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May 12, 1998

Dr. C. W. Jameson
National Toxicology Program
Report On Carcinogens
MD EC-14
P.O. Box 12233
Research Triangle Park, N.C. 27709

Dear Dr. Jameson:

The American Petroleum Institute (API) is pleased to submit comments and data to the National Toxicology Program (NTP) concerning diesel particulates from diesel exhaust as a candidate for listing in the Ninth Report on Carcinogens. API is a trade association representing companies involved with all sectors of the petroleum industry. Included among the many products manufactured by the more than 400 API members are a full array of diesel fuels.

API's intent is to:

- provide insight into the complexity of assessing the carcinogenicity of diesel exhaust particulates;
- provide unpublished data on diesel exhaust emission characterizations;
- provide trends in diesel fuel composition as they relate to health effects;
- provide information on current diesel fuel composition changes, diesel engine improvements, and engine emission control technologies;
- suggest that it is important to distinguish between diesel exhaust particulates from engines and fuels of today versus the engine and fuels from which the existing scientific data base is derived;
- and suggest that it is premature to make any science based determination of current and future diesel exhaust particulate with regard to carcinogenicity.

Diesel particulate is a generic term for the mixture of inorganic and organic carbon and sulfate based mass generated from compression ignition engines. Diesel particulates are mostly less than 1 micron in diameter. The composition of diesel particulates is variable and changes with different diesel engines and diesel fuels. Generation of diesel particulates are affected by engine

speed more than any other variable. At a minimum, diesel engines are categorized as low speed (typically used in marine operations), medium speed (typically used in heavy duty equipment such as trucks and railroad equipment) and high speed (typically used in light duty vehicles such as automobiles and light trucks). Diesel fuels are categorized into four major types - Number 1 (lighter for cold temperature), Number 2 (heavier general purpose for vehicle and off-road), Number 4 and 6 (employed in services involving sustained load and constant speed such as marine propulsion engines). Diesel fuels are themselves complex mixtures and fuel parameters change depending on climate, use, region, state and federal regulations. Fuel composition does affect diesel exhaust but to a lesser degree than engine operating conditions and emission control technologies. Fuel additives and lubricating oils also impact diesel exhaust.

Variability of diesel particle composition directly results in a corresponding variability of lung penetration, bioavailability, and bioactivity - all of which affect health effects including carcinogenesis. Several recent investigations demonstrate that improvements in diesel fuel and engine technology have reduced the carcinogenic potential of diesel exhaust. Studies by the Health Effects Institute (HEI) show that diesel particulates are reduced up to 90% using new emission control technologies such as a particle trap and an oxidation catalytic converter (attachment #1). The California Air Resources Board (CARB) sponsored a recent diesel exhaust study (attachment #2) comparing emissions from current California diesel fuels with a pre-1993 fuel and observed both a reduction of diesel particulate mass and a reduction in specific mutagenic activity. Southwest Research Institute's report "Fuel Property Trends of U.S. Diesel Fuels and Their Effects on Particulate Matter in Diesel Engine Exhausts" (attachment #3) documents the trends in diesel composition that have reduced exhaust particulate mass. Specifically, there was a large decrease in the sulfur content of diesel fuel formulated after 1993, resulting in a corresponding reduction in particulate mass. The report further documents formulation changes in distillation temperature and aromatic content with concomitant reductions in particulate matter. Also attached (attachment #4) is a recent literature search, including data summaries for on-road diesel emission characterization submitted to US EPA as mandated under section 211(b) of the Clean Air Act. This report summarizes a number of studies which characterize the emissions from heavy-duty diesel engines. The data from these studies provide some insight on the generation of particulate matter from key fuel variables and different engine operating conditions.

Emissions from diesel engines are quantitatively and/or qualitatively different today than emissions of 20-40 years ago. The HEI recognizes this and stated in their spring 1998 Update "although much is known about the health effects of diesel exhaust, a great deal of uncertainty surrounds the use of existing data gathered about workers to predict cancer risks for the general population, in part because quantitative exposure data are lacking." As a result, HEI has launched a "Diesel Epidemiology Project" designed to address the risk of exposure to diesel exhaust, especially the risk of ambient exposures to diesel exhaust from newer, cleaner engines.

The HEI project is in the feasibility stage and is scheduled to begin in the year 2000. Another large scale diesel exhaust epidemiology project is underway - the National Institute for Occupational Safety and Health and the National Cancer Institute are studying the effects of diesel exhaust on non-metal mine workers. These studies will provide important information about the potential health effects from diesel exhaust particulates.

API recommends that NTP distinguish between diesel exhaust particulates from engines and fuels of today versus the engine and fuels from which much of the existing scientific data are derived. These older data do not represent today's ambient exposures and it is inappropriate to use the existing data to assess the carcinogenicity of today's diesel particulates for the general population. It would be prudent to await the results of on-going studies before attempting to classify current diesel exhaust particulates for carcinogenicity.

Sincerely,

Carol J. Henry

Carol J. Henry, Ph.D.
Director, Health and Environmental
Sciences Department

Attachments:

1. Characterization of Fuel and Aftertreatment Device Effects on Diesel Emissions (Health Effects Institute)
2. Evaluation of Factors that Affect Diesel Exhaust Toxicity (California Air Resources Board)
3. Fuel Property Trends of U.S. Diesel Fuels and Their Effects on Particulate Matter in Diesel Engine Exhaust (Southwest Research Institute)
4. Literature Review of Tier 1 Requirements of the Clean Air Act 211(b) Regulations

HEI HEALTH EFFECTS INSTITUTE

Characterization of Fuel and Aftertreatment Device Effects on Diesel Emissions

Susan T. Bagley, Kirby J. Baumgard, Linda D. Gratz, John H. Johnson, and David G. Leddy

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Includes the Commentary of the Institute's Health Review Committee

Research Report Number 76
September 1996

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.

Typically, HEI receives half its funds from the U.S. Environmental Protection Agency and half from 28 manufacturers and marketers of motor vehicles and engines in the United States. Occasionally, funds from other public or private organizations either support special projects or provide resources for a portion of an HEI study. However, in all cases HEI exercises complete autonomy in setting its research priorities and in reaching its conclusions. An independent Board of Directors governs HEI. The Institute's Research Committee and the Review Committee serve complementary scientific purposes and draw distinguished scientists as members. The results of HEI-funded studies are made available as Research Reports, which contain both the Investigators' Report and the Review Committee's evaluation of the work's scientific quality and regulatory relevance.

HEI Statement

Synopsis of Research Report Number 76

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

BACKGROUND

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.

APPROACH

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).

RESULTS AND IMPLICATIONS

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.

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

Susan T. Bagley, Kirby J. Baumgard, Linda D. Gratz, John H. Johnson, and David G. Leddy

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 (NO_x), total hydrocarbons (HC), and total particulate matter (TPM); (2) levels of unregulated emissions such as particle-associated soluble organic fraction (SOF), sulfate (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 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 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 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_4 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_2O and H_2SO_4 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_4 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_x 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_x 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_x 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 α-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/μg 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_x 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_x (Gill 1988). Since NO_x is more difficult to treat in diesel exhaust than particulate matter, NO_x 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_x 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 backpressure 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_2) and water (H_2O).

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_2) to sulfur trioxide (SO_3) with the potential for producing sulfuric acid (H_2SO_4) (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_2, OCCs have been shown to oxidize nitric oxide (NO) to nitrogen dioxide (NO_2) 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_2 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_2, SO_3, 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_x, HC, TPM, SOF, SO_4, 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 respired.

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

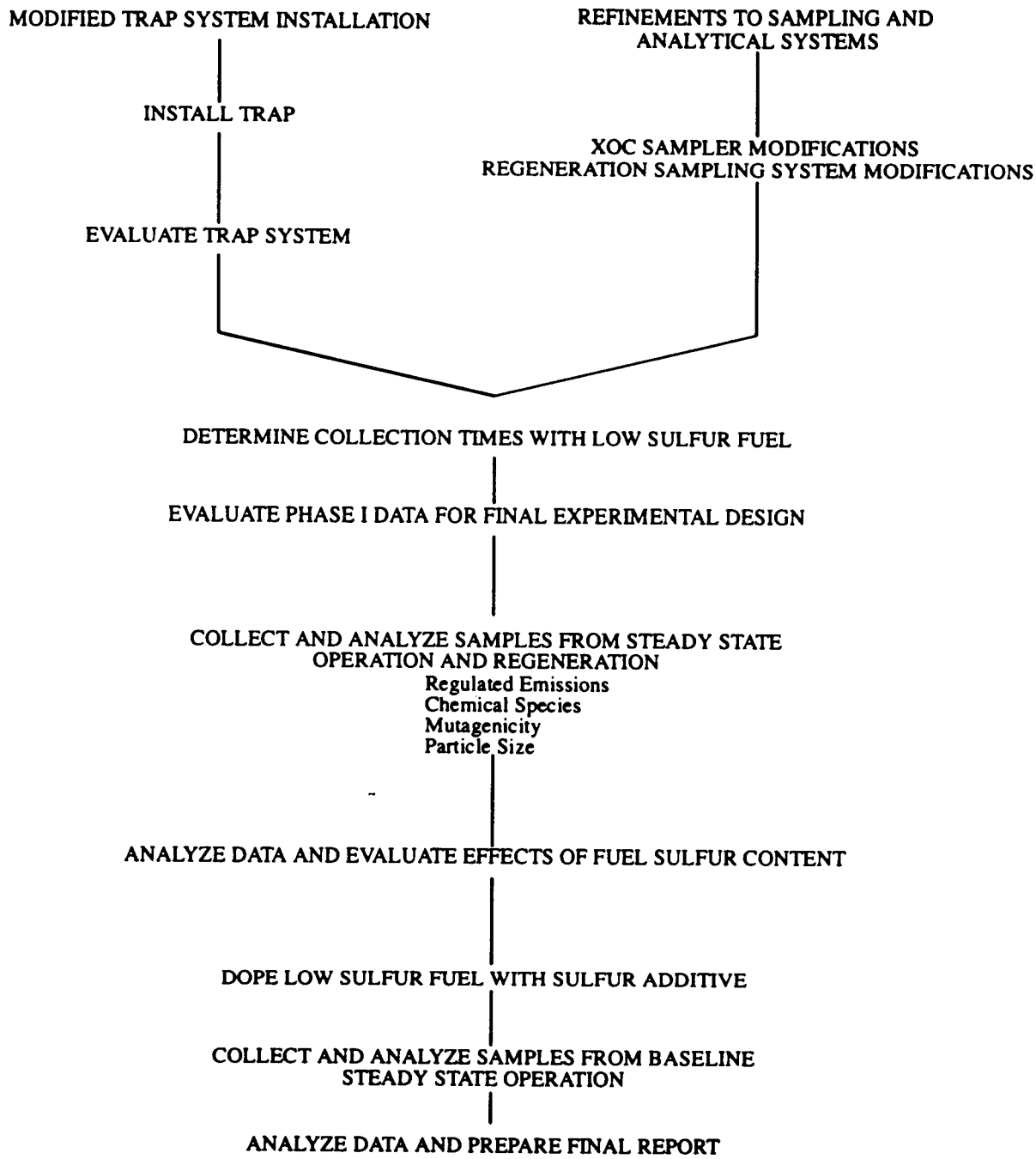

Figure 1A. Specific tasks conducted during the project. Phase I: Cummins 1988 L10 engine and ceramic trap system.

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

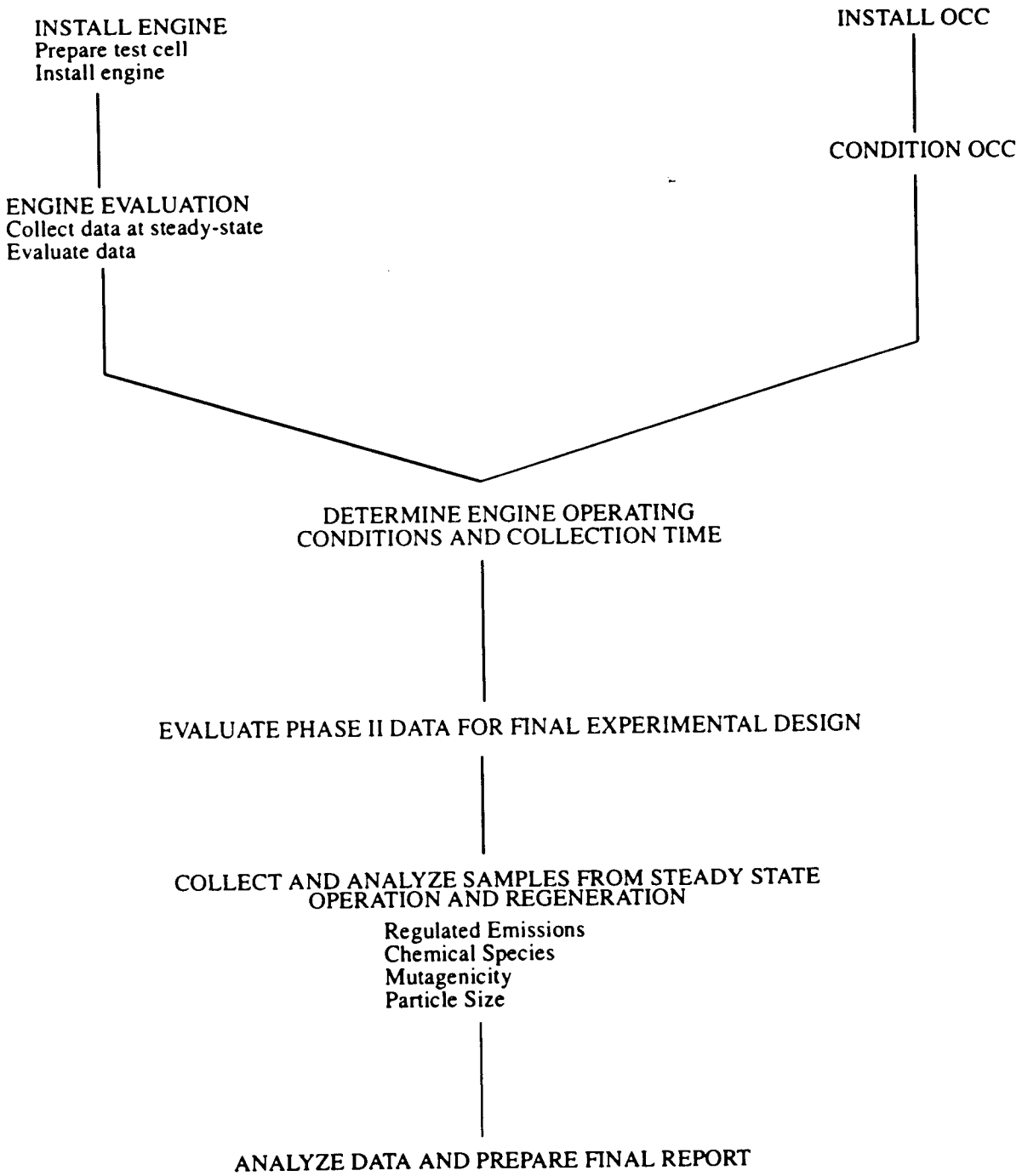

Figure 1B. Specific tasks conducted during the project. Phase II: Cummins 1991 LTA engine and OCC.

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 aftercooled 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

	Conventional Sulfur		Low Sulfur	
Fuel Property	AM 1988[a]	AM 1990[b]	Chev 1990[c]	Chev 1992[d] DS[e]
API gravity[f] (at 16°C)	38.4	NA[g]	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[h])	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

[a] Test performed by AMOCO, Naperville, OH, in 1988.

[b] Test performed by AMOCO in 1990.

[c] Test performed by Chevron Research and Technology Co., Richmond, CA, in 1990.

[d] Test performed by Chevron Research and Technology Co. in 1992.

[e] Low-sulfur fuel doped with di-*tert*-butyl disulfide.

[f] The American Petroleum Institute hydrometer scale for measuring the specific gravity of liquids.

[g] NA = no data available.

[h] FIAM = fluorescence indicator adsorption method.

bard, IL). The NO_x measurements were also made during baseline and trap sampling in the raw and diluted exhaust using a Beckman Instruments Model 955 NO/NO_x 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_x 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-

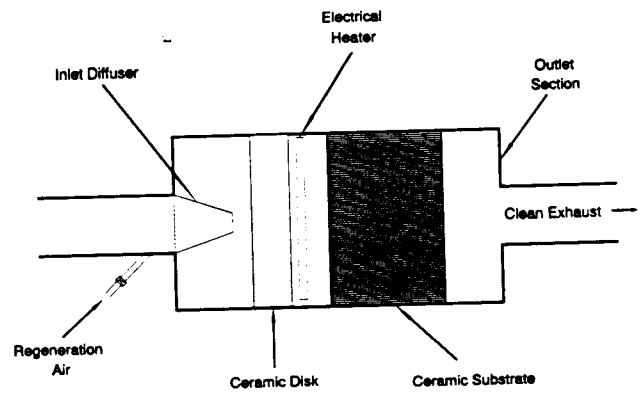

Figure 2. Schematic of the ceramic trap system.

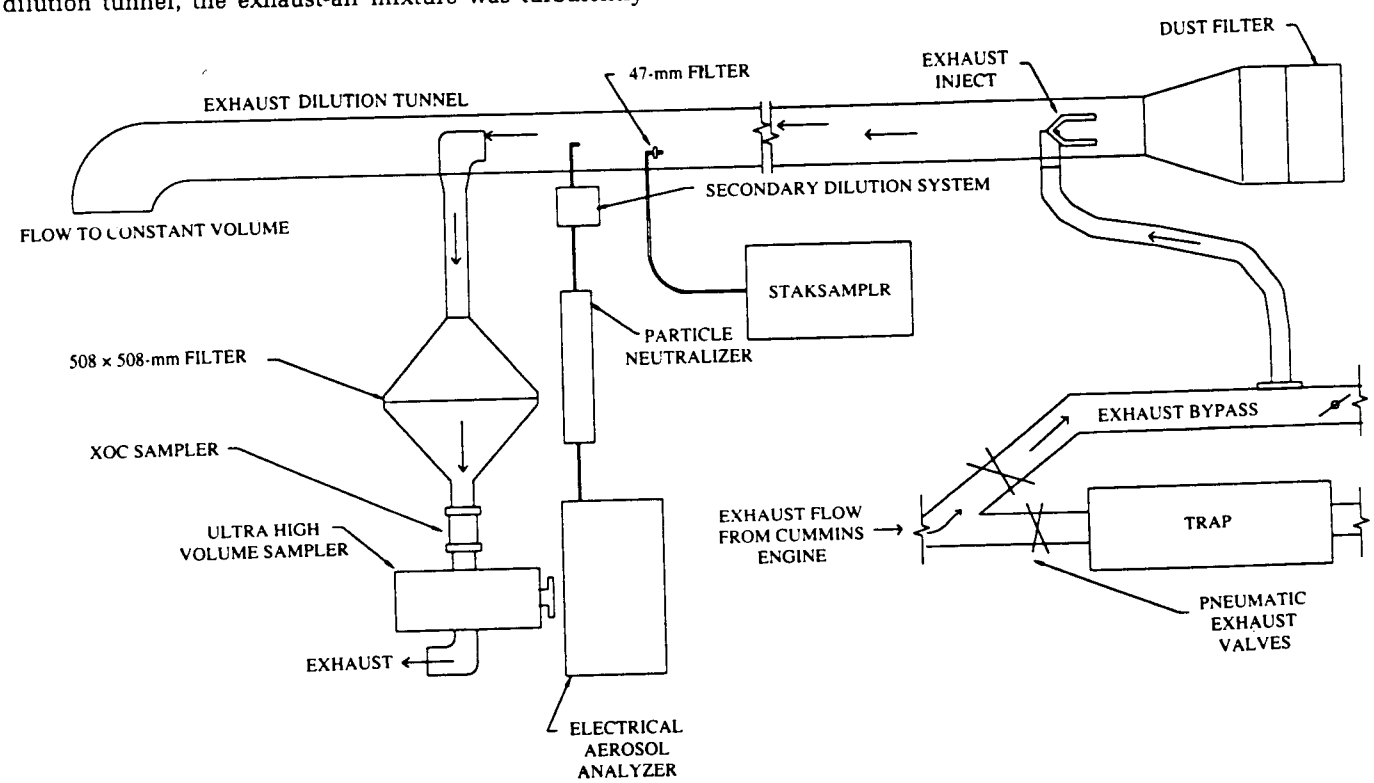

Figure 3. Schematic of the dilution tunnel for baseline sampling with the 1988 Cummins L10 engine.

mm woven glass fiber, Teflon-coated filters (Pallflex TX40HI20-WW, Pallflex Corp., Putnam, CT). The filter face temperature was maintained at 45° ± 1°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_4. 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 μm 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°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, SO_4, SOL, XOC, and Aldehydes All filters used to collect particulate matter were equilibrated in a constant relative humidity chamber (42 ± 3% relative humidity and 25° ± 1°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-μL) 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° ± 4°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 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 SO_4 masses as: SOL (mg) = TPM (mg) − SOF (mg) − SO_4 (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

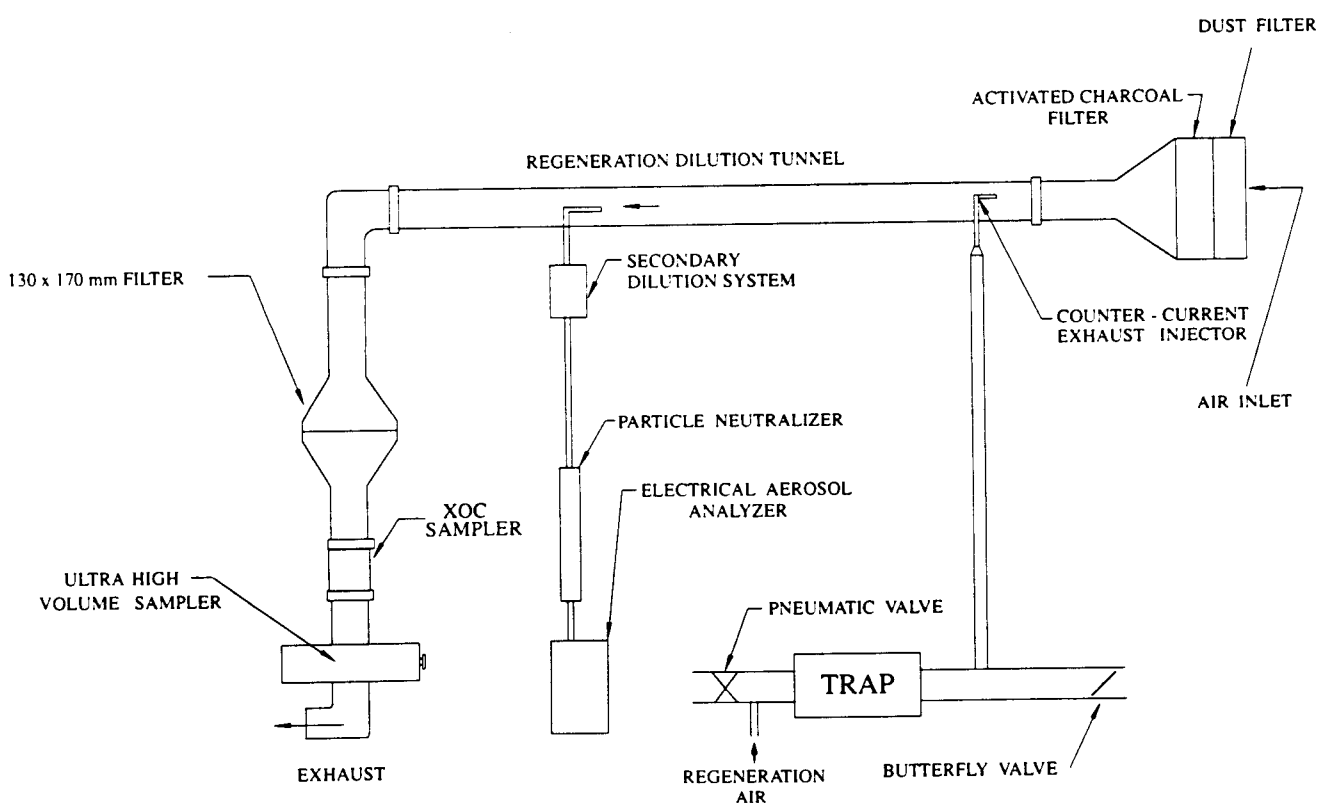

Figure 4. Schematic of the regeneration dilution tunnel.

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 (B*a*A), chrysene (CHR), benzo[*b*]fluoranthene (B*b*F), benzo[*k*]fluoranthene (B*k*F), and benzo[*a*]pyrene (B*a*P). 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 B*a*A 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 B*a*A 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

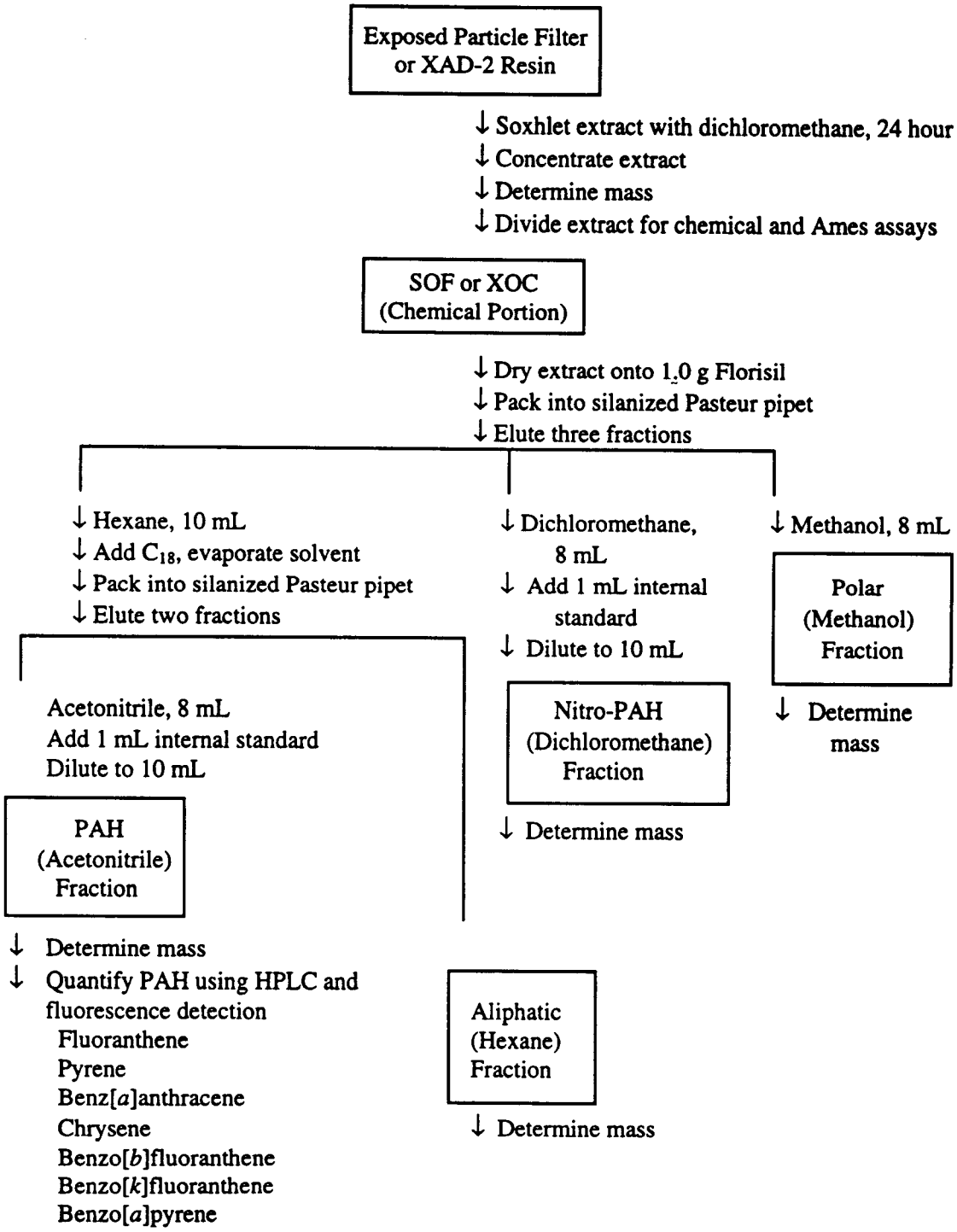

Figure 5. Flow chart for the extraction of SOF and XOC and quantitative analysis of PAHs.

TA98NR (nitroreductase-deficient) and TA98-1,8-DNP$_6$ (*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_2O; 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[a]
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

[a] 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_2O; 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[a]	Excitation and Emission Wave Lengths[b]
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

[a] 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.

[b] 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 $\log_{10}$ 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_4 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_4 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_4, 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_4, 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_2 levels in the raw exhaust at mode 11 were less than 20 ppm, the filter face NO_2 levels would have been less than 2 ppm with dilution ratios around 14:1. Therefore, both temperature and NO_2 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_4 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_x, NO, TPM, SOF, SO_4, 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_4, HC, NO_x, 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^3). 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^3 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^3) of TPM, SOF, SO_4, 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^3) 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-

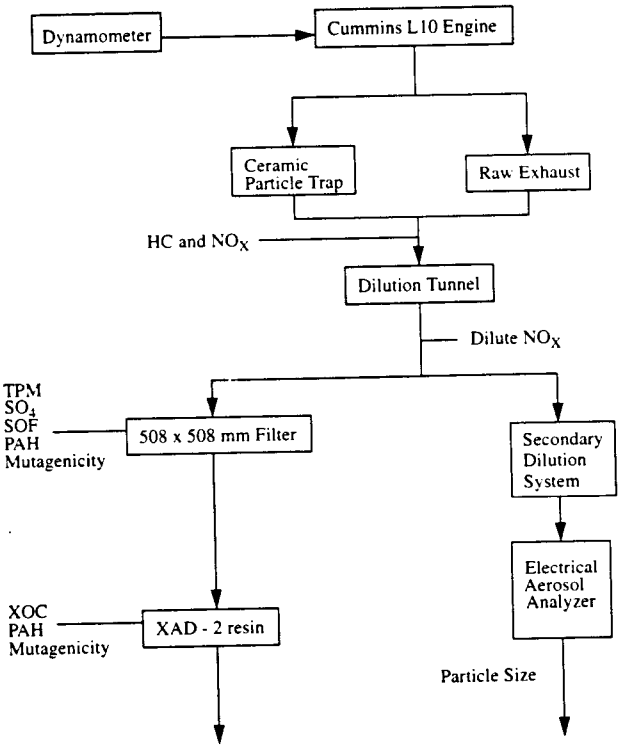

Figure 6. Diesel emissions collection scheme used with the 1988 Cummins L10 engine.

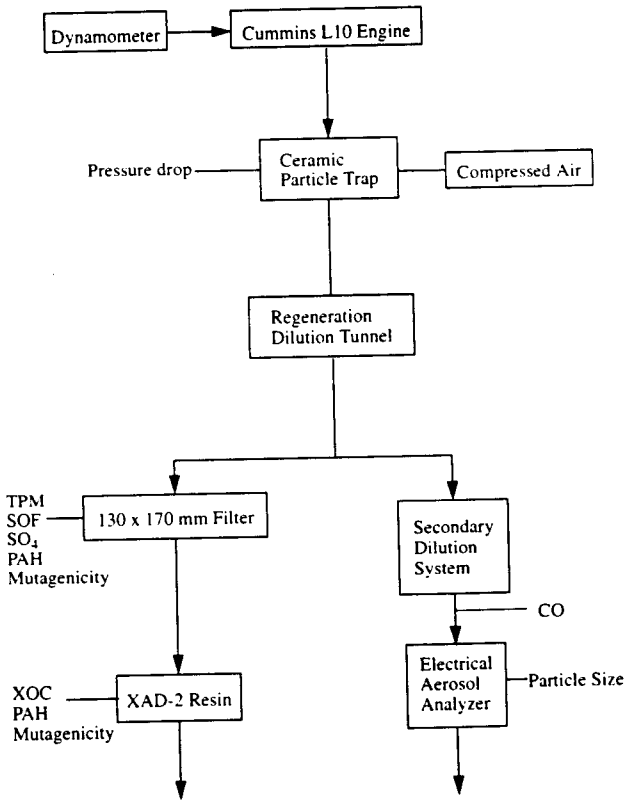

Figure 7. Regeneration emissions collection scheme for the 1988 Cummins L10 engine.

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)[a]	45.1 (1.2)	44.6 (1.9)	45.6 (1.0)	45.2 (0.7)
Sampling time (min)[a]	30 (0.0)	60 (0.0)	30 (0.0)	60 (0.0)
Dilution ratio[a]	14 (2.1)	13 (3.1)	11 (9.6)	10 (7.5)
Approximate NO_2 at filter face (ppm)[a]	3.5 (17)	2.9 (8.2)	2.3 (12)	0.67 (25)

[a] 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

	Mode 9			Mode 11		
Methods and Measures	Baseline	Trap	Trap Regen-eration	Baseline	Trap	Trap Regen-eration
HC, NO_x, NO, and NO_2 measurements	x	x		x	x	
TPM, SOF, SO_4, and SOL measurements[a]	x	x	x	x	x	x
XOC measurements	x	x	x	x	x	x
Particle size distribution	x	x	–[b]	x	x	–[b]
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[c]	x	x	x[c]
Ames assay on subfractions	x	x	x[c]	x	x	x[c]
Quantification of PAHs	x	x	x[c]	x	x	x[c]

[a] 508- × 508-mm filters used with baseline and trap sampling; 130- × 120-mm filters used during regeneration sampling.

[b] Only total particle concentration was measured.

[c] If sufficient mass was available.

tration in mg/m^3. 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_x concentration in the raw exhaust to the NO_x concentration of the dilute exhaust after the NO_x measurements were corrected for the removed water.

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

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

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

Statistical analyses for NO_2 levels were not conducted. With the instrument used for this project, NO_2 levels were determined as the differences between the measured NO_x and NO levels. Considering that the variability of the NO_x and NO measurements were of the same order of magnitude as the calculated NO_2 levels, NO_2 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:

$$[PAH]_{max} < (MDL_{std})(V_i)(SOF_{RE}/m_{SOF}),$$

where $[PAH]_{max}$ is the maximal concentration of the given PAH in ng/m^3; MDL_{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; SOF_{RE} is the concentration of SOF in the raw exhaust in mg/m^3; and m_{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[a]

	Mode 9	Mode 11
Number of samples	3	3
Temperature at filter face (°C)[b]	45.9 (0.63)	45.2 (1.9)
Sampling time (minutes)[b]	30 (0.0)	30 (0.0)
Dilution ratio[b]	15 (1.0)	12 (3.9)
Approximate NO_2 at filter face (ppm)[b]	3.3 (17)	1.5 (13)

[a] Only under baseline conditions.

[b] 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_x 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^3. 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_x 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_x 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_4 (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_4 values; with the LS fuel, the SO_4 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_4 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_x 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 μm in diameter) and an accumulation-mode (0.056 to 1.0 μm 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[a]

	Mode 9		Mode 11	
Emission	Baseline[b]	Trap[b]	Baseline[b]	Trap[c]
NO_x (ppm)[d]	750 (4.2)	800 (0.6)	250 (3.7)	250 (2.0)
NO (ppm)[d]	700 (3.5)	760 (0.9)	220 (4.2)	250 (2.7)
HC (ppm)[e]	140[f] (3.1)	94 (8.7)	170 (2.3)	160 (6.3)
TPM (mg/m^3)[g]	27.5 (3.1)	3.66 (8.8)	37.0f (5.4)	8.73 (12)
SOF (mg/m^3)[h]	8.07 (21)	1.05 (9.6)	8.86[f] (26)	4.35 (3.8)
SO_4 (mg/m^3)	< 0.13[i] ND[j]	< 0.01[i] ND	< 0.02[f,i] ND	< 0.01[i] ND
SOL (mg/m^3)	19.4 (5.6)	1.04 (9.7)	28.2[f] (2.3)	4.33 (3.8)
XOC (mg/m^3)[h]	37.8 (13)	19.3 (20)	43.8[f] (15)	49.1 (14)

[a] 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.

[b] Four samples.

[c] Three samples.

[d] Based on Tukey's test, significant differences between fuels only with mode 9 trap.

[e] Significant differences between fuels at mode 9 baseline and trap.

[f] Two samples.

[g] Significant differences between fuels only at mode 9 baseline.

[h] No significant differences detected between fuels.

[i] Maximum detectable value or highest MDL.

[j] 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 aerosol and has a narrow size range and a GSD between 1.2 and 1.4. The accumulation mode consists of many particles that have agglomerated 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[a]

	Mode 9		Mode 11	
Emission	Baseline[b]	Trap[c]	Baseline[b]	Trap[b]
NO_x (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^3)	33.4 (7.8)	3.16 (18)	38.0 (4.7)	8.44 (11)
SOF (mg/m^3)	9.07 (6.6)	0.75 (23)	12.0 (2.6)	4.50 (16)
SO_4 (mg/m^3)[d]	6.20 (2.5)	1.20 (8.2)	3.09 (18)	2.10 (3.4)
SOL (mg/m^3)[d]	17.3 (19)	0.88 (24)	23.3 (9.2)	3.20 (29)
XOC (mg/m^3)	27.4 (28)	8.83 (29)	41.6 (15)	38.1 (54)

[a] Presented as means of test date means (CV in %) (data from Bagley et al. 1993).

[b] Two samples.

[c] Six samples.

[d] Data obtained from 47-mm filters.

centration units (ng PAH/m^3) 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^3) 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^3) 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 (B*b*F, B*k*F, and B*a*P 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

	Number Fraction		Volume Fraction	
Mode and Condition	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[a]

		Number Mean Diameter		Volume Mean Diameter		Geometric Standard Deviation[c]	
Mode and Condition	n[b]	Nuclei Mode	Accumulation Mode	Nuclei Mode	Accumulation Mode	Nuclei Mode	Accumulation Mode
CS Fuel							
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)
LS Fuel							
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)

[a] All parameters are presented in micrometers as means (CV in %).

[b] Number of samples.

[c] 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 μg/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 B*a*A 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 B*a*A and CHR (for mass and raw exhaust comparisons, with noted significant differences) than the CS fuel.

For B*b*F, B*k*F, and B*a*P, there were generally consistent fuel effects on the basis of both mass and raw exhaust concentration. Although B*k*F and B*a*P were detected only in the particle phase, B*b*F 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 B*b*F at both modes and conditions. In all cases (B*b*F, B*k*F, and B*a*P) 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

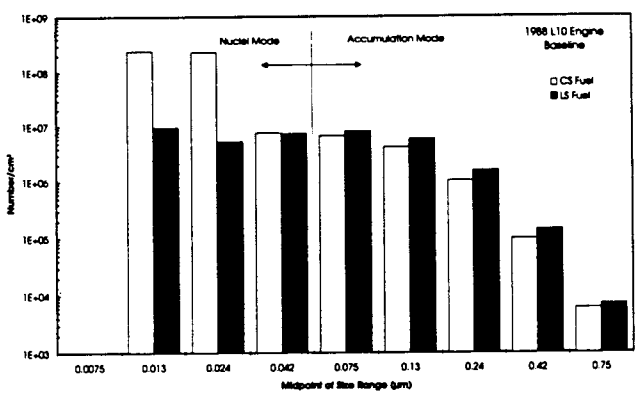

Figure 8. Mode 9 baseline particle number distributions between LS and CS fuels for the 1988 Cummins L10 engine.

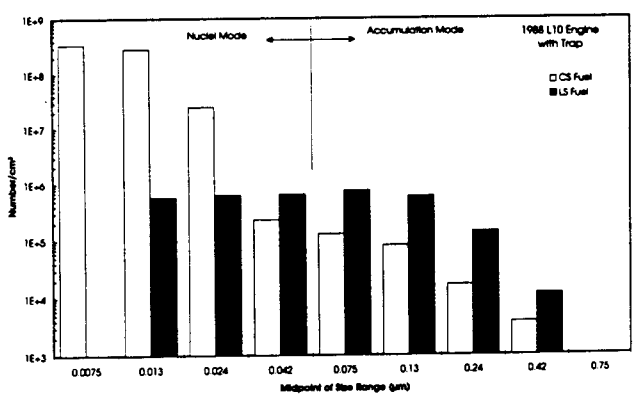

Figure 10. Mode 9 trap particle number distributions between LS and CS fuels for the 1988 Cummins L10 engine.

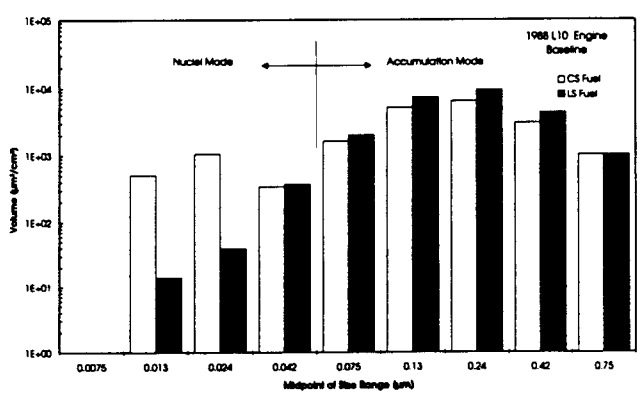

Figure 9. Mode 9 baseline particle volume distributions between LS and CS fuels for the 1988 Cummins L10 engine.

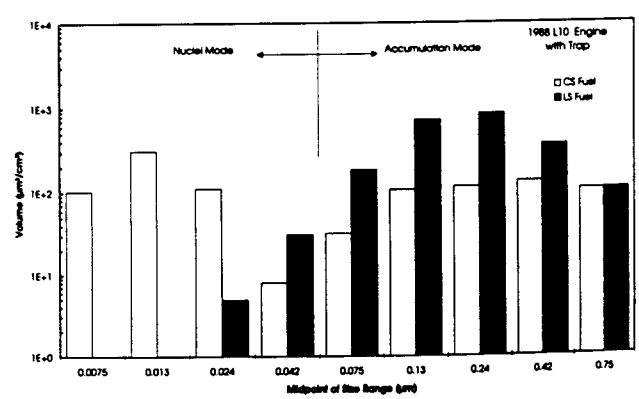

Figure 11. Mode 9 trap particle volume distributions between LS and CS fuels for the 1988 Cummins L10 engine.

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 B*k*F were higher than for the LS fuel, while the PYR, B*a*A, and B*b*F 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/μg 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/μg) 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

			PAH Level (ng/m^3)[b]						
Mode and Condition	Fraction	n[a]	FLU	PYR	B*a*A	CHR	B*b*F	B*k*F	B*a*P
9 Baseline	SOF	4	720 (37)	2300 (12)	1100 (61)	600 (74)	260 (28)	110 (84)	150[c] (82)
	XOC	4	2100 (48)	1800 (28)	320 (29)	240 (28)	4.6 (52)	< 6.0[d] ND[e]	< 6.7[d] ND
9 Trap	SOF	4	170 (24)	330 (18)	140 (25)	180 (24)	41 (48)	< 1.9[f] ND	5.4 (99)
	XOC	4	2700 (83)	1400 (88)	170 (88)	58 (74)	20[c] (> 100)	< 2.2[d] ND	< 3.0[d] ND
11 Baseline	SOF	4	1200 (5.6)	2000 (9.0)	730 (18)	1250 (12)	250[c] (2.9)	91[c] (5.4)	220 (12)
	XOC	3	1200 (14)	910 (14)	250 7.3)	270 (55)	6.5 (18)	< 4.5[d] ND	< 0.63[d] ND
11 Trap	SOF	3	430 (82)	1000 (20)	730 (30)	530 (85)	150 (> 100)	110[g] ND	63[h] (> 100)
	XOC	3	7600 (72)	2500 (78)	490 (56)	250 (55)	≤ 9.7[d] ND	< 7.7[d] ND	< 9.2[d] ND

[a] Number of samples.

[b] Presented as means (CV in %).

[c] $n = 3$.

[d] All values were less than or equal to this MDL.

[e] ND = not determined, because values were less than the MDL or only one value was obtained.

[f] Three of four values were less than this MDL; the fourth value was 9.4 ng/m^3.

[g] $n = 1$.

[h] $n = 2$.

effects are presented in Tables E.7 and E.8 in Appendix E.) A significant fuel effect on activity (revertants/μg 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/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/μg) 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/μg; 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 (ng/m^3)[a]						
Mode and Condition	Fraction	FLU	PYR	BaA	CHR	BbF	BkF	BaP
9 Baseline	SOF	1300[b]	31[b]	140	150	94	3.6	4.4
		(56)	(91)	(89)	(97)	(54)	(99)	(92)
	XOC	1700	300	125	18	< 3[c]	< 3[c]	< 3[c]
		(11)	(8.4)	(19)	(7.0)	ND[d]	ND	ND
9 Trap	SOF	260	53	11	28	3.3	< 3[c]	< 3[c]
		(92)	(79)	(120)	(77)	(4.5)	ND	ND
	XOC	1700	340	11	10	< 10[c]	< 3[c]	< 3[c]
		(37)	(42)	(86)	(79)	ND	ND	ND
11 Baseline	SOF	600	79	170	120	47	5.5	4.3
		(16)	(20)	(19)	(8.8)	(24)	(8.7)	(3.5)
	XOC	2700	470	170	12	< 4[c]	< 5[c]	< 5[c]
		(22)	(22)	(19)	(> 100)	ND	ND	ND
11 Trap	SOF	900	460	140	120	55	< 3[c]	6.4
		(> 100)	(55)	(22)	(16)	(4.5)	ND	(20)
	XOC	3500	1000	150	26	< 3[c]	< 3[c]	< 3[c]
		(36)	(33)	(64)	(45)	ND	ND	ND

[a] Presented as means of mean or median values (CV in %) (data are from Bagley et al. 1993).

[b] The FLU:PYR ratio for this fraction is considered to be atypical.

[c] All values were less than this MDL.

[d] 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 paraffinic-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[a]

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

[a] 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[a]

PAH	Particle-Associated PAH			Vapor-Phase PAH	
	μg/g SOF	μg/g TPM	ng/m^3	μg/g XOC	ng/m^3
Fluoranthene	None	None	None	None	None
Pyrene	All[b]	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[c]	NS
Benzo[*a*]pyrene	All	All	11B	NS	NS

[a] 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^3 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.

[b] Significant differences between PAH levels from LS and CS fuels were found for all combinations of mode and operating condition.

[c] 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[a]

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

[a] 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).

[b] Number of samples.

[c] Based on extractable mass of SOF or XOC.

[d] SOF as a percentage of the TPM.

[e] Data for only two samples.

[f] NA = not applicable to XOC data; NT = not tested; ND = not determined, as only one value was measured.

[g] Sample toxicity may have masked mutagenic response.

[h] Data for only three samples.

[i] Significant differences between LS and CS fuel data.

[j] Data for only one sample.

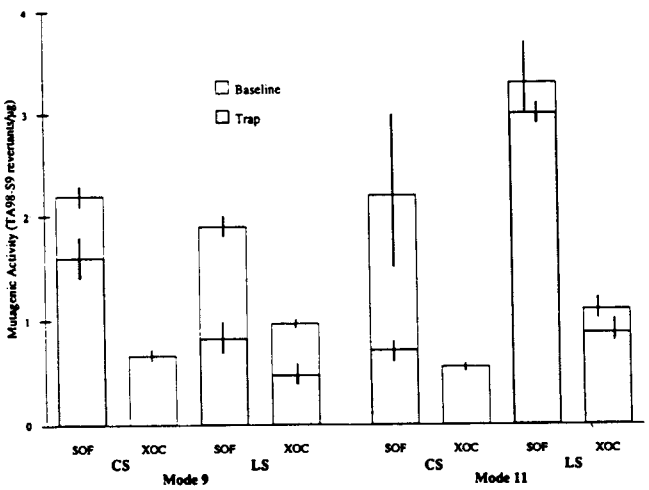

Figure 12. Comparison of mutagenic activity on a mass basis for the LS and CS fuel samples (presented as means ± SE).

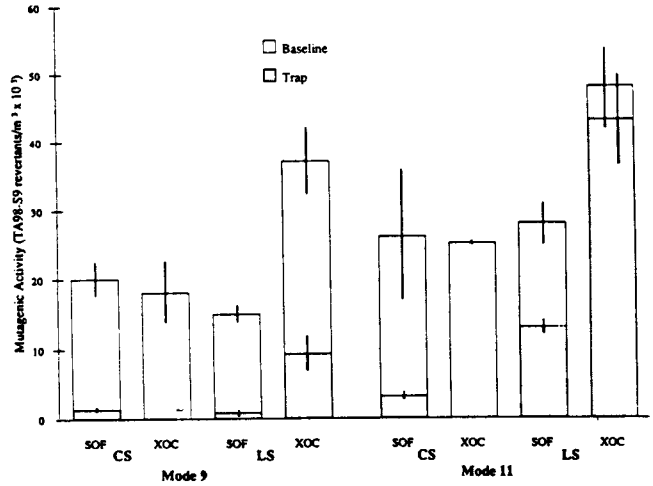

Figure 13. Comparison of mutagenic activity on a raw exhaust concentration basis for the LS and CS fuel samples (presented as means ± SE).

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/µg[a,b]	Revertants/µg[b]	% TA98	Revertants/mg[b]	% TA98
9 Baseline	SOF	1.9 (14)	0.52 (40)	27	0.41 (59)	22
	XOC	0.97 (8.9)	0.20[c] (39)	21	0.38[c] (52)	39
9 Trap	SOF	0.83[d] (40)	0.84[c] (23)	100[d]	2.1[e] (23)	250[d]
	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

[a] For samples listed in Table 15.

[b] Presented as means (CV in %) for four samples, except three samples for mode 11 trap.

[c] Data for three samples.

[d] Sample toxicity may have masked mode 9 trap mutagenic response.

[e] 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 B*a*P 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 combustion 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_4 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[a]

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

[a] Values for % Mass and % Recovered are based on sample mass used in separation. Counts of revertants/µg were measured with TA98–S9. Values for % (mutagenic) Activity were based on activity of unfractionated sample.

[b] Based on separation scheme in Figure 5.

[c] 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.

[d] No response with TA98+S9 above that with TA98–S9.

[e] Response with TA98+S9 was 150% that of TA98–S9.

[f] 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 in Appendix E.) The NO_x 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.

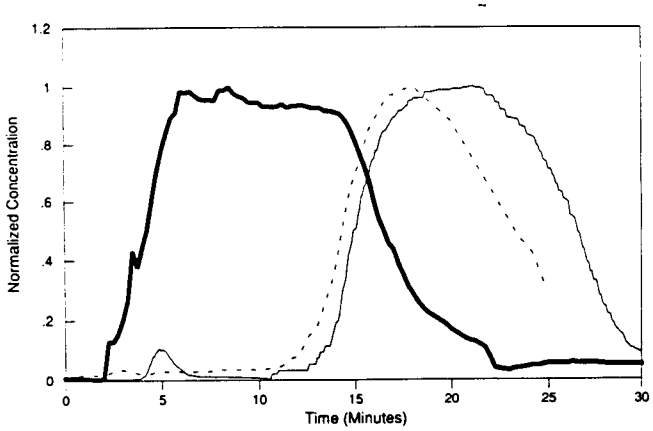

Figure 14. Particle and carbon monoxide emissions during mode 11 regeneration of the particle trap. Heavy line = carbon monoxide with LS fuel; dashed line = EAA measurement of particles with CS fuel; and thin line = EAA measurement of particles with LS fuel.

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

Mode	Test Number[a]	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[b]
	2	7.3	2.3	4.6
	Mean	13.3	4.5	4.6
	(CV in %)	(64)	(68)	NA

[a] 30-Minute sample times.

[b] 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 (%)[a]	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 (%)[a]	0.5	0.5	0.0[b]

[a] Calculated as (mean regeneration/mean trap) × 100, assuming a second trap in the bypass exhaust.

[b] 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_4 fraction should be expected to be the main reason for the TPM increase. The DS fuel produced significantly different SO_4 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_4) 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 (%)[a]
9 SOF	FLU	9,700	2,300	< 0.5	0.0[b]
	PYR	31,000	4,400	< 0.5	0.0[b]
	B*a*A	15,000	1,900	0.2	0.0[b]
	CHR	8,000	2,400	0.5	0.0[b]
	B*b*F	3,500	550	0.7	0.1
	B*k*F	1,500	< 26	0.7	< 2.9
	B*a*P	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
	B*a*A	4,300	2,300	6.1	0.3
	CHR	3,200	780	5.0	0.7
	B*b*F	5,400	270	< 0.1	< 0.1
	B*k*F	< 81	< 30	< 0.1	< 0.5
	B*a*P	< 90	< 40	< 0.1	< 0.3
11 SOF	FLU	11,000	3,900	56	1.5
	PYR	18,000	9,000	43	0.5
	B*a*A	6,500	6,500	17	0.3
	CHR	11,000	4,800	38	0.8
	B*b*F	2,200	1,300	4.1	0.3
	B*k*F	820	990	3.2	0.3
	B*a*P	2,000	570	< 0.1	0.0[b]
11 XOC	FLU	11,000	68,000	264	0.4
	PYR	8,200	22,000	54	0.2
	B*a*A	2,200	4,400	45	1.0
	CHR	2,400	2,200	33	1.5
	B*b*F	58	< 87	2.6	< 3.0
	B*k*F	< 40	< 69	5.8	< 8.4
	B*a*P	< 5	< 82	< 0.0	0.0[b]

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

[b] No increase (or change) detectable.

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

Mode	Test Number	Fraction	Revertants/μg[a] TA98	TA98NR	% TA98	TA98DNP	% TA98	SOF[b] (%)	Revertants/μg TPM[a] TA98	Revertants/min (× 10^3) TA98
9	1	SOF	0.805	0.152	19	0.104	13	58	0.467	0.26
		XOC	0.921	IS[c]	NA[c]	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[c]	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

[a] Without S9.

[b] SOF percentage of the TPM.

[c] 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 (ng/m^3) from the DS fuel study are presented in Table 24; values for the same compounds on a mass basis (μg/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 B*b*F, B*k*F, or B*a*P 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[a] (× 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 (%)[b]	1.3	0.08
11 Baseline	250 (18)	430 (25)
11 Trap	120 (11)	390 (26)
11 Regeneration	0.14[c]	0.06[c]
Increase over trap (%)	0.12	0.02

[a] Presented as means (CV in %); data are from Tables 15 (baseline and trap) and 21 (regeneration).

[b] Calculated as (mean regeneration/mean trap) × 100, assuming a second trap in the bypass exhaust.

[c] Only one sample.

Table 23. Gas-, Vapor-, and Particle-Phase Emissions from the 1988 L10 Engine Using Doped-Sulfur Fuel[a]

Emissions	Mode 9	Mode 11
NO_x (ppm)[b]	770 (1.5)	230 (1.7)
NO (ppm)[b]	710 (0.1)	210 (9.5)
HC (ppm)[c]	130 (3.1)	140 (4.6)
TPM (mg/m^3)[d]	34 (1.1)	43 (6.1)
SOF (mg/m^3)[b]	7.1 (1.5)	12 (3.8)
SO_4 (mg/m^3)[d]	1.8 (15)	1.3 (33)
SOL (mg/m^3)[e]	25 (2.4)	29 (15)
XOC (mg/m^3)[f]	31 (4.4)	54 (7.1)

[a] 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.

[b] Significant differences between the mode 9 and 11 data.

[c] Significant differences between the LS and DS fuel data at mode 11 and between the mode 9 and 11 data.

[d] Significant differences between the LS and DS fuel data at modes 9 and 11 and between the mode 9 and 11 data.

[e] Significant differences between the LS and DS fuel data at mode 9.

[f] 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 B*a*A, which was measured in highest concentrations when the DS fuel was used. Vapor-phase emissions of CHR and B*b*F, 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/μg) 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

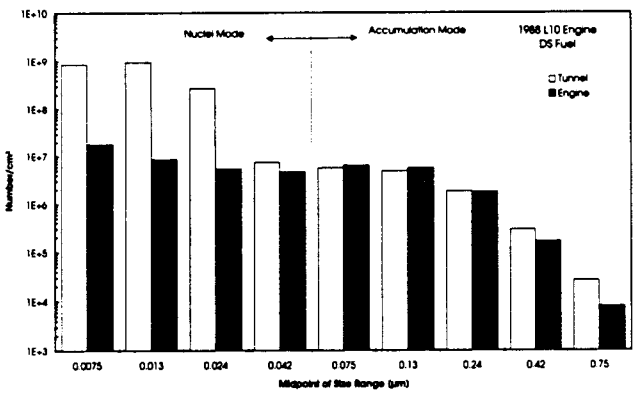

Figure 15. Mode 9 particle number distributions with DS fuel measured at the 1988 Cummins L10 engine manifold and in the dilution tunnel.

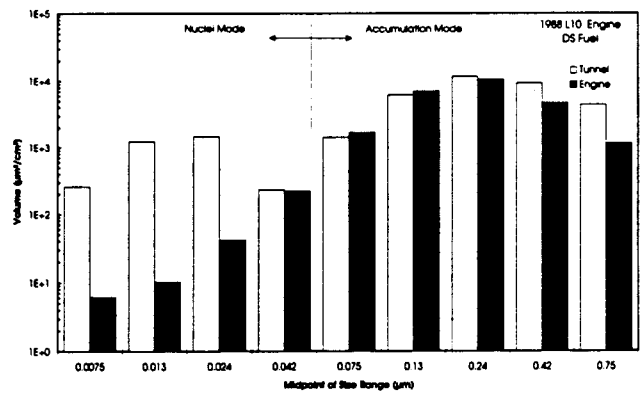

Figure 16. Mode 9 particle volume distributions with DS fuel measured at the 1988 Cummins L10 engine manifold and in the dilution tunnel.

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

			PAH Level (ng/m^3)[b]						
Mode	Fraction	n[a]	FLU	PYR	B*a*A	CHR	B*b*F	B*k*F	B*a*P
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[c] ND[e]	< 5.5[d] ND	< 6.2[d] ND	< 6.5[d] 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[d] ND	< 8.2[d] ND	< 9.3 ND	< 9.7 ND

[a] Number of samples.

[b] Presented as means (CV in %).

[c] Two values less than this MDL and one value was 565 ng/m^3.

[d] All values less than this MDL.

[e] 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[a,b]

PAH	Particle-Associated PAH			Vapor-Phase PAH	
	μg/g SOF	μg/g TPM	ng/m^3	μg/g XOC	ng/m^3
Fluoranthene	11	None[c]	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[c]	NS
Benzo[*a*]pyrene	9, 11	9, 11	9, 11	NS	NS

[a] 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^3 values are in Tables 11 and 24.

[b] 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.

[c] 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[a]

Mode and Condition	Fraction	n[b]	Revertants/μg[c]		SOF[d] (%)	Revertants/μg TPM[e]		Revertants/m^3[f] (× 10^3)	
			−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[g] (29)	NA[h]	NA	NA	13 (12)	11[i] (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)

[a] 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.

[b] Number of samples.

[c] 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.

[d] SOF percentage of the TPM.

[e] Significant differences between LS and DS fuel data are at modes 9 and 11 and between the mode 9 and 11 data.

[f] 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.

[g] Data for only two samples.

[h] 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_x 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_x emissions; Ullman (1989) has shown an inverse correlation between NO_x and cetane number for two direct-injection heavy-duty diesel engines. Emissions from those same engines also showed a direct NO_x 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

	Mode 9			Mode 11		
Subfraction[a]	% Mass[b]	Revertants/μg[c]	% Activity[d]	% Mass[b]	Revertants/μg[c]	% Activity[d]
SOF-HEX	110	NR[e]	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[b]	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[e]	NA[e]	0.6	1.2	1.6
% Recovered[b]	82		0	76		1.6

[a] Based on separation scheme in Figure 5.

[b] Based on sample mass used in separation, rounded to nearest percent.

[c] TA98–S9.

[d] Based on mutagenic activity of unfractionated sample.

[e] NR = no response above spontaneous revertant levels; IS = insufficient sample to test; NA = not applicable to XOC data.

moting NO_x formation. The lack of significant differences in the NO_x 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_x 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

	Percentage of Change from High-Sulfur (CS or DS) Fuel[a]					
	Mode 9			Mode 11		
	LS vs. CS		LS vs. DS	LS vs. CS		LS vs. DS
Parameter	Baseline	Trap	Baseline	Baseline	Trap	Baseline
NO_x (ppm)	+5.6[b]	+8.1[b]	−2.5	+14[b]	+4.2[b]	+9.6
NO (ppm)	+4.5[b]	+5.6[b]	−1.8	+4.8[b]	+4.2[b]	+5.8
HC (ppm)	+87[b]	+120[b]	+9.4	+6.3	+14	+20[b]
TPM (mg/m^3)	−18[b]	+16	−19[b]	−2.6	+3.4	−14[b]
SOF (mg/m^3)	−11	+40	+14	−26	−3.3	−23
SO_4 (mg/m^3)	ND[c]	ND	−93[b,d]	ND	ND	−98[b,d]
SOL (mg/m^3)	ND	ND	−23[b]	ND	ND	−2.1
XOC (mg/m^3)	+38	+120	+23	+5.3	+29	−18
Particle number ($number/cm^3$)[e]	−92	−99	−98	−57	−99	−97
Particle volume ($\mu m^3/cm^3$)[e]	+27	+120	−32	+6.7	+41	−46
Mutagenic activity ($revertants/m^3$)[f]						
SOF	−25	−39	−6.3	+7.7	+310[b]	+27
XOC	+110	NC[c]	+185[b]	+92	NC[c]	+100[b]
Fluoranthene (ng/m^3)						
SOF	−45	−35	−19	+100	−52	+20
XOC	+24	+80	+24	−56	+130	−48
Pyrene (ng/m^3)						
SOF	+7300[b]	+520	+1100[b]	+2400[b]	+120[b]	+33[b]
XOC	+500[b]	+310[b]	+350[b]	+94[b]	+150[b]	−24

[a] Presented as [(LS/CS or DS) − 1] × 100.

[b] Significant difference between LS and CS or DS data.

[c] 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.

[d] Minimum decrease because most LS values were less than the MDL.

[e] Not tested for significant differences.

[f] 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_2 formed in the engine and, consequently, less SO_4 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_2SO_4 was "scrubbing" hydrocarbon compounds out of the gas phase, and (2) the presence of H_2SO_4 (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^3, respectively). However, at mode 11, the difference with the LS fuel was much greater than with the DS fuel (45 mg/m^3 versus 16 mg/m^3, 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_2. He theorized that the hydroxyl radicals formed in the corona discharge section of the EAA are available to react with SO_2 in the aerosol stream; the resultant H_2SO_4 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_2) 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_2 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_2 was below the minimum levels of SO_2 that produced measurable current in the EAA. Assuming that all the sulfur in the DS fuel was converted to SO_2, the SO_2 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_2 (Heywood 1988). When exhaust is diluted and cooled, some SO_2 is converted to SO_3, which combines with water from the combustion process or inlet air and forms H_2SO_4 vapor. Baumgard (1995) showed that heteromolecular nucleation of H_2O and H_2SO_4 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_2O and H_2SO_4 vapor pressures. For our study, based on 4% conversion of the fuel sulfur to H_2SO_4, 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_4 levels on the filter, plus another 2% SO_4 in the vapor phase.) The vapor-phase H_2SO_4 levels were not measured for this project; therefore, measured vapor-phase H_2SO_4 values could change this observation because it is possible to have higher than 4% fuel sulfur conversion to H_2SO_4. 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_2SO_4 and H_2O 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_2O and H_2SO_4 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 (B*a*A, CHR, B*b*F, B*k*F, and B*a*P) 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, B*b*F, B*k*F, and B*a*P), 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^3). 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 consumption. 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/μg) 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/μg) 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_x 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_x 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_4 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^3) 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_4 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_x, 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_2O and H_2SO_4 vapors. When the LS fuel was used, the H_2SO_4 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.

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

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 external-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_2 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.

Table 29. Specifications of the 1991 Prototype Cummins LTA Engine

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

Gaseous HC and NO_x 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_x 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_4, 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^2
Catalyst	Platinum
Precious metal loading	1.06 g/L

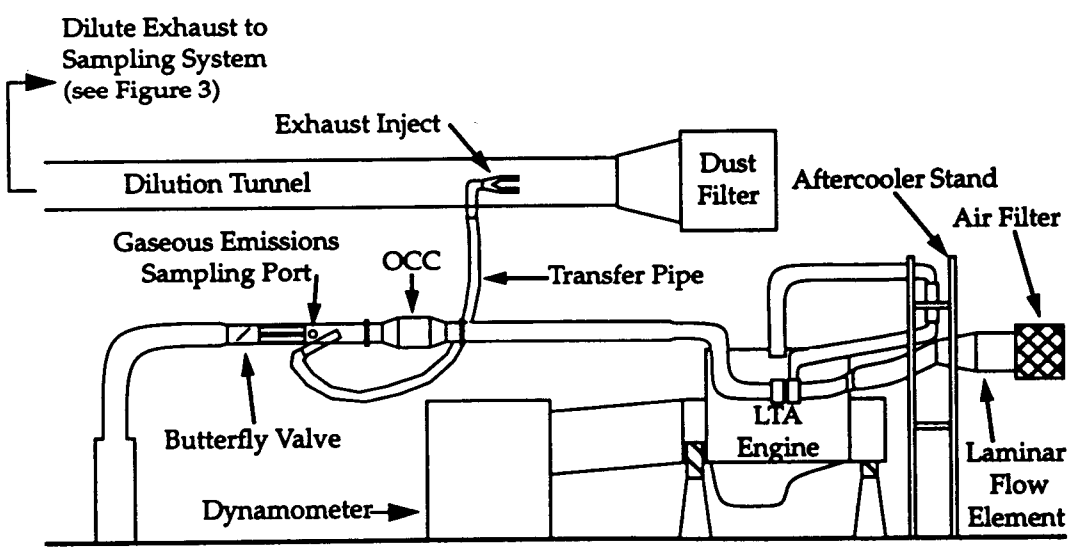

Figure 17. Schematic of the test cell for tests with the 1991 Cummins LTA engine.

