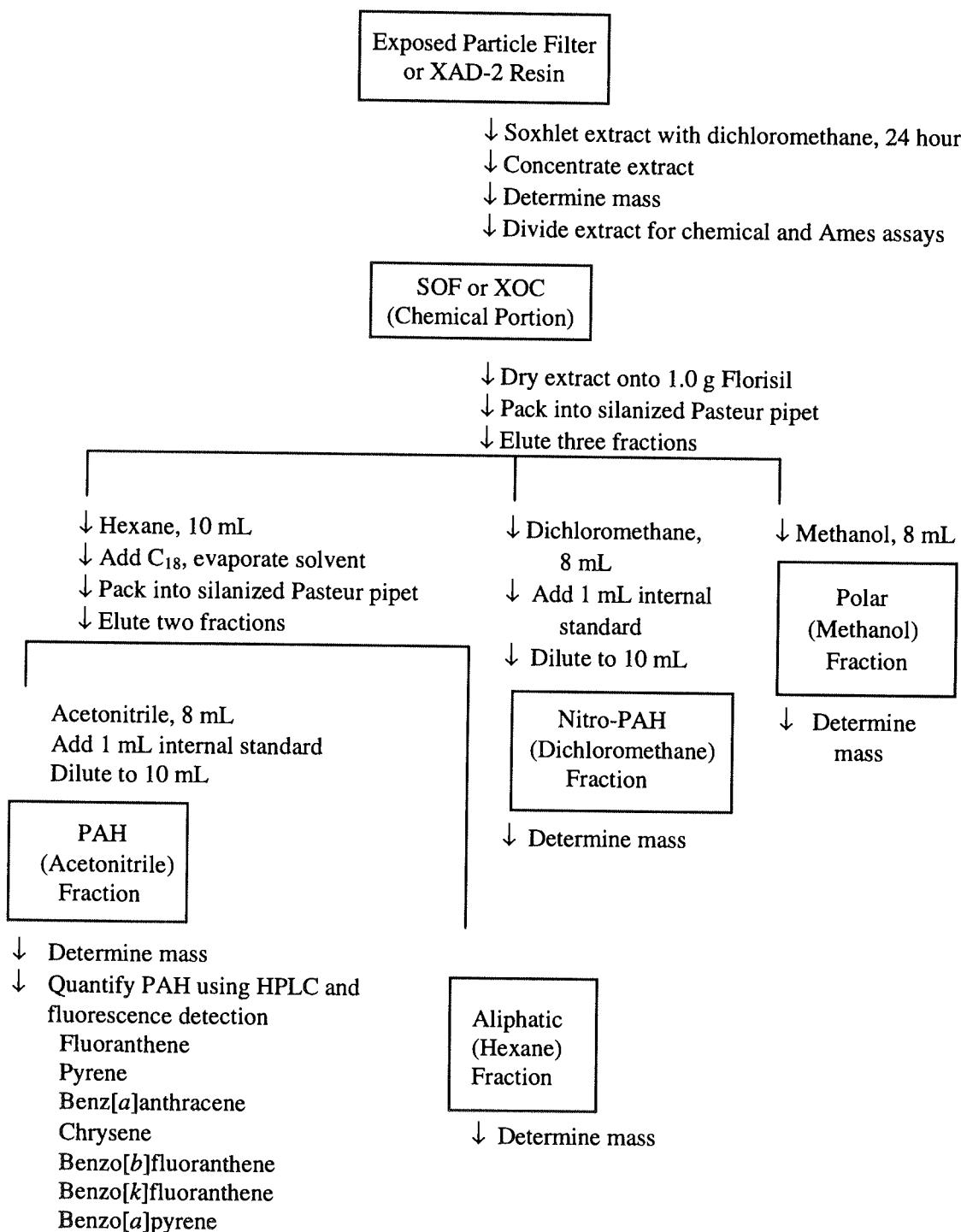


Figure 5. Flow chart for the extraction of SOF and XOC and quantitative analysis of PAHs.

TA98NR (nitroreductase-deficient) and TA98-1,8-DNP<sub>6</sub> (*o*-transacetylase-deficient, referred to as TA98DNP) were provided by Dr. Herbert Rosenkranz, University of Pittsburgh. Tester strain stocks were stored in 2-mL glass vials at -70°C in nutrient broth (Oxoid Broth No. 2, Unipath Co., Oxoid Division, Ogdensburg, NY) with 8% v:v dimethyl sulfoxide (DMSO) (Maron and Ames 1983). Rat liver S9 microsomal fraction (S9) from Arochlor 1254-induced male Sprague-Dawley rats was purchased from Molecular Toxicology, Inc. (Annapolis, MD); the mean (and coefficient of variation [CV] for S9 protein concentration from three lots used during Phase I and Phase II was 38.6 mg/mL (3.6%). 2-Nitrofluorene and 2-aminoanthracene were purchased from Aldrich Chemical Co. (Milwaukee, WI), 1-nitropyrene from Pfaltz and Bauer (Waterbury, CT), and DMSO (99% purity) from Sigma Chemical Co. (St. Louis, MO). As noted above, the SOF and XOC samples were obtained by Soxhlet extraction with DCM. After solvent removal, DMSO was added to an aliquot of known mass for use in mutagenicity testing. These samples were stored at -15° to -20°C prior to analysis.

**Table 2.** HPLC Parameters for Quantifying Selected PAHs in Diesel Exhaust Extracts for the Conventional, High-Sulfur and Low-Sulfur Fuel Studies

HPLC instrument	HP 1084 or equivalent, capable of gradient elution
Column	Vydac 54TP201, 4.6 mm i.d. × 250 mm
Mobile phase	70% methanol, 30% H <sub>2</sub> O; isocratic for 30 min, then linear gradient to 100% methanol in 30 min, then isocratic for 15 min
Flow rate	1.00 mL/min
Injection volume	5 to 20 µL
Detector	Schoeffel FS970
Excitation wave length	267 nm with a 389-nm emission cutoff filter
Compound	Relative Retention Time <sup>a</sup>
Fluoranthene	0.608
Pyrene	0.693
Benz[a]anthracene	1.33
Chrysene	1.40
Benzo[b]fluoranthene	1.61
Benzo[k]fluoranthene	1.70
Benzo[a]pyrene	1.74

<sup>a</sup> Relative to 2-chloroanthracene (used as an internal standard), which elutes at approximately 33 min.

The modified, small-dish (60- × 15-mm) microsuspension assay was conducted in the presence and absence of S9, following the procedures detailed in Bagley and colleagues (1993), except that 0.015 M (pH 7.4) phosphate-buffered saline was used instead of 0.15 M phosphate-buffered saline (DeMarini et al. 1989). All tests were conducted using duplicate dishes per dilution. Revertant colonies on the test dishes were counted after 63 hours of incubation at 37° ± 2°C (Belser et al. 1981) using an Arteck Model 880 automatic colony counter (Arteck Systems Corporation, Farmingdale, NY). All assays were performed under filtered lighting to prevent photooxidation by UV radiation.

**Table 3.** HPLC Parameters for Quantifying Selected PAHs in Diesel Exhaust Extracts for the Doped-Sulfur Fuel Study

HPLC instrument	HP 1090 or equivalent, capable of microbore chromatography and gradient elution
Column	Vydac 52TP201, 2 mm i.d. × 250 mm
Mobile phase	65% methanol, 35% H <sub>2</sub> O; linear gradient to 95% methanol in 20 min, then isocratic for 15 min
Flow rate	200 µL/min
Injection volume	2 to 5 µL
Detector	HP 1046AX

Fluorescence Detector Wavelengths and Expected Retention Times

Compound	Relative Retention Time <sup>a</sup>	Excitation and Emission Wave Lengths <sup>b</sup>
Fluoranthene	0.858	232/440
Pyrene	0.904	232/440
Benz[a]anthracene	1.11	289/413
Chrysene	1.14	267/389
Benzo[b]fluoranthene	1.28	247/418
Benzo[k]fluoranthene	1.33	247/418
Benzo[a]pyrene	1.38	247/418

<sup>a</sup> Relative to 2-chloroanthracene (used as an internal standard), which elutes in this column and solvent at approximately 17.2 min and was detected at 242/440 nm.

<sup>b</sup> Given for the HP 1046AX and may not be appropriate choices for other detectors.

Use of the S9 activation system is designated as +S9 (as in TA98+S9) and no S9 use is -S9 (as in TA98-S9). Direct-acting mutagenicity is detected without S9 activation; indirect-acting mutagenicity is detected with S9 activation.

The protocol first tested each SOF or XOC (or subfraction) sample with TA98 with or without S9 (TA98 ± S9). The SOF or XOC was diluted over a two log<sub>10</sub> concentration range as a series of doses such as 240, 120, 60, 30, 15, 7.5, and 3.75 µg/dish. If sufficient mass was available and the sample demonstrated activity without S9, the sample was retested with TA98NR-S9 and TA98DNP-S9. To eliminate the effect of test-to-test response by the tester strains, samples were grouped together, such as by mode, and run on the same date.

Controls were run on each test date, including solvent (DMSO) controls for spontaneous revertant levels, genotypic checks (ampicillin resistance, crystal violet sensitivity, and histidine-biotin requirement), sterility checks on all assay components, and viability determinations using nutrient agar (Maron and Ames 1983). Sample toxicity to tester strains was monitored by observing whether or not (1) the response levels decreased with increased dose tested, and (2) the background lawn of "microcolonies" varied with increasing dose. The spontaneous revertant and positive control levels found with all tester strains during both Phase I and Phase II are presented in Table C.1 in Appendix C. Extracts from unexposed filters and aliquots of XAD-2 resin were also tested for activity; none of these samples had responses above spontaneous revertant levels.

Preliminary tests were also conducted to determine whether the flowthrough bioassay sampler developed during the previous HEI-funded project (Bagley et al. 1993) could be used as part of this project. This sampler was designed to hold up to eight glass dishes with tester strains that could be exposed to filtered exhaust. In the previous study, this sampler was placed after a 47-mm filter (to remove TPM) and XAD-2 resin (to remove semivolatile organics).

The first tests with the bioassay sampler involved a complex arrangement with both the aldehyde sampler and the bioassay sampler lines located downstream from the XAD-2 resin. This routinely resulted in the aldehyde-trapping solution (DNPH) being drawn into the bioassay sampler, due to the incompatibility of the flow patterns in the 26-L/minute Staksamplr® pump (Research Appliance Co., Allison Park, CA) used with the bioassay sampler, and the 0.5-L/minute pump being used with the aldehyde sampling train. The configuration was changed so that the filtered, diluted exhaust was pulled through the bioassay sampler by a separate, 1.0-L/minute battery-driven constant-volume pump. This eliminated the cross-connection between the

two sampling trains. However, the volume of exhaust to which the dishes were exposed was reduced by a factor of 26 and no responses above spontaneous revertant levels were found in several preliminary tests. There was also increased congestion and difficulty in the engine test facility with trying to operate three separate sampling systems simultaneously, that is, the constant volume, aldehyde, and bioassay sampler systems. Therefore, it was decided to discontinue tests with the bioassay sampler.

**Comparison of Sampling Procedures** The first portion of this study focused on resolving several issues raised as a result of the previous HEI-funded study (Bagley et al. 1993). The specific concerns addressed were (1) whether filter ammoniation to stabilize sulfates also affected the levels of particle-associated PAHs and mutagenicity, and (2) whether increased exposure to exhaust gases affected PAHs and the mutagenicity levels associated with either the SOF or the XOC. These tests were conducted under baseline conditions with the same CS fuel as used in the previous HEI project (Bagley et al. 1993). The data for both of these studies are presented in Appendix D.

**Filter Ammoniation Effects** In order to stabilize filter weights, it has been recommended that the filters be ammoniated after the particulate matter is collected (SAE Handbook 1990). The ammoniation process theoretically converts the SO<sub>4</sub> on the filter to ammonium sulfate; because this compound is fairly stable at room temperature, more stable filter weights should be obtainable, resulting in more repeatable results. The ammoniation should not affect the TPM levels as long as the amount of ammonium sulfate added to the filter is corrected from the filter weight after the SO<sub>4</sub> analysis. However, it was not known what effect the ammoniation process might have on the mutagenicity of the SOF, XOC, or PAH levels in these same fractions.

A test was devised in which the 508- × 508-mm filter samples were collected at modes 9 and 11 using the CS fuel. The filters were either ammoniated for one hour and then frozen, or were frozen without prior ammoniation. The filters were then analyzed for TPM, SOF, SO<sub>4</sub>, mutagenicity, and PAH levels. The data are presented in Tables D.1 to D.4 in Appendix D. The final conclusion was that the ammoniation process had no significant effect on the emissions of interest. Therefore, to obtain more repeatable results, all filter samples were ammoniated for this project.

**Effects of Exposure to Exhaust Gases** The intent of the exhaust gas exposure study was to determine an acceptable sampling time that would produce minimal artifact formation. The procedure involved (1) exposing filters to diluted diesel exhaust for 30 minutes under baseline conditions, using the CS fuel at mode 11, and then (2) reexposing the

filters only to diluted exhaust gas by placing each filter under a clean, unexposed filter. The sampling apparatus was the same as that used in a previous project (Bagley et al. 1987). The reexposure times were 30, 60, and 90 minutes. The reexposed filter was then analyzed for TPM, SO<sub>4</sub>, SOF, SOF-associated PAHs, and mutagenicity. The XOC emissions were collected using the XAD-2 resin, but were not reexposed. The resin samples were continuously collected during the exposing and reexposing sampling times; therefore, the sampling times for the XOC emissions were 60, 90, and 120 minutes. The XOC emissions were also analyzed for PAHs and mutagenicity.

The filter face temperature was maintained at 45° ± 1°C. Assuming that the NO<sub>2</sub> levels in the raw exhaust at mode 11 were less than 20 ppm, the filter face NO<sub>2</sub> levels would have been less than 2 ppm with dilution ratios around 14:1. Therefore, both temperature and NO<sub>2</sub> levels were probably below those believed to cause increases in SOF biological activity or PAH nitration (Bradow et al. 1982; Herr et al. 1982; Saito et al. 1982; Schuetzle 1983).

The complete results are provided in Tables D.5 to D.8 in Appendix D. In general, the data indicated that reexposure of the filters had no effect on TPM, SOF, and SO<sub>4</sub> concentrations. The range of values for SOF-associated PAHs was typical of previous studies, as was the range of mutagenicity values (Bagley et al. 1993). The mass of XOC emissions increased linearly for the longer exposure times, indicating that the resin was not saturated even after a 120-minute sampling time (data not presented). However, the XOC samples analyzed for biological effects showed a proportional increase in direct-acting mutagenicity (measured in the absence of S9; therefore, referred to as -S9) for the sample times greater than 60 minutes. Therefore, the sample times were set at 30 minutes for baseline samples and 60 minutes for trap samples. These sample times allowed for adequate mass to be collected for chemical and biological analysis for all sampling conditions (baseline and trap).

### Experimental Design

All experiments during Phase I were performed using the L10 engine operated under baseline (no trap) and trap conditions, at engine modes 9 and 11; additional samples were collected during periods of trap regeneration. The exhaust system (Figure 3) was designed such that pneumatic valves could be activated to force the exhaust through the trap (trap sampling) or to by-pass the trap (baseline sampling). The general formats used for emissions analyses during steady-state and regeneration operation with the LS fuel are shown in Figures 6 and 7, respectively. The sampling conditions used for the the LS fuel study are shown in Table 4 and the test matrix is presented in Table 5.

For the LS fuel study, a crossed and balanced experimental design was chosen to aid in the statistical analysis of the data. Grand mean values were calculated for this data set because, within a mode-condition combination, each test day or block was equally weighted. This design contrasted with the crossed but unbalanced design used in the previous study (Bagley et al. 1993) with this same engine and a CS fuel, in which there were not only a different number of test days per mode and condition, but also a different number of samples per test day. Due to this unbalanced design, a mean of all test day means was calculated in order to provide equal weightings for each test day. For this LS fuel study, effects of the trap and mode were determined by comparing two factors: (1) aftertreatment (two levels, with and without trap) and (2) EPA steady-state modes (two levels, 9 and 11). Effects of the trap and mode were determined by comparing baseline measurements of HC, NO<sub>x</sub>, NO, TPM, SOF, SO<sub>4</sub>, SOL, XOC, SOF-associated PAHs, XOC-associated PAHs, SOF-associated mutagenicity, and XOC-associated mutagenicity to the same measurements with the trap installed at each mode.

The LS fuel study's experimental design was randomized to the maximum extent possible, given certain constraints. The best design would have been to run all four treatment combinations (baseline or trap at either mode 9 or 11) on one day in a random order. However, the length of time required to set up and perform one replicate (generally two samples) of the experiment, particularly when operating with the trap, precluded the use of this design. At mode 11, in particular, only one sample could be collected before the trap needed regenerating. This meant that the four treatment combinations had to be scheduled on different days with each day representing one block. Each block contained one replicate. Therefore, for three of the treatment combinations, two blocks produced a total of four samples. The exception was the mode 11 trap treatment combination, in which only three samples, scheduled during three separate blocks (or days), were collected. The order in which the LS fuel tests were conducted was as follows: mode 9 trap, mode 9 baseline, mode 11 trap, mode 9 trap, mode 11 trap, mode 11 trap, mode 11 baseline, mode 9 baseline, and mode 11 baseline. A trap regeneration run followed each trap run.

Only a limited number of samples could be collected for the DS fuel study due to the small amount of LS fuel remaining after completion of the above tests. The format used in the DS fuel study was the same as that used with the LS fuel (Figure 6), except that no sampling was conducted with the trap. A balanced experimental design was employed, with one block of test days (four samples per day) per mode (9 or 11) under baseline conditions. Sampling conditions (Table 6) were similar to those for the LS

fuel study. The test matrix was the same as presented in Table 5, except that trap and regeneration samples were not collected.

### Statistical Methods and Data Analysis

The engine-associated data, such as TPM, SOF, XOC, SO<sub>4</sub>, HC, NO<sub>x</sub>, and NO collected during the LS fuel study were analyzed using the MTU diesel emissions computer program on the IBM (White Plains, NY) 4381 mainframe computer (Bagley et al. 1993). Similar data from the DS fuel study were analyzed using a modification of the personal computer-based spreadsheet developed for use in the Phase II studies (Pataky 1992). Means, standard deviations, and CV were calculated by these programs.

The unit of measure selected for raw exhaust data in this study was a standard raw exhaust concentration in milligrams of exhaust per standard cubic meter of air (mg/std m<sup>3</sup>). This unit was used mainly because it is more understandable to health and air pollution scientists and is more common in the health and air pollution literature. Ambient air standards are typically written in these units and estimates of ambient concentration levels may easily be obtained from our data if the dilution ratio is known. One of

the objectives of this research was to provide information about the effects exhaust aftertreatment devices have on emissions; this was accomplished using the mg/m<sup>3</sup> units and comparing the values at each mode. When comparing emissions between the L10 and LTA engines and control technologies (in Phase II), it was more appropriate to normalize the emissions to a brake-specific basis, as mass per kiloWatt-hour (mass/kW-hr).

To determine the standard raw exhaust concentrations (mg/std m<sup>3</sup>) of TPM, SOF, SO<sub>4</sub>, SOL, and XOC, the masses obtained were first divided by the standard volume of raw exhaust that passed through the UHVS sampling system during their respective collection periods. The standard volume of raw exhaust that passed through each filter was determined by first calculating the total dilute exhaust flow that passed through each filter, using the UHVS pump performance curve and correcting this volume to standard conditions of 21.1°C and 101.3 kPa. All concentration data (per m<sup>3</sup>) in this report were corrected to this "standard" condition (referred to as standard temperature and pressure [STP]). This standard volume was then multiplied by the dilution ratio to obtain the standard raw exhaust concen-

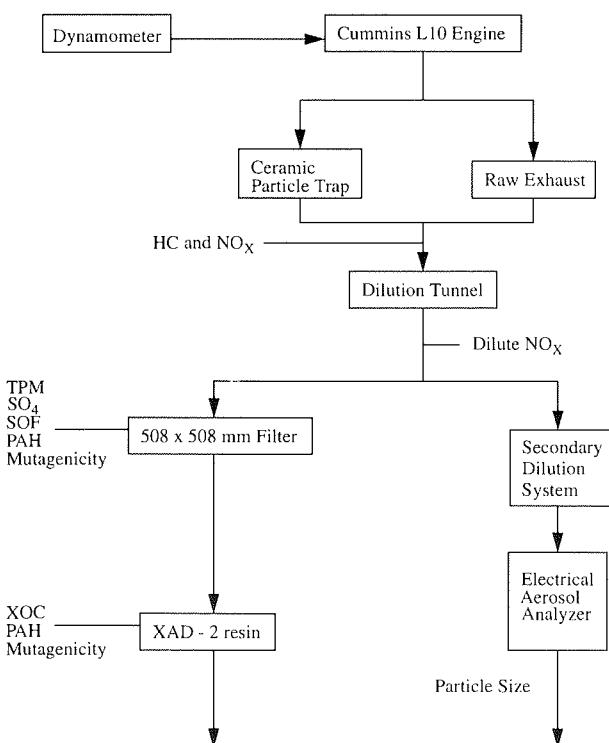


Figure 6. Diesel emissions collection scheme used with the 1988 Cummins L10 engine.

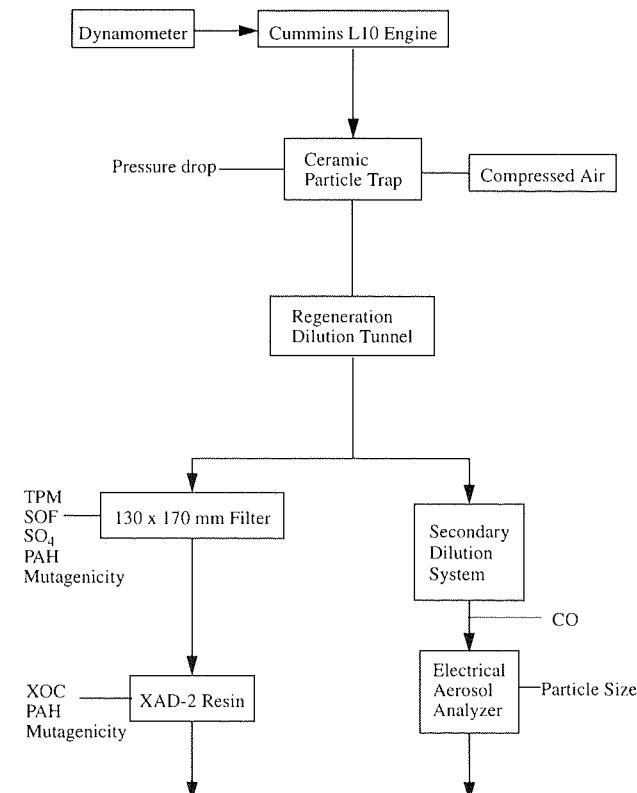


Figure 7. Regeneration emissions collection scheme for the 1988 Cummins L10 engine.

**Table 4.** Steady-State Operating Conditions and Sampling Parameters for the 1988 L10 Engine Using Low-Sulfur Fuel

Operating Conditions	Mode 9	Mode 11		
Load (%)	75	25		
Speed (rpm)	1900	1900		
Torque (N·m)	844	280		
Power (kW)	168	56		
Dry fuel:air ratio	0.032	0.019		
Exhaust flow rate (kg/min)	18.3	12.1		
Fuel flow rate (kg/min)	0.556	0.234		
Sampling Parameters	Baseline	Trap	Baseline	Trap
Number of samples	4	4	4	3
Exhaust temperature (°C)	500	525	338	359
Exhaust backpressure (kPa)	5.5–6.1	17–18.5	3.2–4.3	11–13
Temperature at filter face (°C) <sup>a</sup>	45.1 (1.2)	44.6 (1.9)	45.6 (1.0)	45.2 (0.7)
Sampling time (min) <sup>a</sup>	30 (0.0)	60 (0.0)	30 (0.0)	60 (0.0)
Dilution ratio <sup>a</sup>	14 (2.1)	13 (3.1)	11 (9.6)	10 (7.5)
Approximate NO <sub>2</sub> at filter face (ppm) <sup>a</sup>	3.5 (17)	2.9 (8.2)	2.3 (12)	0.67 (25)

<sup>a</sup> Presented as means (CV in %).

**Table 5.** Test Protocol for Sampling and Quantifying Regulated and Unregulated Emissions from the 1988 L10 Engine Using Low-Sulfur Fuel

Methods and Measures	Mode 9			Mode 11		
	Baseline	Trap	Trap Regeneration	Baseline	Trap	Trap Regeneration
HC, NO <sub>x</sub> , NO, and NO <sub>2</sub> measurements	x	x		x	x	
TPM, SOF, SO <sub>4</sub> , and SOL measurements <sup>a</sup>	x	x	x	x	x	x
XOC measurements	x	x	x	x	x	x
Particle size distribution	x	x	— <sup>b</sup>	x	x	— <sup>b</sup>
Pressure recordings across trap		x			x	
Ames assay on SOF and XOC	x	x	x	x	x	x
Fractionate SOF and XOC samples	x	x	x <sup>c</sup>	x	x	x <sup>c</sup>
Ames assay on subfractions	x	x	x <sup>c</sup>	x	x	x <sup>c</sup>
Quantification of PAHs	x	x	x <sup>c</sup>	x	x	x <sup>c</sup>

<sup>a</sup> 508- × 508-mm filters used with baseline and trap sampling; 130- × 120-mm filters used during regeneration sampling.

<sup>b</sup> Only total particle concentration was measured.

<sup>c</sup> If sufficient mass was available.

tration in mg/m<sup>3</sup>. The dilution ratio was defined as the ratio of the molar flow of dilute exhaust to the molar flow of injected raw exhaust and was estimated by the ratio of NO<sub>x</sub> concentration in the raw exhaust to the NO<sub>x</sub> concentration of the dilute exhaust after the NO<sub>x</sub> measurements were corrected for the removed water.

The raw exhaust data on a brake-specific basis can be obtained by using this formula:

$$C(\text{g/kW-hr}) = [C(\text{mg/m}^3)][M_{\text{exh}}/\rho_{\text{exh}}]/(0.06)(\text{power})$$

where  $C(\text{g/kW-hr})$  = brake-specific value (metric);  $C(\text{mg/m}^3)$  = raw exhaust as a concentration value;  $M_{\text{exh}}$  = mass flow rate (kg/min) and;  $\rho_{\text{exh}}$  = exhaust gas density at STP (1.2 kg/m<sup>3</sup>). The  $M_{\text{exh}}$  and power data for each mode are provided in Table 4.

Statistical analyses for NO<sub>2</sub> levels were not conducted. With the instrument used for this project, NO<sub>2</sub> levels were determined as the differences between the measured NO<sub>x</sub> and NO levels. Considering that the variability of the NO<sub>x</sub> and NO measurements were of the same order of magnitude as the calculated NO<sub>2</sub> levels, NO<sub>2</sub> levels were not considered to be reliable for making a statistical comparison.

The Ames test data were stored in Quattro Pro (Borland International, Inc., Scotts Valley, CA) data files on a personal computer. After a log:log transform of the data, linear regression techniques were used to determine slope and y-intercept values. These values were incorporated into a power function model formula to determine activity as revertants/μg sample (as outlined in Bagley et al. 1993). All PAHs and mutagenic activity values on a mass basis were converted to raw exhaust concentrations using previously determined SOF or XOC concentrations.

The effects of fuel (CS or LS), trap, and engine operating condition (mode) were determined using three-factor ANOVA tests (Zar 1985) for all of the above-listed characteristics. All observations were assumed to follow a linear fixed effects model. The primary hypothesis being tested was: there are no significant differences in emissions when either the CS or LS fuel is used. Secondary hypotheses were: (1) there are no significant differences in emissions with and without the trap as an aftertreatment device; and (2) there are no significant differences in emissions between modes (9 and 11). Tukey's Studentized Range Test (Tukey's test; Zar 1985) was used primarily to assess the effects of the fuel, trap, or mode, if any of the interaction terms were significant. A significance level of  $\alpha = 0.05$  was used for all comparisons. All ANOVA procedures and Tukey's tests were performed using Statistical Analysis System (SAS Institute Inc., 1985) release 5.18, a software package available on MTU's IBM 4381 mainframe computer. The trap regeneration data were not analyzed statistically due to the

limited number of samples, the relatively high variability between regeneration runs, and difficulties in determining concentrations comparable to the steady-state data.

In some cases, the samples were found to have lower concentrations of a given PAH compound than that found in the MDL standard (a suitable dilution of the SRM used for a calibration standard). In those cases, the results were reported as "MDL" and a maximal concentration of the component could be calculated as follows:

$$[\text{PAH}]_{\text{max}} < (\text{MDL}_{\text{std}})(V_i)(\text{SOFRE}/m_{\text{SOF}}),$$

where  $[\text{PAH}]_{\text{max}}$  is the maximal concentration of the given PAH in ng/m<sup>3</sup>;  $\text{MDL}_{\text{std}}$  is the concentration of the given compound in the MDL standard in ng/mL;  $V_i$  is the total volume of the extracted material in the fraction being analyzed in mL; SOFRE is the concentration of SOF in the raw exhaust in mg/m<sup>3</sup>; and  $m_{\text{SOF}}$  is the mass in mg of SOF used for analysis.

For the PAH data sets, values less than the MDL were replaced with one-half MDL values for statistical comparisons (Bagley et al. 1993), unless all of the values were less than the MDL. In these cases, no attempts were made to statistically analyze the data sets and only "less than MDL" was reported as the value. For the mutagenic activity data sets, a value of "no response" above spontaneous revertant levels was considered to be "zero".

Comparisons for fuel sulfur effects on emissions were made with the LS and DS fuel baseline data using two-factor ANOVA tests. The primary hypothesis being tested was: there are no significant differences in emissions with varying fuel sulfur content. The secondary hypothesis was: there are no significant differences in emissions between

**Table 6.** Sampling Parameters During Steady-State Operation of the 1988 L10 Engine Using Doped-Sulfur Fuel<sup>a</sup>

	Mode 9	Mode 11
Number of samples	3	3
Temperature at filter face (°C) <sup>b</sup>	45.9 (0.63)	45.2 (1.9)
Sampling time (minutes) <sup>b</sup>	30 (0.0)	30 (0.0)
Dilution ratio <sup>b</sup>	15 (1.0)	12 (3.9)
Approximate NO <sub>2</sub> at filter face (ppm) <sup>b</sup>	3.3 (17)	1.5 (13)

<sup>a</sup> Only under baseline conditions.

<sup>b</sup> Presented as means (CV in %).

engine modes (9 and 10). The same analytical procedures were used as those for the three-way ANOVA tests described above.

In some cases, levels of certain PAHs measured in the exhaust were tested for correlations or tested against physical parameters (such as vapor pressures) for correlations. A computer spreadsheet (Excel, Microsoft Corporation, Redmond, WA) was used for this purpose, where goodness of fit to least squares, straight line equations, and slopes and intercepts of the calculated straight lines were generated.

## RESULTS

### Gas-, Vapor-, and Particle-Phase Emissions Under Steady-State Conditions

One of the main objectives of this study was to evaluate the overall impact of the trap (Figure 2) on emissions and, therefore, emissions were collected with and without the trap installed in the exhaust stream. This resulted in different exhaust back pressures on the engine for the different operating conditions (see Table 4). The higher back pressures will typically cause the TPM emissions to increase and the NO<sub>x</sub> emissions to decrease. Studies at MTU have indicated that increasing the back pressure by 1.0 kPa at the mode 11 operating condition increases the TPM emissions by 0.58 mg/m<sup>3</sup>. Since this TPM increase is not considered when determining trap TPM efficiency, the results describe the overall effects of adding a trap to existing engines.

The gas-, particle-, and vapor-phase emissions data for the LS fuel are shown in Table 7; for comparison, similar data obtained with the CS fuel (Bagley et al. 1993) are presented in Table 8. The data indicate that the trap caused an increase in both the NO<sub>x</sub> and NO emissions for both the LS and CS fuels. This trend was unexpected because the trap causes an increase in the exhaust back pressure (Table 4), which should lead to lower NO<sub>x</sub> values. The HC emissions were generally lower after the trap with the greatest reductions at mode 9 where the exhaust temperatures were highest (Table 4). The high temperatures in the trap and the large surface area undoubtedly cause some HC oxidation. These emission differences were found to be significant at mode 9 but not at mode 11. The trap effects on HC levels were also significantly different (lower with the trap) only at mode 9; the mode 9 levels were also lower (significantly different) than the mode 11 levels.

For both modes and fuels, the trap was effective at reducing the TPM (76% to 91%), SOF (51% to 92%), and SO<sub>4</sub> (32% to 81%) for the CS fuel. The trap efficiency was higher at mode 9, which has the higher exhaust temperature. The higher temperature causes an increase in the oxidation of HC leading to lower SOF emissions at mode 9 than mode

11. The mode 9 and 11 efficiencies are comparable for both LS and CS fuels. The major fuel emission differences were the SO<sub>4</sub> values; with the LS fuel, the SO<sub>4</sub> values were below the background levels for both baseline and trap conditions. The SOL levels are shown in Tables 9 and 10 for informational purposes as these data were obtained using different sampling systems. Even so, the SOL values are comparable for the two fuels, with reductions of 85% to 95%.

Statistical analyses were performed on all except the SO<sub>4</sub> and SOL data (which were obtained using different sampling systems for the two fuels); the conditions where significant differences were found are provided in Tables E.1 and E.2 in Appendix E. A summary of the results for fuel differences is presented in the Table 7 footnotes. Significant differences were found for fuel, trap, and mode effects for the NO<sub>x</sub> and NO emissions. The HC emissions had mixed results. There were significant differences in fuel effects for both baseline and trap conditions at mode 9 but not at mode 11 (Table 7). The trap effects were also significantly different at mode 9 but not at mode 11. The mode effects (9 versus 11) for HC were significantly different for both baseline and trap conditions.

The fuel effects indicated a significant TPM difference only at mode 9 baseline (Table 7). The differences for mode 9 trap and mode 11 baseline and trap were not large enough to show statistical differences. There were significant differences in TPM and SOF for trap effects at mode 9 and 11 with the LS and CS fuels. This was probably due to minor differences in the traps used in testing the LS and CS fuels. The XOC statistical analysis indicated no differences for mode 9 and 11 fuel effects or mode 11 trap effects; there were significant XOC differences between mode 9 and 11 for trap effects.

### Particle Size Distributions

Mode 9 baseline particle number and volume distributions are shown in Figures 8 and 9, respectively. The data reduction program for the EAA data basically fits a bimodal curve to the data by forcing the curve through limits set on the nuclei and accumulation modes. These limits vary depending on the engine condition or aftertreatment device. Therefore, statistical analyses were not performed on these data and only the final results are presented. If the density of the particles is known, the volume distributions can be converted to the mass distributions. The midpoints of the EAA instrument size ranges are plotted against the particle number or volume on a log scale. The log scale is necessary to cover the several orders of magnitude differences between the concentrations found in the nuclei and accumulation modes. From these plots, the size distribu-

tion is bimodal and consists of a nuclei mode (0.0075 to 0.056  $\mu\text{m}$  in diameter) and an accumulation-mode (0.056 to 1.0  $\mu\text{m}$  in diameter). The number distribution for the LS fuel indicates more than 1 order of magnitude decrease in the nuclei mode from the CS fuel; however, the accumulation-mode number concentrations are nearly the same. The volume distribution indicates similar results; for example, 9.5% of the volume is in the nuclei mode for the CS fuel compared to only 2.2% for the LS fuel.

Mode 11 baseline number and volume distributions are provided in Figures F.1 and F.2 in Appendix F. The results are similar to those found at mode 9, again with the nuclei-mode numbers more than 1 order of magnitude less for the LS fuel. However, the total particle number concentration

for mode 11 is almost 1 order of magnitude less than for mode 9. Consequently, there is very little volume in the mode 11 nuclei mode. Calculations indicate that 2.1% of the particle volume is in the nuclei mode for the LS fuel and a comparable 2.6% for the CS fuel. The accumulation-mode number and volume distributions are also similar for both the CS and LS fuels.

The mode 9 trap distributions are shown in Figures 10 and 11; the comparable mode 11 data are presented in Figures F.3 and F.4 in Appendix F. Note that the abscissa scales are the same for both baseline and trap number distributions, but the volume distributions with the trap are 1 order of magnitude lower than without the trap. For both modes 9 and 11, there are almost 3 orders of magnitude

**Table 7.** Gas-, Vapor-, and Particle-Phase Emissions from the 1988 L10 Engine Using Low-Sulfur Fuel With and Without a Trap<sup>a</sup>

Emission	Mode 9		Mode 11	
	Baseline <sup>b</sup>	Trap <sup>b</sup>	Baseline <sup>b</sup>	Trap <sup>c</sup>
NO <sub>x</sub> (ppm) <sup>d</sup>	750 (4.2)	800 (0.6)	250 (3.7)	250 (2.0)
NO (ppm) <sup>d</sup>	700 (3.5)	760 (0.9)	220 (4.2)	250 (2.7)
HC (ppm) <sup>e</sup>	140 <sup>f</sup> (3.1)	94 (8.7)	170 (2.3)	160 (6.3)
TPM (mg/m <sup>3</sup> ) <sup>g</sup>	27.5 (3.1)	3.66 (8.8)	37.0 <sup>f</sup> (5.4)	8.73 (12)
SOF (mg/m <sup>3</sup> ) <sup>h</sup>	8.07 (21)	1.05 (9.6)	8.86 <sup>f</sup> (26)	4.35 (3.8)
SO <sub>4</sub> (mg/m <sup>3</sup> )	< 0.13 <sup>i</sup> ND <sup>j</sup>	< 0.01 <sup>i</sup> ND	< 0.02 <sup>f,i</sup> ND	< 0.01 <sup>i</sup> ND
SOL (mg/m <sup>3</sup> )	19.4 (5.6)	1.04 (9.7)	28.2 <sup>f</sup> (2.3)	4.33 (3.8)
XOC (mg/m <sup>3</sup> ) <sup>h</sup>	37.8 (13)	19.3 (20)	43.8 <sup>f</sup> (15)	49.1 (14)

<sup>a</sup> Presented as grand means (CV in %); statistical analyses are presented in Tables E.1 and E.2 for comparisons between LS and CS (Table 8) fuel data. References to "significant differences between fuels" compare data in this table with those in Table 8.

<sup>b</sup> Four samples.

<sup>c</sup> Three samples.

<sup>d</sup> Based on Tukey's test, significant differences between fuels only with mode 9 trap.

<sup>e</sup> Significant differences between fuels at mode 9 baseline and trap.

<sup>f</sup> Two samples.

<sup>g</sup> Significant differences between fuels only at mode 9 baseline.

<sup>h</sup> No significant differences detected between fuels.

<sup>i</sup> Maximum detectable value or highest MDL.

<sup>j</sup> ND = not determined because values were < MDL.

decrease in nuclei-mode particle numbers with the LS fuel compared with the CS fuel. The number distributions indicate that, for the CS fuel, the number of particles after the trap decreased by 24% for mode 9 and increased by 400% for mode 11. With LS fuel and the trap, the particle numbers after the trap decreased 91% and 89% for modes 9 and 11, respectively.

Table 9 provides a summary of the number and volume fractions in both the nuclei and accumulation modes for all conditions with the 1988 engine. The number fraction in the nuclei mode for the CS fuel for both baseline and trap conditions ranged between 0.77 to > 0.99. With the LS fuel, the values ranged between 0.44 to 0.60. The data, therefore, indicate that there was a large reduction in nuclei-mode particles when the LS fuel was used.

The particle parameters measured with the EAA are provided in Table 10. The number mean diameter (NMD) and volume mean diameter (VMD) are provided for both the nuclei and accumulation modes in Table 10, along with the geometric standard deviation (GSD) for each mode. The GSD is a measure of the width or spread of the size distribution. Typically, the nuclei mode consists of a fresh aero-

sol and has a narrow size range and a GSD between 1.2 and 1.4. The accumulation mode consists of many particles that have aggregated together and has a wide size range, and a GSD typically between 1.6 and 2.4. The results for baseline conditions, in terms of the overall mean diameters for the nuclei- and accumulation-mode particles, agree with others reported in the literature (Dolan 1977; Verrant and Kittelson 1977; Khatri et al. 1978; Baumgard and Kittelson 1985). The values in Table 10 also indicate that the mean diameters of both the nuclei- and accumulation-mode particles with CS and LS fuels are similar for baseline conditions, but less so with trap conditions. The NMD values for nuclei-mode particles are similar, but the VMD values for accumulation-mode particles are quite different. This was possibly due to differences in trap configuration between the two studies, which might have affected the collection efficiency.

#### PAHs in SOF and XOC Samples

Polynuclear aromatic hydrocarbon levels for particle-associated and vapor-phase samples collected from the L10 engine with the LS fuel are presented in raw exhaust con-

**Table 8.** Gas-, Vapor-, and Particle-Phase Emissions from the 1988 L10 Engine Using Conventional, High-Sulfur Fuel With and Without a Trap<sup>a</sup>

Emission	Mode 9		Mode 11	
	Baseline <sup>b</sup>	Trap <sup>c</sup>	Baseline <sup>b</sup>	Trap <sup>b</sup>
NO <sub>x</sub> (ppm)	710 (7.8)	740 (2.5)	220 (9.0)	240 (2.1)
NO (ppm)	670 (8.0)	720 (2.9)	210 (7.9)	240 (1.5)
HC (ppm)	75 (10.4)	42 (6.4)	160 (0.5)	140 (2.5)
TPM (mg/m <sup>3</sup> )	33.4 (7.8)	3.16 (18)	38.0 (4.7)	8.44 (11)
SOF (mg/m <sup>3</sup> )	9.07 (6.6)	0.75 (23)	12.0 (2.6)	4.50 (16)
SO <sub>4</sub> (mg/m <sup>3</sup> ) <sup>d</sup>	6.20 (2.5)	1.20 (8.2)	3.09 (18)	2.10 (3.4)
SOL (mg/m <sup>3</sup> ) <sup>d</sup>	17.3 (19)	0.88 (24)	23.3 (9.2)	3.20 (29)
XOC (mg/m <sup>3</sup> )	27.4 (28)	8.83 (29)	41.6 (15)	38.1 (54)

<sup>a</sup> Presented as means of test date means (CV in %) (data from Bagley et al. 1993).

<sup>b</sup> Two samples.

<sup>c</sup> Six samples.

<sup>d</sup> Data obtained from 47-mm filters.

centration units (ng PAH/m<sup>3</sup>) in Table 11; PAH levels on a mass basis (µg PAH/g SOF or XOC, and µg PAH/g TPM) are presented in Tables B.2 and B.3, respectively. For comparison purposes, the PAH levels (ng PAH/m<sup>3</sup>) found with the CS fuel (Bagley et al. 1993) are presented in Table 12. Statistical analyses were also conducted on the PAH data sets for LS and CS fuels using the raw exhaust concentration (ng PAH/m<sup>3</sup>) and mass (µg/g SOF, TPM, or XOC) values, although the PAH mass data for the CS fuel (Bagley et al. 1993) are not presented in this report. No statistical analyses were conducted for compounds that had most or all values less than the MDL (BbF, BkF, and BaP for XOC samples). Summaries of statistical analysis results for fuel effects are presented in Table 13; these summaries are based on data contained in Tables E.3 to E.6 in Appendix E, which also include the trap and mode statistical information.

For FLU, the only significant differences were due to the use of the trap. Both particle (TPM) and vapor-phase (XOC)

**Table 9.** Number and Volume Fractions in the Nuclei Mode for the Low-Sulfur and Conventional, High-Sulfur Fuels with the 1988 L10 Engine

Mode and Condition	Number Fraction		Volume Fraction	
	CS	LS	CS	LS
9 Baseline	0.975	0.585	0.095	0.022
9 Trap	0.999	0.553	0.464	0.016
11 Baseline	0.776	0.443	0.026	0.021
11 Trap	0.999	0.604	0.754	0.020

**Table 10.** Particle Parameters from the 1988 L10 Engine Using Conventional, High-Sulfur and Low-Sulfur Fuels With and Without a Trap<sup>a</sup>

Mode and Condition	n <sup>b</sup>	Number Mean Diameter		Volume Mean Diameter		Geometric Standard Deviation <sup>c</sup>	
		Nuclei Mode	Accumulation Mode	Nuclei Mode	Accumulation Mode	Nuclei Mode	Accumulation Mode
<b>CS Fuel</b>							
9 Baseline	2	0.018 (0.8)	0.058 (7.0)	0.019 (0.7)	0.246 (1.8)	1.2 (2.3)	2.01 (2.1)
9 Trap	5	0.010 (4.2)	0.091 (16)	0.023 (6.8)	0.708 (15)	1.37 (2.0)	2.41 (5.0)
11 Baseline	4	0.015 (1.6)	0.075 (3.3)	0.018 (14)	0.167 (9.7)	1.23 (4.7)	1.67 (3.3)
11 Trap	4	0.016 (6.4)	0.091 (14)	0.020 (2.6)	0.789 (27)	1.29 (5.8)	2.32 (5.6)
<b>LS Fuel</b>							
9 Baseline	3	0.011 (10)	0.065 (15)	0.016 (21)	0.299 (31)	1.38 (14)	2.01 (11)
9 Trap	3	0.015 (9.1)	0.067 (11)	0.025 (24)	0.266 (30)	1.48 (8.4)	1.95 (10)
11 Baseline	3	0.015 (5.1)	0.075 (1.5)	0.029 (18)	0.161 (1.0)	1.60 (5.4)	1.65 (1.0)
11 Trap	3	0.017 (15)	0.065 (6.9)	0.021 (26)	0.236 (12)	1.28 (9.3)	1.92 (4.4)

<sup>a</sup> All parameters are presented in micrometers as means (CV in %).

<sup>b</sup> Number of samples.

<sup>c</sup> A measure of the spread of the particle size distribution; see text for further information.

FLU emissions increased on a mass basis when the trap was used. The raw exhaust concentration of FLU in the vapor phase increased and there was a concurrent (although not statistically significant) decrease in the particle-associated concentration of FLU when the trap was used compared to baseline. There were no engine mode or fuel effects that were significant for FLU emissions. Levels of PYR were affected mainly by fuel type, with the LS fuel producing increased raw exhaust concentration levels compared to the CS fuel for both modes, whether or not the trap was used. On a mass basis, the particle-phase PYR was also greater when the LS fuel was used. For the operating conditions tested, there were relatively few significant effects on PYR levels due to the engine mode or the use of the trap. Benz[a]anthracene levels were most consistently different between fuels on a  $\mu\text{g/g}$  SOF or XOC basis (both modes, baseline and trap). There were generally no effects due to engine mode or use of the trap for BaA or CHR. Emissions of CHR were also affected by fuel (on a TPM basis) for both engine modes and independent of trap use. The LS fuel

produced higher levels of both BaA and CHR (for mass and raw exhaust comparisons, with noted significant differences) than the CS fuel.

For BbF, BkF, and BaP, there were generally consistent fuel effects on the basis of both mass and raw exhaust concentration. Although BkF and BaP were detected only in the particle phase, BbF partitioned to a measurable extent between the vapor and particle phases at temperatures and particle concentrations typical of those found in the dilution tunnel during this study. Fuel type also affected the vapor-phase levels of BbF at both modes and conditions. In all cases (BbF, BkF, and BaP) where significant effects were noted due to fuel, the higher levels were found with the LS fuel.

#### PAH Levels in Fuels

The PAH levels obtained for the LS and CS fuels are given in Table 14. These data were not statistically analyzed due to the lack of replicate analyses. Of the nine PAH compounds quantified in these fuel samples, phenanthrene was

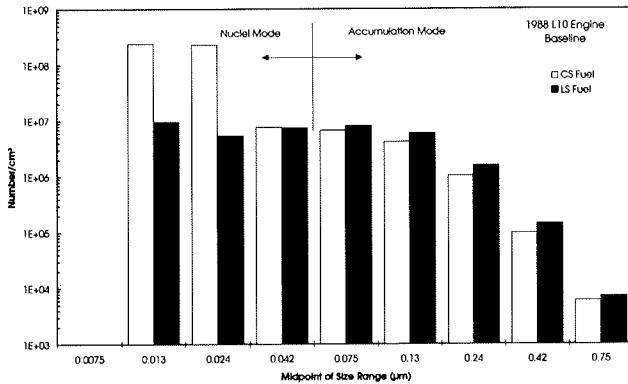


Figure 8. Mode 9 baseline particle number distributions between LS and CS fuels for the 1988 Cummins L10 engine.

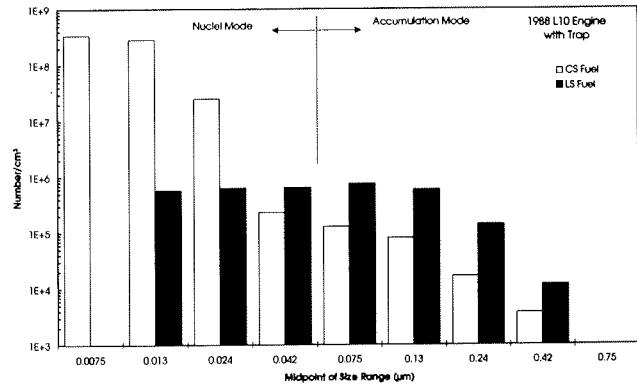


Figure 10. Mode 9 trap particle number distributions between LS and CS fuels for the 1988 Cummins L10 engine.

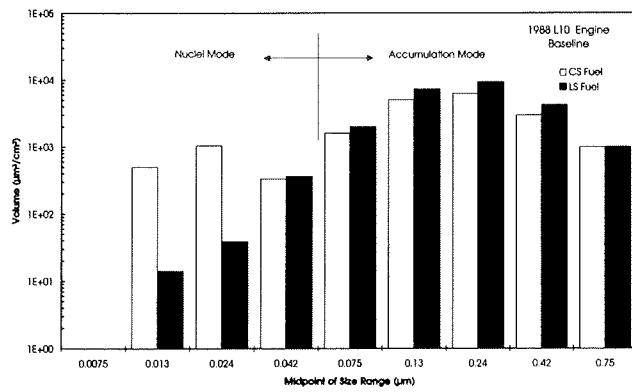


Figure 9. Mode 9 baseline particle volume distributions between LS and CS fuels for the 1988 Cummins L10 engine.

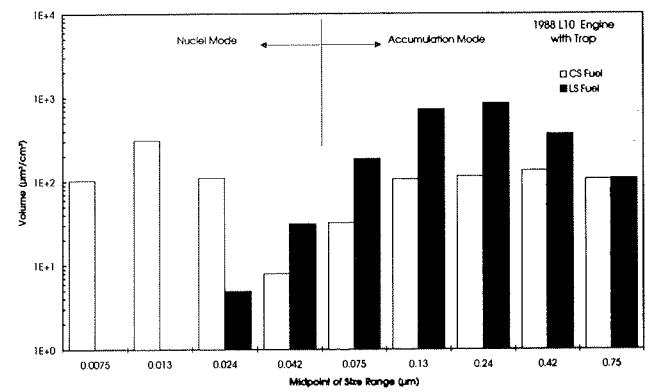


Figure 11. Mode 9 trap particle volume distributions between LS and CS fuels for the 1988 Cummins L10 engine.

the most abundant compound (200 ppm in LS fuel, and 400 ppm in CS fuel). Benzo[a]pyrene was present at the lowest levels (< 1 ppm for either fuel). Although for some compounds there were two- to fourfold differences between fuels, one fuel was not clearly more concentrated in PAHs than the other. The CS fuel levels of phenanthrene, anthracene, FLU, CHR, and BkF were higher than for the LS fuel, while the PYR, BaA, and BbF levels were higher in the LS fuel.

#### Mutagenicity of SOF and XOC Samples

The mutagenic activities observed with the SOF and XOC obtained from use of the LS fuel are shown in Table 15. As has been reported in previous studies at MTU and elsewhere (Ball et al. 1990; Crebelli et al. 1991; Gratz et al. 1991; Westerholm et al. 1991; Bagley et al. 1993), activity obtained with S9 metabolic activation was similar to or

(often) lower than values obtained without S9. The primary exception was with the mode 9 trap SOF samples, where sample toxicity at the higher doses tested was observed without S9. Similar data from the previous HEI-supported study (Bagley et al. 1993) with the CS fuel are presented for comparison purposes in Figures 12 and 13 for mutagenicity activity on a mass (revertants/ $\mu$ g SOF or XOC) or raw exhaust (revertants/ $m^3$ ) basis, respectively.

With either fuel, the general trends for mutagenic activity on a mass basis (revertants/ $\mu$ g) were: (1) reduced activity with trap usage, (2) similar or greater activity at mode 11 than at mode 9, and (3) greater activity in the SOF than the XOC (Figure 12). Similar or greater activity was generally observed with the LS fuel as compared to the CS fuel, particularly for the XOC. As indicated in the Table 15 footnotes, some of these fuel differences were found to be significant. (Statistical test results for fuel, trap, and mode

**Table 11.** Particle-Associated (SOF) and Vapor-Phase (XOC) PAH Emissions from the 1988 L10 Engine Operated with Low-Sulfur Fuel With and Without a Trap

Mode and Condition	Fraction	n <sup>a</sup>	PAH Level ( $ng/m^3$ ) <sup>b</sup>					
			FLU	PYR	BaA	CHR	BbF	BkF
9 Baseline	SOF	4	720 (37)	2300 (12)	1100 (61)	600 (74)	260 (28)	110 (84)
	XOC	4	2100 (48)	1800 (28)	320 (29)	240 (28)	4.6 (52)	< 6.0 <sup>d</sup> ND <sup>e</sup>
9 Trap	SOF	4	170 (24)	330 (18)	140 (25)	180 (24)	41 (48)	< 1.9 <sup>f</sup> ND
	XOC	4	2700 (83)	1400 (88)	170 (88)	58 (74)	20 <sup>c</sup> (> 100)	< 2.2 <sup>d</sup> ND
11 Baseline	SOF	4	1200 (5.6)	2000 (9.0)	730 (18)	1250 (12)	250 <sup>c</sup> (2.9)	91 <sup>c</sup> (5.4)
	XOC	3	1200 (14)	910 (14)	250 (7.3)	270 (55)	6.5 (18)	< 4.5 <sup>d</sup> ND
11 Trap	SOF	3	430 (82)	1000 (20)	730 (30)	530 (85)	150 (> 100)	110 <sup>g</sup> ND
	XOC	3	7600 (72)	2500 (78)	490 (56)	250 (55)	$\leq 9.7^d$ ND	< 7.7 <sup>d</sup> ND

<sup>a</sup> Number of samples.

<sup>b</sup> Presented as means (CV in %).

<sup>c</sup> n = 3.

<sup>d</sup> All values were less than or equal to this MDL.

<sup>e</sup> ND = not determined, because values were less than the MDL or only one value was obtained.

<sup>f</sup> Three of four values were less than this MDL; the fourth value was 9.4  $ng/m^3$ .

<sup>g</sup> n = 1.

<sup>h</sup> n = 2.

effects are presented in Tables E.7 and E.8 in Appendix E.) A significant fuel effect on activity (revertants/ $\mu\text{g}$  SOF, TPM, or XOC) was found at mode 11 with the trap and for XOC activity at mode 11 baseline and mode 9 with the trap. The change in trap XOC-associated activity between the two fuels was the most noticeable fuel effect, changing from not detectable with the CS fuel to approaching baseline levels with the LS fuel. No consistent pattern was observed for significant trap effects on activity, except that differences occurred between the LS and CS fuel results. Significant mode effects on activity were found only for the LS fuel data.

On a concentration basis (revertants/ $\text{m}^3$ ) for both fuels (Figure 13), there were generally (1) reductions in all forms of mutagenic activity with the trap, (2) greater activity at mode 11 than at mode 9, and (3) similar or greater activity with the vapor-phase XOC than with the particle-phase SOF. The LS fuel mutagenic concentrations were typically similar to or greater than those of the CS fuel, especially with the vapor phase. The trap effects were significant for

both fuels, in every case except the XOC-associated activity at mode 9 with the CS fuel and mode 11 with the LS fuel. This was due in large part to the reductions in TPM, SOF, XOC concentrations with trap use (Table 8). Mutagenic activity on a concentration basis was typically greater at mode 11 than at mode 9 (Figure 13), corresponding to the typically higher activities (revertants/ $\mu\text{g}$ ) and SOF and XOC concentrations (Table 8 and Figure 12); these differences were significant in most cases for the LS but not the CS fuel. Due to the similarities in SOF and XOC concentrations (Tables 7 and 8) and mutagenic activities (revertants/ $\mu\text{g}$ ; Figure 12) between the LS and CS fuels, significant fuel effects on raw exhaust activity were found for only one comparison, that is, mode 11 with the trap. No statistical comparisons were made between the SOF- and XOC-associated activities. However, with the exception of the CS fuel and trap samples, the XOC mutagenic activity concentrations represented greater than 50% of the total detected mutagenic activity (particle and vapor phases) for both fuels.

**Table 12.** Particle-Associated (SOF) and Vapor-Phase (XOC) PAH Emissions from the 1988 L10 Engine Operated with Conventional, High-Sulfur Fuel With and Without a Trap

		PAH Level ( $\text{ng}/\text{m}^3$ ) <sup>a</sup>						
Mode and Condition	Fraction	FLU	PYR	BaA	CHR	BbF	BkF	BaP
9 Baseline	SOF	1300 <sup>b</sup> (56)	31 <sup>b</sup> (91)	140 (89)	150 (97)	94 (54)	3.6 (99)	4.4 (92)
	XOC	1700 (11)	300 (8.4)	125 (19)	18 (7.0)	< 3 <sup>c</sup> ND <sup>d</sup>	< 3 <sup>c</sup> ND	< 3 <sup>c</sup> ND
9 Trap	SOF	260 (92)	53 (79)	11 (120)	28 (77)	3.3 (4.5)	< 3 <sup>c</sup> ND	< 3 <sup>c</sup> ND
	XOC	1700 (37)	340 (42)	11 (86)	10 (79)	< 10 <sup>c</sup> ND	< 3 <sup>c</sup> ND	< 3 <sup>c</sup> ND
11 Baseline	SOF	600 (16)	79 (20)	170 (19)	120 (8.8)	47 (24)	5.5 (8.7)	4.3 (3.5)
	XOC	2700 (22)	470 (22)	170 (19)	12 <td>&lt; 4<sup>c</sup> ND</td> <td>&lt; 5<sup>c</sup> ND</td> <td>&lt; 5<sup>c</sup> ND</td>	< 4 <sup>c</sup> ND	< 5 <sup>c</sup> ND	< 5 <sup>c</sup> ND
11 Trap	SOF	900 <td>460 (55)</td> <td>140 (22)</td> <td>120 (16)</td> <td>55 (4.5)</td> <td>&lt; 3<sup>c</sup> ND</td> <td>6.4 (20)</td>	460 (55)	140 (22)	120 (16)	55 (4.5)	< 3 <sup>c</sup> ND	6.4 (20)
	XOC	3500 (36)	1000 (33)	150 (64)	26 (45)	< 3 <sup>c</sup> ND	< 3 <sup>c</sup> ND	< 3 <sup>c</sup> ND

<sup>a</sup> Presented as means of mean or median values (CV in %) (data are from Bagley et al. 1993).

<sup>b</sup> The FLU:PYR ratio for this fraction is considered to be atypical.

<sup>c</sup> All values were less than this MDL.

<sup>d</sup> ND = not determined.

Tests with TA98NR and TA98DNP tester strains for the LS fuel SOF and XOC samples are presented in Table 16. From 20% to 75% reductions in activity were found with these tester strains compared to TA98. The exception was with the mode 9 trap samples, where the same or higher activity levels were found with no evidence of sample toxicity; this response may have been due to the toxicity observed with the TA98 tests. These reductions compared to TA98 are generally similar to those found in the CS fuel study (Gratz et al. 1991; Bagley et al. 1993). Based on these data, it would appear that lower levels of mutagenic nitro-PAHs were associated with the SOF with the trap than without it. Nitro-PAH-related activity was found in both the SOF and XOC at similar levels, except at mode 9 trap.

One set of subfraction samples (see separation scheme in Figure 5) from the SOF and XOC for each mode, fuel, and condition was analyzed for mutagenic activity. As with the previous study with CS fuel (Bagley et al. 1993), all subfraction samples were tested with TA98-S9. S9 was used only with the two less polar fractions, hexane (HEX) and acetonitrile (ACN), which would be expected to contain indirect-acting (+S9) mutagens, if present. Tester strains TA98NR and TA98DNP were used with the more polar fractions, DCM and methanol (MeOH), only if a response was found with TA98 and if sufficient mass was available; these fractions would be expected to contain the direct-acting (-S9) mutagens. The TA98 responses and masses recovered for the modes 9 and 11 LS fuel subfractions are presented in Table 17. The general effects of S9 and the TA98NR and TA98DNP responses are also indicated in this table. There often was insufficient sample to conduct more than the

TA98-S9 tests. None of the mode 9 trap subfractions were assayed as either all of the mass recovered was used for compound quantification or the mass levels were too low for assaying (less than 1 mg). Mass recoveries ranged from 75% to 139% for all subfraction sets. These were higher values than for the CS fuel study due to the inclusion of the HEX fractions and their relatively large masses of parafinic-type compounds. Together, the less polar fractions (HEX and ACN) made up greater than 60% and greater than 75% of the mass recovered for the SOF and XOC samples,

**Table 14.** Levels of PAHs Found in Conventional, High-Sulfur and Low-Sulfur Fuels<sup>a</sup>

Compound	Concentration (ppm, w/w)	
	CS	LS
Phenanthrene	378	199
Anthracene	1.62	1.09
Fluoranthene	34.1	11.9
Pyrene	17.2	65.5
Benz[a]anthracene	93.2	97.9
Chrysene	39.5	11.5
Benzo[b]fluoranthene	9.98	12.5
Benzo[k]fluoranthene	6.22	2.33
Benzo[a]pyrene	0.639	0.803

<sup>a</sup> Quantification by HPLC with fluorescence detection; see Methods and Study Design for details.

**Table 13.** Summary of Statistical Results Comparing PAH Emissions from Low-Sulfur and Conventional, High-Sulfur Fuels<sup>a</sup>

PAH	Particle-Associated PAH			Vapor-Phase PAH	
	μg/g SOF	μg/g TPM	ng/m <sup>3</sup>	μg/g XOC	ng/m <sup>3</sup>
Fluoranthene	None	None	None	None	None
Pyrene	All <sup>b</sup>	All	9B, 11B/T	None	All
Benz[a]anthracene	All	11T	9B	All	None
Chrysene	All	All	11B	All	All
Benzo[b]fluoranthene	All	All	All	None	All
Benzo[k]fluoranthene	11T	11T	All	NS <sup>c</sup>	NS
Benzo[a]pyrene	All	All	11B	NS	NS

<sup>a</sup> All statistical analysis results are in Appendix Tables E.3 through E.6. The μg/g data are in Tables B.2 and B.3. The ng/m<sup>3</sup> values are in Tables 11 and 12. If a mode number (9 or 11)/operating condition (B = baseline or T = trap) is indicated, a significant difference was found between the PAH levels from LS and CS fuel at that mode and operating condition.

<sup>b</sup> Significant differences between PAH levels from LS and CS fuels were found for all combinations of mode and operating condition.

<sup>c</sup> NS = not statistically analyzed because values were less than the MDLs for all samples.

**Table 15.** Effects of the Low-Sulfur Fuel and a Trap (Used with the 1988 L10 Engine) on the Mutagenicity of SOF and XOC<sup>a</sup>

Mode and Condition	Fraction	n <sup>b</sup>	Revertants/µg <sup>c</sup>			Revertants/µg TPM		Revertants/m <sup>3</sup> (× 10 <sup>3</sup> )	
			-S9	+S9	SOF <sup>d</sup> (%)	-S9	+S9	-S9	+S9
9 Baseline	SOF	4	1.9 (14)	2.0 <sup>e</sup> (44)	29 (18)	0.56 (10)	0.51 <sup>e</sup> (55)	15 (13)	13.3 <sup>e</sup> (57)
	XOC	4	0.97 (8.9)	0.54 (62)	NA <sup>f</sup>	NA	NA	37 (22)	20 (54)
9 Trap	SOF	4	0.83 <sup>g</sup> (40)	2.5 <sup>h</sup> (22)	29 (3.1)	0.24 <sup>g</sup> (42)	0.57 <sup>h</sup> (14)	0.86 <sup>g</sup> (40)	22 <sup>h</sup> (13)
	XOC	4	0.48 <sup>i</sup> (34)	0.74 (15)	NA	NA	NA	9.3 (45)	32.6 (24)
11 Baseline	SOF	4	3.3 (21)	NT <sup>f</sup>	24 (21)	0.76 (16)	NT	28 (18)	NT
	XOC	4	1.1 <sup>i</sup> (16)	NT	NA	NA	NA	48 (25)	NT
11 Trap	SOF	3	3.0 <sup>i</sup> (7.1)	2.3 <sup>j</sup> ND <sup>f</sup>	50 (16)	1.5 <sup>i</sup> (23)	1.9 <sup>j</sup> ND	13 <sup>i</sup> (11)	10 <sup>j</sup> ND
	XOC	3	0.88 <sup>i</sup> (13)	0.38 (9.2)	NA	NA	NA	43 <sup>i</sup> (25)	19 (23)

<sup>a</sup> Presented as mean (CV in %) activities using TA98. Statistical analyses for TA98-S9 only are presented in Tables E.7 and E.8 to compare with data for LS and CS fuels (Figures 12 and 13).