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_2 concentration (%)[a]	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)[b]	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)[b]	60 (0.0)	60 (0.0)	60 (0.0)	60 (0.0)	60 (0.0)	60 (0.0)
Dilution ratio[b]	10 (1.7)	11 (0.9)	10 (5.0)	13 (4.6)	9.0 (0.6)	8.9 (1.1)
Approximate NO_2 at filter face (ppm)[b]	2.8 (7.7)	2.9 (5.2)	2.3 (5.7)	1.4 (15)	2.2 (3.3)	0.79 (1.1)

[a] Calculated value.

[b] 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_x, NO, TPM, SOF, SO_4, 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_x, NO, and NO_2 data. The NO_x 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_2. Since ambient air temperature and humidity in the engine intake affect NO_x formation, these intake correction factors adjust NO_x, NO, and NO_2 levels to a reference engine intake humidity and temperature condition. There was no analogous correction factor for HC. The NO_x, NO, and NO_2 data also were corrected to a wet basis by correcting for the water removed by the NO/NO_x 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_4, 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

	Mode 9		Mode 10		Mode 11	
Methods and Measures	Baseline	OCC	Baseline	OCC	Baseline	OCC
HC, NO_x, NO, and NO_2 measurements	x	x	x	x	x	x
TPM, SOF, SO_4, and SOL measurements[a]	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

[a] 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 (NO_x, NO, and HC), vapor-phase (XOC), and particle-phase (TPM, SOF, 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 NO_x, NO, and SOL. It should be noted that, at mode 11 with the OCC installed, three of the four SO_4 measurements were less than the MDL.

The lack of an OCC effect on NO_x emissions was expected since an oxidizing converter generally does not affect NO_x (Ball and Stack 1990). The fact that 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 NO_x. The results for NO levels were similar in all respects to those for 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 NO_x and NO, in that higher operating temperatures produced less HC but more 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 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_4 data in Table 33 indicates that the OCC increased SO_4 at modes 9 and 10 but not at mode 11. Baseline SO_4 levels were similar at modes 9 and 10 and lower at mode 11. While the SO_4 fraction increased from 500% to 600% at modes 9 and 10, respectively, it should be noted that the concentrations of SO_4 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[a]

	Mode 9		Mode 10		Mode 11	
Emissions	Baseline	OCC	Baseline	OCC	Baseline	OCC
NO_x (ppm)[b]	530 (1.3)	540 (0.45)	370 (1.2)	360 (2.9)	210 (1.1)	210 (0.48)
NO (ppm)[b]	510 (1.9)	510 (0.51)	340 (1.8)	350 (2.9)	200 (1.0)	210 (0.78)
HC (ppm)[c]	72 (2.5)	28 (2.1)	96 (1.9)	34 (3.5)	180 (6.8)	53 (3.4)
TPM (mg/m^3)[d]	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^3)[d]	5.1 (5.0)	2.4 (6.5)	5.2 (4.4)	2.1 (12)	12 (5.3)	3.4 (3.1)
SO_4 (mg/m^3)[e]	0.05 (16)	0.28 (12)	0.03 (27)	0.20 (11)	< 0.01 (16)	< 0.01[f] ND[g]
SOL (mg/m^3)[h]	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^3)[c]	21 (6.3)	9.3 (6.3)	29 (7.4)	10 (13)	54 (3.2)	17 (11)

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

[b] Significant differences among data at all modes with and without the OCC.

[c] Significant differences between the baseline and OCC data at all modes.

[d] 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.

[e] Significant differences between the baseline and OCC data at modes 9 and 10 and among all modes with the OCC.

[f] Three of four values less than the MDL.

[g] ND = not determined.

[h] 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_4.

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).

PAHs in SOF and XOC Samples

Table 35 gives the raw exhaust PAH concentrations (ng/m^3) 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 (B*b*F, B*k*F, and B*a*P 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

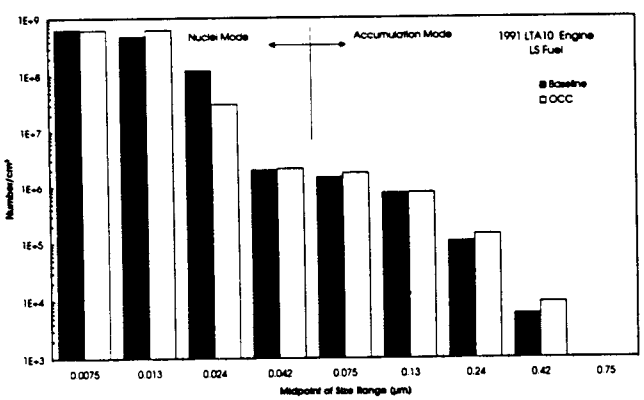

Figure 18. Mode 9 particle number distributions for the 1991 Cummins LTA engine with and without the OCC.

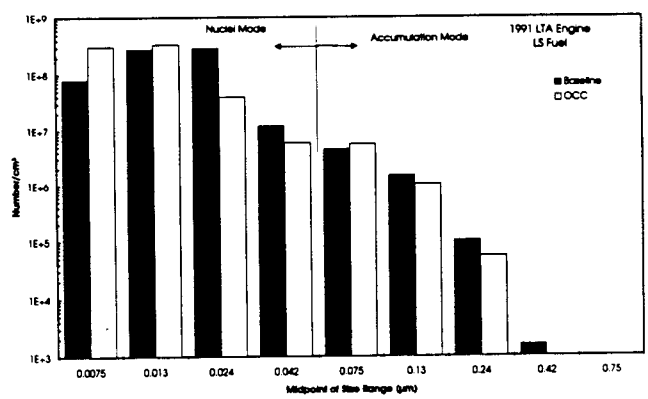

Figure 20. Mode 11 particle number distributions for the 1991 Cummins LTA engine with and without the OCC.

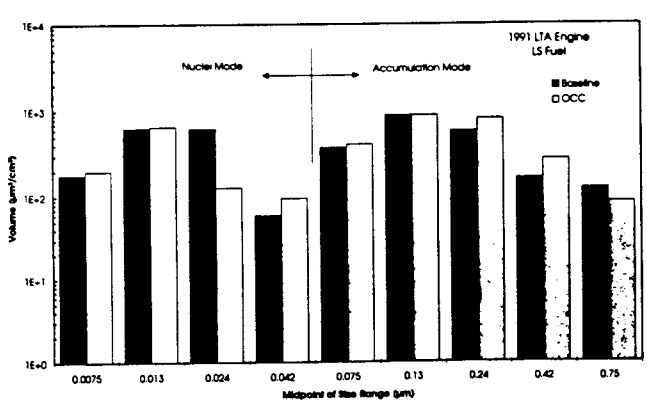

Figure 19. Mode 9 particle volume distributions for the 1991 Cummins LTA engine with and without the OCC.

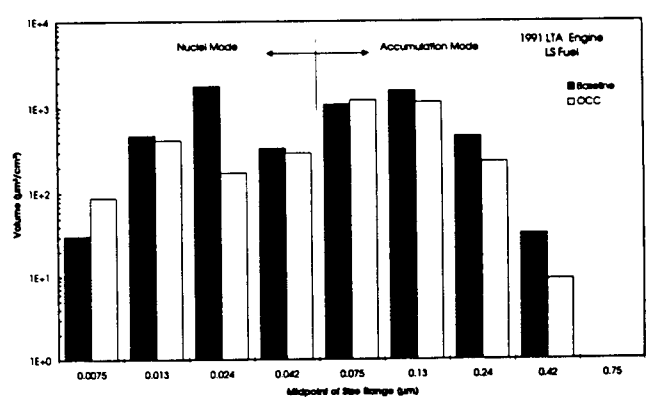

Figure 21. Mode 11 particle volume distributions for the 1991 Cummins LTA engine with and without the OCC.

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 (μg/g), as the raw exhaust concentrations (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 (μg/g TPM) differed among all three modes (see Table H.3). On a μg/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, B*a*A, B*b*F, B*k*F, and B*a*P 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 (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, B*a*A and B*b*F in the vapor phase as well on a ng/m^3 basis. On a mass basis, only the B*b*F 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 (ng/m^3 and μg/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/μg) 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[a]

	Number Mean Diameter		Volume Mean Diameter		Geometric Standard Deviation[b]	
Mode and Condition	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[c]	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)

[a] Reported in micrometers as means of four samples (CV in %).

[b] A measure of the spread of the particle size distribution.

[c] 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/μg) 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) differences 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/μg) 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)[a]						
		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[b] ND[c]	< 2.1[b] 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[b] ND	< 1.0[b] ND	< 1.1[b] 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[b] ND	< 1.1[b] ND
10 OCC	SOF	38 (8.3)	130 (11)	340 (59)	460 (75)	31 (15)	12 (87)	< 2.7[b] ND
	XOC	660 (4.3)	700 (7.1)	540 (2.9)	210 (12)	< 2.4[b] ND	< 2.7[b] ND	< 2.9[b] 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[b] ND	< 1.1[b] 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[b] ND	< 0.87[b] ND

[a] Presented as means (CV in %). $n = 4$ for all data sets.

[b] All values less than this MDL.

[c] 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/μg) and XOC concentrations (mg/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[a]

PAH	Particle-Associated PAH			Vapor-Phase PAH	
	μg/g SOF	μg/g TPM	ng/m^3	μg/g XOC	ng/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[b]	NS
Benzo[*a*]pyrene	9, 10, 11	9, 10, 11	9, 10, 11	NS	NS

[a] All statistical analysis results are in Appendix Tables H.3 through H.6. The μg/g data are in Appendix Tables J.1 and J.2. The ng/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.

[b] 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_2 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[a]

Mode and Condition	Fraction	n[b]	Revertants/μg[c] −S9	Revertants/μg[c] +S9	SOF[d] (%)	Revertants/μg TPM[e] −S9	Revertants/μg TPM[e] +S9	Revertants/m^3[f] (× 10^3) −S9	Revertants/m^3[f] (× 10^3) +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[g]	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[h] (24)	48 (9.1)	0.84 (19)	0.93 (16)	5.8 (20)	6.3 (20)
	XOC	4	1.7 (26)	0.97[i] (84)	NA	NA	NA	28 (18)	18 (91)

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

[b] Number of samples.

[c] 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.

[d] SOF percentage of the TPM.

[e] 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.

[f] 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.

[g] NA = not applicable to XOC data.

[h] $n = 2$.

[i] $n = 3$; 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_2 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

		TA98	TA98NR		TA98DNP	
Mode and Condition	Fraction	Revertants/μg[a,b]	Revertants/μg[b]	% TA98	Revertants/μg[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[c] (34)	39	0.83[c] (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[c] (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[d]		NR[d]	

[a] For samples listed in Table 37.

[b] Presented as means (CV in %) for four samples.

[c] Data for three samples.

[d] 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[a]

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

[a] 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.

[b] Based on separation scheme in Figure 5.

[c] 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.

[d] No response with TA98+S9 above that obtained with TA98–S9.

[e] Responses with TA98NR and TA98DNP from 5% to 25% of the TA98-S9 response.

[f] Responses with TA98NR and TA98DNP about 10% and 40%, respectively, of the TA98–S9 response.

[g] Responses with TA98NR and TA98DNP about 40% and 90%, respectively, of the TA98–S9 response.

[h] 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[a]		
	Mode 9	Mode 10	Mode 11
NO_x (ppm)	+1.9	−2.7	0
NO (ppm)	0	+2.9	+5.0
HC (ppm)	−61[b]	−65[b]	−71[b]
TPM (mg/m^3)	−27[b]	−34[b]	−53[b]
SOF (mg/m^3)	−53[b]	−60[b]	−72[b]
SO_4 (mg/m^3)	+460[b]	+570[b]	NC[c]
SOL (mg/m^3)	+6.7	0.0	−2.6
XOC (mg/m^3)	−56[b]	−66[b]	−69[b]
Particle number (number/cm^3)[d]	+1.9	+76	+4.9
Particle volume (μm^3/cm^3)[d]	−1.6	+19	−38
Mutagenic activity (revertants/m^3)[e]			
SOF	−34	−23	−85[b]
XOC	+100[b]	−79[b]	−64[b]
Fluoranthene (ng/m^3)			
SOF	+110	−50[b]	−84[b]
XOC	+7.4	−51[b]	−63[b]
Pyrene (ng/m^3)			
SOF	−79[b]	−70[b]	−86[b]
XOC	−71[b]	−61[b]	−55[b]

[a] Presented as [(OCC/Baseline) − 1] × 100.

[b] Significant difference between baseline and OCC data.

[c] NC = not calculated because all but one OCC value were less than the MDL.

[d] Not tested for significant differences.

[e] 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_4 (personal communication, D. Psaras, Degussa Corporation 1992). Platinum-based OCCs are very effective for the oxidation of CO, HC, and SO_2 (Horiuchi et al. 1990), and some washcoat formulations can help control the oxidation of SO_2 or the formation of SO_4, while still maintaining satisfactory HC oxidation control. (Washcoat formulations that inhibit SO_4 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_4 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_4 formulations in the same temperature range. In testing two platinum-based SO_4-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_4 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_4 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_4 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_4 at mode 11 (311°C), but significantly increased SO_4 at modes 10 and 9 (370°C and 393°C, respectively). Direct calculation of baseline conversion rates of fuel sulfur to SO_4 (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_4 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_4 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_4 increased by 600% and 500%, respectively, over baseline levels. However, due to the low fuel sulfur levels, the actual SO_4 contribution to TPM was quite low (6%) for all experimental treatment combinations. In fact, the SO_4 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_4 was less than 0.002 g/kW-hr at mode 9 with the OCC. Such low SO_4 levels also may contribute to the large control efficiencies of the OCC, in that small differential changes in SO_4 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 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, ng/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_4-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_4-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^3) 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_4 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[a]

	Engine / Operating Condition / Fuel				
Emissions	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
Mode 9					
NO_x	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)
Mode 11					
NO_x	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)

[a] 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_x transient emission standards have been reduced 53% and the HC standards have not changed (Walsh 1993). Table 41 compares the NO_x, 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[a]

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

[a] All samples were collected from the dilution tunnel (Figure 3) unless otherwise indicated.

[b] 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_2O and H_2SO_4 vapors. These H_2O-H_2SO_4 particles form only when the H_2O and H_2SO_4 dilution tunnel vapor pressures are favorable for nucleation. When these particles are emitted into the atmosphere where the H_2O and H_2SO_4 vapor pressures are considerably lower than in the dilution tunnel, the H_2O-H_2SO_4 particles basically evaporate and revert back to H_2O and H_2SO_4 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_2SO_4 (and H_2O) 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 10^6 particles/cm^3 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_2O-H_2SO_4 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 10^3 $\mu m^3/cm^3$ 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[a]

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

[a] All samples were collected from the dilution tunnel (Figure 3) unless otherwise indicated.

[b] 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 Technogies and Fuels[a]

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
Mode 9					
SOF (g/kW-hr)	0.05	0.04 (−12)	<.01 (−88)	0.03 (−38)	0.02 (−70)
SOL (g/kW-hr)	0.10[b]	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] × 10^3)	110	83 (−25)	4.7[c] (−96)	86 (−22)	57 (−48)
XOC ([rev/kW-hr] × 10^3)	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)
Mode 11					
SOF (g/kW-hr)	0.13	0.10 (−26)	0.05 (−63)	0.14 (8)	0.04 (−69)
SOL (g/kW-hr)	0.26[b]	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] × 10^3)	280	310 (11)	140 (−50)	450 (61)	69 (−76)
XOC ([rev/kW-hr] × 10^3)	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)

[a] Presented as means (percent change), where percent change = [(Condition − 1988 Baseline CS)/1988 Baseline CS] × 100%.

[b] SOL emissions determined from 47-mm filter samples.

[c] 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_x, 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_4 levels increased with the OCC at the two higher-temperature modes (9 and 10), the SO_4 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_4 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

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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PUBLICATIONS RESULTING FROM THIS RESEARCH

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ABBREVIATIONS

ANOVA	analysis of variance
ACN	acetonitrile
B*a*A	benz[*a*]anthracene
B*a*P	benzo[*a*]pyrene
B*b*F	benzo[*b*]fluoranthene
B*k*F	benzo[*k*]fluoranthene
bhp	brake horsepower
CHR	chrysene
CO	carbon monoxide
CO_2	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_2SO_4	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
LTA	Cummins LTA 10-310 engine
MDL	minimum detection limit
MeOH	methanol
MTU	Michigan Technological University
n	number of samples
NIST	National Institute for Standards and Technology
N•m	Newton meter
NMD	number mean diameter
NO	nitric oxide
NO_x	oxides of nitrogen
NO_2	nitrogen dioxide
OCC	oxidation catalytic converter
PAH	polynuclear aromatic hydrocarbon
ppm	parts per million
PYR	pyrene
rpm	revolutions per minute
S9	rat liver microsome preparation
SAE	Society of Automotive Engineers
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SOF	particle-associated soluble organic fraction
SOL	particle-associated solid fraction
SO_4	particle-associated sulfate fraction
SRM	standard reference material
STP	standard temperature and pressure
TA98NR	a nitroreductase-deficient tester strain of *Salmonella typhimurium* TA98
TA98DNP	an *o*-transacetylase–deficient tester strain of *Salmonella typhimurium* TA98
TPM	total particulate matter
UHVS	ultra-high-volume sampler
VMD	volume mean diameter
XOC	XAD-2 resin–bound organic fraction from the vapor phase

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 exhaust 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.

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 μm in diameter, with most particles at around 0.02 μm; the larger class of particles (accumulation mode) are aggregates of the primary particles and range in size from 0.075 to 0.75 μm in diameter, with most particles around 0.2 μm (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 (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 μm 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 μm) particles deposit in several-fold greater numbers and further into the lungs than larger (0.3 μm) particles (International Commission on Radiological Protection 1994); therefore, increased emissions of primary, nuclei-mode particles (0.01 to 0.056 μm 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.

TECHNICAL EVALUATION

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[a]

Parameter	1988 Engine with Ceramic Particle Trap	1991 Engine with Oxidation Catalytic Converter
Gases		
NO	NP[b]	NP
NO_x	NP	NP
HC	↓[c]	↓↓
Fractions		
TPM	↓↓	↓[d]; ↓↓[e]
SOF	↓↓	↓↓
SO_4	–[f]	–[f]
SOL	[↓↓]	NP
XOC	↓[c]	↓↓
Particles		
Number	[↓↓]	NP
Volume	[↓↓]	[↑][g]; [↓][e]
PAHs		
Fluoranthene in SOF	↓↓[c]	↓↓[h]
Fluoranthene in XOC	↑↑[i]	↓↓[h]
Pyrene in SOF	↓↓	↓↓
Pyrene in XOC	NP	↓↓
Mutagenicity		
TA98–S9 in SOF	↓↓	↓↓[e]
TA98–S9 in XOC	↓↓[c]	↑↑[c]; ↓↓[h]

[a] 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.

[b] NP = results not presented because changes were not statistically significant.

[c] At mode 9.

[d] At modes 9 and 10.

[e] At mode 11.

[f] Response not indicated because SO_4 emissions from low-sulfur fuel were below background levels.

[g] At mode 10.

[h] At modes 10 and 11.

[i] 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 limited 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[a]

Parameter	Without Trap	With Trap
Gases		
NO	S[b]	S
NO_x	S	S
HC	↑↑[c]	↑↑[c]
Fractions		
TPM	↓[c]	NP[d]
SOF	NP	NP
SO_4	[↓↓][e]	[↓↓][e]
SOL	[↓][c,e]	[↓][c]
XOC	NP	NP
Particles		
Number	[↓↓]	[↓↓]
Volume	[↑][c]	[↑↑][c] ; [↑][f]
PAHs		
Fluoranthene in SOF	NP	NP
Fluoranthene in XOC	NP	NP
Pyrene in SOF	↑↑	↑↑[f]
Pyrene in XOC	↑↑	↑↑
Mutagenicity		
TA98–S9 in SOF	NP	↑↑[f]
TA98–S9 in XOC	NP	NC[g]

[a] 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.

[b] S = statistically signifcant increase, but < 15%.

[c] At mode 9.

[d] NP = results not presented because changes were not statistically significant.

[e] Statistical significance was not determined because different sampling systems were used for low-sulfur and conventional high-sulfur fuel studies.

[f] At mode 11.

[g] 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 emissions 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.

IMPLICATIONS FOR FUTURE RESEARCH

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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for:

Evaluation of Factors That Affect Diesel Exhaust Toxicity

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1. INTRODUCTION

1.1 Background

Diesel exhaust has been designated by the International Agency for Research on Cancer as a probable human carcinogen, and is undergoing evaluation as a potential toxic air contaminant under the California Air Resources Board's (CARB's) air toxics program. Diesel exhaust is a complex mixture consisting of hundreds of compounds. Effective October 1, 1993, the CARB mandated new highway diesel fuel regulations (CARB, 1991) which limited the maximum sulfur content to 0.05%, the minimum cetane index to 40, and the maximum aromatic content to 10%. These regulations were based upon a review of available data (CARB, 1988) on the impact of fuel properties on criteria pollutant emissions, total hydrocarbons (THC), carbon monoxide (CO), oxides of nitrogen (NO_x), and particulate matter (PM). Since lowering the aromatic content from levels above 30% to those below 10% requires major capital investment and operating costs, CARB has allowed fuel producers the option of producing a less-costly alternative fuel with a higher aromatic content, if equivalent emissions can be demonstrated (CARB, 1988). There is an extensive literature on the effects of diesel fuel parameters on emissions of criteria pollutants, but little is know on the impact of these fuel changes on the complex speciation of the gas-, semivolatile-, and particle-phase components and specifically on emissions of toxic components present in diesel exhaust. This study was designed to provide this information on three diesel fuels: a pre-1993 fuel, a low aromatic fuel, and an alternative formulation fuel. This work has been conducted by a team of researchers from the College of Engineering-Center for Environmental Research and Technology (CE-CERT), the Statewide Air Pollution Research Center (SAPRC) at the University of California (UC) Riverside, and the UC Davis Department of Environmental Toxicology, with emission testing conducted at the Los Angeles County Metropolitan Transit Authority (LACMTA) emission test facility.

1.2 Scope of work

The scope of this project was to obtain a preliminary assessment of the potential impact of diesel fuel formulation on the speciation and toxic components of diesel exhaust. The test bed was a Cummins L10 engine operating over the heavy-duty transient test cycle using three diesel fuels: a pre-1993 diesel fuel, a low aromatic diesel fuel, and an alternative formulation diesel fuel. The sampling/analysis plan included determination of the criteria pollutant emission rates (THC, CO, NO_x, and PM) together with the determination of PM_{10} and $PM_{2.5}$, collection of particulate

samples for elemental, inorganic ion and elemental/organic carbon analyses, collection of bag samples for VOC speciation analyses, collection of 2,4-dinitrophenylhydrazine (DNPH) cartridges for determination of oxygenates, collection of nitrosomorpholine with Thermosorb N cartridges, collection of semi-volatiles on PUF/XAD and particulate samples for PAH, nitro-PAH, and mutagenicity studies. In addition, during the course of this project, the ARB requested that the UC Davis group add sampling and analysis of dioxins for the pre-1993 and alternative formulation diesel fuels. It must be noted that the results obtained in this study may not apply to different engine technologies.

1.3 Intended Use of Data

The data collected in this study are to be used to assess the influence of diesel fuel formulation on the emission of toxic species and will also be used for designing the scope and direction of more comprehensive studies. This study provides information in a research area having limited existing data. The ARB has indicated that this study will provide baseline data only and is not intended to be used to formulate new regulations.

1.4 Project Objectives

The objective of this study was to collect toxic component related data from a Cummins L10 engine with pre-1993 diesel fuel, a low aromatic diesel fuel, and an alternative formulation diesel fuel, operating over the EPA heavy-duty diesel engine transient Federal Test Procedure (FTP). The data quality objectives are to determine the magnitudes of the differences in toxic emissions and their variability among the different fuel types. To meet these data quality objectives, multiple samples were collected during multiday testing for each of the three fuels. For each fuel, the objectives were to:

- Measure all regulated emissions: THC, CO, CO_2, NO_x, total particulates
- Quantify the mass fraction of the particulate below 10 and 2.5 μm aerodynamic diameter
- Collect, identify, and quantify at least 80% of the C_1-C_{12} VOC emissions
- Collect, identify, and quantify at least 80% of carbonyl compounds
- Collect, identify and quantify the elemental and inorganic ion components in the particulate

- Quantify the elemental and inorganic carbon fractions of the particulate
- Collect, identify and quantify the particulate-bound PAH and nitro-PAH emissions
- Collect, identify, and quantify the gas-phase PAH and nitro-PAH emissions
- Determination of mutagenicity

and, for the pre-1993 and reformulated fuel to:

- Collect, identify, and quantify the nitrosomorpholine emissions
- Collect, identify, and quantify the dioxins

2. PROCEDURES

2.1 Engine Set-Up

All testing was performed at the Los Angeles County Metropolitan Transit Authority (LACMTA) engine dynamometer facility which is equipped and calibrated to perform the EPA heavy-duty diesel engine transient FTP. Engine installation, set-up, and operation were performed by LACMTA staff. Specifications for the Cummins L10 test engine are listed below:

Engine Family	:	343E
Engine Model	:	L10-310
Engine S/N	:	34705128
Engine Type	:	In-line 6 cylinder, turbocharged direct injection
Displacement	:	10.0 liters (611 cu. in.)
Advertised HP (SAE)	:	310 @ 1600 RPM
Peak Torque	:	1150 ft-lb @ 1200 RPM

This engine was provided by Cummins Engine Company, Inc. and had been certified to the EPA and California standards for the 1991 to 1993 model years (THC-1.3 g/hp-hr, CO-15.5 g/hp-hr, NO_x-5.0 g/hp-hr, PM-0.25 g/hp-hr). Engine set-up, mapping procedures, and transient cycle

generation were performed according to the procedures outlined in the Code of Federal Regulations (CFR), Title 40, Part 86, Subpart N and as outlined below:

1. Start engine and run at various speeds and loads until the pan and water temperatures have stabilized. Set up the engine at rated speed (1800 rpm)

Intake restriction (in. H_2O)	17.5 ±1.0
Exhaust restriction (in. Hg)	2.4±0.2
Max crossover restriction	4.0
Intake manifold temperature (°F)	115±5
Water supply temperature (°F)	77±4
Engine coolant temperature (°F)	165±10
Fuel in temperature (°F)	100±10

2. Record full load performance data at the following speeds (1800 & 1200 rpm)
3. Run reference torque map
4. Run practice cycles
5. Conduct natural soak until the engine oil sump is stabilized below 86 °F.
6. Run cold cycle, 20 minute soak, and hot cycle. Additional hot cycles run as required by the test matrix.
7. Repeat 5 and 6 to complete test matrix for each fuel.

2.2 Fuel and Fuel Change Procedures

The required specification ranges for the fuels are presented in Table 1. The pre-1993 diesel fuel was supplied by Paramount Petroleum, the low aromatic fuel by Chevron, and the alternative formulation fuel was a splash mixed blend of equal volumes of fuel from the three major retailers in the South Coast Air Basin (Chevron, ARCO, and Texaco). Fuel analyses provided by the supplier and determined by the ARB EL Monte and Core Laboratories are presented inTable 2. All fuels met the required specification ranges.

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Table 1 Diesel Fuel Specification Ranges

Fuel Type	Pre-1993	Low Aromatic	Alternative Formulation
Aromatic HC-Vol. %	33	10 max.	20-25
Sulfur-ppm Wt.	<5000	500 max.	100-300
Cetane Number	>40	48 min.	50-55
PAH - Wt. %	8	1.4 max.	2-5
Nitrogen - ppm Wt.	300-600	10 max.	40-500

Fuel was stored in sealed 55 gallon drums prior to use. Prior to testing with each fuel, the engine oil was drained and filled with new oil, and the oil and fuel filters were changed. Oil analysis results are presented in Table 3. The engine mapping procedures and at least two practice cycles, as outlined in Section 2.1, were conducted at the start of testing with each new fuel. In addition to verifying that the statistical criteria for transient testing were satisfied, the practice cycles also served to precondition the CVS dilution tunnel for the changes in emissions associated with each fuel.

2.3 Test Sequence

To meet the sampling requirements for this project, each fuel was tested under a multi-cycle test sequence. For each fuel, the engine mapping procedures and the practice cycles were run and then the engine was allowed to stand overnight at soak temperatures of 68 to 86°F in preparation for cold-start testing the following day. During each day's testing, a cold-start transient test was followed at 20 minute intervals by a sequence of hot-start transient tests. At the end of the day's testing the engine was again allowed to soak overnight in preparation for the next day's testing. The following fuel testing sequence was followed: pre-1993, low aromatic, alternative formulation, retest with pre-1993. Testing at the beginning (initial) and end (final) of the sampling period with the pre-1993 fuel allowed an assessment of the effects of any drift in engine emissions during the testing period. Table 4 summarizes the test cycles conducted for each fuel. Test cycles, and samples collected during these cycles are designated by the Julian Date, the type of cycle (cold or hot), and for multiple hot cycles run on the same day, the cycle sequence (hot 1, hot 2, hot 3, etc.).

Table 2. Fuel Analyses.

	Pre-1993			Low Aromatic			Reformulated Blend		
Analytical Laboratory	Core Labs	Paramount	CARB	Core Labs	Chevron	Core Labs	CARB "A"	CARB "B"	CARB "C"
API Gravity	32.8	32.8		37.2	37.3	37.1			
Sulfur, ppm wt.	349.7	361		<0.1	<6	71.3	241	50.6	<10
Nitrogen, ppm wt.	352			<1	0.54 microgm/mL	205			
SFC, wt %									
Aromatics	31.0	30.5	28.8	4.3	4.0	22.3	22.5	23.3	23.3
Polynuclear Aromatics	5.9	7.4	6.17	0.7	0.7	4.1	4	4.33	2.4
Non-Aromatics	69.0			95.7		77.7			
Boiling Point Dist., °F									
IBP	389	382		345		386			
5% point	427			408		424			
10% point	448	453		443	440	440			
20% point	476	478		485		466			
30% point	494			509		489			
40% point	512			530		511			
50% point	529	530		546	548	530			
60% point	547			561		550			
70% point	567			575		568			
80% point	592			592		588			
90% point	627	628		616	616	614			
95% point	665			638		641			
EP	708	694		663		661			
% recovery	98.0	98.0		98.2		98.3			
% residue	0.9	1.0		1.0		1.0			
% loss	1.1	1.0		0.8		0.7			
Cetane Number D-613	43.5			54.2		54.4			
Viscosity @ 40°C, cSt	3.50	3.42		3.52		3.27			
Flash Point, °F	169	168		144		162			
Cloud Point, °F	12	20		10		14			
Pour Point, °F	10			10		10			
Ash Content, routine	<0.001			<0.001		<0.001			
Copper Strip Corrosion	1A	1A		1A		1A			
Elemental Analyses (mg/kg)									
Antimony (Sb)	ND			ND		ND			
Arenic (As)	ND			ND		2.1			
Berylium (Be)	ND			ND		ND			
Cadmium (Cd)	ND			ND		ND			
Chromium (Cr)	ND			ND		ND			
Cobalt (Co)	ND			ND		ND			
Copper (Cu)	ND			ND		ND			
Lead (Pb)	ND			ND		ND			
Manganese (Mn)	ND			ND		ND			
Mercury (Hg)	<0.20			<0.2		<0.2			
Nickel (Ni)	ND			ND		ND			
Selenium (Se)	<0.20			<0.1		<0.1			
Chloride	<10			20		56			

PRELIMINARY DRAFT

Table 3 Oil Analysis

OIL	
Analytical Laboratory	Core Labs
Elemental Analyses (mg/kg)	
Antimony (Sb)	ND
Arenic (As)	ND
Berylium (Be)	ND
Cadmium (Cd)	ND
Chromium (Cr)	ND
Cobalt (Co)	ND
Copper (Cu)	ND
Lead (Pb)	ND
Manganese (Mn)	ND
Mercury (Hg)	<0.2
Nickel (Ni)	ND
Selenium (Se)	0.3
Chloride	230

2.4 Los Angeles County Metropolitan Transit Authority (LACMTA) Dilution Tunnel Facility and Measurements of THC, CO, CO_2, NO_x, and PM.

All sampling was performed at the LACMTA test facility using a Horiba CVS-48 HDD constant volume sampler (CVS). The Horiba CVS consists of an 18" primary dilution tunnel and three critical flow venturis providing for dilute bulkstream flow rates of 1500 scfm, 2500 scfm, 3000 scfm and 4000 scfm. 3000 scfm flow was utilized for this study. A Horiba FIA-43A-2 heated flame ionization detector (HFID) analyzer was used for the continuous measurement of HCs. A Horiba CLA-22A heated chemiluminesence (CL) analyzer was used for the continuous measurement of NO_X. A Horiba AIA-23 nondispersive infrared (NDIR) analyzer was used for measurements of CO and CO_2. The Horiba Double Dilution Proportional Sampler was used to collect the total PM emitted during the transient emission test. Samples were extracted from the CVS primary dilution tunnel, diluted with filtered air in the secondary dilution tunnel, and collected on a pair (e.g., primary and secondary) of 70 mm filters. The secondary dilution tunnel is 5" in diameter and the 70 mm filters were Pallflex T60A20 glass fiber filters. Sampling and analysis procedures for THC, CO, CO_2, NO_x, and particulate followed the procedures outlined in CFR 86.1310-1340.

Statistical Analysis Differences in means between the fuel types for the measured emissions were tested using the one-way Analysis of Variance (ANOVA). The one-way ANOVA is the best test for differences in means here because of the different sample sizes within treatments resulting from the vehicle test matrix. The one-way ANOVA also has the advantage of having the maximum number of error degrees of freedom for testing the mean differences between fuel types. For variables where the ANOVA indicated significant differences existed between fuel types, paired comparisons were conducted using the Fisher's Protected Least Significant Difference (PLSD) test for unequal sample sizes (Abacus Concepts, StatView). The Fisher PLSD test is a relatively liberal paired comparison test which is "protected" by the requirement that the test of the main effect must be significant. The sample mean and variance were used to calculate the 95% confidence limits for each variable within each fuel type using the standard formula:

$$\text{Lower Limit} = \text{mean} - t_\alpha * \text{standard error}$$

$$\text{Upper Limit} = \text{mean} + t_\alpha * \text{standard error}$$

where t_α is the two-tailed critical value of the t distribution at level α.

Table 4 Test/Sampling Cycles Run for Each Fuel

Pre-1993 Diesel Fuel

Test Date	12/2/96	12/3/96	12/4/94	12/5/96	12/6/96	1/8/97	1/9/97
Test Cycles	337CS	338CS	339CS	340CS	341CS	8CS	9CS
	337H1	338H1	339H1	340H1	341H1	8H1	9H1
	337H2	338H2	339H2	340H2	341H2	8H2	9H2
	337H3	338H3	339H3	340H3	341H3	8H3	9H3
		338H4	339H4	340H4		8H4	9H4
		338H5	339H5			8H5	9H5
		338H6	339H6			8H6	9H6
		338H7	339H7			8H7	9H7
		338H8					
		338H9					

Low Aromatic Diesel Fuel

Test Date	12/9/96	12/10/96	12/11/96	12/12/19
Test Cycles	344H1	345CS	346CS	347CS
	344H2	345H1	346H1	347H1
	344H3	345H2	346H2	347H2
	344H4	345H3	346H3	347H3
		345H4	346H4	347H4
			346H5	347H5
			346H6	347H6

Reformulated Diesel Blend

Test Date	12/16/96	12/17/96	12/18/96	12/19/96	12/20/96
Test Cycles	351CS	352CS	353CS	354CS	355CS
	351H1	352H1	353H1	354H1	355H1
	351H2	352H2	353H2	354H2	355H2
	351H3	352H3	353H3	354H3	355H3
	351H4	352H4	353H4	354H4	355H4
	351H5	352H5	353H5	354H5	355H5
	351H6	352H6	353H6	354H6	355H6
		352H6	353H7	354H7	355H7

Figure 1 presents a schematic of the LACMTA engine dynamometer dilution tunnel and the associated sampling systems utilized for collection of samples for detailed chemical and physical analysis. Specific procedures utilized are described below.

2.5 Speciated Hydrocarbons (C_1-C_{12})

Samples for the C_1-C_{12} HC speciation were collected in 8 L black Tedlar GC bags. At the end of a test run, a PTFE-coated diaphragm pump was utilized to transfer the samples from the CVS bag system to the GC bags. For each test run a background and emission sample were collected. Final reported results are background corrected. New sets of bags were utilized for each fuel to avoid cross contamination. Prior to use, bags were filled with vehicle emission zero (V.E.Z.) grade nitrogen and checked for impurities. Prior to reuse, bags were evacuated and filled with V. E. Z. grade nitrogen three times. Hydrocarbon speciation analyses utilized the Auto/Oil Phase II protocol (Siegl, et al., 1993). Light hydrocarbons (C_1 through C_4) were measured using a Hewlett-Packard (HP) 6880 Series GC with a flame ionization detector (FID) maintained to 250° C. A 15 m x 0.53 mm polyethylene glycol pre-column and a 50 m x 0.53 mm aluminum oxide "S" deactivation porous layer open tubular (PLOT) column were used. A 5 ml stainless steel sample loop was conditioned with the sample from the GC bag prior to analysis. A second HP 6880 Series GC with a FID maintained to 300° C was used to measure the C_4 to C_{12} hydrocarbons. A 2 m x 0.32 mm deactivated fused silica pre-column and a 60 m x 0.32 mm HP-1 column was used. A 5 ml stainless steel sample loop was conditioned with the sample from the GC bag prior to analysis. Analyses were completed within four hours of sample collection.

2.6 Oxygenated Organics

Samples for analysis of oxygenated organics were collected utilizing Waters Sep-Pak Silica cartridges coated with acidified 2,4-dinitrophenylhydrazine (DNPH) from the CVS dilution tunnel through a heated sample line (110 °C) with the sample probe in the same location as the integrated (i.e., continuous) gaseous and particle sample probes, and from the test cell for a background ambient air measurement. All results presented are background corrected. Sample flows were maintained at approximately 1.0 L/min with needle valves and measured with calibrated dry gas meters located downstream of the DNPH cartridges. DNPH cartridges were sealed and stored at 0°C prior to use and after sampling until analyzed. DNPH cartridges were analyzed using the Auto/Oil Phase II protocol (Siegl, et al., 1993). Cartridges were eluted (via gravity feed) with 5 ml of acetonitrile and transferred to liquid chromatography (LC) vials and capped for analysis.

LOS ANGELES COUNTY METROPOLITAN TRANSPORTATION AUTHORITY
ENGINE DYNAMOMETER SAMPLING SYSTEM

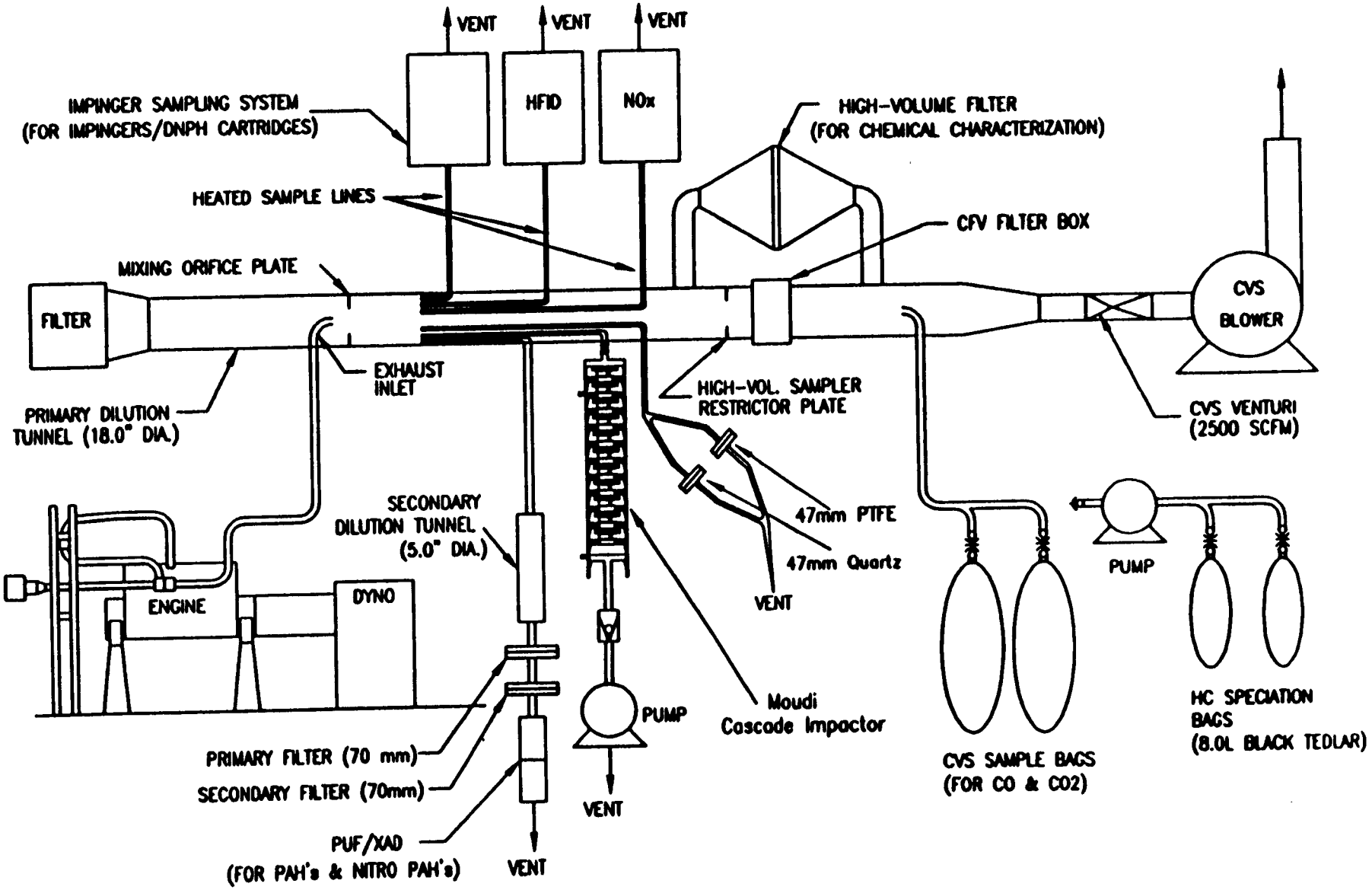

Figure 1

CE-CERT/UC RIVERSIDE	MTA ENGINE DYNAMOMETER SAMPLING SYSTEM	FILE NAME: B:\VERN\MTA.V3	SCALE: NA	DATE: July 6, 1999	REVISED BY: AC	REVISION NO.: 0

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A Shimadzu SCL 10A high performance liquid chromatograph (HPLC) with a variable ultraviolet detector and a 5 μm Deltabond AK C18 column were used for analysis of oxygenates. Analyses were performed within 36 hours of sample collection.

2.7 Particle Size Measurement

A Micro Orifice Uniform Deposit Impactor (MOUDI), manufactured by MSP Corporation (Minneapolis, MN), was used for particle size measurements. Due to limitations in the number of sampling ports, impactor samples were extracted from the primary dilution tunnel with an isokinetic sample probe in the same location as the integrated gaseous and particulate sample probes (see Figure 1). Measurement of the diluted exhaust gas temperature immediately in front of the MOUDI showed a maximum temperature of 38.5 °C, well below the 51.7 °C maximum temperature required by the CFR. The MOUDI was operated at a flow rate of 30 lpm with 4 stages having aerodynamic diameter cut points of 10, 5.6, 3.2, and 1.8 μm, together with a 47 mm 2.0 μm Gelman Teflon Membrane backup filter for collection of particles less than 1.8 μm. Aluminum foil substrates were used for the impaction plates. Filter and substrate samples were stored in sealed and labeled plastic petri dishes in a cooler packed with blue ice for transport to and from the LACMTA test facility. Sample flow was controlled with a needle valve and calibrated orifice with total flow measured with a dry gas meter. Filter and aluminum substrate weights were determined with an ATI Orion Cahn ultra-microbalance to a precision of ±10 μg. Tare and final substrate weights were determined after at least 24 hours equilibration at 25±0.5 °C and a relative humidity of 40±5%.

2.8 Elemental, Inorganic Ion, and Elemental and Organic Carbon

Due to limitations in the number of sampling ports, samples were taken from the primary dilution tunnel with an isokinetic sample probe in the same location (i.e., sample zone) as the integrated (i.e., continuous) and particulate sample probes (see Figure 1). Measurement of the diluted exhaust gas temperature immediately in front of the filters showed a maximum temperature of 38.5 °C, well below the 51.7 °C maximum temperature required by the CFR. The sampling probe was fitted with a flow splitter matted to two 47 mm filter holders. One filter holder was fitted with Pallflex quartz-fiber 2500 QAP-UP filters prefired at 900 °C for three hours to remove background carbon for organic and elemental carbon analyses and determination of sulfate, nitrate, potassium and ammonium ions. A backup quartz fiber filter was collected to assess for artifact organic carbon collection. The other filter holder was fitted with 2.0 μm Gelman Teflon Membrane filters for elemental analysis. Sample flows were maintained at 30 lpm using needle valves in series with

calibrated rotometers and a vacuum pump. All filters were stored in sealed and labeled plastic petri dishes in a cooler packed with blue ice for transport to and from the LACMTA test facility and stored in a refrigerator prior to shipment for analysis. Filter samples were shipped to the Desert Research Institute (DRI) in a cooler with blue ice packs.

Teflon membrane filters were analyzed for elements using x-ray fluorescence (XRF) at DRI. Quartz fiber filters were analyzed for elemental and organic carbon by DRI using the thermal/optical reflectance (TOR) method (Chow et al., 1993) from a 0.512 cm^2 punch from the filter. Sulfate, nitrate, and potassium analyses were performed on the remainder of the quartz fiber filter by ion chromatography, and ammonium analysis by automated colorimetry using the indophenol method.

2.9 Particulate-Bound and Gas-Phase PAH and Nitro-PAH

Sample Collection: The high volume sampling media for PAH and nitro-PAH analysis consisted of 8 in. x 10 in. Teflon-impregnated glass fiber (TIGF) filters backed up by polyurethane foam (PUF) adsorbent in a glass module. Two TIGF filters (front and back) were backed up by two PUF plugs (front and back). The sampling assembly is depicted in Figure 4 with the exception that the PUF sorbent module was not backed up by XAD sorbent. A schematic of the high volume sampling train is shown in Figure 2.

The TIGF filters (Pallflex T60A20) were pre-cleaned by a 20-hr Soxhlet extraction with dichloromethane (DCM, Fisher Optima) followed by drying (60°C, 3 hr) and a 20-hr Soxhlet extraction with methanol (MeOH, Fisher Optima). The filters were dried for four hours at 60 °C and placed onto a rack in a small weighing chamber for equilibration at 18-25°C and 40-50 percent relative humidity. After a 24-hr equilibration, the filters were weighed on a precision balance (Sartorius) and stored individually in pre-labeled glassine envelopes which were placed in numbered manilla envelopes.

The pre-cut PUF plugs were obtained from S&W Plastics (Riverside, CA). Each sampling train consisted of a front PUF plug (3 in. diam. x 3.5 in. long) and a shorter back PUF plug (3 in. diam. x 1 in. long). The purpose of the back PUF plug was to check for breakthrough from the main front plug. The PUF plugs were pre-cleaned by extraction with a large Soxhlet apparatus, first with DCM (20 hr) followed by drying (60°C, 3 hr) and Soxhlet extraction with MeOH (20 hr) and drying. The PUF plugs were wrapped in MeOH-rinsed foil and placed in Ziploc bags inside glass canning jars and stored in the dark at -20 °C. The jars containing the plugs were transported to the LACMTA

Emissions Test Facility in a cooler and just prior to sampling jars were removed from the cooler and allowed to warm to room temperature before opening.

After sampling, the two PUF plugs were wrapped in foil and each was placed in a separate Ziploc bag before returning them to the glass jar. Each filter was folded in half with the particulate-laden faces together and returned to its respective glassine envelope. The glassine envelope containing the filters was then placed in a Ziploc bag, sealed, and returned to the manilla envelope. PUF jars and filters were put promptly into a cooler with blue ice for transport to SAPRC. The samples were transported to SAPRC the same day they were taken and immediately placed in a freezer at -20 °C where they were stored until extracted. The samples taken were either from a single test cycle or from two consecutive test cycles as listed in Table 5.

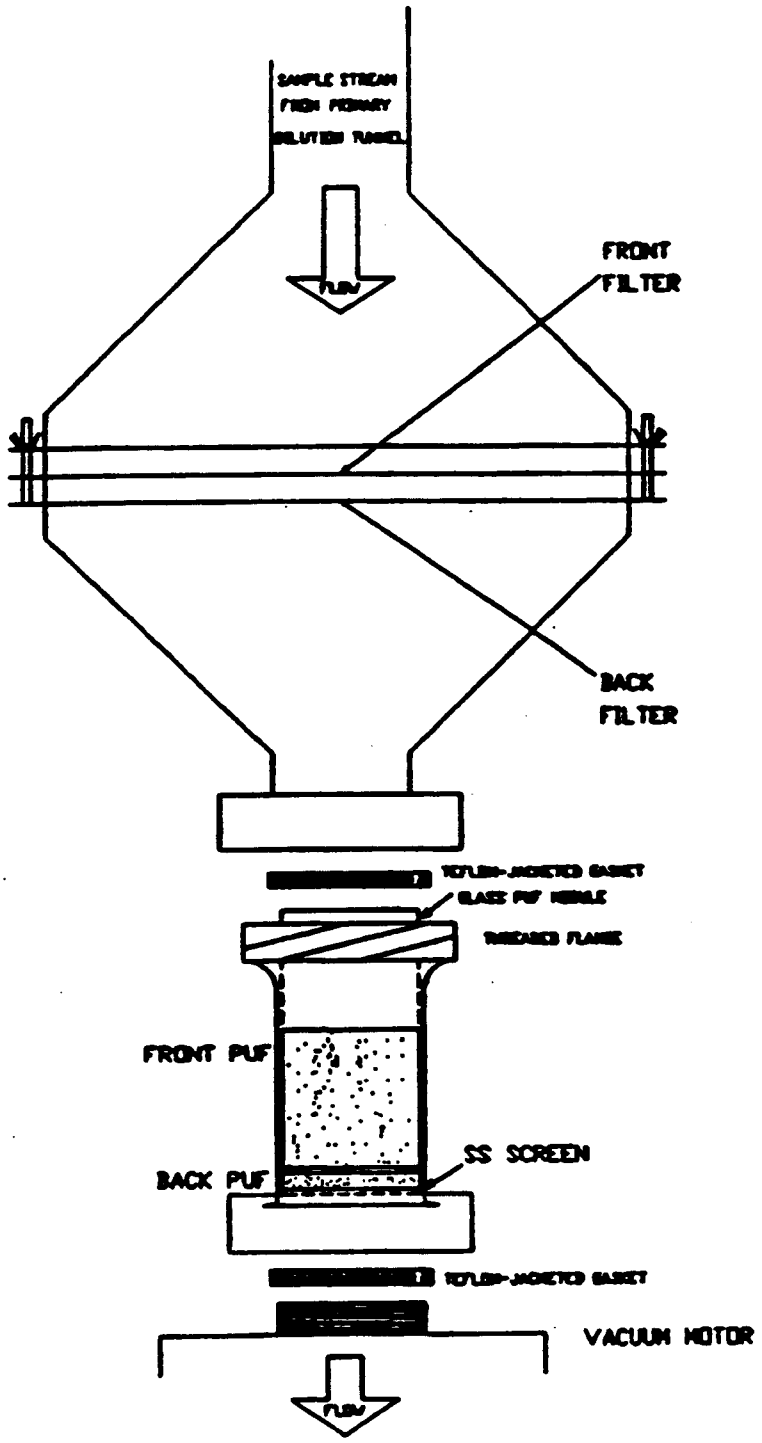
High-Volume Sampler Particulate Weights: Samples were collected at the LACMTA facility in December 1996. Following collection of particulate and gas-phase emissions onto T60Å20 high volume filters and PUF plugs, samples were stored in a freezer at SAPRC until analyzed. Filters were removed from the freezer and equilibrated in a small weighing chamber maintained at 18-25°C and relative humidity of 40-50 percent. Filters were weighed on a Sartorius precision balance after overnight equilibration.

Particulate and gas-phase samples collected on filters and PUFs with the high volume sampling apparatus at LACMTA, along with particulate weights and the hot-cycle samples designated for PAH and nitro-PAH analysis are listed in Table 5. Also noted are the samples that were extracted, fractionated by HPLC and shipped to UC Davis for mutagenicity testing.

Chemicals: HPLC grade acetonitrile, hexane, methanol and methylene chloride were purchased from Fisher Scientific (Optima grade). Standard Reference Material (SRM) 1491, aromatic hydrocarbons in hexane/toluene, was obtained from the National Institute of Standards and Technology (NIST). Other PAH standards included cyclopenta[cd]pyrene, indeno[1,2,3-cd]fluoranthene, dibenzo[a,h]pyrene, and dibenzo[a,i]pyrene (Dr. W. Schmidt, Sieker Landstrasse 19, 2070 Ahrensburg, Germany), benzo[c]phenanthrene, dibenzo[a,e]pyrene, dibenzo[a,l]pyrene, benzo[b]chrysene, benzo[c]chrysene, and benzo[ghi]fluoranthene (BCR), coronene, dibenz[a,c]anthracene, and dibenz[a,j]anthracene (Aldrich).

PRELIMINARY DRAFT

Figure 2 Schematic of high volume sampling system



PRELIMINARY DRAFT

Deuterated PAH standards included naphthalene-d_8 (Aldrich), acenaphthene-d_{10} and fluoranthene-d_{10} (MSD Isotopes), anthracene-d_{10}, phenanthrene-d_{10}, benzo[a]pyrene-d_{12}, perylene-d_{12}, and dibenz[a,h]anthracene-d_{14} (Cambridge Isotopes), chrysene-d_{12} and pyrene-d_{10} (ICN-KOR) and benzo[b]fluoranthene-d_{12} (C/D/N). Deuterated 1-nitronaphthalene-d_7 was purchased from Aldrich. 1-Nitropyrene-d_9 and 2-nitrofluorene-d_9 were previously synthesized in-house.

Sample Extraction and Fractionation of T60A20 Filters and PUF Samples: Three hot/hot cycle particulate samples were selected for chemical analysis for each fuel type (pre-1993 reference, low aromatic, and alternative formulation blend) as listed in Table 5. Prior to Soxhlet extracting these samples, a hot-cycle screening sample was chosen for each diesel fuel to determine the appropriate level of deuterated internal standards (IS) with the goal of adding IS to the 9 samples at levels comparable to the native PAH in the samples. For each sample, the front and back filters were combined, spiked with deuterated IS and Soxhlet extracted 16 hr in DCM. Front and back PUFs were treated as independent samples to allow quantitative collection of an individual PAH to be determined by the absence of break-through onto the back PUF. Each extract was concentrated by rotary evaporation and filtered through a Gelman Acrodisc CR-PTFE 0.2 mm. Table 6 shows the internal standard (IS) amounts of deuterated PAH and deuterated nitro-PAH added to the T60A20 filters prior to extraction, and the IS amounts added to the front and back PUFs are listed in Table 7.

For each filter analysis sample and each front PUF analysis sample, 25% of the soxhlet extract was concentrated for PAH analysis by GC-MS, 50% was fractionated by HPLC for nitro-PAH analysis and 25% was reserved. For each back PUF sample, 25% was used for PAH analysis, 37.5% for fractionation and subsequent nitro-PAH analysis, and 37.5% was reserved..

Samples were fractionated prior to GC-MS nitro-PAH quantification and mutagenicity testing (UCD) using a Hewlett-Packard 1050 HPLC equipped with a Model 1040M Diode-array detector (DAD) interfaced to a Foxy 2200 fraction collector. The HPLC was fitted with a Spherisorb 5 μm Si column with a 7 micron Brownlee Si NewGuard precolumn. The solvent programming and sample collection times were as shown on Table 8.

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Table 5 T60A20 High Volume Samples and PUF Samples Collected at LACMTA

Sampling Date	Fuel	Test Cycles	SAPRC Filter No.	Particulate Wt.[a](mg)	PUF No.[b]	Analysis
12/3/96	Pre-1993	338CS	96-12, 96-13		96-25	
	Pre-1993	338H2,H3	96-14, 96-15	99.6	96-26	HPLC, GC-MS
	Pre-1993	338H4,H5	96-16, 96-17	106.6	96-27	HPLC, GC-MS
	Pre-1993	338H6,H7	96-18, 96-19	88.6	96-28	HPLC, GC-MS
	Pre-1993	338H8,H9	96-20, 96-21	79.9	96-29	Mutagenicity
12/4/96	Pre-1993	339CS	96-22, 96-23		96-30	
	Pre-1993	339H1	96-24, 96-25	34.1	96-31	GC-MS[c]
	Pre-1993	339H2,H3	96-26, 96-27	85.7	96-32	
	Pre-1993	339H4,H5	96-28, 96-29	79.7	96-33	
12/10/96	Low Aromatic	345CS	96-34, 96-35		96-36	
	Low Aromatic	345H1,H2	96-36, 96-37	71.5	96-37	
	Low Aromatic	345H3,H4	96-38, 96-39	55.9	96-38	
12/11/96	Low Aromatic	346CS	96-40, 96-41	38.9	96-39	
	Low Aromatic	346H1,H2	96-42, 96-43	97.3	96-40	
	Low Aromatic	346H3,H4	96-44, 96-45	65.5	96-41	Mutagenicity
	Low Aromatic	346H5,H6	96-46, 96-47	62.2	96-42	HPLC, GC-MS
	Low Aromatic	346H7	96-48, 96-49	40.5	96-43	GC-MS[c]

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Table 5. T60A20 High Volume Samples and PUF Samples Collected at LACMTA (cont.)

Sampling Date	Fuel	Test Cycles	SAPRC Filter No.	Particulate Wt.[a](mg)	PUF No.[b]	Analysis
12/12/96	Low Aromatic	347CS	96-50, 96-51		96-44	
	Low Aromatic	347H1,H2	96-52, 96-53	88.2	96-45	
	Low Aromatic	347H3,H4	96-54, 96-55	93.4	96-46	HPLC, GC-MS
	Low Aromatic	347H5,H6	96-56, 96-57	57.4	96-47	HPLC, GC-MS
12/16/96	Reformulated	351CS	96-60, 96-61		96-50	
	Reformulated	351H1,H2	96-62, 96-63	82.8	96-51	Mutagenicity
	Reformulated	351H3,H4	96-64, 96-65	80.6	96-52	HPLC, GC-MS
	Reformulated	351H5,H6	96-66, 96-67	78.0	96-53	GC-MS[c]
12/17/96	Reformulated	352CS	96-68, 96-69		96-55	
	Reformulated	352H1,H2	96-70, 96-71	76.5	96-56	
	Reformulated	352H3,H4	96-72, 96-73	91.3	96-57	HPLC, GC-MS
	Reformulated	352H5,H6	96-74, 96-75	85.9	96-58	HPLC, GC-MS

[a]Total of front and back filter.

[b]Consists of front and back PUF.

[c]Internal standard screening sample used to determine levels for analysis samples.

Table 6. T60A20 High-Volume Filter Internal Standards (µg per sample).

					Alternative Formulation Blend	
	Screening Sample[a]	Analytical Samples[b]	Screening Sample[a]	Analytical Samples[b]	Screening Sample[b]	Analytical Samples[b]
naphthalene-d_8	8.86	13.3	6.64	13.3	6.64	13.3
acenaphthene-d_{10}	10.5	15.75	7.88	15.75	7.88	15.75
phenanthrene-d_{10}	9.52	14.3	7.14	14.3	7.14	14.3
anthracene-d_{10}	10.19	15.28	7.64	15.28	7.64	15.28
fluoranthene-d_{10}	10.41	15.62	7.81	31.5	7.81	31.5
pyrene-d_{10}	9.73	14.6	7.3	33.7	7.3	33.7
chrysene-d_{12}	8.03	12	6.02	12	6.02	12
benzo[a]pyrene-d_{12}	9.66	14.5	7.24	14.5	7.24	14.5
perylene-d_{12}	10.55	15.82	7.91	15.82	7.91	15.82
dibenz[a,h]anthracene-d_{14}	10.14	15.21	7.6	15.21	7.6	15.21
1-nitronaphthalene-d_7	1.18	1.77	0.89	1.77	0.89	1.77
2-nitrofluorene-d_9	1.69	2.52	1.26	2.52	1.26	2.52
1-nitropyrene-d_9	9.69	14.5	7.27	14.5	7.27	14.5

[a]Single-cycle hot.
[b]Two-cycle hot.

Table 7 PUF Internal Standards (µg per PUF).

	Pre-1993 Reference			Low Aromatic			Alternative Formulation Blend		
	Screening Sample[a,b]	Analytical Samples[c]		Screening Sample[a,b]	Analytical Samples[c]		Screening Sample[b,c]	Analytical Samples[c]	
		Front	*Back*		*Front*	*Back*		*Front*	*Back*
naphthalene-d_8	5.43	10.8		5.43	10.8		10.8	10.8	
phenanthrene-d_{10}	5.14	109	10.9	5.14	109	10.9	10.2	109	10.9
anthracene-d_{10}	3.31	6.62	0.66	3.31	6.62	0.66	6.62	6.62	0.66
fluoranthene-d_{10}	5.94	11.9	1.19	5.94	11.9	1.19	11.9	11.9	1.19
pyrene-d_{10}	24	48.1	0.48	24	48.1	0.48	48.1	48.1	0.48
chrysene-d_{12}	1.92	3.84	0.38	1.92	3.84	0.38	3.84	3.84	0.38
1-nitronaphthalene-d_7	6.03	12.1	1.21	6.03	12.1	1.21	12.1	12.1	1.21
2-nitrofluorene-d_9	6.19	12.4	1.24	6.19	12.4	1.24	12.4	12.4	1.24

[a]Single-cycle hot.

[b]Front PUF only.

[c]Two-cycle hot.

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Table 8 Hewlett Packard 1050 HPLC Solvent Program.

Time (min)	% Hexane	%CH_2Cl_2	% Acetonitrile
0	100	0	0
10	100	0	0
15	95	5	0
40	0	100	0
50	0	100	0
60	0	0	100
70	0	0	100
75	0	100	0
80	0	100	0
85	100	0	0
95	100	0	0

Foxy 2200 Fraction Program

Fraction	Time (min)	Compounds
waste	0 - 1	
1	1 - 10	
2	10 - 19	PAH
3	19 - 26	PAH
4	26 - 37	nitro-PAH
5	37 - 46	dinitro-PAH
6	46 - 55	
7	55 - 64	
8	64 - 73	
9	73 - 82	

GC-MS Analyses for PAH: The PAH were quantified using a Hewlett-Packard Model 5890 Series Gas Chromatograph equipped with a 7673A Automatic Sampler and interfaced to a Model 5970 quadrupole mass selective detector operating in the selected ion monitoring (SIM) mode. As noted above, three replicate emission samples for each of the three fuel types were collected. The 27 samples (9 filter, 9 front PUF, 9 back PUF) were analyzed by triplicate injections onto the GC-MS. Compounds were identified based on their selected ion response and by matching their retention times with those of known standards using a 60m DB-5MS capillary column for separation. Measuring the retention times, as the difference between the compound and the nearest deuterated internal standard corrected for small retention time, shifts between GC runs. Three sets of analyses with different GC-MS conditions and calibration standards were made to quantify the PAH (filter 128-278 Daltons; filter up to 302 Daltons; PUF PAH) and details of the analysis conditions are given in Table 9.

Calibration standards were run to determine response factors for each PAH quantified relative to the appropriate deuterated internal standard (IS). The PAH, ions monitored, and compounds used as IS for each PAH are given in Table 10. Response factors (RF) were calculated as (area/ng PAH)/(area/ng IS). The amount of a given PAH was calculated as [(area PAH) x ng IS]/[(area IS x RF)].

For each 2-cycle sample, the PAH concentrations were calculated on the basis of the weight of particulate matter (PM) collected (µg PAH/mg PM). For each PAH, the PAH emissions rate (µg PAH/bhp-hr) was calculated by dividing the PAH concentration by the mean of the PM emission rate (g/bhp-hr) over the two cycles.

GC-MS Analyses for Nitro-PAH: Two sets of analyses with different GC-MS conditions and standards were run to quantify the nitro-PAH in the filter and PUF samples (see Table 9). Nitro-PAH are more labile than the parent PAH and for this reason the nitro-PAH GC-MS analyses were made using cool on-column manual injections. Unlike the PAH, which generally exhibit only a single major ion peak, $[M]^+$, in their spectra, the nitro-PAH exhibit significant characteristic fragmentation in their mass spectra. Therefore, in addition to the molecular ion, $[M]^+$, characteristic fragment ions were also monitored. The ions monitored for the specific nitro-PAH and the deuterated internal standards are given in Table 11.

Table 9 GC-MS Conditions for Analysis of PAH and Nitro-PAH in Filter and PUF Extracts.