<sup>b</sup> Number of samples.

<sup>c</sup> Based on extractable mass of SOF or XOC.

<sup>d</sup> SOF as a percentage of the TPM.

<sup>e</sup> Data for only two samples.

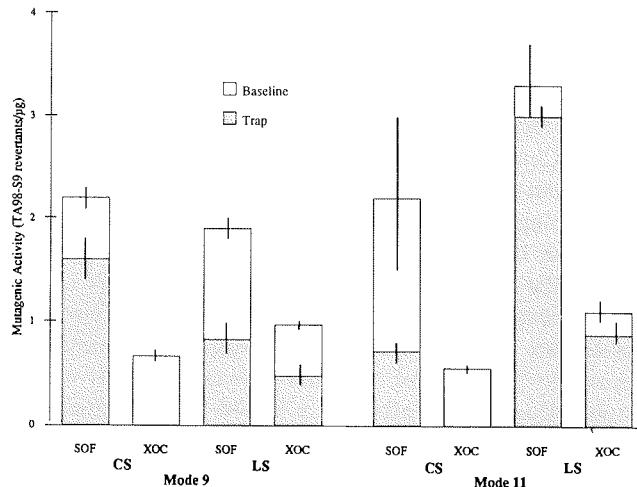
<sup>f</sup> NA = not applicable to XOC data; NT = not tested; ND = not determined, as only one value was measured.

<sup>g</sup> Sample toxicity may have masked mutagenic response.

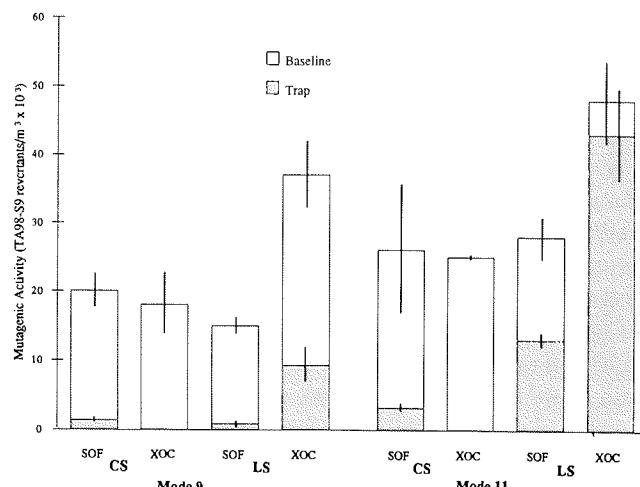
<sup>h</sup> Data for only three samples.

<sup>i</sup> Significant differences between LS and CS fuel data.

<sup>j</sup> Data for only one sample.



**Figure 12.** Comparison of mutagenic activity on a mass basis for the LS and CS fuel samples (presented as means  $\pm$  SE).



**Figure 13.** Comparison of mutagenic activity on a raw exhaust concentration basis for the LS and CS fuel samples (presented as means  $\pm$  SE).

**Table 16.** Response of Tester Strains TA98, TA98NR, and TA98DNP (in the Absence of S9) to SOF and XOC from the 1988 L10 Engine Operated at Modes 9 and 11 Using Low-Sulfur Fuel With and Without a Trap

Mode and Condition	Fraction	TA98		TA98NR		TA98DNP	
		Revertants/ $\mu$ g <sup>a,b</sup>	Revertants/ $\mu$ g <sup>b</sup>	% TA98	Revertants/mg <sup>b</sup>	% TA98	
9 Baseline	SOF	1.9 (14)	0.52 (40)	27	0.41 (59)	22	
	XOC	0.97 (8.9)	0.20 <sup>c</sup> (39)	21	0.38 <sup>c</sup> (52)	39	
9 Trap	SOF	0.83 <sup>d</sup> (40)	0.84 <sup>c</sup> (23)	100 <sup>d</sup>	2.1 <sup>e</sup> (23)	250 <sup>d</sup>	
	XOC	0.48 (34)	0.36 (35)	75	0.33 (24)	69	
11 Baseline	SOF	3.3 (21)	0.84 (34)	25	0.55 (30)	17	
	XOC	1.1 (16)	0.43 (15)	39	0.24 (31)	22	
11 Trap	SOF	3.0 (7.1)	1.2 (20)	40	1.1 (30)	37	
	XOC	0.88 (13)	0.21 (25)	24	0.34 (13)	39	

<sup>a</sup> For samples listed in Table 15.

<sup>b</sup> Presented as means (CV in %) for four samples, except three samples for mode 11 trap.

<sup>c</sup> Data for three samples.

<sup>d</sup> Sample toxicity may have masked mode 9 trap mutagenic response.

<sup>e</sup> Data for two samples.

respectively. As found in the CS fuel study, the SOF samples had more mass associated with the more polar fractions (DCM and MeOH) than did the XOC samples.

Some general patterns were found with the mutagenicity responses in the subfractions. No activity was detected with any of the HEX fractions; this was expected as this fraction should contain the least polar, paraffinic-type HC. The ACN fractions, which should contain those unsubstituted PAHs requiring metabolic activation, had little activity in the SOF and no activity in the XOC, even with S9. As shown in Table 11, very low levels of PAHs such as BaP were found in the SOF and none were detected in the XOC. As with the CS fuel study (Bagley et al. 1993), almost all of the detected activity was found in the more polar DCM and MeOH subfractions. Higher activity was typically found with the SOF subfractions than with the XOC subfractions, reflecting the higher levels of direct-acting, polar compounds present with the SOF samples. This is also indicated by the results obtained with TA98NR-S9 and TA98DNP-S9 (see also Table 17 footnotes). Total recovery of mutagenic activity from the SOF and XOC subfractions ranged from 35% to 67% of the SOF activity, with much lower recoveries from the XOC.

### Regeneration and Regeneration Emissions

The regeneration process entailed loading the trap at either mode 9 or 11 to the specified level and then activating pneumatic valves to by-pass the exhaust around the trap. The 4000-W electric heater was turned on and air was supplied to the inlet of the trap at the rate of 219 L/min. The heater and air combination quickly increased the temperature at the trap face to 500°C. The heater remained on for five minutes to ensure that the regeneration was thoroughly initiated and the combustion air was maintained at 219 L/min throughout the 30-minute regeneration process.

Figure 14 shows the normalized EAA data (indication of particle concentration) for both the LS and CS mode 11 regeneration data, plus the normalized CO data for the LS tests. The curves represent the average of all the data collected for mode 11 regeneration and are normalized in order to compare the trends between the two fuels. The CO data provide information on when regeneration or combustion is occurring. The results indicate that about five minutes were required for the combustion wave to become fully developed, and then an additional ten minutes were required for the wave to travel through the trap. The EAA data indicated that, with both fuels, low particle concentrations were present as the combustion wave traveled through the trap and then the concentrations increased as the combus-

tion wave was extinguished. The origin of these particles is still not fully understood. Similar results were obtained with the mode 9 regeneration data.

The mass emissions collected for the LS fuel electrical by-pass regeneration are provided in Table 18. As indicated by the CVs, considerable variability was found for all the data, even after improving the sampling systems for the LS fuel testing. As with the steady-state samples, all SO<sub>4</sub> levels with the LS fuel were below the background levels. To assess the impact of regeneration emissions, the LS fuel steady-state trap and regeneration TPM, SOF, and XOC mass data were converted to rate values (mg/minute), as provided in Table 19. For these comparisons, it was assumed that trap installation on a vehicle would consist of two traps in parallel so that, when one trap was regenerating, the other would be filtering the exhaust stream. The regeneration emissions would then combine with the emissions being emitted from the other trap. The data in the table indicate that the increase in tailpipe emissions from the regeneration process was less than 2% of the total emissions out the tailpipe. These results are similar to those previously reported for the CS fuel studies (Bagley et al. 1993).

The PAH regeneration emission rates (ng/minute) at mode 9 were generally lower than at mode 11 (Table 20). The mode 9 samples, in fact, had very few of the PAHs present above MDLs. The highest levels overall were seen in XOC collected at mode 11. This was not an unexpected result since PAH levels are generally engine-mode dependent with higher levels at lower-load modes (Wall and Hoekman 1984). It is possible that some fraction of the PAH compounds could be stored in the trap and liberated during regeneration.

The PAH emission rate comparisons between baseline, trap, and regeneration conditions with the LS fuel are also provided in Table 20. The PAH emission rates with the trap were generally lower for both the SOF and XOC at both modes. The contribution of PAH emissions during regeneration was typically less than 1% of the total emissions out of the tailpipe.

Mutagenicity assays were conducted on all of the SOF and XOC samples collected from all of the mode 9 regeneration tests listed in Table 21. Separate SOF and XOC samples were analyzed from the mode 11 regeneration tests. Mutagenic activity was detected with all of the samples tested. The two mode 9 SOF samples had similar activity levels on a mass of SOF basis (revertants/µg), but varied considerably for all other comparisons, including activity associated with the XOC. As noted earlier, relatively high levels of variability in emissions were generally found for the regeneration data. The activity (revertants/µg) detected with the regeneration samples was about the same

**Table 17.** Mutagenicity of SOF and XOC Subfractions from the 1988 L10 Engine Using Low-Sulfur Fuel With and Without a Trap<sup>a</sup>

Subfraction <sup>b</sup>	Mode 9						Mode 11					
	Baseline			Trap			Baseline			Trap		
	% Mass	Revertants/ $\mu$ g	% Activity	% Mass	Revertants/ $\mu$ g	% Activity	% Mass	Revertants/ $\mu$ g	% Activity	% Mass	Revertants/ $\mu$ g	% Activity
SOF-HEX	47	NR <sup>c,d</sup>	0	16	IS <sup>c</sup>	NA <sup>c</sup>	48	NR <sup>d</sup>	0	53	NRd	0
SOF-ACN	17	0.22	6.2	15	IS	NA	15	0.21	1.2	12	1.7 <sup>e</sup>	6.3
SOF-DCM	14	2.1 <sup>f</sup>	18	15	IS	NA	12	5.6 <sup>f</sup>	25	8.7	6.5 <sup>f</sup>	17
SOF-MeOH	16	4.4 <sup>f</sup>	43	28	IS	NA	14	4.1 <sup>f</sup>	21	20	1.9 <sup>f</sup>	12
% Recovered	95		67	75		NA	89		47	94		35
XOC-HEX	32	NR <sup>d</sup>	0	33	NR <sup>d</sup>	0	44	NR <sup>d</sup>	0	45	NR <sup>d</sup>	0
XOC-ACN	49	NR <sup>d</sup>	0	43	NR <sup>d</sup>	0	54	NRd	0	77	NR <sup>d</sup>	0
XOC-DCM	3.1	IS	NA	3.0	NR	0	6.3	T <sup>c</sup>	NA <sup>c</sup>	6.9	NR	0
XOC-MeOH	2.2	1.4 <sup>f</sup>	2.9	3.3	1.6 <sup>f</sup>	20	3.5	1.8 <sup>f</sup>	5.1	10	1.3	15
% Recovered	86		2.9	82		20	110		5.1	139		15

<sup>a</sup> Values for % Mass and % Recovered are based on sample mass used in separation. Counts of revertants/ $\mu$ g were measured with TA98-S9. Values for % (mutagenic) Activity were based on activity of unfractionated sample.

<sup>b</sup> Based on separation scheme in Figure 5.

<sup>c</sup> NR = no response above spontaneous revertant levels; IS = insufficient sample to test; NA = not applicable to this situation; T = toxic response to sample and no mutagenic activity detected.

<sup>d</sup> No response with TA98+S9 above that with TA98-S9.

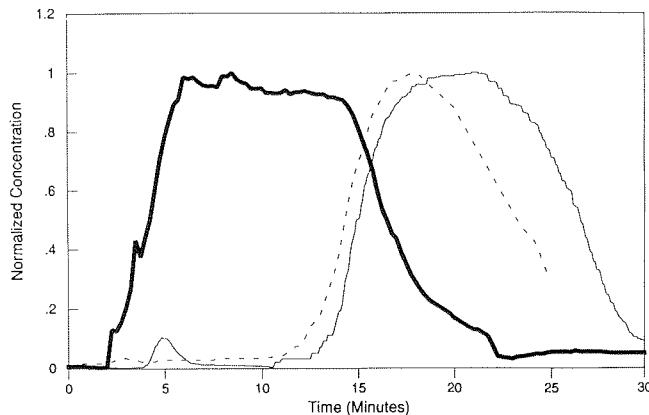
<sup>e</sup> Response with TA98+S9 was 150% that of TA98-S9.

<sup>f</sup> Response with TA98NR and TA98DNP from 5% to 20% of the TA98-S9 response.

(mode 9) or lower (mode 11) than that found during steady-state operation with the trap (Table 15). Due to the much lower flow rates during the period of trap regeneration, however, the activity emission rates (revertants/minute) during trap regeneration were roughly 10-fold lower than when operating with the trap (Table 22). Assuming operation of a trap system that uses a second trap while on-board trap regeneration is in process, the regeneration emissions would contribute about 1% or less to the mutagenicity of the SOF or XOC emitted during this time period.

### Doped-Sulfur Fuel Study

It was apparent after analyzing the LS and CS fuel data that the differences in emissions might be due not only to the fuel sulfur level, but probably also due to different cetane numbers and aromatic contents and to differences in the specific chemical composition of the fuels (Table 1). As noted earlier, the original intent of this project was to study the effects on emissions of an available LS (< 0.05 wt %) fuel. Therefore, in order to investigate the effect of fuel sulfur only, the remaining LS fuel was doped with di-*tert*-butyl disulfide to levels comparable to the CS fuel level. The test matrix and statistical comparisons were made only between the LS and DS fuel baseline data and are presented in the Statistical Methods and Data Analysis section. The mean values and the CVs for particle-, vapor-, and gas-phase data for the DS fuel study are given in Table 23. These data can be compared to those presented for the LS and CS fuels (Tables 7 and 8, respectively). Summaries of the statistical results are presented in Table 23 (footnotes) for the comparison of modes 9 and 11 baseline emissions for the LS and DS fuels to evaluate the effects of a change only in fuel sulfur content on emissions. (Tables showing all of the statistical test results are presented in Tables E.9 and E.10)



**Figure 14. Particle and carbon monoxide emissions during mode 11 regeneration of the particle trap.** Heavy line = carbon monoxide with LS fuel; dashed line = EAA measurement of particles with CS fuel; and thin line = EAA measurement of particles with LS fuel.

in Appendix E.) The NO<sub>x</sub> and NO levels at both mode 9 and 11 were not fuel-dependent; only the engine operating condition had a significant effect. The results indicated significant differences in the HC levels between the two fuels at mode 11 but not at mode 9. The XOC levels were not affected by the fuel sulfur level. Only the engine operating condition (mode) had a significant effect on the XOC levels; this difference was found only with the DS fuel.

**Table 18.** Mass Emissions Collected During Electrical Regeneration of the Particle Trap with the 1988 L10 Engine Using Low-Sulfur Fuel

Mode	Test Number <sup>a</sup>	TPM Mass (mg)	SOF Mass (mg)	XOC Mass (mg)
9	1	16	9.5	4.7
	2	7.4	1.9	3.3
	Mean	11.8	5.7	4.0
	(CV in %)	(54)	(95)	(26)
11	1	19.3	6.7	NA <sup>b</sup>
	2	7.3	2.3	4.6
	Mean	13.3	4.5	4.6
	(CV in %)	(64)	(68)	NA

<sup>a</sup> 30-Minute sample times.

<sup>b</sup> NA = no data available.

**Table 19.** Emission Rate Comparisons Between Baseline, Trap, and Regeneration Conditions with the Low-Sulfur Fuel

Mode and Condition	TPM (mg/min)	SOF (mg/min)	XOC (mg/min)
9 Baseline	370	110	510
9 Trap	48	14	260
9 Regeneration	0.4	0.2	0.1
Increase over trap (%) <sup>a</sup>	0.8	1.4	0.0b
11 Baseline	330	79	390
11 Trap	78	39	440
11 Regeneration	0.4	0.2	0.2
Increase over trap (%) <sup>a</sup>	0.5	0.5	0.0b

<sup>a</sup> Calculated as (mean regeneration/mean trap) × 100, assuming a second trap in the bypass exhaust.

<sup>b</sup> No increase (or change) detectable.

The LS fuel TPM levels were significantly different (lower with the LS fuel) when compared to the DS fuel TPM levels. Since the only difference between the two fuels was the fuel sulfur content, the higher SO<sub>4</sub> fraction should be expected to be the main reason for the TPM increase. The DS fuel produced significantly different SO<sub>4</sub> levels at both engine operating conditions, with lower levels with the LS fuel. The fuel sulfur conversion efficiencies (from sulfur in fuel to sulfur in SO<sub>4</sub>) were comparable for the two fuels and ranged from 0.5% to 1.5%. No significant difference in SOF levels between the two fuels was determined at either

mode. The data indicated no changes in the SOL emissions at mode 11. However, at mode 9, the DS fuel generated significantly different SOL levels (30% higher than with the LS fuel).

The particle size distributions for the DS fuel were obtained in the normal location from the dilution tunnel and also from the exhaust manifold. By sampling at both locations and comparing the distributions, it can be determined where specific sizes of particles are formed. The sampling from the exhaust manifold required designing an additional dilution system that rapidly diluted the exhaust sample.

**Table 20.** PAH Emission Rates Under Baseline, Trap, and Regeneration Conditions with the 1988 L10 Engine Using Low-Sulfur Fuel

Mode and Fraction	Compound	Baseline (ng/min)	Trap (ng/min)	Regeneration (ng/min)	Increase over Trap (%) <sup>a</sup>
9 SOF	FLU	9,700	2,300	< 0.5	0.0 <sup>b</sup>
	PYR	31,000	4,400	< 0.5	0.0 <sup>b</sup>
	BaA	15,000	1,900	0.2	0.0 <sup>b</sup>
	CHR	8,000	2,400	0.5	0.0 <sup>b</sup>
	BbF	3,500	550	0.7	0.1
	BkF	1,500	< 26	0.7	< 2.9
	BaP	2,000	72	< 0.0	0.1
9 XOC	FLU	28,000	36,000	67	0.2
	PYR	24,000	19,000	35	0.2
	BaA	4,300	2,300	6.1	0.3
	CHR	3,200	780	5.0	0.7
	BbF	5,400	270	< 0.1	< 0.1
	BkF	< 81	< 30	< 0.1	< 0.5
	BaP	< 90	< 40	< 0.1	< 0.3
11 SOF	FLU	11,000	3,900	56	1.5
	PYR	18,000	9,000	43	0.5
	BaA	6,500	6,500	17	0.3
	CHR	11,000	4,800	38	0.8
	BbF	2,200	1,300	4.1	0.3
	BkF	820	990	3.2	0.3
	BaP	2,000	570	< 0.1	0.0 <sup>b</sup>
11 XOC	FLU	11,000	68,000	264	0.4
	PYR	8,200	22,000	54	0.2
	BaA	2,200	4,400	45	1.0
	CHR	2,400	2,200	33	1.5
	BbF	58	< 87	2.6	< 3.0
	BkF	< 40	< 69	5.8	< 8.4
	BaP	< 5	< 82	< 0.0	0.0 <sup>b</sup>

<sup>a</sup> Calculated as (mean regeneration PAHs/mean trap PAHs) × 100, assuming a second trap in the bypass exhaust.

<sup>b</sup> No increase (or change) detectable.

**Table 21.** Mutagenicity of SOF and XOC Samples Emitted During Trap Regeneration

Mode	Test Number	Fraction	Revertants/ $\mu\text{g}^{\text{a}}$					SOF <sup>b</sup> (%)	Revertants/ $\mu\text{g}$ TPM <sup>a</sup>	Revertants/min ( $\times 10^3$ )
			TA98	TA98NR	% TA98	TA98DNP	% TA98			
9	1	SOF	0.805	0.152	19	0.104	13	58	0.467	0.26
		XOC	0.921	IS <sup>c</sup>	NA <sup>c</sup>	IS	NA	NA	NA	0.15
	2	SOF	0.949	0.257	27	0.204	21	25	0.237	0.06
		XOC	0.413	IS	NA	IS	NA	NA	NA	0.05
11	1	SOF	0.637	0.230	36	0.357	56	35	0.223	0.14
		XOC	NT <sup>c</sup>	NT	NA	NT	NA	NA	NA	NT
	2	SOF	NT	NT	NA	NT	NA	32	NT	NT
		XOC	0.413	IS	NA	0.173	42	NA	NA	0.06

<sup>a</sup> Without S9.<sup>b</sup> SOF percentage of the TPM.<sup>c</sup> IS = insufficient sample to test; NA = not applicable to this situation; NT = not tested.

This dilution system consisted of two air ejectors operating in series. The orifice on the first ejector was designed such that nearly isokinetic sampling from the exhaust pipe could be performed. The dilution ratio at the engine varied from 200:1 to 700:1, and the dilution system was necessary to reduce the particle concentration to a range suitable for the EAA and also to stop the particle growth process. With the rapid dilution, there was virtually no time for gas-phase material to form particles. However, at the dilution sampling point, the exhaust was mixed with the fresh air and there were about two seconds for gas reactions to occur and new particles to form.

The mode 9 particle size distributions for the DS fuel are provided in Figures 15 and 16. The number concentrations measured at the tunnel location for the mode 9 DS fuel are similar to the CS data (Figure 8) and more than 2 orders of magnitude larger than the LS concentrations (Figure 8). The mode 11 data (Figures F.5 and F.6 in Appendix F) show similar trends to the mode 9 data. The percent volumes in the nuclei mode for mode 9 with the CS and DS fuels were 9.5 and 8.0, respectively, compared to 2.2 for the LS fuel. The size distributions for the CS and the DS fuels measured from the engine raw exhaust and the dilution tunnel have similar accumulation modes, but the dilution tunnel distributions have higher number and volume concentrations in

the nuclei mode. This indicates that the majority of the nuclei-mode particles are formed during the dilution process and originate from the fuel sulfur.

PAH concentrations ( $\text{ng}/\text{m}^3$ ) from the DS fuel study are presented in Table 24; values for the same compounds on a mass basis ( $\mu\text{g}/\text{g}$ ) are presented in Table B.4 in Appendix B. These values can be compared to those found with the LS and CS fuel studies (Tables 11, 12, B.2, and B.3). Summaries of the statistical analyses for comparison of the PAH data between the LS and DS fuels are presented in Table 25 (based on statistical test results found in Tables E.11 to E.14 in Appendix E). No statistical analyses were conducted for BbF, BkF, or BaP levels in the vapor phase as all values were less than the MDLs.

These tests indicated that most of the significant differences for PAHs were due to the fuel, with relatively few mode effects independent of fuel. The exceptions were FLU, for which there were no significant differences noted in the XOC or SOF due to either fuel or mode, and PYR, for which there were differences due to engine mode as well as the fuel. These LS versus DS fuel statistical comparisons (Table 25) were similar to those found between the LS and CS fuels PAH data (Table 13). On a raw exhaust concentration basis, the DS fuel produced PAH levels that were usually lower than for the LS fuel but higher than the CS

**Table 22.** Comparison of Trap Regeneration Effects on Mutagenic Activity of Emissions

Mode and Condition	Revertants/min <sup>a</sup> ( $\times 10^3$ )	
	SOF	XOC
9 Baseline	200 (13)	490 (22)
9 Trap	12 (40)	120 (45)
9 Regeneration	0.16 (97)	0.10 (74)
Increase over trap (%) <sup>b</sup>	1.3	0.08
11 Baseline	250 (18)	430 (25)
11 Trap	120 (11)	390 (26)
11 Regeneration	0.14 <sup>c</sup>	0.06 <sup>c</sup>
Increase over trap (%)	0.12	0.02

<sup>a</sup> Presented as means (CV in %); data are from Tables 15 (baseline and trap) and 21 (regeneration).

<sup>b</sup> Calculated as (mean regeneration/mean trap)  $\times 100$ , assuming a second trap in the bypass exhaust.

<sup>c</sup> Only one sample.

**Table 23.** Gas-, Vapor-, and Particle-Phase Emissions from the 1988 L10 Engine Using Doped-Sulfur Fuel<sup>a</sup>

Emissions	Mode 9	Mode 11
NO <sub>x</sub> (ppm) <sup>b</sup>	770 (1.5)	230 (1.7)
NO (ppm) <sup>b</sup>	710 (0.1)	210 (9.5)
HC (ppm) <sup>c</sup>	130 (3.1)	140 (4.6)
TPM (mg/m <sup>3</sup> ) <sup>d</sup>	34 (1.1)	43 (6.1)
SOF (mg/m <sup>3</sup> ) <sup>b</sup>	7.1 (1.5)	12 (3.8)
SO <sub>4</sub> (mg/m <sup>3</sup> ) <sup>d</sup>	1.8 (15)	1.3 (33)
SOL (mg/m <sup>3</sup> ) <sup>e</sup>	25 (2.4)	29 (15)
XOC (mg/m <sup>3</sup> ) <sup>f</sup>	31 (4.4)	54 (7.1)

<sup>a</sup> Presented as means (CV in %) of three samples collected under baseline conditions. Statistical analyses are presented in Tables E.9 and E.10 for comparisons between LS (Table 7) and DS fuel data.

<sup>b</sup> Significant differences between the mode 9 and 11 data.

<sup>c</sup> Significant differences between the LS and DS fuel data at mode 11 and between the mode 9 and 11 data.

<sup>d</sup> Significant differences between the LS and DS fuel data at modes 9 and 11 and between the mode 9 and 11 data.

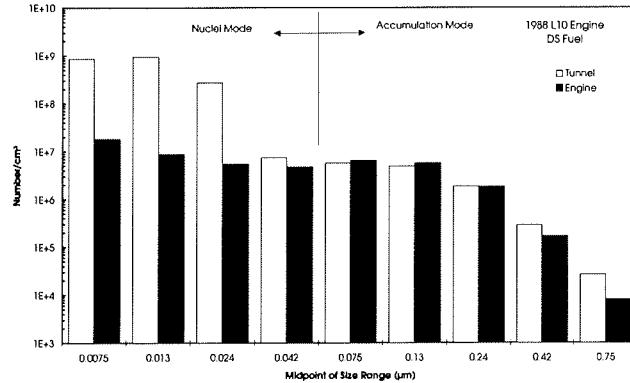
<sup>e</sup> Significant differences between the LS and DS fuel data at mode 9.

<sup>f</sup> Significant differences between the mode 9 and 11 data for the DS fuel.

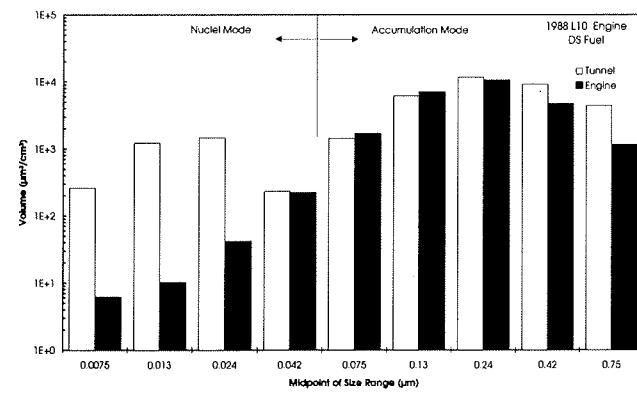
fuel. This was generally true for both engine modes and for the particle and vapor phases, with the notable exception of BaA, which was measured in highest concentrations when the DS fuel was used. Vapor-phase emissions of CHR and BbF, which were present in quantifiable levels when the LS fuel was used, were below detection limits when the LS fuel was doped with sulfur.

The mean and CV results from the mutagenicity tests of the SOF and XOC samples from DS fuel are presented in Table 26 and can be compared to the baseline mutagenic activity data previously obtained with the LS and CS fuels in Table 15 and Figures 12 and 13. As with the LS fuel samples, there was relatively little effect due to the use of the S9 metabolic activation system. Due to the limited nature of this additional study, none of the SOF or XOC

samples (or subfractions) were tested with TA98NR or TA98DNP. Statistical comparisons were made only with the LS fuel baseline data; a summary of these results for fuel and mode effects is presented in the Table 26 footnotes, based on the data presented in Tables E.15 and E.16 in Appendix E. The mutagenic activity of the DS fuel SOF and XOC was lower than the corresponding LS fuel data. This is similar to that found for the comparisons of the activity between the LS and CS fuels' SOF and XOC. As noted in Table 26, all the LS and CS fuel differences were significant except for the SOF-associated activity, which was significant only for the mode 11 activity (revertants/ $\mu\text{g}$ ) data. Differences between engine operating conditions also were found to be significant between the LS and DS fuels, with higher mutagenic activity at mode 11 than at mode 9. The increased ability to detect significant differences between



**Figure 15.** Mode 9 particle number distributions with DS fuel measured at the 1988 Cummins L10 engine manifold and in the dilution tunnel.



**Figure 16.** Mode 9 particle volume distributions with DS fuel measured at the 1988 Cummins L10 engine manifold and in the dilution tunnel.

**Table 24.** Particle-Associated (SOF) and Vapor-Phase (XOC) PAH Emissions from the 1988 L10 Engine Operated with Doped-Sulfur Fuel Under Baseline Conditions

Mode	Fraction	<i>n</i> <sup>a</sup>	PAH Level (ng/m <sup>3</sup> ) <sup>b</sup>						
			FLU	PYR	BaA	CHR	BbF	BkF	BaP
9	SOF	3	890 (2.4)	190 (5.3)	810 (3.9)	460 (13)	290 (45)	33 (42)	10 (5.9)
	XOC	3	1700 (24)	400 (8.9)	1000 (32)	< 5.0 <sup>c</sup> ND <sup>e</sup>	< 5.5 <sup>d</sup> ND	< 6.2 <sup>d</sup> ND	< 6.5 <sup>d</sup> ND
11	SOF	3	1000 (6.4)	1500 (1.4)	1400 (1.8)	560 (2.0)	510 (4.9)	80 (9.0)	19 (77)
	XOC	3	2300 (1.8)	1200 (4.6)	2400 (16)	< 7.3 <sup>d</sup> ND	< 8.2 <sup>d</sup> ND	< 9.3 ND	< 9.7 ND

<sup>a</sup> Number of samples.

<sup>b</sup> Presented as means (CV in %).

<sup>c</sup> Two values less than this MDL and one value was 565 ng/m<sup>3</sup>.

<sup>d</sup> All values less than this MDL.

<sup>e</sup> ND = not determined, because values were less than the MDL.

**Table 25.** Summary of Statistical Results Comparing PAH Emissions from Low-Sulfur and Doped-Sulfur Fuels<sup>a,b</sup>

PAH	Particle-Associated PAH			Vapor-Phase PAH	
	µg/g SOF	µg/g TPM	ng/m <sup>3</sup>	µg/g XOC	ng/m <sup>3</sup>
Fluoranthene	11	None <sup>c</sup>	None	None	None
Pyrene	9	9, 11	9, 11	9	9
Benz[a]anthracene	None	9, 11	9, 11	9, 11	9, 11
Chrysene	9, 11	9, 11	9, 11	None	9, 11
Benzo[b]fluoranthene	None	9, 11	11	11	None
Benzo[k]fluoranthene	None	9, 11	9, 11	NS <sup>c</sup>	NS
Benzo[a]pyrene	9, 11	9, 11	9, 11	NS	NS

<sup>a</sup> All statistical analysis results are in Appendix Tables E.3 through E.14. The µg/g data are in Appendix Tables B.2 through B.4. The ng/m<sup>3</sup> values are in Tables 11 and 24.

<sup>b</sup> If a mode number is indicated (9 or 11), a significant difference was found between the LS and DS fuel and PAH levels at that mode.

<sup>c</sup> None = not statistically significant at either mode. NS = not statistically analyzed because values were less than the MDLs for all samples.

**Table 26.** Effects of the Doped-Sulfur Fuel (Used with the L10 Engine) on the Mutagenicity of SOF and XOC<sup>a</sup>

Mode and Condition	Fraction	n <sup>b</sup>	Revertants/µg <sup>c</sup>		SOF <sup>d</sup> (%)	Revertants/µg TPM <sup>e</sup>		Revertants/m <sup>3</sup> f (× 10 <sup>3</sup> )	
			-S9	+S9		-S9	+S9	-S9	+S9
9 Baseline	SOF	3	2.2 (9.0)	2.3 (9.3)	21 (2.5)	0.46 (6.6)	0.47 (9.5)	16 (7.7)	16 (1.4)
	XOC	3	0.43 (8.1)	0.36 <sup>g</sup> (29)	NA <sup>h</sup>	NA	NA	13 (12)	11 <sup>i</sup> (23)
11 Baseline	SOF	3	1.9 (8.6)	2.3 (4.5)	27 (8.0)	0.52 (15)	0.63 (12)	22 (9.9)	27 (6.4)
	XOC	3	0.45 (6.8)	0.30 (17)	NA	NA	NA	24 (2.7)	16 (3.7)

<sup>a</sup> Presented as mean (CV in %) activities using TA98. Statistical analyses (TA98-S9 only) are presented in Tables E.15 and E.16 for comparisons between LS (Table 15) and these DS fuel data.

<sup>b</sup> Number of samples.

<sup>c</sup> Based on extractable mass of SOF or XOC. For SOF, significant differences are between LS and DS fuel data at mode 11; for XOC, significant differences are between the LS and DS fuel data at both modes 9 and 11.

<sup>d</sup> SOF percentage of the TPM.

<sup>e</sup> Significant differences between LS and DS fuel data are at modes 9 and 11 and between the mode 9 and 11 data.

<sup>f</sup> For SOF there are significant differences between the mode 9 and 11 data; for XOC, there are significant differences between the LS and DS fuel data at modes 9 and 11 and between the mode 9 and 11 data.

<sup>g</sup> Data for only two samples.

<sup>h</sup> NA = not applicable to XOC data.

the LS and DS fuel data may be related both to having a balanced experimental design (the design for the CS fuel study was unbalanced) and also to using a two-way ANOVA test instead of a three-way ANOVA test that also included effects of trap versus baseline operation.

One set of DS fuel subfractions was also screened for mutagenic activity using TA98-S9 (Table 27). The percentage of SOF or XOC masses and activity recovered were similar to those previously found with the LS fuel (Table 17). The same general trends were observed for mass distribution between the four subfractions as for the LS and CS fuel samples, with most of the mass in the less polar subfractions and more mass in the DCM and MeOH subfractions for the SOF compared to the XOC samples. In general, most of the activity was also detected with these more polar subfractions.

## DISCUSSION

A summary of LS versus CS and LS versus DS fuel effects on emissions is shown in Table 28. As shown in the previous section, the particle trap and the engine operating mode also were found to affect emissions; these effects are similar to those reported in other studies (MacDonald 1983; Baumgard and Kittelson 1985; Wiczynski and Johnson 1986; Bagley et al. 1987, 1993). It should be noted that the

CS fuel study was conducted approximately two years before the LS fuel studies and four years before the DS fuel studies. Some of the differences — or lack thereof — found for fuel effects also may relate to variations in experimental design, engine operation, and sampling and analytical procedures. However, a comparison of data from studies with these three fuels does provide (1) evidence of fuel sulfur level effects on specific emissions, and (2) indications that other types of fuel components may affect certain types of regulated and unregulated emissions (because not all of the observed differences could be explained only by differences in fuel sulfur levels).

As indicated in Table 28, NO<sub>x</sub> and NO levels changed less than 10% for the different fuels; these differences were significant for the LS versus CS but not the LS versus DS fuel comparisons. Fuel cetane number may affect NO<sub>x</sub> emissions; Ullman (1989) has shown an inverse correlation between NO<sub>x</sub> and cetane number for two direct-injection heavy-duty diesel engines. Emissions from those same engines also showed a direct NO<sub>x</sub> dependency on fuel aromatic content. A significantly lower cetane number would increase the ignition delay and would cause a larger fraction of the diesel fuel to be homogeneously mixed with the air before ignition. This would result in higher instantaneous temperatures and pressures within the cylinder, pro-

**Table 27.** Mutagenicity of SOF and XOC Subfractions from the 1988 L10 Engine During Steady-State Operation in Modes 9 and 11 Baseline Conditions Using Doped-Sulfur Fuel

Subfraction <sup>a</sup>	Mode 9			Mode 11		
	% Mass <sup>b</sup>	Revertants/µg <sup>c</sup>	% Activity <sup>d</sup>	% Mass <sup>b</sup>	Revertants/µg <sup>c</sup>	% Activity <sup>d</sup>
SOF-HEX	110	NR <sup>e</sup>	0	46	NR	0
SOF-ACN	14	4.0	27	22	0.48	5.2
SOF-DCM	15	3.0	22	8.2	4.7	19
SOF-MeOH	9.8	8.5	34	5.0	5.7	14
% Recovered <sup>b</sup>	148		83	82		38
XOC-HEX	51	NR	0	26	NR	0
XOC-ACN	28	NR	0	46	NR	0
XOC-DCM	2.4	NR	0	3.3	NR	0
XOC-MeOH	0.9	IS <sup>e</sup>	NA <sup>e</sup>	0.6	1.2	1.6
% Recovered <sup>b</sup>	82		0	76		1.6

<sup>a</sup> Based on separation scheme in Figure 5.

<sup>b</sup> Based on sample mass used in separation, rounded to nearest percent.

<sup>c</sup> TA98-S9.

<sup>d</sup> Based on mutagenic activity of unfractionated sample.

<sup>e</sup> NR = no response above spontaneous revertant levels; IS = insufficient sample to test; NA = not applicable to XOC data.

moting NO<sub>x</sub> formation. The lack of significant differences in the NO<sub>x</sub> emissions between the LS and DS fuels agrees with studies by Wall and Hoekman (1984), Heywood (1988), and Ullman (1989).

Some significant differences in HC levels were found in this study, but it is unlikely that the fuel sulfur content caused them. Ullman and associates (1990a,b) conducted several tests in order to assess the effects of different fuel properties on regulated emissions. The engine used in their tests was a Detroit Diesel Company heavy-duty engine, which had characteristics similar to the Cummins L10 engine used in the present study. They reported that HC

emissions decreased with increased engine operating hours, whereas the NO<sub>x</sub> emissions increased over time. This study showed a similar trend, but it is uncertain whether the time factor really influenced the HC levels as much as the measurements indicate. This trend usually correlates with an advance in the injection timing but, in both studies, nonintrusive inspection of the engine identified no mechanical or electronic shift of injection timing. Wall and Hoekman (1984) and Ullman (1989) concluded that fuel sulfur concentration should not affect the HC levels.

**Table 28.** Summary of Fuel Effects on Emissions from the 1988 L10 Engine During Steady-State Operation at Modes 9 and 11

Parameter	Percentage of Change from High-Sulfur (CS or DS) Fuel <sup>a</sup>					
	Mode 9			Mode 11		
	LS vs. CS		LS vs. DS	LS vs. CS		LS vs. DS
	Baseline	Trap	Baseline	Baseline	Trap	Baseline
NO <sub>x</sub> (ppm)	+5.6 <sup>b</sup>	+8.1 <sup>b</sup>	-2.5	+14 <sup>b</sup>	+4.2 <sup>b</sup>	+9.6
NO (ppm)	+4.5 <sup>b</sup>	+5.6 <sup>b</sup>	-1.8	+4.8 <sup>b</sup>	+4.2 <sup>b</sup>	+5.8
HC (ppm)	+87 <sup>b</sup>	+120 <sup>b</sup>	+9.4	+6.3	+14	+20 <sup>b</sup>
TPM (mg/m <sup>3</sup> )	-18 <sup>b</sup>	+16	-19 <sup>b</sup>	-2.6	+3.4	-14 <sup>b</sup>
SOF (mg/m <sup>3</sup> )	-11	+40	+14	-26	-3.3	-23
SO <sub>4</sub> (mg/m <sup>3</sup> )	ND <sup>c</sup>	ND	-93 <sup>b,d</sup>	ND	ND	-98 <sup>b,d</sup>
SOL (mg/m <sup>3</sup> )	ND	ND	-23 <sup>b</sup>	ND	ND	-2.1
XOC (mg/m <sup>3</sup> )	+38	+120	+23	+5.3	+29	-18
Particle number (number/cm <sup>3</sup> ) <sup>e</sup>	-92	-99	-98	-57	-99	-97
Particle volume (μm <sup>3</sup> /cm <sup>3</sup> ) <sup>e</sup>	+27	+120	-32	+6.7	+41	-46
Mutagenic activity (revertants/m <sup>3</sup> ) <sup>f</sup>						
SOF	-25	-39	-6.3	+7.7	+310 <sup>b</sup>	+27
XOC	+110	NC <sup>c</sup>	+185 <sup>b</sup>	+92	NC <sup>c</sup>	+100 <sup>b</sup>
Fluoranthene (ng/m <sup>3</sup> )						
SOF	-45	-35	-19	+100	-52	+20
XOC	+24	+80	+24	-56	+130	-48
Pyrene (ng/m <sup>3</sup> )						
SOF	+7300 <sup>b</sup>	+520	+1100 <sup>b</sup>	+2400 <sup>b</sup>	+120 <sup>b</sup>	+33 <sup>b</sup>
XOC	+500 <sup>b</sup>	+310 <sup>b</sup>	+350 <sup>b</sup>	+94 <sup>b</sup>	+150 <sup>b</sup>	-24

<sup>a</sup> Presented as [(LS/CS or DS) - 1] × 100.

<sup>b</sup> Significant difference between LS and CS or DS data.

<sup>c</sup> ND = not determined because different sampling systems were used for LS and CS fuel studies; NC = not calculated because no response was detected for CS fuel.

<sup>d</sup> Minimum decrease because most LS values were less than the MDL.

<sup>e</sup> Not tested for significant differences.

<sup>f</sup> TA98-S9.

A number of studies demonstrated that TPM emissions are related to fuel properties. Ryan and colleagues (1981) showed that a high initial-boiling point and a low end-boiling point are important fuel properties that can reduce TPM levels. Ullman and associates (1990a,b) identified cetane number and aromatic content as important. Wall and colleagues (1987), Baranescu (1988), and Lange (1991) also determined strong correlations between fuel sulfur content and TPM levels. Lowering the fuel sulfur level reduces the amount of SO<sub>2</sub> formed in the engine and, consequently, less SO<sub>4</sub> is formed to contribute to the TPM. In the present study, significant differences in TPM levels were found when only fuel sulfur content was varied (LS versus DS fuels). However, differences in TPM levels noted for the LS and CS fuels indicated the potential influence of fuel composition and other properties.

Wall and Hoekman (1984), using steady-state testing, found that increasing the fuel sulfur may increase the SOF levels up to 30%. They concluded that two effects contributed to this finding: (1) the H<sub>2</sub>SO<sub>4</sub> was "scrubbing" hydrocarbon compounds out of the gas phase, and (2) the presence of H<sub>2</sub>SO<sub>4</sub> (and the water bonded to it) improved the filtration efficiency.

The flame ionization detection signal reflects the total concentration of hydrocarbons including those species collected as SOF and XOC, as well as some lower-molecular-weight species that would not be collected as either SOF or XOC. Assuming that the collection efficiencies of the HC and XOC sampling systems did not change within a mode, the difference between the sum of SOF + XOC and the HC measurement can be expected to be constant for similar engine operating conditions and fuel properties. At mode 9, the difference between the total HC and the sum of SOF + XOC was, in fact, similar for both the LS and the DS fuels (32 and 36 mg/m<sup>3</sup>, respectively). However, at mode 11, the difference with the LS fuel was much greater than with the DS fuel (45 mg/m<sup>3</sup> versus 16 mg/m<sup>3</sup>, respectively).

The particle size distributions indicated there were considerably more particles with the CS and DS fuels than with the LS fuel. Stelson (1989) reported that there is a potential for artifact formation when using the EAA in the presence of SO<sub>2</sub>. He theorized that the hydroxyl radicals formed in the corona discharge section of the EAA are available to react with SO<sub>2</sub> in the aerosol stream; the resultant H<sub>2</sub>SO<sub>4</sub> would be measured as particles. Experimental data generated as a part of that study demonstrated that sensitivity to this artifact increased with decreasing particle diameter; that is, the nuclei-mode measurements were much more susceptible to positive errors (in the presence of SO<sub>2</sub>) than were the accumulation-mode particles.

Since the use of CS and DS fuel produced substantial nuclei-mode particles and the LS fuel did not, calculations were performed to determine the maximum amount of SO<sub>2</sub> present at the aerosol gas inlet stream to the EAA. Then these values were compared to Stelson's experimental observations to determine if the concentration of SO<sub>2</sub> was below the minimum levels of SO<sub>2</sub> that produced measurable current in the EAA. Assuming that all the sulfur in the DS fuel was converted to SO<sub>2</sub>, the SO<sub>2</sub> concentration at the EAA would still be lower than the observed minimum level for artifact measurements.

The nuclei mode typically is thought to consist of primary carbon spherules and hydrocarbon particles (Dolan 1977). Studies by MacDonald (1983), Baumgard and Kittelson (1985), and Wiczynski and Johnson (1986) considered that the nuclei-mode particles measured downstream of a particle trap were formed from the nucleation of hydrocarbon vapors that were able to pass through the trap and to nucleate during dilution and cooling. However, the results from this study with the L10 engine indicate that formation of nuclei-mode particles is dependent on the fuel sulfur level.

At the temperature and pressure in the combustion chamber, most of the fuel sulfur is converted to SO<sub>2</sub> (Heywood 1988). When exhaust is diluted and cooled, some SO<sub>2</sub> is converted to SO<sub>3</sub>, which combines with water from the combustion process or inlet air and forms H<sub>2</sub>SO<sub>4</sub> vapor. Baumgard (1995) showed that heteromolecular nucleation of H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> vapor can occur during dilution tunnel sampling and can form particles of nuclei-mode size range. These particles are collected on the filter as part of the TPM. Whether or not heteromolecular nucleation occurs is dependent upon the H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> vapor pressures. For our study, based on 4% conversion of the fuel sulfur to H<sub>2</sub>SO<sub>4</sub>, the dilution tunnel vapor pressures were favorable for nucleation when using the CS and DS fuels, and were below the vapor pressures required for nucleation when using the LS fuel. (The 4% conversion factor includes the typical 2% SO<sub>4</sub> levels on the filter, plus another 2% SO<sub>4</sub> in the vapor phase.) The vapor-phase H<sub>2</sub>SO<sub>4</sub> levels were not measured for this project; therefore, measured vapor-phase H<sub>2</sub>SO<sub>4</sub> values could change this observation because it is possible to have higher than 4% fuel sulfur conversion to H<sub>2</sub>SO<sub>4</sub>. Barsic (1977) measured the size distributions from premixed propane flames with fuel containing 7 or 4 ppm sulfur, and the results indicated typical nuclei and accumulation modes for combustion-generated particles. He also attributed the nuclei mode to heteromolecular nucleation of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O vapor based on agreement with nucleation theory and on the fact that nuclei-mode number con-

centration increased with the higher fuel sulfur level. The different fuels had no measurable effect on the accumulation mode.

The particle size distributions measured in the exhaust from the 1988 L10 engine and in the dilution tunnel (Figures 15 and 16) for the DS study provided information on where the diesel particles were formed. The accumulation-mode particles were similar at both locations. This similarity indicates that the majority of the agglomerated particles occurred in the engine or in the exhaust manifold, and that the tunnel did not affect the particles in the accumulation mode. Agglomeration is mainly due to the high particle concentrations in the engine and exhaust manifold, where the probability that the particles will collide with one another is high. In the dilution tunnel, the exhaust particle concentration was reduced by more than a factor of 10; consequently, the agglomeration process was greatly reduced. However, the nuclei mode was more than 2 orders of magnitude greater when sampling from the tunnel than when sampling at the engine. Because the nuclei mode was much greater at the tunnel location, these particles were formed during the dilution process, probably by heteromolecular nucleation of the H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> vapors, as explained by Baumgard (1995).

Generally, statistically significant fuel effects on raw exhaust concentrations of most of the measured PAHs were noted when the CS and LS fuel data sets were compared. In most of the cases where differences were found, higher levels were obtained with the LS fuel. There were relatively few significant mode effects, which were independent of fuel type.

In addition to sulfur levels, the LS and CS fuels also differed in their distillation profiles, specific gravities, cetane numbers, and aromatic content. The LS fuel was a denser, petroleum distillate fraction with a higher boiling point, a considerably lower cetane number (longer ignition delay), and greater proportion of aromatic compounds than the CS fuel. It is therefore reasonable to expect that the combustion products of two such fuels would differ, as would the levels of uncombusted fuel components in the exhaust. Analysis of these two fuels for PAH levels (Table 14) showed that these differed as well. The fuel and emission levels of PAHs were not clearly correlated in this limited study.

The LS and CS fuels were considerably different in PAH content compared to diesel fuels used in the United Kingdom (Williams et al. 1986, 1989; Abbass et al. 1989). The more volatile PAHs (phenanthrene, FLU, and PYR) are present in generally lower concentrations, and the least

volatile compounds (BaA, CHR, BbF, BkF, and BaP) are present in higher concentrations than in the United Kingdom fuels.

Five commercially available (U.S.) fuels were analyzed by Wall and Hoekman (1984) and found to contain similar levels of FLU, but lower levels of several other PAHs analyzed (CHR, BbF, BkF, and BaP), than either fuel used in the present study. Wall and Hoekman also compared fuel PAH levels to exhaust (particle-associated) PAH emissions and reported no clear relationship between these two parameters, although variability in PAH emission rates from the Cummins NTC 290 engine prevented ruling out with absolute certainty any correlations between fuel PAHs and emissions.

McClure and coworkers (1992) reported a study in which emissions were measured from a Caterpillar 3304 heavy-duty diesel engine typical of those used in the mining industry. Particle- and vapor-phase samples were collected over a light-duty transient test cycle from a dilution tunnel. The two fuels tested were a low-aromatic (11 wt %) and low-sulfur (0.03 wt %) fuel, and a high-aromatic (20 wt %) and low-sulfur (0.04 wt %) fuel that was adjusted to the same cetane number as the low-aromatic fuel. In the cases where significant differences in PAH levels were noted between fuels (for roughly half of the PAHs measured), the cetane-adjusted, higher-aromatic fuel produced the lowest PAH concentrations in the raw exhaust (when SOF and XOC levels were summed, in ng/m<sup>3</sup>). In the present study, lower PAH values were associated with the LS fuel, the fuel containing the higher-aromatic composition.

This study noted DS versus LS fuel effects on PAH levels. One explanation is that the presence of sulfur affected the combustion process itself. Since the DS fuel was prepared by doping the LS fuel stock, the resulting fuel PAH composition should be identical, and emissions of PAHs unaffected by the combustion process should be similar for both fuels. In this study, the only PAH measured that showed no fuel effects on particle- or vapor-phase emissions was FLU. Fluoranthene was also the only PAH showing no mode or fuel effects when LS and CS fuels were compared. This provided additional evidence that FLU emissions either originated from the fuel and did not combust, or were produced during the combustion process via a pathway not affected by the fuel sulfur level.

Williams and coworkers (1986) have reported the "survivability" of fuel PAHs, defined as the percentage of PAHs that are measured in the exhaust relative to what was measured in the fuel before combustion. The PAHs were assumed to have survived combustion because the ratio of the mass of exhaust PAHs to the mass of PAHs in the fuel was similar to the ratio of the mass of unburned hydrocar-

bons to the mass of fuel consumed. This similarity was not as obvious at low-load conditions as it was for mid- or high-load engine conditions. The range in reported "survivabilities" for 2- to 4-ring PAHs was 0.03 to 0.4 wt % at high load and 0.04 to 1 wt % at low load for a single-cylinder Petter direct-injection engine with a power output of 3.7 kW at 1500 rpm.

"Survivabilities" of the PAHs measured were calculated for modes 9 and 11 baseline for the CS and LS fuels of this study. Using the combined SOF and XOC emissions, the range in survivabilities was 0.008 to 0.2 wt % at mode 9 and 0.004 to 0.4 wt % at mode 11 for CS fuel. For the LS fuel, these survivabilities were greater: 0.04 to 0.6 wt % for mode 9 and 0.05 to 1 wt % for mode 11. These calculations included all of the analyzed PAHs (4 and 5 rings). It is interesting to note that, generally speaking, the PAHs with the highest vapor pressures have generally higher "survivabilities".

Because varying fuel sulfur levels altered particle size distributions, it is also possible that the chemical nature of the particles, as well as the size, number, and total surface area of the particles were also changed. One expected consequence of such changes in diesel fuel exhaust particles might be altered partitioning between the vapor and particle phases of PAHs (as well as of other semivolatile hydrocarbons). The principles of adsorption theory, which have been used to describe the partitioning process in ambient air (Junge 1977; Yamasaki et al. 1982; Bidleman et al. 1986; Ligocki and Pankow 1989), have been applied to the dynamic diesel exhaust sampling process (Opris et al. 1993). As in the case of ambient air measurements, linear log-log correlations exist between the vapor:particle ratios of similar PAHs (as measured in the dilution tunnel) and their respective vapor pressures. The intercept of such a linear relationship is dependent upon the temperature, the total surface of suspended particles, and the thermodynamic properties that influence the interaction of PAHs and particles. Thus, altered partitioning of PAHs would be an expected result of any qualitative or quantitative changes in particle emissions. (For further discussion, see Appendix G.)

Schuetzle and Frazier (1986) compiled and reported the ratios of several particle-associated PAHs emitted from various types of engines for possible further study as source apportionment tools for light- and heavy-duty diesel and light-duty gasoline engines. They inferred that the emissions of FLU and PYR are nearly equal regardless of engine type or make, and engine timing or fuel. For heavy-duty diesels, the average particle-associated FLU:PYR ratio was reported to be 0.8 in two literature references containing PAH measurements. In the present and previous HEI-

supported studies (Bagley et al. 1993), the ratio of these two compounds appeared to vary somewhat depending on the fuel type, engine mode, and presence or absence of a particle trap.

In the present study with LS fuel with and without the particle trap, FLU:PYR ratios ranged from 0.31 to 0.60 for particle-associated (SOF) samples and from 0.69 to 1.7 for vapor-phase (XOC) samples. For the previous study with CS fuel (Bagley et al. 1993), the FLU:PYR ratios were 2.0 to 9.1 for seven of eight SOF and XOC measurements; the eighth value, probably an outlier or extreme value, was 42. The ratios were considerably higher when the trap was used with the CS fuel (compared to baseline). When the LS fuel was doped with sulfur, the range of FLU:PYR ratios for particle and vapor phases collected and analyzed separately was 0.67 to 4.7.

FLU:PYR ratios notably lower or higher than approximately 1 have been reported in other studies. Westerholm and coworkers (1991) measured FLU and PYR levels (among other PAHs) in a study of adsorbents used for the collection of the vapor-phase emissions during transient operation of a heavy-duty diesel engine. The FLU:PYR ratios measured using gas chromatography with mass spectrometry (GC/MS) produced ratios of 1.3 for cryotrapping, 1.7 for polyurethane adsorbent, and 3.6 for XAD-2; the ratio for particle-associated FLU:PYR was 1.6. In an earlier study of fuels and aftertreatment devices (Westerholm et al. 1986), particle-associated PAHs were measured using GC with flame ionization detection (GC/FID). PAH emissions were higher and FLU:PYR ratios lower with a conventional, high-sulfur (0.26 wt %) fuel compared to a low-sulfur (0.03 wt %) fuel (ratios of 0.37 and 0.65, respectively). The use of an oxidation catalyst or catalyzed diesel particle filter produced higher FLU:PYR ratios (about 0.9).

Using GC/FID, particle-associated FLU and PYR levels found in a study of two different conventional, high-sulfur fuels produced a range of ratios of 1.1 to 2.6 (Abass et al. 1989). Gibson and associates (1980) also reported a high range (1.9 to 2.6) for particle-associated emissions from light-duty diesel cars, using HPLC with thin-layer chromatography as the analytical technique. Previous studies at MTU, in collaboration with the U.S. Bureau of Mines, produced a range of 1.2 to 2.9 for ratios (measured by HPLC with fluorescence detection) obtained from particle-phase emissions from a heavy-duty diesel engine operated on low-sulfur fuel with and without a catalyzed diesel particle filter (Bagley et al. 1991).

In a recent study (Mitchell et al. 1994; ORTECH 1994) for which particle- and vapor-phase emissions were collected separately but subsequently combined for analysis, PAH levels were measured from two heavy-duty diesel engines

operated over the federal test procedure transient cycle, using one of four different fuels and one of two different oxidation catalysts (for baselines). For three of the four fuels, the FLU:PYR ratios were 0.50 to 0.89; for the fourth fuel, the ratios were only 0.13 to 0.22. Very low ratios (0.03 to 0.22) also were found in the ambient air collected in a dieselized Canadian hard rock mine (Mogan et al. 1986a), and analyzed using thin layer chromatography with fluorescence.

In summary, although the average FLU:PYR ratio for heavy-duty particle- and vapor-phase emissions appears to be near the value of 1 reported by Schuetzle and Frazier (1986), ratios both higher and lower than approximately 1 have been observed with various engines, fuels, and engine operating conditions (and using several different analytical techniques).

Mutagenic activity, both in the presence and absence of S9, was measured in the present study. In general, the effects on mutagenic activity from using the particle trap, or different engine operating conditions, and the LS fuel were not different from those previously reported for CS fuel (Bagley et al. 1993). In particular, no increases in activity on a mass of SOF basis (revertants/ $\mu$ g) were found with trap use with this engine and operating conditions. This result contrasts with studies of earlier model heavy-duty diesel engines operated with different fuels and under different conditions (Mogan et al. 1986b; Bagley et al. 1987; Draper et al. 1987). One notable difference between the LS and CS fuels was the increased level of vapor-phase XOC activity with trap and LS fuel use. Vapor-phase organic compounds contributed over 60% of the total detected mutagenic activity with the LS fuel, even with trap use. This is a greater contribution than found in other studies. For example, Westerholm and coworkers (1991) reported only 10% to 40% of the -S9 mutagenicity was present in the vapor phase in transient diesel testing without a control device, using XAD-2 resin as the collection medium for the semivolatile XOC vapor-phase organic compounds.

The underlying basis for the observed differences in mutagenic activities between the CS and LS fuels probably is related (at least in part) to differences in fuel composition. The CS and LS fuels differ in more than sulfur content (Table 1). Other parameters such as aromatic content, cetane number, and 90% boiling point have been suggested as influencing emissions (Wall et al. 1987; Ullman et al. 1990a,b; Rantanen et al. 1993). Rasmussen (1990) conducted a study on the activity of particle emissions from a heavy-duty diesel engine operated with nine fuels, which varied primarily in sulfur (0.04 to 0.30 wt %) and aromatic (11 to 47 vol %) contents. He reported a negative correlation between particle-associated mutagenic activity on a mass

basis (revertants/ $\mu$ g) and fuel sulfur content; this correlation was not significant for raw exhaust activity on a brake-specific basis. A positive correlation was found between mutagenic activity on a brake-specific basis (revertants/hp-hr) and fuel aromatic content.

Significantly higher raw exhaust mutagenic activity also was reported by Westerholm and coworkers (1986) for two different diesel fuels with similar aromatic contents, but different sulfur levels (0.03 and 0.26 wt %) and 90% boiling points (224°C and 326°C). The higher activities were found with the fuel having the higher sulfur level. Rantanen and coworkers (1993) more recently reported the results of a study on diesel fuel composition effects on emissions from a heavy-duty diesel engine meeting the 1990 Economic Commission for Europe NO<sub>x</sub> limit (ECE R49/01). Fuel total aromatic contents varied from 15 to 33 vol %, and sulfur levels ranged from 6 to 845 ppm. In general, particle-associated mutagenic activity on mass and raw exhaust concentration bases decreased with decreasing levels of fuel sulfur and total aromatic contents, with the key difference in activity with the diesel fuels appearing to be due mainly to fuel sulfur and triaromatic compound levels. Schuetzle and Frazier (1986) also reported a possible relationship between increases in fuel aromaticity and particle-associated mutagenic activity in raw exhaust. In these three studies, however, the variation in fuel aromatic content ranged from about 10% up to 55%, far above the 20% to 30% range for the fuels used in this study. Other studies involving mutagenic activity emissions from fuels with less variation in aromatic content, however, reported no conclusive links between fuel aromatic content and mutagenic activity emissions from both light- and heavy-duty diesel engines (Jensen et al. 1988; Smith 1989; McClure et al. 1992). One of the difficulties in comparing fuel aromatic contents, however, is that these values do not necessarily indicate other similarities or differences in fuel composition that directly relate to the combustion and the particle formation process.

The comparison of the LS and DS activity data, in particular, appears to indicate that the increase in fuel sulfur might be related to the decrease in mutagenic activity with the mode 11 SOF and all of the XOC samples. This observation is in general agreement with the findings of Rasmussen (1990), for which the fuel sulfur contents also were adjusted using di-*tert*-butyl disulfide. Assays of this compound at concentrations higher than those used in the fuel showed neither mutagenic activity nor toxicity, indicating that the decrease in activity was not directly related to the presence of the sulfur additive. In the present study, the higher activities on a mass basis for both the SOF and XOC were generally found with the LS fuel. This fuel also had a

higher aromatic content and, in general, higher mutagenic activities on a raw exhaust concentration basis than the CS fuel.

The specific reasons for the observed differences in mutagenic activity between the various fuels is, therefore, still unclear. Rasmussen (1990) suggested that increased sulfur levels may interfere with formation of combustion products that might have biological activity, but did not pursue this area further. Westerholm and associates (1986) considered particle-associated emissions of PAHs and 1-nitropyrene to be fuel-dependent; however, increased levels of 1-nitropyrene and many PAHs, including FLU, PYR, and CHR were found when using the fuel with the higher (0.26 wt %) sulfur content. In our study, SOF and XOC PAH levels were generally greater with the LS fuel compared to both the CS and DS fuels, with many of the differences found to be significant for the same comparisons. The greater mutagenic activity generally associated with the LS fuel SOF and XOC samples may relate to the higher percentage of sample mass recovered from the more polar (DCM and MeOH) subfractions from the LS than the DS fuels.

When this study with LS fuel is compared with the regeneration measurements made with the same engine and CS fuel (Laymac et al. 1991; Bagley et al. 1993), many of the emissions measured show less variability. In part, this may be due to sampling during more of the regeneration process than was done previously. Also, more data were collected for mutagenic activity and chemical characterization, in order to evaluate potential regeneration process contributions to emissions. As was concluded from the previous CS fuel study, the trap regeneration process shows nearly undetectable contributions to overall emissions, provided a second trap is used in the by-pass exhaust. This configuration of traps was expected to be used (Kojetin et al. 1993), although recent trap research has been directed at using a fuel additive in conjunction with a trap to lower the particulate matter regeneration temperature, so that a heated regeneration system is not needed (for example, see Harvey et al. 1994 and Tan et al. 1996).

## CONCLUSIONS

This study focused on the effects of fuel composition on diesel engine emissions. A 1988 Cummins L10 engine was operated on fuels with varying composition including widely varying sulfur levels. Studies were performed with and without an uncatalyzed ceramic trap at two steady-state modes (9 and 11) and a trap regeneration mode. In some cases, statistically significant differences attributable to fuel as well as to trap and mode effects were noted. Trap

and mode effects were, as expected, basically consistent with previous studies. The fuel effects are summarized below.

### Low-Sulfur Fuel Effects

When comparing emissions between the LS (0.01 wt % sulfur) and CS (0.32 wt % sulfur) fuels, a number of effects could be attributed to use of the LS fuel, even though these two fuels had other compositional differences than sulfur level.

1. NO and NO<sub>x</sub> levels were generally higher (by approximately 5%), and HC levels were higher (by about 100%) at mode 9 (baseline and trap) with the LS fuel than with CS fuel. Although SO<sub>4</sub> emissions were reduced 2 orders of magnitude with the LS fuel, TPM emissions were reduced (20%) only at mode 9 without the trap. SOF and XOC levels were not significantly different between the two fuels.
2. Bimodal particle size distribution measurements indicated that the accumulation-mode particles were similar between fuels but that the numbers of nuclei-mode particles were several orders of magnitude lower for the LS fuel.
3. Most particle-associated SOF and vapor-phase XOC raw exhaust PAH levels (ng/m<sup>3</sup>) were at least 100% higher (except for FLU) with the LS fuel, but not necessarily for all modes and conditions. Particle FLU:PYR ratios also varied with fuel type; however, no correlation was found between fuel and exhaust levels of specific PAH compounds in this study.
4. Mutagenic activity generally increased (both on a mass and a raw exhaust concentration basis) with use of the LS fuel, although results varied depending on mode. The greatest increases (over 100%) were found in the activity associated with XOC.