Column: 60 m DB-5MS, 0.25 mm i.d.; 0.25 μm film thicknss.
Scan mode: SIM

Sample	Injector	Injector Mode	Inj. Temp.	Detector	Column Program
Filter PAH (128 to 278 Daltons)	Splitless	Autosampler	250 C	320 C	Initial 40 C, 8 C/min to 340 C; hold 10 min
Filter PAH (up to 302 Daltons)	Splitless	Autosampler	300 C	320 C	Initial 40 C, 15 C/min to 200 C; then 4 C/min to 340 C; hold 5 min
PUF PAH	Splitless	Autosampler	250 C	300 C	Initial 40 C, 8 C/min to 300 C; hold 15 min
Filter Nitro-PAH	On-column	Manual	Cool	300 C	Initial 40 C, 15 C/min to 200 C; 4 C/min to 320 C; hold 4.5 min
PUF Nitro-PAH	On-column	Manual	Cool	300 C	Initial 40 C, 8 C/min to 300 C

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Table 10 Analytes and Internal Standards (IS) for GC-MS SIM Analyses.

Polycyclic Aromatic Hydrocarbon	SIM Ion	IS[a]	IS Ion
2,3,5-trimethylnaphthalene	170	PH-d10	188
phenanthrene	178	PH-d10	188
anthracene	178	AN-d10	188
Me-phenanthrenes/anthracenes	192	PH-d10	188
fluoranthene	202	FL-d10	212
pyrene	202	PY-d10	212
benzo[c]phenanthrene	228	CH-d12	240
benzo[ghi]fluoranthene	226	CH-d12	240
cyclopenta[cd]pyrene	226	CH-d12	240
benz[a]anthracene	228	CH-d12	240
chrysene + triphenylene	228	CH-d12	240
benzo[b+j+k]fluoranthene	252	BAP-d12	264
benzo[e]pyrene	252	BAP-d12	264
benzo[a]pyrene	252	BAP-d12	264
perylene	252	PRY-d12	264
indeno[1,2,3-cd]fluoranthene	276	DBA-d14	292
benzo[c]chrysene	278	DBA-d14	292
dibenz[a,j]anthracene	278	DBA-d14	292
indeno[1,2,3-cd]pyrene	276	DBA-d14	292
dibenz[a,h + a,c]anthracene	278	DBA-d14	292
benzo[b]chrysene	278	DBA-d14	292
benzo[ghi]perylene	276	DBA-d14	292
coronene	300	DBA-d14	292
dibenzo[a,l]pyrene	302	DBA-d14	292
dibenzo[a,e]pyrene	302	DBA-d14	292
dibenzo[a,i]pyrene	302	DBA-d14	292
dibenzo[a,h]pyrene	302	DBA-d14	292

[a]Abbreviations: PH-d10, phenanthrene-d_{10}; AN-d10, anthracene-d_{10}; FL-d10, fluoranthene-d_{10}; PY-d10, pyrene-d_{10}; CH-d12, chrysene-d_{12}; BAP-d12, benzo[a]pyrene-d_{12}; PRY-d12, perylene-d_{12}; DBA-d14, dibenz[a,h]anthracene-d_{14}.

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Table 11 Analytes and Deuterated Internal Standards for GC-MS SIM Analyses.

	SIM Ions				
Nitro-PAH	$[M]^+$	$[M-NO]^+$	$[M-NO_2]^+$	$[M-HNO_2]^+$	$[M-NO-CO]^+$
1-nitronaphthalene-d_7	180		134		
1-nitronaphthalene	173		127		115
2-nitronaphthalene	173		127		115
methylnitronaphthalenes	187				115[a]
2-nitrobiphenyl	199			152	
4-nitrobiphenyl	199			152	
5-nitroacenaphthene	199			152	
2-nitrofluorene-d_9	220		174		
2-nitrofluorene	211	194[b]	165		
9-nitroanthracene	223	193		176	165
1-nitropyrene-d_9	256	226	210		
1-nitropyrene	247	217	201	200	189
3-nitrofluoranthene	247	217	201	200	189
4-nitropyrene	247	217	201	200	189
7-nitrobenz[a]anthracene	273	243		226	
6-nitrochrysene	273	243		226	
6-nitrobenzo[a]pyrene	297	267		250	239

[a]Fragment ion is indenyl ion, characteristic of substituted naphthalenes; $[M-72]^+$ from methylnitronaphthalenes.
[b]Fragment ion is $[M-OH]^+$.

Quantification was made on the basis of the molecular ion, with the fragment ion(s) serving to confirm the identity of the nitro-PAH. As discussed above for the PAH, response factors relative to a deuterated IS were determined and used for quantification. 1-Nitronaphthalene-d_7 served as the IS for 1- and 2-nitronaphthalene. 1-Nitropyrene-d_9 was used as the internal standard to quantify 1-nitropyrene, 9-nitroanthracene and 6-nitrobenzo[a]pyrene. The emission rates of the nitro-PAH as µg/bhp-hr were also calculated as described above for the PAH.

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2.9 Vapor Phase PAH

Chemicals: HPLC grade methanol, acetone, hexane, and water were obtained from Fisher Scientific. Dichloromethane (DCM, OmniSolve) was from EM Science. Acetonitrile (ChromPure) and hexane (UV, High Purity) were from Burdick and Jackson.

Deuterated standards included methyl naphthalene-d_{10}, fluorine-d_{10}, anthracene-d_{10}, fluoranthene-d_{10}, and pyrene-d_{10} were obtained from Cambridge Isotopes Laboratories (Andover, MA). Naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} were from AccuStandard (New Haven, CT). Standard Reference Material SRM 2260, native PAHs in toluene (nominal 60 ng/ul), were obtained from NIST (Gatherberg, Maryland).

Adsorbents Pre-cut PUF plugs were obtained from North Carolina Foam, Inc. (Mount Airy, NC). Two sizes of PUF plugs were used. The PUF plugs used for the low volume sampler were nominally 3" in length and 2" in diameter. The PUF plugs used for the high volume sampler were nominally 1" in length and 3" in diameter. All PUF plugs were pre-cleaned by sequential sonication in methanol (3x) and DCM (3x) and dried in a Baker BioChemgard hood, equipped with HEPA filters.

Purified XAD-4 resin was from Alltech (Philadelphia, PA). The XAD was further purified to remove potential background interferences by sequential 15 min sonications in methanol (3x) and dichloromethane (3x). The resin was dried for 5 days under vacuum at 50°C and then stored in solvent-cleaned amber glass jars.

Low Volume Sampling Apparatus PAH samples were collected from both a high volume sampler and a low volume sampler. The low volume sampling unit is illustrated in Figure 3 and consisted of two sampling trains that were connected by a stainless steel "Y" whereby two parallel samples were collected during a single dynamometer run for bioassay and PAH analysis. Each diesel exhaust sampling train consisted of two Teflon-coated glass fiber filters, a sorbent module containing three PUF plugs, one 40 mL bed of XAD, and a rotometer connected in series. Teflon sorbent modules containing PUF and XAD were from Savillex Corp. (Minnetonka, MN). Teflon tubing was used to connect both the filter holder assembly to the complete sampling train and to the vacuum pump.

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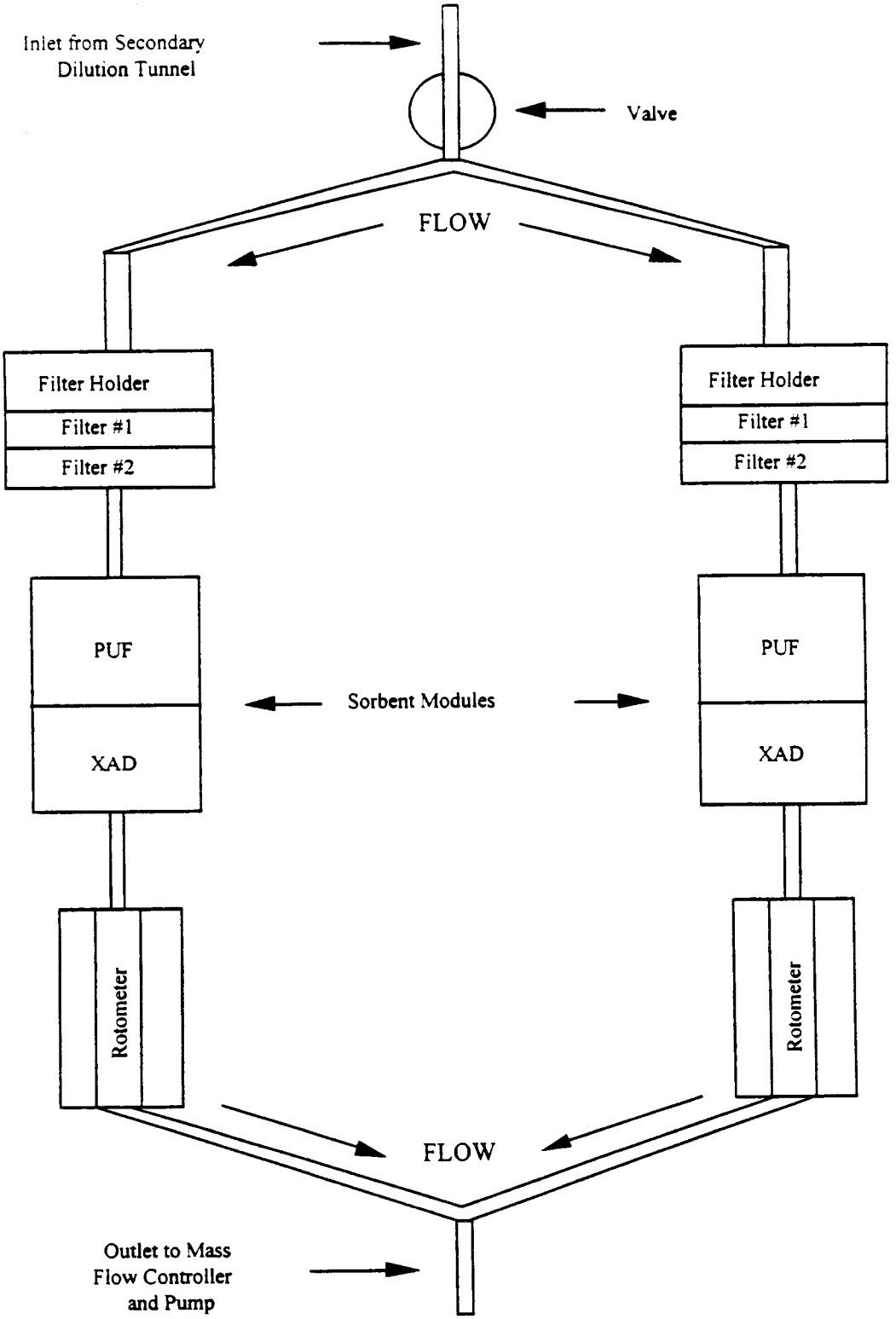

Figure 3 Particulate and Vapor-Phase Sampler.

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High Volume Sampler: The high volume sampling train is illustrated in Figure 4 and consisted of a filter assembly that housed two Teflon-coated glass fiber filters, a sorbent module containing three 3" diameter x 1" thick PUF plugs and one 60 mL bed of XAD-4, a vacuum pump, and a laminar flow element connected in series. The sampling train was inserted into the six inch diameter by-pass on the primary tunnel. The filter assembly, sorbant holder, and vacuum pump were from Grasby GMW (Village of the Cleves, Ohio) and the Lamanir Flow Element was from Meriam Instruments (Cleveland, Ohio). Glass sorbent modules (6 in. long x 76.2 mm ID) containing PUF and XAD were from R&D Glass (Berkeley, CA). A Variac was used to control the vacuum pump speed by varying the voltage which in turn controlled the flow rate through the sampler. A laminar flow element was used to measure the flow rate. Two manometers were used to measure the delta P and pressure in the tunnel. The temperature probe from the digital thermometer was located near the inlet end of the laminar flow element. Pressure and temperature measurements were immediately put into a spreadsheet and the flow was calculated in standard cubic feet per minute. Using the updated flowrate the voltage output from the Variac was made to ensure a consistent flowrate. Corrections to the flow rate were made every 2 minutes.

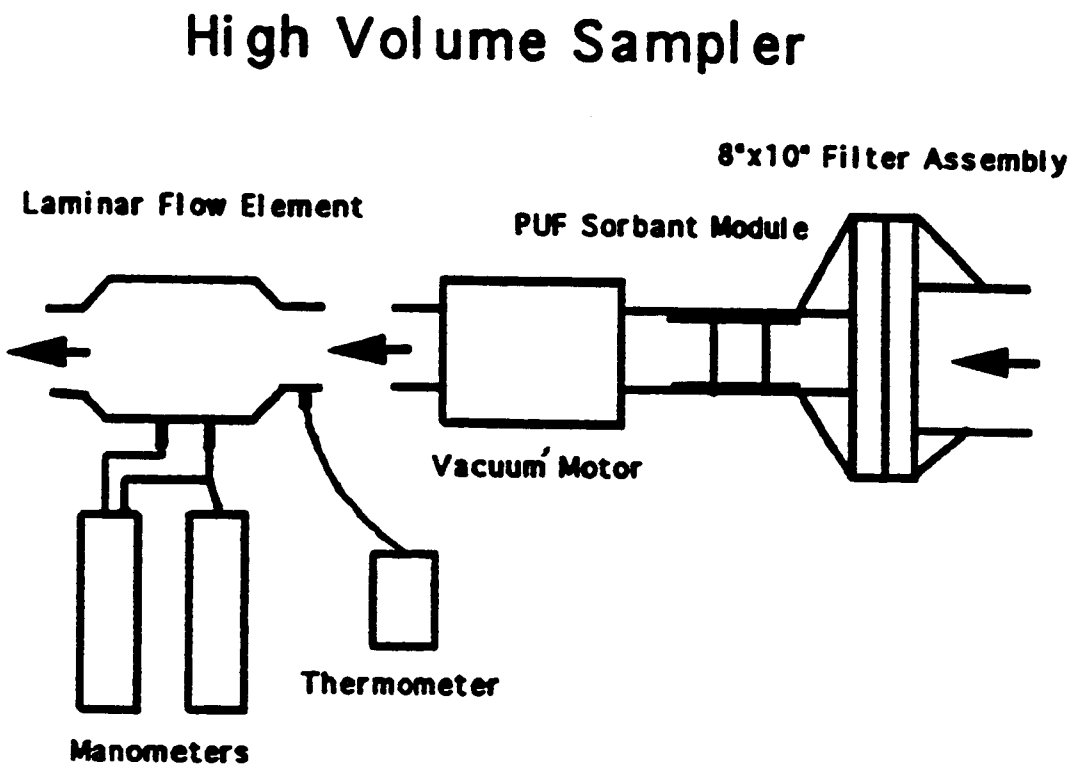

Figure 4 Schematic of High Volume Sampler used for PAH sampling.

Diesel Exhaust Sampling: In preparation for collecting diesel exhaust samples for the main study, a series of Pretest experiments were conducted at the Los Angeles County Metropolitan Transit District (LACMTA) dynamometer facility. A diagram of the diesel exhaust sampling set-up at the LACMTA facility is illustrated in Figure 5.

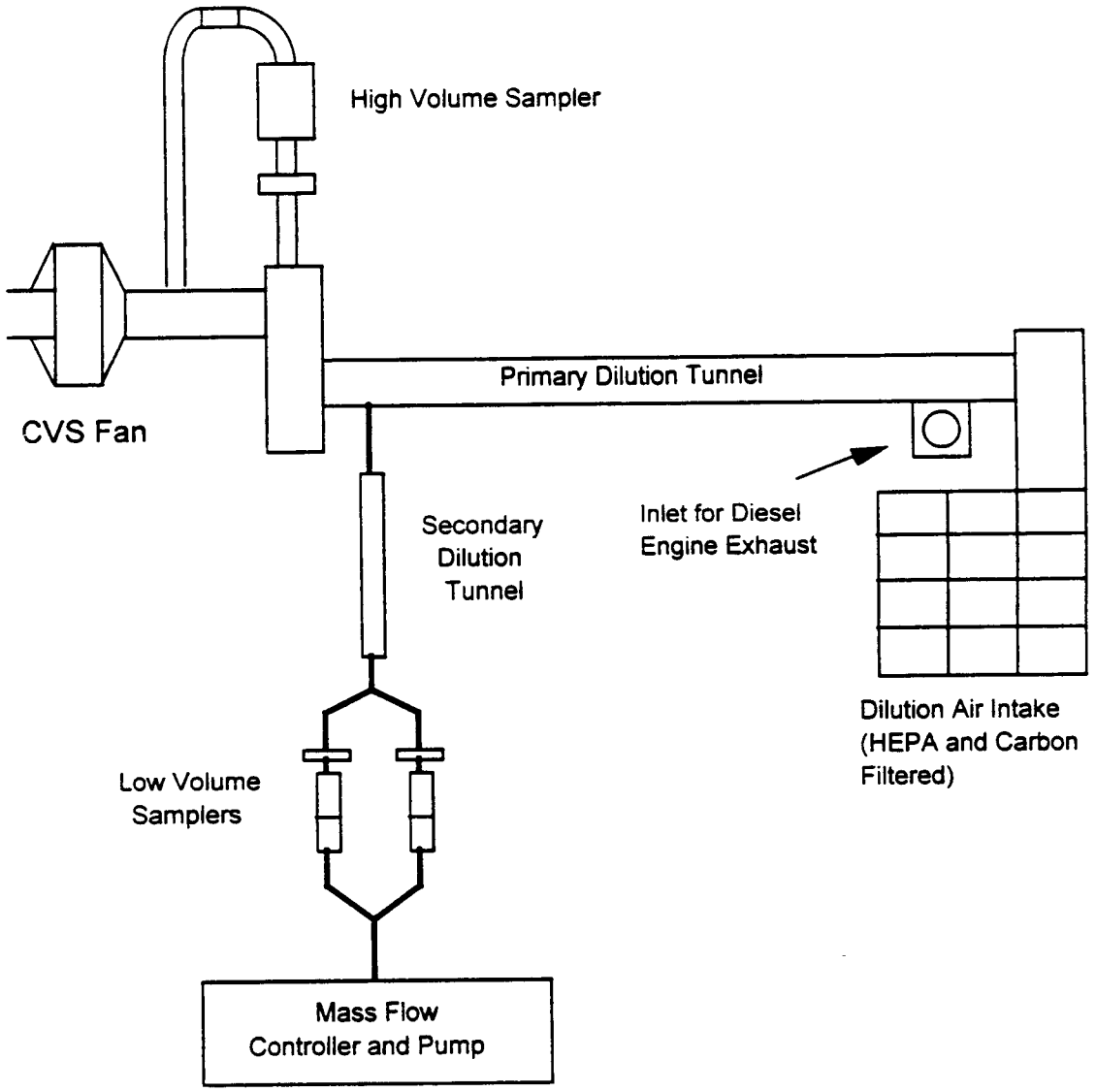

Figure 5 Dilution Tunnel for Heavy-Duty Diesel Exhaust and Sampler at the LACMTA Facility.

Initial pre-tests were conducted to test the feasibility of modifying the original Horiba high volume particulate sampler to a high volume sampler capable of collecting both particulates and semi-volatile compounds. This modification required that a sorbant module containing PUF and XAD be added to the sampling train. After numerous tests, it became apparent that the original sampler and flow meter were not compatible with the addition of the sorbant module. A substantial increase in the pressure drop, caused by the sorbant module, dropped the flow rate below the lower limit of the Venturi flow meter. Increasing the flow rate through the passive high volume sampler required that a flow restricter be placed in the main tunnel. This increases the back pressure in the main tunnel thereby forcing more flow into the high volume sampler. Concerns were raised as to whether the restricter caused the main tunnel Venturi, which controls the flow rate in the main tunnel, to run sub-critical or out of calibration. Since this would be a unacceptable condition, the high volume sampler was redesigned as an active high volume sampler that did not require a flow restricter.

In subsequent pre-tests, the flow rate through the system was increased by the addition of a high volume vacuum motor. Flow rate measurements were made by replacing the Venturi (rated from 60-200CFM) with a laminar flow element calibrated from 5cfm to 60cfm.

In the October 1996 pre-test, a blank and a sample were collected to estimate the concentration of PAHs found in the diesel exhaust.

The Main Study was also conducted at the LACMTA Emissions Test facility using 1) a Pre-October 1993 (Pre-Oct. '93) specification fuel, 2) a low aromatic fuel (Reformulated) and 3) a blend of three fuels (Reformulated Blend).

Low volume Teflon sorbent modules and high volume glass sorbant modules containing the samples, spikes, and requisite blanks were wrapped in aluminum foil throughout the sampling period to minimize potential photo-oxidation. Immediately after each sampling period, the sample and blank modules were stored at 4°C, until they were transported back to the laboratory, where they continued to be stored at 4°C until further processing.

<u>High Volume Sample Preparation:</u> The high volume diesel exhaust vapor-phase samples consisted of two filters, two PUF plugs followed by 60 mls of XAD-4 resin. The PUF and XAD were extracted separately by SFE and the filters were extracted by sonication. High volume PUF plugs were cut in half, and one half of each PUF plug was used for PAH analysis. Prior to extraction, one half of the PUF sample was spiked with 120 µl of a 20 ng/µl deuterated PAH internal

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standard mixture and 1 mls of methanol modifier was added. The PUF was extracted by SFE using supercritical carbon dioxide and the final volume of each extract was approximately 2 mls. Summary of the SFE conditions are given in Table 12.

Table 12. SFE Extraction Conditions for High Volume and Low Volume PUF and XAD-4 Samples.

Extraction Condition	PUF	XAD-4
Pressure	5000 psi	7000 psi
Temperature	75°C	100°C
Time	90 min	60 min
Modifier	10% methanol	10% methanol

A 660 µl aliquot of the SFE extract was loaded onto a Waters C18 SepPak cartridge to remove some of the hydrocarbons that interfere with GC/MS analysis. The C18 was extracted with 2 mls of methanol. The methanol extract was transferred to a Waters Silica SepPak cartridge. The methanol was allowed to evaporate on the cartridge before eluting 3 mls of hexane through the cartridge. The hexane fraction was saved for GC/MS analysis. DCM was added to a measured aliquot of SFE extract to adjust the final volume to 200 µL. The diluted extract was analyzed by GC/MS.

XAD-4 resin from the high volume sampler was well mixed and approximately 10 mls of XAD from each sample was prepared for GC/MS analysis. The XAD sample was spiked with 100 µl of a 20 ng/µl deuterated PAH internal standard mixture and 1 mls of methanol modifier was added. The XAD was extracted by SFE using supercritical carbon dioxide and the final volume of each extract was approximately 2.0 mls. Summary of the SFE conditions are given in Table 12. A 400 µl aliquot of the SFE extract was added to a Waters C-18 SepPak cartridge to remove some of the hydrocarbon interferences. The C-18 was extracted with 2 mls of methanol. The methanol extract was transferred to a Waters Silica SepPak cartridge. The methanol was allowed to evaporate on the cartridge before eluting 3 mls of hexane through the cartridge. The hexane fraction was saved for GC/MS analysis. DCM was added to a measured aliquot of the methanol extract and to just the final volume of 200 ul.

Prior to extraction the filters were divided in two with one half dedicated to bioassay analysis and the other half to PAH analysis. One half of the front and backup filter was cut into pieces and placed in an Erlmeyer flask with a screw cap. 40 µl of 5ng/ul internal standards were added to the filters. The filters were extracted 4 times in 25 mls of DCM for 20 minutes. After each sonication the sample was filtered through a 2 A filter. The flask and filter were rinsed with DCM and the washes and extractions were combined. The combined extract was concentrated to 1 ml. One-half of the sample was then added to a Waters C-18 SepPak cartridge. The DCM from the extract was allow to evaporate before the C-18 cartridge was eluted with 2mls methanol. The methanol extract was transfered to a Silica SepPak cartridge and the methanol was allowed to evaporate before eluting with 3 mls of hexane. The hexane extract was concentrated to 1 ml and prepared for GC/MS analysis.

Low Volume Sample Preparation: The low volume diesel exhaust vapor-phase samples consisted of three sets of filters, a three inch long PUF plug followed by 40 mL of XAD-4 resin. The PUF and XAD were extracted separately by SFE. The filters were extracted by sonication. The PUF samples were spiked with 100 µl of a 20 ng/µl deuterated PAH internal standard mixture and 1 mls of methanol modifier was added. The PUF was extracted by SFE and the final volume of each extract was approimately 2 mls. Summary of the SFE conditions are given in **Error! Reference source not found.**. A 660 µl aliquot of the SFE extract was loaded onto a Waters C-18 SepPak cartridge to remove some of the hydrocarbons that interfere with GC/MS analysis. The C-18 was extracted with 2 mls of methanol. The methanol extract was transferred to a Waters Silica SepPak cartridge. The methanol was allowed to evaporate on the cartridge before eluting 3 mls of hexane through the cartridge. The hexane fraction was saved for GC/MS analysis. DCM was added to a measured aliquot of SFE extract to adjust the final volume to 200 µl. The diluted extract was injected into the GC/MS for analysis.

The low volume XAD-4 resin was well mixed and approximately 10 mls of XAD from each sample was prepared for SFE extraction and for GC/MS analysis. Prior to SFE, the XAD sample was spiked with 75 µl of a 20 ng/µl deuterated PAH internal standard mixture and 1 mls of methanol modifier was added. The XAD was extracted by SFE and the final volume of each extract was approximately 2 mls. A 660 ul aliquot of the SFE extract was loaded onto a Waters C-18 SepPak cartridge to remove some of the hydrocarbons that interfere with GC/MS analysis. The C-18 was extracted with 2 mls of methanol. The C-18 was extracted with 2 mls of methanol. The methanol extract was transferred to a Waters Silica SepPak cartridge. The methanol was allowed to evaporate on the cartridge before eluting 3 mls of hexane through the cartridge. The hexane fraction was saved for

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GC/MS. DCM was added to a measured aliquot of the methanol extract to adjust the final volume to 200 µl and each diluted extract analyzed by GC/MS run in selective ion monitoring (SIM) mode.

The six filters from each sample were cut into pieces and placed in an Erlmeyer flask with a screw cap. 100 µl of 5ng/µl internal standards were added to the filters. The filters were extracted 4 times in 25 mls of DCM for 20 minutes. After each sonication the sample was filtered through a 2 A filter. The flask and filter were rinsed with DCM and the washes and extracts were combined. The combined extract was concentrated to 1 ml. One-half of the sample was then added to a Waters C-18 SepPak cartridge. The DCM from the extract was allow to evaporate before the C-18 cartridge was eluted with 2mls methanol. The methanol extract was transfered to a Silica SepPak cartridge and the methanol was allowed to evaporate before eluting with 3 mls of hexane. The hexane extract was concentrated to 1 ml and prepared for GC/MS analysis.

Instrumental conditions and column selection: The SFE extracts were analyzed using a Hewlett-Packard Model 5890 Series II Gas Chromatograph (GC) equipped with a Model 8290 autosampler interfaced to a Hewlett-Packard Model 5970A quadrupole mass selective detector (MSD). The GC was equipped with a split/splitless injector and an electronic pressure controller. The injector was run in the splitless mode and the electronic pressure controller was programmed for vacuum compensation and constant flow mode. The GC was equipped with a 30 m x 0.25 mm i.d. DB-5MS fused silica capillary column (0.5 µm film thickness; Hewlett-Packard). The MSD was run in selective ion monitoring (SIM) mode. The final instrument conditions are summarized in Table 13.

The target and substituted PAHs that were quantitated are listed in Table 14. The PAHs were analyzed using an isotope dilution method to improve the quality of quantitation. This table includes all of the C_1 and most of the C_2-substituted isomers of naphthalenes, as well as other mono-methylated vapor-phase PAHs.

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Table 13. GC/MS Conditions for Analysis of PUF and XAD-4 Extracts

Carrier gas / velocity	He; 32 cm/sec
Temperature program	40°C hold for 10 min
	5°C/min to 270°C
	5 min hold @ 270°C
	10°C/min to 310°C
	10 min hold @ 310°C
Injector temperature	295°C
Detector temperature	285°C
Solvent delay	10 min
Run time	40 min
Scan mode	SIM

Table 14. List of Analytes and Internal Standards for PAH Analysis by GC/MS.

Compound No.	Compound	Quantitation ion
1	naphthalene-d_8*	136
2	naphthalene	128
3	methylnaphthalene-d_{10}*	152
5	2-methylnaphthalene	142
6	1-methylnaphthalene	142
8	2,6- & 2,7-dimethylnaphthalene	141
15	acenaphthene-d_{10}*	160
16	acenaphthylene	153
17	acenaphthene	152
18	fluorene-d_{10}*	176
19	fluorene	166
20	anthracene-d_{10}*	188
24	1-methylphenanthrene	192
28	phenanthrene-d_{10}*	188
29	phenanthrene	178
30	anthracene	178
31	fluoranthene-d_{10}*	212
32	fluoranthene	202
33	pyrene-d_{10}*	212
34	pyrene	202
35	chrysene-d_{12}*	240
36	benzo[a]anthracene	228
37	chrysene	228

* internal standard

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Quality Assurance and Control: The collection and storage of samples followed specifically defined procedures. All testing conditions for the Main Study were recorded on Field Data Sheets. For each sampling run, the date, time, type of sample (bioassay or chemical analysis), flow rate, temperature, and pressure of the sampling system were recorded. The parameters for each cycle were also recorded. All samples were identified in a Master Log that was used throughout the main study. The Master Log contained sample ID, sample type, and date of collection. Finally, all sample transfers were tracked from collection to analysis using Chain of Custody forms. The Chain of Custody contained samples ID's, sample type, dates of transfer and acceptance, and the initials of the personnel who transferred and accepted the samples.

For the sampling and chemical analysis, adsorbent and solvent blanks were analyzed along with the actual samples in order to determine possible background interferences. Field samples were stored on blue ice during transport to the laboratory where they were stored at 4°C before sample work-up and extraction. All SFE extracts were chemically analyzed immediately following extraction or stored at -20°C until sample analysis and mutagenicity testing could be completed.

Prior to sample analysis, the MSD was manually tuned using perfluorotributylamine. The MSD was optimized for SIM analysis for PAHs by first injecting a reagent blank into the GC/MS to determine background contamination levels. If the background levels were acceptable, then a multi-point calibration curve was established by injecting 5 standards at 5 different concentrations. The actual samples were analyzed after the analysis of the calibration standards was completed. After every ten (10) samples, a calibration standard check sample was run to ensure that the instrument was still properly calibrated. If the target compounds were found at levels above the calibration curve, the samples were diluted and analyzed again. Duplicate analyses were performed for each sample.

All PAH analysis incorporated adsorbent blanks. All PAH procedures were carried out in a room fitted with yellow fluorescent lights (G.E. F40Go) to minimize potential photo-oxidation of chemicals.

Samples: A summary of the PUF and XAD-4 samples collected from the emissions of a heavy-duty diesel engine using pre-1993, low aromatic, and reformulated blends that have been extracted by SFE is presented in Table 15. There were numerous samples collected from the hot cycles for each fuel type. No cold start samples were collected.

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Table 15. Summary of PUF and XAD-4 Samples Collected from Pre-1993, Low Aromatic and Reformulated Blend Fuels and Extracted by SFE.

Sample ID	Fuel Type	Cycle/Start Type [a]	Sampler type	Chem. Analysis	
				XAD-4	PUF
H3	Pre-1993	2FTP/Hot[b]	High Vol	X	X
H4	Low Aromatic	2FTP/Hot	High Vol	X	X
H6	Reformulated	2FTP/Hot	High Vol	X	X
UV2	No Diesel	Tunnel Blank[c]	High Vol	X	X
UV3	No Diesel	Tunnel Blank	High Vol	X	X
UV4	No Diesel	Tunnel Blank	High Vol	X	X
TR1	No Diesel	Trip Blank	High Vol	X	X
H110	Pre-1993	6FTP/Hot[d]	Low Vol	X	X
H127	Low Aromatic	6FTP/Hot	Low Vol	X	X
H145	Reformulated	6FTP/Hot	Low Vol	X	X
H150	Reformulated	6FTP/Hot	Low Vol	X	X
H170	Pre-1993	6FTP/Hot	Low Vol	X	X
UL100	No Diesel	Tunnel blank	Low Vol	X	X
UL120	No Diesel	Tunnel blank	Low Vol	X	X
UL134	No Diesel	Tunnel blank	Low Vol	X	X
TRL1	No Diesel	Trip Blank	Low Vol	X	X

[a] All data are from FTP (Federal Test Procedure) runs.
[b] All data are from 2 FTP cycles run in the hot start mode.
[c] Tunnel blank = sample dilution tunnel without engine running.
[d] All data are from 6 FTP cycles run in the hot start mode.
X Sample has been extracted for chemical analysis.

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Materials: Thermosorb-N cartridges were purchased from Thermedics (Woburn, Mass). Pretest-Calibration calibrated against Gilmont Flow meters.

Sampling: The sampler consisted of a filter module, sorbant module, rotometer, and sample pump. The filter module consisted of the stainless steel filter holder used at the LAMTA facility. The holder housed two 70 mm Teflon membrane filters separated by a stainless steel screen. A 1/8" diameter Teflon tube connected the Filter holder to two Thermosorb-N cartridges connected in series. The second cartridge was connected to a rotometer. The purpose of the second cartridge was to trap any NAs that were not trapped by the front cartridge. A bellows pump was attached to the exit of the rotometer. Nitrosoamine samples were taken from a side port on the secondary dilution tunnel. See Figure 6.

The sampling flow was set at a nominal 2 liters per minute. Samples were collected during FTP cycles. To obtain a sufficient sample, emissions from six FTP cycles were collected on each set of cartridges. Each cycle lasted approximately 20 minutes with a total sample time of 120 minutes. This resulted in a total sample volume of 240 liters corresponding to a quantitation limit of 2.5 $\mu g/m^3$ in the undiluted diesel exhaust for all NA samples. Filters were changed after every cycle. A leak check was performed prior to each series of sampling runs and after each time the cartridges were disconnected from the sampling train.

The particles collected on the filters were archived. The volatile emissions were collected on the Thermosorb-N cartridges. After sampling the cartridges were immediately capped and sealed in aluminum foil packages until shipped to Lancaster laboratory for analysis. All the front cartridges were analyzed. One backup cartridge was analyzed to determine whether breakthrough had occurred.

Analytical Procedure: A mixture of 25% methanol and 75% dichloromethane was eluted through a Thremosorb-N cartridge. The first 1.5-1.8 mls of eluant was collected for GC/TEA analysis. 4 µls of sample was injected for analysis. The GC is equipped with a 10' long x 1/8" O.D. stainless steel column packed with 10% Carbowax 20M and 2% KOH on Chromsorb W-AH and a Thermal Energy Analyzer Detector. Lancaster Laboratories analyzed the samples for N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosdipropylamine (NDPA),

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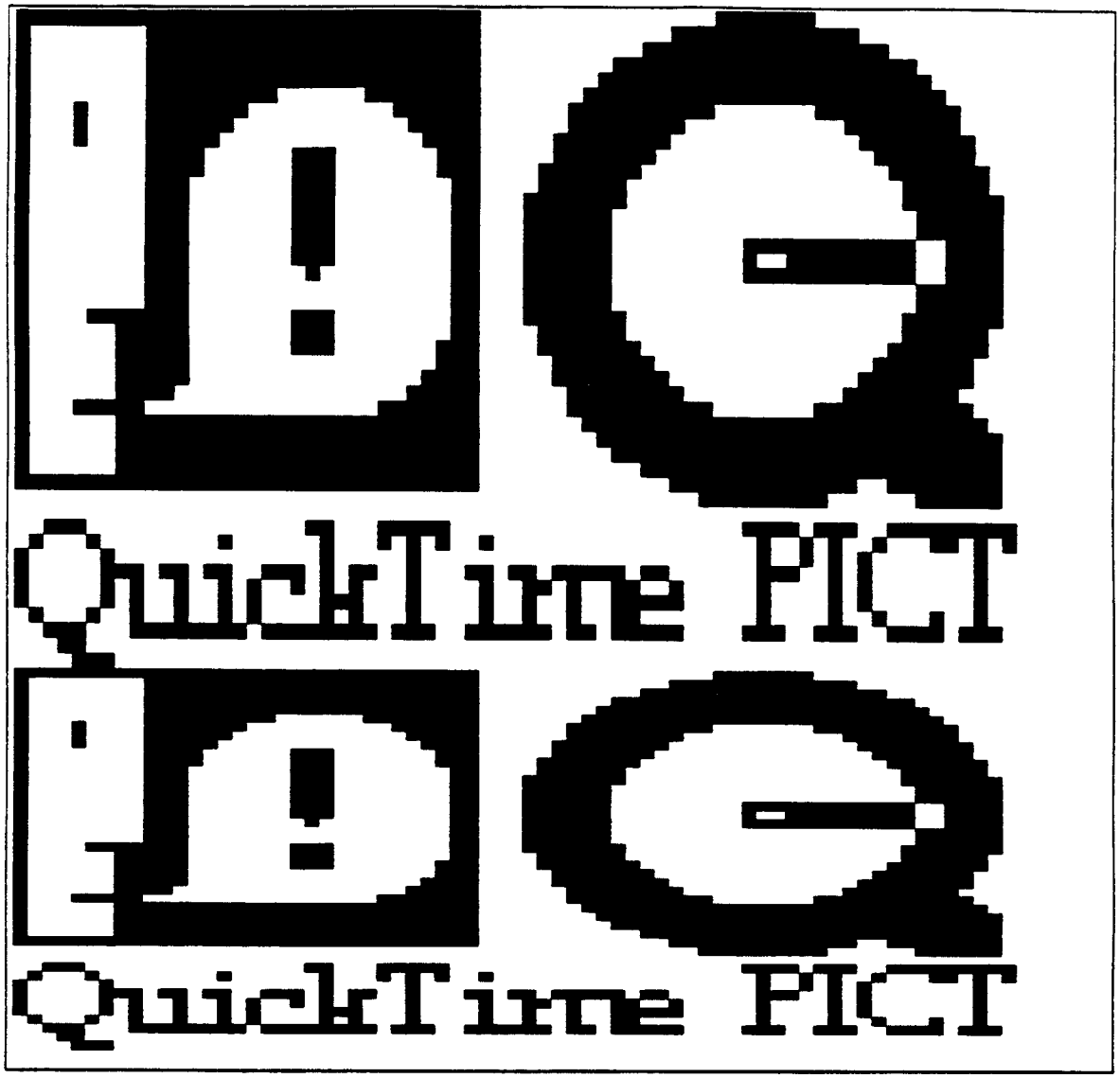

Figure 6. Nitrosamine Sampler at the LAMTA Facility

N-nitrosodibutylamine (NDBA), N-nitrosopiperidine (NPIP), N-nitrosopyrolidine (NPYR), and N-nitrosomorpholine (NMOR).

2.11 Dioxins

Chemicals: HPLC grade hexane and methanol were obtained from Fisher Scientific. PUF sheets were obtained from Graseby GMW (Village of Cleves, Ohio). The sheets were cut into 3" diameter x 1" thick PUF plugs. 8"x10" Teflon coated glass fiber filters were obtained from Pallflex (Putnam, CT). 76.2 mm x 6" diameter Glass PUF holders were obtained from R&D glass (Berkeley, CA). The filters, PUF, and glass holders were pre-cleaned by Alta Laboratories (El Dorado Hills, CA). All utensils and aluminum foil used in the test were pre-cleaned in methanol.

The filter holder, sorbant holder and vacuum motor were obtained from Graseby GMW (Village of Cleves, OH). The laminar flow element was obtained from Meriam Instruments (Cleveland, OH).

Sampling-EPA Proposed Test Procedure: No standardized testing procedures were available for PCDD and PCDF testing. PCDD and PCDF methodologies developed for this study were adapted from a test plan outlined in a USEPA Memo, "Method Validation and Confirmatory Testing for the Identification and Quantification of Dioxin and Dioxin-Like Compounds from Diesel Emissions" (Jan 31, 1996). The test plan was based on recommendations made by a USEPA dioxin work group. Modifications to the Test plan were made based on comments by the ARB/CE-CERT committee which was formed for this study.

Test Plan: The Test plan was based on the criteria for dioxin sampling in diesel exhaust as outlined in a USEPA Memo, "Method Validation and Confirmatory Testing for the Identification and Quantification of Dioxin and Dioxin-Like Compounds from Diesel Emissions" (Jan 31, 1996). The memo was issued by the National Vehicle and Fuel Emissions Laboratory of the USEPA. Much of this test plan was based on Phase 1 of that memo. Most of the criteria listed in the memo were implemented into this plan. Listed below are the criteria adopted from the USEPA test plan.

1. The test engine was connected to a engine dynamometer and run using a FTP cycle.

2. Dioxin diesel exhaust samples were collected from a dilution tunnel.

3. A high volume sampler was used to collect the diesel exhaust samples.

4. Chlorine, a dioxin precursor, and copper, a catalyst, were measured in the emissions, fuel and oil.

5. A qualified commercial laboratory using standardized Dioxin EPA method was used to analyze the samples.

6. EPA criteria and assumptions for estimating sample size were adapted. The sampler was designed to collect enough sample to obtain a toxic equivalent factor detection limit of 100 pg/l.

Additional validation not included in the EPA plan but incorporated into the current study included:

1. Analysis of dioxins in the fuel and oil.

2. Validation of the sampler in a pretest trial.

3. Test for breakthrough of the PUF.

4. Incorporation of additional QA procedures such as tunnel blanks.

Other criteria could not be included because they required major modifications to the main test plan. The major differences are summarized below.

1. *Engine Selection.* The EPA memo recommends a Detroit Diesel Series 60 or a Caterpillar 3176 engine. For this test a Cummins LC10 engine was used. The selection of the engine for this test was determined by the ARB/CE-CERT committee.

2. *Ambient Chlorine.* EPA recommends measuring atmospheric chlorine at the air intake of the engine. Atmospheric chlorine could not be measured for this test. Modifications to the system were beyond the resources and scope of this project. No practical way could be found to measure atmospheric chlorine without affecting the operation of the engine.

3. *Tunnel Conditioning Time.* Due to time constraints conditioning time in the tunnel was changed from 30 hours to 2 hours.

4. *Selection of Fuels.* The fuels were changed from a chlorine and a high chlorine diesel certification fuel to a pre-1993 California fuel and a reformulated blend of post-October 1993 fuels.

To acquire sufficient sample a high volume sampler equipped with a filter and sorbant module was interfaced to the dilution tunnel. Multiple cycles were collected on one sample train. The pooled samples were analyzed for PCDDs and PCDFs.

Characterization of dioxins not only requires analysis of diesel emissions but also of dioxins in the fuel and oil. Also needed is the characterization of chlorine and copper in the emissions, fuel, and oil. Chlorine is a dioxin precursor that is found in diesel fuel and oil. Copper is a catalyst that has been shown to increase the rates of formation of dioxins in diesel exhaust (1).

Estimating Sample Size: Initial estimates of sample size were based on USEPA estimates. that .5% of the total diesel emissions need to be collected in a single sampling run and that sufficient samples would be collected in two FTP cycles. The following assumptions were used in this estimation. 1) The diesel emission factor is 100 pg toxic equivalence per liter of diesel fuel (TEQ/l). This emission factor is based on a study by Marklund et al., 1987. 2) The congener profiles for diesel exhaust resembles the congener profile for municipal waste incinerators. 3) The amount of fuel used per test is 4 liters. 4) Assumes four congeners, TCDD, PeCDD, HxCDD, and PeCDF make up over 80% of the body burden TEQ for the general population. 5) Five tenths of a percent of the total diesel emissions can be collected in a single FTP cycle. 6) The overall extraction efficiency of the method is 80%. 7) The GC/MS can quantify 2-4 pgs of 2,3,7,8 TCDD and 20-40 pg for other congeners.

For the sampling setup at the MTA facility an estimated 1.5% of the total diesel emissions can be collected in a single FTP cycle. This requires a high volume sampler with a sampling rate of 39 cubic feet per minute and a 32:1 dilution of the diesel exhaust. Sufficient sample should be collected in pooling 1-2 cycles on a single sampling train to achieve a 100 pg TEQ/l. Lower detection limits can be achieved by pooling more cycles on a single sample. The maximum number of cycles is limited by the number of filter changes required. Filter changes occur after every 2 or 3 cycles because of the increased pressure drop due to particle loading. The number of filters is limited to three because of the amount of space in the soxhlet used for extracting the sample. The maximum number of cycles per pooled sample is eight.

Sampling System: The Horiba High Volume Sampler installed on the dilution tunnel was not suitable for dioxin emission sampling. It was removed for this diesel test and was replaced by a modified Grasby GMW high volume sampler. The sampler consisted of a filter module, sorbant module, vacuum motor and laminar flow element as shown in Figure 7. The unit was connected to the main tunnel by a bi-pass. Part of the diesel emissions were diverted through the bi-pass into the sampler and then channeled back into the main tunnel.

The sampler collected particulates on a 8"x10" Pallflex T60A20 rectangular filter. Gaseous emissions were trapped by two 1" thick x 3" diameter PUF plugs. Sample was pulled from the main tunnel by a motor and flow was measured by a laminar flow element. Pressure was measured by a U- tube oil manometer and a water manometer. Flow was regulated by using a Variac to control the voltage on the motor. Flow rates were measured and adjusted every two minutes. Temperature in the laminar flow element was measured by electronic digital thermometer.

Sample Preparation: The PUF sheets were cut to size using a three inch diameter dye. 3" id. x 6" long Glass sorbant modules were used to house the PUF. PUF, sorbant modules, and filters were cleaned by Alta Laboratories. Alta loaded the PUF in the glass modules. Prior to sampling, the upstream PUF was spiked with a cocktail of labeled dioxins and furans, and the list of surrogates are presented in Table 16.

Sample Tracking and Chain of Custody: The spiked sorbants were wrapped in aluminum foil and labeled. Filters were cleaned, wrapped in pre-cleaned foil, and labeled prior to sampling. The samples were packed on blue ice and shipped via over-night delivery to MTA. After delivery to MTA, the sorbant modules were stored in a freezer at 4°C until use.

Leak checks were performed before a sample was collected and after each filter change. Emissions from seven hot and one cold start FTC cycles were collected on a single set of PUFs. The filters were changed after the first 2 cycles and every 3 cycles thereafter. After emission sampling, the filters were folded and put into the glass sorbant module. The module was then wrapped in aluminum foil, labeled, and sealed in plastic bags. The samples were stored in a freezer at 4°C. The samples were packed with blue ice and shipped by overnight delivery to Alta Laboratories for analysis. Samples were analyzed within 1 month of sampling.

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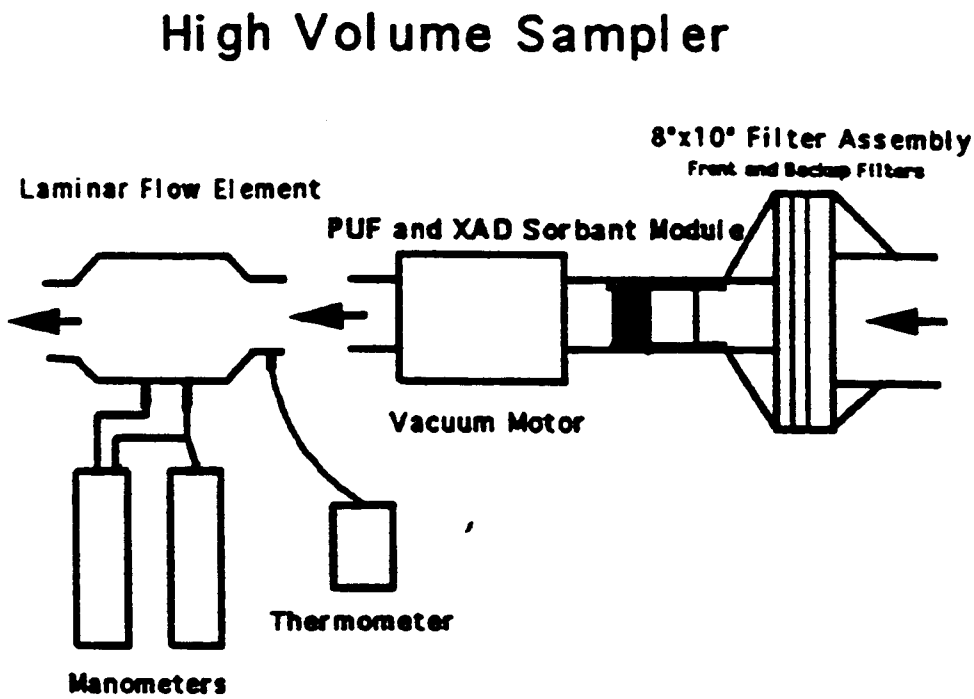

Figure 7. Diagram of PCDD and PCDF high volume sampler.

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Table 16. Surrogate Standards

^{37}Cl-2,3,7,8-TCDD	^{13}C-2,3,4,7,8-PeCDF
^{13}C-1,2,3,4,7,8, -HxCDD	^{13}C-1,2,3,4,7,8-HxCDF
	^{13}C-1,2,3,4,7,8,9 -HpCDF

Fuel, oil, and particle samples were collected in pre-cleaned Teflon lined screw cap bottles. Fuel and particle samples were shipped from MTA to UCD, where they were processed and prepared for shipping to Alta for analysis.

All samples were labeled, all pertinent information was put in a master log, and chain of custodies were used to track all samples.

Analysis of Diesel Exhaust Samples: The analytical procedures used for the analysis of PCDDs and PCDFs emission samples followed the analytical procedures given in Air Resources Board Stationary Source Test Method 428: Determination of Polychlorinated Dibenzo-p-dioxin (PCDD), Polychlorinated Dibenzofuran (PCDF), and Polychlorinated Biphenyl Emissions from Stationary Sources, (ARB Stationary Source Test Methods Vol. 3).

The PUF, PUF module, and filters from a pooled sample were put into a sohxlet. The samples were spiked with PCDDs and PCDFs internal standards and then extracted in toluene for 24 hours. The sample extract was concentrated by roto-evaporation. Half the extract was further concentrated by nitrogen evaporation and the other half was archived. The concentrated extract was cleaned up by using silica gel, alumina, and carbopak/celite. Recovery standards were added to the sample and the analysis was performed by HRGC/HRMS. The GC was equipped with a 60 meter x .25 mm ID DB-5MS column. The mass spectrometer was capable of accurately resolving masses to four decimal places and a resolving power of >10,000. The PCDDs and PCDFs analyzed are listed in Table 17.

Table 17. List of Target Compounds

PCDDs	PCDFs
2,3,7,8-TCDD	2,3,7,8-TCDF
total TCDD	total TCDF
1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDF
total PeCDD	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDD	total PeCDF
1,2,3,6,7,8-HxCDD	1,2,3,4,7,8-HxCDF
1,2,3,7,8,9-HxCDD	1,2,3,6,7,8-HxCDF
total HxCDD	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDD	total HxCDF
total HpCDD	1,2,3,4,6,7,8-HpCDF
total OCDD	1,2,3,4,7,8,9-HpCDF
	total HpCDF
	total OCDF

Analysis of Diesel Fuel, Oil, and Tunnel Particulate Matter. Fuel and oil samples were prepared and analyzed by EPA method 8270. 10 to 100 mls of fuel was spiked with internal standards and diluted with dichloromethane. Clean-up by column chromatography was performed to remove hydrocarbon interferences. One-half of each sample was concentrated by roto-evaporation. Tetradecane, a keeper solvent, was added and each sample was further concentrated by nitrogen evaporation. Recovery standards were added and each sample was analyzed by HRGC/HRMS.

Tunnel particulates and manifold particulate samples were spiked with internal standards and sohxlet extracted in toluene. Further clean-up was done by column chromatography. One-half of each sample was concentrated by roto-evaporation. Tetradecane, a keeper solvent, was added and each sample was further concentrated by nitrogen evaporation. Recovery standards were added and each sample was analyzed by HRGC/HRMS.

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2.12 Bioassay

Chemicals: All organic solvents were HPLC grade or at least equivalent in purity. Methanol, acetone, hexane, and water (HPLC grade) were obtained from Fisher Scientific. For mutagenicity experiments, benzo(a)pyrene and dimethylsulfoxide (DMSO; spectrophotometric grade) were from Aldrich Chemical Co. and were used without further purification. Dichloromethane (DCM, OmniSolve) was from EM Science. For solid phase extractions (SPE), acetonitrile (ChromPure) and hexane (UV, High Purity) were from Burdick and Jackson.

Filter Samples: Particulate samples extracted for bioassay analyses were collected from a high-volume sampler described in the methods section on PAH. In a typical sampling procedure, particles were collected on pre-cleaned 8" x 10" Teflon-coated glass fiber filters (T60A20 - Pallflex, Putnam, Conn.). Particulate matter from each sample were collected on primary and secondary (backup) filter. Filters were extracted either by SAPRAC using DCM and Soxhlet extraction (48 hr), or by UCDavis using DCM and sonication. The DCM extract was further concentrated using roto- and nitrogen-evaporation. The mass of particulate matter which was collected and extracted is summarized in Table 18. The entire scope of samples processed and tested in bioassay are also presented in this table.

All particle masses represent the particulate matter collected during 2 consecutive FTP transient cycles. The particle mass extracted and used for HPLC fractionation, and the particle mass ufractionated extract, are reported in Table 19. An extraction blank for the HPLC fractions was also tested. The HPLC was used to fractionate the whole extract into nine fractions, with the least polar compounds eluting in fraction 1, and the most polar fractions eluting in fraction 9. Details of the procedure are presented by SAPRC for the analyses of nitro-PAHs in the Methods section. Filter blanks wer also incorporated. These blanks included: 1) trip blanks - filters handled and extracted as experimental samples, and 2) field or tunnel blanks - filters used to collect tunnel air without the engine running.

Table 18. Samples extracted and tested in bioassay.

Fuel Type	Test Cycle ID	Ave Particle Emissions (g/brhp-hr)	Laboratory Sample ID	Particle Wt Per Filter (2 cycles each) (mg)	Samples Tested
Pre-1993	338H8,H9	0.201	96-20,96-21 a	79.9	PM, HPLC
Pre-1993	337H1,H2	0.212	H1FV b	76.6	PM, VP
Pre-1993	339H6,H7	0.223	H3FV b	76.1	PM, VP
Low Aromatic	346H3, H4	0.177	96-44,96-45 a	65.5	PM, HPLC
Low Aromatic	344H1, H2	0.1979	H4FV b	55.9	PM, VP
Low Aromatic	344H3, H4	0.187	H5FV b	60.2	PM, VP
Reformulated	351H1, H2	0.172	96-62, 96-63 a	82.8	PM, HPLC
Reformulated	348H1,H2	0.172	H6FV b	46.7	PM, VP
Reformulated	351H7,352H7	0.171	H7FV b	60.6	VP

a SAPRC UC Riverside ID. Sample extracted and fractionated by SAPRC.
b UC Davis ID. Sample extracted and fractionated by UC Davis.
PM=particulate matter; VP=Vapor-phase, HPLC = high performance liquid chromatography.

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Table 19. Mass of Particulate Matter Collected and Extracted.

Fuel	Total [a] Collected Particulate mass (mg)	Particulate mass Fractionated (HPLC) (mg)	Particulate mass Unfractionated (mg)
Pre-1993	79.9	26.6	13.3
Low Aromatic	65.5	21.8	10.9
Reformulated Formulation	82.8	27.6	13.8

a Particulate matter collected for two consecutive FTP cycles. All of the particulate matter was extracted and portions indicated were divided for fractionation, unfractionated, and archived samples. HPLC fractionation was conducted at UC Riverside.

The unfractionated extract (neat complex mixture extract) was used to determine relative potencies of each extract. A portion of the extract was transferred to a pre-cleaned 0.5 dram vial and taken to dryness under a gentle flow of nitrogen. The extract was then redissolved in DMSO for the bioassay. Doses were developed by serially diluting the redissolved solution in DMSO. To prepare the HPLC fractions for bioassay, a known aliquot of each fraction was transferred to a pre-cleaned 1/2 dram vial, dried under a gentle stream of nitrogen, and redissolved in DMSO. Dose-response relationships were developed for each fraction.

Collection of Vapor-Phase Sample: Samples were collected using the Hi-Vol system detailed in the Methods section for the collection of PAHs. The sampling train consisted of two 8" x 10" Teflon-coated glass fiber filters (T60A20; Pallflex, Putnam, Conn.), followed in series by two PUF plugs, and 60 ml of XAD-4 resin. The filters were extracted by solvent as described above, while the PUF and XAD were extracted using supercritical carbon dioxide (supercritical extraction).

Extraction of Vapor-phase Samples - Supercritical Fluid Extractionn: Supercritical fluid extraction (SFE) of the organic compounds from the PUF and XAD samples was accomplished using liquid

carbon dioxide (CO_2) as the extraction solvent at pressures and temperatures above its critical point of 72.9 atm and 31°C. Since CO_2 is a gas at atmospheric pressure, this technique produces a concentrated extract without residual solvent. The concentrated extract can be directly analyzed by both GC-MS and the mutagenicity assay.

All supercritical fluid extractions were carried out using an ISCO Model 260D syringe pump (Lincoln, NE), an ISCO SFX2-10 extractor, and SFC/SFE grade CO_2 (Air Products, Allentown, PA) under a helium headspace of 2000 psi. Prior to sample extractions, the PUF and XAD adsorbents were placed into a 10 mL stainless steel extraction cell. For chemical recovery studies, the adsorbents were spiked with either target or substituted PAHs (for example alkyl-PAHs) in DCM. After spiking, the DCM was allowed to evaporate for a period of 10 minutes., after which approximately 1 mL of methanol was added as a modifier to the top of the adsorbent. For actual samples, approximately 1 mL of methanol was added as a modifier to the top of the adsorbent. The cell was then closed and placed into the extractor for a 5 minute temperature equilibration period. A static extraction (SFE without CO_2 flow into the collection vial) was conducted for 10 minutes prior to conducting the dynamic extraction (SFE with CO_2 flow into the collection vial). The syringe pump was operated at 5000 psi, 75°C, 90 min for the PUF samples and at 7000 psi, 100°C, 60 min for XAD samples. A length of stainless steel capillary tubing was used as a depressurizing flow restrictor to maintain supercritical conditions within the extraction cell. As the supercritical CO_2 (s-CO_2) exits the restrictor, it expands to a gas upon reaching ambient pressure. The effluent from the outlet of the capillary was directed into a graduated collection vial with a screw top fitted with a Teflon septum. The collection vial contained approximately 2 mL of methanol and was placed in a dry ice-ethanol bath to trap and concentrate the semi-volatile chemicals for direct mutagenicity and chemical analyses.

Fractionation of Samples: Samples were fractionated using solid phase extraction (SPE) to develop mutagenic profiles of the extracts. The extracts are processed through columns packed with C18 and silica sorbents. The solvent series and volumes used are summarized in Table 20. Each fraction was stored at -20° C in amber glass vials fitted with a Teflon-lined screw cap.

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Table 20. Fractionation Sorbents and Solvents for Vapor-Phase Samples.

Sorbent	Solvent	Vol (mL)
C18 - Fraction 1	Methanol	2
C18 - Fraction 2	Methanol:Acetonitrile (1:1)	1
C18 - Fraction 3	Acetonitrile	1
C18 - Fraction 4	Dichloromethane	1
C18 - Fraction 5	Hexane	1
Silica - Fraction 1	Hexane	4
Silica - Fraction 2	Dichloromethane	1
Silica - Fraction 3	Dichloromethane:Methanol (1:1)	1
Silica - Fraction 4	Methanol	1

Bioassay: Bioassay experiments were conducted to determine the specific mutagenic activity of the particulate and vapor-phase extracts. For these samples, the specific mutagenic activity is reported as the number of revertants per microgram equivalent of sample extract (rev/µg equiv) or per µl equivalent solvent volume (rev/µl equiv), respectively. The term "equivalent" refers to the addition of an extract of particulate matter that represents the original mass of particulate matter collected, or in the case of a vapor-phase sample, the addition of a volume of extract that represents a specified volume of the original extract. The specific mutagenic activity is determined using the slope obtained from the linear portion of the dose-response curve. All particulate extracts were then tested for mutagenicity using the microsuspension bioassay procedure (Kado et al, 1983) with tester strain TA98. This tester strain is the primary strain used for detecting the mutagens present in diesel exhaust. Particulate extracts were prepared for bioassay by first taking a portion of the extract which is in DCM, evaporating the DCM to dryness under a gentle stream of nitrogen, and redissolving the extract in DMSO. Doses of the extract were prepared by serially diluting the redissolved extract in DMSO. Vapor-phase samples were tested in tester strains TA98 and TA100.

For the microsuspension procedure, bacteria were grown overnight in Oxoid Nutrient Broth No. 2 (Oxoid Ltd., Hants, England) to approximately 1 - 2 x 10^9 cells/ml and harvested by centrifugation (5,000 x gravity, 4°C, 10 min). Cells were resuspended in ice-cold phosphate-buffered saline (0.15M phosphate-buffered saline, pH 7.4) to a concentration of approximately 1 x 10^{10} cells/ml. The S9 (metabolic enzymes) and S9 mix (enzyme co-factors) were prepared and 300 µg S9/ml final concentration was used. The S9 from Aroclor 1254 pretreated male Sprague-Dawley rats was obtained from Molecular Toxicology, Inc. (Annapolis, MD.) and contained 39.2 mg protein/ml. For the microsuspension assay, the following ingredients were added, in order, to 12 x 75 mm or 12 x 65 mm (screw cap) sterile glass culture tubes kept on ice: 0.1 mL S9 mix, 0.005 mL sample in DMSO,

and 0.1 mL concentrated bacteria in PBS (1 x 10^{10} / mL phosphate-buffered saline). The mixture was incubated in the dark at 37°C with rapid shaking. After 90 min, the tubes were placed in an ice bath and taken out one at a time immediately before adding 2 ml molten top agar containing 90 nanomoles of histidine and biotin. The combined solutions were vortex-mixed and poured onto minimal glucose plates. Plates were incubated at 37°C in the dark for 48 hrs and counted using an automatic plate counter. Benzo(a)pyrene, 2-nitrofluorene, and nitroquinoline-N-oxide were used as a positive controls. Tester strain markers were routinely determined for each experiment.

3.0 Results and Discussion

3.1 Emission Rates for NO_x, THC, CO, and PM

Attachment A contains NO_x, THC, CO, and PM emission results for individual test cycles, run with pre-1993 fuel in Table A1, low aromatic fuel in Table A2, and the reformulated blend in Table A3. All cold- and hot-start transient emissions data reported were verified to meet the FTP validation criteria for transient engine operation. Table 21 presents the means and standard deviations for each fuel during the cold- and hot-start transient cycles with plots of the means and 95% confidence intervals for cold-start results presented in Figure 8, and for hot-start results presented in Figure 9. The means and standard deviations for the pre-1993 fuel were calculated from all test results obtained with this fuel, including the initial and final (repeat) tests run at the end of the main sampling study as described in Section 3.2. Table 22 summarizes statistical results from an analysis of variance (ANOVA) and an analysis of pairwise differences between fuels, using the Fischer's protected least square difference method. Values of p 0.05 indicate significant differences among the fuel types at the 95% confidence level. Statistically significant differences at the 95% confidence level for pairwise comparisons are indicated by an S in the table.

Table 21. Average Emission Test Results on Cummins L10 Engine for Pre-1993, Low Aromatic, and Reformulated Fuels.