### Doped-Sulfur Fuel Effects

This portion of the study used LS fuel doped to approximately the same sulfur level (0.29 wt % sulfur) as the CS fuel (0.32 wt % sulfur). Particle- and vapor-phase samples were collected at modes 9 and 11, baseline only. Comparing the emissions from LS and DS fuels, the following effects were attributed to fuel sulfur level:

1. At both modes, SO<sub>4</sub> and TPM were reduced (roughly 95% and 17%, respectively) using LS fuel compared to DS fuel. HC emissions were increased (20%) only at mode 11. There were no significant differences in NO, NO<sub>x</sub>, SOF, or XOC levels.
2. With the DS fuel, particle size distribution measurements at the engine exhaust manifold and in the dilu-

tion tunnel indicated that accumulation-mode particles were formed in the engine, whereas the nuclei-mode particles were formed during the dilution process. The formation of the nuclei-mode particles with the DS and CS fuels and the L10 engine was attributed to heteromolecular nucleation of the H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> vapors. When the LS fuel was used, the H<sub>2</sub>SO<sub>4</sub> vapor was likely below the threshold vapor pressure required for nucleation.

3. The general trends in PAH levels and mutagenicity were similar to those found in the comparison of LS to CS fuels, that is, SOF- and XOC-associated PAH levels (except for FLU) and mutagenicity were generally higher with the LS than the DS fuel.

### Regeneration Emissions

Regeneration emissions collected after loading the trap at mode 9 or 11 and using either LS or CS fuel indicated that there would be negligible contributions to gaseous, particle, or PAH emissions or mutagenic activity, compared to steady-state emissions, provided a second trap was used to treat the by-pass exhaust during regeneration.

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## PHASE II. EMISSIONS FROM A CUMMINS 1991 LTA10-310 ENGINE AND AN OXIDATION CATALYTIC CONVERTER USING A LOW-SULFUR FUEL

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### METHODS AND STUDY DESIGN

#### Engine, Oxidation Catalytic Converter, and Test Cell

The engine used for this study was a 1991 prototype Cummins model LTA10-310. Its prototype status was due to several prototype parts, so that the engine did not completely conform to the engine actually certified for the 1991 model year. However, the engine's emissions characteristics were representative of 1991 model engines; according to tests by Cummins, it produced emissions less than the 1991 heavy-duty diesel emission standards. Engine specifications are given in Table 29. When the engine was installed at MTU at the start of this study, it was estimated to have accumulated less than 100 hours of running time. The LS fuel and the oil used in Phase II were the same as those used in Phase I. (See Table 1 for fuel specifications.)

The engine incorporated a two-step injection timing control mechanism, called step timing control, which advanced injection timing at light loads by routing oil to appropriate tappets in the rocker housing. An oil pressure gauge was installed on the step timing control oil line in order to determine the state of injection timing. For exter-

nal-charge air cooling, the engine also used a water-to-air heat exchanger (which had been modified from an air-to-air version for laboratory purposes). This system consisted of two Cummins water-air aftercooler units mounted back-to-back on an external stand. A schematic of the MTU test cell showing the arrangement of the LTA engine is presented in Figure 17. One difference between the 1991 LTA engine and the 1988 L10 engine is that the LTA engine used a higher fuel-injection pressure than the L10 engine.

The OCC used for this study was supplied by Degussa Corporation (South Plainfield, NJ). The OCC employs a flow-through metallic substrate and a platinum catalyst. The washcoat technology is proprietary. Specifications of the OCC are given in Table 30.

The engine was installed in the same MTU diesel engine test facility as the 1988 Cummins engine used for Phase I. The engine was coupled to the opposite end of the double-ended, eddy-current dynamometer from the 1988 engine. During testing, all pertinent temperatures, pressures, speeds, and flows were recorded.

The location of the OCC in the exhaust system can influence its overall effectiveness, since OCC oxidation efficiencies for HC, CO, and SO<sub>2</sub> depend in part upon OCC operating temperature. A location closer to the exhaust manifold will produce higher OCC operating temperatures than if placed further downstream. Using guidelines supplied by Degussa and Cummins, the OCC substrate was placed 2.44 m downstream from the engine (Figure 17). Flanges were welded to the ends of the OCC canister to facilitate installation and removal. The canister was also modified to enable measurement of the bulk inlet and outlet exhaust gas temperatures as well as the pressure drop across the OCC substrate.

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**Table 29.** Specifications of the 1991 Prototype Cummins LTA Engine

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Type	In-line, 6-cylinder, 4-cycle, direct-injection
Aspiration	Turbocharged and charge-air cooled
Bore × stroke	125 mm × 136 mm
Displacement	10 L
Compression ratio	16.6:1
Maximum power at governed speed	321 kW at 1800 rpm
Maximum torque at governed speed	1227 N•m at 1800 rpm

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Gaseous HC and NO<sub>x</sub> measurements were obtained using the same instruments as during Phase I. Particle size distributions also were obtained in a similar manner as Phase I testing.

#### Emission Sampling

All samples for determining TPM and XOC-associated emissions and particle sizes were collected utilizing the MTU dilution tunnel, as described in the Phase I Methods and Study Design section. The dilution ratio was determined from the NO<sub>x</sub> concentrations in the raw and diluted exhaust.

Temperatures were monitored at numerous points in the dilution tunnel and its related equipment, using type K thermocouples (Omega Engineering, Inc., Stamford, CT). These points included the inlet and outlet of the transfer pipe, the dilution tunnel inlet, a downstream dilution tunnel location near the UHVS sample train, the 508- × 508-mm filter face, and the UHVS pump inlet and outlet. Magnehelic gauges were used to measure the pressure differential across the 508- × 508-mm filter and the dilution tunnel

gauge pressure. A mercury manometer was used to measure the gauge pressure at the UHVS pump inlet, and pump speed was measured using a phototachometer.

#### Chemical Characterization and Mutagenicity Assays

The methods used for determining TPM, SOF, SO<sub>4</sub>, SOL, XOC, and mutagenic activity levels were the same as used during Phase I. The procedures used in Phase II for the quantification of PAHs were the same as those used in Phase I for the DS fuel studies.

**Table 30.** Specifications of the DeGussa Corporation OCC

#### Substrate parameters

Manufacturer	Emitec
Dimensions	213-mm diameter × 152-mm length
Material	Stainless steel
Cell structure	Sinusoidal
Cell density	46.5 cells/cm <sup>2</sup>
Catalyst	Platinum
Precious metal loading	1.06 g/L

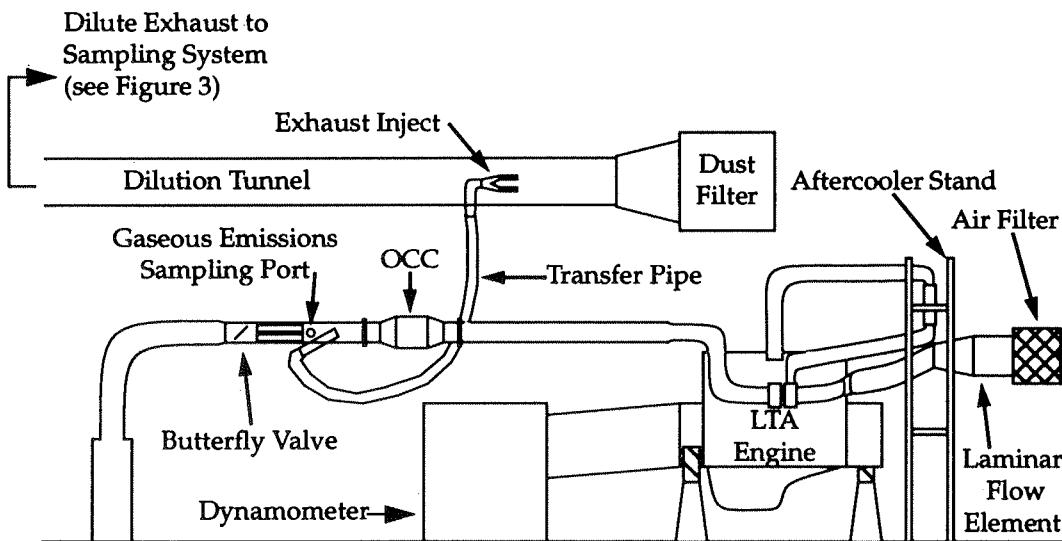


Figure 17. Schematic of the test cell for tests with the 1991 Cummins LTA engine.

### Selection of Test Conditions

The three modes chosen were EPA steady-state modes 9, 10, and 11, which are defined as 75%, 50%, and 25% load, respectively, at rated engine speed. In this study, the rated speed was taken to be the governed speed of 1800 rpm specified by Cummins, and the corresponding loads for modes 9, 10, and 11 thus were 920, 614, and 307 N·m, respectively. Modes 9 and 11 were selected to provide qualitative comparisons to Phase I tests with the 1988 L10 engine. Since these two modes would provide a range of exhaust temperatures as well a range of emission characteristics, mode 10 was selected to obtain intermediate exhaust temperatures.

### Experimental Design

All experiments were conducted with the engine operated under baseline (no OCC) and OCC conditions at three steady-state engine operating modes. The baseline tests were conducted by using a straight flow-through pipe in

place of the OCC (Figure 17). The general format followed for these experiments was similar to the Phase I LS fuel study (Figure 6). The sampling conditions used for this study are shown in Table 31 and the test matrix is presented in Table 32.

On each test day, prior to the sampling period, the dilution tunnel and UHVS sampling system were conditioned for a period of 2 to 3 hours at the tested steady-state engine condition with the filter face temperature set at approximately 45°C (with a "dummy" filter installed). The purposes of this conditioning period were (1) to allow chemical and physical interactions in the dilution tunnel to occur; (2) to allow the UHVS sampling system to reach equilibrium; and (3) to allow the analysis equipment to warm up.

Each test day's sampling period consisted of collecting dilute exhaust samples on filters and XAD-2 resin, each at 60-minute sample times. During each 60-minute collection time, gaseous emission data and test cell temperatures and pressures were measured at approximately 5, 15, 25, 35, 45, and 55 minutes. One control filter and XAD-2 resin sample

**Table 31.** Steady-State Operating Conditions and Sampling Parameters for the 1991 LTA Engine Using Low-Sulfur Fuel

Operating Conditions	Mode 9		Mode 10		Mode 11	
Load (%)	75		50		25	
Speed (rpm)	1800		1800		1800	
Torque (N·m)	920		614		307	
Power (kW)	173		116		58	
Dry fuel:air ratio	0.032		0.029		0.021	
Exhaust flow rate (kg/min)	21.0		16.3		13.5	
Fuel flow rate (kg/min)	0.615		0.444		0.269	
Exhaust O <sub>2</sub> concentration (%) <sup>a</sup>	10.9		11.8		14.2	
OCC space velocity (L/sec)	51.5		41.4		33.5	
OCC inlet temperature (°C)	393		370		311	
Sampling Parameters	Baseline	OCC	Baseline	OCC	Baseline	OCC
Number of samples	4	4	4	4	4	4
Temperature at filter face (°C) <sup>b</sup>	45.0 (0.0)	45.0 (0.0)	46.0 (0.5)	45.5 (0.7)	45.6 (0.0)	45.6 (0.0)
Sampling time (min) <sup>b</sup>	60 (0.0)	60 (0.0)	60 (0.0)	60 (0.0)	60 (0.0)	60 (0.0)
Dilution ratio <sup>b</sup>	10 (1.7)	11 (0.9)	10 (5.0)	13 (4.6)	9.0 (0.6)	8.9 (1.1)
Approximate NO <sub>2</sub> at filter face (ppm) <sup>b</sup>	2.8 (7.7)	2.9 (5.2)	2.3 (5.7)	1.4 (15)	2.2 (3.3)	0.79 (1.1)

<sup>a</sup> Calculated value.

<sup>b</sup> Presented as means (CV in %).

were treated similarly to the exposed samples, and therefore the exposed samples could be corrected for sample handling errors.

As with the Phase I studies, a crossed and balanced two-factor experimental design was chosen to facilitate statistical analyses of the data. Effects of the OCC and mode were determined by comparing two factors: (1) aftertreatment (two levels, baseline, or OCC installed), and (2) modified EPA steady-state modes (three levels, 9, 10, and 11). Effects of the OCC and mode were determined specifically by comparing baseline measurements of HC, NO<sub>x</sub>, NO, TPM, SOF, SO<sub>4</sub>, SOL, XOC, SOF-associated PAHs, XOC-associated PAHs, SOF-associated mutagenicity, and XOC-associated mutagenicity to the same measurements with the OCC installed at each of the three steady-state operating conditions.

The experimental design was randomized to the maximum extent possible, given certain constraints. The best design would have been to run all six treatment combinations (two aftertreatment levels at three modes) in one day in a random order. However, the length of time required to set up and perform one run of the experiment dictated that each treatment combination be scheduled on one day (six days total), with each day representing one block. Furthermore, because the limited quantity of LS fuel available precluded performing replicate experiments (as had been done in Phase I), each treatment combination could be run only once. Four filter samples were collected for each treatment combination to obtain the number of samples sufficient to determine the effects of each factor and the associated experimental errors.

The effect of these randomization restrictions was to confound the effects of scheduling with the experimental

error, since there was only one collection day for each treatment condition. Essentially, this means that the variability due to running the experiment on different days could not be discerned from the experimental error, because any given treatment combination was run on only one day. This consequence was accepted as part of the experimental design. The experimental running order of the six blocks (days) was randomized as mode 9 with OCC, mode 11 baseline, mode 10 baseline, mode 10 with OCC, mode 9 baseline, and mode 11 with OCC.

### Statistical Methods and Data Analysis

During each sample collection period, engine test data were entered into a spreadsheet specifically set up for this experimental design (Pataky 1992). Intake corrections were applied to the NO<sub>x</sub>, NO, and NO<sub>2</sub> data. The NO<sub>x</sub> intake correction factor used was that recommended by the EPA and SAE as determined by Krause and colleagues (1973), who also determined intake corrections for NO and NO<sub>2</sub>. Since ambient air temperature and humidity in the engine intake affect NO<sub>x</sub> formation, these intake correction factors adjust NO<sub>x</sub>, NO, and NO<sub>2</sub> levels to a reference engine intake humidity and temperature condition. There was no analogous correction factor for HC. The NO<sub>x</sub>, NO, and NO<sub>2</sub> data also were corrected to a wet basis by correcting for the water removed by the NO/NO<sub>x</sub> analyzer. The HC analyzer measured HC concentrations on a wet basis and therefore the HC data required no water correction.

Levels of SOF, SOL, SO<sub>4</sub>, TPM, XOC, PAHs, and mutagenic activity were assessed and converted to raw exhaust concentrations using the procedures set forth in the Phase I Statistical Methods and Data Analysis section. The engineering values for engine operations are given in Table 31.

**Table 32.** Test Protocol for Sampling and Quantifying Regulated and Unregulated Emissions from the 1991 LTA Engine Using Low-Sulfur Fuel

Methods and Measures	Mode 9		Mode 10		Mode 11	
	Baseline	OCC	Baseline	OCC	Baseline	OCC
HC, NO <sub>x</sub> , NO, and NO <sub>2</sub> measurements	x	x	x	x	x	x
TPM, SOF, SO <sub>4</sub> , and SOL measurements <sup>a</sup>	x	x	x	x	x	x
XOC measurements	x	x	x	x	x	x
Particle size distribution	x	x	x	x	x	x
Ames assay on SOF and XOC	x	x	x	x	x	x
Fractionate SOF and XOC samples	x	x	x	x	x	x
Ames assay on subfractions	x	x	x	x	x	x
Quantification of PAHs	x	x	x	x	x	x

<sup>a</sup> 508- × 508-mm filters used.

Since accurate determinations of volume flow through the UHVS pump were required to determine emission concentrations in the diluted exhaust, the UHVS pump was calibrated to determine the volumetric flow through the pump. A pump performance curve was generated after the first two test dates in the test matrix, using the SAE Handbook (1990) as a guideline for the tests.

The effects of the OCC and engine operating condition (or mode) were determined using two-factor ANOVA tests (Zar 1985) for all of the above-listed characteristics. All observations were assumed to follow a linear fixed-effects model. The hypotheses tested were: (1) there are no significant differences in emissions with and without the OCC as an aftertreatment device; (2) there are no significant differences in emissions between modes (9, 10, or 11); and (3) there are no significant interactions between mode and aftertreatment. For purposes of statistical analyses, sample values that were "less than the MDL", "not tested", etc., were handled as noted for the Phase I samples. Tukey's test (Zar 1985) was used to assess the effects of the OCC within modes and also to determine differences among the levels of mode within aftertreatment levels. A significance level of  $\alpha = 0.05$  was used for all comparisons. As with the Phase I analyses, all ANOVA and Tukey's tests were performed using the SAS statistical package.

Due to the differences in engine and control system configurations and engine operation between the Phase I and Phase II studies, no attempt was made to statistically compare these two data sets. However, qualitative comparisons and observations were made.

## RESULTS

### Gas-, Vapor-, and Particle-Phase Emissions

All OCC performance results presented in this report are shown as a function of steady-state engine mode, which can be directly related to OCC operating temperature. However, other parameters, such as exhaust oxygen concentration (since oxygen is necessary for the desired oxidation reactions) and OCC space velocity, may affect OCC performance. Space velocity is a measure of the exhaust gas residence time in the OCC and is found by calculating the volumetric flow rate of the exhaust divided by the gross OCC volume, thereby obtaining units of reciprocal time. Table 31 shows the engine fuel:air ratio, exhaust oxygen concentration, OCC space velocity, and OCC inlet temperature as observed or calculated during the tests with the OCC installed, all as a function of engine mode.

The experimental means and CVs for the gas-phase ( $\text{NO}_x$ , NO, and HC), vapor-phase (XOC), and particle-phase (TPM,

SOF,  $\text{SO}_4$ , and SOL) phase emissions are shown in Table 33. The summary results of the statistical analyses for the effects of aftertreatment and mode on these emissions are also presented in Table 33 (footnotes), based on the data presented in Tables H.1 and H.2 in Appendix H. Mode effects were found to be significant for all of these emission, and significant aftertreatment effects and mode-aftertreatment interactions were present for all but  $\text{NO}_x$ , NO, and SOL. It should be noted that, at mode 11 with the OCC installed, three of the four  $\text{SO}_4$  measurements were less than the MDL.

The lack of an OCC effect on  $\text{NO}_x$  emissions was expected since an oxidizing converter generally does not affect  $\text{NO}_x$  (Ball and Stack 1990). The fact that  $\text{NO}_x$  production was highest at mode 9 and lowest at mode 11 can be attributed to the progressively higher operating temperatures from mode 11 to mode 9, with the higher operating temperatures producing more  $\text{NO}_x$ . The results for NO levels were similar in all respects to those for  $\text{NO}_x$  (Table 33).

The OCC had a significant effect on HC emissions at all modes (Table 33); differences between modes with and without the OCC were found for mode 11 versus modes 9 and 10. Baseline HC emissions were highest at mode 11 and lowest at mode 9. Hydrocarbon emissions thus followed an inverse relationship to  $\text{NO}_x$  and NO, in that higher operating temperatures produced less HC but more  $\text{NO}_x$  and NO. The greatest difference in HC levels due to OCC use was at mode 11 and the least difference was at mode 9, indicating that the OCC was most effective against HC at mode 11 (lowest temperature) and least effective at mode 9 (highest temperature).

The XOC general trends and statistical results (Table 33) are very similar to those observed for the HC. The XOC concentrations measured in the dilute exhaust appeared to be affected by the OCC in the same manner as was the gaseous HC measured in the raw exhaust. Apparently, the XOC was composed of compounds that are representative of the HC in the raw exhaust or at least of those that are affected in a similar manner by the OCC.

Use of the OCC significantly affected TPM levels at all three modes. The greatest difference between mean levels with and without the OCC was at mode 11 and the least at mode 9, again indicating higher control efficiencies at lower operating temperatures. After examination of data on the main constituents of the TPM, it is apparent that the OCC decreased SOF at all three modes, increased  $\text{SO}_4$  at modes 9 and 10 (which still contributed minimally to TPM levels), and did not affect SOL.

The SOF statistical analyses (Table 33) showed many similarities to those of the HC and XOC, which was understandable since all three are composed of hydrocarbons.

The trends found for the HC and the XOC also applied to the SOF as for the XOC, except that the SOF means at modes 9 and 10 baseline were not significantly different.

Examination of the SO<sub>4</sub> data in Table 33 indicates that the OCC increased SO<sub>4</sub> at modes 9 and 10 but not at mode 11. Baseline SO<sub>4</sub> levels were similar at modes 9 and 10 and lower at mode 11. While the SO<sub>4</sub> fraction increased from 500% to 600% at modes 9 and 10, respectively, it should be noted that the concentrations of SO<sub>4</sub> produced at all treatment combinations were still 1 to 2 orders of magnitude lower than the TPM concentrations and thus did not contribute significantly to the TPM. Sulfate contribution was minimal due to the low-sulfur content of the test fuel (0.01 wt % sulfur).

The SOL statistical results (Table 33) indicated that only the mode significantly affected the SOL concentrations; the

OCC did not affect SOL at any mode. The SOL levels at mode 11 with and without the OCC were significantly different from those at mode 9.

### Particle Size Distributions

The particle size distributions for the 1991 prototype LTA engine are considerably different than the distributions for the 1988 L10 Cummins engine. The particle number and volume distributions for modes 9 and 11 are shown in Figures 18 through 21. The midpoints of the EAA instrument size ranges are plotted versus the particle number or volume on a log scale. The log scale is necessary to cover the several orders of magnitude differences between the concentrations found in the nuclei and accumulation modes. The mode 10 distributions were similar and are provided in Figures I.1 and I.2 in Appendix I. The baseline

**Table 33.** Gas-, Vapor-, and Particle-Phase Emissions from the 1991 LTA Engine Using Low-Sulfur Fuel With and Without the OCC<sup>a</sup>

Emissions	Mode 9		Mode 10		Mode 11	
	Baseline	OCC	Baseline	OCC	Baseline	OCC
NO <sub>x</sub> (ppm) <sup>b</sup>	530 (1.3)	540 (0.45)	370 (1.2)	360 (2.9)	210 (1.1)	210 (0.48)
NO (ppm) <sup>b</sup>	510 (1.9)	510 (0.51)	340 (1.8)	350 (2.9)	200 (1.0)	210 (0.78)
HC (ppm) <sup>c</sup>	72 (2.5)	28 (2.1)	96 (1.9)	34 (3.5)	180 (6.8)	53 (3.4)
TPM (mg/m <sup>3</sup> ) <sup>d</sup>	8.1 (4.9)	5.9 (2.8)	8.7 (3.5)	5.7 (6.1)	15 (2.1)	7.0 (7.8)
SOF (mg/m <sup>3</sup> ) <sup>d</sup>	5.1 (5.0)	2.4 (6.5)	5.2 (4.4)	2.1 (12)	12 (5.3)	3.4 (3.1) <sup>f</sup>
SO <sub>4</sub> (mg/m <sup>3</sup> ) <sup>e</sup>	0.05 (16)	0.28 (12)	0.03 (27)	0.20 (11)	< 0.01 (16)	< 0.01 ND <sup>g</sup>
SOL (mg/m <sup>3</sup> ) <sup>h</sup>	3.0 (5.1)	3.2 (2.6)	3.5 (3.2)	3.5 (3.3)	3.8 (8.4)	3.7 (16)
XOC (mg/m <sup>3</sup> ) <sup>c</sup>	21 (6.3)	9.3 (6.3)	29 (7.4)	10 (13)	54 (3.2)	17 (11)

<sup>a</sup> Presented as means (CV in %) of four samples. Statistical analyses for comparisons are presented in Tables H.1 and H.2.

<sup>b</sup> Significant differences among data at all modes with and without the OCC.

<sup>c</sup> Significant differences between the baseline and OCC data at all modes.

<sup>d</sup> Significant differences between the baseline and OCC data at all modes and between the mode 11 and modes 9 and 10 data with and without the OCC.

<sup>e</sup> Significant differences between the baseline and OCC data at modes 9 and 10 and among all modes with the OCC.

<sup>f</sup> Three of four values less than the MDL.

<sup>g</sup> ND = not determined.

<sup>h</sup> Significant differences between the baseline mode 9 and 11 data.

data indicated the typical bimodal distribution with a well-defined nuclei mode. More than 98% of the total number of particles were found in the nuclei mode for all conditions, and between 27% and 47% by volume were in the nuclei mode depending on the engine condition. In Phase I using LS fuel, only about 2% by volume of the particles were in the nuclei mode, and less than 10% when using the CS fuel. In further analysis of these data, Baumgard (1995) reasons that the nuclei mode for the LTA engine contains individual carbon spheres with HC adsorbed as SOF and insignificant associated SO<sub>4</sub>.

The size distributions with the OCC are similar to the baseline size distributions with virtually no change in either the nuclei or accumulation mode. Table 34 summarizes the particle parameters for both the baseline and OCC NMD and VMD for the nuclei mode and the accumulation mode. The parameters for both the nuclei and accumulation modes tended to be less than the parameters for the LS and CS data (Table 10).

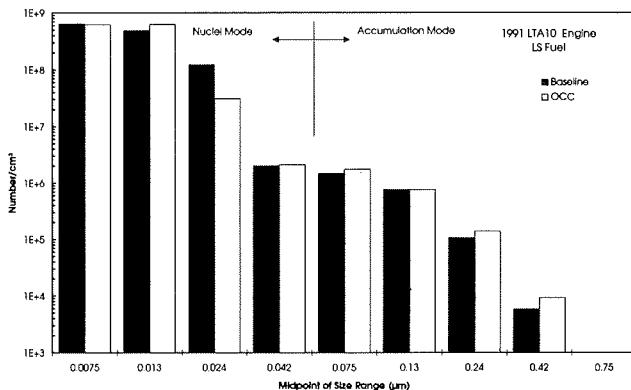


Figure 18. Mode 9 particle number distributions for the 1991 Cummins LTA engine with and without the OCC.

### PAHs in SOF and XOC Samples

Table 35 gives the raw exhaust PAH concentrations (ng/m<sup>3</sup>) measured in particle-associated SOF and vapor-phase XOC samples collected at modes 9, 10, and 11 from the LTA engine operated on LS fuel with and without the OCC. Data for PAH levels on a mass basis (µg/g) are presented in Tables J.1 and J.2 in Appendix J. As with the Phase I data, no statistical analyses were conducted for compounds that had most or all values less than the MDL (BbF, BkF, and BaP for XOC samples). Summaries of the statistical results for aftertreatment effects for all other PAH levels are presented in Table 36. The statistical analyses for the aftertreatment and mode comparisons are presented in Tables H.3 to H.6 in Appendix H.

The use of the OCC had an effect on FLU emissions in both the particle and vapor phases. At mode 9, there was an increase in FLU in both phases on a mass basis. At modes

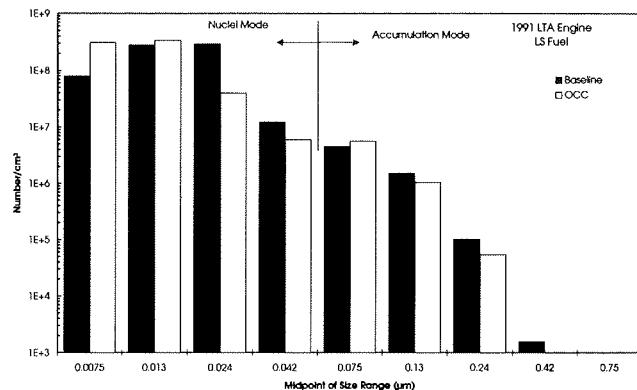


Figure 20. Mode 11 particle number distributions for the 1991 Cummins LTA engine with and without the OCC.

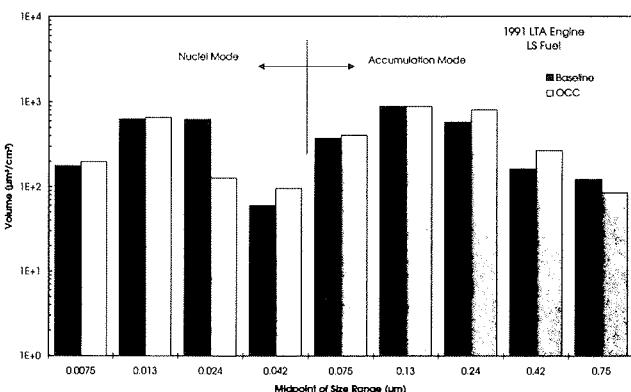


Figure 19. Mode 9 particle volume distributions for the 1991 Cummins LTA engine with and without the OCC.

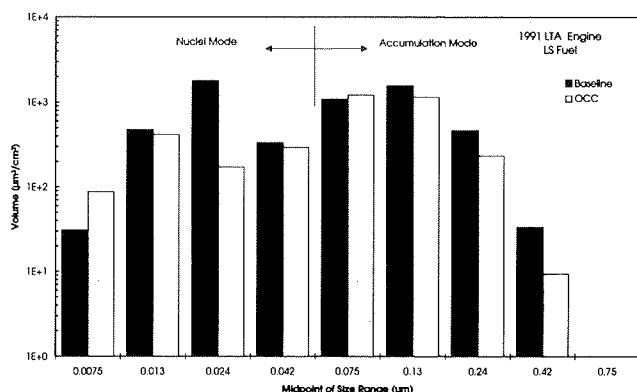


Figure 21. Mode 11 particle volume distributions for the 1991 Cummins LTA engine with and without the OCC.

10 and 11, the raw exhaust concentrations decreased in the particle and vapor phase when the OCC was used. All of these changes were found to be significant (Table 36).

Under baseline conditions there were significant differences in raw exhaust FLU emissions (particle and vapor phases) among engine modes. When the OCC was used, mode effects were observed only on a mass basis ( $\mu\text{g/g}$ ), as the raw exhaust concentrations ( $\text{ng/m}^3$ ) were not significantly different among modes when the OCC was used. Since three modes were being considered, a statistically significant difference among modes did not necessarily imply differences among all modes. For example, although FLU baseline emissions are affected by engine mode, only particle-associated levels ( $\mu\text{g/g TPM}$ ) differed among all three modes (see Table H.3). On a  $\mu\text{g/g SOF}$  basis, there was a difference between mode 9 and modes 10 and 11, that is, modes 10 and 11 were not statistically different.

Particle-associated PYR, BaA, BbF, BkF, and BaP levels all decreased when the OCC was used both in terms of their mass relative to that of SOF or TPM and on a raw exhaust ( $\text{ng/m}^3$ ) basis; all of these differences were significant. There were also significant mode effects on the levels of these compounds in the particle phase whether or not the OCC was used. Use of the OCC significantly affected (decreased) emissions of PYR, BaA and BbF in the vapor phase as well on a  $\text{ng/m}^3$  basis. On a mass basis, only the BbF

levels in the XOC were measurably affected by the OCC; again the levels decreased compared to baseline. Benzo[*a*]pyrene levels in the vapor phase were below detection limits, probably due to its low vapor pressure.

Although particle-phase CHR levels varied with engine mode, there was a measurable effect of the OCC on this particular compound on a mass basis only at mode 10 and at modes 10 and 11 on a raw exhaust concentration basis. For CHR in the vapor phase ( $\text{ng/m}^3$  and  $\mu\text{g/g XOC}$ ), levels with the OCC were significantly different only at mode 10. In all cases of significant differences for CHR levels, lower levels were obtained with the OCC compared to baseline.

#### Mutagenicity of SOF and XOC Samples

The mean and CV results from the mutagenicity tests for the SOF and XOC samples are presented in Table 37. As with the Phase I samples, there was relatively little effect due to the use of the S9 metabolic activation system. A summary of the statistical results for aftertreatment and mode effects is presented in Table 37, based on the data presented in Tables H.7 and H.8 in Appendix H.

The following observations can be made about the mutagenic activity on a mass basis (revertants/ $\mu\text{g}$ ) for SOF, TPM, or XOC: (1) the effect of the OCC is mode-dependent, with generally increased or similar activity at modes 9 and 10 but reduced activity at mode 11; (2) mode effects vary

**Table 34.** Particle Parameters from the 1991 LTA Engine Using Low-Sulfur Fuel With and Without an OCC<sup>a</sup>

Mode and Condition	Number Mean Diameter		Volume Mean Diameter		Geometric Standard Deviation <sup>b</sup>	
	Nuclei Mode	Accumulation Mode	Nuclei Mode	Accumulation Mode	Nuclei Mode	Accumulation Mode
9 Baseline	0.011 (27.8)	0.071 (25.5)	0.017 (5.5)	0.171 (21.1)	1.46 (10.5)	1.71 (14.4)
9 OCC	0.010 (7.3)	0.047 (13.6)	0.013 (4.0)	0.185 (8.2)	1.32 (3.5)	1.97 (5.1)
10 Baseline	0.011 (13.6)	0.064 (21.4)	0.016 (4.2)	0.140 (12.2)	1.44 (6.8)	1.67 (10.8)
10 OCC	0.009 (0.7)	0.043 (5.0)	0.010 (2.2)	0.185 (8.8)	1.26 (1.2)	2.00 (3.1)
11 Baseline <sup>c</sup>	0.017 (8.8)	0.073 (8.7)	0.024 (7.6)	0.120 (8.8)	1.38 (6.0)	1.50 (0)
11 OCC	0.011 (26.1)	0.055 (2.3)	0.014 (9.1)	0.098 (1.8)	1.34 (10.8)	1.55 (0.6)

<sup>a</sup> Reported in micrometers as means of four samples (CV in %).

<sup>b</sup> A measure of the spread of the particle size distribution.

<sup>c</sup> Three samples.

with OCC use, with mode 11 activities generally higher under baseline conditions and mode 9 activities higher with the OCC; and (3) SOF-associated activities were generally higher than the XOC-associated activities. Many of these differences were also found to be significant (Table 37). The OCC significantly affected activity (revertants/ $\mu$ g) for the SOF at modes 10 and 11, TPM at mode 11, and XOC at mode 9. Significant differences for modes were found between the mode 11 values and those for modes 9 or 10 for all but SOF without the OCC.

The general trends found with activity on a raw exhaust concentration basis (revertants/ $m^3$ ) were (1) use of the OCC reduced both SOF- and XOC-associated activity; (2) differ-

ences between modes varied with the type of activity and whether or not the OCC was used; and (3) approximately 50% or more of the detected mutagenic activity was XOC-associated, with levels about 80% at modes 9 and 11 with the OCC. The OCC effects were significant for the SOF at mode 11 and for the XOC at all modes. In these cases, any increases in mutagenic activity on a mass basis (revertants/ $\mu$ g) were more than offset by the OCC's lowering of SOF and XOC concentrations (Table 33). At modes 9 and 10, the decreases in SOF concentrations were not proportionately as great as at mode 11 and did not fully compensate for the increases in SOF mutagenic activity. The only significant difference among modes for SOF activity concentrations was between baseline values for mode 11 com-

**Table 35.** Particle-Associated (SOF) and Vapor-Phase (XOC) PAH Emissions from the 1991 LTA Engine With and Without the OCC

Mode and Condition	Fraction	PAH Level ( $ng/m^3$ ) <sup>a</sup>						
		FLU	PYR	BaA	CHR	BbF	BkF	BaP
9 Baseline	SOF	17 (41)	210 (8.0)	970 (5.2)	150 (12)	730 (7.5)	130 (5.1)	100 (7.8)
	XOC	1080 (23)	1730 (26)	2500 (31)	100 (30)	86 (30)	< 2.0 <sup>b</sup> ND <sup>c</sup>	< 2.1 <sup>b</sup> ND
9 OCC	SOF	35 (32)	44 (16)	130 (10)	51 (11)	18 (18)	5.4 (7.0)	2.8 (22)
	XOC	1160 (1.7)	500 (5.8)	930 (2.4)	77 (8.2)	< 0.87 <sup>b</sup> ND	< 1.0 <sup>b</sup> ND	< 1.1 <sup>b</sup> ND
10 Baseline	SOF	76 (12)	430 (5.0)	2250 (5.6)	3300 (6.2)	1280 (8.0)	500 (6.2)	540 (7.0)
	XOC	1350 (6.1)	1790 (5.6)	1390 (24)	1500 (7.3)	106 (44)	< 1.0 <sup>b</sup> ND	< 1.1 <sup>b</sup> ND
10 OCC	SOF	38 (8.3)	130 (11)	340 (59)	460 (75)	31 (15)	12 (87)	< 2.7 <sup>b</sup> ND
	XOC	660 (4.3)	700 (7.1)	540 (2.9)	210 (12)	< 2.4 <sup>b</sup> ND	< 2.7 <sup>b</sup> ND	< 2.9 <sup>b</sup> ND
11 Baseline	SOF	220 (9.7)	1640 (2.0)	5510 (1.5)	800 (5.5)	5950 (1.2)	1730 (4.0)	440 (14)
	XOC	2120 (26)	2530 (25)	3580 (28)	190 (34)	230 (29)	< 0.75 <sup>b</sup> ND	< 1.1 <sup>b</sup> ND
11 OCC	SOF	36 (10)	230 (3.4)	1020 (5.0)	110 (9.5)	950 (6.0)	240 (6.6)	57 (8.8)
	XOC	780 (5.6)	1140 (2.2)	1890 (6.9)	83 (13)	130 (6.3)	< 0.83 <sup>b</sup> ND	< 0.87 <sup>b</sup> ND

<sup>a</sup> Presented as means (CV in %). n = 4 for all data sets.

<sup>b</sup> All values less than this MDL.

<sup>c</sup> ND = not determined because values were less than the MDL.

pared to modes 9 and 10, reflecting at least in part the higher SOF concentrations at the lower load mode (Table 33). Most of the XOC activity concentrations differed significantly between modes, reflecting differences in activity levels (revertants/ $\mu\text{g}$ ) and XOC concentrations ( $\text{mg}/\text{m}^3$ ).

The responses of these SOF and XOC samples to tester strains TA98NR and TA98DNP (both -S9) are presented in Table 38. Varying levels of response were found for the baseline SOF samples, with the lowest relative amount of TA98NR activity found with the samples having the highest TA98 activity (mode 11). For the baseline XOC samples, the level of TA98NR responses (as a percentage of the TA98 response) was inversely proportional to the TA98 response level; for example, the highest TA98NR percentage was with the lowest TA98 response at mode 9. Similar patterns were not observed with the TA98DNP responses. All of the OCC SOF samples had similar, low percentage responses with TA98NR, indicating the presence of mononitro-PAHs. The lowest percentage TA98DNP level was found with the OCC SOF sample having the highest TA98 activity, that is mode 10. The responses for these tester strains with the OCC XOC samples appeared to relate to the TA98 activity level, with low percentage responses with the samples with the highest activity (mode 9) and vice versa.

As with the Phase I study, one set of SOF and XOC subfractions from each mode (9, 10, or 11) and condition (baseline or OCC) was analyzed for mutagenic activity. Summaries of the mass recoveries and activity data are presented in Table 39. The mass recovery values were consistently high, ranging from 77% to 104%. With most sets, the highest percentage of mass was recovered from the least polar HEX subfraction. There was a difference in mass distribution between the SOF and XOC samples. For all SOF samples,

most of the recovered mass was found in the HEX subfraction (50% to 70%) with roughly equal distribution of the remaining mass between the ACN, DCM, and MeOH subfractions. In contrast, the XOC samples had about 70% to 80% of the recovered mass about equally distributed between the HEX and ACN fractions and about 5% or less of the recovered mass in the more polar DCM and MeOH subfractions.

The subfractions were assayed for mutagenic activity using the same guidelines described for the Phase I subfraction tests. No mass was available to assay some of the subfractions even with TA98 (Table 39) and some of the XOC, ACN, and DCM subfractions had toxic responses. No activity was detected with any of the HEX subfractions and relatively little with the ACN subfractions, even with S9 (see Table 39). If present, most of the activity was found with the DCM and MeOH subfractions; the tests with TA98NR and TA98DNP also indicated the presence of direct-acting nitro-PAHs in these subfractions. Recovery of mutagenic activity was fairly good for the SOF samples (up to 90%), but relatively poor for the XOC samples (as low as 0% where some subfractions were not available for testing). In general, activities per subfraction and activity recoveries were higher for the baseline than the OCC samples.

## DISCUSSION

### Effects of Oxidation Catalytic Converter and Mode on Emissions

A summary of the effects on some of the regulated and unregulated emissions of using this OCC as an aftertreatment device is presented in Table 40. Heywood (1988)

**Table 36.** Summary of Statistical Results for OCC Effects on PAH Emissions<sup>a</sup>

PAH	Particle-Associated PAH			Vapor-Phase PAH	
	$\mu\text{g}/\text{g}$ SOF	$\mu\text{g}/\text{g}$ TPM	$\text{ng}/\text{m}^3$	$\mu\text{g}/\text{g}$ XOC	$\text{ng}/\text{m}^3$
Fluoranthene	9	9	10, 11	9	10, 11
Pyrene	9, 10, 11	9, 10, 11	9, 10, 11	None	9, 10, 11
Benz[a]anthracene	9, 10, 11	9, 10, 11	9, 10, 11	None	9, 11
Chrysene	10	10	10, 11	9	9
Benzo[b]fluoranthene	9, 10, 11	9, 10, 11	9, 10, 11	9, 10, 11	9, 10, 11
Benzo[k]fluoranthene	9, 10, 11	9, 10, 11	9, 10, 11	NS <sup>b</sup>	NS
Benzo[a]pyrene	9, 10, 11	9, 10, 11	9, 10, 11	NS	NS

<sup>a</sup> All statistical analysis results are in Appendix Tables H.3 through H.6. The  $\mu\text{g}/\text{g}$  data are in Appendix Tables J.1 and J.2. The  $\text{ng}/\text{m}^3$  data are presented in Table 35. If a mode number is indicated (9, 10, or 11), a significant difference was found between the baseline and OCC PAH levels at that mode.

<sup>b</sup> NS = not statistically analyzed because values were less than the MDLs for all samples.

reported that an OCC's efficiency should increase with operating temperature. The apparent disparity found in this study may be due to several reasons.

Several physical grounds may explain the behavior of the data in Table 40. The inlet HC and O<sub>2</sub> concentrations to the OCC decreased from mode 11 to 9 (see Tables 33 and 31,

**Table 37.** Effects of the OCC and LS Fuel (Used with the 1991 LTA Engine) on the Mutagenicity of SOF and XOC<sup>a</sup>

Mode and Condition	Fraction	<i>n</i> <sup>b</sup>	Revertants/ $\mu\text{g}$ <sup>c</sup>			Revertants/ $\mu\text{g}$ TPM <sup>e</sup>		Revertants/ $\text{m}^3$ <sup>f</sup> ( $\times 10^3$ )	
			-S9	+S9	SOF <sup>d</sup> (%)	-S9	+S9	-S9	+S9
9 Baseline	SOF	4	2.6 (14)	3.3 (10)	63 (0.83)	1.7 (14)	2.1 (10)	14 (10)	17 (64)
	XOC	4	0.57 (34)	0.48 (31)	NA <sup>g</sup>	NA	NA	12 (29)	10 (28)
9 OCC	SOF	4	3.9 (16)	4.1 (7.7)	41 (4.0)	1.6 (15)	1.6 (9.0)	9.3 (16)	9.7 (11)
	XOC	4	2.6 (18)	2.7 (25)	NA	NA	NA	24 (13)	25 (20)
10 Baseline	SOF	4	2.5 (20)	3.3 (21)	60 (1.6)	1.5 (18)	1.9 (21)	13 (16)	17 (23)
	XOC	4	0.98 (12)	0.96 (15)	NA	NA	NA	29 (12)	28 (17)
10 OCC	SOF	3	4.9 (44)	5.2 (39)	36 (6.4)	1.8 (45)	2.2 (12)	10 (49)	12 (20)
	XOC	3	0.60 (20)	0.52 (32)	NA	NA	NA	6.1 (28)	5.4 (39)
11 Baseline	SOF	4	3.3 (12)	3.3 (7.8)	75 (1.3)	2.5 (8.9)	2.5 (6.0)	38 (7.3)	38 (4.6)
	XOC	4	1.4 (3.0)	1.1 (11)	NA	NA	NA	78 (4.0)	57 (13)
11 OCC	SOF	4	1.7 (22)	1.9 <sup>h</sup> (24)	48 (9.1)	0.84 (19)	0.93 (16)	5.8 (20)	6.3 (20)
	XOC	4	1.7 (26)	0.97 <sup>i</sup> (84)	NA	NA	NA	28 (18)	18 (91)

<sup>a</sup> Presented as mean (CV in %) activities using TA98. Statistical analyses for comparisons are presented in Tables H.7 and H.8.

<sup>b</sup> Number of samples.

<sup>c</sup> Based on extractable mass of SOF or XOC. For SOF, significant differences were found between the baseline and OCC data at modes 10 and 11, and between the mode 11 and mode 9 or 10 data with the OCC; for XOC, significant differences were found between the baseline and OCC data at mode 9, among all modes for the baseline data, and between modes 9 and 11 with the OCC.

<sup>d</sup> SOF percentage of the TPM.

<sup>e</sup> Significant differences were found between the baseline and OCC data at mode 11, between the mode 11 and mode 9 or 10 baseline data, and between the mode 10 and 11 data with the OCC.

<sup>f</sup> For SOF, significant differences were found between the baseline and OCC data at mode 11, and between the mode 11 and 9 or 10 baseline data; for XOC, significant differences were found among the baseline and OCC data at all modes, among all modes for the baseline data, and between modes 10 and 9 or 11 for the OCC.

<sup>g</sup> NA = not applicable to XOC data.

<sup>h</sup> *n* = 2.

<sup>i</sup> *n* = 3; sample toxicity may have masked mutagenic response.

respectively). Lower reactant concentrations, particularly those of HC, may lower HC conversion efficiency due to smaller concentration gradients to the catalyst, resulting in smaller HC "driving forces" to the catalyst. Differences in O<sub>2</sub> concentration among modes would likely have been too small to noticeably affect the degree of oxidation. The space velocity also increased from mode 11 to mode 9, as shown in Table 31, decreasing the time for catalytic oxidation of the HC. The space velocity is essentially the number of volume changes (at standard conditions) per unit of time through the converter and is a measure of the residence time of the exhaust gas in the OCC. Under isothermal conditions,

conversion efficiency decreases as space velocity increases (Zelenka et al. 1990b; Porter et al. 1991; Barris 1992). Additionally, Kummer (1981) stated that, in the presence of NO up to 1000 ppm, HC oxidation was strongly inhibited, with low NO concentrations causing relatively more inhibition than higher concentrations. Nitric oxide was present at all three modes from about 200 to 500 ppm and increased from mode 11 to 9. Thus, a combination of these factors may have affected HC conversion efficiencies and may explain why the HC conversion efficiencies decreased as the OCC inlet temperature increased.

**Table 38.** Response of Tester Strains TA98, TA98NR, and TA98DNP (in the Absence of S9) to SOF and XOC from the 1991 LTA Engine Operated at Modes 9, 10, and 11 With and Without the OCC

Mode and Condition	Fraction	TA98		TA98NR		TA98DNP	
		Revertants/ $\mu\text{g}^{\text{a},\text{b}}$	Revertants/ $\mu\text{g}^{\text{b}}$	% TA98	Revertants/ $\mu\text{g}^{\text{b}}$	% TA98	
9 Baseline	SOF	2.6 (14)	1.2 (6.7)	44	0.51 (10)	19	
	XOC	0.57 (34)	0.41 (19)	91	0.15 (35)	28	
9 OCC	SOF	3.9 (16)	0.71 (13)	18	1.2 (33)	30	
	XOC	2.6 (18)	0.89 <sup>c</sup> (34)	39	0.83 <sup>c</sup> (38)	35	
10 Baseline	SOF	2.5 (20)	1.4 (17)	60	0.87 (50)	46	
	XOC	0.98 (12)	0.47 (31)	49	0.37 (9.2)	38	
10 OCC	SOF	4.2 (44)	0.81 (23)	19	0.38 (12)	8.8	
	XOC	0.60 (20)	0.55 (1.9)	94	0.31 (39)	50	
11 Baseline	SOF	3.3 (12)	0.28 (16)	8.4	1.1 (16)	34	
	XOC	1.4 (30)	0.27 <sup>c</sup> (6.9)	19	0.54 (43)	38	
11 OCC	SOF	1.7 (22)	0.22 (46)	12	0.67	55	
	XOC	1.7 (26)	NT <sup>d</sup>		NR <sup>d</sup>		

<sup>a</sup> For samples listed in Table 37.

<sup>b</sup> Presented as means (CV in %) for four samples.

<sup>c</sup> Data for three samples.

<sup>d</sup> NT = not tested; NR = no response above spontaneous revertant levels.

**Table 39.** Mutagenicity of SOF and XOC Subfractions from the 1991 LTA Engine Using the Low-Sulfur Fuel With and Without the OCC<sup>a</sup>

Subfraction <sup>b</sup>	Mode 9						Mode 10						Mode 11					
	Baseline			OCC			Baseline			OCC			Baseline			OCC		
	% Mass	Revertants/µg	% Activity	% Mass	Revertants/µg	% Activity	% Mass	Revertants/µg	% Activity	% Mass	Revertants/µg	% Activity	% Mass	Revertants/µg	% Activity	% Mass	Revertants/µg	% Activity
SOF-HEX	57	NR <sup>c,d</sup>	0	66	NR <sup>d</sup>	0	64	NR <sup>d</sup>	0	74	NR <sup>d</sup>	0	53	NR <sup>d</sup>	0	48	NR <sup>d</sup>	0
SOF-ACN	11	0.55 <sup>d</sup>	2.4	13	1.2 <sup>d</sup>	4.6	12	0.96 <sup>d</sup>	6.1	ML <sup>c</sup>	IS <sup>c</sup>	NA <sup>c</sup>	10	0.31 <sup>d</sup>	1.0	15	0.13 <sup>d</sup>	1.5
SOF-DCM	11	9.5 <sup>e</sup>	43	13	8.2 <sup>e</sup>	31	9.0	6.4 <sup>e</sup>	29	15	4.0 <sup>e</sup>	8.8	10	4.8 <sup>f</sup>	16	9.9	2.9 <sup>e</sup>	21
SOF-MeOH	13	6.6 <sup>e</sup>	35	11	3.9 <sup>e</sup>	13	14	7.9 <sup>e</sup>	57	ML	IS	NA	20	2.1 <sup>g</sup>	14	19	1.9 <sup>e</sup>	26
% Recovered	92		80	104		49	98		92	89		8.8	94		25	92		49
XOC-HEX	42	NR <sup>d</sup>	0	30	NR <sup>d</sup>	0	39	NR <sup>d</sup>	0	34	NR <sup>d</sup>	0	45	NR <sup>d</sup>	0	45	NR <sup>d</sup>	0
XOC-ACN	36	NR <sup>d</sup>	0	42	T <sup>c</sup>	0	38	NR <sup>d</sup>	0	51	NR <sup>d</sup>	0	26	0.31 <sup>d</sup>	5.7	38	0.28 <sup>d</sup>	7.8
XOC-DCM	3.7	T	0	3.6	T	0	4.5	NR	0	3.5	T	0	4.6	T	0	4.3	T	0
XOC-MeOH	4.3	1.6 <sup>h</sup>	21	1.7	4.5	3.5	4.0	2.0	6.9	5.6	IS	NA	4.7	2.6 <sup>e</sup>	8.5	4.9	0.84 <sup>h</sup>	3.1
% Recovered	86		21	77		3.5	85		6.9	95		0	80		14	92		11

<sup>a</sup> Values for % Mass and % Recovered are based on sample mass used in separation, rounded to the nearest percent. Counts of Revertants/µg were measured with TA98-S9. Values for % (mutagenic) Activity were based on activity of unfractionated sample.

<sup>b</sup> Based on separation scheme in Figure 5.

<sup>c</sup> NR = no response above spontaneous revertant levels; ML = mass too low to determine; IS = insufficient sample to test; NA = not applicable to this situation; T = toxic response to sample and no mutagenic response detected.

<sup>d</sup> No response with TA98+S9 above that obtained with TA98-S9.

<sup>e</sup> Responses with TA98NR and TA98DNP from 5% to 25% of the TA98-S9 response.

<sup>f</sup> Responses with TA98NR and TA98DNP about 10% and 40%, respectively, of the TA98-S9 response.

<sup>g</sup> Responses with TA98NR and TA98DNP about 40% and 90%, respectively, of the TA98-S9 response.

<sup>h</sup> Responses with TA98NR and TA98DNP about 50% and 25%, respectively, of the TA98-S9 response.

Direct comparisons of OCC effects on emissions between this study and literature values for the gas, vapor, and particle phase emissions are complicated, because OCC performance is affected by numerous factors (Zelenka et al. 1990b). One important factor is the type of test, steady-state or transient. Under steady-state testing, the load and speed of the engine is held constant. This condition may or may not reflect the nature of the other processes associated with the test. If no time-dependent effects are present (a distinctly idealized case), then all test-associated processes will also be steady-state. Some time-dependent processes such as occur in the loading of a particle trap may well be present under steady-state testing. Many of the processes associated with steady-state OCC testing are expected to be near steady-state; these include exhaust gas temperatures, OCC space velocity, and various pollutant concentrations

before and after the OCC. Some storage and release mechanisms of various particulate constituents on the OCC substrate may occur.

Further, comparisons among steady-state tests are complicated by factors such as different steady-state temperatures, different OCC space velocities, and different OCC formulations. However, steady-state testing yields valuable information as to how an OCC performs at various operating conditions, indicating specific performance at these conditions. Ideally, knowledge gained from steady-state testing assists in designing OCCs that perform well under transient conditions. Additionally, steady-state testing simulates OCC performance for a significant portion of the operating time of a heavy-duty vehicle, such as when it is traveling down a level highway at a constant speed.

Numerous other parameters also affect OCC performance, such as fuel sulfur content, precious metal loading,

**Table 40.** Summary of OCC Effects on Emissions from the 1991 LTA Engine During Steady-State Operation at Modes 9, 10, and 11

Parameter	Percentage of Change from Baseline <sup>a</sup>		
	Mode 9	Mode 10	Mode 11
NO <sub>x</sub> (ppm)	+1.9	-2.7	0
NO (ppm)	0	+2.9	+5.0
HC (ppm)	-61 <sup>b</sup>	-65 <sup>b</sup>	-71 <sup>b</sup>
TPM (mg/m <sup>3</sup> )	-27 <sup>b</sup>	-34 <sup>b</sup>	-53 <sup>b</sup>
SOF (mg/m <sup>3</sup> )	-53 <sup>b</sup>	-60 <sup>b</sup>	-72 <sup>b</sup>
SO <sub>4</sub> (mg/m <sup>3</sup> )	+460 <sup>b</sup>	+570 <sup>b</sup>	NC <sup>c</sup>
SOL (mg/m <sup>3</sup> )	+6.7	0.0	-2.6
XOC (mg/m <sup>3</sup> )	-56 <sup>b</sup>	-66 <sup>b</sup>	-69 <sup>b</sup>
Particle number (number/cm <sup>3</sup> ) <sup>d</sup>	+1.9	+76	+4.9
Particle volume (μm <sup>3</sup> /cm <sup>3</sup> ) <sup>d</sup>	-1.6	+19	-38
Mutagenic activity (revertants/m <sup>3</sup> ) <sup>e</sup>			
SOF	-34	-23	-85 <sup>b</sup>
XOC	+100 <sup>b</sup>	-79 <sup>b</sup>	-64 <sup>b</sup>
Fluoranthene (ng/m <sup>3</sup> )			
SOF	+110	-50 <sup>b</sup>	-84 <sup>b</sup>
XOC	+7.4	-51 <sup>b</sup>	-63
Pyrene (ng/m <sup>3</sup> )			
SOF	-79 <sup>b</sup>	-70 <sup>b</sup>	-86 <sup>b</sup>
XOC	-71 <sup>b</sup>	-61 <sup>b</sup>	-55 <sup>b</sup>

<sup>a</sup> Presented as [(OCC/Baseline) - 1] × 100.

<sup>b</sup> Significant difference between baseline and OCC data.

<sup>c</sup> NC = not calculated because all but one OCC value were less than the MDL.

<sup>d</sup> Not tested for significant differences.

<sup>e</sup> TA98-S9.

substrate material, washcoat formulation, cell design and density, and OCC position in the exhaust stream. Thus, with knowledge of the various parameters influencing OCC performance, general trends can be discerned from among the numerous OCC evaluations available in the scientific and engineering literature.

The platinum-containing OCC used for this study was designed to produce low levels of SO<sub>4</sub> (personal communication, D. Psaras, Degussa Corporation 1992). Platinum-based OCCs are very effective for the oxidation of CO, HC, and SO<sub>2</sub> (Horiuchi et al. 1990), and some washcoat formulations can help control the oxidation of SO<sub>2</sub> or the formation of SO<sub>4</sub>, while still maintaining satisfactory HC oxidation control. (Washcoat formulations that inhibit SO<sub>4</sub> formation tend to reduce HC oxidation efficiencies.) Although the washcoat formulation of the OCC used in this study is proprietary and few washcoat formulations are discussed in detail in the literature, comparisons can add understanding to the effectiveness of formulations that result in low SO<sub>4</sub> formation. Thus, how this OCC performed with a LS-fueled 1991 engine can be compared to the various OCC data found in the literature.

The control efficiencies for HC in this study (Table 40) vary from 62% to 70% for temperatures ranging from approximately 300°C to 400°C. In general, this efficiency was acceptable, because it was similar to other platinum-based low-SO<sub>4</sub> formulations in the same temperature range. In testing two platinum-based SO<sub>4</sub>-inhibiting OCC formulations, Cooper and Roth (1991) measured HC decreases of about 40% to 50% for one OCC and about 60% to 65% for a second OCC, in the 300°C to 400°C temperature range. Zelenka and associates (1990b) tested numerous platinum-based OCCs with various design parameters, including ones to control SO<sub>4</sub> formation, and measured HC decreases ranging from 50% to nearly 80% in the 300°C to 400°C temperature range. Horiuchi and coworkers' (1990) steady-state evaluation of three different OCC formulations measured 65% to 95% reductions in HC in the 300°C to 400°C temperature range. In a review of numerous OCC evaluations prior to 1988, which included steady-state and transient evaluations of a variety of OCCs, McClure and associates (1988) found average HC reductions of 54%; however, these OCCs were early types not designed to produce low SO<sub>4</sub> emissions.

Although the decreases of gaseous HC were expected with the OCC, the primary purpose of the OCC was to decrease TPM levels by decreasing SOF without appreciable SO<sub>4</sub> formation. The OCC decreased SOF by 53% to 71% (Table 33) in the 300°C to 400°C range, a decrease similar in magnitude to the HC decreases. Various OCC evaluations have demonstrated reductions in SOF (or other similarly

denoted particulate fractions, such as organic solubles, volatile organic fractions, or oil and fuel particulates) of up to 90%, with many control efficiencies in the range of 50% to 80% (Hunter et al. 1981a,b; Andrews et al. 1987; Gill 1988; Needham et al. 1989; Ball and Stack 1990; Horiuchi et al. 1990; Zelenka et al. 1990a,b; Arai 1991, 1992; Horiuchi et al. 1991; Porter et al. 1991; Brear et al. 1992; Harayama 1992; Henk et al. 1992; McClure et al. 1992). These evaluations include numerous transient and steady-state tests, various OCC formulations, and fuels of differing sulfur content. The SOF control efficiencies observed in this study therefore fall in about the middle range of those found in the various studies mentioned above.

The OCC used in this study had no significant effect on SO<sub>4</sub> at mode 11 (311°C), but significantly increased SO<sub>4</sub> at modes 10 and 9 (370°C and 393°C, respectively). Direct calculation of baseline conversion rates of fuel sulfur to SO<sub>4</sub> (as a mole or mass percentage of fuel sulfur that ends up as sulfur in the sulfates) resulted in rates on the order of 0.1% to 0.4%. These values are similar to those reported by Wall and coworkers (1987) (0.6% to 2% conversion) and Baranescu (1988) (0.3% to 1.0% conversion) when their data are calculated on a mass-of-sulfur-in-fuel to mass-of-sulfur-in-SO<sub>4</sub> basis. Wall and coworkers (1987) claimed that calculated sulfur conversion rates at low fuel sulfur levels can lead to very high conversion rates due to measurement variability; however, this was not observed in this study. The direct sulfur-to-SO<sub>4</sub> conversion rates for modes 9 and 10 with the OCC were around 2%, which was a considerable increase over the baseline conversion rates for the corresponding modes.

The data showed that, at modes 9 and 10 with the OCC, SO<sub>4</sub> increased by 600% and 500%, respectively, over baseline levels. However, due to the low fuel sulfur levels, the actual SO<sub>4</sub> contribution to TPM was quite low (6%) for all experimental treatment combinations. In fact, the SO<sub>4</sub> measurements observed in this study (including the OCC treatment combinations) were all well below the 0.007 g/kW-hr background level observed by Wall and coworkers (1987) in their tests of a sulfur-free fuel. In this study, the maximum value of SO<sub>4</sub> was less than 0.002 g/kW-hr at mode 9 with the OCC. Such low SO<sub>4</sub> levels also may contribute to the large control efficiencies of the OCC, in that small differential changes in SO<sub>4</sub> at low levels will show up as large OCC conversion efficiencies. It is not known whether similar results would be found at higher fuel sulfur levels.

The OCC in this study did not affect SOL at any mode. This indicates that any storage and release or combustion of carbonaceous material on the OCC substrate had reached equilibrium. Unlike this study, some studies have shown

that OCCs increase or decrease SOL or the carbon fraction of the particulate matter (Hunter et al. 1981a,b; Osborne et al. 1986; Porter et al. 1991; Arai 1992; McClure et al. 1992). Thus, the OCC used in this study would be less effective for TPM control under conditions that increase the SOL/SOF ratio or when high fuel sulfur level offsets decreases in SOF.

In this study, the combination of the 53% to 71% decrease in SOF, low  $\text{SO}_4$  formation, and no influence on SOL resulted in a net 27% to 54% decrease in TPM, when the OCC was installed in the exhaust system. Particulate matter control efficiencies found in the literature approach 70% (Arai 1992; Brear et al. 1992; Harayama et al. 1992; McClure et al. 1992). Of course, direct comparisons are difficult because those evaluations include steady-state and transient tests for a variety of OCC formulations, and they include each OCC's influence on each fraction of the particulate matter. Under the conditions observed in this study, this OCC is effective at decreasing emissions of particulate matter, mostly via SOF oxidation in the 300°C to 400°C range.

The differences in particle size distributions between the 1988 L10 and 1991 LTA engines were probably due to the different fuel injection systems on the engines. The LTA engine incorporated a high-pressure fuel-injection system that injects fuel at 152,000 kPa compared to 124,000 kPa for the L10. The higher-pressure system created more nuclei-mode particles and, by analyzing the baseline and OCC data, it can be deduced that the nuclei-mode particles probably consisted mainly of solid particles (Baumgard 1995). This was due to the fact that the OCC did not decrease the number of nuclei-mode particles. If these particles were of hydrocarbon origin, the OCC should oxidize and remove them, especially at the higher exhaust temperature modes.

The trends observed during OCC use included decreased particle- and vapor-phase levels of most of the PAHs measured on a raw exhaust concentration basis and generally decreased particle-associated PAH emissions on a mass basis. These results are similar to those found by McClure and coworkers (1992) using a Caterpillar 3304 heavy-duty engine (typical for mining applications), an Englehard PTX 10 DVC OCC, and two fuels that differed mainly in total aromatic content (11 wt % compared to 20 wt %). Particle- and vapor-phase samples were collected from a dilution tunnel over a light-load transient test cycle. Total PAH emissions (SOF plus XOC levels,  $\text{ng}/\text{m}^3$ ) were significantly lower for all PAHs measured (except BaP) when the OCC was used for both of the fuels tested.

The particle:vapor ratios for FLU and PYR were lower than those reported by Schuetzle and Frazier (1986). The PYR ratios (which varied between modes) were 0.12 to 0.65

for baseline and 0.088 to 0.24 for OCC, compared to a reported value of 0.75 obtained in a study without use of control devices (Schuetzle and Frazier 1986). Fluoranthene particle:vapor ratios were 0.015 to 0.10 for baseline and 0.030 to 0.058 with the OCC, compared to a reported value of 0.75. These differences may be due to the fact that the newer heavy-duty diesel engines are more efficient in terms of combustion, have low engine oil consumption, and emit lower levels of particles, especially in conjunction with lower-sulfur fuels. If the chemical make-up of the exhaust particles or their total surface area changes, one would expect that the partitioning of semivolatile organic species onto the surfaces of these particles from the vapor phase would be altered as well. (See Opris et al. 1993 for a discussion, and see Appendix G.)