Fuel	Pre-1993		Low Aromatic		Reformulated	
Cycle	Cold		Cold		Cold	
	Average	*STD DEV*	*Average*	*STD DEV*	*Average*	*STD DEV*
Emission Rates (GM/BHP/HR)						
NOx	4.98	0.13	4.60	0.06	4.85	0.05
THC	0.56	0.02	0.41	0.01	0.47	0.02
CO	2.38	0.11	2.47	0.01	2.30	0.06
CO2	547.3	8.1	545.6	1.4	549.2	2.2
Particulate	0.259	0.016	0.193	0.003	0.212	0.019
BSFC (LB/BHP-HR)	0.385	0.007	0.387	0.001	0.385	0.002
Work (BHP-HR)	22.254	0.087	21.962	0.034	22.128	0.043

Fuel	Pre-1993		Low Aromatic		Reformulated	
Cycle	Hot		Hot		Hot	
	Average	*STD DEV*	*Average*	*STD DEV*	*Average*	*STD DEV*
Emission Rates (GM/BHP/HR)						
NOx	4.74	0.12	4.41	0.06	4.61	0.19
THC	0.52	0.02	0.48	0.02	0.50	0.02
CO	2.24	0.19	2.44	0.04	2.30	0.05
CO2	518.0	3.9	511.7	6.2	511.6	4.4
Particulate	0.218	0.010	0.181	0.008	0.182	0.012
BSFC (LB/BHP-HR)	0.364	0.003	0.364	0.004	0.359	0.003
Work (BHP-HR)	22.327	0.046	22.035	0.222	22.198	0.047

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Figure 8. Cold-Start Emission Rates and 95% Confidence Intervals

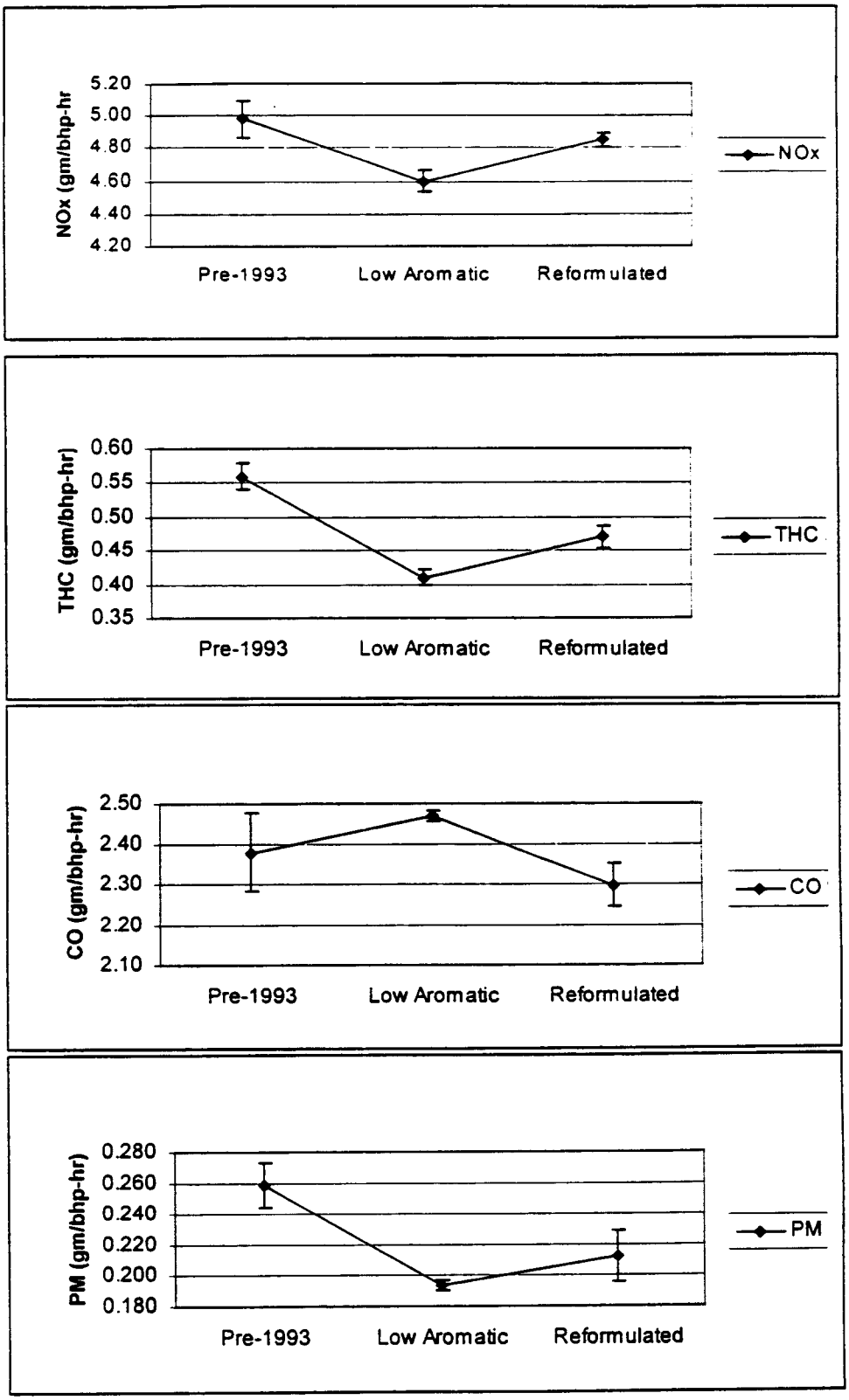

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Figure 9. Hot-Start Emission Rates and 95% Confidence Intervals

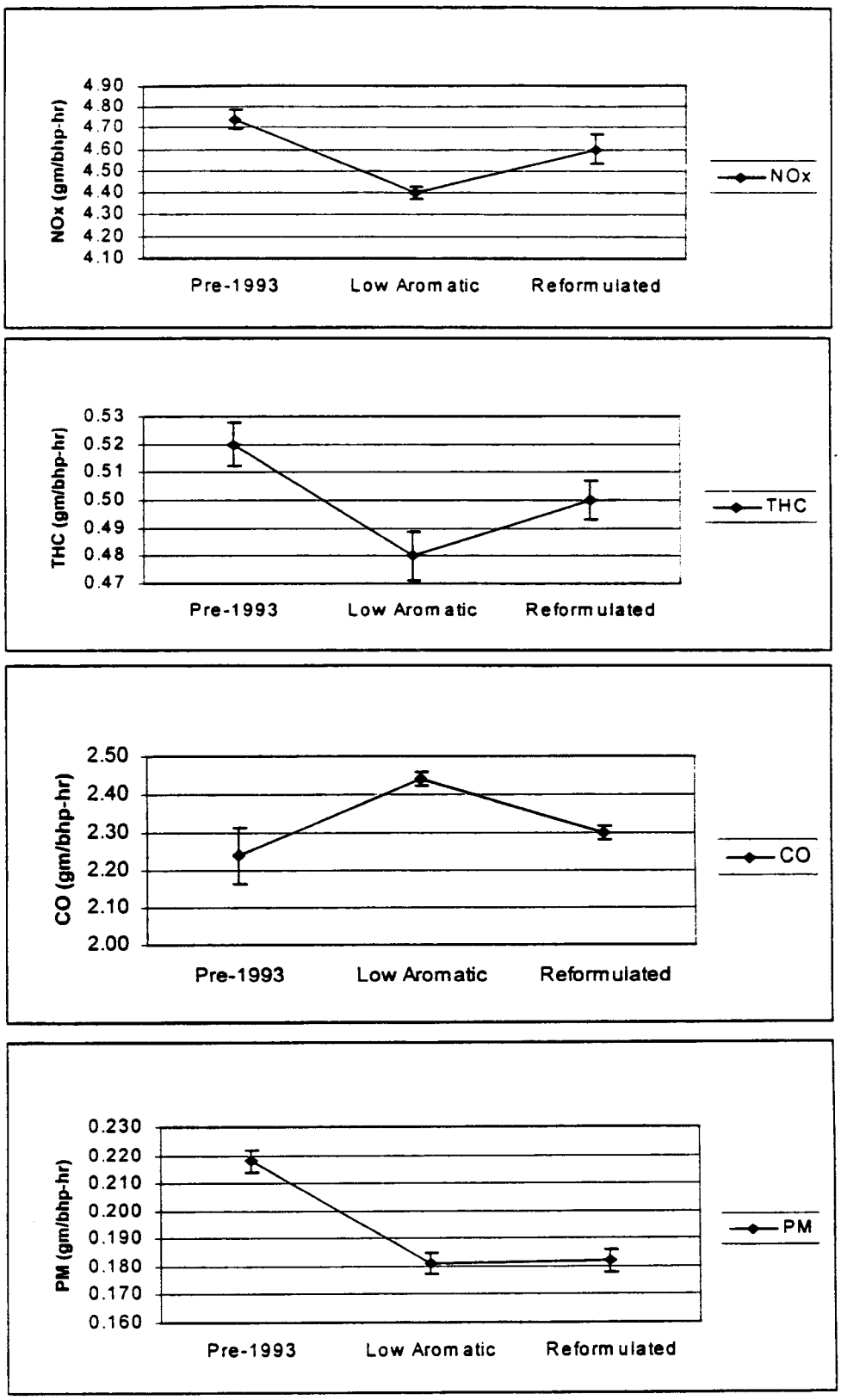

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Table 22. Analysis of variance (ANOVA) and pairwise Fisher's protected least square difference results for NOx, THC, CO, and PM

	NOx		THC		CO		PM	
Cycle	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
P-value	.005	<.0001	<.0001	<.0001	.0579	<.0001	<.0001	<.0001
Low Ar. vs. Pre-93	S	S	S	S		S	S	S
Low Ar. vs. Reform.	S	S	S	S		S		
Pre-93 vs. Reform.	S	S	S	S		S	S	S

NO_x, THC, and PM show reductions in emission rates for both the cold- and hot-start cycles with the low aromatic and reformulated fuels in comparison to the pre-1993 fuel. For NO_x and THC, all of the pairwise differences between fuel types are statistically significant at the 95% confidence level. For PM, the low aromatic and reformulated fuels show a statistically significant difference compared to the pre-1993 fuel, but are not different from each other. The low aromatic fuel indicates an increase and the reformulated fuel a decrease in cold-start CO emissions compared to the pre-1993 fuel, but none of the differences are significant at the 95% confidence level. Both the low aromatic and reformulated fuels show increases in hot-start CO emission rates in comparison to the pre-1993 fuel. All of the differences in hot-start CO emission rates are statistically significant at the 95% confidence level.

The reductions in NO_x emission rates with the low aromatic and reformulated fuels range from 2.6 to 7.6%. Cold-start THC emissions were reduced by 26.7% with the low aromatic fuel and 16.1% with the reformulated fuel, while hot-start THC emissions were reduced by 7.6 and 3.8% with the low aromatic and reformulated fuels, respectively. The low aromatic and reformulated fuels have the largest impact on PM emission rates, with reductions ranging from 16.5 to 25.5% compared to the pre-1993 fuel.

The present study was designed to examine differences between specific fuels rather than the effects of fuel parameters on emissions. As a consequence, there is a high correlation between fuel parameters for the three fuels studied which makes it difficult to conduct a detailed analysis of the impact of specific fuel parameters on emissions. The emission results are consistent with the general trends reported for the effects of changes in diesel fuel parameters on emissions. CARB's original decision to limit the sulfur and aromatic content of diesel fuel was based upon available data at that time which indicated these parameters had a significant impact upon emissions. This included data generated in a Coordinating Research Council (CRC) study to assess the impact of aromatic content, 90% boiling point, and sulfur content (Ullman, 1989a, 1989b). These results indicated that reduction of the aromatic content reduced HC, CO, NO_x, and PM emissions, and that reduced sulfur levels resulted in lower PM emissions. During this phase of the CRC project, the aromatic content and fuel cetane number were highly correlated. Work done in the next phase of the CRC project (Ullman et. al., 1990a, 1990b) separated the effects of aromatic content and cetane number and concluded that increased cetane number was the key to reducing HC and CO emissions, and that both increased cetane number and lowered aromatic content decreased NO_x and PM emissions. From the reformulated fuel analysis results presented in Table 2, it is apparent that refiners have utilized both reduced aromatic content and increased cetane number to certify alternative formulations (Nikanjam, 1993). It should be noted that the emissions results for the reformulated blend should not necessarily be expected to be equivalent to or less than the low aromatic fuel studied in this project. First, the equivalency testing for CARB certification is specified to be performed on a Detroit Diesel Corporation Series 60 engine and it has been shown that the effects of fuel changes are dependent upon engine type (Ullman, 1989a, 1989b). Second, the low aromatic fuel has substantially lower aromatic content than the maximum allowed for CARB reference fuel (4.3% vs. 10%) and higher cetane number than the minimum allowed for the reference fuel (54.2 vs. 48).

3.2 Assessment of Engine Emissions Drift during Testing

The main sampling phase of this project was conducted over a three week period in December, 1996 with the following sequence: pre-1993 fuel tested the week of December 1, low aromatic fuel tested the week of December 8, and reformulated fuel tested the week of December 16. To assess whether any drift occurred with the engine emissions over this test period which would affect interpretation of the results and to provide an additional opportunity to collect samples for analysis, emission tests were also conducted with the pre-1993 fuel at the end of the main test the week of January 5, 1997. Complete results are presented in Table A1 in Appendix A. Means and 95% confidence intervals for NO_x, THC, CO, and PM emission rates obtained during the initial (week of 12/1/96) and final (week

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of 1 5 97) tests with the pre-1993 fuel are presented in Figure 10. An analysis of variance (ANOVA) shows that the increase in hot-start NO_x ($p<0.001$) and decrease in cold-start CO ($p=0.0133$) are statistically significant at the 95% confidence level. None of the other emission differences were found to be statistically significant at the 95% confidence level. Since the statistically significant emission trends associated with fuel changes are opposite to the trends in time sequence, it is concluded that any drift in engine emissions throughout the testing period cannot account for the emission trends observed with the different fuels.

3.3 Particle Size Distributions

Particle size distribution results form the MOUDI cascade impactor presented as per cent of total particulate mass below 10 and 2.5 μm for each fuel are presented in Table 23.

Table 23. Particle Size Distributions

Fuel	Percent <10μm	Stand. Dev.	Percent <2.5 μm	Stand. Dev.
		Cold-Start		
Pre-1993	99.6	0.1	98.0	0.4
Low Aromatic	99.1	0.5	95.0	0.8
Reformulated	99.2	0.7	97.3	0.8
		Hot-Start		
Pre-1993	99.8	0.6	98.7	0.7
Low Aromatic	99.3	0.2	96.9	0.4
Reformulated	99.3	0.6	97.9	1.4

No significant differences were noted in the particle size distributions between the three fuels and as expected the majority of the particles (>95%) were found to be less than 2.5 μm in aerodynamic diameter.

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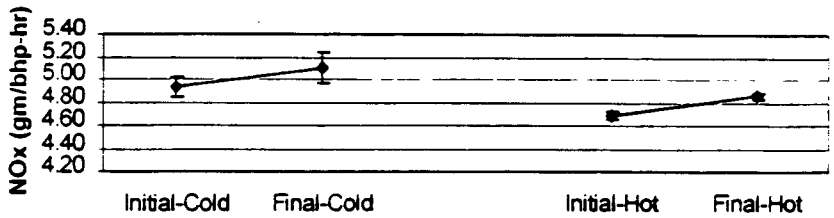
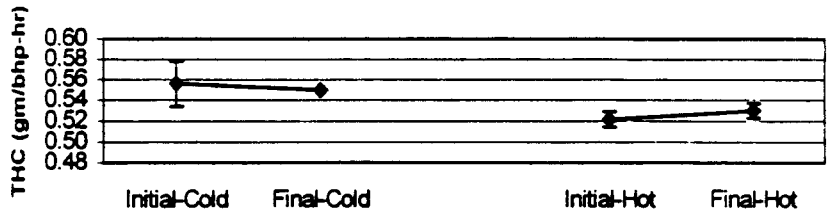
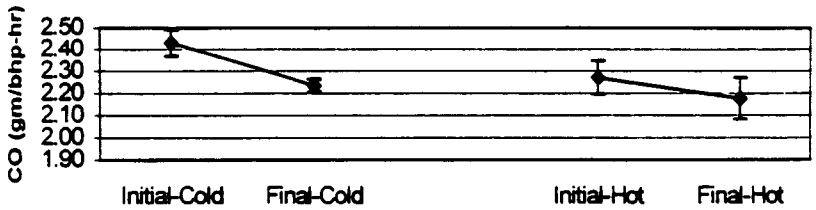
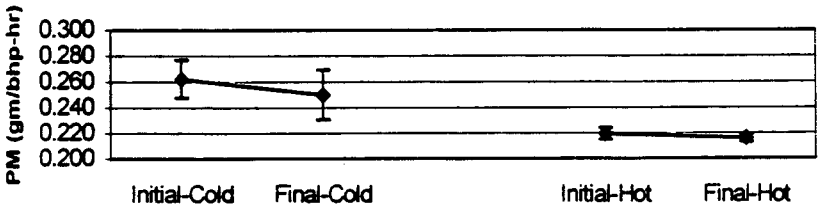
Figure 10. Initial and Final Emissions with Pre-1993 Diesel Fuel









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3.4 Elemental and Organic Carbon, Ion, and Elemental Analyses of Particulates

Complete ion and organic and elemental carbon analysis results are summarized in Table A4 of Appendix A. Elemental analysis results are summarized in Table A5 of Appendix A. Table 24 presents results for components that were detected at levels at least twice the analytical uncertainty. All results have been background corrected. Elemental and organic carbon dominate the composition of the particulate matter for all fuels and represent more than 97% of the total identified mass, consistent with previous studies of diesel particulate (Watson, et al., 1994, Hildemann, et al., 1991). The organic carbon as a percent of total carbon is relatively constant for all three fuels and ranges from 33 to 40%. The major changes in emission rates associated with the fuel are found in nitrate, sulfur and sulfate, and elemental and organic carbon. The low aromatic and reformulated fuels show lower elemental and organic carbon emission rates associated with the lower total PM emission rates for these fuels. Selected backup quartz fiber filters were analyzed by the TOR method to assess the contribution of organic carbon artifact formation. These results show that the backup filters contain organic carbon equivalent to 14-20% of the primary filter organic carbon contents which can be ascribed to sampling artifacts resulting from adsorption of gas phase organics on the filter media.

Nitrate emission rates are higher for the low aromatic and reformulated fuels. This may be a result of the use of organonitrates as cetane improvers in the reformulated fuel, but is unexplained for the low aromatic fuel. Sulfur and sulfate emissions follow the trend pre-1993 > reformulated > low aromatic which is the same order as the fuel sulfur levels. Mg, P, Ca, and Zn emission rates are relatively constant. This is expected as these are known engine oil components. The emission rates of these oil derived components and Fe (due to engine wear) are consistently higher during the cold-start cycles than the hot-start cycles. Si emissions are relatively constant for all fuels and all cycles with the source of these emissions being unknown. Cl and Cu are minor components and are observed at levels close to or slightly above twice the analytical uncertainties.

The sum of the identified species represents 83 to 95% of the total PM mass for these results. Similar results have been reported in previous studies (Lowenthal, et al., 1994) and have been ascribed to non-uniform filter deposits and to the fact that these analyses do not measure species such as hydrogen and oxygen which contribute to the total PM mass.

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Table 24. Ion, Elemental, and Organic and Elemental Carbon

Pre-1993

	Cold Start Emission Rate *mg/bhp-hr*	Cold Start Std. Dev. *mg/bhp-hr*	Hot Start Emission Rate *mg/bhp-hr*	Hot Start Std. Dev. *mg/bhp-hr*
Nitrate	*0.07*	0.08	*0.08*	0.01
Sulfate	1.10	0.97	1.11	0.09
Ammonium	0.59	0.19	0.58	0.12
Organic Carbon	89.00	9.02	66.51	8.57
Elemental Carbon	133.98	4.24	125.87	7.96
Mg	0.081	0.044	0.066	0.034
Si	0.619	0.109	0.748	0.092
P	0.079	0.017	0.044	0.011
S	1.725	0.187	1.349	0.060
Cl	*0.022*	0.001	*0.026*	0.025
Ca	0.084	0.046	0.079	0.045
Fe	0.451	0.339	0.213	0.135
Cu	0.012	0.006	0.008	0.013
Zn	0.156	0.032	0.096	0.019
Sum	227.90		196.70	
Total PM	259		218	

Low Aromatic

	Cold Start Emission Rate *mg/bhp-hr*	Cold Start Std. Dev. *mg/bhp-hr*	Hot Start Emission Rate *mg/bhp-hr*	Hot Start Std. Dev. *mg/bhp-hr*
Nitrate	0.37	0.04	0.39	0.05
Sulfate	0.39	0.10	*0.10*	0.02
Ammonium	0.37	0.04	0.30	0.05
Organic Carbon	56.28	1.73	51.29	3.33
Elemental Carbon	109.86	7.98	118.87	6.54
Mg	0.080	0.049	*0.039*	0.012
Si	0.674	0.081	0.637	0.081
P	0.089	0.018	0.060	0.013
S	0.530	0.068	0.264	0.034
Cl	0.048	0.012	0.039	0.004
Ca	0.064	0.013	0.030	0.008
Fe	0.441	0.041	0.067	0.024
Cu	0.006	0.001	*0.000*	0.001
Zn	0.174	0.042	0.107	0.013
Sum	169.38		172.19	
Total PM	193		181	

Reformulated Blend

	Cold Start Emission Rate *mg/bhp-hr*	Cold Start Std. Dev. *mg/bhp-hr*	Hot Start Emission Rate *mg/bhp-hr*	Hot Start Std. Dev. *mg/bhp-hr*
Nitrate	0.19	0.07	0.17	0.04
Sulfate	1.05	0.81	0.43	0.04
Ammonium	0.43	0.20	0.34	0.05
Organic Carbon	58.27	5.83	51.24	7.06
Elemental Carbon	113.87	18.75	103.70	14.82
Mg	*0.077*	0.046	*0.051*	0.041
Si	0.628	0.185	0.512	0.088
P	0.110	0.056	0.072	0.018
S	0.925	0.327	0.570	0.033
Cl	*0.028*	0.013	0.033	0.010
Ca	0.095	0.066	0.045	0.011
Fe	0.331	0.311	0.089	0.026
Cu	0.009	0.005	*0.005*	0.004
Zn	0.267	0.136	0.153	0.019
Sum	176.28		157.41	
Total PM	212		182	

Values in Italics are < twice the analytical uncertainty

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3.5 Oxygenated Organics and Speciated Hydrocarbons

Emission rates for oxygenated organics are presented in Table 25 with means and 95% confidence limits plotted for toxic oxygenates in Figure 11. Table 26 summarizes statistical results for the toxic oxygenates from an analysis of variance (ANOVA) and an analysis of pairwise differences between fuels using the Fischer's protected least square difference method. Results presented in **Error! Reference source not found.** show that the same patterns and similar emission rates are observed for each fuel with the highest emissions observed for formaldehyde followed by acetaldehyde. The low aromatic fuel has lower formaldehyde and acetaldehyde emissions than the pre-1993 and reformulated fuels during the cold-start cycle which are statistically significant at the 95% confidence level. This trend is not observed for the hot-start. The pre-1993 fuel has lower hot-start acetaldehyde emissions than the low aromatic and reformulated fuels. The other statistically significant difference is higher cold- and hot-start acrolein emissions for the low aromatic fuel in comparison to the pre-1993 and reformulated fuels.

Complete hydrocarbon speciation results are presented in Table A6 in Appendix A. Emission rates of toxic components are presented in Table 27 with means and 95% confidence limits plotted in Figure 13. As with the oxygenate results, the toxic hydrocarbon emissions show the same emission trends and similar emission rates for all fuels. Table 28 summarizes statistical results from an analysis of variance (ANOVA) and an analysis of pairwise differences between fuels using the Fischer's protected least square difference method. The low aromatic fuel has higher hot-start 1,3-butadiene, higher cold- and hot-start benzene, higher hot-start toluene, lower cold-start o-xylene, and lower hot-start m&p-xylene emissions than the other fuels. All of these trends are statistically significant at the 95% confidence level. No statistically significant differences are observed between the pre-1993 and reformulated fuels.

Very little data exists on the possible effects of diesel fuel composition on oxygenate and speciated hydrocarbon emissions. Spreen, et al., 1995, have reported limited results from heavy-duty engine dynamometer studies with the conclusion that lowering the aromatic content did not appear to have a significant impact on emission rates for individual oxygenates or hydrocarbon species. Hublin, et al., 1996, have reported results on the effects of diesel fuel parameters on emissions of benzene, 1,3-butadiene, formaldehyde, and acetaldehyde from studies of light-duty diesel vehicles on a chassis dynamometer. The overall observation was that emissions of these species varied more with engine technology than with fuel composition.

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Table 25. Emission Rates for Oxygenates

	Pre - 1993			
	Cold Start Cycle		Hot Start Cycle	
	Average mg/bhp-hr	SDEV mg/bhp-hr	Average mg/bhp-hr	SDEV mg/bhp-hr
Formaldehyde	62.33	1.37	56.26	0.95
Acetaldehyde	20.23	0.31	17.81	0.20
Acrolein	2.18	1.12	2.13	0.74
Acetone	7.66	0.02	5.90	0.69
Propionaldehyde	4.45	0.08	3.56	0.43
Crotonaldehyde	1.32	0.50	1.39	0.28
Methacrolein	0.00	0.00	0.00	0.00
Methyl Ethyl Ketone	0.00	0.00	0.00	0.00
Butyraldehyde	4.72	1.21	4.52	1.12
Benzaldehyde	1.23	0.75	1.53	0.42
Valeraldehyde	0.50	0.05	0.42	0.03
Tolualdehyde	2.84	1.50	3.74	0.96
Hexadehyde	0.54	0.10	0.39	0.06

	Low Aromatic			
	Cold Start Cycle		Hot Start Cycle	
	Average mg/bhp-hr	SDEV mg/bhp-hr	Average mg/bhp-hr	SDEV mg/bhp-hr
Formaldehyde	54.75	2.10	59.42	5.77
Acetaldehyde	17.66	0.45	19.34	1.72
Acrolein	5.49	0.69	5.84	0.91
Acetone	6.23	0.65	6.81	0.66
Propionaldehyde	3.90	0.22	3.92	0.49
Crotonaldehyde	2.09	0.34	2.55	0.37
Methacrolein	0.10	0.09	0.32	0.44
Methyl Ethyl Ketone	0.00	0.00	0.00	0.00
Butyraldehyde	1.85	1.02	3.86	1.96
Benzaldehyde	2.82	0.36	2.03	1.40
Valeraldehyde	0.87	0.23	0.78	0.21
Tolualdehyde	2.35	0.58	3.05	0.61
Hexadehyde	0.47	0.06	0.45	0.26

	Reformulated Diesel			
	Cold Start Cycle		Hot Start Cycle	
	Average mg/bhp-hr	SDEV mg/bhp-hr	Average mg/bhp-hr	SDEV mg/bhp-hr
Formaldehyde	59.69	2.71	59.85	1.00
Acetaldehyde	20.10	1.10	19.90	0.58
Acrolein	2.52	0.44	2.41	1.71
Acetone	6.29	1.39	5.67	0.75
Propionaldehyde	4.28	0.84	4.11	0.47
Crotonaldehyde	1.46	0.29	1.47	0.47
Methacrolein	0.00	0.00	0.14	0.34
Methyl Ethyl Ketone	0.00	0.00	0.00	0.00
Butyraldehyde	5.21	0.54	4.30	1.07
Benzaldehyde	1.32	0.39	1.49	0.64
Valeraldehyde	1.28	0.21	1.04	0.24
Tolualdehyde	4.12	1.27	4.20	1.06
Hexadehyde	0.69	0.04	0.62	0.07

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Figure 11. Means and 95% Confidence Intervals for Toxic Oxygenates

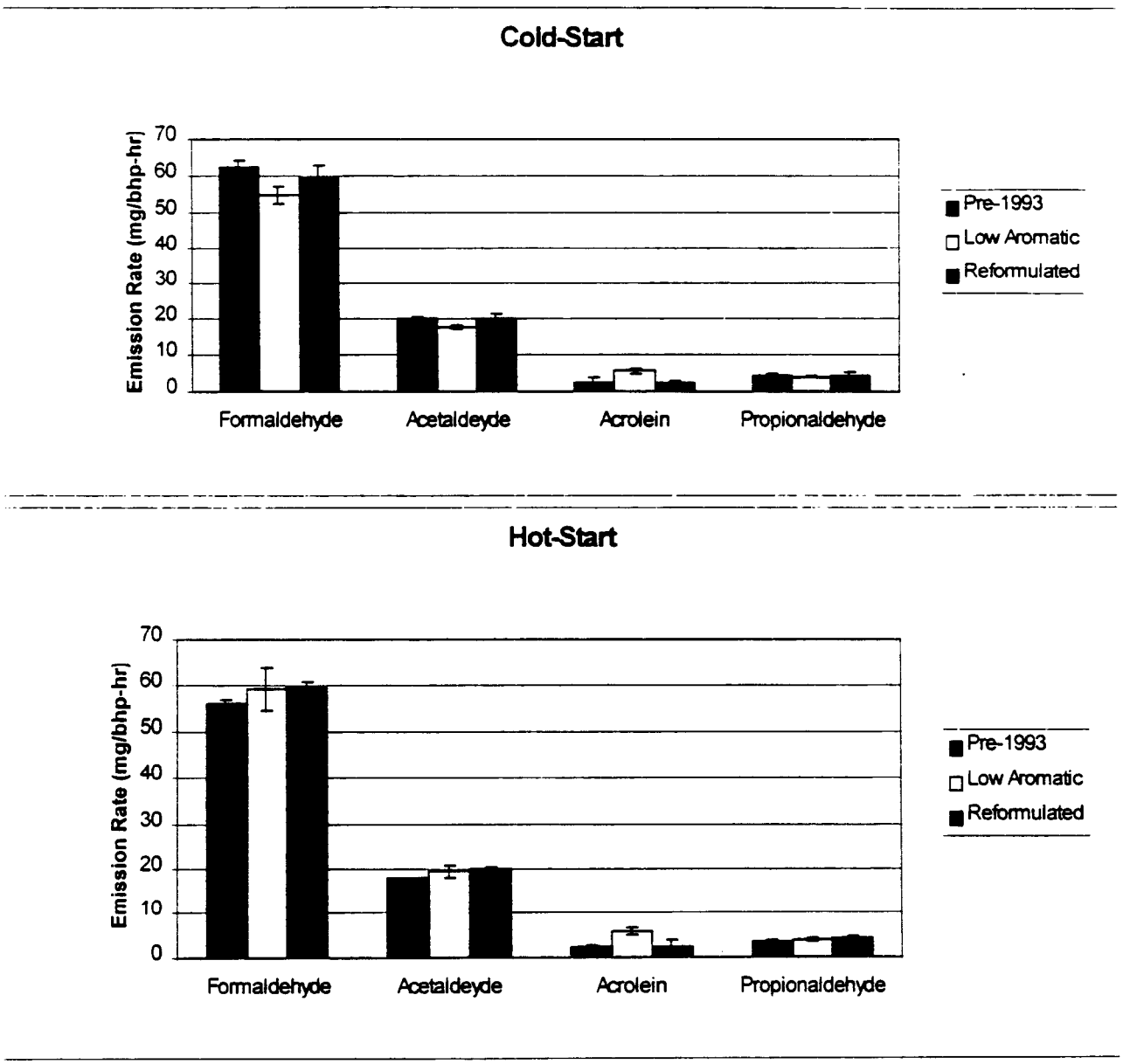

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Table 26. Analysis of variance (ANOVA) and pairwise Fisher's protected least square difference results for toxic oxygenates

	Formaldehyde		Acetaldehyde		Acrolein		Propionaldehyde	
	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
P-value	.0316	.2581	.0178	.0245	.0055	<.0001	.5384	.1746
Low Ar. vs. Pre-93	S		S	S	S	S		
Low Ar. vs. Reform.	S		S		S	S		
Pre-93 vs. Reform.				S				

Table 27. Emission Rates for Toxic Gas Phase Hydrocarbons

Pre-1993

	Cold-Start		Hot-Start	
	Emission Rate	Std. Dev.	Emission Rate	Std. Dev.
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
1,3-Butadiene	**2.08**	0.52	**1.75**	0.11
Benzene	**6.49**	0.04	**5.80**	0.30
Toluene	**2.17**	0.10	**1.89**	0.27
Ethylbenzene	**0.74**	0.06	**1.30**	0.66
o-xylene	**0.85**	0.09	**0.77**	0.09
m&p-xylene	**1.90**	0.23	**2.12**	0.55
Styrene	**0.97**	0.34	**1.32**	0.31
Naphthalene	**1.33**	0.09	**1.75**	0.50

Low Aromatic

	Cold-Start		Hot-Start	
	Emission Rate	Std. Dev.	Emission Rate	Std. Dev.
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
1,3-Butadiene	**2.19**	0.53	**2.50**	0.13
Benzene	**7.29**	0.38	**8.15**	1.17
Toluene	**1.96**	0.23	**2.31**	0.33
Ethylbenzene	**0.54**	0.11	**0.69**	0.20
o-xylene	**0.58**	0.05	**0.62**	0.11
m&p-xylene	**1.24**	0.20	**1.24**	0.34
Styrene	**2.10**	1.60	**1.49**	0.21
Naphthalene	**1.55**	0.54	**1.77**	0.25

Reformulated Blend

	Cold-Start		Hot-Start	
	Emission Rate	Std. Dev.	Emission Rate	Std. Dev.
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
1,3-Butadiene	**1.72**	0.04	**1.87**	0.15
Benzene	**6.78**	0.19	**5.65**	0.80
Toluene	**1.86**	0.55	**1.86**	0.25
Ethylbenzene	**1.03**	0.65	**1.20**	0.72
o-xylene	**0.99**	0.11	**0.86**	0.24
m&p-xylene	**1.84**	0.39	**2.19**	0.36
Styrene	**1.36**	0.19	**1.46**	0.31
Naphthalene	**1.18**	0.07	**1.29**	0.25

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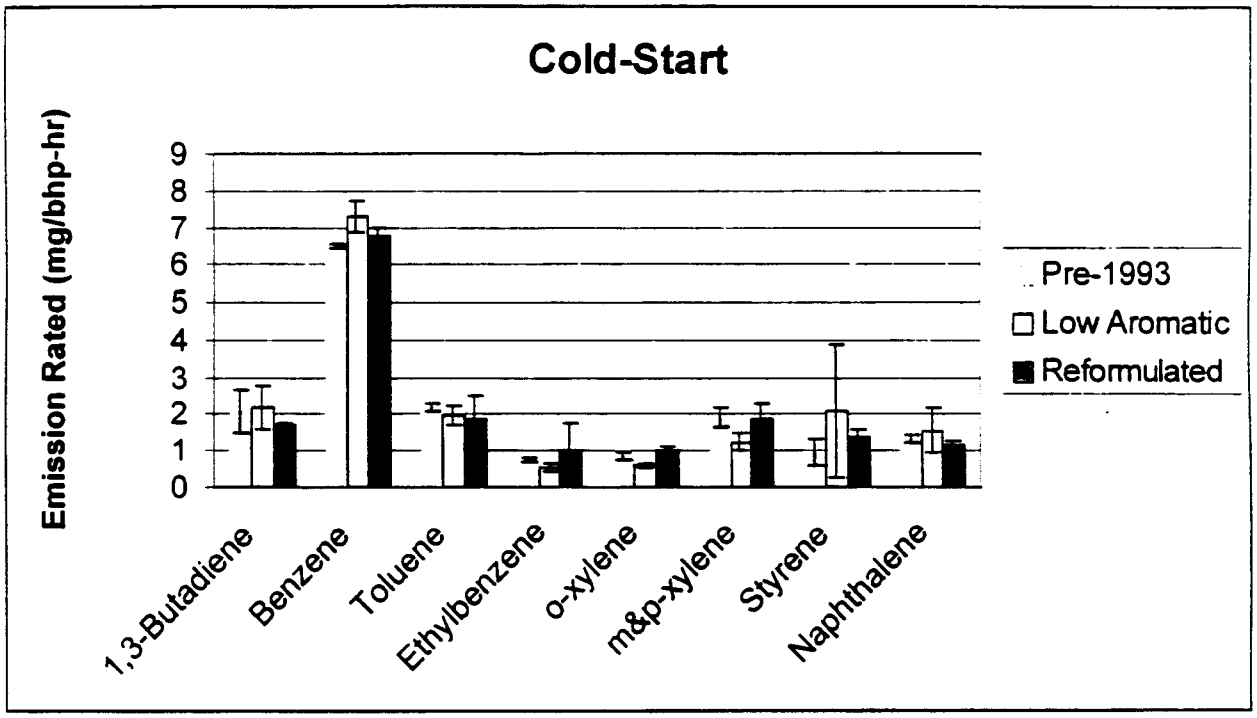
Figure 13. Means and 95% Confidence Intervals for Toxic Hydrocarbons



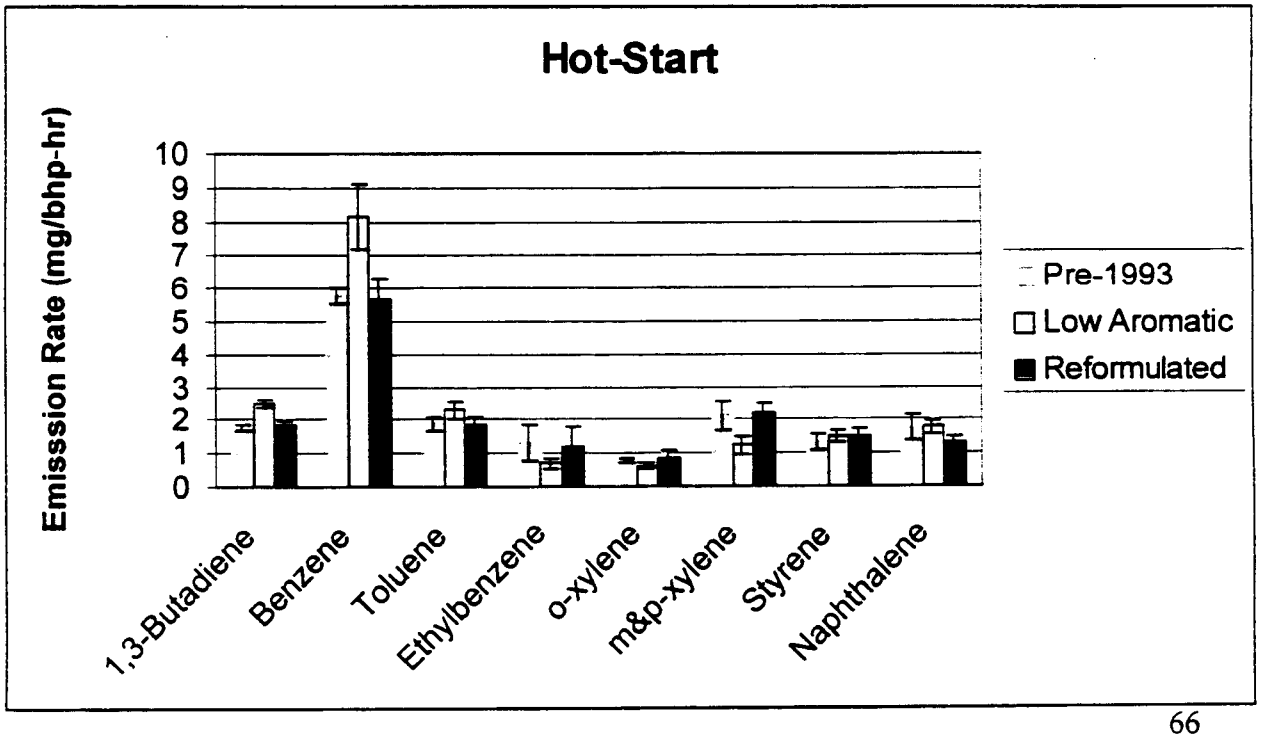


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Table 28. **Analysis of variance (ANOVA) and pairwise Fosher's protected least square difference results for toxic hydrocarbons.**

	1,3-but.	ben.	tol.	e-ben.	o-xyl.	m&p-xyl.	Sty.	Naph.
	Cold-Start							
P-value	.4293	.0195	.5877	.3527	.0034	.0553	.3898	.4123
Low Ar. vs. Pre-93		S			S			
Low Ar. vs. Reform.		S			S			
Pre-93 vs. Reform.								
	Hot-Start							
P-value	<.0001	<.0001	.0247	.1769	.0627	.0024	.5426	.0526
Low Ar. vs. Pre-93	S	S	S			S		
Low Ar. vs. Reform.	S	S	S			S		
Pre-93 vs. Reform.								

The following trends were observed with changes in fuel properties. Reduced polyaromatics increased benzene emissions, had little effect on 1,3-butadiene emissions, and reduced formaldehyde and acetaldehyde emissions. Increased cetane number reduced benzene, 1,3-butadiene, formaldehyde, and acetaldeyde emissions. Reduced 95% boiling point increased benzene and formaldehyde emissions but mixed and complex results were observed for the 1,3-butadiene and

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acetaldehyde emissions. Reduced density reduced benzene, 1,3-butadiene, and formaldehyde emissions. Due to the interaction of fuel parameters in this study, it is difficult to interpret the present results based upon the findings of Hublin, et al. The trend observed in this study for increased benzene emissions with the low aromatic fuel may be consistent with the results of Hublin, et al., if the effects of reduced polyaromatics and 95% BP are dominant over the density and cetane effects. However, at this stage such conclusions are probably no better than speculation.

3.6 PAH and Nitro-PAH

Gas-Particle Distribution of PAH under High Volume Sampling Conditions: In order to collect the total PAH emissions from the diesel exhaust, high volume and low volume emission samples were collected for analysis at SAPRC and UCD. Experience with ambient sampling using high volume collection suggested that for the 4-ring and smaller PAH, some fraction of these PAH will be gas-phase and not particle-associated (Arey et al., 1987; 1989; Coutant et al, 1988; Wilson et al., 1995). The high volume sampling system used to collect the emission samples reported below was designed to be complementary to the low volume sampling system whose samples were analyzed and reported on by UCD. The high volume sampling system consisted of two T60A20 teflon-coated glass fiber filters backed up by two polyurethane foam plugs (PUFs), with the smaller back PUF allowing compound breakthrough from the first PUF to be determined. In the UCD low volume system the addition of XAD adsorbent after a PUF was designed for quantitative collection of even the most volatile PAH naphthalene (Westerholm et al., 1991).

The distributions of the PAH between the filters and PUFs are shown in Table 29 and Figure 14. The 4-ring PAH, benz[a]anthracene and chyrsene (m.w. 228 Daltons) were quantitatively collected on the filters with no significant amount (<5% of total) found in the front PUF extracts. The 4-ring PAH, fluoranthene and pyrene (m.w. 202 Daltons) were distributed between the filter and the front PUF, with no detectable fluoranthene or pyrene on the back PUF. Interestingly, a consistently higher fraction of the PAH was found on the particles from the low aromatic fuel samples (see Figure 14).

Because of the lack of available standards, the areas of the five methylphenanthrene/methylanthracene peaks (m.w. 192 Daltons) were summed and the response factor for 1-methylphenanthrene relative to deuterated phenanthrene was used to quantify all isomers. Prior reports have suggested that methylphenanthrenes may be used as a marker for diesel exhaust (Benner et al., 1989), and methylphenanthrene isomers have previously been quantified in heavy-duty diesel emissions (Westerholm and Li, 1994). Summing the areas of the five peaks may

Table 29. Distribution of PAH between Filter and PUFs during High Volume Sampling.

Pre- 1993 Fuel

PAH	Average % on Filter	SDEV	Average % on Front PUF	SDEV	Average % on Back PUF	SDEV
2,3,5-Trimethylnaphthalene	0.0	0.0	88.2	1.5	11.8	1.5
Phenanthrene	8.6	1.3	91.2	1.3	0.2	0.2
Anthracene	13.7	1.9	86.3	1.9	0.0	0.0
Methylphenanthrenes	18.9	3.3	81.0	3.3	0.1	0.0
Fluoranthene	43.3	7.2	56.7	7.2	0.0	0.0
Pyrene	52.7	7.6	47.3	7.6	0.0	0.0

Low Aromatic Fuel

PAH	Average % on Filter	SDEV	Average % on Front PUF	SDEV	Average % on Back PUF	SDEV
2,3,5-Trimethylnaphthalene	0.0	0.0	84.2	2.4	15.8	2.4
Phenanthrene	16.0	1.5	83.7	1.3	0.3	0.2
Anthracene	28.1	2.8	71.9	2.8	0.0	0.0
Methylphenanthrenes	27.6	3.3	71.6	3.9	0.8	1.1
Fluoranthene	71.7	7.9	28.3	7.9	0.0	0.0
Pyrene	78.4	6.4	21.6	6.4	0.0	0.0

Reformulated Diesel Blend

PAH	Average % on Filter	SDEV	Average % on Front PUF	SDEV	Average % on Back PUF	SDEV
2,3,5-Trimethylnaphthalene	0.0	0.0	81.4	3.3	18.6	3.3
Phenanthrene	7.6	0.6	91.8	0.6	0.6	0.6
Anthracene	13.0	1.4	87.0	1.4	0.0	0.0
Methylphenanthrenes	12.4	1.8	87.4	1.8	0.2	0.1
Fluoranthene	41.7	3.3	58.3	3.3	0.0	0.0
Pyrene	51.3	3.6	48.7	3.6	0.0	0.0

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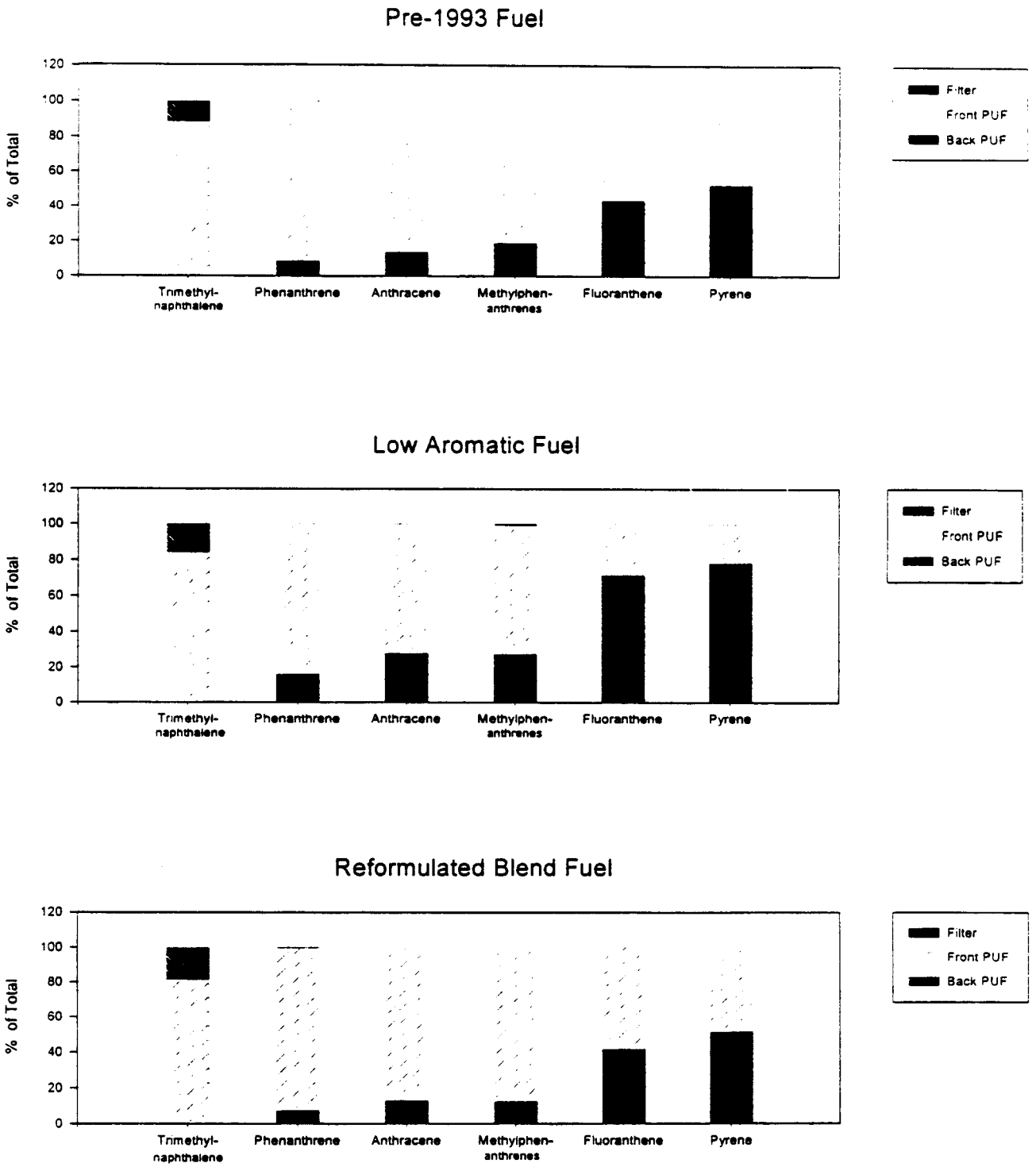
Figure 14. Distribution of PAH between Filter and PUFs during High Volume Sampling



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cause some systematic error in the quantification, but since the pattern of isomers present was consistent, the relative amounts from each of the fuel types can be reliably determined. Methylphenanthrene/methylanthracenes were found mainly on the front PUFs, but with a significant fraction (up to 30%) on the filters and minimal breakthrough (<0.3%, except for a single sample of 2%) on the back PUF (see Figure 14).

The 3-ring PAH phenanthrene and anthracene (m.w. 178 Daltons) were again mainly collected on the front PUFs with up to 17% for phenanthrene and 31% for anthracene present on the low aromatic fuel filters and minimal (≤0.5%, except for a single sample of 1.3%) present on the back PUF.

Breakthrough onto the back PUF became significant for the alkylnaphthalenes. Figure 14 shows the distribution of 2,3,5-trimethylnaphthalene (m.w. 170 Daltons) between the front and back PUF. Therefore, the quantification of C_3-naphthalenes using the high volume sampling system strictly gives only lower limits to the true emissions.

In summary, the fraction of the PAH present on the PUFs decreased with the volatility of the PAH in the order: C_3-naphthalene > phenanthrene > anthracene > C_1-phenanthrene/anthracene > fluoranthene > pyrene. The PAH more volatile than the C_3-naphthalenes were not quantitatively collected using the filter/PUF sampling system. Only analysis of the filter samples was required to quantify the PAH of molecular weight 228 Daltons and above.

PAH in the Emissions are Fuel-derived and Formed *In-situ*: Table A3 in Attachment B lists the results for micrograms of individual PAH emissions per brake horse power hour for the three replicate (sum of high volume filter plus PUF) samples from the three fuel types: pre-1993 fuel, low aromatic fuel, and blend of reformulated fuels. Table 30 lists the average PAH emissions and standard deviation for the three fuels. Figure 15 through Figure 20 show the means and 95% confidence intervals for the PAH in the emissions from the three fuel types. As may be seen from Figure 15, there were large variations in emissions for PAH of ≤3-rings. Fuel analysis of the pre-1993 fuel showed the presence of alkylnaphthalenes, phenanthrene and methylphenanthrenes derivatives. The concentrations of these PAH present in the exhaust is consistent with the majority of these emissions resulting from the PAH initially present in the fuel, with the highest levels in the pre-1993 fuel (6.9 mass% PAH), followed by the reformulated fuel (4.1 mass% PAH) and with very low levels found in the emissions from the low aromatic fuel (0.7 mass%PAH). In contrast, the similarity of the emissions for PAH≥4-ring independent of the fuel type (see Figures 14-19) suggests that these PAH are formed *in-situ* during the combustion process.

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Table 30. Average Emission Rates for Polycyclic Aromatic Hydrocarbons.

PAH	Pre-1993 Diesel Fuel Average µg/bhp-hr	Pre-1993 Diesel Fuel SDEV µg/bhp-hr	Low Aromatic Diesel Fuel Average µg/bhp-hr	Low Aromatic Diesel Fuel SDEV µg/bhp-hr	Reformulated Diesel Blend Average µg/bhp-hr	Reformulated Diesel Blend SDEV µg/bhp-hr
2,3,5-trimethylnaphthalene[a,b]	283.68	5.27	14.77	2.42	56.21	2.82
phenanthrene[c]	336.71	9.08	160.92	15.54	220.73	52.65
anthracene[d]	38.89	1.43	18.54	2.13	26.16	6.86
Me-phenanthrenes/anthracenes[c,e]	331.32	16.07	25.17	1.41	111.98	28.74
fluoranthene[d]	128.45	7.60	132.36	18.30	123.07	26.21
pyrene[d]	193.03	16.51	211.19	37.35	206.82	39.04
benzo[c]phenanthrene	3.03	0.24	1.74	0.14	1.54	0.26
benzo[ghi]fluoranthene[f]	24.84	2.68	18.93	2.14	16.94	2.31
cyclopenta[cd]pyrene	21.44	4.11	26.15	3.12	21.25	3.46
benz[a]anthracene	16.42	1.67	10.57	1.15	10.96	2.42
chrysene + triphenylene[g]	17.36	1.66	10.38	0.54	12.20	2.72
benzo[b+j+k]fluoranthene[g]	31.05	4.17	23.17	1.98	29.18	7.93
benzo[e]pyrene	16.71	2.72	14.55	1.34	18.99	5.58
benzo[a]pyrene	20.46	3.27	16.48	1.56	20.59	5.75
perylene	4.32	0.88	3.71	0.74	4.18	1.16
indeno[1,2,3-cd]fluoranthene	0.34	0.07	0.21	0.02	0.17	0.00
benzo[c]chrysene	0.29	0.05	0.18	0.05	0.14	0.04
dibenz[a,j]anthracene	0.93	0.05	0.55	0.10	0.67	0.09
indeno[1,2,3-cd]pyrene	19.45	2.71	14.04	1.99	22.16	9.11
dibenz[a,h + a,c]anthracene[g]	1.54	0.15	0.87	0.12	1.48	0.67
benzo[b]chrysene	0.40	0.01	0.15	0.05	0.27	0.05
benzo[ghi]perylene	49.17	9.63	39.81	7.22	60.74	26.60
coronene	9.49	3.13	4.93	0.47	7.48	1.59
dibenzo[a,l]pyrene	2.84	0.45	1.25	0.15	2.31	0.48
dibenzo[a,e]pyrene	1.10	0.29	0.61	0.06	1.13	0.15
dibenzo[a,i]pyrene	0.91	0.21	0.27	0.09	0.71	0.15
dibenzo[a,h]pyrene	1.33	0.25	0.75	0.07	0.84	0.20

[a] Lower limit based on summing amounts on front PUF and back PUF (amount on filter negligible).
[b] The area of the molecular ion peak (m/z 170) and the response factor for 2,3,5-trimethylnapthalene relative to deuterated phenanthrene were used to quantify 2,3,5-trimethylnaphthalene and a co-eluting isomer
[c] Sum of amounts on filter, front PUF and back PUF
[d] Sum of amounts on filter and front PUF; negligible amount found on back PUF
[e] The areas of the molecular ion of the five isomers present were summed and the response factor for 1-methyl-phenanthrene relative to deuterated phenanthrene was used to quantify all isomers.
[f] Standard not available, response factor for cyclopenta[cd]pyrene relative to deuterated chrysene used for quantification
[g] Co-eluting isomers

Figure 15. Means and 95% Confidence Intervals for 2-4 Ring PAH and Alkyl-PAH

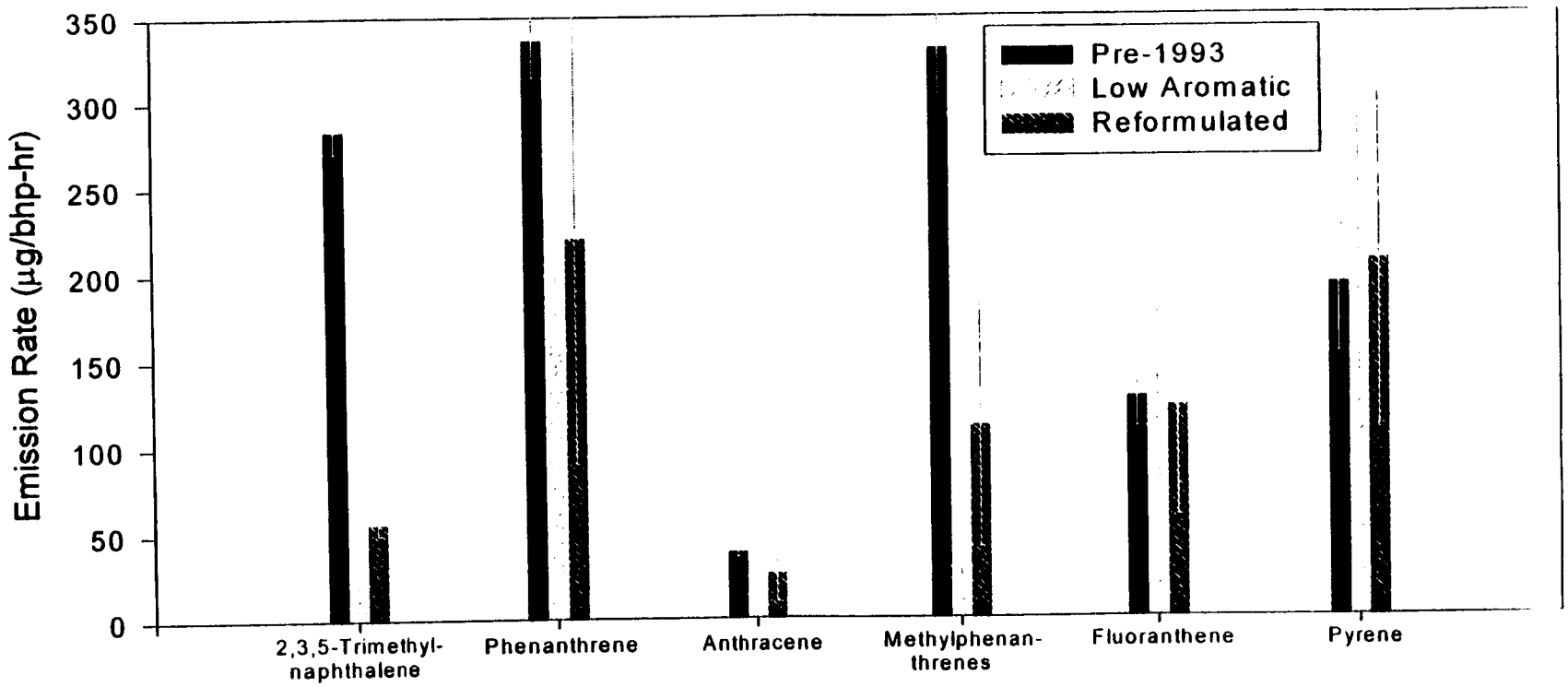


Figure 15. Means and 95% Confidence Intervals for 4-Ring PAH of Molecular Weight Range 226-228 Daltons.

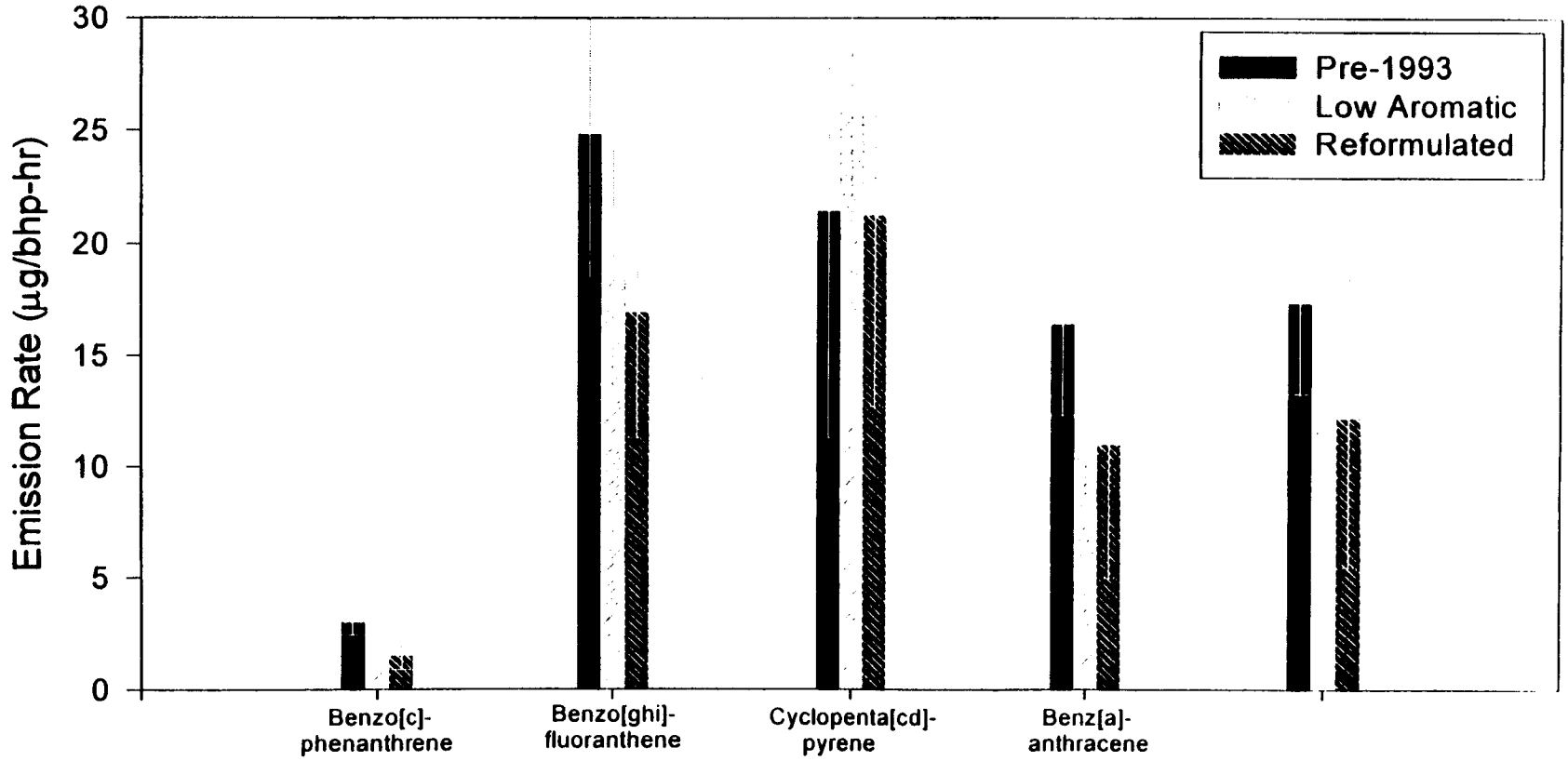


Figure 16. Means and 95% Confidence Intervals for 5-Ring PAH of Molecular Weight 252 Daltons.

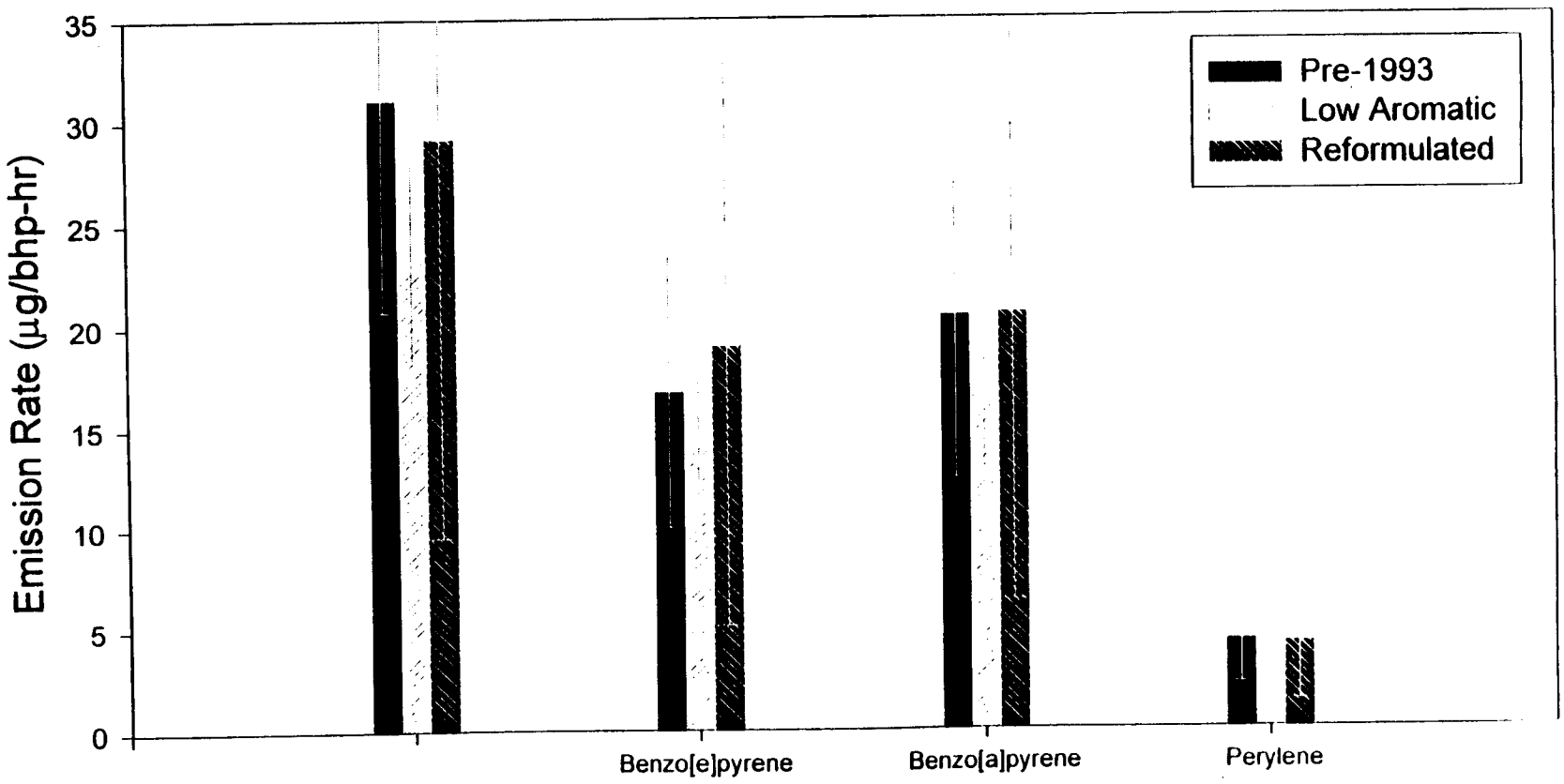


Figure 17. Means and 95% Confidence Intervals for Most Abundant PAH of Molecular Weights 276 and 300 Daltons.

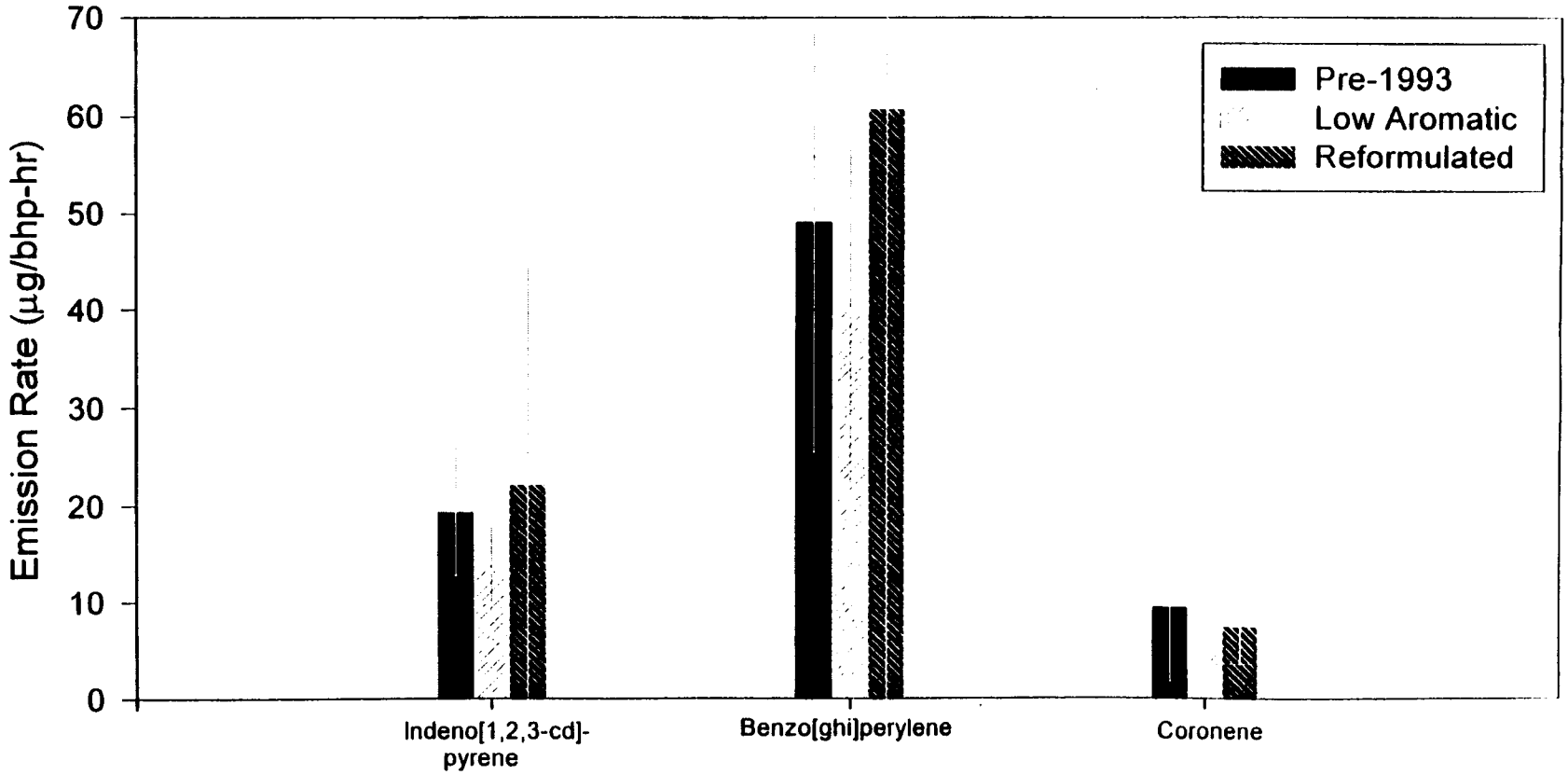


Figure 18. Means and 95% Confidence Intervals for PAH of Molecular Weights 276 and 278 Daltons.

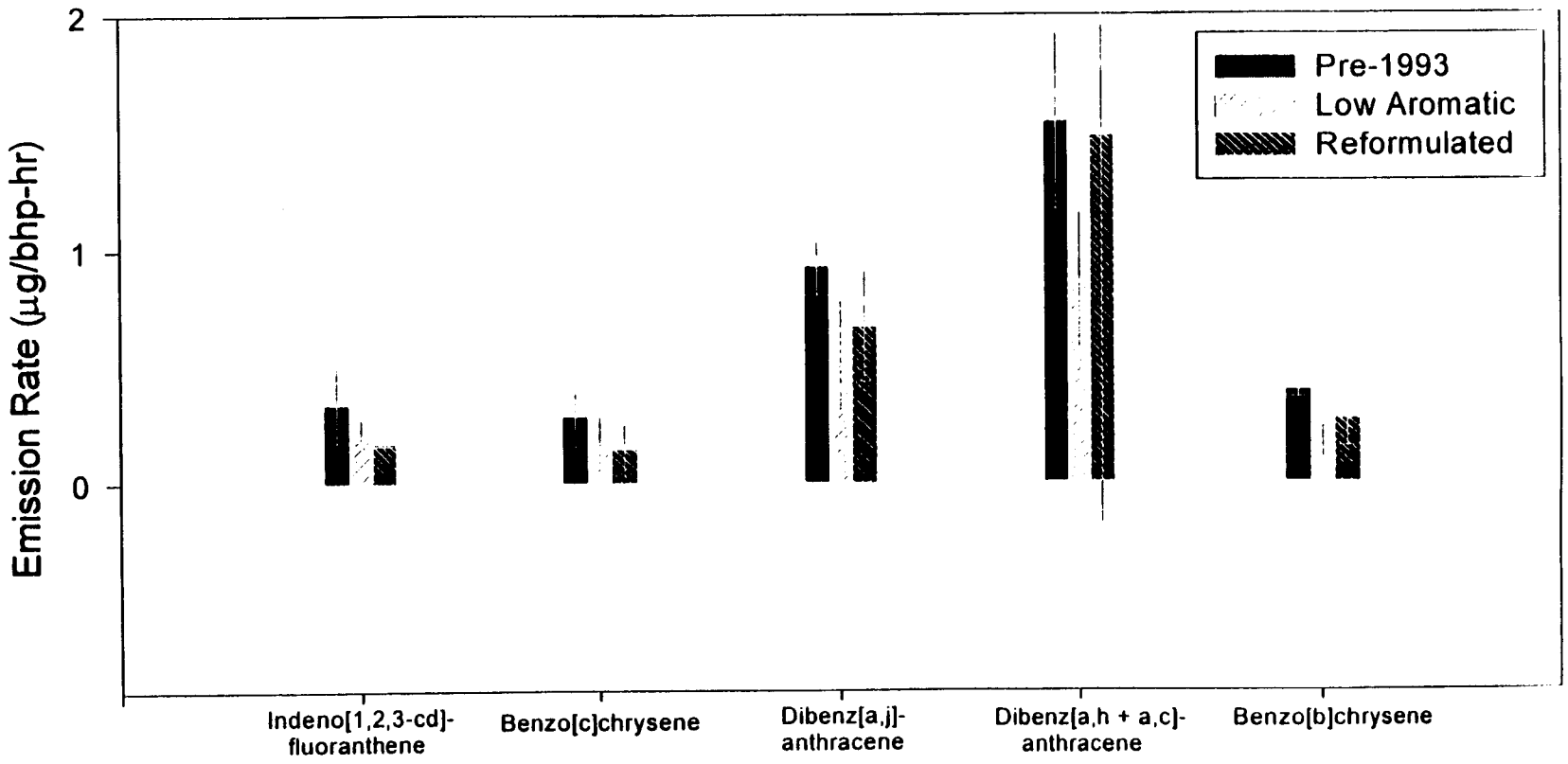
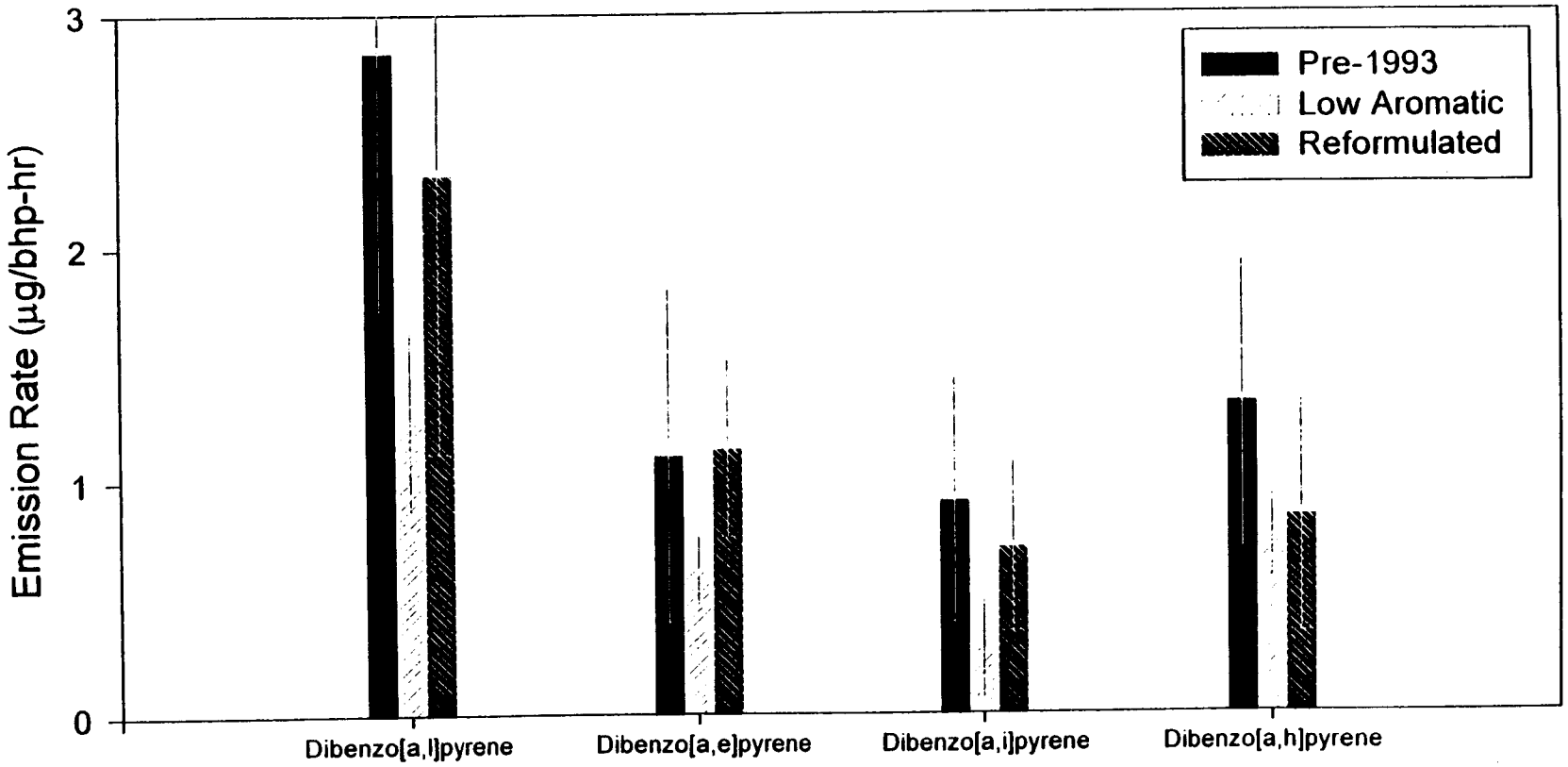


Figure 20. Means and 95% Confidence Intervals for Isomeric Dibenzopyrenes (302 Daltons)



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As may be seen from Figure 15, the alkyl-PAH are statistically different in each of the three fuel types. Phenanthrene and anthracene are statistically higher in the pre-1993 fuel emission than in the low aromatic fuel emissions, but the 95% confidence intervals for the reformulated fuel blend overlaps with both the remaining fuel types. This is consistent with phenanthrene and anthracene being present at higher levels in the pre-1993 fuel, but also being formed *in situ* in the combustion process. Alkyl-PAH reportedly are formed in lower abundance than their parent PAH in high temperature combustion processes (Benner et al., 1989). Generally for the higher molecular weight PAH, beginning with fluoranthene and pyrene (see Figure 15), the 95% confidence intervals of the emissions from the three fuel types overlap. In a few instances, the 95% confidence interval for the pre-1993 fuel emissions does not overlap with the low aromatic fuel emissions, and the lowest emission rate for the majority of the PAH was for the low aromatic fuel.

Nitro-PAH: Table A4 in the Appendix lists the results for micrograms of individual nitro-PAH emissions per brake horse power hour for the three replicate samples from the three fuel types. Because the distribution of the PAH between the filter and PUF plugs closely resembled the distribution previously observed under ambient sampling conditions (Arey et al., 1987), any nitronaphthalenes, methylnitronaphthalenes, nitrobiphenyls and nitroacenaphthene were expected to be on the PUFs. The three-ring nitro-PAH were expected to be particle-associated. 2-Nitrofluorene was looked for in both the filter and PUF extracts.

The average nitro-PAH emissions are given in Table 31. Only five nitro-PAH were detected. 1-Nitronaphthalene and 2-nitronaphthalene were quantified in the PUF plug extracts and analysis of the back PUF showed that no breakthrough during sampling had occurred. The most abundant nitro-PAH was 1-nitropyrene. 6-Nitrobenzo[a]pyrene and 9-nitroanthracene were also quantified in each of the filter extracts. The means and 95% confidence intervals for the nitro-PAH are shown in Figure 20. The levels of the particle-associated nitro-PAH were similar for the three fuel types. The low aromatic fuel had lower levels of the nitronaphthalenes, perhaps reflecting lower naphthalene emissions (although these were not statistically lower at the 95% confidence level).

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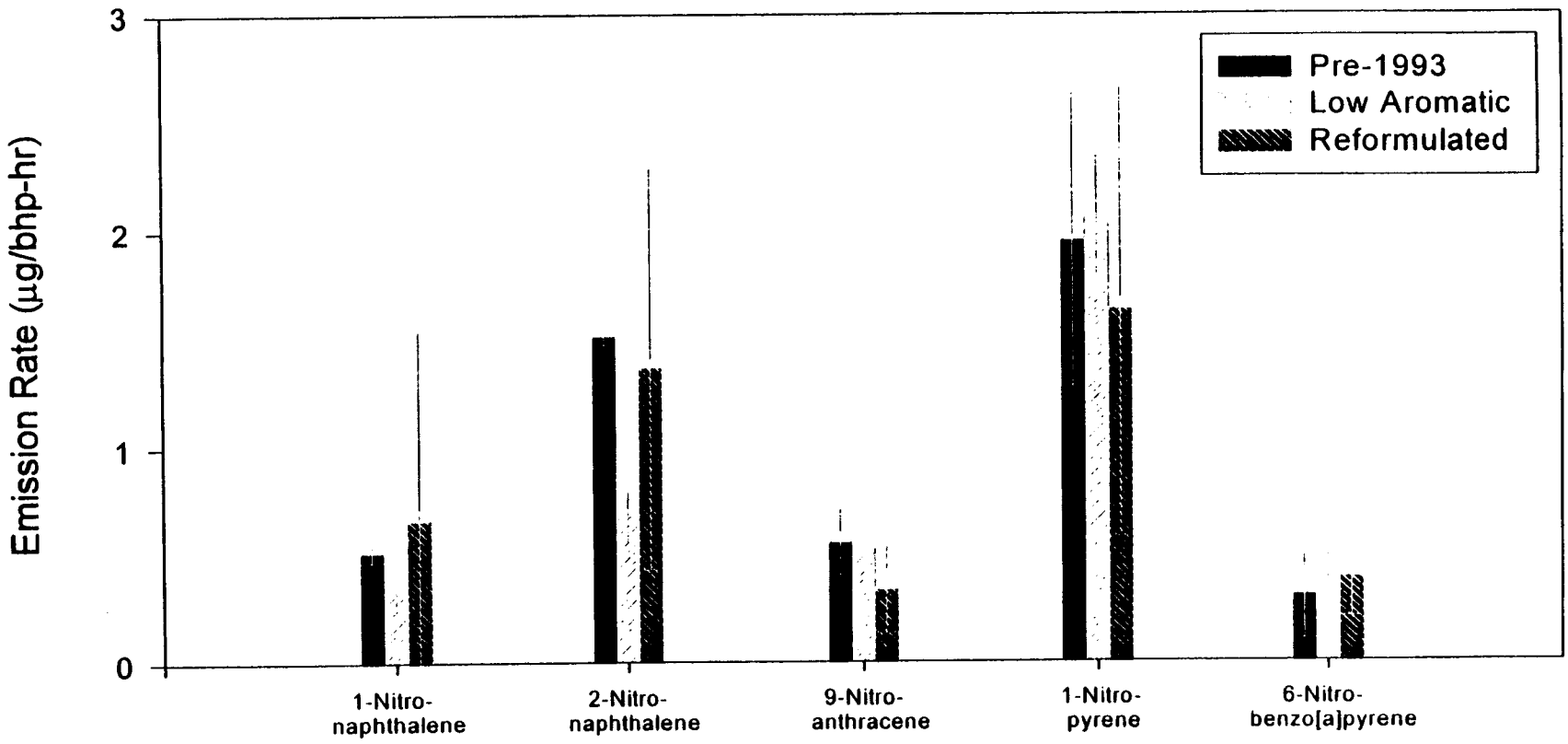
Table 31. Average Emission Rates for Nitro-Polycyclic Aromatic Hydrocarbons.

	Pre-1993 Diesel Fuel		Low Aromatic Fuel		Reformulated Fuel	
Nitro-PAH	**Average** µg/bhp-hr	**SDEV** µg/bhp-hr	**Average** µg/bhp-hr	**SDEV** µg/bhp-hr	**Average** µg/bhp-hr	**SDEV** µg/bhp-hr
1-nitronaphthalene	0.52	0.02	0.32	0.02	0.66	0.35
2-nitronaphthalene	1.51	0.02	0.69	0.05	1.37	0.38
methylnitronaphthalenes	<0.5		<0.5		<0.5	
2-nitrobiphenyl	<0.5		<0.5		<0.5	
4-nitrobiphenyl	<0.5		<0.5		<0.5	
5-nitroacenaphthene	<0.5		<0.5		<0.5	
2-nitrofluorene	<0.3		<0.3		<0.3	
9-nitroanthracene[a]	0.56	0.06	0.54	0.01	0.34	0.08
1-nitropyrene	1.95	0.27	2.07	0.11	1.64	0.43
3-nitrofluoranthene	<0.06		<0.06		<0.06	
4-nitropyrene	<0.06		<0.06		<0.06	
7-nitrobenz[a]anthracene	<0.1		<0.1		<0.1	
6-nitrochrysene	<0.1		<0.1		<0.1	
6-nitrobenzo[a]pyrene	0.31	0.08	0.42	0.04	0.39	0.08

[a]For the Pre-1993 Fuel and the Reformulated Blend, interferences prevented quantification using the molecular ion at m/z 223 and the $[M-NO]^+$ fragment ion was used.

Figure 20. Means and 95% Confidence Intervals for the Nitro-PAH.



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Upper limits are given in Table 31 for the particle-associated nitro-PAH that were not detected. These limits are based on the response from injections of a standard solution made from SRM 1587 and containing sub-ng levels of the nitro-PAH analytes, or in the case of 4-nitropyrene and 3-nitrofluoranthene, estimating what fraction of the observed isomeric 1-nitropyrene would clearly be detected. Figure 21 shows GC-MS ion traces of the molecular ion, m/z 247, for the nitropyrenes (NP) and nitrofluoranthenes (NF) for a solution containing all eight isomers (upper trace) and an injection of the filter extract from the reformulated fuel sample (351H3,H4) showing the 1-nitropyrene present and arrows at the retention times for 3-NF and 4-NP (lower trace). Assuming that a peak with 3% of the area of the 1-nitropyrene peak would be readily detected, an upper limit for 3-NF and 4-NP of 0.06 μg/bhp-hr is given. Solutions containing the 14 methylnitronaphthalenes and the isomeric 199 Daltons species (nitrobiphenyls and nitroacenaphthene) were used to determine the retention times for these analytes and their characteristic fragmentation patterns. Careful comparisons with the ion chromatograms from the PUF sample extracts showed no evidence for the presence of these volatile nitro-PAH. A conservative upper limit of 5 μg/bhp-hr is reported in Table 31 for these volatile nitro-PAH.

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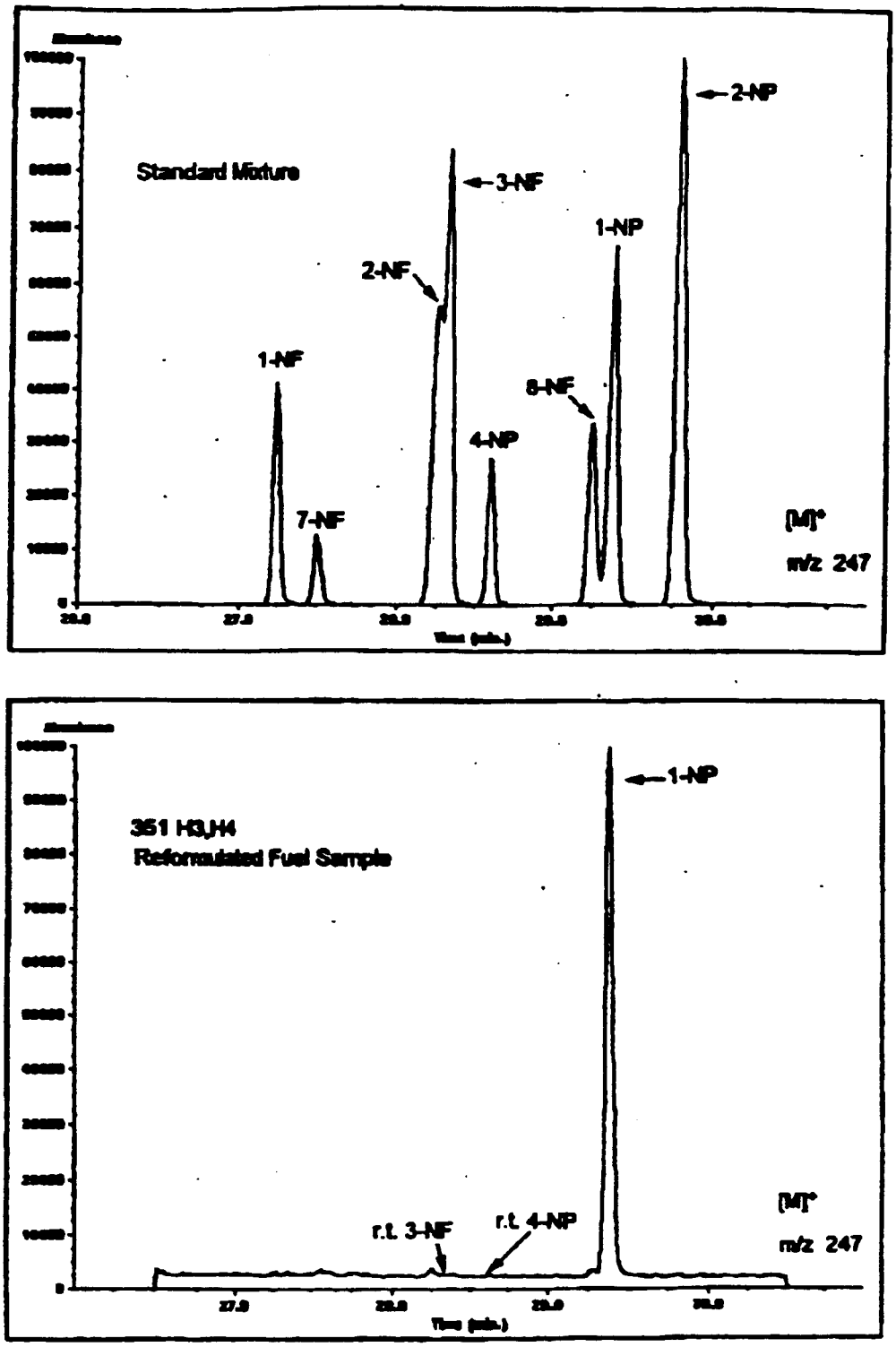

Figure 21 GC-MS SIM Traces of the Molecular Ion for the Nitrofluoranthenes (NF) and Nitropyrenes (NP).

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3.7 Vapor Phase PAH

High volume and low volume emission samples were collected from the exhaust of the diesel engine using three fuels. In addition requisite trip blanks, tunnel blanks, and trip spikes were collected. Included in this report are the vapor-phase PAH results from the low volume and high volume samples. For the purposes of this report PAHs distributed between the filter, XAD, and PUF are considered vapor phase PAHs. In all samples the filter, PUF and XAD were analyzed separately. To estimate the total emissions of individual vapor phase PAHs the chemical results from the filter, PUF and XAD were combined.

2,6 dimethyl naphthalene co-elutes with 2,7 dimethyl naphthalene and is reported as the sum of the two dimethyl naphthalenes. Also 2,3,5-trimethyl naphthalene co-elutes with another trimethyl naphthalene and they are reported as the sum of the two trimethyl naphthalenes. A compound that co-elutes with acenaphthene prevented its quantitation. In some of the samples there were interferences with one of the qualifier ions of fluorene and the identification was based on two of the three ions.

PAHs measured in the PUF portion of the low volume sample: Presented in Table 32 are the PAH emission rates of the PAHs collected on the PUF. Naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, biphenyl, dimethyl naphthalene, trimethyl naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene were detected in all the samples. Fluoranthene and pyrene were detected in all the samples with none reported in the PUF trip blank. All the tunnel blanks PUF contained fluoranthene and pyrene except for fluoranthene in the reformulated fuel emission sample (H145) at levels above 20% of the samples. Those results are highlighted in bold. Since the dilution tunnel is higher than the trip blank, this indicates that the fluoranthene and pyrene are being stripped off the tunnel during sampling of the blank. This happens even after the tunnel has been conditioned by running ambient air through the tunnel for 2 hours prior to collecting the tunnel blanks. It is uncertain how to correct for tunnel blanks since they are not conducted under identical conditions to the samples. For example, tunnel blanks are run at cooler temperatures and when the engine is not running. For this reason, sample data is highlighted in bold where tunnel blanks are over 20% of the sample values.

The PUF extract contained many other alkyl PAHs that were not quantified. To quantitate on the target compounds the PUF extracts were cleaned up using C-18 and Silica cartridges. The PAH

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fractions revealed a whole series of alkylated PAHs. Among them a series of C1, C2, C3, - naphthalenes were detected in the analysis of the target compounds.

Table 32. PAH emissions from the PUF in the low volume sampler.

	pre-1993[a]	pre-1992	reform[b]	reform	low aromatic[c]
	H110[d]	H170	H145	H150	H127
	ug/brhphr[e]	ug/brhphr	ug/brhphr	ug/brhphr	ug/brhphr
naphthalene	241	282	168	240	140
2-methyl naphthalene	573	610	287	356	71
1-methyl naphthalene	424	434	181	217	54
biphenyl	345	327	266	268	61
2,6/2,7-dimethyl naphthalene	848	727	277	294	58
acenaphthylene	355	399	358	294	263
acenaphthene	CoE[f]	CoE	CoE	CoE	CoE
2,3,5-trimethyl naphthalene[g]	347	301	106	102	22
fluorene	197	184	129	71	40
phenanthrene	285	217	184	140	89
anthracene	34	29	12	17	9
fluoranthene	18	12	13	7	4
pyrene	22	12	11	9	6

a. pre-1993 fuel
b. reformulated blend
c. low aromatic fuel
d. Sample Identification
e. brake horse power hour
f. Another compound coelutes with Acenaphthene and it cannot be quantitated.
g. 2,3,5-trimethyl naphthalene coelutes with another naphthalene, quanitation is based on 2,3,5-trimethyl naphthalene

PAHs measured in XAD portion of the low volume sampler: The PAH emission rates for the XAD resin are presented in Table 33. The main PAHs in the XAD samples were naphthalene, 1-methyl naphthalene, and 2-methyl naphthalene, although many other unquantified alkylated naphthalenes were present in the samples. Other quantitated PAHs included biphenyl, 2,4 dimethyl naphthalene, and acenaphthylene.

Analysis of the trip blank and tunnel blanks showed high levels of naphthalene contamination. In the low aromatic fuel emission XAD sample blank, levels of naphthalene contributed to over half the total naphthalene measured. Naphthalene XAD blank levels for the pre-1993 and reformulated blend emission XAD samples were lower, but still significant at 23% and 42% respectively of the total naphthalene measured. Naphthalene is a contaminant inherent in XAD and cannot be completely removed. Levels of acenaphthene, 2,3,5-trimethyl naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene were comparable in the trip, tunnel blanks and samples. Inspection of the PUF data showed that most of these PAHs were efficiently trapped by the PUF, and little broke through from the PUF to XAD. PAHs with tunnel blank values higher than 20% are highlighted in bold.

In order to obtain the total emission rates of PAHs found in the vapor phase, the diesel particulate filter samples needed to be analyzed. 2,3,5-trimethyl naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene can partition between the filter and PUF. Presented in Table 34 are the PAH emission results from the filter analysis.

Table 33. PAH emissions from the XAD in the low volume sampler

	pre-1993[a]	pre-1993	reform[b]	reform	low aromatic[c]
	H110[d]	H170	H145	H150	H127
	µg/brhphr[e]	µg/brhphr	µg/brhphr	µg/brhphr	µg/brhphr
naphthalene	**2100**	**1674**	**1616**	**1739**	**841**
2-methyl naphthalene	1043	703	555	542	74
1-methyl naphthalene	631	396	282	263	46
biphenyl	58	17	61	25	9
2,6/2,7-dimethyl naphthalene	118	45	56	33	11
acenaphthylene	0	0[h]	0	0	0
acenaphthene	CoE[f]	CoE	CoE	CoE	CoE
2,3,5-trimethyl naphthalene[g]	**28**	**38**	**41**	**38**	**33**
fluorene	33	**23**	**19**	**17**	**13**
phenanthrene	**32**	**72**	**50**	**43**	**34**
anthracene	**4**	**10**	**7**	**5**	**5**
fluoranthene	**0**	**3**	**0**	**2**	**0**
pyrene	**18**	**18**	**10**	**3**	**0**

a. pre-1993 fuel
b. reformulated blend
c. low aromatic fuel
d. Total PAH
e. brake horse power hour
f. Another compound coelutes with Acenaphthene and it cannot be quantitated.
g. 2,3,5-trimethyl naphthalene coelutes with another naphthalene, quanitation is based on 2,3,5-trimethyl naphthalene

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these XAD levels are not added to the PUF and filter values to calculate emission rates, then the blanks levels fall well below 20% for all samples except for naphthalene.

Naphthalene, 2-methyl naphthalene, 1-methyl naphthalene, biphenyl, 2,4-dimethyl naphthalene, and acenaphthylene are distributed between the PUF and XAD, the 2,3,5 trimethyl naphthalene, phenanthrene, and anthracene are mainly in the PUF, and the fluoranthene and pyrene are mainly in the particulate matter.

Table 35. Sum of PAH emissions from the Filter, PUF and XAD in the low volume sampler.

	pre-1993[a]	pre-1993	reform[b]	reform	low aromatic[c]
	H110[d]	H170	H145	H150	H127
	µg/brhphr[e]	µg/brhphr	µg/brhphr	µg/brhphr	µg/brhphr
naphthalene	2340	**1956**	**1784**	**1980**	**980**
2-methyl naphthalene	1617	1313	842	899	145
1-methyl naphthalene	1055	830	463	480	101
biphenyl	403	345	326	293	69
2,6/2,7-dimethyl naphthalene	966	771	358	327	68
acenaphthylene	355	399	148	294	263
acenaphthene	CoE[f]	CoE	CoE	CoE	CoE
2,3,5-trimethyl naphthalene[g]	384	343	**149**	**141**	**57**
fluorene	199	208	17	89	54
phenanthrene	**368**	333	263	210	**158**
anthracene	**45**	**46**	**23**	**27**	**20**
fluoranthene	72	75	70	**55**	67
pyrene	125	118	114	101	104

a. pre-1993 fuel
b. reformulated blend
c. low aromatic fuel
d. Sample Identification
e. brake horse power hour
f. Another compound coelutes with Acenaphthene and it cannot be quantitated.
g. 2,3,5-trimethyl naphthalene coelutes with another naphthalene, quanitation is based on 2,3,5-trimethyl naphthalene

Table 34. PAH emissions from the Filter in the low volume sampler.

	pre-1993[a]	pre-1993	reform[b]	reform	low aromatic[c]
	H110[d]	H170	H145	H150	H127
	µg/brhphr[e]	µg/brhphr	µg/brhphr	µg/brhphr	µg/brhphr
2,3,5-trimethyl naphthalene[f]	5	4	1	1	2
Fluorene	2	2	1	1	1
phenanthrene	50	44	29	27	35
anthracene	7	7	4	5	5
fluoranthene	54	60	57	47	63
pyrene	85	87	93	89	98

a. pre-1993 fuel
b. reformulated blend
c. low aromatic fuel
d. Sample Identification
e. brake horse power hour
f. 2,3,5-trimethyl naphthalene coelutes with another naphthalene, quanitation is based on 2,3,5-trimethyl naphthalene

Total PAH Emission Rates of the Combined Filter/XAD/PUF from the Low Volume Samples: PAH emission rates determined from the low volume samples for the heavy-duty diesel engine using the three fuels are given in Table 35. Emission rates are calculated by summing the PAHs measured in the Filter, PUF and XAD. The Pre-1993 fuel had the highest emissions rates for the all the alkyl-PAHs, including 1 and 2 methyl-naphthalene, 2,4,dimethyl naphthalene, and trimethyl naphthalene, while the low aromatic fuel had the lowest emission rates for these alkyl PAHs. For the reformulated fuel the emission rates of these alkyl PAHs were intermediate between the low aromatic and pre-1993 fuel.

Prior to an engine test of a new fuel, a tunnel blank was taken. PAH levels in the tunnel blank were compared with PAH levels in the exhaust samples. PAH measurements where tunnel blank levels were greater than 20% of the sample values are highlighted in bold. Since trimethyl naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene levels in the XAD blank are comparable to XAD sample levels, it is assumed that these compounds are at background levels. If

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High Volume PAH: Table 36 shows the total PAHs emitted in the diesel exhaust of the three fuels. The high volume PAH emission profile is similar to the low volume emission profile with the PAH emission rate of the pre-1993 fuel being the highest and the low aromatic PAH emission rate being the lowest. The results from the reformulated blend must be considered suspect since the sample leaked during collection. The magnitude of the leak cannot be determined and it is not known if it affected the integrity of the sample. One trip blank and one tunnel blank for each fuel was taken for the high volume samples. All levels measured in the blanks were significantly less than 20% of the sample.

The volatile PAH emissions rates for the PUF are presented in Table 37 and volatile PAHs emission rates for the XAD are presented in Table 38. In general, the PUF samples contained napthalene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene. Alkyl naphthalenes quantitated were 1 and 2 methyl naphthalene, 2,4 dimethyl naphthalene, and 2,3,5 trimethylnaphthalenes. Other C2 and C3 napthalenes were detected at similar levels. PAHs with a molecular weight greater than 202 were not detected in the PUF samples.

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Table 36. High volume Total PAH emissions.

	pre-1993[a]	reform[b]	low aromatic[c]
	H3[d]	H6	H4
	µg/brhphr[e]	µg/brhphr	µg/brhphr
naphthalene	2921	2078	1905
2-methyl naphthalene	1637	949	225
1-methyl naphthalene	1118	547	158
biphenyl	481	379	110
2,6/2,7-dimethyl naphthalene	720	264	54
acenaphthylene	250	196	191
acenaphthene	CoE[f]	CoE	CoE
2,3,5-trimethyl naphthalene[g]	572	156	48
fluorene	159	55	43
phenanthrene	248	169	166
anthracene	32	25	18
fluoranthene	155	76	93
pyrene	242	145	189

a. pre-1993 fuel
b. reformulated blend
c. low aromatic fuel
d. Sample Identification
e. brake horse power hour
f. Another compound coelutes with Acenaphthene and it cannot be quantitated.
g. 2,3,5-trimethyl naphthalene coelutes with another naphthalene, quanitation is based on 2,3,5-trimethyl naphthalene

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Table 37. PUF high volume PAHs Emission rates of a diesel engine using three fuels.

	pre-1993[a]	reform[b]	low aromatic[c]
	H3[d]	H6	H4
	µg/brhphr[e]	µg/brhphr	µg/brhphr
naphthalene	12	32	22
2-methyl naphthalene	14	48	5
1-methyl naphthalene	11	30	4
biphenyl	17	49	7
2,6/2,7-dimethyl naphthalene	25	39	4
acenaphthylene	25	130	119
acenaphthene	CoE[f]	CoE	CoE
2,3,5-trimethyl naphthalene[g]	68	82	12
fluorene	55	55	20
phenanthrene	187	123	92
anthracene	23	17	8
fluoranthene	104	22	12
pyrene	134	26	13

a. pre-1993 fuel
b. reformulated blend
c. low aromatic fuel
d. Sample ID
e. brake horse power hour
f. Another compound coelutes with Acenaphthene and it cannot be quantitated.
g. 2,3,5-trimethyl naphthalene coelutes with another naphthalene, quanitation is based on 2,3,5-trimethyl naphthalene

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Table 38. Emission rates of PAHs found in the high volume XAD.

	pre-1993[a]	reform[b]	low aromatic[c]
	H3[d]	H6	H4
	µg/brhphr[e]	µg/brhphr	µg/brhphr
naphthalene	2910	2046	1893
2-methyl naphthalene	1626	901	219
1-methyl naphthalene	1106	517	154
biphenyl	465	330	104
2,6/2,7-dimethyl naphthalene	695	225	50
acenaphthylene	224	66	73
acenaphthene	CoE[f]	CoE	CoE
2,3,5-trimethyl naphthalene[g]	495	73	35
fluorene	104	0	23
phenanthrene	24	23	41
anthracene	4	3	5
fluoranthene	0	2	0
pyrene	6	15	9

a. pre-1993 fuel
b. reformulated blend
c. low aromatic fuel
d. Sample Identification
e. brake horse power hour
f. Another compound coelutes with Acenaphthene and it cannot be quantitated.
g. 2,3,5-trimethyl naphthalene coelutes with another naphthalene, quanitation is based on 2,3,5-trimethyl naphthalene

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Compared to the PUF samples, the XADs sample contained higher concentrations of naphthalene, 1- and 2-methyl naphthalene. The XAD had lower levels of acenaphthylene, fluorene, phenanthrene, and anthracene than the PUF. The reformulated fuel emission sample contained fluoranthene, and all three emission samples contained pyrene which indicates that some of these PAHs broke through the PUF.

Comparison of PAH results from the High Volume and Low Volume Sampler. During a series of pretest the high volume sampler was compared with the low volume sampler. Particulate emission rates from both samplers were compared. The pretest results showed that particle emission rates in the high volume samplers were about 15% lower than in the low volume sampler. Results were sufficiently close to allow for sample collection from both samplers.

During the main test, UCD collected vapor phase PAH samples from both the high and low volume samplers. Since most of UCD's previous work was done on the low volume sampler, low volume samples were collected to serve as a baseline for comparison between the low volume and high volume samplers, where SAPRC and UCD collected most of the PAH samples. UCD collected a single replicate for each fuel which was taken with the high volume sampler. The comparision between the high volume and low volume must be taken with cavets since the sampling times and conditions between the two sets of samples were not identical. To collect sufficient sample for the low volume sampler, six test cycles were collected for a single sample. The high volume sample consisted of two test cycles. High volume samples were collected off the main dilution tunnel, while the low volume samples were collected off the second dilution tunnel, which resulted in a higher dilution volume and a lower sampling temperature for the low volume sampler. Also the low volume sampler was about 10 feet upstream of the high volume sampler. Due to scheduling limitations, high and low volume samples were not collected in parallel. Presented in Table 39 are the PAHs results for the high volume and low volume samples.

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Table IV-10. Emission rates of PAHs found in the high volume Filters.

	pre-1993[a] H3[d] ug/brhphr[e]	reform[b] H6 ug/brhphr	low aromatic[c] H4 ug/brhphr
2,3,5-trimethyl naphthalene[f]	8	2	2
phenanthrene	36	23	34
anthracene	6	5	5
fluoranthene	50	52	81
pyrene	102	113	162

a. pre-1993 fuel
b. reformulated blend
c. low aromatic fuel
d. Sample Identification
e. brake horse power hour
f. 2,3,5-trimethyl naphthalene coelutes with another naphthalene, quanitation is based on 2,3,5-trimethyl naphthalene

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Table 39. Average of the high and low volume PAH emission rates for the diesel engine using low aromatic fuel.

Pre1993

	H3 Hivol µg/bkhphr	H110 Low Vol µg/bkhphr	H170 Low Vol µg/bkhphr	ave µg/bkhphr	stdev µg/bkhphr
naphthalene	2921	2340	1956	2406	486
2-methyl naphthalene	1637	1617	1313	1522	182
1-methyl naphthalene	1118	1055	830	1001	151
biphenyl	481	403	345	410	69
2,6-dimethyl naphthalene	720	966	771	819	130
acenaphthylene	250	355	399	335	77
acenaphthene	CoE	CoE	CoE		
2,3,5-trimethyl naphthalene	572	384	343	433	122
fluorene	159	199	208	189	26
phenanthrene	248	368	333	316	62
anthracene	32	45	46	41	8
fluoranthene	155	72	75	100	47
pyrene	242	125	118	161	70

Reformulated Fuel

	H6 Hivol µg/bkhphr	H145 Low Vol µg/bkhphr	H150 Low Vol µg/bkhphr	ave µg/bkhphr	stdev
naphthalene	2078	1784	1980	1947	150
2-methyl naphthalene	949	842	899	896	53
1-methyl naphthalene	547	463	480	497	44
biphenyl	379	326	293	333	44
2,6-dimethyl naphthalene	264	333	327	308	38
acenaphthylene	196	358	294	282	82
acenaphthene	CoE	CoE	CoE		
fluorene	55	149	89	98	47
phenanthrene	169	263	210	214	47
anthracene	25	23	27	25	2
fluoranthene	76	70	55	67	11
pyrene	145	114	101	120	23

Low Aromatic Fuel

	H4 Hivol µg/bkh phr	H127 Low Vol µg/bkhphr	ave µg/bkhphr	stdev
naphthalene	1915	980	1448	661
2-methyl naphthalene	225	145	185	56
1-methyl naphthalene	158	101	129	40
biphenyl	110	69	90	29
2,6-dimethyl naphthalene	54	68	61	10
acenaphthylene	191	263	227	51
acenaphthene	CoE	CoE		
2,3,5-trimethyl naphthalene	48	57	52	6
fluorene	43	54	49	8
phenanthrene	166	158	162	6
anthracene	18	20	19	1
fluoranthene	93	67	80	18
pyrene	189	104	146	60

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Presented in Table 40 is the comparision of the high volume sample results with the XAD corrected low volume sample results. Levels for 2,3,5-trimethyl naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene are slightly lower with the XAD correction.

Table 40. Comparision of the high volume sample results with the XAD corrected low volume sam results.

Sample ID;	H6	H145	H150			H4	H127			H3	H110	H170		
Sampler type:	Hivol	Low Vol	Low Vol			Hivol	Low Vol			Hivol	Low Vol	Low Vol		
	µg/bk	µg/bk	µg/bk	ave	stdev	µg/bk	µg/bk	ave	stdev	µg/bk	µg/bk	µg/bk	ave	stdev
naphthalene	2078	1784	1980	1947	150	1915	980	1448	661	2921	2340	1956	2406	272
2-methyl naphthalene	949	842	899	896	53	225	145	185	56	1637	1617	1313	1522	215
1-methyl naphthalene	547	463	480	497	44	158	101	129	40	1118	1055	830	1001	159
biphenyl	379	326	293	333	44	110	69	90	29	481	403	345	410	41
2,6-dimethyl naphthalene	264	333	327	308	38	54	68	61	10	720	966	771	819	138
acenaphthylene	196	358	294	282	82	191	263	227	51	250	355	399	335	32
2,3,5-trimethyl naphthalene	156	107	103	122	30	48	24	36	17	572	351	305	409	33
fluorene	55	130	74	86	39	43	41	42	2	159	199	186	181	9
phenanthrene	169	213	145	176	34	166	124	145	30	248	335	261	281	52
anthracene	25	17	17	20	5	18	15	16	2	32	41	36	36	4
fluoranthene	76	70	63	70	7	93	67	80	18	155	72	72	100	0
pyrene	145	104	97	115	26	189	104	146	60	242	107	100	150	5

µg/bk = micrograms per brakehorsepower hour.

For the main test, naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, dimethyl naphthalene, biphenyl, acenaphthylene, fluorene, trimethyl naphthalene, and phenanthrene, anthracene, fluoranthene, and pyrene were detected in all the high and low volume samples. Generally high volume volatile PAH emission rates were similar to the low volume volatile PAH emission rates

The trends for emission rates of the three fuels in the low and high volumes samples were similar. For both the high and low volumes samples, individual alkyl PAH emission rates were highest in the pre-1993 fuel and lowest in the low aromatic fuel. High volume naphthalene emission rates were higher than the low volume naphthalene emission rates in spite of the high blank contribution to the low volume naphthalene.

Blanks: Tunnel blank levels are not directly comparable to the sample levels. The procedure for taking tunnel blanks into account require that the tunnel is first conditioned for two

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hours by running ambient air through the tunnel. The tunnel blank is taken only when the CVS is running and at ambient temperature, a temperature lower than during an FTP run. Alkyl PAH exhaust levels from the low aromatic fuel were considerably lower than in the exhausts of the other two fuels and closer to the background levels found in the tunnel blank. Some PAHs appeared to be desorbing off the tunnel. Continued PAH desorption off the tunnel continuing after the tunnel blank was taken could account for the tunnel blank PUFs levels being higher than the trip blank PUFs.

Unlike the low volume sampler blank levels the high volume blank levels were an insignificant part of the measured PAH emissions. Two factors explain the differences. First, sufficient sample was collected in the high volume sampler (approximately 9 times more sample than the low volume sampler) to obtain PAH values significantly higher than the blank levels. Second, because the high volume sampler was operated at a higher flow rate and temperature more of the heavy PAHs broke through the filter and were trapped on the PUF. This resulted in a greater fraction of the heavy PAHs trapped on the PUF and proportionally increased sample levels above the blank levels. Both these factors contributed in increasing the levels of heavier PAHs in the PUF compared to levels in the tunnel blank.

Discussion: With respect to the chemical characterization of diesel exhaust, Bagley et al (1987) chemically characterized compounds in diesel particulate matter and in the vapor-phase as trapped on XAD-2 resin using an ultra-high volume sampler. The lowest boiling point compounds reported included parent and substituted naphthalenes, fluorenones, anthracenes, phenanthrenes, and fluorenes. Westerholm et al (1991) reported a number of semi-volatile PAHs collected using PUF and XAD-2 including phenanthrene or substituted phenanthrenes, fluoranthene, pyrene, and anthracene. The authors used volumetric sampling flow rates of 240 and 340 LPM for XAD-2 and PUF sorbants, respectively.

In a previous study (Kado et al, 1997) an L10 Detroit heavy-duty diesel engine was run on a engine dynamometer using the same pre-1993 fuel that was used in this study. In addition, an interim fuel which was allowed to be produced after 1993 and did not meet all the specifications of a reformulated fuel was tested. The fuel was low in sulfur but contained comparable levels of aromatics to the pre-1993 fuel. Total PNA were 7.3% in the pre-1993 fuel and 4.7% in the post-1993 fuel. That study used the same low volume sampler design which was used in this study. Volatile PAHs were trapped on PUF and XAD-4 sorbant. Generally vapor phase PAHs were lower in the emissions of the post-1993 fuel. In general, the PUF samples contained considerable amounts of naphthalene, acenaphthylene, acenaphthene, fluorene, and phenanthrene, along with lower

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amounts of anthracene, fluoranthene, and pyrene. PAHs containing four or more fused benzene rings were not detected in the PUF samples. The XAD samples contained higher concentrations of naphthalene, but much lower levels of acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene. The XAD samples did not contain PAHs with four or more fused benzene rings.

Our current study showed greater differences in some volatile PAH emission rates from a heavy-duty diesel engine using three different fuels. A comparison of the total PAH emissions rates based on the average of the low volume and high volume is given in Figure V-1 and Figure V-2.

The pre-1993 fuel had the highest emissions rates for all the alkyl-PAHs including 1 and 2 methyl-naphthalene, 2,4 dimethyl naphthalene, and trimethyl naphthalene, while the low aromatic fuel had the lowest emission rates for these alkyl naphthalenes. For the reformulated fuel the emission rates of these alkyl PAHs were intermediate between the low aromatic and pre-1993 fuel. The profiles of the two and three ring unsubstituted PAH, such as naphthalene, acenaphthylene, fluorene, phenanthrene and anthracene, do not show such a marked fuel dependence suggesting that a greater fraction of these PAHs are formed during the combustion process. The exact magnitude of PAH fuel dependence cannot be measured since all these data fall within the 95% confidence levels. For fluoranthene and pyrene, the two-four ring PAHs that were measured appeared to show little if no fuel dependence.

These vapor phase PAH results were in agreement with PAH work conducted by SAPRC. SAPRC was responsible for determining emission rates for PAHs trapped on filters and on PUF. 2,3,5-trimethyl naphthalene, phenanthrene, anthracene, fluoranthene, and pyrene were analyzed by both SAPRC and UCD. Evaluation of both sets of data show the same trend for both alkyl PAHs and PAHs. Both sets of data show that emission levels of alkyl PAHs are highly fuel dependent. For phenanthrene and anthracene both data sets show that they are mainly produced during the combustion process although some fuel dependence is indicated. For fluoranthene and pyrene both data sets indicate that they are primarily formed during combustion and no fuel dependence could be discerned.

The total emission rates between SAPRC and UCD match well, even without considering that different types of samplers were used to collect samples and that samples were collected during different engine cycles. Results of the comparison are presented in Table 41.

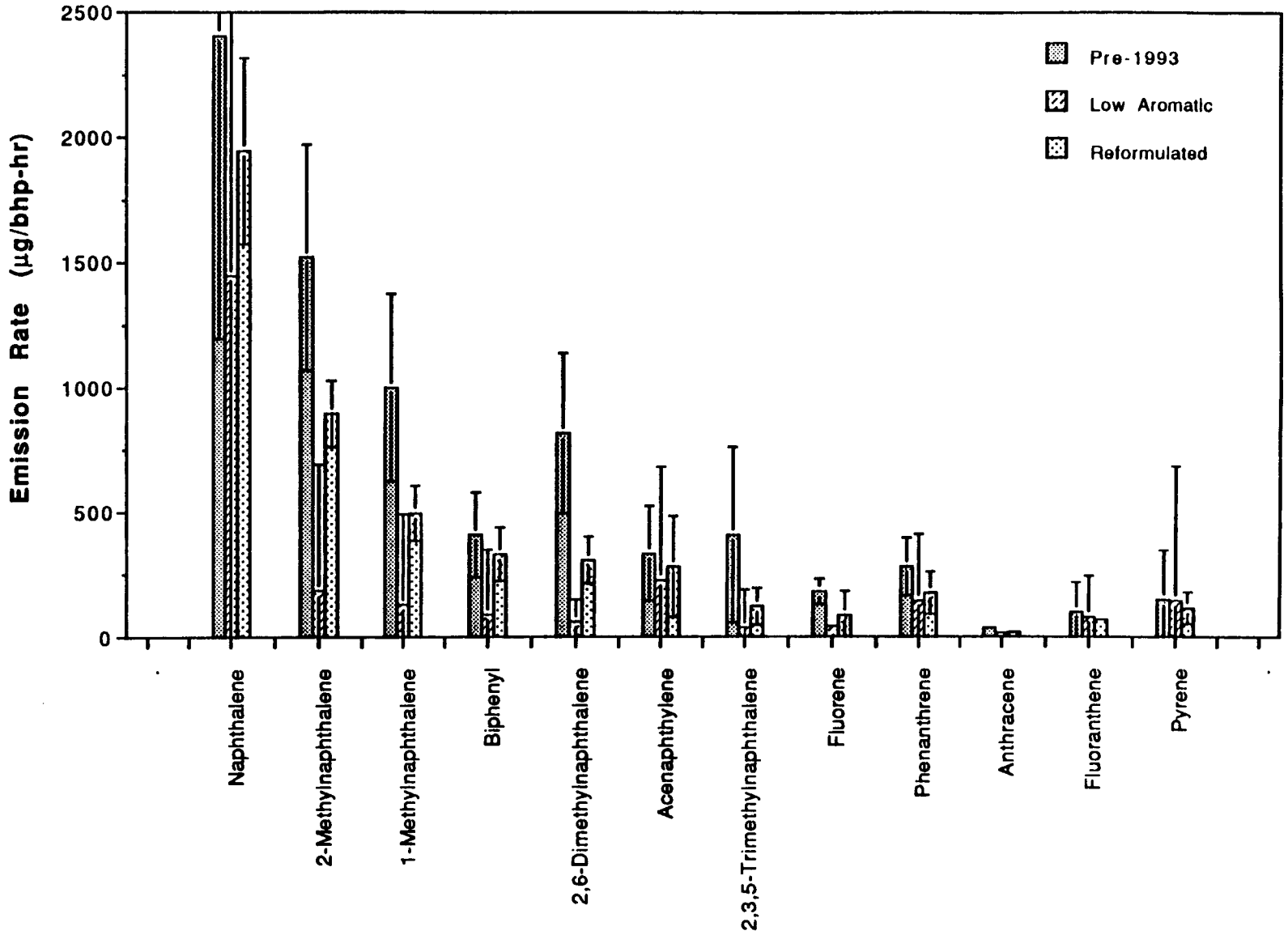
Emission Rate (µg/bhp-hr)
2500
2000
1500
1000
500
0
Pre-1993
Low Aromatic
Reformulated
Naphthalene
2-Methylnaphthalene
1-Methylnaphthalene
Biphenyl
2,6-Dimethylnaphthalene
Acenaphthylene
2,3,5-Trimethylnaphthalene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene

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Table 41. A Comparision of certain 2-4 ring PAHs emission as determined by SAPRAC and UCD.

PAH emission rates corrected for XAD background*	pre-1993		Low Aromatic		Reformulated	
	UCD µg/bhh	SAPRC µg/bhh	UCD µg/bhh	SAPRC µg/bhh	UCD µg/bhh	SAPRC µg/bhh
2,3,5-trimethyl naphthalene	409	284	36	15	122	56
phenanthrene	281	337	145	161	176	221
anthracene	36	39	16	19	20	26
fluoranthene	100	129	80	132	70	123
pyrene	150	193	146	208	115	207

PAH emission rates not corrected for XAD blanks	pre-1993		Low Aromatic		Reformulated	
	UCD µg/bhh	SAPRC µg/bhh	UCD µg/bhh	SAPRC µg/bhh	UCD µg/bhh	SAPRC µg/bhh
2,3,5-trimethyl naphthalene	433	284	52	15	149	56
phenanthrene	316	337	162	161	214	221
anthracene	41	39	19	19	25	26
fluoranthene	100	129	80	132	67	123
pyrene	161	193	146	208	120	207

* XAD background levels were comparable to sample levels so XAD values were not included in the total emission calculations.

Another way to view the data would be to plot the total concentration of the PAH in the fuel versus the concentration in the exhaust. Assuming that the profile of PAHs in all three fuels is similar, than there may be a relationship between total PAHs in the fuel when plotted against individual PAHs in the exhaust. Figures V-3 and V-4 show the results. Intercepts through zero indicate none of the PAHs are formed during combustion and intercept values indicate the amount formed during combustion. Figure V-3 shows the intercepts for all the alkyl naphthalene are near zero indicating that they are from the fuel. For the unsubstituted PAHs the intercepts indicate that most of them are formed during combustion. Phenanthrene may have the largest fuel dependence with almost half coming from the fuel.

Conclusions: Our goal was two fold: 1) to investigate the vapor-phase emissions from a heavy duty engine using three different fuel formulations, a Pre-1993 and a low aromatic Post-1993 fuel and a Reformulated blend and 2) to design and run a high volume sampler capable of collecting sufficient sample to detect and quantitate low level PAHs, dioxins and nitro-PAHs. Both goals were

achieved by comparing volatile PAH emission rates of a heavy-duty diesel engine using three fuels and using data collected from both high and low volume samplers. A high volume sampler designed to collecte larger sample volumes was successfully designed and tested at the LCMTA facility. The sampler was used to collect samples for PAHs, nitro-PAHs, mutagencity, and PCDDs and PCDFs.

A comparison of the emission profiles of the heavy-duty diesel engine using three different fuels shows a similar distribution of volatile alkyl PAHs but at significantly different emission rates. Two and three ring PAHs show some fuel dependence, although the majority of these PAHs may be formed during combustion. Four ring PAHs such as fluoranthene and pyrene do not show any fuel dependence and are formed mainly from combustion.

A high volume sampler was designed and used to collect PAH samples as well as mutagenicity, dioxin, and nitro-PAH samples. The purpose of the high volume sampler was to collect a larger sample mass critical for the detection and quantitation of low level nitro-PAHs, dioxins, and some low level PAHs. The main advantage of the high volume sampler over the low volume sampler was the detection and quantification of low level PAHs that could not be done by low volume sampling. PAH results between the low and high volume samplers are comparable.

3.8 Nitrosamines

The emissions of the reformulated blend and Pre-1993 fuels were sampled along with a tunnel blank and a trip blank. Samples, date sampled, type of fuel, and sample identification are summarized in Table 42.

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Table 42. Summary of Nitrosamine samples obtained from the emissions of a heavy duty diesel engine using pre-1993 and reformulated blend fuels.

Sample ID	Fuel Type	Date Sampled	Cycle/Start Type
76798	Pre-1993	12/05/96	FTP/Hot
76806	Pre-1993	01/08/97	FTP/Hot
76815	Reformulated	12/16/97	FTP/Hot
76803	Reformulated	12/16/96	FTP/Hot
76813	none	12/13/97	Tunnel Blk
76800	none	02/04/97	Trip Blk

a. 6 hot start FTP transient cycles.
b. Blk = blank

Hydrocarbon, nitrogen oxides, carbon monoxide, and carbon dioxide pollutant levels taken during NA sampling are presented in Table 43. All samples were sent to Lancaster Laboratories and analysis was completed by 2/27/97. In addition to the analysis of the front cartridges, one backup cartridge was analyzed. No NA were detected in the backup cartridge so none of the other backup cartridges were analyzed.

The results of NA are given in μg per brake horsepower hour are reported in Table 44.

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Table 43. Summary of the average pollutant levels for the pooled NA samples.

Sample	Fuel	HC[a] g/hp-hr[d]	Std Dev[b] g/hp-hr	NOx[c] g/hp-hr	Std Dev g/hp-hr
	Pre-1993	.53	.012	4.63	.052
	Pre-1993	.53	.010	4.88	.034
	blend	.50	.010	4.56	.026
	blend	.50	.019	4.60	.054
	blend	.50	.019	4.60	.054

	Fuel	CO[d] g/hp-hr	Std Dev g/hp-hr	CO_2[e] g/hp-hr	Std Dev g/hp-hr
	Pre-1993	2.39	.063	520.9	1.01
	Pre-1993	2.25	.040	494.8	2.57
	blend	2.30	2.17	510.7	6.58
	blend	2.26	.051	512.9	1.39

a. Total Hydrocarbon Emissions
b. Standard Deviation
c. Nitrogen Oxide Emissions
d. Carbon Monoxide Emissions
e. Carbon Dioxide Emissions

Table 44. Nitrosoamine emission rate

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Nitrosamine	Pre-1993 76798 µg/hphr[b]	Pre-1993 76806 µg/hphr	average (precision) µg/hphr	Reform [a] 76803 µg/hphr	Reform 76811 µg/hphr	average (precision) µg/hphr
N-nitrosodimethylamine (NDMA)	5.81	7.02	6.41 (9.41)	7.84	8.00	7.92 (1.01)
N-nitrosodiethylamine (NDEA)	<7.7	<7.9		<7.8	<7.9	
N-nitrosodipropylamine (NDPA)	8.28	<7.9		<7.8	7.2	
N-nitrosobutylamine (NDBA)	<12	<12		<12	<12	
N-nitrospiperidine (NPIP)	<7.7	<7.9		<7.8	<7.9	
N-nitrosopyrolidine (NPYR)	<7.7	<7.9		<7.8	<7.9	
N-nitrosomorpholine (NMOR)	<7.7	<7.9		<7.8	<7.9	

a. reformulated blend is a blend of 3 fuels obtained from 3 refineries
b. micrograms per brake-horse power hour

The average NDMA emission per cycle was 143 µg (6.41 µg/hp-hr) in the pre-1993 fuel and 176 µg (7.92 µg/hp-hr) in the reformulated blend fuel. One pre-1993 fuel emission sample and one reformulated blend fuel emission sample contained measurable levels of NDPA at 185 µg (8.28 µg/hp-hr) and 160 µg (7.2 µg/hp-hr) respectively. No other nitrosamines, including NMOR, were detected in any of the samples.

To test for breakthrough one backup cartridge was tested. No NAs were detected in the backup cartridge. No NAs were detected in either the tunnel blank or in the trip blank.

Discussion: As reported in the literature, NA have been detected in the emissions from diesel and gasoline powered vehicles. Most of the studies have centered on emissions from catalyst equipped vehicles. NDMA has been detected when in malfunctioning catalyst equipped vehicles.

No other study has reported the emission of NDPA which in this study was detected in two samples and emitted at similar levels to NDMA. Only one sample from the emission of each fuel showed measurable levels of NDPA.

Conclusion: The objective of the nitrosamine component of this study was to determine whether NA were present in diesel exhaust. NDMA and NDPA were detected in the exhaust near the detection limit of the method. If other NAs are present at lower levels then larger sample volumes need to be collected to detect them. Additional QA procedures to test for NA artifacts and GC/MS confirmation are recommended but were not included in this study. GC/MS confirmation would have required a larger sample volume than was collected at this test and would have required designing and validating a sampler with a significantly higher flow rate. Artifacts are attenuated by the nitrogen dioxide suppressing layer in the Thermosorb-N sampler but additional information could be obtained by running a parallel sample train to sample for dialkyl amines. Dialkyl amines can react with nitrogen dioxide to form NA. Detection of dialkyl amines will help in calculating the upper limit of artifactual NA formation.

3.9 Dioxins

Structure and Toxic Equivalent: There are 210 polychlorinated dibenzo-p-dioxin (PCDD) and dibenzofuran (PCDF) isomers. Each isomer has a different cancer potency. To assess cancer risk of PCDD and PCDF exposure, a system based on toxic equivalence factors (TEQ) has been developed. The isomer 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) which is considered the most potent isomer is given a TEQ of 1. PCDD and PCDF isomers with chlorines in the 2,3,7,8 position are considered carcinogenic and are also given TEQ factors. Isomers of PCDD and PCDF not chlorinated in the 2,3,7,8 position are not given TEQ factors. A number of TEQ schemes have been proposed. Currently the US EPA, Department of Toxic Substance Control (DTSC) and other nations use the international system (I-TEQ), and Cal/EPA and OEHHA use a different a different system, although Cal/EPA and OEHHA are currently considering adopting the I-TEQ system. The two TEQ systems are shown in Table 45.

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Table 45. CA EPA/OEHHA and International Toxic Equivalence Factors for PCDDs and PCDFs.

Toxic Equivalence Factors (TEQ)

	CAL EPA/OEHHA Factors	US EPA/Int. Factors
Dioxins		
2,3,7,8-TCDD	1	1
Total TCDD	0	0
1,2,3,7,8-PeCDD	1	0.5
Total PeCDD	0	0
1,2,3,4,7,8-HxCDD	0.03	0.1
1,2,3,6,7,8-HxCDD	0.03	0.1
1,2,3,7,8,9-HxCDD	0.03	0.1
Total HxCDD	0	0
1,2,3,4,6,7,8-HpCDD	0.03	0.01
Total HpCDD	0	0
OCDD	0	0.001
Furans		
2,3,7,8-TCDF	1	0.1
Total TCDF	0	0
1,2,3,7,8-PeCDF	1	0.05
2,3,4,7,8-PeCDF	1	0.5
Total PeCDF	0	0
1,2,3,4,7,8-HxCDF	0.03	0.1
1,2,3,6,7,8-HxCDF	0.03	0.1
2,3,4,6,7,8-HxCDF	0.03	0.1
1,2,3,7,8,9-HxCDF	0.03	0.1
Total HxCDF	0	0
1,2,3,4,6,7,8-HpCDF	0.03	0.01
1,2,3,4,7,8,9-HpCDF	0.03	0.01
Total HpCDF	0	0
OCDF	0	0.0001

Pretest High Volume Sampler and Diesel Exhaust Studies: A series of pretests were conducted at the MTA Engine Emissions Test Facility located in Los Angeles in August and September of 1996. The purpose of the first set of pre-tests was to modify the existing Horiba high volume particulate sampler which is part of the dilution tunnel. The sampler was modified to include a sorbant module to collect semi-volatile compounds including PCDDs and PCDFs in the vapor phase. In October of 1996 a main pre-test was performed to 1) Evaluate the performance of the high volume sampler, 2) Collect a diesel emission sample to determine whether dioxins could be detected, and 3) Test for breakthrough of the PUF. A tunnel blank was collected during the main pre-test. A tunnel blank is when the blower in the tunnel is run but the engine is not.

PreTest: A tunnel blank was taken to determine background levels of dioxins in the main dilution tunnel. Prior to collecting the tunnel blank, the tunnel was conditioned for approximately two hours by running the CVS fan without running the engine. Only HEPA and charcoal filtered ambient air at ambient temperature was used to purge the tunnel.

Diesel exhaust from six hot start FTP cycles was collected on a single high volume sample. The high volume sample consisted of filters and a PUF module. The flow rate was approximately 60 CFM. A large volume of sample needed to be collected to achieve the required detection limit. This raised concerns for breakthrough of dioxins. Breakthrough was tested by spiking the front half of the PUF with a cocktail of PCDDs and PCDFs. The front half and the back half of the PUF were analyzed separately to test for breakthrough. Also native PCDDs and PCDFs were analyzed in the backup PUF to determine the amount of PCDDs and PCDFs that broke through the front PUF.

Presented in Table 46 are the PCDDs and PCDFs detected in the front half PUF, in the back PUF, and in the tunnel blank. Virtually all the PCDDs and PCDFs were detected in the front half PUF. The back half PUF PCDD and PCDF levels were virtually the same as in the tunnel blank.

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Table 46. Pretest PCDDs and PCDFs Analytical Results for the Front and Back Half of Sample 96101 and the Blank.