The PAH ratios for particle-associated compounds were found to be considerably lower, in general, than those expected (nearly unity) based on inferences made by Schuetzle and Frazier (1986). The ratios of FLU:PYR varied with engine mode and increased when the OCC was used compared to baseline. At mode 9, the FLU:PYR ratio was 0.08 for baseline and 0.80 with the OCC. The effect of the OCC was less at the lower temperature modes (10 and 11). At mode 10, the ratios were 0.29 with and 0.18 without the OCC; for mode 11, these ratios were 0.16 and 0.13 with and without the OCC, respectively. The same trends were observed for the vapor-phase PAH ratios, which varied from 0.56 (mode 11 without the OCC) to 2.2 (mode 9 with the OCC). Summing the FLU and PYR levels from both phases (SOF + XOC) produced ratios in the same range (0.56 to 2.2) as found with the XOC alone, because the XOC levels were considerably higher than the SOF levels.

Ratios were calculated from measurements made in recent studies (Mitchell et al. 1994; ORTECH 1994) in which an OCC was used in transient cycle testing with LS fuels having varied composition in terms of aromatic content. Such ratios range between 0.13 and 0.89. Westerholm and associates (1986) reported FLU and PYR levels giving ratios of 0.65 to 0.87 in a study using an OCC or a catalyzed diesel particle filter, LS fuel, and a transient test cycle. In the Westerholm and coworkers (1986) study, where only particle-associated PAHs were measured, the ratios were slightly higher for control devices compared to baseline. In the ORTECH study, SOF and XOC were collected and combined for analysis; use of the OCC usually produced lower ratios than for baseline conditions.

A number of studies have reported the effects of OCCs on mutagenic activity, although relatively few have been conducted with newer OCCs and LS fuels. In an earlier study

at MTU, Hunter and colleagues (1981a,b) found that the use of a higher SO<sub>4</sub>-producing OCC with an on-highway diesel engine increased SOF mutagenic activity at most of the tested steady-state modes. Several other earlier evaluations demonstrated that use of OCCs, particularly pelleted converters, increased particle-associated mutagenic activity from diesels used in underground mines, on both a mass and raw exhaust concentration basis (Mogan et al. 1986a,b). Mogan and associates (1986b) also reported that mono- and dinitro-PAHs might have large contributions to the observed responses, based on TA98NR and TA98DNP tests, with larger contributions found with OCC use.

In a more recent study, McClure and coworkers (1992) evaluated an OCC with a SO<sub>4</sub>-inhibiting formulation over a low load-factor transient cycle, using a diesel engine typical of those used in mining operations. Results were presented for two different low-sulfur fuels (0.03 to 0.04 wt % sulfur) varying in cetane number and aromatic content; mutagenic activity was assayed at MTU using the same bioassay procedures as used in this present study. In contrast to the present HEI study, McClure and coworkers (1992) reported reductions in particle-associated mutagenic activity (mass and raw exhaust concentration basis) for both fuels with OCC use. Vapor-phase-associated mutagenic

activity appeared to increase with the OCC, although there was also an increase in sample toxicity that made evaluation of mutagenic activity difficult. With the LTA engine and OCC, XOC toxicity was found only with the mode 11 samples. Decreases in overall mutagenic activity concentrations (revertants/m<sup>3</sup>) were reported for most heavy-duty diesel steady-state conditions tested by Hansen and associates (1994) when using an OCC that produced low levels of SO<sub>4</sub> and a low-sulfur (0.032 wt %) fuel.

The varied results from all of these studies, including those presented in this report, are due to a combination of factors, including differences in engine type and operation, fuel composition, and OCC type and catalyst formulation. In the case of the studies by Mogan and associates (1986a,b), in particular, differences in sample collection and handling also may have been factors.

As shown in this study, the decrease of TPM, which is the primary intent of this OCC, was achieved, at least under the conditions observed in this study. The OCC generally decreased the PAHs quantified in the SOF and XOC. On a per-mass of SOF or XOC extract basis, the OCC increased mutagenic activity; however, this increase was typically offset by the reduction in SOF and XOC concentration levels.

**Table 41.** Summary of Regulated Emissions from the 1988 and 1991 Cummins Engines with Different Control Technologies and Fuels<sup>a</sup>

Emissions	Engine   Operating Condition   Fuel				
	1988 L10 Baseline CS Fuel	1988 L10 Baseline LS Fuel	1988 L10 Trap LS Fuel	1991 LTA Baseline LS Fuel	1991 LTA OCC LS Fuel
<b>Mode 9</b>					
NO <sub>x</sub>	7.3	7.7 (6)	8.2 (13)	6.1 (-16)	6.2 (-15)
HC	0.23	0.44 (91)	0.29 (26)	0.25 (9)	0.10 (-57)
TPM	0.18	0.15 (-17)	0.02 (-89)	0.05 (-73)	0.04 (-80)
<b>Mode 11</b>					
NO <sub>x</sub>	4.5	5.1 (14)	5.1 (14)	4.7 (3)	4.7 (3)
HC	0.99	1.1 (6)	0.99 (0)	1.2 (21)	0.35 (-65)
TPM	0.42	0.40 (-5)	0.10 (-77)	0.18 (-57)	0.08 (-80)

<sup>a</sup> Presented as means (percent change), where percent change = [(Condition – 1988 Baseline CS)/1988 Baseline CS] × 100, all in g/kW-hr.

### Effects of Engine, Control Device, and Fuel on Emissions

Between the years 1988 to 1994, the EPA particulate transient standards for over-the-road heavy-duty trucks have been reduced by 83%. The EPA NO<sub>x</sub> transient emission standards have been reduced 53% and the HC standards have not changed (Walsh 1993). Table 41 compares the NO<sub>x</sub>, HC, and TPM emissions for the 1988 L10 and 1991 LTA Cummins engines with the respective control technologies. The emissions are normalized to a brake-specific (g/kW-hr) basis for both steady-state modes 9 and 11. Both modes are at rated speed and 75 or 25 percent load, respectively. Since the engines are from the same engine family, the differences in emissions can be attributed to design improvements.

The 1991 engine incorporates charge air-to-air aftercooling of the intake air compared to an aftercooler using the engine coolant to cool the inlet air on the 1988 engine. The charge air aftercooling allows the inlet air temperature to

be about 40°C with the 1991 engine instead of 60°C with the 1988 engine. The 1991 engine also incorporates a higher output turbo, and therefore the boost pressure is higher. The combination of lower inlet air temperature and higher boost pressure leads to more air entering the engine and, consequently, the 1991 engine runs slightly leaner than the 1988 engine and generates about 3% more power. The fuel:air ratio for the 1988 engine at mode 9 is 0.032 compared to 0.030 for the 1991 engine. The 1991 engine also uses high-pressure injectors, which lead to better mixing of the fuel and air and result in less TPM generated.

Table 41 also provides the percent decrease in TPM emissions for both engines and control technologies. The 1988 engine with CS fuel was considered the baseline condition. With the LS fuel, the baseline TPM emissions were decreased about 17% and 5% depending on the engine mode. With the trap and the LS fuel, the emissions were decreased 89% and 77%, depending on mode. Using

**Table 42.** Comparison of Particle Number Concentrations<sup>a</sup>

Engine	Fuel	Mode and Condition	Particle Number (number/cm <sup>3</sup> )		
			Nuclei Mode	Accumulation Mode	Total
1988 L10	CS	9 Baseline	$4.8 \times 10^8$	$1.2 \times 10^7$	$4.9 \times 10^8$
		9 Trap	$6.5 \times 10^8$	$2.3 \times 10^5$	$6.5 \times 10^8$
		11 Baseline	$8.2 \times 10^7$	$2.4 \times 10^7$	$1.1 \times 10^8$
		11 Trap	$4.7 \times 10^8$	$2.0 \times 10^5$	$4.7 \times 10^8$
	LS	9 Baseline	$2.2 \times 10^7$	$1.6 \times 10^7$	$3.8 \times 10^7$
		9 Trap	$1.8 \times 10^6$	$1.5 \times 10^6$	$3.3 \times 10^6$
		11 Baseline	$2.0 \times 10^7$	$2.6 \times 10^7$	$4.6 \times 10^7$
		11 Trap	$3.1 \times 10^6$	$2.0 \times 10^6$	$5.1 \times 10^6$
1991 LTA	DS	9 Baseline <sup>b</sup>	$3.6 \times 10^7$	$1.4 \times 10^7$	$5.0 \times 10^7$
		9 Trap	$2.1 \times 10^9$	$1.3 \times 10^7$	$2.1 \times 10^9$
		11 Baseline <sup>b</sup>	$4.4 \times 10^7$	$1.8 \times 10^7$	$6.2 \times 10^7$
		11 Trap	$1.6 \times 10^9$	$3.0 \times 10^7$	$1.6 \times 10^9$
		9 Baseline	$1.3 \times 10^9$	$2.4 \times 10^6$	$1.3 \times 10^9$
		9 OCC	$1.3 \times 10^9$	$2.7 \times 10^6$	$1.3 \times 10^9$
		10 Baseline	$8.1 \times 10^8$	$3.4 \times 10^6$	$8.2 \times 10^8$
		10 OCC	$1.4 \times 10^9$	$3.7 \times 10^6$	$1.4 \times 10^9$
		11 Baseline	$6.6 \times 10^8$	$6.1 \times 10^6$	$6.7 \times 10^8$
		11 OCC	$6.9 \times 10^8$	$6.8 \times 10^6$	$7.0 \times 10^8$

<sup>a</sup> All samples were collected from the dilution tunnel (Figure 3) unless otherwise indicated.

<sup>b</sup> Samples were collected at the engine in the raw exhaust.

the 1991 engine and LS fuel, the emissions were decreased 73% and 57%. Finally, with the 1991 engine and OCC, the TPM emissions were decreased about 80%.

Even though the TPM emissions were decreased in all cases, the particle number concentrations were not necessarily reduced. Table 42 presents the nuclei-mode, accumulation-mode, and total particle number concentrations for both the 1988 and 1991 engines for all conditions tested. Baumgard (1995) has shown that the majority of the nuclei-mode particles produced, using the 1988 engine with either the CS or the DS fuel, were formed in the dilution tunnel by heteromolecular nucleation of the H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> vapors. These H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> particles form only when the H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> dilution tunnel vapor pressures are favorable for nucleation. When these particles are emitted into the atmosphere where the H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> vapor pressures are considerably lower than in the dilution tunnel, the H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> particles basically evaporate and revert back to H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> vapors. A definite shift toward more nuclei-mode particles and less accumulation-mode particles was noted with LS fuel in the 1991 engine compared with the 1988 engine; the increase was attributed to the increase in solid nuclei-mode particles with the 1991 engine compared with the 1988 engine (Baumgard and Johnson 1996).

When using the 1988 engine and the LS fuel, the dilution tunnel H<sub>2</sub>SO<sub>4</sub> (and H<sub>2</sub>O) vapor pressures are below the threshold for particle formation; the nuclei-mode particles measured under these conditions are considered to be solid particles that would survive in the atmosphere (Baumgard 1995). However, the nuclei-mode number concentration is more than 1 order of magnitude less with the LS fuel as compared with the CS or DS fuel. If a ceramic trap is used, the concentration is more than 2 orders of magnitude lower than with the CS fuel.

With the 1988 engine, the accumulation-mode particles are considered to be mainly solid particles and the concentrations are similar for the CS, DS, and LS fuels for both modes 9 and 11. The trap is effective at removing the solid particles and, therefore, the accumulation mode is reduced more than 1 order of magnitude when using either the CS or DS fuel, as shown in Table 42. The trap also reduced levels of the LS fuel nuclei-mode particles, providing further evidence that these particles are solid in origin.

The accumulation-mode particle number concentrations with the 1991 engine and the LS fuel are similar to those obtained with the 1988 engine using LS fuel and a ceramic trap (in the 10<sup>6</sup> particles/cm<sup>3</sup> range). However, the nuclei-mode particle number concentrations are somewhat higher than with the 1988 engine using the CS or DS fuel, and 30 to 60 times higher using the LS fuel under baseline conditions. Because no change was noted in the nuclei and

accumulation number concentrations for the 1991 engine with and without the OCC, these particles are considered to be mainly solid in origin.

The particle volume concentrations for the 1988 and 1991 engines are provided in Table 43. The 1988 engine accumulation-mode concentrations are similar for all fuels, but when the trap is used, the concentration is reduced about 1 order of magnitude. There is also a difference in the nuclei-mode volume concentrations between the CS and LS fuels in the 1988 engine, again mainly due to the H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> particle formation.

With the 1991 engine, the accumulation-mode volume concentrations are comparable to the 1988 engine with LS fuel and the ceramic trap (in the 10<sup>3</sup> μm<sup>3</sup>/cm<sup>3</sup> range). However, the nuclei-mode volume concentrations are greater than with the 1988 engine and LS fuel. Depending on the engine mode, the percent by volume in the nuclei mode with the 1991 engine varies from 18% to 41%. The data indicate a reduction in the accumulation volume concentrations in the 1991 engine as compared to the 1988 engine with the LS fuel. This is to be expected, since the EPA standards on a mass basis were 0.6 g/bhp-hr in 1988 and 0.25 g/bhp-hr in 1991.

Comparisons of engine, control device, and fuel effects on a variety of unregulated emissions are presented in Table 44. All emissions are also presented on a brake-specific basis to facilitate comparisons between the two engines. SOF levels are decreased in general with use of the LS fuel compared to the CS fuel, while the effect on XOC levels depends on mode. The overall effect of the OCC with the 1991 LTA engine compared to the trap with the 1988 L10 engine is little change in SOF levels but great decreases in XOC levels, indicating the increased effectiveness of the OCC on more volatile, vapor-phase hydrocarbons. Levels of SOL were also low for trap use with the L10 engine and for the LTA engine with or without the OCC. The use of an uncatalyzed trap with certain types of diesel engines or the use of later-model engines with improved combustion systems, therefore, should effectively decrease the emissions of the SOL component and the TPM, which has been linked to diesel particle-associated health effects (Heinrich 1994; Mauderly et al. 1991, 1994).

The brake-specific emissions for particle-associated (SOF) and vapor-phase (XOC) FLU are also given in Table 43. Fluoranthene was chosen for comparison because measurable levels were found in both the particle and vapor phases for all test matrices and, therefore, the effects of fuel types and control devices on the partitioning of this type of compound could be assessed. For mode 9, the lowest emis-

sions were obtained with the LTA engine under baseline conditions; at mode 11, the levels were lowest when the OCC was used with the LTA engine. All of the measurements obtained with the LTA engine utilized a LS fuel. Comparing fuels, the L10 engine FLU emissions were difficult to assess; there was no clear cut improvement in total (SOF + XOC) levels with a decrease in fuel sulfur without a trap control device. The highest levels were obtained in the vapor-phase emissions of the L10 with a ceramic trap (both modes). Generally speaking, decreasing the levels of sulfur and employing a control device tended to decrease the particle:vapor ratio. This is a reasonable result since alterations in the number of particles (which would affect collision frequency) or the nature of the particles (which would affect physicochemical interactions) would ultimately affect phase distributions of semivolatile compounds such as PAHs.

In general, use of the LS fuel and either engine and aftertreatment device greatly reduced particle-associated (SOF) mutagenic activity at both engine operating conditions (Table 44). The effects of the OCC with the 1991 LTA engine were greatest at mode 11 (with the higher SOF levels). A different pattern was observed with the vapor-phase-associated (XOC) mutagenic activity. In this case, use of the LS fuel resulted in increases in activity, particularly at mode 11 and with the OCC and the LTA engine.

## CONCLUSIONS

The Phase II study focused on the effects of an OCC on the emissions from a Cummins 1991 LTA engine operated on LS fuel at three different steady-state modes (9, 10, and 11). The emissions obtained from the 1988 and 1991 engines, fuels, and control devices in the Phase I and II studies also were compared.

**Table 43.** Comparison of Particle Volume Concentrations<sup>a</sup>

Engine	Fuel	Mode and Condition	Particle Volume ( $\mu\text{m}^3/\text{cm}^3$ )		
			Nuclei Mode	Accumulation Mode	Total
1988 L10	CS	9 Baseline	$1.9 \times 10^3$	$1.6 \times 10^4$	$1.8 \times 10^4$
		9 Trap	$4.3 \times 10^2$	$5.0 \times 10^2$	$9.3 \times 10^2$
		11 Baseline	$6.3 \times 10^3$	$2.3 \times 10^4$	$2.4 \times 10^4$
		11 Trap	$1.3 \times 10^3$	$4.3 \times 10^2$	$1.7 \times 10^3$
	LS	9 Baseline	$4.3 \times 10^2$	$2.3 \times 10^4$	$2.3 \times 10^4$
		9 Trap	$3.7 \times 10^1$	$2.2 \times 10^3$	$2.3 \times 10^3$
		11 Baseline	$5.5 \times 10^2$	$2.5 \times 10^4$	$2.6 \times 10^4$
		11 Trap	$4.8 \times 10^1$	$2.4 \times 10^3$	$2.5 \times 10^3$
	DS	9 Baseline <sup>b</sup>	$2.8 \times 10^2$	$2.4 \times 10^4$	$2.4 \times 10^4$
		9 Trap	$3.2 \times 10^3$	$2.9 \times 10^4$	$3.2 \times 10^4$
		11 Baseline <sup>b</sup>	$4.2 \times 10^2$	$2.1 \times 10^4$	$2.1 \times 10^4$
		11 Trap	$1.5 \times 10^3$	$4.6 \times 10^4$	$4.7 \times 10^4$
1991 LTA	LS	9 Baseline	$1.5 \times 10^3$	$2.1 \times 10^3$	$3.6 \times 10^3$
		9 OCC	$1.1 \times 10^3$	$2.4 \times 10^3$	$3.5 \times 10^3$
		10 Baseline	$1.0 \times 10^3$	$2.3 \times 10^3$	$3.4 \times 10^3$
		10 OCC	$7.3 \times 10^2$	$3.3 \times 10^3$	$4.0 \times 10^3$
		11 Baseline	$2.6 \times 10^3$	$3.1 \times 10^3$	$5.7 \times 10^3$
		11 OCC	$9.7 \times 10^2$	$2.6 \times 10^3$	$3.6 \times 10^3$

<sup>a</sup> All samples were collected from the dilution tunnel (Figure 3) unless otherwise indicated.

<sup>b</sup> Samples were collected at the engine in the raw exhaust.

**Table 44.** Summary of Unregulated Emissions from the 1988 and 1991 Cummins Engines with Different Control Technologies and Fuels<sup>a</sup>

Emissions	Engine   Operating Condition   Fuel				
	1988 L10 Baseline CS Fuel	1988 L10 Baseline LS Fuel	1988 L10 Trap LS Fuel	1991 LTA Baseline LS Fuel	1991 LTA OCC LS Fuel
<b>Mode 9</b>					
SOF (g/kW-hr)	0.05	0.04 (-12)	<.01 (-88)	0.03 (-38)	0.02 (-70)
SOL (g/kW-hr)	0.10 <sup>b</sup>	0.11 (12)	0.01 (-85)	0.02 (-81)	0.02 (-79)
XOC (g/kW-hr)	0.15	0.21 (38)	0.11 (-30)	0.13 (-15)	0.06 (-62)
Mutagenic Activity					
SOF ([rev/kW-hr] × 10 <sup>3</sup> )	110	83 (-25)	4.7 <sup>c</sup> (-96)	86 (-22)	57 (-48)
XOC ([rev/kW-hr] × 10 <sup>3</sup> )	99	200 (10)	51 (-48)	74 (-25)	150 (52)
FLU					
SOF (μg/kW-hr)	7.2	3.5 (-51)	1.6 (-78)	0.096 (-99)	0.29 (-96)
XOC (μg/kW-hr)	9.9	12 (21)	17 (72)	6.7 (-32)	7.6 (-23)
<b>Mode 11</b>					
SOF (g/kW-hr)	0.13	0.10 (-26)	0.05 (-63)	0.14 (8)	0.04 (-69)
SOL (g/kW-hr)	0.26 <sup>b</sup>	0.31 (21)	0.05 (-81)	0.05 (-82)	0.04 (-83)
XOC (g/kW-hr)	0.46	0.48 (5)	0.54 (18)	0.64 (40)	0.20 (-56)
Mutagenic activity					
SOF ([rev/kW-hr] × 10 <sup>3</sup> )	280	310 (11)	140 (-50)	450 (61)	69 (-76)
XOC ([rev/kW-hr] × 10 <sup>3</sup> )	270	530 (96)	470 (74)	920 (240)	330 (22)
FLU					
SOF (μg/kW-hr)	6.9	1.5 (-78)	5.0 (-27)	2.7 (-61)	0.43 (-94)
XOC (μg/kW-hr)	31	14 (-55)	90 (190)	25 (-19)	9.2 (-70)

<sup>a</sup> Presented as means (percent change), where percent change = [(Condition – 1988 Baseline CS)/1988 Baseline CS] × 100%.<sup>b</sup> SOL emissions determined from 47-mm filter samples.<sup>c</sup> Sample toxicity may have masked the mutagenic response.

### Effects of Oxidation Catalytic Converter and Mode on Emissions

The following statements can be made concerning the effect of an OCC on the LTA engine operated in different modes on the measured regulated and unregulated emissions.

1. The OCC had no effect on NO<sub>x</sub>, NO, and SOL concentrations, but HC, SOF, TPM, and XOC concentrations were decreased by up to 70% at all modes. The TPM reductions were primarily due to decreases in SOF. Although SO<sub>4</sub> levels increased with the OCC at the two higher-temperature modes (9 and 10), the SO<sub>4</sub> contributions to TPM levels due to the use of the LS fuel were less than 6%.
2. The OCC had no effects on the number or volume of either the nuclei-mode or the accumulation-mode particles.
3. With the exception of FLU at mode 9, particle- and vapor-phase PAH emissions were generally decreased by at least 50% when the OCC was used.
4. The OCC effects on particle-associated mutagenic activity were mode-related, with reductions in activity ranging from about 30% (modes 9 and 10) to 84% (mode 11). Use of the OCC resulted in about 60% reductions in vapor-phase-associated mutagenic activity at modes 10 and 11, but a 100% increase was found at mode 9 due to a fivefold increase in activity on a mass basis.

### Comparisons Between Engines, Control Devices, and Fuels

The following statements can be made for comparisons of regulated and unregulated emissions levels between the 1988 L10 and 1991 LTA engines operated with an uncatalyzed ceramic trap (L10) or an OCC (LTA) and different fuels (CS, DS, or LS fuels with the L10 engine, and LS fuel with the LTA engine).

1. Compared to the reduction in emissions obtained by operating the L10 engine on LS fuel with a particle trap (over the use of the CS fuel and no trap), operating the LTA engine on LS fuel with an OCC produced similar decreases in TPM and SOF (about 70% to 80% in each case). However, greater decreases (up to 60 times) in HC and XOC emissions were found for the LTA engine with the OCC versus the L10 engine with the trap and CS fuel.
2. There were large differences in the particle size distributions between engines, with 27% to 47% of the particle volume in the nuclei mode for the LTA engine compared to only 2% for the L10 engine. As was found

in comparison to the L10 engine with CS fuel, the numbers of nuclei-mode particles produced with the LTA engine (with and without the OCC) were several orders of magnitude greater than the numbers produced with the L10 engine with LS fuel and a particle trap. Because the OCC had no effect on the nuclei mode (with LS fuel), the nuclei-mode particles with the LTA engine are considered to consist mainly of solid carbon particles.

3. In general, lower PAH levels were produced with the LTA engine and the OCC than with the L10 engine and the trap, when using the same LS fuel. Comparisons between the PAH levels obtained from using the CS and LS fuels are less clear as, in most cases, higher PAH concentrations were found when using the LS fuel (with either engine or control device).
4. The effects of changing the engine and control device had differing effects on mutagenic activity. Use of the LTA engine and the OCC generally produced lower reductions in activity at mode 9 than the L10 engine with a trap and LS fuel (compared to the L10 engine with CS fuel). However, the opposite effect was generally found at mode 11.

### IMPLICATIONS OF THE FINDINGS

A number of important implications follow from the findings of this study. One significant aspect is that the fuel sulfur level (lowered from 0.32 to 0.01 wt %) reduces the number of smaller, nuclei-mode particles in the dilution tunnel. The SO<sub>4</sub> particles appear to form in the dilution tunnel with the higher-sulfur fuel. Another aspect is that changes in particle size distributions can affect both the total particle mass and the species adsorbed onto the particles. The atmospheric reactions that diesel exhaust compounds may undergo will in turn be affected by the partitioning of the hydrocarbon reactants between the particle and the vapor phases. The end result of reducing fuel sulfur levels could be a beneficial impact on human respiratory systems, due to this potential decrease in the number of smaller, nuclei-mode particles. A reduction in the number of nuclei-mode particles as a result of using low-sulfur fuel also should have a positive effect on the environment, as reduction in the number of particles (particularly the smaller sizes) can improve visibility.

In general, using the LS fuel in conjunction with the trap or with the OCC decreased the levels of regulated emissions (HC and TPM) as well as levels of PAHs and mutagenic activity associated with the particle- and vapor-phase organic fractions, as compared to using a CS fuel or compared

to using no control device. The data also indicated that using LS fuel without a trap or OCC can increase PAH concentrations, even though the reduced sulfur content clearly decreases TPM emissions. Fuel sulfur variation and the use of a trap or a catalyst also affect the particle- and vapor-phase partitioning of PAHs.

The SOL control efficiencies for the trap and the OCC were determined. The trap, compared to the OCC, showed greater control efficiencies (90% or greater) on the SOL component of the TPM. The OCC primarily reduced the SOF and had no effect on the SOL. The data showed that high-pressure-optimized combustion systems effectively decrease the SOL levels in the 1991 engine to the same tailpipe output levels as the trap does with the 1988 engine. The data also show that the solid carbon spheres in the nuclei mode greatly increase in the 1991 engine with or without the OCC as compared to the 1988 engine without the particle trap.

The OCC was highly effective in decreasing HC in general, whether in the vapor or particle phase. Beginning in 1994, this technology has been used on medium-duty engines due to the fact that it decreases TPM because of the decrease in the SOF component of the TPM. The decrease of the vapor-phase hydrocarbons by the catalyst also should have a positive effect on the environment.

As a result of these findings, several recommendations for future research are important.

- (1) The fact that the concentrations of several of the biologically active compounds were found to increase with particle control technology indicates that future studies should be expanded to include additional compounds that could have important implications in atmospheric reactions. Newkirk and colleagues (1993) indicated some compounds that are of interest.
- (2) Aldehydes should be measured using the recently available, commercially prepared DNPH sampling cartridges.
- (3) Additional work, using advanced technology such as exhaust gas recirculation and lean catalysts, is necessary to judge whether the unregulated compounds also have been decreased enough to meet future vehicle emission standards. Unregulated transient cycle emissions also need study.
- (4) Alternative fuels such as methanol, natural gas, and reformulated diesel fuels also should be studied.
- (5) Interlaboratory studies of the precision and accuracy of HPLC and GC/MS methods for measuring PAHs and nitro-PAHs need to be conducted. Methods need to be

developed that have lower variability for nitro-PAHs, in particular, and are reliable for large and long-term studies.

- (6) More engines and other operating conditions should be studied to determine whether wide spread increases in the number of nuclei-mode particles also occur in engines with higher-pressure fuel-injection systems.
- (7) Atmospheric transformation studies need to investigate whether an increase in the number of nuclei-mode particles might cause adverse health effects.

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#### APPENDICES AVAILABLE ON REQUEST

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The following appendices may be obtained by writing to the Health Effects Institute, 955 Massachusetts Avenue, Cambridge, MA 02139. Please provide first author's name, the Report title, and the appendix title.

- A. Aldehyde Measurements
- B. Phase I. PAH Chromatograms and Data
- C. Phase I. Mutagenicity Data
- D. Resolution of Sampling Procedures Effects Data
- E. Phase I. Statistical Tables
- F. Phase I. Particle Size Distribution Data
- G. PAH Phase Distributions
- H. Phase II. Statistical Tables
- I. Phase II. Particle Size Distribution Data
- J. Phase II. PAH Data

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#### ABOUT THE AUTHORS

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**Susan T. Bagley** is an Associate Professor in the Department of Biological Sciences at Michigan Technological University in Houghton, MI. She received her Ph.D. in Microbiology in 1978 from Oregon State University and her post-doctoral training at the University of California, Davis. Dr. Bagley has conducted research on and published articles about the effects of fuels and emission controls on the physical, chemical, and biological character of diesel exhaust, and the mutagenicity and toxicity of environmental pollutants.

**Kirby J. Baumgard** is currently an Engineer in the Performance and Emissions Group with the John Deere Company in Waterloo, IA. During the course of the study reported here, he received his Ph.D. in Environmental Engineering (1995) from Michigan Technological University, working in the area of diesel fuel and aftertreatment device effects on particle size distributions. Dr. Baumgard also has had extensive experience at the U.S. Bureau of Mines in the Diesel Health and Safety Division, researching the application of exhaust control technology to underground mine vehicles.

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**John H. Johnson** is a Presidential Professor in the Department of Mechanical Engineering-Engineering Mechanics at Michigan Technological University. He received his Ph.D. in Mechanical Engineering from the University of Wisconsin in 1964. He has extensive research and publishing experience in the characterization and modeling of diesel emissions with and without use of particle control technology for various fuels.

**David G. Leddy** is an Associate Professor in the Department of Chemistry at Michigan Technological University. He received his Ph.D. in Chemistry at the University of Kansas in 1966. Dr. Leddy has conducted research and has published articles about the characterization of diesel particulate emissions and the effects of fuels and control systems on diesel exhaust.

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#### PUBLICATIONS RESULTING FROM THIS RESEARCH

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#### ABBREVIATIONS

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ANOVA	analysis of variance
ACN	acetonitrile
BaA	benz[a]anthracene
BaP	benzo[a]pyrene
BbF	benzo[b]fluoranthene
BkF	benzo[k]fluoranthene
bhp	brake horsepower
CHR	chrysene
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
CS	conventional, high-sulfur (0.32 wt %) fuel
CV	coefficient of variation
DCM	dichloromethane
DNPH	2,4-dinitrophenylhydrazine
DMSO	dimethyl sulfoxide
DS	doped-sulfur (0.29 wt %) fuel
EAA	electrical aerosol analyzer
EPA	U.S. Environmental Protection Agency
FLU	fluoranthene
g/bhp-hr	grams per brake horsepower-hour
g/KW-hr	grams per kiloWatt-hour
GC/FID	gas chromatography with flame ionization detection
GSD	geometric standard deviation
H <sub>2</sub> SO <sub>4</sub>	sulfuric acid
HC	hydrocarbon, hydrocarbons
HEX	hexane
HP	Hewlett Packard
HPLC	high-performance liquid chromatography
L10	Cummins LTA10-300 engine

LS	low-sulfur (0.01 wt %) fuel	SAE	Society of Automotive Engineers
LTA	Cummins LTA 10-310 engine	SO <sub>2</sub>	sulfur dioxide
MDL	minimum detection limit	SO <sub>3</sub>	sulfur trioxide
MeOH	methanol	SOF	particle-associated soluble organic fraction
MTU	Michigan Technological University	SOL	particle-associated solid fraction
<i>n</i>	number of samples	SO <sub>4</sub>	particle-associated sulfate fraction
NIST	National Institute for Standards and Technology	SRM	standard reference material
N•m	Newton meter	STP	standard temperature and pressure
NMD	number mean diameter	TA98NR	a nitroreductase-deficient tester strain of <i>Salmonella typhimurium</i> TA98
NO	nitric oxide	TA98DNP	an <i>o</i> -transacetylase-deficient tester strain of <i>Salmonella typhimurium</i> TA98
NO <sub>x</sub>	oxides of nitrogen	TPM	total particulate matter
NO <sub>2</sub>	nitrogen dioxide	UHVS	ultra-high-volume sampler
OCC	oxidation catalytic converter	VMD	volume mean diameter
PAH	polynuclear aromatic hydrocarbon	XOC	XAD-2 resin-bound organic fraction from the vapor phase
ppm	parts per million		
PYR	pyrene		
rpm	revolutions per minute		
S9	rat liver microsome preparation		



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INTRODUCTION

The environment contains a wide variety of pollutants generated by human activities, particularly in heavily industrialized and urbanized settings. A significant portion of these pollutants consists of emissions, or atmospheric transformation products of emissions, derived from burning gasoline and diesel fuel, and from internal combustion engines consuming lubricants. Since 1983, the Health Effects Institute has conducted a multidisciplinary program to fund, review, and evaluate scientific research to understand better the health consequences of motor vehicle emissions and their individual constituents. Included in this program are studies of diesel engine exhaust and the effects of pollution control devices on engine emissions.