	PUF Front Half Sample ID: 96101		PUF Back Half Sample ID: 96101		Tunnel Blank Sample ID: 96101-1.2	
Compound	Conc[a] pg/sample	DL[b]	Conc pg/sample	DL	Conc pg sample	DL
2,3,7,8-TCDD	ND[c]	4.2	ND	2.8	ND	2.4
Total TCDD	60		ND	2.8	16	
1,2,3,7,8-PeCDD	ND	2.1	ND	4.1	ND	2.2
Total PeCDD	19		ND	4.1	ND	2.2
1,2,3,4,7,8-HxCDD	ND	1.7	ND	2.5	ND	5.1
1,2,3,6,7,8-HxCDD	ND	1.7	ND	3.2	ND	4.6
1,2,3,7,8,9-HxCDD	ND	1.5	ND	2.9	ND	5
Total HxCDD	15		ND	3.2	ND	5.1
1,2,3,4,6,7,8-HpCDD	7.7		ND	2.6	ND	2.5
Total HpCDD	14		ND	2.6	ND	2.5
OCDD	37		6.9		12	
2,3,7,8-TCDF	4.7		ND	2.6	ND	2
Total TCDF	200		ND	2.6	26	
1,2,3,7,8-PeCDF	2.2		ND	2.3	ND	2.8
2,3,4,7,8-PeCDF	2.2		ND	2.2	ND	2.7
Total PeCDF	28		ND	2.3	ND	2.8
1,2,3,4,7,8-HxCDF	2.1		ND	1.6	ND	1.4
1,2,3,6,7,8-HxCDF	1.2		ND	1.4	ND	1.4
2,3,4,6,7,8-HxCDF	1		ND	1.7	ND	1.5
1,2,3,7,8,9-HxCDF	ND	0.61	ND	1.9	ND	1.7
Total HxCDF	10		ND	1.9	ND	1.7
1,2,3,4,6,7,8-HpCDF	4.1		ND	1.3	ND	1.5
1,2,3,4,7,8,9-HpCDF	ND	1.3	ND	1.7	ND	1.9
Total HpCDF	4.1		ND	1.7	ND	1.9
OCDF	4.5		ND	5.7	ND	3.7

a. Conc. = concentration
b. D.L. = detection limit
c. ND = not detected

A cocktail of 5 isotopically labeled PCDDs and PCDFs were spiked on the front half of PUF sample 96101. After the sample was collected, the PUF was analyzed to determined the amount of recovery standards that were lost from the front cartridge. Recoveries were from 89% to 115%, suggesting that there was no loss of recovery standards due to breakthrough. (Table 47).

Table 47. Recoveries of pre-spike standards added to the front half of the PUF.

Pre-spike Recovery Standard	%R
^{37}Cl-2,3,7,8-TCDD	89
^{13}C-2,3,4,7,8-PeCDF	104
^{13}C-1,2,3,4,7,8-HxCDD	111
^{13}C-1,2,3,4,7,8-HxCDF	115
^{13}C-1,2,3,4,7,8,9-HpCDF	114

*%R = Recovery of standards

After the main pretest it was determined that the original Horiba high volume sampler was not suitable for dioxin sampling. Modifications to the high volume sampling system (see PAH section) were successfully completed in November for subsequent testing.

Summary of Main Test Sampling: The main test was conducted at the MTA Emissions Test Facility. Testing started on 12/2/97, was suspended for the holidays on 12/19/97, resumed on 1/8/97 and was completed on 1/9/97. Fuel and oil samples were collected throughout the test. Tunnel and manifold particulate samples were collected on 1/9/97 and again on 5/1/97. A summary of the PCDDs and PCDFs samples are given in Table 48.

Criteria Pollutant Results: A total of six PCDDs and PCDFs diesel exhaust samples were collected. Diesel exhaust samples D1, D5, and D6 were collected when the engine was running on pre-1993 fuel. Diesel exhaust samples D2, D3, and D4 were collected when the diesel engine was running on the reformulated blend. Each sample consisted of 7 hot and 1 cold FTP cycles. For each pollutant the sample's average emission rate of regulated pollutants for all 8 cycles is given in Table 49.

Table 48. Summary information of PCDDs and PCDF samples collected at the LA MTA.

Sample ID	Lab ID	Date sampled	Type	Matrix	sample type	fuel
	Pretest					
96101-1,2	96101-1,2	10/2/97	filter/PUF	emission	6HFTP[a]	pre-1993
96101-1,2	96101-1,2		Back PUF	emission	6HFTP	pre-1993
96101	96101	10/2/97	filter/PUF	emission	blank[b]	pre-1993
	Main test					
ULFV0	ULFV1	12/2/96	filter/PUF	emission	blank	pre-1993
D1FV0	D1FV1	12/5/96	filter/PUF	emission	1C/7HFTP[c]	pre-1993
D5	Sample 1	1/8/97	filter/PUF	emission	1C/7HFTP	pre-1993
D6	Sample 2	1/9/97	filter/PUF	emission	1C/7HFTP	pre-1993
DVL2	DVL	12/13/96	filter/PUF	emission	blank	reformulated
D2	D2	12/18/96	filter/PUF	emission	1C/7HFTP	reformulated
D3	D3	12/19/96	filter/PUF	emission	1C/7HFTP	reformulated
D4	D4	12/20/96	filter/put	emission	1C/7HFTP	reformulated
	Fuel/Oil					
DPF-0	DPF-1	12/6/96	fuel	fuel		pre-1993
DMF-1	DMF-2	12/19/96	fuel	fuel		reformulated
DO-1	DO-1	12/6/97	oil	new oil		
DPO-2	DPO-2	12/6/96	oil	used oil		pre-1993
DMO-3	DMO-3	12/19/96	oil	used oil		reformulated
	Tunnel and Manifold					
DEP-1	DEP-1	1/9/97	particulates	exhaust line	exhaust	near manifold[d]
97051-2	97051-2	5/1/97	particulates	exhaust line	exhaust	near tunnel[e]
DTP-1	DTP-1	1/9/97	particulates	tunnel	exhaust	by 2nd dil
97051-1	97051-1	5/1/97	particulates	tunnel	exhaust	by 2nd dil
97051-3	97051-3	5/1/97	particulates	tunnel	exhaust	by bag filter

a.. 6 hot transient Federal Test Procedures (FTP) cycles
b. Tunnel blank
c. 1 cold and 7 hot transient FTP cycles
d. Sample taken near engine manifold
e. Sample taken just before main tunnel

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Table 49. Summary of Regulated Pollutant Emission Taken Concurrently During the Collection of Dioxin Samples.

Sample	Date	HC[a] emission rate	standard deviation	NO_x[b] emission rate	standard deviation
		g/hp-hr[c]	g/hp-hr	g/hp-hr	g/hp-hr
D1 (pre)[d]	12/5/97	0.53	0.015	4.64	0.097
D5 (pre)	1/8/97	0.54	0.7	4.87	0.074
D6 (pre)	1/9/97	0.52	0.017	4.84	0.13
D2 (MB)[e]	12/18/97	0.52	0.31	4.61	0.11
D3 (MB)	12/19/97	0.5	0.025	4.62	0.09
D4 (MB)	12/20/97	0.49	0.013	4.6	0.111

Sample	Date	CO[f] Emission Rate	Standard Deviation	CO_2[g] Emission Rate	Standard Deviation
		g/hp-hr	g/hp-hr	g/hp-hr	g/hp-hr
D1 (pre)	12/5/97	2.36	0.086	525	10.917
D5 (pre)	1/8/97	2.23	0.022	496	13.17
D6 (pre)	1/9/97	2.12	0.229	502.3	10.461
D2 (MB)	12/18/97	2.27	0.037	510.4	14.9
D3 (MB)	12/19/97	2.28	0.048	512.3	13.12
D4 (MB)	12/20/97	2.3	0.036	511.6	14.76

a. Total hydrocarbon emissions
b. Total Nitrogen Oxide emissions
c. grams per brake-horsepower hour
d. pre-Oct. '93 fuel
e. Market basket blend
f. Total Carbon Monoxide Emissions
g. Total Carbon Dioxide Emissions

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Dioxin Exhaust Sample Volume: Due to the low level of PCDDs and PCDFs found in the pre-test, a large sample volume was needed to detect their levels in the diluted diesel exhaust. Sample flow rates and the fraction of a single FTP cycle is given in Table 50.. Approximately 10 % of the total exhaust was collected in each pooled sample of 8 FTP cycles. The flow rate averaged between 36.15 and 39.63 CFM. The flow rate decreased as the particulates loading on the 8"x10" filter increased. Also, it was observed that as the particulate loading on the main tunnel bag filter increased, the high volume sampler flow rate concurrently decreased.

Fuel Consumption during the FTP Cycle: Fuel consumption during a cycle was determined by two methods. In the first method, hydrocarbons (HC) from the diesel exhaust were used to calculate the mass of fuel consumed during a test. The second method was to directly measure the weight loss of the fuel drum by using a scale. The weight before and after a test was recorded to obtain the fuel consumption during each test. Initial weight measurements drifted when the scale was exposed to direct sunlight. Shade was provided for the scale which resulted in more reproducible data. The fuel weight determined directly was in good agreement with the HC calculated weight. Since there was a complete data set for the calculated HC weight the calculated fuel consumption data was used. Average calculated fuel consumption per sample is also reported in Table 50.

Table 50. Average Flow Rate and Fuel Consumption for PCDDs and PCDFs Samples.

	D1	D2	D3	D4	D5	D6
Avg. (SCFM)[a]	39.63	33.61	36.59	36.15	35.85	37.32
Std. Dev.[b]	3.81	4.05	4.68	4.90	5.07	5.38
Total Volume (CF)[c]	6,341	5,377	5,855	5,784	5,736	5,970
Total CVS Volume (CF)[d]	61,078	60,985	60,765	60,576	60,776	60,954
Fraction Sampled[e]	0.10	0.09	0.10	0.10	0.09	0.10
Fuel Consumed (L)[f]	7.27	6.27	6.27	6.27	7.24	7.27

a. Average sample flow rate in standard cubic feet per minute of 8 FTP cycles.
b. Standard Deviation of flow rate
c. Total volume collected per sample
d. Average total exhaust per FTP transient cycle
e. Fraction of total volume collected per sample
f. Average fuel consumed per cycle

PCDDs and PCDFs in Diesel Emission Results: For each fuel tested, 3 diesel exhaust samples (8 cycle equivalents) and one tunnel blank were collected. For the tunnel blank, the CVS tunnel was run with dilution air only and the sample volume collected was comparable to the emissions samples. The emission sample consisted of 8 FTP cycles. The filter was changed after the completion of the first set of a cold and a hot cycle. Subsequent filters were changed after every third cycle.

Sample D1 had lower than expected concentrations of dioxins. A re-extraction and analysis of the sample D1 was performed to recheck the extraction procedure. Analysis of the re-extraction (sample D1RA) detected no additional PCDDs or PCDFs. This data is shown in Table 51 along with emission PCDDs and PCDFs data from samples ULFV1, D5, and D6. A comparison of the blank with the emission samples reveal that the total TCDDs, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDD, total HpCDD, OCDD, 1,2,3,4,6,7 HpCDF, and total HpCDF in the blank are between 25 and 50 percent of the emission samples. Levels in the tunnel blank may be a significant part of the total dioxin emissions measured in the emission samples. Concentration of PCDDs and PCDFs in the blank for the tunnel are also reported.

Samples D2, D3, and D4 and the tunnel blank DVL were collected from the CVS tunnel with the diesel engine running on the reformulated fuel. The reformulated fuel was a blend of three commercially available fuels. Levels of some PCDDs and PCDFs detected in the diesel exhaust were also found in the blank. A comparison of the blank with the emission samples (see Table 52) show that the total TCDDs, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDD, total HpCDD, and OCDD are between 25 and 50 percent of the emission samples. Again the tunnel blank levels may be a significant part of the emission sample.

The diesel exhaust from the reformulated blend contained lower levels of all PCDDs and PCDFs isomer classes than in the pre-1993 fuel. In the pre-1993 fuel, TCDFs were found in the highest concentration of all the PCDD and PCDF classes. OCDDs were found in the highest levels of all the PCDD classes. In the reformulated blend, TCDFs were also found in the highest concentration for all PCDD and PCDF classes. For PCDD classes, THxCDDs were detected at the highest concentration. This is unusual in that OCDDs are usually found in the highest level. A comparison of PCDD and PCDF isomer classes between the pre-1993 and reformulated blend are given in Figure 21.

Table 51. PCDDs and PCDFs Concentrations in the Exhaust of Heavy Duty Diesel Engine Using Pre-1993 Fuel.

	Sample ID: UL1FV1		Sample ID: D1		Sample ID: D1RA		Sample ID: D5		Sample ID: D6	
Compound	Con	D.L.[a]	Con.	D.L.	Con.	D.L.	Con.	D.L.	Con.	D.L.
2,3,7,8-TCDD	ND	2.3	ND	4.4	ND	2.5	ND	2.2	ND	3.2
Total TCDD	5.1		24		ND	2.5	13		11	
1,2,3,7,8-PeCDD	ND	1	ND	1.9	ND	0.52	ND	2.6	ND	1.7
Total PeCDD	2.8		11		ND	0.52	11		9.4	
1,2,3,4,7,8-HxCDD	ND	1.3	ND	1.5	ND	1.1	ND	3.1	ND	1.8
1,2,3,6,7,8-HxCDD	ND	1.3	2.4		ND	1.1	ND	3.0	ND	3.1
1,2,3,7,8,9-HxCDD	ND	1.2	ND	1.5	ND	1	ND	2.7	ND	2.2
Total HxCDD	ND	3	19		ND	1.1	14.0		14.0	
1,2,3,4,6,7,8-HpCDD	5.5		9		ND	0.8	12		8.4	
Total HpCDD	11		18		ND	0.8	23		18	
OCDD	35		42		7.8		69		40	
2,3,7,8-TCDF	ND	2.1	ND	3.7	ND	1.7	3.6		ND	2.6
Total TCDF	ND	2.1	91		ND	1.7	90		75	
1,2,3,7,8-PeCDF	ND	0.94	ND	1.6	ND	0.69	ND	1.7	ND	1.7
2,3,4,7,8-PeCDF	ND	0.91	ND	1.6	ND	0.67	ND	1.6	ND	2.1
Total PeCDF	ND	1.2	13		ND	0.69	12		5.7	
1,2,3,4,7,8-HxCDF	ND	0.65	1.9		ND	0.25	ND	2.8	ND	1.7
1,2,3,6,7,8-HxCDF	ND	0.56	ND	0.88	ND	0.22	ND	2.5	ND	1.1
2,3,4,6,7,8-HxCDF	ND	0.7	ND	1.1	ND	0.3	ND	1.5	ND	1.2
1,2,3,7,8,9-HxCDF	ND	0.77	ND	0.68	ND	0.3	ND	1.6	ND	1.2
Total HxCDF	ND	1.2	8.8		ND	0.3	3.2		3	
1,2,3,4,6,7,8-HpCDF	1.9	1.2	3.5		ND	0.35	6.3		4.6	
1,2,3,4,7,8,9-HpCDF	ND		ND	1.1	ND	0.45	ND	1.4	ND	2.4
Total HpCDF	1.9	3.2	3.5		ND	0.45	6.3		4.6	
OCDF	ND		ND	2.9	ND	2.5	ND	9.4	ND	6

a. Detection limit in picograms per sample

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Table 52. PCDDs and PCDFs in exhaust samples of a diesel engine using reformulated blend.

	Sample ID: DVL		Sample ID: D2		Sample ID: D3		Sample ID: D4	
Compound	Conc.[a]	D.L.[b]	Conc.	D.L.	Conc.	D.L.	Conc.	D.L.
2,3,7,8-TCDD	ND[c]	2.2	ND	3.0	ND	4.7	ND	3.5
Total TCDD	6		10		12		11	
1,2,3,7,8-PeCDD	ND	2.8	ND	2.8	ND	3.8	ND	1.5
Total PeCDD	ND	2.8	7.2		7.8		8.4	
1,2,3,4,7,8-HxCDD	ND	2.6	ND	2.0	ND	2.1	ND	2.9
1,2,3,6,7,8-HxCDD	ND	2.5	ND	2.0	ND	2.1	ND	2.9
1,2,3,7,8,9-HxCDD	ND	2.3	ND	1.8	ND	1.9	ND	2.6
Total HxCDD	ND	2.6	14		17.0		13	
1,2,3,4,6,7,8-HpCDD	2.5		9.0		5.4		6.8	
Total HpCDD	4.8		17		11		14	
OCDD	13		33		22		37	
2,3,7,8-TCDF	ND	2.0	3.3		ND	3.5	ND	3.2
Total TCDF	6.8		66		55		61	
1,2,3,7,8-PeCDF	ND	1.5	ND	3.8	ND	4.0	ND	4.0
2,3,4,7,8-PeCDF	ND	1.5	ND	3.7	ND	3.8	ND	3.9
Total PeCDF	ND	1.5	ND	3.8	ND	4.0	ND	4.2
1,2,3,4,7,8-HxCDF	ND	0.96	ND	2.0	ND	2.3	ND	1.7
1,2,3,6,7,8-HxCDF	ND	0.84	ND	1.7	ND	2.0	ND	1.5
2,3,4,6,7,8-HxCDF	ND	1.0	ND	2.0	ND	2.3	ND	1.8
1,2,3,7,8,9-HxCDF	ND	1.1	ND	2.3	ND	2.7	ND	2
Total HxCDF	ND	1.1	ND	2.3	ND	2.7	3.1	
1,2,3,4,6,7,8-HpCDF	ND	1.2	2.8		3.0		3.0	
1,2,3,4,7,8,9-HpCDF	ND	1.6	ND	1.4	ND	1.5	ND	2.1
Total HpCDF	ND	1.6	2.8		3.0		3.0	
OCDF	ND	6.5	ND	6.2	ND	4.2	ND	6.1

a. Concentration in picograms per sample
b. Detection limit in picograms per sample
c. Not detected

One of the goals of this study was to collect sufficient sample to obtain a detection limit of 100 pg TEQ/L. This goal was exceeded with the lowest TEQ measured for the pre-1993 fuel emission samples being 10 pg TEQ/l and for the Market Basket blend being 15 pg TEQ/l. These values were calculated by adding the TEQ of compounds detected with the TEQ of the compounds not detected. The upper limit TEQ of undetected compounds was calculated by multiplying its TEQ factor with the detection limit of that compound. Even with the lower detection limit obtained in this study many of the PCDDs and PCDFs with TEQ factors were not detected. The average TEQ profiles (three samples each) of the pre-1993 and reformulated blend emission samples are illustrated in Figure 22. The TEQ profile of the market basket blend emission samples were lower than the pre-1993 emission samples.

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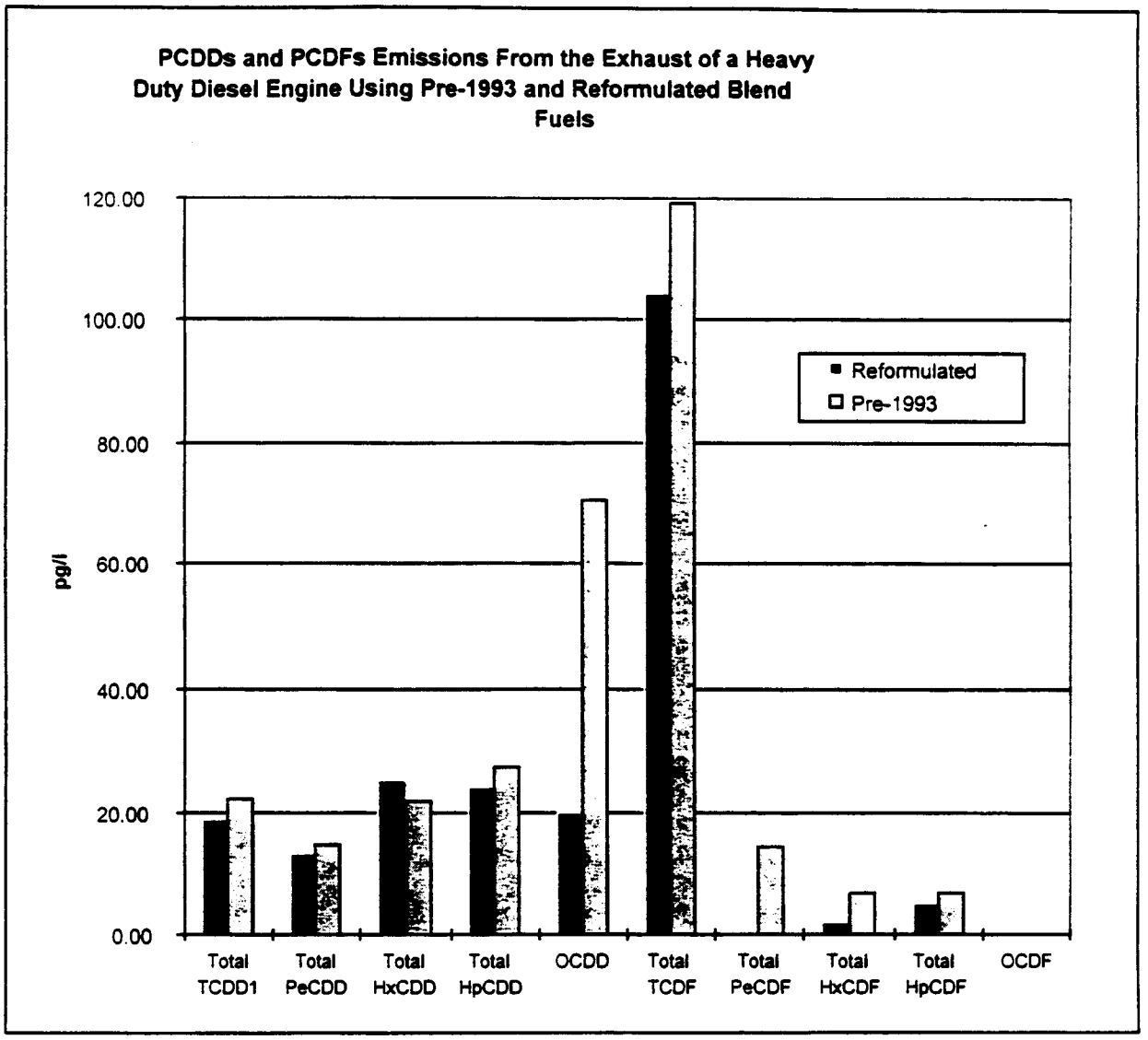

Figure 21. Profile of PCDDs and PCDFs isomer classes from the emissions from the exhaust of a heavy duty engine using Pre-1993 and Reformulated blend.

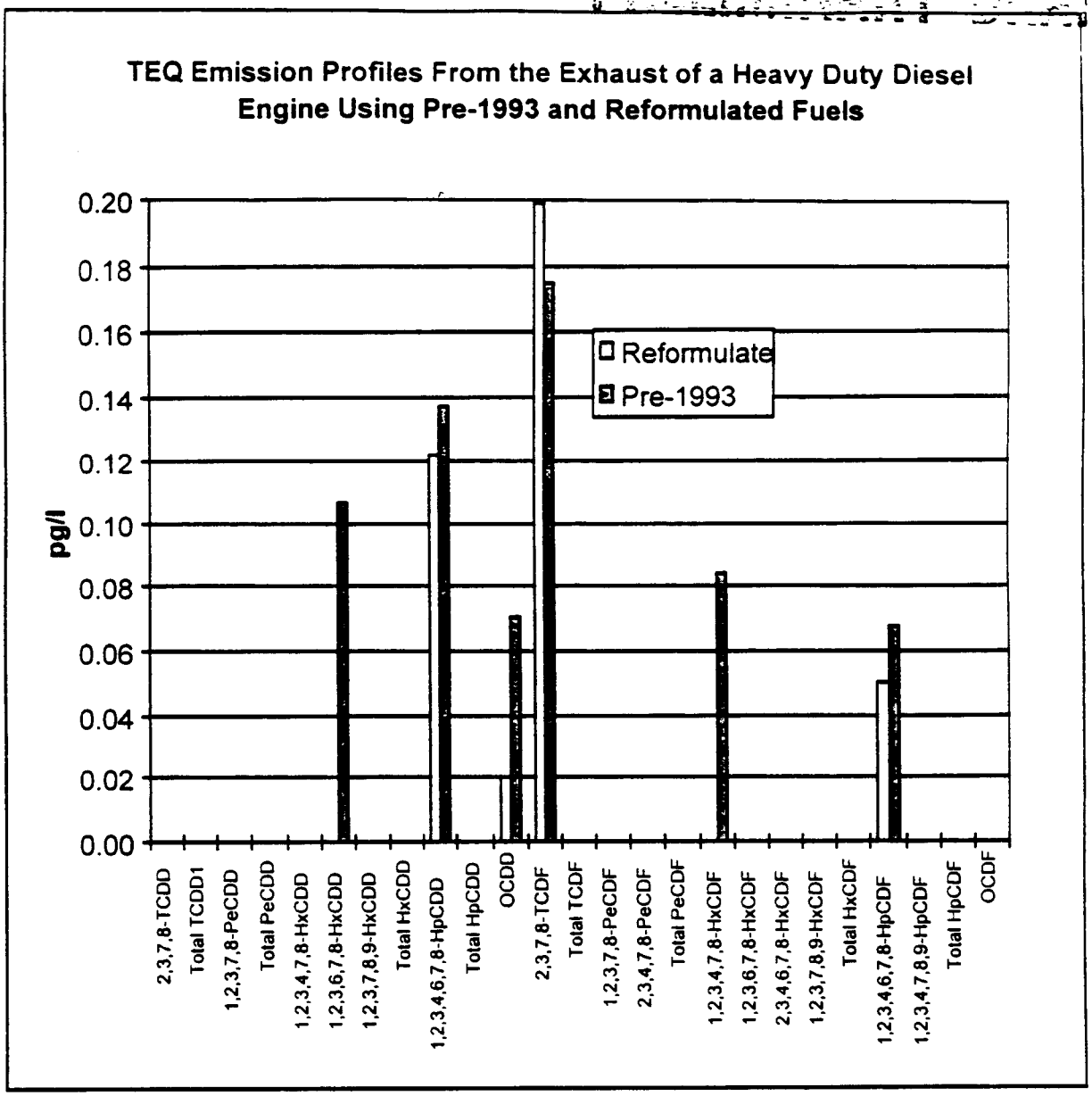

Figure 22. TEQ profiles for the pre-1993 and Market basket blend diesel emission samples taken at the LA MTA Test Emissions Facility.

Fuel and Oil Dioxin Results: PCDDs and PCDFs present in the fuel may be detected in the exhaust because some of the fuel is not burned during combustion. Both the pre-1993 and the reformulated blend fuels were analyzed for PCDDs and PCDFs. The results are presented in Table 53. OCDD levels in the pre-1993 fuel and the reformulated blend were 1400 pg/l and 720 pg/l, respectively. This corresponds to a TEQ of 1.4 pg/l for the pre-1993 fuel and .72 pg/l for

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the reformulated blend. The measured TEQ in the fuels can be misleading because not all the PCDDs and PCDFs with TEQ factors were above the detection limit. This is magnified because the detection limit in the pre-1993 fuel is much higher than in the reformulated blend. Levels below the detection limit of the pre-1993 fuel and above that of the reformulated blend could raise the TEQ for the pre-1993 fuel.

Table 53. PCDD and PCDF levels in the pre-1993 and Reformulated Blend Fuels.

	Sample ID: DPF-1 Pre-1993		Sample ID: DMF-1 Reformulated blend	
Compound	Conc.[a] (pg/l)[c]	D.L.[b] (pg/l)	Conc. (pg/l)	D.L. (pg/l)
2,3,7,8-TCDD	ND [d]	100	ND	26
Total TCDD	ND	100	ND	26
1,2,3,7,8-PeCDD	ND	89	ND	21
Total PeCDD	ND	89	ND	21
1,2,3,4,7,8-HxCDD	ND	110	ND	21
1,2,3,6,7,8-HxCDD	ND	120	ND	23
1,2,3,7,8,9-HxCDD	ND	110	ND	20
Total HxCDD	ND	120	ND	23
1,2,3,4,6,7,8-HpCDD	ND	230	ND	47
Total HpCDD	ND	230	ND	76
OCDD	1400		720	
2,3,7,8-TCDF	ND	21	ND	11
Total TCDF	ND	21	ND	11
1,2,3,7,8-PeCDF	ND	110	ND	8.1
2,3,4,7,8-PeCDF	ND	100	ND	11
Total PeCDF	ND	110	ND	11
1,2,3,4,7,8-HxCDF	ND	36	ND	6.4
1,2,3,6,7,8-HxCDF	ND	34	ND	6.1
2,3,4,6,7,8-HxCDF	ND	66	ND	17
1,2,3,7,8,9-HxCDF	ND	36	ND	7.5
Total HxCDF	ND	66	ND	17
1,2,3,4,6,7,8-HpCDF	ND	92	ND	48
1,2,3,4,7,8,9-HpCDF	ND	98	ND	50
Total HpCDF	ND	98	ND	50
OCDF	ND	260	ND	41

a. Concentration in picograms per liter
b. Detection limit in picograms per liter
c. Picograms per liter
d. Not detected

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PCDDs and PCDFs Level in Oil: Samples of the new oil and used oil were collected and analyzed for PCDDs and PCDFs. After each fuel change on the diesel engine the oil was also changed. Used oil samples from the pre-1993 fuels test and reformulated blend were collected and analyzed for PCDDs and PCDFs. Levels in the new oil were the lowest, while levels in the used market basket oil were the highest. The TEQ of the used market basket oil was 13 pg/l of oil. This sample contained 1,2,3,4,6,7,8-HpCDD at 810 pg/l and OCDD at 5200 pg/l. Table 54 summarizes the oil results. From our current study, it is uncertain how dioxin levels in the oil affect levels in diesel exhaust.

Table 54. Summary of PCDDs and PCDFs measured in new and used oil.

	Sample DPO-1 new oil		Sample DPO-2 used after pre-1993 test		Sample DMO-3 used after reformulated fuel test	
Compound	Conc.[a] (pg/l)[c]	D.L.[b] (pg/l)	Conc. (pg/l)	D.L. (pg/l)	Conc. (pg/l)	D.L. (pg/l)
2,3,7,8-TCDD	ND[d]	96	ND	46	ND	55
Total TCDD	ND	96	ND	46	ND	55
1,2,3,7,8-PeCDD	ND	300	ND	210	ND	210
Total PeCDD	ND	300	ND	210	ND	210
1,2,3,4,7,8-HxCDD	ND	300	ND	130	ND	150
1,2,3,6,7,8-HxCDD	ND	340	ND	150	ND	180
1,2,3,7,8,9-HxCDD	ND	290	ND	130	ND	160
Total HxCDD	ND	340	ND	150	ND	180
1,2,3,4,6,7,8-HpCDD	ND	370	ND	220	810	0
Total HpCDD	ND	370	ND	220	810	0
OCDD	2000	0	1100	0	5200	0
2,3,7,8-TCDF	ND	77	ND	64	ND	76
Total TCDF	370	0	320	0	330	0
1,2,3,7,8-PeCDF	ND	160	ND	180	ND	150
2,3,4,7,8-PeCDF	ND	170	ND	150	ND	150
Total PeCDF	ND	170	ND	180	ND	150
1,2,3,4,7,8-HxCDF	ND	110	ND	64	ND	62
1,2,3,6,7,8-HxCDF	ND	120	ND	78	ND	74
2,3,4,6,7,8-HxCDF	ND	120	ND	80	ND	71
1,2,3,7,8,9-HxCDF	ND	160	ND	110	ND	100
Total HxCDF	ND	160	ND	110	ND	100
1,2,3,4,6,7,8-HpCDF	ND	480	ND	140	ND	160
1,2,3,4,7,8,9-HpCDF	ND	470	ND	140	ND	210
Total HpCDF	ND	480	ND	140	ND	210
OCDF	ND	700	ND	470	ND	450

a. Concentration in picograms per liter
b. Detection limit in picograms per liter
c. Picograms per liter
d. Not detected

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Emission Analysis Results of Dioxin Precursors and Catalyst Emissions of chloride, chlorine (Cl), iron (Fe), and copper (Cu) are presented in Table 55. Emission samples were taken by CE-CERT personnel. The data listed in this table are pertinent to the PCDD and PCDF study. Listed in this table are the total chloride, chlorine, copper and iron levels. Chlorine is considered a dioxin precursor and copper and iron are considered catalysts for dioxin formation.

Table 55. Summary of Dioxin precursors and catalyst that were measured in the diesel exhaust.

Species	Pre-1993 Cold Start Cycle Emission Rate mg/bhp-hr	SDEV mg/bhp-hr	Pre-1993 Hot Start Cycle Emission Rate mg/bhphr	SDEV mg/bhp-hr
Chloride	-	-	0.01	0.01
Cl	0.022	0.001	0.026	0.025
Fe	0.451	0.339	0.213	0.135
Cu	0.012	0.006	0.008	0.013

Species	Reformulated Blend Cold Start Cycle Emission Rate mg/bhp-hr	SDEV mg/bhp-hr	Reformulated Blend Hot Start Cycle Emission Rate mg/bhphr	SDEV mg/bhp-hr
Chloride	0.03	0.03	0.07	0.11
Cl	0.028	0.013	0.033	0.010
Fe	0.331	0.311	0.089	0.026
Cu	0.009	0.005	0.005	0.004

Isotope Recoveries: Part of the Quality Assurance procedures is to measure the recoveries of the internal standards spiked on the samples. Percent recoveries are calculated by dividing the amount measured in the sample by the amount added, multiplied by 100. Recoveries between 60-140% are considered adequate and levels outside this range are flagged. Because isotope dilution compensates for recoveries, internal standard levels outside this range are considered acceptable as long as there is sufficient signal to accurately measure the internal standard. Internal standard recoveries in diesel

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emission samples are presented in Table 56. ^{13}C-1,2,3,7,8-PeCDD in samples D2 and D4, ^{13}C-1,2,3,6,7,8-HxCDD in sample D2 and ^{13}C-1,2,3,6,7,8-HxCDF in sample D2, D3, and D4 had recoveries greater than 140%. Recoveries of the alternate standard for samples D1, D5 and D6 were less than 60%.

Table 56. Recoveries of Internal Standards in Diesel Emission Samples.

	D1	D2	D3	D4	D5	D6	UL1FV1	UL2FV1
Internal Standard:	%R[a]	%R	%R	%R	%R	%R	%R	%R
^{13}C-2,3,7,8-TCDD	109	116	115	118	86	80	99	92
^{13}C-1,2,3,7,8-PeCDD	138	143[b]	139	142[b]	104	96	116	103
^{13}C-1,2,3,6,7,8-HxCDD	96	143[b]	132	137	117	105	98	99
^{13}C-1,2,3,4,6,7,8-HpCDD	89	133	136	133	89	94	110	96
^{13}C-OCDD	69	88	93	88	50	81	104	90
^{13}C-2,3,7,8-TCDF	106	92	92	93	89	79	97	91
^{13}C-1,2,3,7,8-PeCDF	112	98	100	99	91	84	104	92
^{13}C-1,2,3,6,7,8-HxCDF	91	148[b]	149[b]	146[b]	111	102	94	96
^{13}C-1,2,3,4,6,7,8-HpCDF	87	128	123	127	71	77	97	96
Pre-spike Recovery Standard:								
^{37}Cl-2,3,7,8-TCDD	100	106	108	108	105	106	99	107
^{13}C-2,3,4,7,8-PeCDF	98	106	104	108	98	98	99	106
^{13}C-1,2,3,4,7,8-HxCDD	95	110	124	123	90	96	98	91
^{13}C-1,2,3,4,7,8-HxCDF	101	106	114	116	101	105	100	99
^{13}C-1,2,3,4,7,8,9-HpCDF	108	111	121	114	118	120	114	112
Alternate Recovery Standard:								
^{13}C-1,2,3,7,8,9-HxCDF	11[b]	70	73	73	49[b]	47[b]	106	106

a. Recovery of internal standard
b. Recovery of internal standard flagged because outside specified range of 60-140%

Recoveries of internal standards spiked in the fuel and oil samples are presented in Table 57. ^{13}C-2,3,7,8-TCDD in sample DPF-1 and ^{13}C-2,3,4,6,7,8-HxCDF and ^{13}C-OCDD in sample DMO-3 are flagged.

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Table 57. Recoveries of internal standards in fuel and oil samples.

	DPF-1	DMF-2	DO-1	DPO-2	DMO-3
Internal Standard:	%R[a]	%R	%R	%R	%R
^{13}C-2,3,7,8-TCDD	53[b]	74	97	100	100
^{13}C-1,2,3,7,8-PeCDD	69	69	71	74	63
^{13}C-1,2,3,4,7,8-HxCDD	99	131	127	129	130
^{13}C-1,2,3,6,7,8-HxCDD	84	105	104	96	106
^{13}C-1,2,3,4,6,7,8-HpCDD	95	91	96	92	90
^{13}C-OCDD	73	64	75	83	49[b]
^{13}C-2,3,7,8-TCDF	65	111	101	103	100
^{13}C-1,2,3,7,8-PeCDF	77	134	87	81	77
^{13}C-2,3,4,7,8-PeCDF	82	129	74	77	68
^{13}C-1,2,3,4,7,8-HxCDF	108	144[b]	148[b]	139	52
^{13}C-1,2,3,6,7,8-HxCDF	95	129	117	112	130
^{13}C-2,3,4,6,7,8-HxCDF	114	137	129	130	148[b]
13C-1,2,3,7,8,9-HxCDF	121	138	118	116	136
13C-1,2,3,4,6,7,8-HpCDF	88	96	102	89	104
13C-1,2,3,4,7,8,9-HpCDF	116	101	118	112	116
Cleanup Recovery Standard:					
37Cl-2,3,7,8-TCDD	121	98	119	128	112

a. Recovery of internal standard
b. Recovery of internal standard flagged because outside specified range of 60-140%

Internal standard recoveries for tunnel and manifold particulate matter are presented in Table 58.. ^{13}C-1,2,3,7,8-PeCDD recovery for sample DTP-2 was 148%.

Comparisons to Other Studies: Very few studies of dioxin incorporating sampling from a dynamometer have been reported. Marklund et al, (1987) conducted a test of a heavy-duty diesel vehicle on a chassis dynamometer. Due to difficulties in the analytical procedures the detection limit (I-TEQs) was less than 100 pg/km. Hagenmeyer et al, (1992) conducted two runs of a heavy-duty diesel engine on an engine dynamometer and reported I-TEQs of 70 and 81 pg/l. In a transportation study, Gertler et al, (1996) had reported I-TEQs of 170 pg/km emitted from a fleet of vehicles consisting of 20% heavy-duty diesel vehicles. The study was conducted in the Fort McHenry tunnel. Oehme's transportation study conducted in Norway reported I-TEQs at 5100 pg/km where there were leaded gasoline vehicles and only 3% heavy-duty diesel vehicles.

Table 58. Recoveries of internal standards in tunnel and manifold particulate matter.

	DEP-1	DTP-2	97051-1	97051-2	97051-3
Internal Standard:	%R[a]	%R	%R	%R	%R
^{13}C-2,3,7,8-TCDD	100	120	106	108	105
^{13}C-1,2,3,7,8-PeCDD	117	146[b]	114	109	109
^{13}C-1,2,3,4,7,8-HxCDD	100	137	117	116	118
^{13}C-1,2,3,6,7,8-HxCDD	105	137	90	91	88
^{13}C-1,2,3,4,6,7,8-HpCDD	97	124	95	96	96
^{13}C-OCDD	74	108	80	82	86
^{13}C-2,3,7,8-TCDF	99	128	110	106	108
^{13}C-1,2,3,7,8-PeCDF	113	113	132	150	136
^{13}C-2,3,4,7,8-PeCDF	102	128	123	126	125
^{13}C-1,2,3,4,7,8-HxCDF	87	122	99	90	99
^{13}C-1,2,3,6,7,8-HxCDF	86	112	81	72	79
^{13}C-2,3,4,6,7,8-HxCDF	84	120	84	80	84
^{13}C-1,2,3,7,8,9-HxCDF	96	62	98	102	97
^{13}C-1,2,3,4,6,7,8-HpCDF	80	106	79	82	81
^{13}C-1,2,3,4,7,8,9-HpCDF	83	109	90	106	95
Cleanup Recovery Standard:					
^{37}Cl-2,3,7,8-TCDD	99	122	103	104	106

a. Recovery of internal standard
b. Recovery of internal standard flagged because outside specified range of 60-140%

The concentration of individual PCDDs and PCDFs in diesel exhaust in this study were at lower levels than in other studies. Total PCDDs and PCDFs from the diesel exhaust for the market basket blend and the pre-1993 fuels were at 250 pg/l and 320 pg/l, respectively. This is an order of magnitude less than Hagenmeyer et al reported where there was 4340 pg/l and 2778 pg/l of PCDDs and PCDFs emitted from two diesel exhaust runs.

In this study, levels of some PCDDs and PCDFs congeners could not be detected and therefore the corresponding TEQs could not be determined. This was compounded because the congeners 2,3,7,8 TCDD, 1,2,3,7,8 PeCDD, and 2,3,4,7,8 PeCDF, with the highest potency factors were not detected. Using the detection limit as an estimate of the upper limit for the concentration of these compounds, the maximum I-TEQ in the diesel exhaust would be 9.3 pg/l for the pre-1993 fuel and 15.7 pg/l for the reformulated blend. A summary of each TEQ measured and a calculated maximum TEQ of undetected PCDDs and PCDFs are summarized in Table 59.

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The calculated maximum TEQ levels are still considerably lower than that which was reported in the Hagenmeyer et al (1992) study.

A comparison of total PCDDs and PCDFs in diesel emissions from the two fuels of this study and the two heavy-duty diesel emissions runs from the Hagenmeyer et al (1992) study are illustrated in Figure 23. Because PCDDs and PCDFs levels in the Hagenmeyer study are much higher than in this study, the profiles of classes of PCDDs and PCDFs are normalized to their total PCDD and PCDF emissions. The results are given in units of picograms per liter of fuel burned by the diesel engine. The Hagenmeyer et al (1992) study profile shows PCDFs as a larger fraction of the total mass than in this study, except for total TCDFs which are a smaller fraction in the Hagenmeyer study. In this study, TCDFs were the largest fraction whereas in the Hagenmeyer study OCDDs were the largest fraction.

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Table 59. Measured and potential TEQ for diesel emissions from pre-1993 and Reformulated blend fuel.

	Pre-1993		Reformulated Blend	
Compound	I-TEQ Measured pg/l	I-TEQ D.L. pg/l	I-TEQ Measured pg/l	I-TEQ D.L. pg/l
2,3,7,8-TCDD	0.00	4.33	0.00	6.38
Total TCDD	0.00	0.00	0.00	0.00
1,2,3,7,8-PeCDD	0.00	1.37	0.00	2.31
Total PeCDD	0.00	0.00	0.00	0.00
1,2,3,4,7,8-HxCDD	0.00	0.28	0.00	0.40
1,2,3,6,7,8-HxCDD	0.11	0.40	0.00	0.40
1,2,3,7,8,9-HxCDD	0.00	0.28	0.00	0.36
Total HxCDD	0.00	0.00	0.00	0.00
1,2,3,4,6,7,8-HpCDD	0.13	0.00	0.12	0.00
Total HpCDD	0.00	0.00	0.00	0.00
OCDD	0.07	0.00	0.05	0.00
2,3,7,8-TCDF	0.16	0.00	0.19	0.38
Total TCDF	0.00	0.00	0.00	0.00
1,2,3,7,8-PeCDF	0.00	0.11	0.00	0.34
2,3,4,7,8-PeCDF	0.00	1.17	0.00	3.25
Total PeCDF	0.00	0.00	0.00	0.00
1,2,3,4,7,8-HxCDF	0.08	0.30	0.00	0.34
1,2,3,6,7,8-HxCDF	0.00	0.20	0.00	0.30
2,3,4,6,7,8-HxCDF	0.00	0.17	0.00	0.35
1,2,3,7,8,9-HxCDF	0.00	0.15	0.00	0.40
Total HxCDF	0.00	0.00	0.00	0.00
1,2,3,4,6,7,8-HpCDF	0.06	0.00	0.05	0.00
1,2,3,4,7,8,9-HpCDF	0.00	0.02	0.00	0.03
Total HpCDF	0.00	0.00	0.00	0.00
OCDF	0.00	0.01	0.00	0.01
Total	0.61	8.79	0.41	15.23

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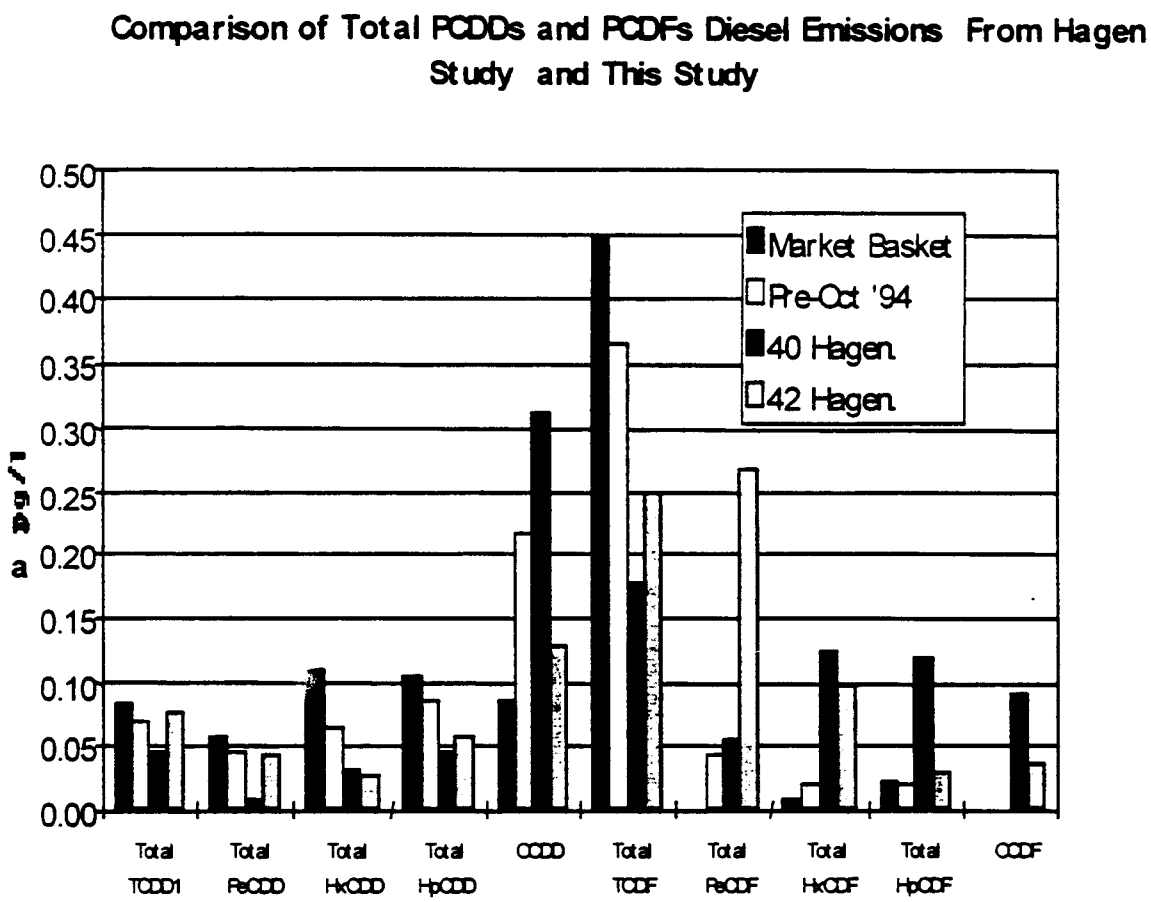


Figure 23. Comparison of Total PCDDs and PCDFs Diesel Emissions from Hager Study and this Study.

In the pre-test, PCDDs and PCDFs were not detected in the tunnel blank, except for low levels of OCDDs, which is a common background contaminant that is often found even in the method blanks. The tunnel blanks taken during the main test had elevated background levels, with some as high as 50% of the emission samples. It is unknown why there was an increase in tunnel blank level since the same protocols were used. Corrections for the tunnel blanks is not a simple subtraction from sample levels since they were not taken under identical conditions as the emission samples. No blank corrections were applied to the emission data, and tunnel background levels are reported.

PRELIMINARY DRAFT

Other Factor Affecting Low Emission Levels: To address the significantly lower results of this study than have been reported in other dynamometer studies, a comprehensive review of the test including a review of all sampling methodologies and procedures was undertaken. Flow rate measurements were validated against a low volume sampler and the results were similar. Breakthrough of dioxins through the PUF was investigated in the pre-test by analyzing the front and backup PUF separately. No breakthrough was detected in the backup PUF. In every sample a pre-spike of dioxin and furan surrogates was added to the front PUF. All recoveries of spiked surrogate standards were excellent, which also indicates that breakthrough was not a problem.

In this study and in the studies by Marklund et al (1987) and Hagenmeyer et al (1992), the emissions samples were collected differently. Both Marklund and Hagenmeyer collected the exhaust using a Grimmer's full-stream collection method where no dilution tunnel was used. The hot diesel exhaust was collected directly into the sampler by cryogenically cooling the exhaust. In this study, samples from a dilution tunnel were collected by a high volume sampler equipped with a filter and PUF. In a dilution tunnel the exhaust is cooled with filtered ambient air. To determine whether tunnel losses were a problem, particles which had adhered to the side of the tunnel were collected and analyzed.

The concentrations of PCDDs and PCDFs in tunnel scrapings taken at two locations in the tunnel and at two locations in the exhaust line that connected the engine to the main tunnel are presented in Table 60.

Two manifold samples were taken. DM-1 was taken in an area after the exhaust manifold and DM-2 was taken just before the juncture to the main tunnel. Samples DTP-1A and DTP-1B were taken in the main tunnel near the secondary dilution probe. DTP-2 was taken at a site located after the high volume sampler and just before the bag filters. The tunnel particulate matter showed high concentration of PCDDs and PCDFs. In the main tunnel I-TEQ concentrations were 125 pg/g, a concentration significantly higher than in the high volume samples. The second tunnel particulate matter was collected downstream of the first sample and it had a concentration of 42 pg TEQ/g. To estimate the total mass of PCDDs and PCDFs in the tunnel, the total mass of particulate in the tunnel is needed. Also, a dioxin concentration gradient through the tunnel is needed. To estimate the tunnel losses per run the number of FTP cycles run, types of fuels, and types of engine tested are needed.

PRELIMINARY DRAFT

Table 60. PCDDs and PCDFs Concentrations in Tunnel, Engine Manifold, and Engine Exhaust Line Particulate Matter.

	Sample ID: DTP-1A Conc. pg/g	Sample ID: DTP-1B Conc. pg/g	Sample ID: DTP-2 Conc. pg/g	Sample ID: DM-1 Conc. pg/g	Sample ID: DM-2 Conc. pg/g
Compound					
2,3,7,8-TCDD	ND	ND	ND	ND	ND
Total TCDD	460	600	190	ND	ND
1,2,3,7,8-PeCDD	33	46	ND	ND	ND
Total PeCDD	1200	1200	250	ND	ND
1,2,3,4,7,8-HxCDD	56	50	12	ND	ND
1,2,3,6,7,8-HxCDD	110	100	24	ND	ND
1,2,3,7,8,9-HxCDD	42	54	19	ND	ND
Total HxCDD	1800	1500	330	ND	ND
1,2,3,4,6,7,8-HpCDD	400	550	130	4	ND
Total HpCDD	750	1100	260	4	ND
OCDD	940	2500	670	61	120
2,3,7,8-TCDF	11	24	20	ND	ND
Total TCDF	450	520	320	ND	ND
1,2,3,7,8-PeCDF	51	55	22	ND	ND
2,3,4,7,8-PeCDF	80	83	34	ND	ND
Total PeCDF	880	730	280	ND	ND
1,2,3,4,7,8-HxCDF	94	96	30	ND	ND
1,2,3,6,7,8-HxCDF	110	110	29	ND	ND
2,3,4,6,7,8-HxCDF	78	96	74	14	29
1,2,3,7,8,9-HxCDF	17	20	ND	ND	ND
Total HxCDF	1200	680	260	14	29
1,2,3,4,6,7,8-HpCDF	210	310	98	ND	ND
1,2,3,4,7,8,9-HpCDF	10	ND	ND	ND	ND
Total HpCDF	280	330	98	ND	ND
OCDF	60	180	61	ND	ND

PRELIMINARY DRAFT

incomplete due to the low level detected. An estimated 10 times more sample would be needed to obtain a complete TEQ profile.

Analysis of the tunnel particulate matter indicates there may be tunnel losses. Using a crude mass balance that accounts for tunnel losses, levels in the exhaust are lower than in other studies.

High background levels from the tunnel make quantitation of these samples difficult. Accurate measurements of these compounds in the tunnel need to be investigated. Finally, modifications to current dilution sampling methodologies may be needed.

3.10 Bioassay Analyses

Diesel exhaust is composed of a complex mixture of compounds present in the particle as well as the vapor phase. These compounds include known and unknown genotoxic compounds. Since genotoxic compounds are present in both the particle and vapor-phase, health effects associated with diesel exhaust needs to be performed for all phases. Specific important classes of compounds such as the polycyclic aromatic hydrocarbons (PAHs) can be quantitated in these complex mixtures as detailed in this report. There are however, as yet unidentified compounds in these mixtures that can be important in the exposure of the population to toxic compounds. Therefore, a supplemental approach or approaches to help identify and help screen for toxic compounds present in the complex mixture of diesel exhaust would be an important assessment tool.

One approach for examining compound classes and to identify potentially toxic compounds, is to use bioassay in conjunction with chemical analyses. The approach, termed "bioassay-directed chemical analyses" has been used in the chemical analyses of diesel particulate as well as airborne particulate matter (Schuetzle, et al., 1986; Arey et al, 1992). In a typical experiment, particulate matter is extracted using organic solvents, concentrated by evaporation, and the concentrate fractionated typically by using HPLC. The fractions are then individually tested in a bioassay. The bioassay generally used is the Salmonella/microsome test of Ames et al (1975) or more recently, its modifications that requires less material. Mutagenic activity of each fraction is then obtained resulting in a profile of relative mutagenic activities, or "mutagrams". These mutagrams are profiles of different compound classes present in the complex mixture of the particulate extract. The mutagrams can be used to compare mutagenic activities and compound profiles

The engine side dilution tunnel was recently installed and was therefore relatively new. Besides this study only one other test program was run on it. Three engines and approximately 150 test cycles were run on this tunnel with this test comprising most of the test time and most of the recent test time. Total mass in the main part of tunnel alone could account for an additional— pg TEQ /cycle. Taking into account the incomplete TEQ profiles and tunnel losses, levels in this study are still considerably lower than in the Hagenmeyer study.

It is interesting that Hagenmeyer compared the Grimmer's sampler system to a dilution tunnel sampling system and found the results were comparable. This would indicate that tunnel losses should not be a problem. The comparison was done with a heavy-duty diesel engine and with a tunnel run with a 5 to 1 dilution. One difference is that in this test the tunnel was run with a 32:1 dilution. This indicates that this tunnel was run at a lower temperature than Hagenmeyer's tunnel. The cooler tunnel temperatures could increase tunnel loses.

Total dioxin and furans in this study are about an order of magnitude lower than in Hagenmeyer's study but TEQ levels were two orders of magnitude lower. Part of the reason is that none of the 2,3,7,8 TCDD, 1,2,3,7,8 PeCDD, and 2,3,4,7,8 PCDF were detected in any of the samples. If these compounds were present at levels below the detection limits, the TEQs would certainly increase. Even in the tunnel scraping, 2,3,7,8 TCDD was not detected although 1,2,3,7,8 PeCDD and 2,3,4,7,8 PCDF were detected. This certainly adds to the possibility that the later two compounds were present in the exhaust at levels below the detectable limit of the method.

Another factor that may contribute to lower emissions was that the engine was brand new, and the system was in peak operating condition. The oil was changed after each week of testing.

Chlorine levels in the pre-1993 fuel were less than 10 mg/kg and in the reformulated blend were 56 mg/kg. The lower chlorine pre-1993 fuel had higher levels of PCDDs and PCDFs in the diesel engine exhaust. Oil used for the test had chlorine concentrations of 230 mg/kg which is relatively high for lubricating oil and would contribute to increased PCDDs and PCDFs emission levels.

Conclusions: Achieved detection limits for the samples collected were between 6 and 10 times lower than the target detection limits of 100 pg I-TEQ/l. Evaluation of the emission data suggest PCDDs and PCDFs levels in the diesel exhaust were at very low levels. TEQ profiles were

from different sources, locations, or collection variables. In the current study, the mutagrams were developed to examine the mutagen profiles from different diesel fuel particulate phase and the vapor-phase.

Prior to developing the mutagrams, the potency - referred to as specific mutagenic activity - was determined for each particle and vapor phase sample. The specific mutagenic activity is reported as the mutagenic activity (revertants) per µg of particulate matter or per µl of extract. Although the potency value is important to consider in assessing toxicity, an index of exposure requires emission values. Emissions for genotoxic compounds will be reported as the level of mutagenic activity emitted per unit of work of the engine, or per brake horsepower-hr.

Particulate Matter Genotoxic or mutagenic activity is reported as "revertants per plate". Revertants are the number of mutated bacterial cells present per incubation plate, and is representative of the level of DNA damage to the target cells. Dose-response relationships are established by measuring the number of cells that mutate (number of revertants) over a series of doses. The dose-response relationships of the particle extracts collected from the combustion of each fuel are presented in Figures 24 and 25 for the all fuels and blanks when using tester strain TA98 with (+S9) and without (-S9) metabolic enzymes added, respectively. These enzymes are routinely used in this type of bioassay and are known to metabolically activate toxic compounds to their reactive forms where they can damage target molecules such as DNA.

The hi-volume particulate samples were extracted using two methods -- Soxhlet extraction (samples designated with 96 prefixes) and by sonication (samples designated H1, H3, ...). The blanks were collected for equivalent times as the samples from the tunnel, except that the engine was not engaged. The samples were extracted by the two methods because one set of extracts (the Soxhlet extracted samples) was used for HPLC fractionation and one set exclusively for mutagenicity testing. Both methods are considered comparable for bioassay analyses.

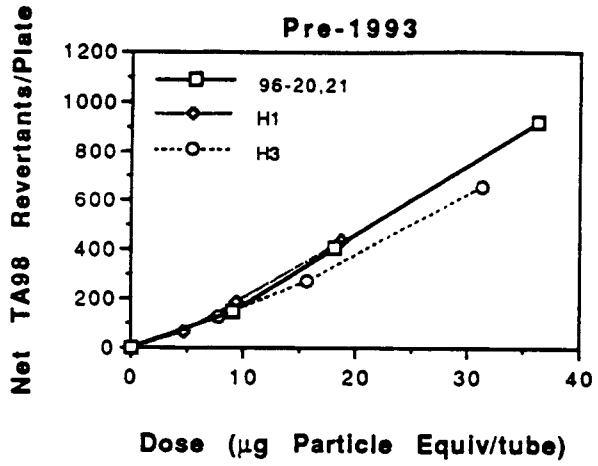
The most potent extracts (revertants per mg of particle extracted - or particle equivalents) were the pre-1993 fuel particulate matter, both when tested with and without metabolic enzymes added. The potencies of the reformulated blend as well as the low aromatic fuel were similar in potency with or without the addition of metabolic enzymes, but were lower than the Pre-1993 fuel particulate matter. The overall potency of the particulate emission extracts was higher when no metabolic enzymes were added, especially for Soxhlet extracted samples. The blanks had very little or no activity. Relative genotoxic potencies of the extracts are summarized in Table 61. The specific mutagenic activities and the r^2 values for the slopes are provided. The slopes for the pre-1993 fuel particulate matter extracts were the highest relative to the other two fuels. The

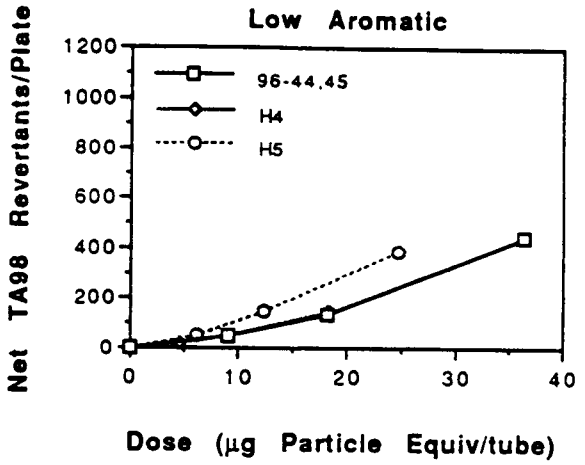
comparisons of potencies between the fuels should be made with samples extracted in an identical manner (for example, Soxhlet-extracted samples for all three fuels). For the Soxhlet extracted samples, the Pre-1993 fuel had the highest specific mutagenic activity (+ or -S9) relative to the Low Aromatic and Reformulated fuels. For the samples extracted using sonication, the Pre-1993 fuel had the greatest activity, followed by the Low Aromatic fuel followed by The Reformulated fuel particle sample.

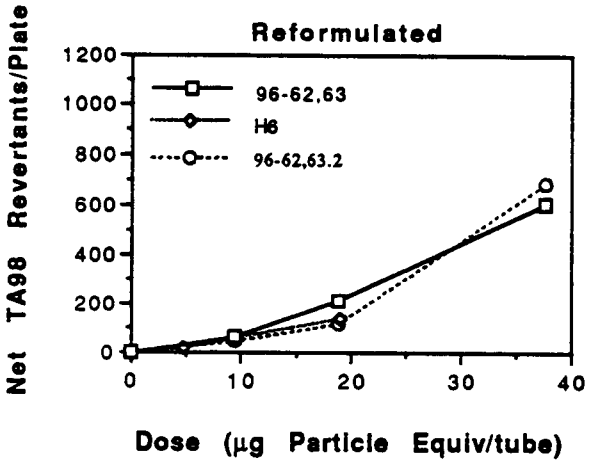
Figure 24. Dose-response curves for pre-1993, low aromatic, and reformulated fuel particulate matter. Samples were tested using tester strain TA98 with metabolic enzymes added (+S9).

PRELIMINARY DRAFT

TA98 +S9







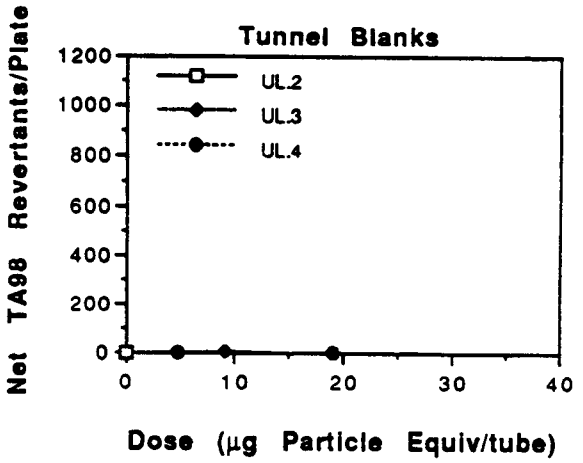
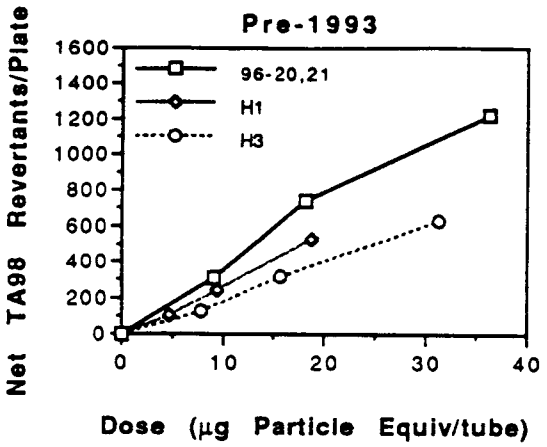
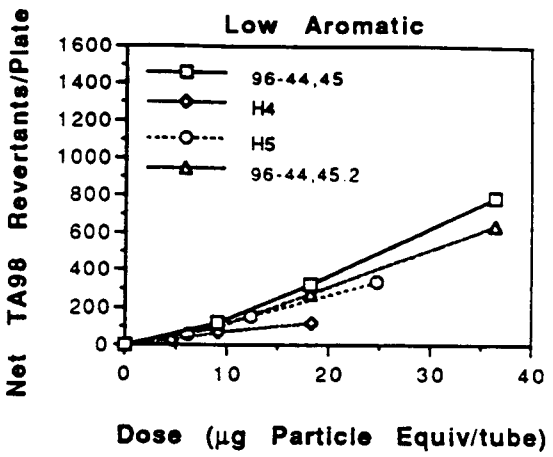


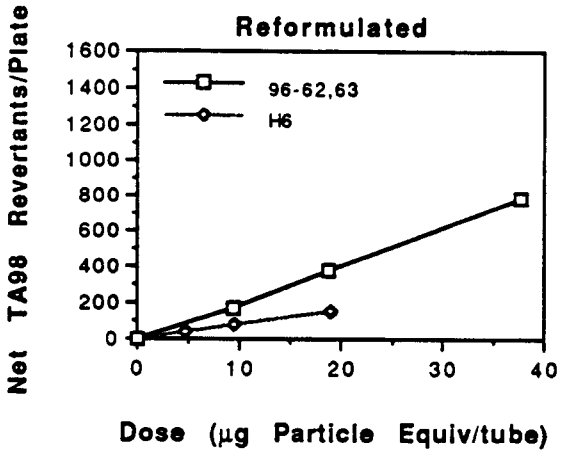
Figure 25. Dose-response curves for pre-1993, low aromatic, and reformulated fuel particulate matter. Samples were tested using tester strain TA98 without metabolic enzymes added (-S9).

PRELIMINARY DRAFT

TA98 -S9







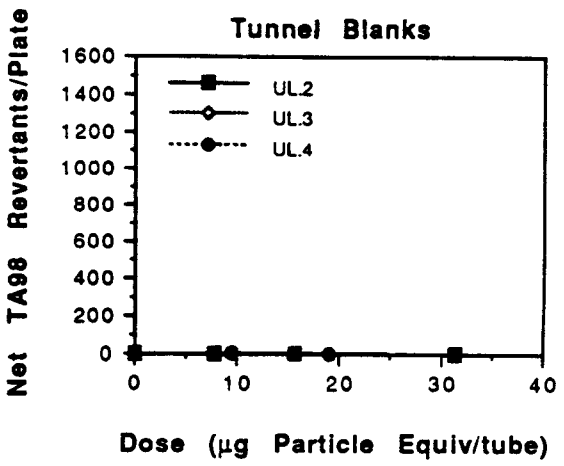


Table 61. Specific Mutagenic Activities and Emissions of the Particulate Matter Collected from the High Volume Sampler.

Fuel Type	Test Cycle ID	Lab Sample ID	Sp. Act Rev/µg (+)	Sp. Act r 2	Emission TA98 (+ S9) Rev/hp-hr (x10 6)	Sp. Act Rev/µg (-)	Sp. Act r2	Emission TA98 (- S9) Rev/hp-hr (x10 6)
Pre-1993	338H8,H9	96-20,96-21	28.332	0.959	**5.69**	32.729	0.964	**6.58**
Pre-1993	337H1,H2	H1FV	24.498	0.968	**5.19**	29.006	0.988	**6.15**
Pre-1993	339H6,H7	H3FV	21.738	0.989	**4.85**	20.797	0.99	**4.64**
				Ave	**5.25**		Ave	**5.79**
				SD	**(0.43)**		SD	**(1.0)**
Low Aromatic	346H3, H4	96-44,96-45	12.886	0.927	**2.28**	20.731	0.96	**3.67**
Low Aromatic	344H1, H2	H4FV	8.445	0.969	**1.67**	6.538	0.985	**1.29**
Low Aromatic	344H3, H4	H5FV	16.659	0.965	**3.11**	14.079	0.984	**2.63**
				Ave	**2.36**		Ave	**2.53**
				SD	**(0.72)**		SD	**(1.19)**
Reformulated	351H1, H2	96-62, 96-63	18.81	0.918	**3.23**	25.6	0.911	**4.4**
Reformulated	348H1,H2	H6FV	7.74	0.974	**1.33**	7.955	0.992	**1.37**
				Ave	**2.28**		Ave	**2.89**

[a] Particulate mass collected per filter from 2 consecutive hot start cycles.
[b] Specific mutagenic activity is the number of revertants per microgram of particulate matter. Sample added for the assay is actually an extract of the particulate matter. Therefore, the mass is an equivalent mass.
[c] + or - S9 indicates that the test included or did not include adding metabolic enzymes.

Although genotoxic potency is an important property to help in the evaluation of potential toxicity, an index for the levels of genotoxic compounds being emitted is needed to help evaluate potential exposure to diesel emissions. As mentioned, since the emissions are a complex mixture of compounds, only a few toxic genotoxic compounds can realistically be measured. Mutagenic activity could therefore serve as an index to some of these complex emissions. An emission value that incorporated both the potency and yield of these compounds would serve to meet this need. The emissions based on the bioassay results can be presented as mutagenic activity emitted per mile or per brake horsepower hr (bhp-hr), or more specifically as revertants / bhp-hr. These emission values were calculated by using the specific mutagenic activity and emissions of particulate matter for each fuel.

The emissions for genotoxic activity for each fuel type are summarized in Table 61. The pre-1993 fuel particulate matter had on the average the highest emissions both with and without the addition of metabolic enzymes. The low aromatic and reformulated fuel particulate matter had similar emissions based on the average values from all extracts within a fuel type.

To test the reproducibility of the bioassay for these complex samples, a specific series of samples from each fuel were tested. The samples used for this analyses were extracted by Soxhlet extraction using DCM (Sample ID prefixes "96" for all fuel types) and were tested for dose response relationships. The results are presented in Figure 26. The experiments were conducted on separate days. The dose-response curves for these samples using the microsuspension bioassay were reproducible. Also, within these samples, the differences between the pre-1993 fuel and the low aromatic and reformulated fuels can be seen. To further examine the variability between assays, the specific mutagenic activity derived from these specific samples (rev/µg particulate matter) and the particle emissions (g/bhp-hr) were used calculate the average mutagen emissions and 95 percent confidence interval of each fuel (Figure 27). The emissions for the pre-1993 fuel for these samples was higher than the emission from the other two fuels with and without S9. Although the Reformulated fuel emissions appear higher than the low aromatic fuel emissions, the 95% confidence intervals overlap, especially without S9 added. To investigate the chemical characteristics of the mutagenic compounds, hi-volume samples were fractionated using HPLC.

PRELIMINARY DRAFT

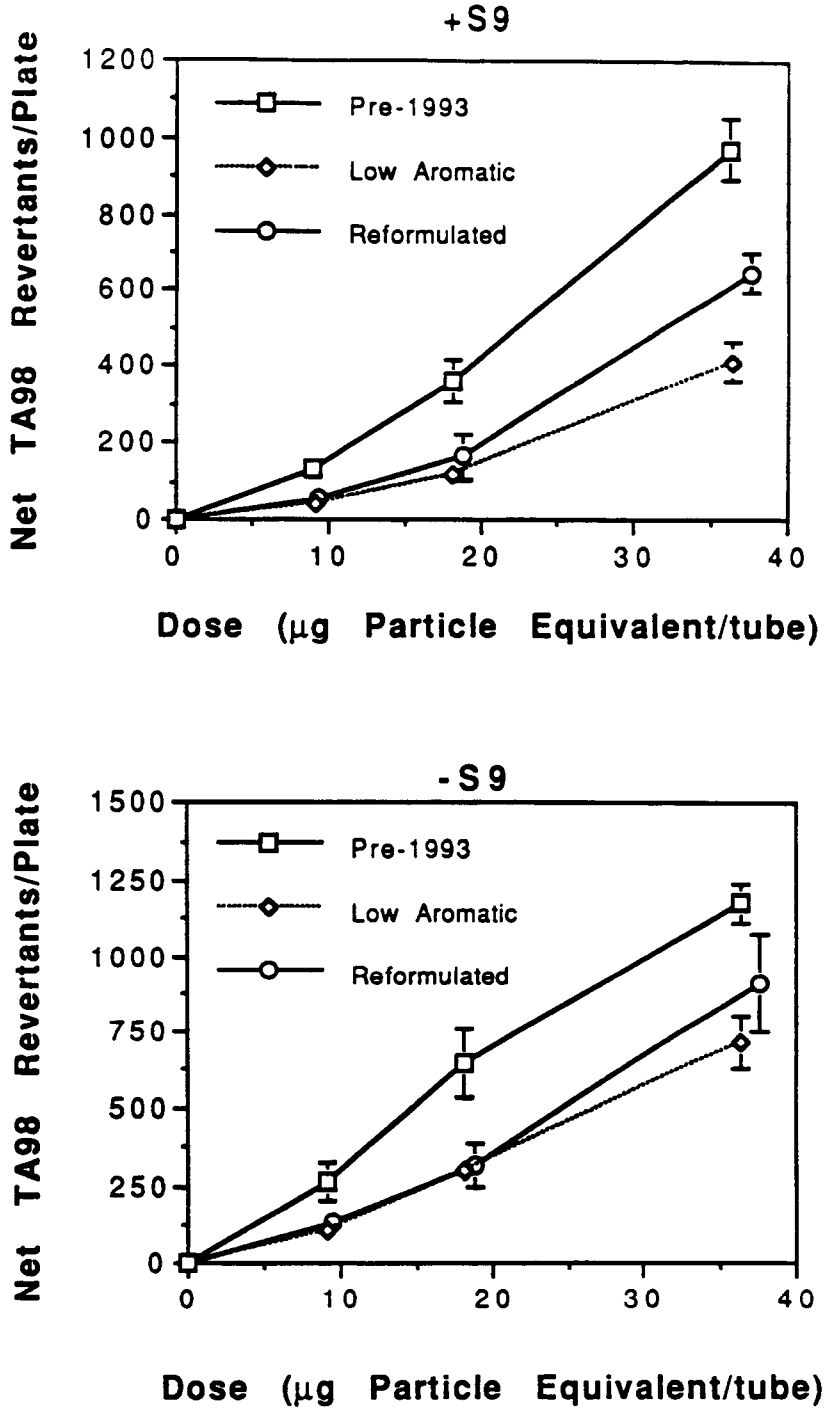


Figure 26. Dose-response curves to check for bioassay reproducibility of testing particulate matter from the combustion of Pre-1993, low aromatic, and reformulated fuel formulations. Samples were extracted using Soxhlet and the extracts tested using tester strain TA98 with metabolic enzymes added (+S9) and no metabolic enzymes added (-S9). Results represent data from two separate experiments with average (± SD) responses.

PRELIMINARY DRAF

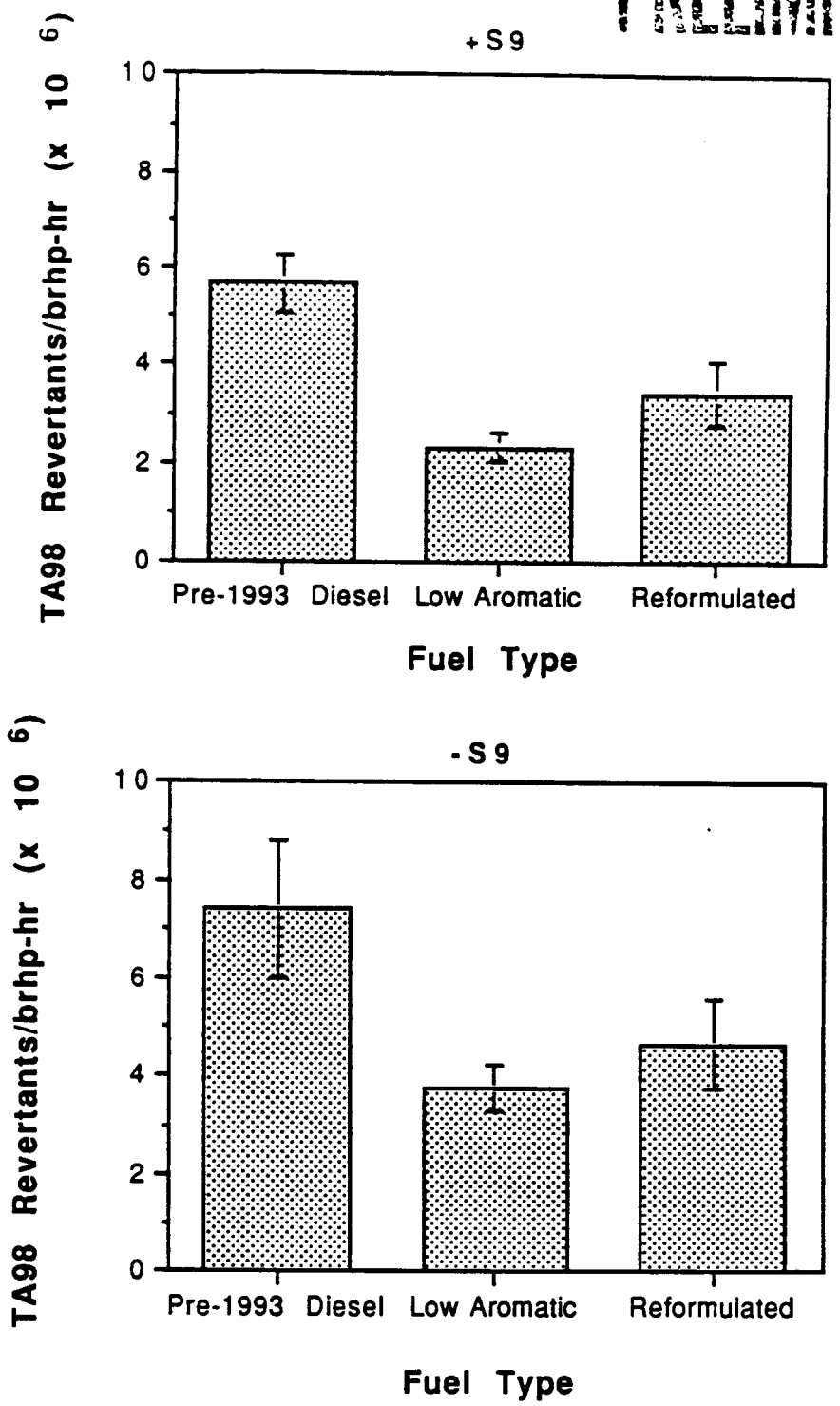


Figure 27. Emissions of mutagenic compounds for the three fuel types from Hi volume samples represented in Figure 26. The rectangles represent the average emissions (and 95 % confidence intervals) determined from two separate experiments from samples extracted with Soxhlet (Sample No. with "96" prefix). Each sample represents two consecutive cycles collected. Samples were tested using tester strain TA98 with (+S9) and without (-S9) the addition of metabolic enzymes.

PRELIMINARY DRAFT

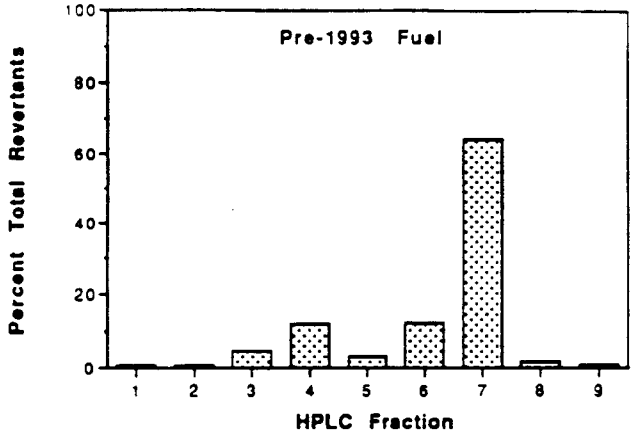
HPLC Fractions and Mutagrams The HPLC fractions from each particle sample were tested for mutagenic activity using three doses, in duplicate. Dose-response curves were developed for each HPLC fraction and the specific genotoxic activities were determined. The relative genotoxic activity of each fraction is presented in a bar graph, or "mutagram", where the relative percent of activity is illustrated. The mutagrams for all the fuel particulate matter are presented in Figures 28 and 29 with (+S9) and without (-S9) metabolic enzymes added, respectively. For the pre-1993 fuel, HPLC fraction 7 typically had the most mutagenic activity, accounting for approximately 64% of the total mutagenic activity with S9 added and approximately 50% of the total mutagenic activity without S9 added. Relative to Fraction 7, the next most mutagenic fraction was Fraction 6 which accounted for approximately 12 % and 28% with and without S9, respectively. The rest of the activity is spread over the other fractions especially fractions 3,4 and 5. The relative activity in fraction 6 without S9 is approximately 2 times the activity when S9 is added.

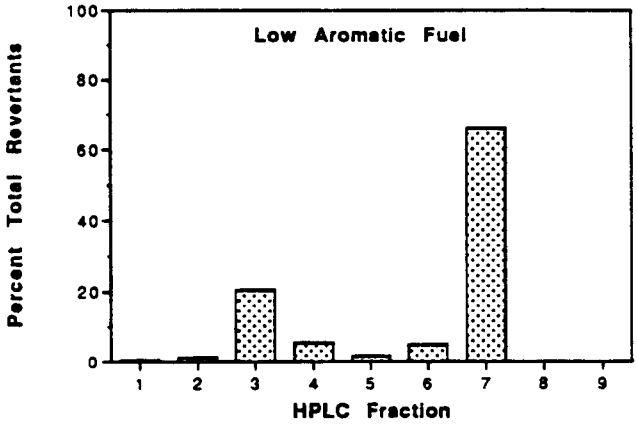
The mutagram for the low aromatic fuel particulate matter also has fraction 7 with the greatest mutagenic activity. The relative activity with metabolic activation (+S9) was approximately 66% and was approximately 41% without activation (-S9). Unlike the Pre-1993 fuel, the low aromatic fuel has a higher relative mutagenic activity in Fraction 3, especially when S9 was added. Fraction 3 represented approximately 23 % of the total mutagenic activity measured in the fractions. There was virtually no activity in Fraction 3 without S9. Fraction 6 (-S9) contained approximately 38% of the activity. The remainder of the activity was spread out over fractions 4 and 5 (+S9) and 8 and 9 (-S9).

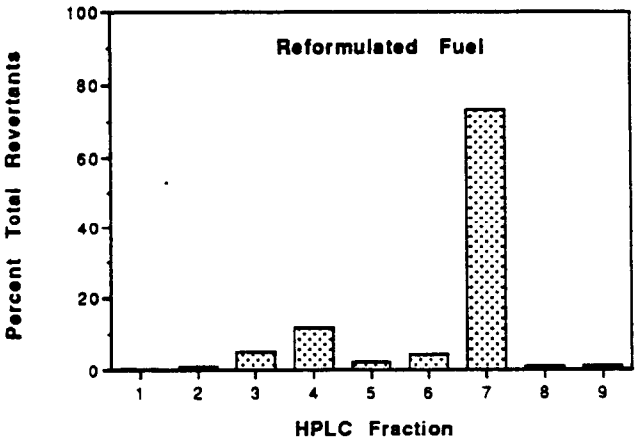
Fraction 7 is also the most mutagenic fraction from the reformulated blend fuel particulate matter accounting for approximately 73% and 57% of the activity, with and without S9, respectively. Fraction 4 contained approximately 12 % of the total activity with metabolic activation, while without metabolic enzymes added, Fraction 6 is the second highest peak with approximately 21% of the total activity. The mutagrams for the particulate matter extracts appear unique for each fuel, but there are similarities such as for the Pre-1993 and Reformulated fuel mutagrams.

PRELIMINARY DRAFT

Figure 28. Percent total mutagenic activity of HPLC fractions ("mutagram") of particle extract collected from combustion emission of Pre-1993, low aromatic, and reformulated fuel. Tester strain TA98 used with metabolic enzymes added (+S9). HPLC fractions are presented in order of increasing polarity. Fraction 1 represents the most non-polar fraction and Fraction 9 represents the most polar fraction.

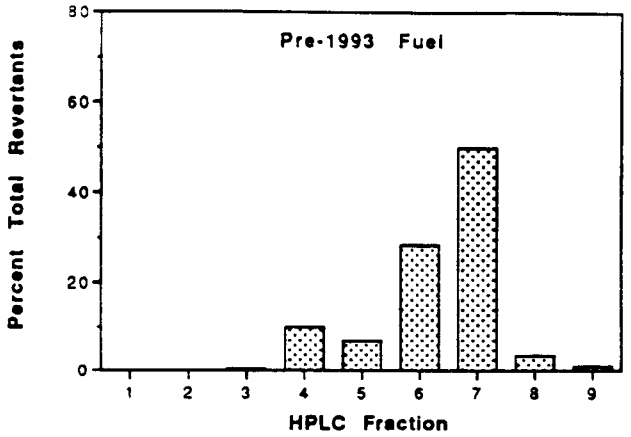

Pre-1993 Fuel
Percent Total Revertants
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9
HPLC Fraction

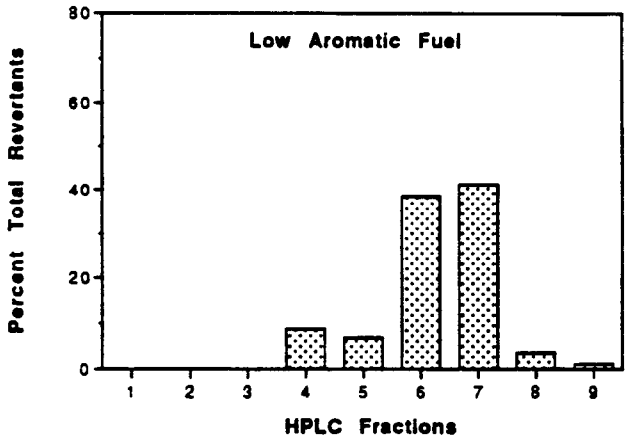

Low Aromatic Fuel
Percent Total Revertants
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9
HPLC Fraction

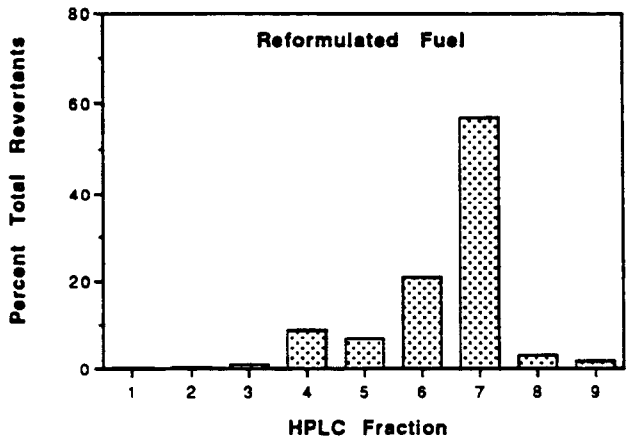

Reformulated Fuel
Percent Total Revertants
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9
HPLC Fraction

PRELIMINARY DRAFT

Figure 29. Percent Total Mutagenic activity of HPLC fractions ("mutagram") of particle extract collected from combustion emission of Pre-1993, low aromatic, and reformulated fuel. Tester Strain TA98 used without the addition metabolic enzymes (-S9). HPLC fractions are presented in order of increasing polarity. Fraction 1 represents the most non-polar fraction and Fraction 9 represents the most polar fraction.


Pre-1993 Fuel
Percent Total Revertants
0
20
40
60
80
1
2
3
4
5
6
7
8
9
HPLC Fraction


Low Aromatic Fuel
Percent Total Revertants
0
20
40
60
80
1
2
3
4
5
6
7
8
9
HPLC Fractions


Reformulated Fuel
Percent Total Revertants
0
20
40
60
80
1
2
3
4
5
6
7
8
9
HPLC Fraction

PRELIMINARY DRAFT

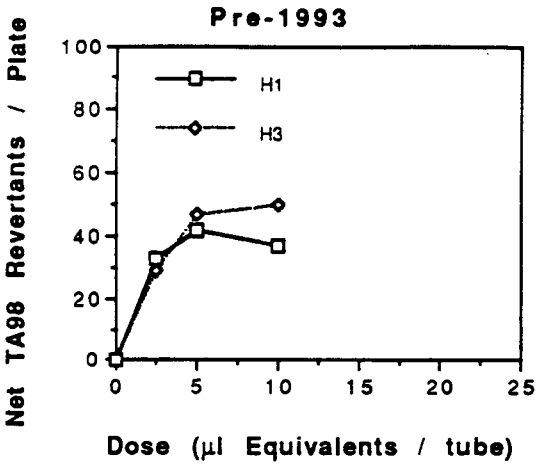
Vapor-Phase Samples: Vapor-phase samples were collected onto PUF and XAD adsorbents, extracted by supercritical fluid extraction, and tested in the bioassay for mutagenicity. Dose response curves were developed for each fuel type in duplicate or triplicate using tester strains TA98 and TA100. Each PUF sample represented two consecutive hot cycles and the dose response curves for each fuel type are presented in Figures 30 and 31. The dose response relationships for the trip blanks and tunnel blanks are also presented. For the Pre-1993 fuel, the extracts were mutagenic in both TA98 and TA100. In tester strain TA98 however, there is a decrease in the response at the highest dose tested (10 µl). This might indicate that there is some toxicity to the tester strain used. This plateau was not observed for the samples tested with strain TA100. The samples, H1 thru H6 are from two consecutive hot start cylces and are extracted and were tested independently. The dose response curves for a specific fuel have slopes that are very reproducible.

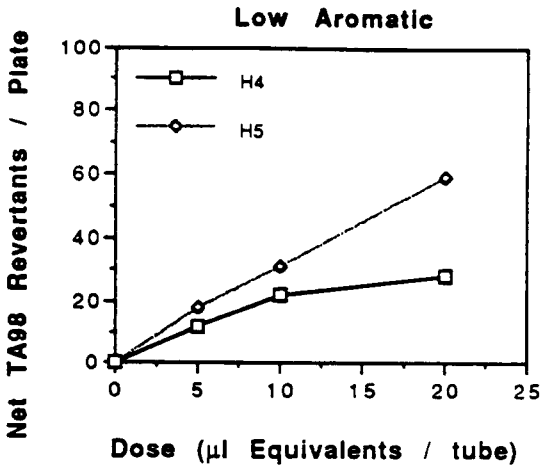
The slope of the linear portion dose response curve was used to determine the specific mutagenic activity of each sample and are reported as revertants per µl equivalent. These values reflect the potency of the samples. The specific mutagenic activities are presented in Table 62. An increase in the slope of the dose-response curve results in an increase in an increase the potency of the extract. The highest specific mutagenic activity in both tester strains were observed in emissions from the Pre-1993 fuel. For all fuels, tester strain TA100 is more sensitive than TA98 for the mutagens present in these extracts. For example, specific activities for the Pre-1993 PUF samples increased approximately 3-fold from using TA98 to using TA100.

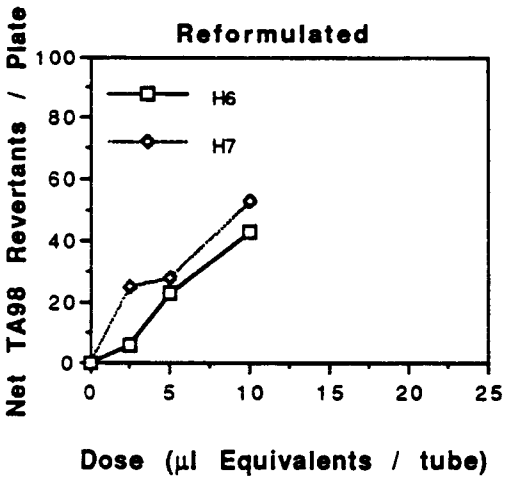
Total emission of mutagenic activity for the vapor-phase samples were determined and are reported as revertant per brake-horsepower hour (rev /brhp-hr) in Table 62. The highest relative mutagenic emissions for TA98 were found in the Pre-1993 fuel, followed by the reformulated fuel and the low aromatic fuel which like the particulate matter. Tester strain TA100 had higher emission values compared to TA98, and the relative order of emissions was similar to that observed for TA98 for the PUF samples. However, for TA100, there is very little difference in the emissions for the XAD samples across all fuels. For the Low Aromatic and Reformulated fuels, the XAD sample is higher relative to the matching PUF sample. The XAD samples appeared to have greater activity in TA100 compared to TA98. The emission value from a PUF sample and its matching XAD sample are also presented as the sum of the two values. The XAD was placed in series behind the PUF in the sampling stream. The combined values represent the mutagenic vapor-phase compounds adsorbed and extracted from the adsorbents. Based on the sum of emission values determined using TA100, the Pre-1993 fuel has the highest emissions, and the Low ARomatic and Reformulated fuels are similar in emissions.

PRELIMINARY DRAFT

Vapor-Phase PUF TA98







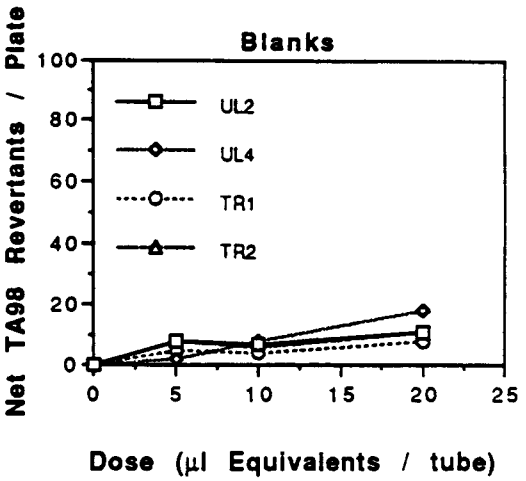
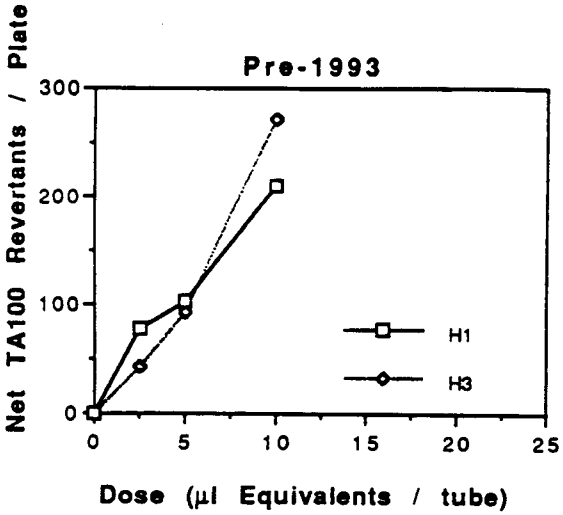
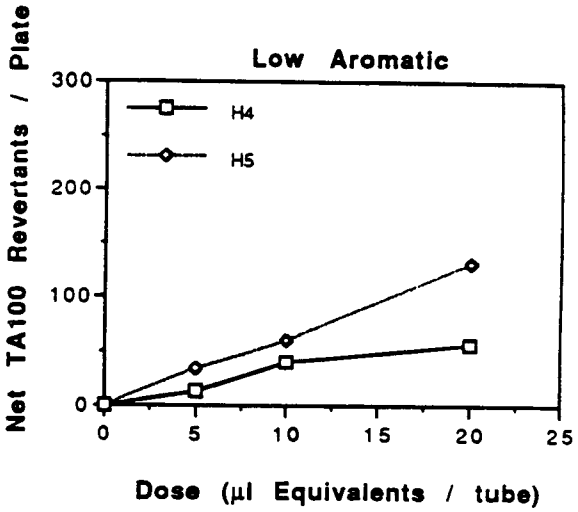


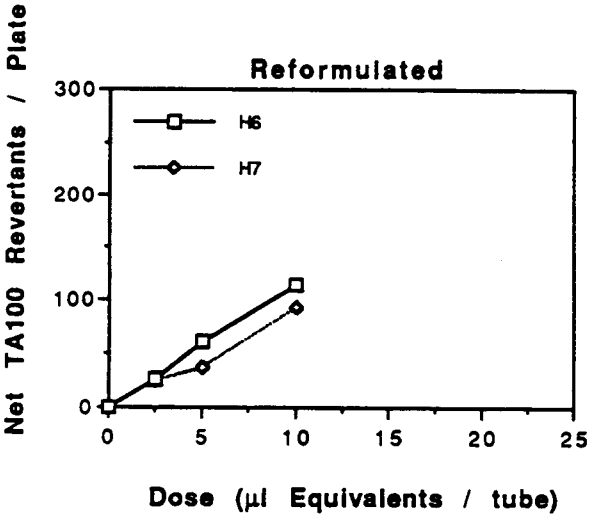
Figure 30. Dose-response curves for fuel types and blanks in the vapor-phase PUF samples using tester strain TA98 with the addition of metabolic enzymes. Each extract that was tested represents two FTP cycles run consecutively and each data point represents the values obtained from duplicate determinations. UL= tunnel blanks; TR = trip blanks (blanks taken on the trip to the dynamometer facility and not used for sampling.

PRELIMINARY DRAFT

Vapor-Phase PUF TA100







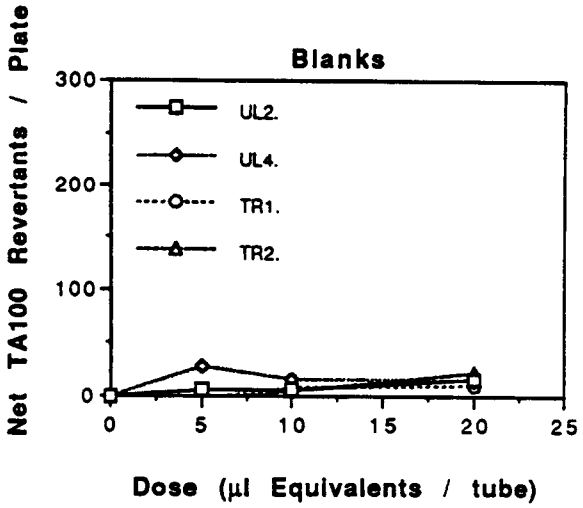


Figure 31. Dose-response curves for fuel types and blanks in the vapor-phase PUF samples using tester strain TA98 without the addition of metabolic enzymes. Each extract that was tested represents two FTP cycles run consecutively and each data point represents the values obtained from duplicate determinations.

PRELIMINARY DRAFT

Table 62 Specific Mutagenic Activity and Emissions of Mutagenicity in PUF and XAD samples.

Fuel Type	Test Cycle ID	Lab Sample ID	Sample Type a	Sp. Act TA98 Rev/µl	Sp.Act r 2	Emissions (+ S9) TA98 Rev/hp-hr (x10 5)	Sp. Act TA100 Rev/µl	Sp.Act r2	Emissions (+ S9) TA100 Rev/hp-hr (x10 5)
Pre-1993	337H1,H2	H1PV	PUF	8.50	0.831	**0.96**	20.14	0.964	**2.30**
Pre-1993	339H6,H7	H3PV	PUF	9.50	0.925	**1.16**	27.57	0.969	**3.42**
Pre-1993	337H1,H2	H1XV	XAD	0.70	0.564	**0.26**	4.79	0.755	**2.80**
		Total b	Vapor	Phase	H1	**1.22**			**5.10**
Low Aromatic	344H1, H2	H4PV	PUF	1.22	0.757	**0.19**	2.88	0.792	**0.44**
Low Aromatic	344H3, H4	H5PV	PUF	2.92	0.985	**0.37**	6.45	0.996	**0.81**
Low Aromatic	344H1, H2	H4XV	XAD	0.45	0.893	**0.19**	6.21	0.869	**2.70**
		Total b	Vapor	Phase	H4	**0.38**			**3.14**
Reformulated	348H1,H2	H6PV	PUF	4.47	0.963	**0.73**	11.58	0.967	**1.89**
Reformulated	351H7, 352H7	H7PV	PUF	4.91	0.891	**0.68**	9.19	0.907	**1.27**
Reformulated	351H7, 352H7	H7XV	XAD	2.76	0.971	**0.70**	8.55	0.975	**2.24**
		Total b	Vapor	Phase	H7	**1.38**			**3.51**

a All samples represent 2 consecutive hot start cycles.

b Total of PUF and XAD sample (sample no. H1, H4, or H7).

PRELIMINARY DRAFT

Mutagenic profiles - Mutagrams of Vapor Phase Samples. The extracts from PUF and XAD samples were fractionated using SPE as described in the Methods section. The five fractions from C18 were individually tested in the bioassay. Fraction 1 was subfractionated using a silica SPE cartridge with a series of solvents that included hexane, DCM, DCM:methanol, and finally methanol. These subfractions were also tested in bioassay. The results for the C18 fractions and silica subfractions are presented in Figures 32 and 33 for the PUF samples fractionated using C18 and silica, respectively and tested in TA98, and in Figures 34 and 35 for the PUF samples fractionated using C18 and silica, respectively and tested in TA100. Fraction 1 (from the C18 SPE) was selected for subfractionation since this fraction had one of the higher relative mutagenic activities for the Pre-1993 and the reformulated fuel vapor phase emissions in comparison with the other C18 fractions. The Low Aromatic fuel emissions had higher relative activities in C18 Fraction 5 (non-polar fraction). The C18 Fraction 1 (methanol) was analyzed for PAHs and the results are presented in the PAH analyses section. Most of the PAHs were present in this fraction. When comparing the mutagrams between the fuel types, each fuel type had distinct distributions of the percent total mutagenic activity. For the pre-1993 fuel tested in both TA98 and TA100 tester strains, Fraction 1 in the C18 fractionation and silica subfraction 3 from were the dominant peaks of mutagenic activity. Subfraction 3 is a polar fraction. For the low aromatic fuel, C18 Fraction 5 silica subfraction 2 were the most active fractions. Finally, for the reformulated fuel, C18 Fractions 1 and 5 were the most active, with Fraction 5 having more activity when metabolic enzymes were added (+S9). For the reformulated fuel, silica subfraction 1 was the most active (hexane fraction). These differences in mutagrams are indicative of different classes of compounds representing a range of polarities, or are indicative of different concentrations of compounds present in the various fractions.

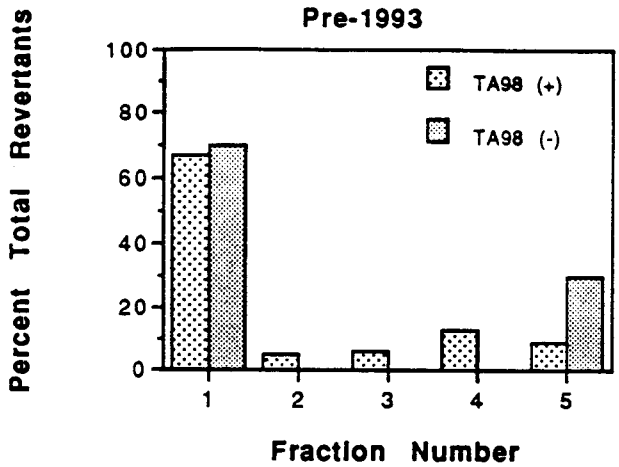
Mutagrams were also developed for the XAD samples and are presented in Figures 36 through 39. In Figure 35, the primary mutagenic activity was observed in Fraction 5 for the Pre-1993 and the Reformulated fuels. The mutagram is similar to the trip blank (blank XAD taken on the trip and returned, stored, extracted and tested in an identical manner as the samples). The low aromatic fuel SPE fractions were toxic. The silica SPE subfractions were tested using TA98 with metabolic enzymes added (Figure 36). The emission samples did not follow or align with the mutagram of the blank where most of the activity was in Silica subfraction 3. All the fuels had their own specific mutagram. In the more sensitive of the two tester strains used (TA100) , the C18 mutagram followed the TA98 mutagram including the observation that the low aromatic fuel was toxic when fractionated. The reformulated fuel fractions in C18 were also toxic to the tester strains. The mutagram for the silica subfractions are illustrated in Figure 38. No two fuel mutagrams were alike in the silica subfractions.

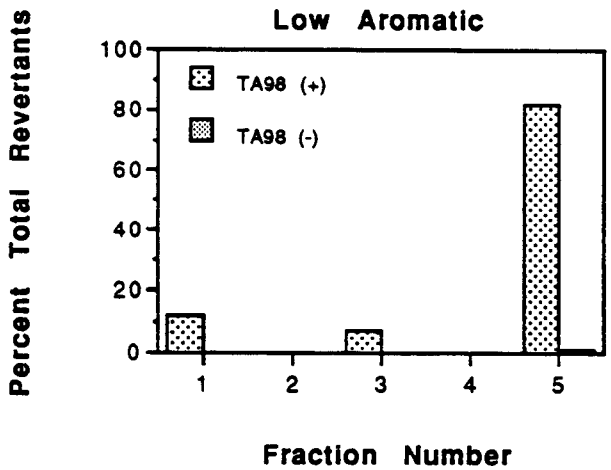
PRELIMINARY DRAFT

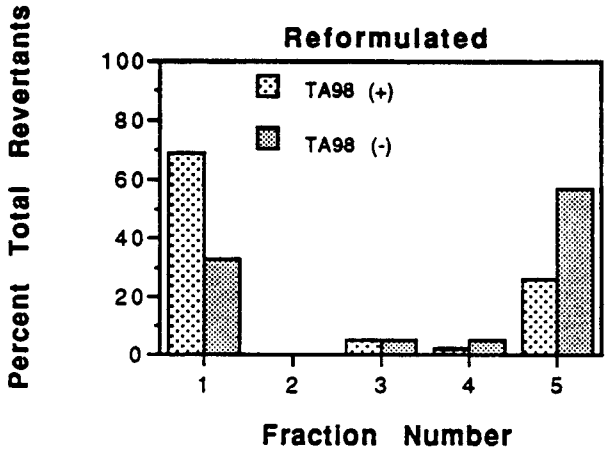
Figure 32. Mutagrams of Pre-1993, low aromatic, and reformulated fuel vapor-phase emissions collected on PUF and fractionated using C18 solid phase extraction (SPE). Fractions tested in tester strain TA98 with metabolic enzymes added.

PRELIMINARY DRAFT

C18 Fractionation TA98





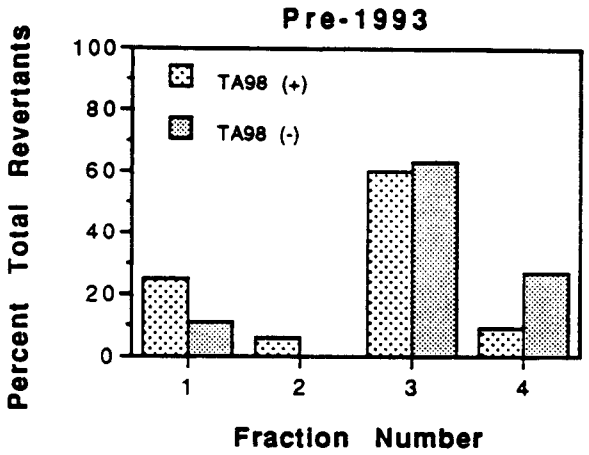


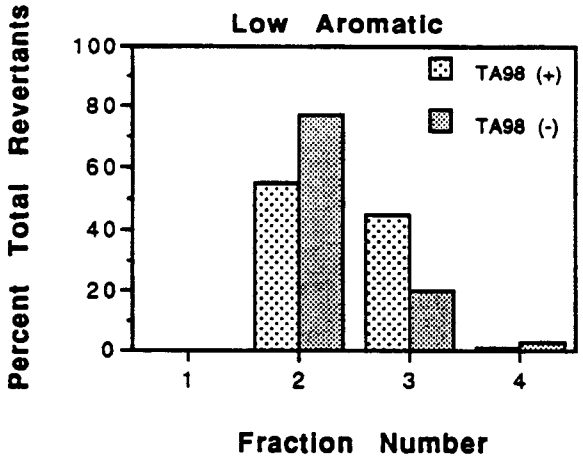
PRELIMINARY DRAFT

Figure 33. Mutagrams of Pre-1993, low aromatic, and reformulated fuel vapor-phase emissions collected on PUF and fractionated using silica solid phase extraction (SPE). Fractions tested in tester strain TA98 with metabolic enzymes added.

PRELIMINARY DRAFT

Silica Fractionation TA98





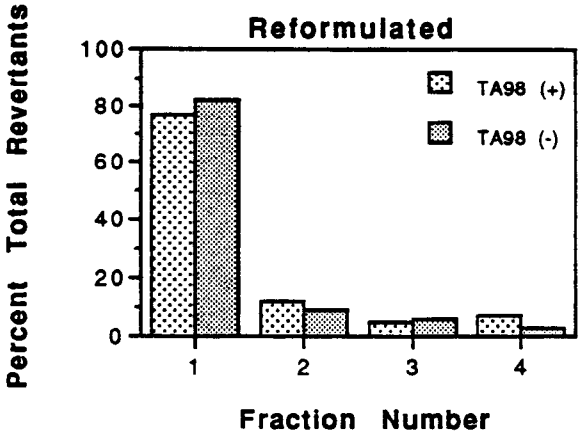
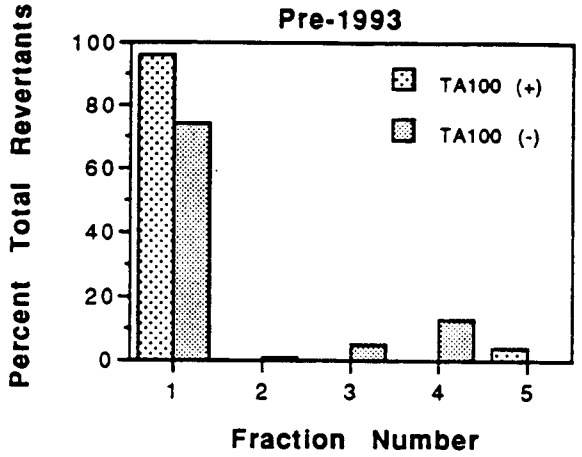
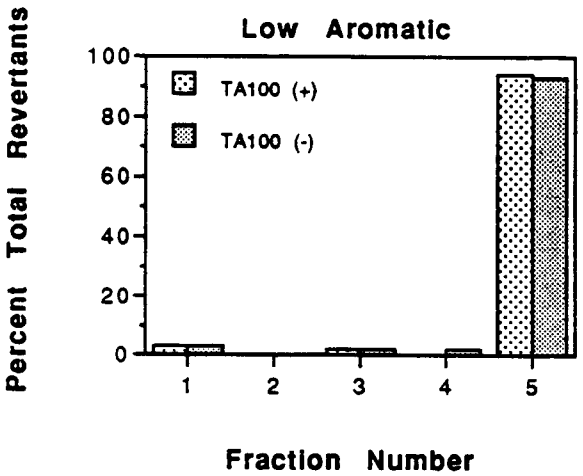


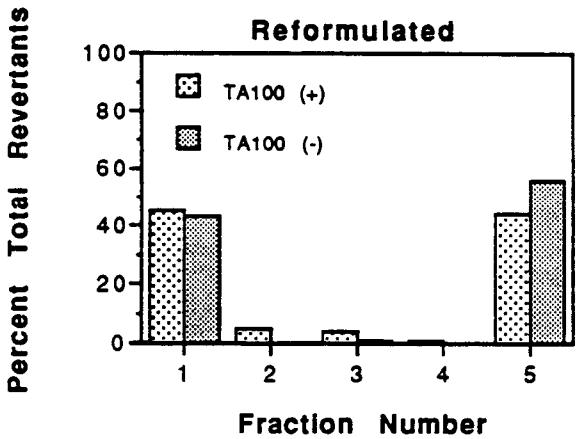
Figure 34. Mutagrams of Pre-1993, low aromatic, and reformulated fuel vapor-phase emissions collected on PUF and fractionated using C18 solid phase extraction (SPE). Fractions tested in tester strain TA100 with metabolic enzymes added.

PRELIMINARY DRAFT

C18 Fractionation TA100





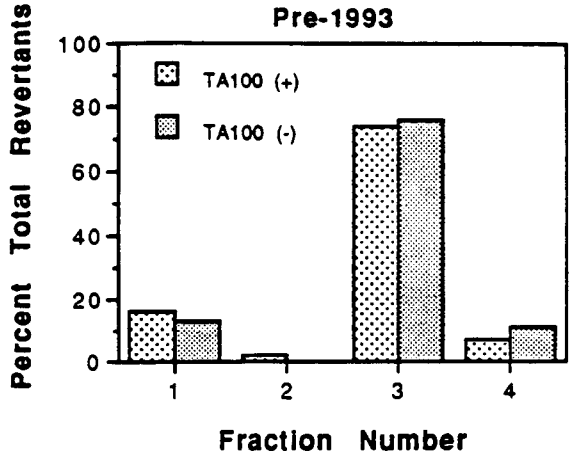


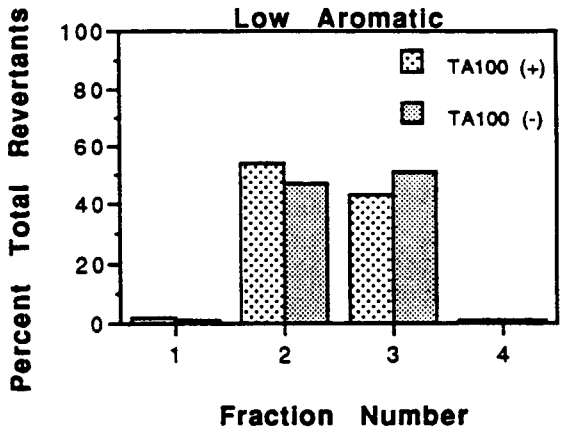
PRELIMINARY DRAFT

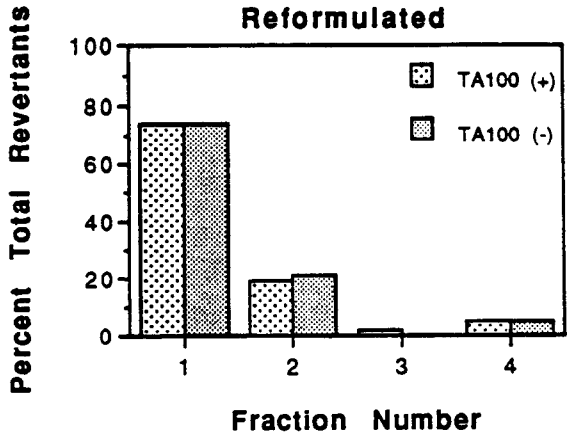
Figure 35. Mutagrams of Pre-1993, low aromatic, and reformulated fuel vapor-phase emissions collected on PUF and fractionated using silica solid phase extraction (SPE). Fractions tested in tester strain TA100 with metabolic enzymes added.

PRELIMINARY DRAFT

Silica Fractionation PUF TA100





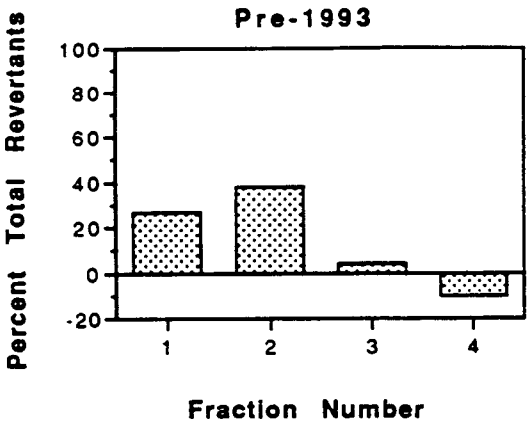


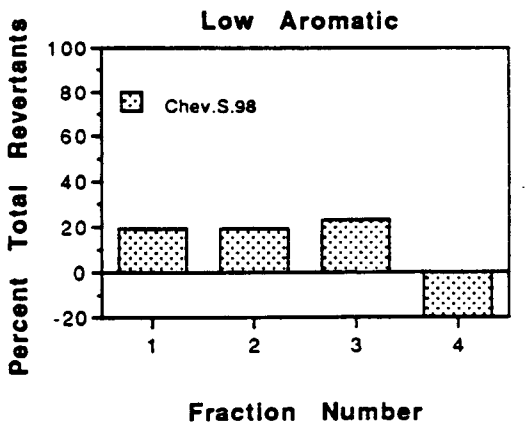
PRELIMINARY DRAFT

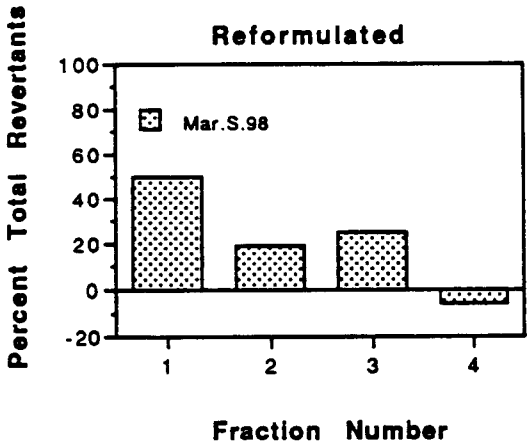
Figure 37. Mutagrams of Pre-1993, low aromatic, and reformulated fuel vapor-phase emissions collected on XAD and fractionated using silica solid phase extraction (SPE). Fractions tested in tester strain TA98 with metabolic enzymes added.

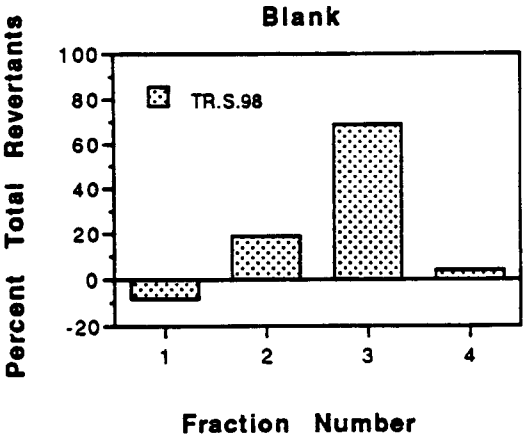
PRELIMINARY DRAFT

Silica Fractionation XAD TA98







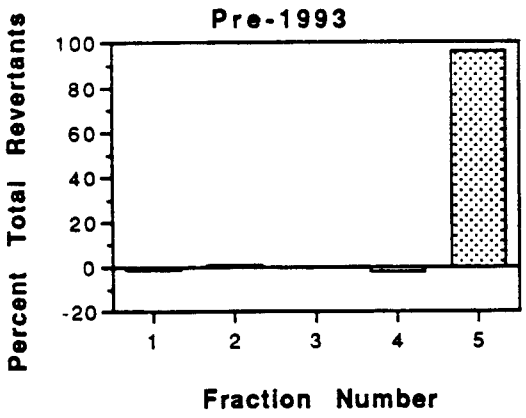


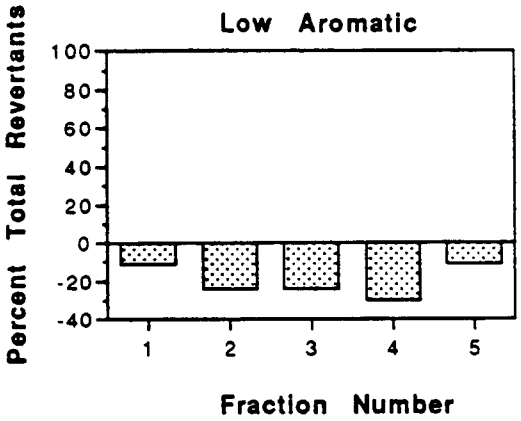
PRELIMINARY DRAFT

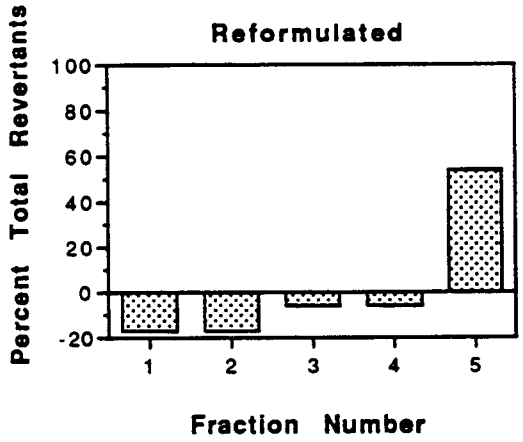
Figure 36. Mutagrams of Pre-1993, low aromatic, and reformulated fuel vapor-phase emissions collected on XAD and fractionated using C18 solid phase extraction (SPE). Fractions tested in tester strain TA98 with metabolic enzymes added.

PRELIMINARY DRAFT

C18 Fractionation XAD TA98







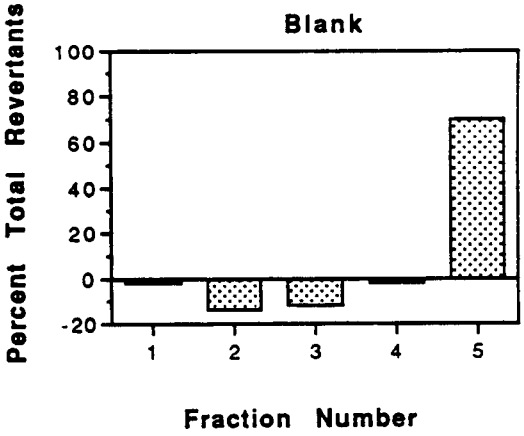
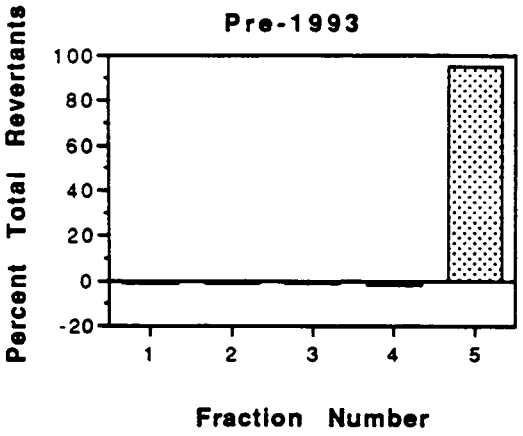


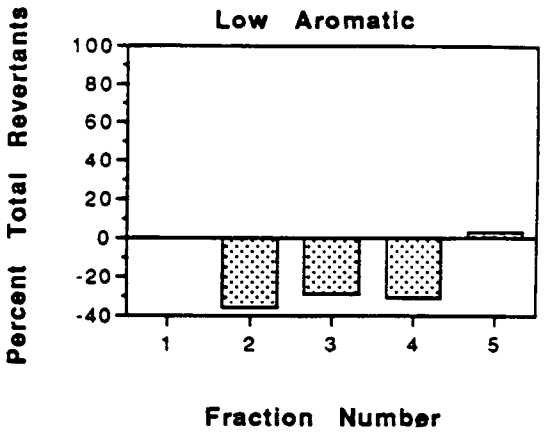
Figure 38. Mutagrams of Pre-1993, low aromatic, and reformulated fuel vapor-phase emissions collected on XAD and fractionated using C18 solid phase extraction (SPE). Fractions tested in tester strain TA100 with metabolic enzymes added.

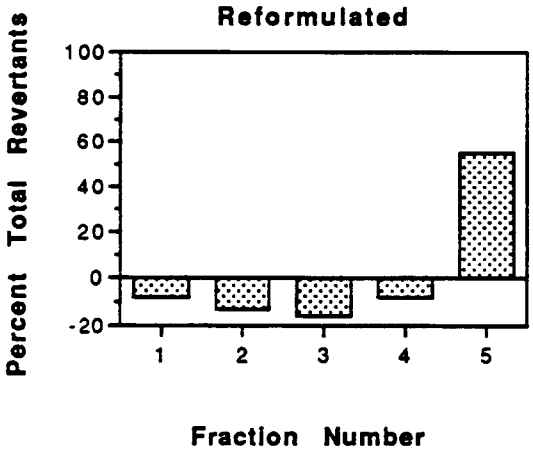
Figure 39. Mutagrams of Pre-1993, low aromatic, and reformulated fuel vapor-phase emissions collected on XAD and fractionated using silica solid phase extraction (SPE). Fractions tested in tester strain TA100 with metabolic enzymes added.

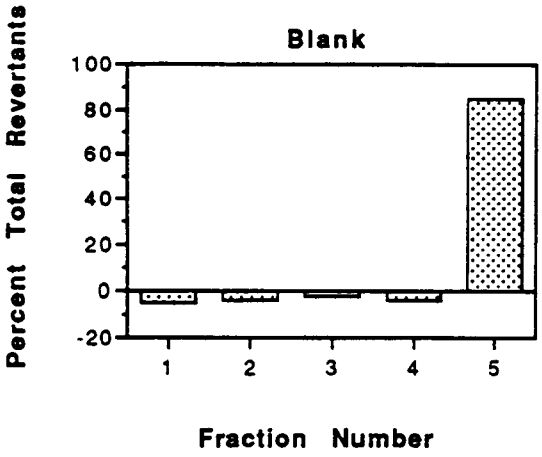
PRELIMINARY DRAFT

C18 Fractionation XAD TA100



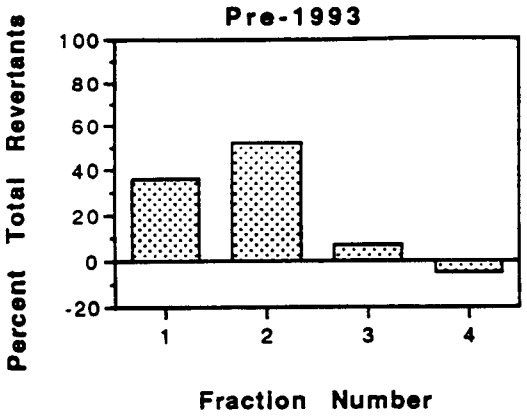


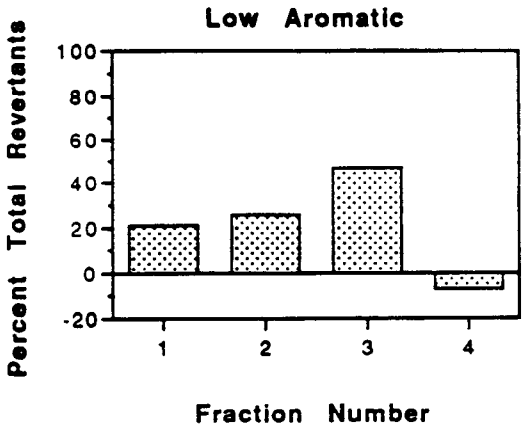


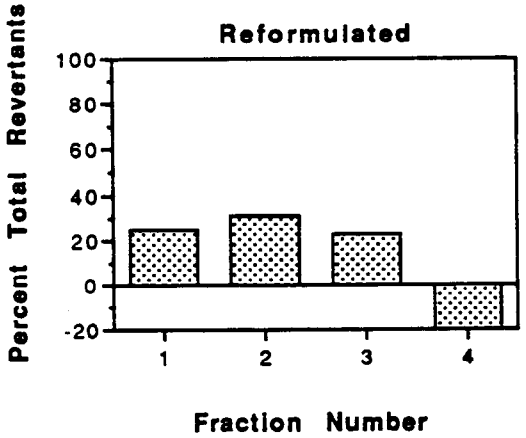


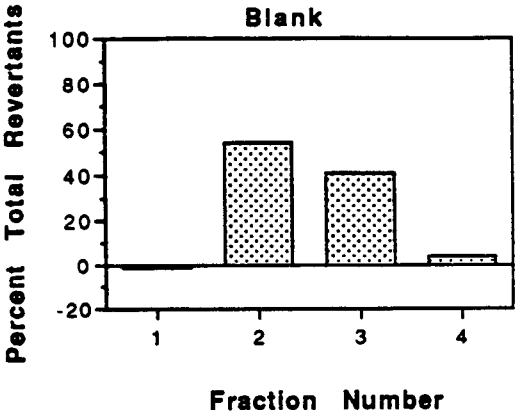
PRELIMINARY DRAFT

Silica Fractionation XAD TA100









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Discussion: The dose response curves for the particulate matter and vapor-phase samples allowed us to determine a potency value. This value in turn was used to calculate emissions for all fuels tested. For the particulate matter, the specific mutagenic activity (revertants per μg of particulate matter extracted) for the Pre-1993 fuel was higher both with and without S9 compared to the other fuels. The activity for the Reformulated blend fuel particulate matter was similar to the activity of the Low Aromatic fuel when tested with S9 or without S9. The difference in specific activities between fuels, with and without S9, support the hypothesis that different compounds may be present in the extracts, or that the there are differences in the concentrations of similar compounds. For example, nitro-PAHs are potent mutagens often detected without S9. Further analyses of compound classes can be analyzed using HPLC fractionation with subsequent bioassay analyses of the fractions. These mutagrams can be informative with respect to compound class identification.

HPLC fractionation using a normal phase (silica) column produces fractions that range from a typically non-polar fraction (Fraction 1) that progressively increases in polarity to Fraction 9 which contains the most polar compounds. HPLC Fraction 7 was the most mutagenic fraction for the particulate matter from all 3 fuels, both with and without S9. Each fuel did have distinctive mutagrams, however. For example, for the Pre-1993 fuel, HPLC Fractions 4 and 6 each had levels of mutagenic activity that were similar to each other and were the next highest peak relative to Fraction 7 with S9 added. For the reformulated blend fuel particulate matter, Fraction 4 had the next highest mutagenic activity peak and Fraction 6 was considerably lower than Fraction 4. For the low aromatic fuel, Fraction 3 had the next highest peak in the mutagram. Fractions 2 and 3 typically contain the PAHs.

Differences in the mutagrams are observed when comparing activity with and without metabolic enzymes added. For example, for all three fuels, Fraction 6 is relatively low compared to Fraction 7 when metabolic enzymes are added. Fraction 6 dramatically increases relative to Fraction 7 when no metabolic enzymes are added. This is indicative of what is referred to as "direct-acting" mutagenic compounds, or compounds that do not typically require the addition of enzymes for their detection. Arey and colleagues (1992) have reported that the nitro-PAHs are typically present in HPLC Fraction 4, and the di-nitro PAHs are in Fraction 5.

Historic work by Arey and colleagues (1994) have isolated from ambient and controlled chamber experiments, highly mutagenic nitro-phenanthrene-lactone compounds that are present in HPLC Fraction 6. The most mutagenic compounds present in HPLC Fraction 7 remain unknown, and are considerably more polar than classical PAHs or nitro-PAHs. One possible candidate class of

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compounds that may be present in this fraction are substituted PAHs (such as oxygenated PAH) that are more polar than the classical nitro-PAHs.

The levels of activity and the relative activities of emissions using different fuels was evaluated from other studies. Rasmussen et al. (1990) tested particulate matter collected from diesel exhaust using the Salmonella microsuspension assay. A number of fuels of varying aromaticity were tested. They reported that the levels of activity were generally related to the level of aromaticity.

We found in our sample that based on either potency and emission values, this relationship of aromaticity to mutagenicity was not necessarily related quantitatively. The percent aromatics for the Pre-1993, Low Aromatic, and Reformulated fuels were approximately 30, 4, and 23, respectively. The specific mutagenic activity and emission values for the Pre-1993 fuel were higher than the two other fuels. However, the specific mutagenic activity for the Low aromatic and Reformulated fuels were very similar both in the particle and vapor phases, and especially when no metabolic enzymes were added to the bioassay. The Low aromatic fuel itself also had the lowest total polyaromatics as determined by fuel analyses (0.7 %) compared to the Pre-1993 (approximately 6-7%) and the Reformulated fuel (approximately 4 %). The studies by Rassmussen et al were not originally designed to test for fuel differences using mutagenic activity.

With respect the vapor-phase compounds collected and tested in the bioassay, the testing of the complex mixture of the vapor-phase was challenging in many regards. First, the extraction, handling, and bioassay testing of the extracts or their fractions had to be carefully completed since the compounds are semi-volatile. Care was taken to minimize loss of semi-volatile compounds. Second, there appeared to be toxicity or concurrent masking of mutagenic activity in some of the extracts. For example, the supercritical extracts from the Pre-1993 PUF sample were toxic to TA98 at very low concentrations of the extract and SPE fractions of the XAD were toxic. Finally, collection of the sample is highly labor intensive starting from the preparation and pre-testing of the media (PUF and XAD), to collecting a high volume sample from the dynamometer, to extraction of the sample, to chemical and bioassay testing of the sample. Alternative approaches for this entire process could be investigated. Vapor-phase samples were previously tested for emissions collected from a medium heavy duty diesel truck (Kado et al, 1996). Tester strain TA100 was the most sensitive strain for these and current vapor-phase samples. Tester strain TA98 is the more sensitive strain when testing the diesel particulate matter. We found this to be the case (data not shown) when we tested the fuel extracts in both tester strains TA98 and TA100 and found that the relative increase in activity for TA98 is approximately 2 -fold when adding S9 and approximately 5-fold when no S9 is added. With respect to the mutagrams of the vapor-phase

compounds, a number of factors should be noted. For example, the mutagrams for the C18 fractions are different between the fuels. As indicated, these differences could be due to differences in the chemical composition of the vapor-phase mutagenic compounds, and varying relative concentration of these compounds. The mutagrams between strains for a given fuel type are very similar, but the relative mutagenic activities are higher in tester strain TA100.