The U.S. Environmental Protection Agency (EPA)\* regulates emissions from diesel-powered vehicles by promulgating allowable levels of various emission components. Diesel emissions can be reduced by modifying engine design and diesel fuel composition, and by employing exhaust aftertreatment devices. Although they remove undesirable components from the exhaust, these approaches may alter the physical and chemical characteristics of the emission constituents with possible consequences for human health.

In 1989, Dr. Susan T. Bagley and her colleagues from Michigan Technological University submitted a research proposal entitled "Characterization of Fuel Effects on Diesel Emissions." The proposed study was an extension of a previously completed investigation funded by HEI (Bagley et al. 1993), which had examined the emissions from a 1988-model heavy-duty engine using conventional-sulfur diesel fuel and equipped with a particle trap. During the first phase of this proposed study, the investigators planned to characterize the chemical composition and the mutagenicity of the emissions as well as the physical properties of the particles in the emissions from the same 1988 engine and trap system, using low-sulfur diesel fuel. A second phase of the study was proposed to characterize the emissions from a more recent 1991-model heavy-duty diesel engine equipped with an oxidative catalytic converter. This engine was designed to use low-sulfur diesel fuel and to meet the EPA's 1991 emission standard for particles.

The HEI Health Research Committee approved Dr. Bagley's proposal to address concerns that the use of ex-

haust aftertreatment devices or changes in diesel fuel composition might adversely affect public health. The study began in November 1989 and was completed in March 1993, with total expenditures of \$450,104. Dr. Bagley's final report was received in January 1994. Following discussion by the Health Review Committee, the investigators submitted a revised report in August 1995, which was accepted for publication in November 1995. During the review of the Investigators' Report, the Review Committee and the investigators had an opportunity to exchange comments and to clarify issues in the Investigators' Report and in the Review Committee's Commentary. This Commentary is intended to place the Investigators' Report in perspective, as an aid to the sponsors of HEI and to the public.

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REGULATORY BACKGROUND

Heavy-duty diesel engines are employed primarily in trucks, buses, locomotives, agricultural and construction equipment, and ships. Light-duty diesel engines are utilized in some light trucks and automobiles. In the U.S., only about 2% of recently manufactured light-duty trucks and automobiles are equipped with diesel engines (Sawyer and Johnson 1995). In contrast, about 25% of new automobiles in Europe are powered by diesel engines. However, several advantages, including increased fuel efficiency, decreased emissions of carbon monoxide and hydrocarbons, and 10% to 25% less emission of carbon dioxide (a gas implicated in global warming), have renewed some interest in using diesel engines rather than gasoline or spark-ignition engines in automobiles in the U.S. (DeLuchi 1992; Hammerle et al. 1994; Sawyer and Johnson 1995).

In response to concerns about the potential health consequences of inhaling diesel engine exhaust, the EPA sets emission standards for diesel engines and vehicles under the Clean Air Act, as amended in 1990. With respect to on-highway heavy-duty diesel engines and vehicles, the EPA first issued emission standards in the early 1970s. The limits specified for hydrocarbons, carbon monoxide, and nitrogen oxides were applicable to engines and vehicles produced in the 1974 model year.

The Clean Air Act contains provisions for regulating emissions from diesel engines and vehicles, and for diesel fuel composition. For heavy-duty diesel engine applications (in vehicles with a gross vehicle weight of greater than 8,500 lbs), 1994 emission standards for nitrogen oxides, hydrocarbons, and carbon monoxide are 5.0, 1.3, and 15.5 grams/brake horsepower-hour (g/bhp-hr), respectively. Beginning with the 1998 model year, emissions of nitrogen

\* A list of abbreviations appears at the end of the Investigators' Report for your reference.

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oxides will be further reduced to 4.0 g/bhp-hr. The 1994 emission standard for particulate matter from heavy-duty diesel trucks was set at 0.1 g/bhp-hr, with a stricter standard of 0.07 g/bhp-hr for urban buses. In 1996, urban bus emission of particulate matter will be further limited to 0.05 g/bhp-hr. In order to help achieve the more stringent particulate emission standards in 1994, the EPA also implemented regulations for diesel fuel quality. The limitation of sulfur content in diesel fuels to 0.05% by weight represents a fivefold reduction in sulfur over previously uncontrolled levels. Furthermore, a maximum aromatic content of 35% by volume or a minimum cetane number of 40 (an index of the ease of igniting the fuel) was specified.

One approach to attain current and projected emission standards is the use of exhaust aftertreatment devices to reduce emissions of exhaust components. Although such devices markedly reduce selected emissions, they also may increase or alter the composition of other exhaust components in unexpected ways that may affect public health. The Clean Air Act Amendments of 1990 state that an effort to comply with emission requirements should not "cause or contribute to an unreasonable risk to public health, welfare, or safety in its operation or function." It is, therefore, appropriate to measure the effects these devices have on the physical and chemical composition of diesel exhaust, and to assess the potential of the exhaust to cause harm to biological systems.

## SCIENTIFIC BACKGROUND

### COMPOSITION OF DIESEL EXHAUST

Diesel exhaust contains thousands of pollutants, including components of unburned fuel and lubricating oil and products of incomplete combustion of the fuel and oil (Schuetzle 1983; International Agency for Research on Cancer 1989). These pollutants are emitted either as gases (vapor phase) or as particles (particle phase). Vapor-phase pollutants include carbon monoxide, nitrogen oxides, and sulfur oxides, as well as a variety of low-molecular-weight organic compounds, such as hydrocarbons, aldehydes, and small polynuclear aromatic hydrocarbons (PAHs). Those organic compounds that can be trapped on appropriate resins for chemical analysis comprise what is termed the semivolatile organic component of the vapor phase (XOC).

The particle phase, also known as total particulate matter (TPM), is the filterable portion of diesel exhaust and contains two size classifications of particles. The small, primary (nuclei mode) particles range in size from 0.01 to 0.056  $\mu\text{m}$  in diameter, with most particles at around 0.02  $\mu\text{m}$ ; the larger class of particles (accumulation mode) are

aggregates of the primary particles and range in size from 0.075 to 0.75  $\mu\text{m}$  in diameter, with most particles around 0.2  $\mu\text{m}$  (Sawyer and Johnson 1995). The particle phase contains three components: (1) a carbonaceous fraction composed mainly of solid-carbon-core particles (SOL), (2) a sulfate ( $\text{SO}_4$ ) fraction containing small hydrated sulfate particles, and (3) a soluble organic fraction (SOF) that contains compounds that are soluble in organic solvents and adsorbed or condensed onto the carbon core particles. These soluble organic compounds consist mainly of higher-molecular-weight hydrocarbons and PAHs and may contribute 15% to 45% of the weight of the total particulate matter (Schuetzle 1983; International Agency for Research on Cancer 1989).

### HEALTH EFFECTS OF DIESEL EXHAUST

Using conventional diesel fuel without emission controls causes heavy-duty diesel engines to emit much higher levels of nitrogen oxides, sulfate, and total particulate matter than do light-duty spark-ignition engines with emission controls (National Research Council 1981; Sawyer and Johnson 1995). Although the number of diesel-powered vehicles in the U.S. is relatively small, these vehicles consume substantial amounts of fuel because of the large amount of work they perform. Projections for the year 2000 suggest that heavy-duty diesel trucks will be the largest contributor of nitrogen oxides and particle emissions from on-road vehicles (reviewed by Sawyer and Johnson 1995).

Diesel emissions are a public health concern for several reasons. They are a major contributor to particulate air pollution (Cass and Gray 1995), and the particles contain many adsorbed chemicals that are well-known mutagens in bacteria and mammalian cells and are carcinogens in laboratory animals (reviewed by International Agency for Research on Cancer 1983, 1989, and by Shirnamé-Moré 1995). The emission vapors also contain many known mutagens and carcinogens, as well as many lung irritants and chemicals involved in atmospheric formation of ozone that also may be mutagenic and carcinogenic.

Epidemiologic data indicate that long-term exposure to diesel exhaust in a variety of occupational settings is associated with small increases in the relative risk of lung cancer occurrence (reviewed by Cohen and Higgins 1995). These increases do not appear to be due to confounding by cigarette smoking. However, other potential confounders have not been evaluated, and these studies did not include measurements of diesel exhaust. Inhalation studies clearly indicate that long-term exposure to high concentrations of diesel exhaust induces lung tumors in rats (reviewed by Mauderly 1992, and Busby and Newberne 1995). It appears

that the inorganic carbon portion of the particles, and not the adsorbed organic compounds, is responsible for these tumors. This was documented when the same amounts and kinds of lung tumors were found when rats were comparably exposed to diesel exhaust or to carbon black particles that are almost entirely free of organic compounds and, therefore, serve as a surrogate for the solid-carbon-core particles in diesel exhaust (Mauderly et al. 1994; Heinrich et al. 1995; Nikula et al. 1995; reviewed by Busby and Newberne 1995).

Other epidemiologic evidence suggests that relatively small elevations in indices of particulate air pollution are associated with increased daily mortality and morbidity from cardiopulmonary disease (Dockery and Pope 1994; Samet et al. 1995). Diesel exhaust particles are so small (over 90% by weight are less than 1  $\mu\text{m}$  in diameter) that they are respirable, and are transported deep into the alveolar regions of the lungs, where they may remain (Schlesinger 1989; Snipes 1989). Smaller (0.02  $\mu\text{m}$ ) particles deposit in several-fold greater numbers and further into the lungs than larger (0.3  $\mu\text{m}$ ) particles (International Commission on Radiological Protection 1994); therefore, increased emissions of primary, nuclei-mode particles (0.01 to 0.056  $\mu\text{m}$  in diameter) in diesel exhaust may have special health significance, particularly because deposited particles are cleared or removed from the lungs more slowly by humans than rodents (Morrow et al. 1996).

## EMISSION CONTROL TECHNOLOGY

Most reductions in diesel engine emissions to date have come from engine design modifications, such as optimizing fuel-to-air mixing to improve fuel combustion in the cylinder, and minimizing consumption of lubrication oil, the source of approximately 20% of particle emissions in recent engines (Zelenka et al. 1990; Sawyer and Johnson 1995). Future reductions in specific components of diesel emissions may require treatment of engine exhaust as well as the use of reformulated fuels (reviewed by Sawyer and Johnson 1995). For example, particle traps reduce particle emissions by physically removing particles and their associated organic compounds from the exhaust flow. At some point, the collected particles must be removed from the trap by a regeneration process, which could involve (1) sporadically burning the particles by heating the trap, or (2) continuously oxidizing the particles with a catalytic coating in the trap, or with a catalyst fuel additive that deposits in the trap with the particles. Passing the exhaust stream through a catalytic converter is an alternative treatment that oxidizes emission products and results in decreased concentrations of carbon monoxide, vapor-phase hydrocarbons,

and organic compounds adsorbed onto particles. Unlike particle traps, catalytic converters have relatively little effect on the levels of the solid-carbon-core particles in diesel engine emissions.

Modifications in fuel composition are currently viewed as a cost-effective approach to meeting projected diesel emission standards, and involve reducing sulfur and aromatic hydrocarbon content in fuel and raising the cetane number (reviewed by Sawyer and Johnson 1995). Lowering fuel sulfur content reduces particle emissions by diminishing the contribution of sulfates to the total particulate matter. Increasing the cetane number, and reducing the aromatic hydrocarbon content and the distillation temperature of the fuel decreases nitrogen oxides and total particulate matter emissions. Adding oxygenated compounds to diesel fuel also is being considered because of their observed ability to diminish particulate emissions.

In summary, a number of strategies can effectively reduce diesel engine emissions. However, because each approach to the problem selectively decreases different components of diesel exhaust, a combination of technologies will most likely be required to reach the desired emission objectives. Decisions about the kinds of control technologies that will be implemented in different kinds of engines and operating circumstances are being considered. In addition to efficiency and cost factors, the effects of these technologies on the physical, chemical, and biological properties of the exhaust components need to be appraised to prevent undue and unforeseen impacts on public health.

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## TECHNICAL EVALUATION

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### OBJECTIVES AND STUDY DESIGN

Dr. Bagley and colleagues examined selected physical, chemical, and biological properties of the exhaust from heavy-duty diesel engines equipped with either a ceramic particle trap or an oxidation catalytic converter to decrease engine emissions. Emission characteristics investigated included (1) concentrations of the regulated pollutants nitric oxide, nitrogen oxides, and hydrocarbons in the hot, undiluted exhaust; (2) the mass of the fractions in the cool, diluted diesel exhaust, including semivolatile vapor-phase organic compounds, total particulate matter, and components of the particulate matter, which in turn included sulfate and carbon-core particles and the organic compounds associated with them; (3) the total number and volume of particles, and their distribution according to size; (4) the bacterial mutagenicity of the vapor-phase and parti-

cle-associated organic compound fractions; and (5) the concentrations of 12 biologically active PAHs and nitro-PAHs in these organic compound fractions.

The work, which began in 1989, was conducted in two phases. In Phase I, the investigators examined the effects of a particle trap on the emission characteristics of a 1988 heavy-duty diesel engine that met the 1988 California state standard for particle emissions. The engine was fueled with a low-sulfur fuel (0.01% sulfur by weight) and operated under constant-speed conditions corresponding to a 25% (mode 11) or a 75% (mode 9) load on the engine. In addition, selected emissions were characterized during trap regeneration when the trapped particles in the loaded trap were removed by controlled combustion. Limited emission data at both engine loads without the particle trap also were obtained with a low-sulfur fuel that was doped with sufficient sulfur to raise its sulfur content to that found in a conventional, high-sulfur fuel containing 0.32% sulfur by weight.

In Phase II, Dr. Bagley and coworkers examined the effect of an oxidation catalytic converter on the emission characteristics of a 1991 heavy-duty diesel engine, which met the 1991 EPA particulate matter standard. Only low-sulfur fuel was used in these experiments, and the engine was operated under three steady-state conditions corresponding to a 25% load (mode 11), a 50% load (mode 10), and a 75% load (mode 9).

#### Attainment of Study Objectives

The Investigators' Report thoroughly documents a meticulously conducted study on two heavy-duty engines operated under different conditions. It describes a wealth of data on the effects of some pertinent fuel modification and exhaust aftertreatment technologies for controlling diesel emission constituents. Key results are summarized in Tables 1 and 2 of this Commentary. The experiments were carried out in a systematic and carefully managed fashion and the investigators interpreted their results cautiously in the context of current knowledge.

The investigators met all of the original study objectives; however, during the review of their draft report, some questions arose about the accuracy of their nitro-PAH measurements. The chromatographic separation procedure used for these analyses did not completely resolve the individual nitro-PAH peaks, and a second separation and measurement technique was not available to confirm the data. Consequently, the investigators did not include these nitro-PAH data in their revised report.

#### Engine Operating Conditions

The three steady-state operating conditions selected by the investigators in this study (modes 9, 10, and 11) were run at intermediate engine loads (75%, 50%, and 25%, respectively) while the engine speed was held constant at a maximum or "rated" speed (1800 or 1900 rpm). Considering the time and cost constraints, these conditions were appropriate choices because the resulting emissions were comparable to those from heavy-duty engines operating on the highway or in the EPA transient cycle used for emission certification purposes (Bagley et al. 1993). Furthermore, these conditions kept exhaust temperatures below the ignition temperature of the particles retained in the particle trap in Phase I of the study, an important consideration to prevent particle oxidation before the trap regeneration experiments.

In actual use, diesel engines are not always run under well-controlled, steady-state conditions. Sometimes the engines may run at idle for extended periods in urban settings. The relatively lower engine operating temperatures at idling result in less efficient oxidation of the fuel and lead to comparatively higher concentrations of emission constituents in the exhaust. In other instances, diesel engines may not be maintained sufficiently to optimize fuel combustion, which also results in increased emissions. In these examples, public exposure to emissions from individual engines can be higher than would be expected from properly maintained engines operating under highway conditions. It should be noted, however, that the purpose of this study was not to relate diesel emissions to human exposure, but only to examine the effects of advanced exhaust control technologies on engine emissions under controlled conditions.

#### Analysis and Expression of Data

An outstanding aspect of this study is the complete analysis of particle emissions in terms of total particle number, total particle volume, and the size distribution of these particles within the discrete classes of the small, primary, nuclei-mode particles and the larger, accumulation-mode particles.

The investigators expressed their emission data in terms of mass (or mutagenicity)/exhaust volume. This convention is generally acceptable because they were making relative comparisons of a single variable (the absence or presence of an emissions control device) under fixed engine operating conditions. At the conclusion of this report, when the investigators compared the emissions from different engines with different control technologies and fuels, they appropriately expressed emissions in terms of mass/engine

work output. The investigators have also included in their report a formula for converting [mass/exhaust volume] to [mass emissions rate/engine power output].

The principal statistical technique employed in analyzing these data was factorial analysis of variance (ANOVA). This is a suitable tool for this study, in which a small number of independent variables were manipulated at discrete levels in various combinations. It was appropriate for the investigators not to perform a statistical analysis of the particle number and volume distributions because the curve-fitting technique used to analyze such data gives variable limits for the nuclei- and accumulation-mode particles depending upon engine operating conditions, thus rendering any statistical comparisons meaningless.

## RESULTS AND INTERPRETATION

### Phase I Studies

**Low-Sulfur Fuel** The effects of a ceramic particle trap on the characteristics of low-sulfur fuel emissions are summarized in Table 1. Independent of engine load, the trap significantly decreased both particle emissions and those emission components associated with the particles. In terms of concentration in undiluted exhaust, the trap substantially lowered emissions of the total particulate matter by 76% to 87%, the solid-carbon-core component of the particles by 85% to 95%, and the soluble particle-associated organic compounds by 51% to 87%. The number and volume of the particles were decreased by over 85%. The sulfate fraction, another component of the total particulate matter, was not measurable when the low-sulfur fuel was used. These large decreases in particle-associated emissions were accompanied by small decreases in vapor-phase-associated emissions of the hydrocarbon fraction (HC) and the resin-bound organic fraction of the vapor phase (XOC).

With few exceptions, the particle trap decreased the concentration of seven measured PAHs in the particle-associated organic compound fraction. This outcome is expected because most of the mass of this fraction was removed from the emissions along with the particle phase. Four of these PAHs also were present in the resin-bound organic fraction of the vapor phase at levels consistently above the minimum detection limit. Some measurements indicated that the particle trap increased the amount of fluoranthene in this fraction by up to sixfold, whereas the effect of the trap on the other three PAHs was variable and not statistically significant. Only data for fluoranthene and pyrene are summarized in Tables 1 and 2 because the levels of these compounds were substantially higher than the other PAHs and were consistently elevated well above the minimum detection limit for all samples analyzed.

Another consequence of the decline in the particle-associated organic compound fraction was the decrease in mutagenicity of this fraction by 54% to 94%. The mutagenicity of the semivolatile organic compounds in the vapor phase showed a moderate decrease at a high engine load (75%),

**Table 1.** Effects of a Particle Trap or an Oxidation Catalytic Converter on Emissions from Heavy-Duty Diesel Engines Operated with Low-Sulfur Fuel<sup>a</sup>

Parameter	1988 Engine with Ceramic Particle Trap	1991 Engine with Oxidation Catalytic Converter
Gases		
NO	NP <sup>b</sup>	NP
NO <sub>x</sub>	NP	NP
HC	↓ <sup>c</sup>	↓↓
Fractions		
TPM	↓↓	↓ <sup>d</sup> ; ↓↓ <sup>e</sup>
SOF	↓↓	↓↓
SO <sub>4</sub>	— <sup>f</sup>	— <sup>f</sup>
SOL	[↓↓]	NP
XOC	↓ <sup>c</sup>	↓↓
Particles		
Number	[↓↓]	NP
Volume	[↓↓]	[↑] <sup>g</sup> ; [↓] <sup>e</sup>
PAHs		
Fluoranthene in SOF	↓↓ <sup>c</sup>	↓↓ <sup>h</sup>
Fluoranthene in XOC	↑↑ <sup>i</sup>	↓↓ <sup>h</sup>
Pyrene in SOF	↓↓	↓↓
Pyrene in XOC	NP	↓↓
Mutagenicity		
TA98-S9 in SOF	↓↓	↓↓ <sup>e</sup>
TA98-S9 in XOC	↓↓ <sup>c</sup>	↑↑ <sup>c</sup> ; ↓↓ <sup>h</sup>

<sup>a</sup> Comparisons are based on raw exhaust measurements. Results from different engine operating modes are combined, except where noted. Number and direction of arrows approximate the extent of change from an engine without to an engine with a trap or OCC. ↑ or ↓ means 15% to 50% change; ↑↑ or ↓↓ means > 50% change. Arrows without brackets indicate statistically significant responses. Arrows in brackets indicate the response was not analyzed for significance.

<sup>b</sup> NP = results not presented because changes were not statistically significant.

<sup>c</sup> At mode 9.

<sup>d</sup> At modes 9 and 10.

<sup>e</sup> At mode 11.

<sup>f</sup> Response not indicated because SO<sub>4</sub> emissions from low-sulfur fuel were below background levels.

<sup>g</sup> At mode 10.

<sup>h</sup> At modes 10 and 11.

<sup>i</sup> Analyzed by three-way ANOVA only.

but little or no change at a low engine load (25%). These measurements of mutagenicity were obtained in the absence of S9, a rat liver preparation that contains enzymes necessary to metabolize many chemicals (such as PAHs) into substances that are mutagenic. Because most PAHs are not mutagenic without S9, the observed decrease in mutagenicity in the particle-associated organic compound fraction does not reflect any decrease in PAH levels. However, this finding could indicate a loss of nitro-PAHs, a group of PAH derivatives that are often highly mutagenic in the absence of S9. By contrast, mutagenicity assessed in the presence of S9 would be expected to decrease in parallel to a generalized decrease in PAH emissions. This data set, however, was incomplete because some of the samples had insufficient mass for mutagenicity measurements.

Finally, regenerating the loaded particle trap by combustion induced by electric heating increased emission levels and mutagenicity by only 1% to 2% above emissions measured with normal trap operation.

**Conventional, High-Sulfur Fuel** Dr. Bagley and coworkers compared the emissions data they obtained in the current study with low-sulfur fuel to the results obtained in an earlier study in which a conventional, high-sulfur fuel had been used in the same engine and trap system (Bagley et al. 1993). Table 2 presents a summary of the effects of low-sulfur fuel compared with the effects of conventional, high-sulfur fuel on the emissions in undiluted exhaust from a 1988 heavy-duty diesel engine with and without the particle trap. The major, consistent differences with the low-sulfur fuel were a more than 99% decrease in sulfate emissions and a more than 90% reduction in particle numbers. Little or no change in the mass of the total particulate matter in the emissions was noted because the sulfate particles were too small to have any effect on total particle mass. Changes reported for the other emission constituents might be due to differences in the hydrocarbon composition of the two fuels.

Because the high-sulfur fuel study was performed approximately two years earlier than the low-sulfur fuel study, the experimental results from the two studies may not be entirely comparable, due to potential variations in engine operation and condition, and in exhaust sampling and analytic procedures. Also, apart from sulfur content, there were other differences between the two fuels. The low-sulfur fuel had a different hydrocarbon content as indicated by a higher boiling point, a lower cetane number, and a 35% higher aromatic content than the conventional, high-sulfur fuel.

**Doped-Sulfur Fuel** Because of chemical differences other than sulfur content between the low-sulfur and the conventional, high-sulfur fuels, the investigators conducted lim-

ited studies without a particle trap, using a doped-sulfur fuel. The sulfur content in this low-sulfur fuel was raised to match approximately the sulfur content of the conventional, high-sulfur fuel by adding di-*tert*-butyl disulfide. As expected, the emissions from the doped-sulfur fuel contained increased sulfate concentrations and numbers of

**Table 2.** Effects of Low-Sulfur Fuel Compared with Conventional, High-Sulfur Fuel on Emissions from a 1988 Heavy-Duty Diesel Engine Without and With a Particle Trap<sup>a</sup>

Parameter	Without Trap	With Trap
Gases		
NO	S <sup>b</sup>	S
NO <sub>x</sub>	S	S
HC	↑↑ <sup>c</sup>	↑↑ <sup>c</sup>
Fractions		
TPM	↓ <sup>c</sup>	NP <sup>d</sup>
SOF	NP	NP
SO <sub>4</sub>	[↓↓] <sup>e</sup>	[↓↓] <sup>e</sup>
SOL	[↓] <sup>c,e</sup>	[↓] <sup>c</sup>
XOC	NP	NP
Particles		
Number	[↓↓]	[↓↓]
Volume	[↑] <sup>c</sup>	[↑↑] <sup>c</sup> ; [↑] <sup>f</sup>
PAHs		
Fluoranthene in SOF	NP	NP
Fluoranthene in XOC	NP	NP
Pyrene in SOF	↑↑	↑↑ <sup>f</sup>
Pyrene in XOC	↑↑	↑↑
Mutagenicity		
TA98-S9 in SOF	NP	↑↑ <sup>f</sup>
TA98-S9 in XOC	NP	NC <sup>g</sup>

<sup>a</sup> Comparisons are based on raw exhaust measurements. Results from different engine operating modes are combined, except where noted. Number and direction of arrows approximate the extent of change: ↑ or ↓ means 15% to 50% change; ↑↑ or ↓↓ means > 50% change. Arrows without brackets indicate statistically significant responses ≥ 15% change. Arrows in brackets indicate the response was not analyzed for significance.

<sup>b</sup> S = statistically significant increase, but < 15%.

<sup>c</sup> At mode 9.

<sup>d</sup> NP = results not presented because changes were not statistically significant.

<sup>e</sup> Statistical significance was not determined because different sampling systems were used for low-sulfur and conventional high-sulfur fuel studies.

<sup>f</sup> At mode 11.

<sup>g</sup> NC = not calculated because no measurement was obtained for conventional, high-sulfur fuel.

particles that were comparable to results obtained with the conventional, high-sulfur fuel. Unlike the comparison between low-sulfur fuel and conventional, high-sulfur fuel, however, unexplained small (15% to 20%), but statistically significant, decreases were measured in the mass of the total particulate matter, which also were reflected in decreases (30% to 45%) in total particle volume.

#### Phase II Studies

The effects of an oxidation catalytic converter on the composition and mutagenicity of low-sulfur fuel emissions in raw exhaust are summarized in Table 1. The catalytic converter decreased emissions of all organic compounds, including total hydrocarbons in the hot, undiluted exhaust, and the emissions of vapor-phase and particle-associated organic compounds in the cooled, diluted exhaust. The investigators attributed the 25% to 50% decrease in total particulate matter, which was dependent on mode of operation, to the decrease in particle-associated organic compounds. Unlike the particle trap, the catalytic converter had little or no effect on the number or volume of particles.

Consistent with the generalized decrease of organic compound emissions, using the catalytic converter resulted in a decrease in the concentration of selected PAHs in the vapor and particle phases in most instances. Also, the mutagenicity measured in the absence of S9 was significantly reduced, which was most likely due to a decrease in nitro-PAH levels. One exception was an unexplained increase of mutagenicity in the semivolatile vapor-phase fraction at the 75% engine load at mode 9.

#### Comparisons Between Engines

The 1991 engine used in this study differed from the 1988 engine primarily by a higher fuel-injection pressure, higher turbo-boost pressure, and the use of an air-to-air aftercooler to lower the temperature of air on intake. The net results of these engine design changes were to provide better mixing of the fuel with the air, resulting in better fuel combustion in the combustion chamber. Using emission data from the 1988 engine with conventional-sulfur fuel without the particle trap as a baseline (Bagley et al. 1993), and correcting emissions data to a work-output basis, the investigators found that emissions of total particulate matter and associated organic chemicals were reduced by 70% to 80% using both the 1988 engine with low-sulfur fuel and a particle trap and the 1991 engine with low-sulfur fuel and a catalytic converter. However, the 1991 engine with the catalytic converter was up to 70% more effective in lowering emis-

sions of total hydrocarbons in the undiluted exhaust and of semivolatile organic compounds in the vapor phase of the diluted exhaust than the 1998 engine with the particle trap.

Further analysis of the particle emissions from the 1988 and 1991 engines showed some provocative findings (see Tables 42 and 43 in the Investigators' Report and in Baumgard and Johnson 1996). Using low-sulfur fuel in the absence of a particle trap or a catalytic converter, the total volume of the particles from the 1991 engine compared to the 1988 engine was reduced by 78% at mode 11 and 85% at mode 9. However, the total number of particles emitted from the 1991 engine was nearly 15-fold higher at mode 11 and nearly 35-fold higher at mode 9 than the number of particles emitted from the 1988 engine. This increase was due to a 30- to 60-fold elevation in the number of small, primary, nuclei-mode particles emitted at modes 11 and 9, respectively. These particles are thought by the investigators to consist mainly of solid carbonaceous material, because the catalytic converter did not appreciably decrease the number or volume of these particles in the exhaust of the 1991 engine. The possibility that these nuclei-mode particles could be sulfate particles was eliminated because a low-sulfur fuel was used in these experiments.

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#### IMPLICATIONS FOR FUTURE RESEARCH

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The results of this study provide some assurance that advances in fuel and engine technology can lead to substantial decreases in the mass of total particulate emissions from heavy-duty diesel engines. However, it is of concern that successful attempts to reduce the mass of total particulate emissions also may cause changes in the physical size distribution characteristics of the particles. This concern is based on the observation, from a single set of experiments, that a more recent model engine produced a much larger number of small, primary, nuclei-mode particles than an older model engine. This preliminary finding from a single engine needs to be verified with representative advanced engines from different manufacturers. If this finding is confirmed, it will be necessary to assess possible control technologies to decrease nuclei-mode particle emissions. Furthermore, it will be important to test this finding under engine operating conditions other than those studied in this project. For example, emissions could be sampled directly from vehicles during actual operation, or representative vehicles with new model engines from different manufacturers could be tested with a reference fuel over a standard test cycle or similar driving conditions.

Modifying fuel is a major strategy for meeting the next round of emission standards for engines and vehicles by the year 2004. Some examples of proposed fuel modifiers include cyanuric acid precursors to lower nitrogen oxide emissions, cerium, copper, platinum, and other substances to oxidize particles, oxygenates to decrease carbon monoxide and particulate emissions, and cetane enhancers to improve ignition quality. A comparative survey of the impact of these new fuel modifiers on emissions and their potential health effects before they are implemented would complement the current study on fuel sulfur content.

Other possible supplements to the information in this report might include studies on emissions from alternative fuels (natural gas, alcohol, etc.), from alternative combustion strategies (e.g., exhaust gas recirculation), or from the use of advanced lubricants.

## CONCLUSIONS

Dr. Bagley and coworkers found that, independent of the type of engine and exhaust aftertreatment device, the primary effect of reducing sulfur content in diesel fuel was to decrease substantially the sulfate emissions and the number of respirable particles. However, because sulfate particles are so small, decreases in the emission of these particles did not significantly diminish the emission of the total particulate matter. Using a low-sulfur fuel had no significant effect on emissions of semi-volatile organic compounds in the vapor phase or of soluble organic compounds in the particle phase. However, the emission of hydrocarbon gases, the emission of some PAHs in the particle and vapor phases, and the mutagenicity of particle-phase fractions were significantly elevated under some operating conditions. The investigators attributed these effects to differences in the hydrocarbon composition of the low-sulfur and conventional, high-sulfur fuels, and not to changes in the sulfur content of the fuel.

In this study, the particle trap was highly effective in decreasing emission of particles (total particulate matter, the solid-carbon-core component of the particulate phase, and total number and total volume of particles), particle-associated organic chemicals, and the mutagenicity of these chemicals in the absence of S9. In general, the trap did not appreciably alter either the emission or the mutagenicity of organic chemicals not adsorbed to particles. Regeneration of particle-loaded traps by electrical heating and combustion of the trapped particles increased emissions by only 1% to 2% above tailpipe emissions when the trap was in use.

In contrast to the particle trap, the oxidation catalytic converter had little or no effect on the total number and volume of particles, or on the mass of the solid carbon component of the particles emitted. However, the catalytic converter efficiently decreased emission of organic chemicals present in the vapor- and particle-phase fractions. The reduced emission of these organic compounds also was reflected in generally decreased emission and mutagenicity of specific PAHs in these fractions, and decreased emission of total particulate matter.

In the absence of exhaust aftertreatment devices, the more advanced 1991-model engine was found to emit 15 to 35 times more particles than the 1988 engine, despite a substantial reduction in total particle volume and mass. Further analysis indicates that this unexpected finding was due to large increases (30- to 60-fold) in the numbers of small, primary, nuclei-mode particles. Because the main objective of the study was to examine the effect of fuel composition and exhaust aftertreatment devices on emissions, rather than to compare different engines, these data should be considered preliminary. Only one engine of each model was studied, and the two studies with two engines were performed about two years apart. Further systematic inquiry is needed to clarify this potentially important finding.

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