The emission values from the vapor-phase are difficult to compare directly with the emissions of the particle phase due to differences in tester strain sensitivity to each phase. The tester strains appear to be sensitive to different compounds in the extracts, and therefore the vapor-phase activity detected is an indication that there are different mutagenic compounds or changes in compound concentrations. For the Pre-1993 fuel, for example, when comparing the most sensitive strain for particle or vapor-phase samples, the vapor-phase mutagen emissions are approximately 10 times lower (10^5 vs 10^6 Rev/brhp-hr) than the particle phase. However, it needs to be stated that 10^5 revertants / brhp-hr multiplied by the number of brhp-hr in a typical cycle (approximately 12 in the current study) translates into compounds emitted to equal approximately 10^6 revertants, or 10^7 revertants for the particulate matter for a 20 minute transient cycle.

The emission levels of both particle and vapor-phase associated mutagenic compounds are important to evaluate as an index of potential exposure to the complex mixture of compounds present. The mutagenic activity is also used in conjunction to bioassay to chemically characterize the most genotoxic compounds or groups of compounds present in the particle and vapor phase. These integrated approaches using chemical analyses and bioassay could prove to be valuable in evaluating human and ecological health risks.

Future studies for comparing different fuels and engines (and vehicles) would provide valuable information regarding the factors important in affecting mutagen emissions. The factors which modulate these emissions could also be evaluated.

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ATTACHMENT A

Table A1 - Emission Test Results on Cummins L10 Engine using Pre-1993 Fuel.

Table A2 - Emission Test Results with Cummins L10 Engine using Low Aromatic Fuel.

Table A3 - Emission Test Results with Cummins L10 Engine using Reformulated Diesel Blend.

Table A4 - Ion and Carbon Analysis Results of Particulate.

Table A5 - Elemental Analysis Results of Particulate.

Table A6 - Emission Rates for Speciated Hydrocarbons.

Table A1. Emission Test Results on Cummins L10 Engine using Pre-1993 Fuel.

Test Date	12/2/96	12/2/97	12/2/97	12/2/96
Test Number	337CS	337H1	337H2	337H3
Cycle Type	Cold	Hot 1	Hot 2	Hot 3
Emissions (GM/BHP-HR)				
NOx	4.89	4.53	4.61	NA
THC	0.53	0.52	0.48	NA
CO	2.47	2.43	2.34	NA
CO2	552.5	519.6	518.2	NA
Particulate	0.237	0.218	0.206	NA
BSFC (LB/BHP-HR)	0.394	0.371	0.364	NA
Work (BHP-HR)	22.282	22.379	22.417	NA

Test Date	12/3/96	12/3/96	12/3/96	12/3/96	12/3/96	12/3/96	12/3/96	12/3/96	12/3/96	12/3/96
Test Number	338CS	338H1	338H2	338H3	338H4	338H5	338H6	338H7	338H8	338H9
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7	Hot 8	Hot 9
Emissions(GM/BHP-HR)										
NOx	5.09	4.72	4.87	4.77	4.75	4.74	4.80	4.77	4.73	4.74
THC	0.56	0.55	0.52	0.53	0.54	0.54	0.50	0.51	0.54	0.53
CO	2.40	2.32	2.24	1.77	1.79	2.32	2.36	2.39	2.40	2.36
CO2	551.7	525.7	518.6	520.8	517.7	511.9	518.4	515.1	515.4	515.3
Particulate	0.257	0.231	0.218	0.212	0.212	0.208	0.206	0.201	0.202	0.200
BSFC (LB/BHP-HR)	0.387	0.369	0.364	0.365	0.363	0.360	0.364	0.362	0.362	0.362
Work (BHP-HR)	22.336	22.391	22.370	22.402	22.414	22.397	22.397	22.412	22.431	22.417

Test Date	12/4/96	12/4/96	12/4/96	12/4/96	12/4/96	12/4/96	12/4/96	12/4/96
Test Number	339CS	339H1	339H2	339H3	339H4	339H5	339H6	339H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions(GM/BHP-HR)								
NOx	4.93	4.50	4.63	4.70	4.62	4.74	4.69	4.66
THC	0.58	0.54	0.48	0.53	0.52	0.51	0.51	0.51
CO	2.35	2.30	2.28	2.27	2.12	2.31	2.33	2.43
CO2	552.7	526.8	523.6	522.1	518.0	520.8	527.3	522.0
Particulate	0.276	0.232	0.220	0.222	0.212	0.223	0.218	0.228
BSFC (LB/BHP-HR)	0.388	0.370	0.368	0.367	0.364	0.366	0.370	0.367
Work (BHP-HR)	22.283	22.375	22.391	22.361	22.399	22.399	22.417	22.417

Table A1-cont. Emission Test Results on Cummins L10 Engine using Pre-1993 Fuel.

Test Date	12/5/96	12/5/96	12/5/96	12/5/96	12/5/96
Test Number	340CS	340H1	340H2	340H3	340H4
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4
Emissions(GM/BHP-HR)					
NOx	4.80	4.50	4.59	4.62	4.63
THC	0.53	0.50	0.51	0.54	0.54
CO	2.41	2.21	2.31	2.36	2.38
CO2	549.7	520.7	520.7	521.9	521.5
Particulate	0.264	0.231	0.219	0.229	0.231
BSFC (LB/BHP-HR)	0.386	0.366	0.366	0.367	0.366
Work (BHP-HR)	22.311	22.427	22.393	22.354	22.361

Test Date	12/6/96	12/6/96	12/6/96	12/6/96
Test Number	341CS	341H1	341H2	341H3
Cycle Type	Cold	Hot 1	Hot 2	Hot 3
Emissions(GM/BHP-HR)				
NOx	4.94	4.60	4.72	4.77
THC	0.58	0.53	0.53	0.53
CO	2.53	2.47	2.43	1.82
CO2	553.2	521.3	519.3	520.8
Particulate	0.278	0.246	0.231	0.228
BSFC (LB/BHP-HR)	0.389	0.366	0.365	0.365
Work (BHP-HR)	22.306	22.408	22.363	22.341

Test Date	1/8/97	1/8/97	1/8/97	1/8/96	1/8/97	1/8/97	1/8/97	1/8/97
Test Number	8CS	8H1	8H2	8H3	8H4	8H5	8H6	8H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions(GM/BHP-HR)								
NOx	5.03	4.80	4.87	4.84	4.89	4.89	4.94	4.86
THC	2.39	0.54	0.55	0.54	0.54	0.53	0.53	0.52
CO	2.22	2.20	2.21	2.24	2.20	2.22	2.26	2.31
CO2	536.2	509.8	514.6	513.0	514.7	515.5	515.8	512.0
Particulate	0.260	0.220	0.227	0.221	0.213	0.215	0.215	0.209
BSFC (LB/BHP-HR)	0.376	0.356	0.361	0.360	0.361	0.362	0.362	0.360
Work (BHP-HR)	22.131	22.170	22.175	22.222	22.225	22.211	22.213	22.223

Table A1-cont. Emission Test Results on Cummins L10 Engine using Pre-1993 Fuel.

Test Date	1/9/97	1/9/97	1/9/97	1/9/97	1/9/97	1/9/97	1/9/97	1/9/97
Test Number	9CS	9H1	9H2	9H3	9H4	9H5	9H6	9H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions(GM/BHP-HR)								
NOx	5.18	4.83	4.84	4.84	4.81	4.85	4.88	4.84
THC	0.55	0.52	0.54	0.52	0.53	0.54	0.50	0.52
CO	2.25	2.21	2.22	2.29	2.28	1.78	1.79	2.30
CO2	534.9	509.7	520.2	517.3	513.4	515.3	513.7	515.1
Particulate	0.240	0.222	0.214	0.219	0.208	0.588	0.210	0.214
BSFC (LB/BHP-HR)	0.376	0.358	0.365	0.363	0.360	0.362	0.361	0.361
Work (BHP-HR)	22.128	22.226	22.234	22.181	22.275	22.220	22.193	22.233

Table A2. Emission Test Results with Cummins L10 Engine using Low Aromatic Fuel.

Test Date	12/9/96	12/9/96	12/9/96	12/9/96
Test Number	344H1	344H2	344H3	344H4
Cycle Type	Hot 1	Hot 2	Hot 3	Hot 4
Emissions(GM/BHP-HR)				
NOx	4.31	4.45	4.49	4.36
THC	0.43	0.49	0.48	0.48
CO	2.46	2.43	2.46	2.48
CO2	516.9	509.6	507.9	504.6
Particulate	0.213	0.182	0.187	0.187
BSFC (LB/BHP-HR)	0.367	0.362	0.361	0.359
Work (BHP-HR)	22.012	21.962	21.931	21.936

Test Date	12/10/96	12/10/96	12/10/96	12/10/96	12/10/96
Test Number	345CS	345H1	345H2	345H3	345H5
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4
Emissions(GM/BHP-HR)					
NOx	4.67	4.31	4.39	4.41	4.45
THC	0.40	0.50	0.50	0.48	0.50
CO	2.47	2.34	2.46	2.43	2.46
CO2	545.9	519.1	513.2	513.7	511.3
Particulate	0.195	0.180	0.178	0.178	0.177
BSFC (LB/BHP-HR)	0.368	0.369	0.365	0.365	0.363
Work (BHP-HR)	21.957	21.954	21.979	21.936	21.978

Test Date	12/11/96	12/11/96	12/11/96	12/11/96	12/11/96	12/11/96	12/11/96
Test Number	346CS	346H1	346H2	346H3	346H4	346H5	346H6
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6
Emissions(GM/BHP-HR)							
NOx	4.58	4.37	4.46	4.38	4.48	4.35	4.37
THC	0.42	0.48	0.50	0.47	0.50	0.47	0.49
CO	2.47	2.45	2.42	2.43	2.43	2.48	2.46
CO2	546.8	518.2	516.0	511.3	514.6	525.7	515.1
Particulate	0.195	0.180	0.175	0.179	0.176	0.186	0.181
BSFC (LB/BHP-HR)	0.368	0.368	0.367	0.363	0.366	0.374	0.366
Work (BHP-HR)	21.998	22.020	22.043	22.047	22.963	21.978	21.955

Table A2-cont. Emission Test Results with Cummins L10 Engine using Low Aromatic Fuel.

Test Date	12/12/96	12/12/96	12/12/96	12/12/96	12/12/96	12/12/96	12/12/96
Test Number	347C8	347H1	347H2	347H3	347H4	347H5	347H6
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6
Emissions(GM/BHP-HR)							
NOx	4.55	4.28	4.46	4.46	4.42	4.42	4.48
THC	0.42	0.47	0.49	0.48	0.49	0.48	0.48
CO	2.48	2.51	2.40	2.44	2.42	2.42	2.45
CO2	544.0	514.7	502.7	506.5	501.6	505.5	506.2
Particulate	0.190	0.185	0.177	0.175	0.175	0.177	0.177
BSFC (LB/BHP-HR)	0.386	0.366	0.357	0.360	0.357	0.359	0.360
Work (BHP-HR)	21.930	22.022	22.015	21.984	21.976	22.015	22.008

Table A3. Emission Test Results with Cummins L10 Engine using Reformulated Diesel Blend.

Test Date	12/16/96	12/16/96	12/16/96	12/16/96	12/16/96	12/16/96	12/16/96
Test Number	351CS	351H1	351H2	351H3	351H4	351H5	351H6
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6
Emissions(GM/BHP-HR)							
NOx	4.92	4.53	4.65	4.57	4.58	4.55	4.59
THC	0.46	0.46	0.49	0.49	0.50	0.51	0.49
CO	2.28	2.23	2.26	2.25	2.31	2.33	2.29
CO2	550.2	517.9	516.8	515.6	509.5	506.5	504.7
Particulate	0.245	0.177	0.168	0.180	0.172	0.179	0.167
BSFC (LB/BHP-HR)	0.386	0.364	0.363	0.362	0.358	0.356	0.355
Work (BHP-HR)	22.093	22.189	22.149	22.196	22.233	22.229	22.280

Test Date	12/17/96	12/17/96	12/17/96	12/17/96	12/17/96	12/17/96	12/17/96	12/17/96
Test Number	352CS	352H1	352H2	352H3	352H4	352H5	352H6	352H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions(GM/BHP-HR)								
NOx	4.81	4.42	4.36	4.51	4.55	4.51	4.54	4.59
THC	0.51	0.47	0.48	0.50	0.50	0.49	0.49	0.50
CO	2.41	2.35	2.32	2.33	2.37	2.41	2.41	2.43
CO2	551.2	516.9	511.3	513.5	512.9	510.1	507.8	510.2
Particulate	0.203	0.183	0.176	0.170	0.170	0.214	0.204	0.206
BSFC (LB/BHP-HR)	0.387	0.363	0.359	0.361	0.360	0.358	0.357	0.359
Work (BHP-HR)	22.077	22.150	22.148	22.179	22.163	22.215	22.177	22.203

Test Date	12/18/96	12/18/96	12/18/96	12/18/96	12/18/96	12/18/96	12/18/96	12/18/96
Test Number	353CS	353H1	353H2	353H3	353H4	353H5	353H6	353H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions(GM/BHP-HR)								
NOx	4.82	4.52	4.48	4.57	4.59	4.66	4.68	4.74
THC	0.46	0.50	0.53	0.55	0.54	0.54	0.51	0.50
CO	2.27	2.24	2.20	2.27	2.27	2.28	2.32	2.29
CO2	547.2	522.6	509.5	505.8	506.8	509.8	509.2	509.2
Particulate	0.205	0.205	0.186	0.190	0.172	0.174	0.176	0.181
BSFC (LB/BHP-HR)	0.384	0.367	0.358	0.355	0.356	0.358	0.358	0.358
Work (BHP-HR)	22.154	22.182	22.244	22.278	22.245	22.191	22.212	22.194

Table A3-cont. Emission Test Results with Cummins L10 Engine using Reformulated Diesel Blend.

Test Date	12/19/96	12/19/96	12/19/96	12/19/96	12/19/96	12/19/96	12/19/96	12/19/96
Test Number	354CS	354H1	354H2	354H3	354H4	354H5	354H6	354H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions(GM/BHP-HR)								
NOx	4.81	4.53	4.63	4.67	4.57	4.60	4.66	4.67
THC	0.45	0.48	0.48	0.50	0.53	0.51	0.49	0.49
CO	2.30	2.17	2.29	2.27	2.27	2.31	2.31	2.33
CO2	546.4	517.0	513.8	512.6	509.2	509.6	512.1	512.1
Particulate	0.198	0.196	0.194	0.183	0.185	0.185	0.174	0.163
BSFC (LB/BHP-HR)	0.383	0.363	0.361	0.36	0.358	0.358	0.36	0.36
Work (BHP-HR)	22.182	22.278	22.208	22.19	22.264	22.201	22.231	22.202

Test Date	12/20/96	12/20/96	12/20/96	12/20/96	12/20/96	12/20/96	12/20/96	12/20/96
Test Number	355CS	355H1	355H2	355H3	355H4	355H5	355H6	355H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions(GM/BHP-HR)								
NOx	4.88	4.63	4.59	4.54	4.59	4.62	4.62	4.58
THC	0.46	0.47	0.50	0.48	0.49	0.48	0.48	0.50
CO	2.25	2.30	2.27	2.24	2.34	2.29	2.32	2.33
CO2	550.9	519.1	515.6	509.9	510.2	511.0	511.2	504.0
Particulate	0.208	0.192	0.183	0.171	0.175	0.177	0.177	0.173
BSFC (LB/BHP-HR)	0.387	0.364	0.362	0.358	0.358	0.359	0.359	0.354
Work (BHP-HR)	22.132	22.230	22.243	22.165	22.110	22.111	22.098	22.131

Table A4. Results of Particulate Ion and Carbon Analysis

Pre - 1993

	Cold Start Cycle		Hot Start Cycle	
	Emission Rate *mg/Bhp-hr*	SDEV *mg/Bhp-hr*	Emission Rate *mg/Bhp-hr*	SDEV *mg/Bhp-hr*
Chloride	-	-	0.01	0.01
Nitrate	0.07	0.08	0.08	0.01
Sulfate	**1.10**	0.97	**1.11**	0.09
Ammonium	**0.59**	0.19	**0.58**	0.12
Organic Carbon	**89.00**	9.02	**66.51**	8.57
Elemental Carbon	**133.98**	4.24	**125.87**	7.96
Total Carbon	**222.99**	11.39	**192.39**	15.58
Sum of species	**224.68**	11.34	**194.14**	15.63

Low Aromatic

	Cold Start Cycle		Hot Start Cycle	
	Emission Rate *mg/Bhp-hr*	SDEV *mg/Bhp-hr*	Emission Rate *mg/Bhp-hr*	SDEV *mg/Bhp-hr*
Chloride	0.01	0.02	0.04	0.03
Nitrate	**0.37**	0.04	**0.39**	0.05
Sulfate	**0.39**	0.10	0.10	0.02
Ammonium	**0.37**	0.04	**0.30**	0.05
Organic Carbon	**56.28**	1.73	**51.29**	3.33
Elemental Carbon	**109.86**	7.98	**118.87**	6.54
Total Carbon	**166.15**	8.55	**170.16**	8.53
Sum of species	**167.28**	8.44	**170.99**	8.49

Reformulated Diesel

	Cold Start Cycle		Hot Start Cycle	
	Emission Rate *mg/Bhp-hr*	SDEV *mg/Bhp-hr*	Emission Rate *mg/Bhp-hr*	SDEV *mg/Bhp-hr*
Chloride	0.03	0.03	0.07	0.11
Nitrate	**0.19**	0.07	**0.17**	0.04
Sulfate	**1.05**	0.81	**0.43**	0.04
Ammonium	**0.43**	0.20	**0.34**	0.05
Organic Carbon	**58.27**	5.83	**51.24**	7.06
Elemental Carbon	**113.87**	18.75	**103.70**	14.82
Total Carbon	**172.15**	23.40	**154.94**	19.49
Sum of species	**173.84**	24.49	**155.94**	19.50

Bold values indicate rates > 2 (analytical uncertainty)

Table A5. Elemental Analysis of Particulate

	Pre - 1993				Low Aromatic				Reformulated Diesel				
	Cold Start		Hot Start		Cold Start		Hot Start		Cold Start		Hot Start		
	Emission Rate ug/Bhp-hr	SDEV ug/Bhp-hr	Emission Rate ug/Bhp-hr	SDEV ug/Bhp-hr	Emission Rate ug/Bhp-hr	SDEV ug/Bhp-hr	Emission Rate ug/Bhp-hr	SDEV ug/Bhp-hr	Emission Rate ug/Bhp-hr	SDEV ug/Bhp-hr	Emission Rate ug/Bhp-hr	SDEV ug/Bhp-hr	
Na	2.45	4.24	19.83	36.07	-	-	-	-	-	-	10.55	11.80	Na
Mg	80.73	43.84	65.89	33.56	79.80	46.63	38.95	11.80	77.01	46.04	50.58	41.45	Mg
Al	3.00	3.19	20.44	18.43	9.42	16.32	2.63	4.16	0.17	0.29	4.13	3.86	Al
Si	619.16	108.92	749.36	91.55	674.07	61.06	638.53	81.27	627.86	165.36	611.61	86.08	Si
P	78.77	16.65	44.32	10.79	69.12	17.69	69.62	12.60	109.81	56.23	71.61	18.35	P
S	1,725.44	186.94	1,349.44	60.45	629.94	68.16	263.78	34.04	924.93	327.38	569.87	32.66	S
Cl	21.87	0.94	26.35	25.01	47.92	11.56	38.94	4.27	28.32	12.60	32.89	10.06	Cl
K	15.17	13.60	13.92	12.32	1.31	2.27	2.16	3.57	7.08	6.36	3.41	3.62	K
Ca	83.96	45.85	79.32	45.69	63.61	13.17	30.41	7.63	94.96	66.33	45.46	11.30	Ca
Ti	1.26	2.19	1.72	3.27	-	-	-	-	-	-	-	-	Ti
V	-	-	0.13	0.32	-	-	-	-	-	-	-	-	V
Cr	0.81	1.38	0.72	1.05	-	-	0.06	0.15	-	-	0.03	0.06	Cr
Mn	1.04	1.43	0.36	0.88	1.39	1.54	0.02	0.05	1.37	2.37	-	-	Mn
Fe	461.36	336.13	212.66	134.66	441.41	41.07	67.22	24.35	330.50	310.58	89.23	25.90	Fe
Co	-	-	0.06	0.12	-	-	-	-	-	-	0.18	0.30	Co
Ni	2.23	3.12	1.34	2.32	-	-	-	-	2.96	2.63	1.11	0.89	Ni
Cu	11.64	6.20	8.46	12.69	6.22	1.43	0.33	0.54	8.57	5.47	4.54	4.39	Cu
Zn	156.07	32.44	96.87	18.77	174.19	41.68	106.65	13.41	267.49	136.00	152.52	19.12	Zn
Ga	-	-	-	-	-	-	-	-	-	-	-	-	Ga
As	-	-	0.06	0.21	-	-	-	-	-	-	0.06	0.19	As
Se	-	-	-	-	-	-	-	-	-	-	-	-	Se
Br	0.30	0.37	0.43	0.50	0.42	0.50	0.35	0.29	0.70	0.58	0.37	0.44	Br
Rb	-	-	-	-	-	-	0.06	0.13	0.06	0.13	0.01	0.02	Rb
Sr	0.61	1.06	0.56	0.74	0.23	0.40	0.02	0.04	0.49	0.43	0.06	0.11	Sr
Y	-	-	-	-	-	-	-	-	-	-	-	-	Y
Zr	-	-	0.73	1.79	-	-	0.00	0.01	0.42	0.73	-	-	Zr
Mo	-	-	-	-	-	-	-	-	-	-	-	-	Mo
Pd	-	-	0.34	0.62	-	-	0.66	1.62	-	-	-	-	Pd
Ag	1.31	2.26	6.24	6.06	0.96	1.35	8.55	14.16	2.76	2.39	3.41	5.11	Ag
Cd	1.28	2.22	2.42	2.52	2.89	2.55	2.76	3.86	1.66	2.77	1.86	2.65	Cd
In	-	-	1.09	2.16	2.45	4.24	2.61	2.65	3.60	6.23	1.25	1.40	In
SN	-	-	1.01	1.26	5.04	8.73	6.66	9.03	6.33	4.73	2.98	4.20	SN
Sb	0.90	1.55	-	-	-	-	3.72	3.29	0.16	0.28	4.64	6.93	Sb
Ba	-	-	4.59	11.24	25.23	33.91	9.63	23.59	2.85	4.94	18.51	22.23	Ba
La	2.62	4.53	12.22	17.66	33.67	26.53	27.28	47.85	9.30	16.10	18.38	22.72	La
Au	-	-	-	-	-	-	-	-	-	-	-	-	Au
Hg	-	-	-	-	-	-	-	-	-	-	-	-	Hg
Tl	-	-	-	-	-	-	-	-	-	-	-	-	Tl
Pb	-	-	0.31	0.77	-	-	-	-	-	-	0.01	0.02	Pb
Ur	-	-	-	-	-	-	0.10	0.18	0.17	0.29	0.00	0.01	Ur
Sum	3,261.86	750.87	2,719.02	332.05	2,189.19	186.65	1,309.03	136.33	2,609.81	1,150.13	1,599.30	144.91	Sum

Bold values indicate measured rates > 2 (analytical uncertainty)

Table A6. Emission Rates for Speciated Hydrocarbons.

	Pre - 1993				Low Aromatic				Reformulated Diesel			
	Cold Start Cycle Average *mg/bhp-hr*	Cold Start Cycle SDEV *mg/bhp-hr*	Hot Start Cycle Average *mg/bhp-hr*	Hot Start Cycle SDEV *mg/bhp-hr*	Cold Start Cycle Average *mg/bhp-hr*	Cold Start Cycle SDEV *mg/bhp-hr*	Hot Start Cycle Average *mg/bhp-hr*	Hot Start Cycle SDEV *mg/bhp-hr*	Cold Start Cycle Average *mg/bhp-hr*	Cold Start Cycle SDEV *mg/bhp-hr*	Hot Start Cycle Average *mg/bhp-hr*	Hot Start Cycle SDEV *mg/bhp-hr*
Methane	18.23	7.66	14.66	2.47	21.04	5.49	18.17	6.15	22.64	0.36	13.00	5.67
Ethane	0.76	0.26	0.75	0.17	0.70	0.02	0.81	0.08	0.99	0.21	0.74	0.12
Propane	0.14	0.25	0.12	0.18	0.14	0.12	0.07	0.08	0.25	0.03	0.10	0.12
Butane	0.03	0.05	0.03	0.06	0.05	0.09	0.01	0.02	0.00	0.00	0.06	0.10
Pentane	0.00	0.00	0.00	0.01	0.08	0.14	0.04	0.07	0.00	0.00	0.01	0.01
Hexane	3.69	0.33	3.29	0.55	0.60	0.27	0.85	0.12	0.00	0.00	0.10	0.25
Heptane	0.38	0.65	0.42	0.79	1.00	0.41	0.79	0.37	0.00	0.00	0.14	0.35
Octane	1.05	0.11	1.10	0.08	1.35	0.14	1.57	0.21	0.78	0.09	0.76	0.33
Nonane	0.82	0.03	0.78	0.05	0.72	0.09	0.68	0.07	0.62	0.14	0.56	0.39
Decane	1.04	0.12	1.07	0.17	0.83	0.06	0.92	0.09	0.92	0.03	1.17	0.62
Undecane	2.14	0.36	2.73	0.33	1.47	0.04	1.48	0.21	1.56	0.13	1.87	0.31
Dodecane	1.54	0.28	3.92	1.38	2.18	0.60	2.05	0.30	1.14	1.01	1.99	0.81
2-Methylpropane	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.28	0.42	0.41	0.54	0.61
2,2-Dimethylpropane	0.54	0.02	0.42	0.14	0.41	0.08	0.30	0.17	0.55	0.18	0.43	0.23
2-Methylbutane	0.03	0.05	0.00	0.00	0.03	0.06	0.03	0.06	0.00	0.00	0.03	0.04
2,2-Dimethylbutane	1.09	0.16	1.13	0.37	0.56	0.17	0.68	0.39	0.69	0.13	0.65	0.56
2,3-Dimethylbutane	0.00	0.00	0.00	0.00	0.68	0.15	0.19	0.30	0.00	0.00	0.00	0.00
2-Methylpentane	2.62	0.90	2.01	1.04	3.72	2.00	4.01	2.04	1.25	2.16	2.58	2.05
3-Methylpentane	1.00	0.08	1.27	0.38	0.69	0.36	0.38	0.23	0.91	0.28	0.87	0.39
2,2,3-Trimethylbutane	0.17	0.29	0.00	0.00	0.23	0.39	0.09	0.22	0.00	0.00	0.00	0.00
2,2-Dimethylpentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3-Dimethylpentane	0.83	0.36	0.91	0.15	1.06	0.49	1.16	0.44	0.95	0.12	0.88	0.46
2,4-Dimethylpentane	0.00	0.00	0.00	0.00	0.15	0.25	0.17	0.27	0.00	0.00	0.00	0.00
3,3-Dimethylpentane	0.33	0.29	0.27	0.30	0.49	0.04	0.61	0.11	0.40	0.36	0.43	0.22
2-Methylhexane	0.14	0.24	0.17	0.26	0.76	0.70	0.49	0.56	0.30	0.26	0.36	0.29
3-Methylhexane	1.23	0.31	1.05	0.23	1.42	0.21	1.35	0.23	1.25	0.05	1.05	0.15
2,2,4-Trimethylpentane (I-Octane)	0.00	0.00	0.13	0.33	0.29	0.51	0.11	0.24	0.15	0.26	0.00	0.00
2,3,3-Trimethylpentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3,4-Trimethylpentane	0.00	0.00	0.23	0.25	0.21	0.36	0.00	0.00	0.36	0.62	0.15	0.36
3-Ethylpentane	0.00	0.00	0.10	0.25	0.72	0.07	0.68	0.37	0.00	0.00	0.00	0.00
2,2-Dimethylhexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.66	0.27	0.43
2,3-Dimethylhexane	0.22	0.38	0.00	0.00	0.00	0.00	0.45	0.38	0.18	0.31	0.24	0.40
2,4-Dimethylhexane	0.17	0.30	0.00	0.00	0.00	0.00	0.19	0.30	0.00	0.00	0.00	0.00
2,5-Dimethylhexane	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.24	0.00	0.00	0.00	0.00

Table A6. Emission Rates for Speciated Hydrocarbons.

	Pre - 1993				Low Aromatic				Reformulated Diesel			
	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
3,3-Dimethylhexane	0.00	0.00	0.08	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Methylheptane	0.00	0.00	0.10	0.24	0.47	0.43	0.37	0.30	0.00	0.00	0.00	0.00
3-Methylheptane	0.00	0.00	0.00	0.00	0.36	0.33	0.27	0.30	0.00	0.00	0.00	0.00
4-Methylheptane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3-Dimethylheptane	0.00	0.00	0.00	0.00	0.68	0.10	0.70	0.10	0.30	0.53	0.16	0.38
2,4-Dimethylheptane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3,5-Dimethylheptane	2.03	0.45	2.51	0.66	2.25	1.45	0.94	0.91	1.08	1.87	0.49	0.78
2,2,5-Trimethylhexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3,5-Trimethylhexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Methyloctane	0.00	0.00	0.00	0.00	0.64	0.11	0.67	0.11	0.00	0.00	0.00	0.00
3-Methyloctane	1.21	0.10	1.34	0.28	0.87	0.09	1.13	0.16	1.59	0.62	1.59	0.29
2,2-Dimethyloctane	0.00	0.00	0.33	0.38	0.45	0.39	0.24	0.39	0.00	0.00	0.19	0.46
2,4-Dimethyloctane	1.96	0.36	1.94	0.41	1.24	0.09	1.30	0.17	2.21	0.18	2.29	0.41
Cyclopentane	0.72	0.12	0.66	0.18	1.16	0.10	1.04	0.19	0.57	0.08	0.48	0.28
Methylcyclopentane	0.22	0.38	0.10	0.25	0.75	0.44	0.37	0.20	0.23	0.40	0.19	0.30
Cyclohexane	1.05	0.23	1.00	0.14	1.38	0.45	1.79	0.23	0.93	0.23	1.20	0.18
t-1,2-Dimethylcyclopentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
c-1,3-Dimethylcyclopentane	0.00	0.00	0.00	0.00	0.55	0.14	0.47	0.25	0.00	0.00	0.00	0.00
Methylcyclohexane	0.87	0.40	0.98	0.32	1.82	0.05	2.35	0.31	0.42	0.38	0.49	0.39
1c,2t,3-Trimethylcyclopentane	1.35	0.08	0.90	0.29	0.18	0.30	0.09	0.23	1.05	0.43	1.16	0.34
c-1,2-Dimethylcyclohexane	0.00	0.00	0.00	0.00	0.14	0.25	0.31	0.48	0.00	0.00	0.00	0.00
c-1,3-Dimethylcyclohexane	0.00	0.00	0.00	0.00	1.45	0.55	1.49	0.42	0.00	0.00	0.00	0.00
t-1,3-Dimethylcyclohexane	0.00	0.00	0.00	0.00	0.83	0.08	1.30	0.30	0.00	0.00	0.00	0.00
t-1,4-Dimethylcyclohexane	0.00	0.00	0.00	0.00	0.15	0.27	0.17	0.26	0.00	0.00	0.00	0.00
Ethylcyclohexane	0.00	0.00	0.07	0.18	0.54	0.51	4.42	4.94	12.98	11.28	9.34	7.58
Ethene	28.54	0.70	25.93	1.13	25.58	0.90	28.09	0.99	27.39	0.47	26.52	0.94
Propene	11.01	0.28	10.20	0.37	9.41	1.43	9.90	0.30	9.55	0.40	9.68	0.16
1-Butene	2.85	0.11	2.55	0.17	2.40	0.13	2.64	0.07	2.85	0.09	2.77	0.13
c-2-Butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.53
t-2-Butene	0.64	0.03	0.60	0.08	0.55	0.09	0.61	0.07	0.41	0.36	0.49	0.24
2-Methylpropene	1.92	0.18	1.98	0.30	1.54	0.13	1.69	0.33	1.95	0.20	1.94	0.30
1-Pentene	1.25	0.27	1.27	0.37	1.13	0.10	1.17	0.21	1.04	0.07	1.29	0.40
c-2-Pentene	0.64	0.78	0.37	0.30	0.37	0.65	0.49	0.78	0.00	0.00	0.08	0.20

Table A6. Emission Rates for Speciated Hydrocarbons.

	Pre - 1993				Low Aromatic				Reformulated Diesel			
	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
t-2-Pentene	0.21	0.36	0.32	0.26	0.00	0.00	0.16	0.25	0.31	0.27	0.11	0.27
2-Methyl-1-Butene	0.97	0.21	0.87	0.32	0.97	0.10	0.81	0.13	0.75	0.07	0.79	0.10
3-Methyl-1-Butene	0.80	0.07	0.76	0.07	0.78	0.36	0.35	0.28	0.54	0.10	0.33	0.26
2-Methyl-2-Butene	0.26	0.44	0.21	0.32	0.62	0.14	0.34	0.22	0.14	0.24	0.00	0.00
1-Hexene	1.24	0.22	1.26	0.16	1.26	0.42	1.12	0.26	1.50	0.28	1.16	0.15
c-2-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
t-2-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
c-3-Hexene	0.00	0.00	0.07	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
t-3-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Methyl-1-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-Methyl-1-Pentene	1.13	0.16	0.83	0.19	0.74	0.11	0.85	0.19	0.79	0.13	0.66	0.51
4-Methyl-1-Pentene	1.32	0.11	1.25	0.25	1.19	0.15	1.27	0.20	1.10	0.14	1.12	0.20
2-Methyl-2-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-Methyl-c-2-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.23	0.22	0.39	0.18	0.44
3-Methyl-t-2-Pentene	0.16	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Methyl-c-2-Pentene	0.00	0.00	0.94	1.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Methyl-t-2-Pentene	1.89	1.62	1.25	0.47	2.45	2.09	1.97	2.57	2.40	1.73	1.26	1.96
3,3-Dimethyl-1-Butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Heptene	1.06	0.15	0.90	0.47	1.30	0.26	1.45	0.28	1.13	0.18	1.09	0.27
c-2-Heptene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
t-2-Heptene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
t-3-Heptene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3-Dimethyl-2-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3,4-Dimethyl-1-Pentene	0.16	0.27	0.00	0.00	0.00	0.00	0.09	0.23	0.00	0.00	0.00	0.00
3-Methyl-1-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Methyl-2-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-Methyl-t-3-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Octene	0.71	0.09	0.71	0.22	0.86	0.09	0.92	0.09	0.48	0.42	0.74	0.09
c-2-Octene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
t-2-Octene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
t-4-Octene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,4,4-Trimethyl-1-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,4,4-Trimethyl-2-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-Ethyl-c-2-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Nonene	0.75	0.16	0.55	0.07	1.12	0.24	1.27	0.13	0.77	0.04	0.76	0.20
Propadiene	0.19	0.11	0.03	0.06	0.00	0.00	0.00	0.01	0.03	0.06	0.04	0.04
1,3-Butadiene	2.08	0.52	1.75	0.11	2.19	0.53	2.60	0.13	1.72	0.04	1.87	0.15

Table A6. Emission Rates for Speciated Hydrocarbons.

	Pre - 1993				Low Aromatic				Reformulated Diesel			
	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
2-Methyl-1,3-Butadiene	0.74	0.17	0.86	0.23	0.68	0.59	1.09	0.25	0.69	0.22	0.81	0.41
Cyclopentadiene	0.00	0.00	0.05	0.12	0.62	0.09	0.51	0.32	0.00	0.00	0.00	0.00
Cyclopentene	0.35	0.30	0.50	0.47	0.38	0.33	0.22	0.25	0.00	0.00	0.00	0.00
1-Methylcyclopentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-Methylcyclopentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cyclohexene	0.00	0.00	0.09	0.23	0.36	0.33	0.24	0.39	0.00	0.00	0.00	0.00
Ethyne	7.93	1.01	6.67	0.55	6.81	0.46	6.17	0.56	6.74	0.24	5.48	0.55
Propyne	0.00	0.00	0.06	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Butyne	0.00	0.00	0.32	0.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Butyne	1.56	0.21	1.65	1.24	1.65	0.72	1.31	1.20	0.47	0.81	0.19	0.47
Benzene	6.49	0.04	5.80	0.30	7.29	0.38	8.15	1.17	6.78	0.19	5.65	0.80
Toluene	2.17	0.10	1.89	0.27	1.96	0.23	2.31	0.33	1.86	0.55	1.86	0.25
Ethylbenzene	0.74	0.06	1.30	0.66	0.54	0.11	0.69	0.20	1.03	0.65	1.20	0.72
o-Xylene	0.85	0.09	0.77	0.09	0.58	0.05	0.62	0.11	0.99	0.11	0.86	0.24
m&p-Xylene	1.90	0.23	2.12	0.55	1.24	0.20	1.24	0.34	1.84	0.39	2.19	0.36
n-Propylbenzene	0.77	0.19	0.25	0.28	0.18	0.30	0.24	0.26	0.16	0.28	0.57	0.34
i-Propylbenzene	0.25	0.43	0.00	0.00	0.96	0.07	0.91	0.10	0.00	0.00	0.00	0.00
1-Methyl-2-ethylbenzene	0.68	0.10	0.79	0.29	0.15	0.26	0.26	0.29	0.57	0.98	0.78	1.00
1-Methyl-3-ethylbenzene	1.22	0.05	1.23	0.12	0.37	0.64	0.57	0.48	1.62	0.33	1.47	0.19
1-Methyl-4-ethylbenzene	0.81	0.09	0.75	0.09	0.00	0.00	0.09	0.22	0.92	0.21	0.88	0.16
1,2-Dimethyl-3-ethylbenzene	0.45	0.48	0.20	0.32	0.14	0.24	0.11	0.27	0.00	0.00	0.00	0.00
1,2-Dimethyl-4-ethylbenzene	0.57	0.51	0.66	0.37	0.00	0.00	0.00	0.00	0.81	0.16	0.74	0.10
1,3-Dimethyl-2-ethylbenzene	0.54	0.01	0.51	0.19	0.28	0.25	0.46	0.26	0.36	0.62	0.57	0.43
1,3-Dimethyl-4-ethylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,4-Dimethyl-2-ethylbenzene	0.51	0.12	0.51	0.11	0.62	0.12	0.62	0.10	0.56	0.15	0.61	0.12
1,2,3-Trimethylbenzene	1.37	0.55	1.25	0.54	0.00	0.00	0.00	0.00	0.60	0.14	1.06	0.29
1,2,4-Trimethylbenzene	1.71	0.06	1.76	0.14	1.15	0.29	1.13	0.14	1.90	0.26	2.04	0.18
1,3,5-Trimethylbenzene	0.93	0.13	0.96	0.36	0.19	0.33	0.29	0.32	0.90	0.36	0.96	0.23
Indan	0.16	0.28	0.28	0.46	0.00	0.00	0.00	0.00	0.61	0.12	0.56	0.16
i-Butylbenzene	0.00	0.00	0.10	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
s-Butylbenzene	0.58	0.05	0.73	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Methyl-Butylbenzene	0.00	0.00	3.85	5.96	1.84	3.18	2.44	3.78	0.00	0.00	0.00	0.00
tert-1-Butyl-2-Methyl-Benzene	0.91	0.43	0.52	0.49	1.03	0.91	1.01	0.81	0.74	0.32	0.45	0.24

Table A6. Emission Rates for Speciated Hydrocarbons.

	Pre - 1993				Low Aromatic				Reformulated Diesel			
	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
tert-1-Butyl-3,5-Dimethyl-Benzene	1.03	0.19	0.71	0.72	0.19	0.34	0.07	0.17	0.58	0.05	0.58	0 07
1,2-Diethylbenzene	0.00	0.00	0.00	0.00	0.29	0.50	0.16	0.23	0.22	0.38	0.00	0 00
1,3-Diethylbenzene	1.12	0.47	0.79	0.47	0.54	0.08	0.63	0.22	1.03	0.28	0.84	0 22
1,4-Diethylbenzene	0.13	0.23	0.33	0.46	0.00	0.00	0.07	0.17	0.09	0.16	0.00	0 00
1-Methyl-2-n-Propylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.32	0.37	0.64	0 36
1-Methyl-3-n-Propylbenzene	0.57	0.07	0.58	0.61	0.00	0.00	0.00	0.00	1.72	0.35	1.50	0 32
1-Methyl-4-n-Propylbenzene	1.00	0.33	0.81	1.14	0.00	0.00	0.13	0.33	2.34	0.26	2.37	0 39
1-Methyl-2-i-Propylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0 00
1-Methyl-3-i-Propylbenzene	0.76	0.19	0.77	0.39	0.00	0.00	0.23	0.36	0.00	0.00	0.14	0 34
1-Methyl-4-i-Propylbenzene	0.75	0.36	0.99	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0 00
1,2,3,4-Tetramethylbenzene	1.11	0.22	1.06	1.15	0.93	1.03	0.83	0.79	1.21	0.07	1.25	0 12
1,2,3,5-Tetramethylbenzene	0.67	0.05	0.64	0.21	0.44	0.76	0.47	0.74	1.07	0.22	1.24	0 13
1,2,4,5-Tetramethylbenzene	11.17	1.35	7.50	5.96	4.85	4.21	5.15	4.07	12.22	4.14	9.98	2 13
n-Pent-Benzene	0.00	0.00	0.68	0.63	0.30	0.52	0.33	0.39	2.17	0.21	2.27	0 23
Styrene	0.97	0.34	1.32	0.31	2.10	1.60	1.49	0.21	1.36	0.19	1.46	0 31
Naphthalene	1.33	0.09	1.75	0.50	1.55	0.54	1.77	0.25	1.16	0.07	1.29	0 25
Methyl-t-Butyl-Ether	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0 00
Ethyl-t-Butyl-Ether	0.00	0.00	3.26	1.27	0.00	0.00	2.72	0.35	0.00	0.00	0.37	0 90
Unknown (C1-C4)	0.42	0.42	0.27	0.34	0.28	0.11	0.31	0.10	0.40	0.13	0.58	0 35
Unknown (C4-C12)	31.42	3.62	37.72	7.17	23.72	0.77	24.35	5.70	38.43	4.21	41.05	8 86
Total	194.04		196.97		176.09		185.21		207.61		194.11	

PRELIMINARY DRAFT

ATTACHMENT B

QUALITY CONTROL / QUALITY ASSURANCE REPORT

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PRELIMINARY DRAFT

QUALITY CONTROL / QUALITY ASSURANCE REPORT

This chapter discusses QA/QC activities and results as described in the QA Project Plan (Norbeck et al, 1996). Please see that document for additional information on QA/QC procedures and goals.

Section 1.1 of this chapter presents Data Quality Goals and Data Quality Results. The types of QC data collected during the study are described in Section 1.2. The quantitative QC data are shown in Section 1.3. Section 1.4 describes variability in replicate tests and compares this variability to QC results. Section 1.5 summarizes data quality achieved with data quality goals and discuses the adequacy of the data set for its intended use.

1 Data Quality Goals and Results

1.1 Primary Goals and Results

Goals were to collect at least 2 valid samples from each fuel/cycle combination. Criteria for validity of samples were: conformity of the dynamometer load test cycle with requirements specified in the Code of Federal Regulations (CFR); conformity of analytical procedures and QC check tolerances with requirements specified in the CFR for criteria gases and total particulates; comparability of sampling procedures and sampling performance with industry standards for various speciated measurements. The number of valid samples collected is shown in Table 1-1. All primary goals were met.

Table 1-1 Primary Goals

Fuel:	Pre 93		Reformulated		Low Aromatic	
Cycle:	Cold	Hot	Cold	Hot	Cold	Hot
Criteria gases	7	38	5	34	3	20
Speciated HC	3	6	3	6	3	6
Oxygenates	2	5	3	6	3	7
Mass	7	38	5	34	3	20
Ions	3	7	3	6	3	6
EC/OC	3	7	3	6	3	6
Elements	3	7	3	6	3	6
MOUDI	2	4	2	4	3	6

PRELIMINARY DRAFT

1.2 Supplementary Goals and Results

Supplementary goals were to achieve analytical accuracies and precisions comparable with data from standard emission test protocols and with results from other studies.

The supplementary goals are shown in Table 1-2. The values achieved during the study are shown in Table 1-3.

Table 1-2 Supplemental Data Quality Goals

Species	Accuracy	Precision	Detection Limit
Exhaust Emissions[a]			
Total PM	20%	10%	0.01 g/bhp-hr
THC	35%	15%	0.01 g/bhp-hr
NOx	10%	5%	0.01 g/bhp-hr
CO	35%	20%	0.06 g/bhp-hr
Size Fractionated PM	20%	10%	0.01 g/bhp-hr
Elements	30%	20%	0.003-.130 mg/bhp-hr
Ions	30%	20%	0.124 mg/bhp-hr
Carbon(elem./organic)	30%	20%	0.248 mg/bhp-hr
Chemical Analyses[b]			
C1-C4 Hydrocarbons	10%	20%	0.01 ppm carbon
C4-C12 Hydrocarbons	10%	20%	0.01 ppm carbon
Carbonyls	2%	20%	0.02 ug/ml
Nitrosomopholine	N.D.	±0.014 ug/sample	0.05 ug/sample
Nitro-PAH	N.D.	20%	2-6 ug/sample
PAH	N.D.	20%	2-6 ug/sample
Dioxins			

a-engine testing/sampling/analysis b-analytical N.D.-Not Determined

Table 1-3 Supplemental Data Quality Results

Species	Accuracy	Precision	Detection Limit
Exhaust Emissions[a]			
Total PM	<3%	5.5%	0.002 g/bhp-hr
THC	< 2%	4.0%	0.042 g/bhp-hr
NOx	<2%	1.9%	0.064 g/bhp-hr
CO	<2%	4.7%	0.058 g/bhp-hr
Size Fractionated PM	<1%	<1%	0.002 g/bhp-hr
Elements	%	14% to 111%	0.003 to 0.130 mg/bhp-hr
Ions	%	22% to 55%	0.124 mg/bhp-hr
Carbon(elem./organic)	%	9% / 11%	0.248 mg/bhp-hr
Chemical Analyses[b]			
C1-C4 Hydrocarbons	-0.1% to 2.8%	<1.1%	0.01 ppm carbon
C4-C12 Hydrocarbons	-5.6% to 2.4%	<3.5%	0.01 ppm carbon
Carbonyls	<2.2%	<2.4%	0.02 ug/ml

a-engine testing/sampling/analysis b-analytical N.D.-Not Determined

PRELIMINARY DRAFT

2 QA/QC Activities

The quality of results for all emissions measurements in this program includes dependence on a common baseline:

conformity of the dynamometer load test cycle with requirements specified in the CFR

adherence to sampling procedures defined in the CFR

the accuracy and precision of the CVS system

correctness of data calculations

completeness of record keeping and data archiving

In addition to these base requirements, the quality of individual measurement types depend on one or more of the following:

accuracy and precision of criteria gas analyzers

accuracy and precision of sample collection flow rates

accuracy and precision of laboratory analyses

For some measurements, the quality of results can also be assessed by comparing data from two methods to provide additional validation.

The QA/QC activities undertaken in each of these areas is summarized below. The results of these activities are given in Section 3.

Dynamometer Loads

The LACMTA dynamometer system includes a test labeled "EPA Heavy Duty Transient Regression Report." This report includes two test pass/fail checks labeled "Regression Analysis" and "Power Validation." These tests were conducted and reviewed for each emission test run.

CVS

The CVS system and mass flow controllers on the secondary dilution tunnel received an external audit by Dick Munns Company on April 27, 1997.

Data Calculations

Equations for calculation of emission rate data from sample concentrations, background concentrations and flow rates, were obtained from the CFR. The results of computer data processing were spot-checked by manual calculation for particle mass and particle species, for speciated hydrocarbons, and for carbonyls.

Data Record Completeness

The raw source data archives consist of three ring binders containing hand-written field data sheets and hard copy printouts of analytical data. The presence of the appropriate data sheets and printouts was checked for each test run.

Criteria Gas Analyzers

The criteria gas analyzers received audits by the ARB on 5/16/96, 5/20/96, 7/11/96, 1/16/97, and 1/23/97. The criteria gas analyzers receive a zero and span check with 2% tolerance for each species before and after each sample bag analysis.

Sample Collection

The mass flow controllers for total particle sampling received an external audit by Dick Munns Company on April 22, 1997.

Flow meters for Teflon filter (elemental analysis) and quartz filter sampling (ions and OC/EC analysis) were calibrated against a NIST traceable dry gas meter at CE-CERT prior to sampling.

The Method 5 sampler for impactor sampling (particle size distribution) includes a dry gas meter. This meter was cross checked against a NIST traceable dry gas meter at CE-CERT prior to sampling.

The carbonyl sampler includes a dry gas meter. This meter was cross checked against a NIST traceable dry gas meter by CE-CERT prior to sampling.

A dilution tunnel particle sampling blank was collected for each fuel type.

Laboratory Analyses

Gravimetric procedures for total mass analyses at LACMTA were conducted in accordance with CFR requirements and tolerances.

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Gravimetric analyses at CE-CERT were checked against zero every fifth weighing, against a calibration weight every twentieth weighing, and against reference filters once per weighing session.

Carbonyl analyses were checked each run against control standards.

Speciated hydrocarbon analyses were checked each day against a 23-component control mixture.

Intermethod Comparisons

Total hydrocarbons by FID were compared with the sum of speciated hydrocarbons.

MTA total particle mass was compared with sum of particle species.

Particle sulfur was compared with particle sulfate.

3 QA/QC Data

3.1 Dynamometer load cycles

Dynamometer cycle Regression Analysis and Power Validation test tolerances were met for all tests. The cycle validation test results are archived at CE-CERT. Table 1-4 shows the cycle validation tests results archived at CE-CERT.

3.2 CVS flows

CVS flow system and mass flow controllers for secondary dilution tunnel were calibrated by LACMTA at installation. Results archived at LACMTA.

External audit test results for the CVS flow rate showed LACMTA flow rate within 2% of audit flow rate (Dick Munns Co., 1997).

3.3 Criteria gas analyzers THC, CO, NOx, CO_2

Adherence to CFR procedures

The LACMTA operates a dedicated emissions testing facility designed specifically to operate in conformance with CFR requirements.

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Calibrations

Six-point calibrations were performed on the THC, CO, NOx, and CO_2 analyzers by LACMTA on November 24, 1996 and January 6, 1997. Results were within requirements as specified in CFR 1321-24. Records are archived at LACMTA.

QC Checks

Zero and span checks were conducted before and after each bag analysis for every test cycle. On three occasions NOx zero checks slightly exceeded tolerances, being 2% to 5% of full-scale. Otherwise all post analytical zero and span checks met the 2% or less drift limit as required in CFR 86.1340. Table 1-4 shows the status of zero and span QC checks. QC check printouts for the first four runs and a scattered few other runs are missing.

Table 1-4 Validation Results for MTA Cycle and Criteria Gases

Test Date	Test Time	Fuel Type	Test Code	data sheets present	CO2 span corr. made	zero	span	regr	power
12/2/96	8:00	Pre-93							
12/2/96	12:10:19	Pre-93	337CS	yes		b	b	ok	ok
12/2/96	12:10:19	Pre-93	337H1	yes		b	b	ok	ok
12/2/96	13:46:37	Pre-93	337H2	yes		b	b	ok	ok
12/2/96	14:30:00	Pre-93	337H3	no		b	b	ok	ok
12/3/96	7:10:47	Pre-93	338CS	yes		ok	ok	ok	ok
12/3/96	7:10:47	Pre-93	338H1	yes		ok	ok	ok	ok
12/3/96	8:46:13	Pre-93	338H2	yes		ok	ok	ok	ok
12/3/96	9:26:09	Pre-93	338H3	yes		ok	ok	ok	ok

12/3/96	10:17:43	Pre-93	338H4	yes		ok	ok	ok	ok
12/3/96	10:57:11	Pre-93	338H5	yes		ok	ok	ok	ok
12/3/96	11:46:36	Pre-93	338H6	yes		ok	ok	ok	ok
12/3/96	12:29:51	Pre-93	338H7	yes		ok	ok	ok	ok
12/3/96	13:16:28	Pre-93	338H8	yes		ok	ok	ok	ok
12/3/96	13:57:08	Pre-93	338H9	yes		ok	ok	ok	ok
12/4/96	7:25:21	Pre-93	339CS	yes		ok	NOx	ok	ok
12/4/96	7:25:21	Pre-93	339H1	yes		ok	NOx	ok	ok
12/4/96	8:58:04	Pre-93	339H2	yes		ok	NOx	ok	ok
12/4/96	9:44:22	Pre-93	339H3	yes		ok	ok	ok	ok
12/4/96	10:34:34	Pre-93	339H4	yes		ok	ok	ok	ok
12/4/96	11:20:47	Pre-93	339H5	yes		ok	ok	ok	ok
12/4/96	13:05:02	Pre-93	339H6	yes		ok	ok	ok	ok
12/4/96	13:50:31	Pre-93	339H7	yes		ok	ok	ok	ok
12/5/96	7:31:33	Pre-93	340CS	yes		ok	ok	ok	ok
12/5/96	7:31:33	Pre-93	340H1	yes		ok	ok	ok	ok
12/5/96	9:12:47	Pre-93	340H2	yes		ok	ok	ok	ok
12/5/96	9:52:18	Pre-93	340H3	yes		ok	ok	ok	ok
12/5/96	10:36:21	Pre-93	340H4	yes		ok	ok	ok	ok
12/6/96	12:54:33	Pre-93	341CS	yes		ok	ok	ok	ok
12/6/96	12:54:33	Pre-93	341H1	yes		ok	ok	ok	ok
12/6/96	14:28:25	Pre-93	341H2	yes		ok	ok	ok	ok
12/6/96	15:18:36	Pre-93	341H3	a		ok	ok	ok	ok
12/9/96	9:33:00	LowArom	344header						
12/9/96	13:47:24	LowArom	344H1	yes		ok	ok	ok	ok
12/9/96	14:44:28	LowArom	344H2	yes		ok	ok	ok	ok
12/9/96	15:32:18	LowArom	344H3	yes		ok	ok	ok	ok
12/9/96	16:14:19	LowArom	344H4	yes		ok	ok	ok	ok
12/10/96	8:00	LowArom	345tunnel						
12/10/96	10:39:21	LowArom	345CS	yes		ok	ok	ok	ok
12/10/96	10:39:21	LowArom	345H1	yes		ok	ok	ok	ok
12/10/96	12:21:25	LowArom	345H2	yes		ok	ok	ok	ok
12/10/96	13:10:54	LowArom	345H3	yes		ok	ok	ok	ok
12/10/96	13:56:45	LowArom	345H4	yes		ok	ok	ok	ok
12/11/96	7:32:18	LowArom	346CS	yes		ok	ok	ok	ok
12/11/96	7:32:18	LowArom	346H1	yes		ok	ok	ok	ok
12/11/96	9:03:43	LowArom	346H2	yes		ok	ok	ok	ok
12/11/96	9:48:53	LowArom	346H3	yes		ok	ok	ok	ok
12/11/96	10:34:12	LowArom	346H4	yes		ok	ok	ok	ok
12/11/96	13:25:31	LowArom	346H5	yes		ok	ok	ok	b
12/11/96	14:26:29	LowArom	346H6	yes		ok	ok	ok	ok
12/11/96	15:15:58	LowArom	346H7	yes		ok	ok	ok	ok
12/12/96	7:33:31	LowArom	347CS	yes		ok	ok	ok	ok
12/12/96	7:33:31	LowArom	347H1	yes		ok	ok	ok	ok
12/12/96	9:00:02	LowArom	347H2	yes		ok	ok	ok	ok
12/12/96	10:01:15	LowArom	347H3	yes		ok	ok	ok	ok
12/12/96	10:47:17	LowArom	347H4	yes		ok	ok	ok	ok
12/12/96	12:00:31	LowArom	347H5	yes		ok	ok	ok	ok
12/12/96	13:01:41	LowArom	347H6	yes		ok	ok	ok	ok

12/13/96		Reform	348 header						
12/13/96	13:59:39	Reform	348H1	yes		ok	ok	ok	ok
12/13/96	14:51:32	Reform	348H2	yes		ok	ok	ok	ok
12/16/96	7:00	Reform	351tunnel						
12/16/96	8:19:31	Reform	351CS	yes		ok	ok	ok	ok
12/16/96	8:19:31	Reform	351H1	yes		ok	ok	ok	ok
12/16/96	9:54:11	Reform	351H2	yes		ok	ok	ok	ok
12/16/96	10:52:37	Reform	351H3	yes		ok	ok	ok	ok
12/16/96	11:47:06	Reform	351H4	yes		ok	ok	ok	ok
12/16/96	12:34:18	Reform	351H5	yes		ok	ok	ok	ok
12/16/96	13:16:19	Reform	351H6	yes		ok	ok	ok	ok
12/16/96	14:12:00	Reform	351H7	yes		ok	ok	ok	ok
12/17/96	7:22:39	Reform	352CS	yes		ok	ok	ok	ok
12/17/96	7:22:39	Reform	352H1	yes		ok	ok	ok	ok
12/17/96	8:53:01	Reform	352H2	yes		ok	ok	ok	ok
12/17/96	9:39:23	Reform	352H3	yes		ok	ok	ok	ok
12/17/96	10:35:04	Reform	352H4	yes		b	ok	ok	ok
12/17/96	11:27:06	Reform	352H5	yes		ok	ok	ok	ok
12/17/96	12:09:43	Reform	352H6	yes		ok	ok	ok	ok
12/17/96	12:51:34	Reform	352H7	yes		ok	ok	ok	ok
12/18/96	7:25:42	Reform	353CS	yes		ok	ok	ok	ok
12/18/96	7:25:42	Reform	353H1	yes		ok	ok	ok	ok
12/18/96	8:55:44	Reform	353H2	yes		ok	ok	ok	ok
12/18/96	9:53:58	Reform	353H3	yes		ok	ok	ok	ok
12/18/96	10:34:41	Reform	353H4	yes		ok	ok	ok	ok
12/18/96	11:29:25	Reform	353H5	yes		ok	ok	ok	ok
12/18/96	12:14:57	Reform	353H6	yes		ok	ok	ok	ok
12/18/96	12:58:38	Reform	353H7	yes		ok	ok	ok	ok
12/19/96	7:47:52	Reform	354CS	yes		ok	ok	ok	ok
12/19/96	7:47:52	Reform	354H1	yes		ok	ok	ok	ok
12/19/96	9:18:51	Reform	354H2	yes		ok	ok	ok	ok
12/19/96	10:15:28	Reform	354H3	yes		ok	ok	ok	ok
12/19/96	10:59:24	Reform	354H4	yes		ok	ok	ok	ok
12/19/96	11:45:20	Reform	354H5	yes		ok	ok	ok	ok
12/19/96	12:34:16	Reform	354H6	yes		ok	ok	ok	ok
12/19/96	13:18:06	Reform	354H7	yes		ok	ok	ok	ok
12/20/96	7:34:07	Reform	355CS	yes		ok	ok	ok	ok
12/20/96	7:34:07	Reform	355H1	yes		ok	ok	ok	ok
12/20/96	9:13:03	Reform	355H2	yes		ok	ok	ok	ok
12/20/96	10:01:01	Reform	355H3	yes		ok	ok	ok	ok
12/20/96	10:49:23	Reform	355H4	yes		ok	ok	ok	ok
12/20/96	11:35:51	Reform	355H5	yes		ok	ok	ok	ok
12/20/96	12:27:08	Reform	355H6	yes		ok	ok	ok	ok
12/20/96	13:09:36	Reform	355H7	yes		ok	ok	ok	ok
1/7/97		Pre-93	7header						
1/8/97	8:12:48	Pre-93	8CS	yes	yes	ok	ok	ok	ok
1/8/97	8:12:48	Pre-93	8H1	yes	yes	ok	ok	ok	ok
1/8/97	9:53:41	Pre-93	8H2	yes	yes	ok	ok	ok	ok
1/8/96	10:40:19	Pre-93	8H3	yes	yes	ok	ok	ok	ok

1/8/97	11:22:11	Pre-93	8H4	yes	yes	ok	ok	ok	ok
1/8/97	12:09:51	Pre-93	8H5	yes	yes	ok	ok	ok	ok
1/8/97	13:01:52	Pre-93	8H6	yes	yes	ok	ok	ok	ok
1/8/97	13:42:20	Pre-93	8H7	yes	yes	b	ok	ok	ok
1/9/97	7:52:22	Pre-93	9CS	yes	yes	ok	ok	ok	ok
1/9/97	7:52:22	Pre-93	9H1	yes	yes	ok	ok	ok	ok
1/9/97	9:44:30	Pre-93	9H2	yes	yes	ok	ok	ok	ok
1/9/97	10:28:00	Pre-93	9H3	yes	yes	ok	ok	ok	ok
1/9/97	11:09:16	Pre-93	9H4	yes	yes	ok	ok	ok	ok
1/9/97	11:56:33	Pre-93	9H5	yes	yes	ok	ok	ok	ok
1/9/97	12:44:18	Pre-93	9H6	yes	yes	ok	ok	ok	ok
1/9/97	13:29:57	Pre-93	9H7	yes	yes	ok	ok	ok	ok

a - Cover page of test report printout is missing; data recovered from emission summary pages of test report.

b - Hardcopy printout is missing from archive; no data quality problems were noted by emissions test operator; data for these tests are consistent with data for the other tests of this fuel.

NO_x - Span checks for NO_x analyzer were slightly above tolerance, ranging from 2% to 5% of full scale. Other QC results are within tolerance. Emission results for these tests are consistent with the emission rates from the other 44 emission tests on this fuel.

Audits

The following external audits were conducted as part of this program:

1. Instrument train verification conducted by CARB El Monte laboratories on 5/16/96 with the following results (ARB, 1996):
   - -NOx linearity test – pass
   - -NOx conversion efficiency test found to be 98.96%-pass
   - -Analyzer accuracy using NIST gases

Instrument/Range		% Difference	Status
NOx	100ppm	-0.21	Pass
NOx	300ppm -	0.93	Pass
NOx	1000ppm	+1.58	Pass
CO_2	1%	+1.06	Pass
CO_2	6%	-0.03	Pass
CO	100ppm	+3.30	Fail
CO	300ppm -	0.87	Pass
CO	1500ppm	+5.22	Fail

   - -THC analyzer was not verified because the instrument ran out of zero pot.
   - -Barometric readings were verified with +0.06% difference-Pass

   Corrective Action: A follow-up Verification/Inspection was conducted by ARB on May 20, 1996. All instruments passed. CVS propane injection/recovery passed.

2. Instrument train verification conducted by CARB El Monte laboratories on 1/16/97 with the following results (ARB, 1997):
   - -Analyzer accuracy using NIST gases

Instrument/Range		% Difference	Status
HC	100ppm	-1.229	Pass
		-0.198	Pass
CO	100ppm	+0.770	Pass
		+0.862	Pass
CO	300ppm	-0.019	Pass
		+0.131	Pass
CO_2	1%	+3.409	Fail
CO_2	6%	-8.9574	Fail
NOx	100ppm	-1.686	Pass
NOx	300ppm	+0.477	Pass
		+0.543	Pass

   Corrective Action: LACMTA was actioned to correct the problem with the CO_2 analyzer. LACMTA found that a span cylinder had been changed, but the span point had not been updated. This was done and a new calibration conducted. A follow-up visit was conducted by CARB on 1/23/97 with the following results:

CO_2	1%	+0.633	Pass
		+0.626	Pass
CO_2	6%	-0.155	Pass
		+0.316	Pass

Corrective Action: It was determined from LACMTA that the problems with the CO_2 span had occurred on January 6, 1997 and affected the CO_2 emission results obtained on January 8 and 9, 1997. The CO_2 emission results for these dates were corrected with the new calibration numbers.

Estimation of Accuracy, Precision, and Detection Limit

The accuracies shown in Table 1-3 are based upon meeting the audit tolerance of 2%. The precisions are based upon replicate test variability. The detection limits are calculated as two times the standard deviation of zero checks for a random sample of twenty zero checks. The values were converted to g/bhp-hr using nominal values for total CVS flow and total power.

3.4 Sample collection

Calibrations

The flow meters used for PTFE (elemental analyses) and Quartz Fiber (ion and carbon analyses) were calibrated with a dry gas meter traceable to NIST prior to sampling.

The Method 5 box used for particle size samples contains a dry gas meter. This meter was cross checked against a NIST traceable dry gas meter.

Audits

Dick Munns Company conducted an audit of the CVS system and the flow controllers on the secondary dilution tunnel on April 22, 1997 with the following results (Dick Munns Co., 1997):

-CVS flow found to be within 2% of calibration value-Pass

-Mass flow controllers on secondary dilution tunnel found to be within 2% of calibration values-Pass

Tunnel Backgrounds

Three dilution tunnel background samples were collected during testing. The following emission rates were obtained with the tunnel blanks:

1. 1.78 mg/bhp-hr equivalent
2. 1.90 mg/bhp-hr equivalent
3. 1.78 mg/bhp-hr equivalent

All tunnel backgrounds were <1% of the engine emission rates

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3.5 Particle analyses

Cahn Microbalance

The microbalance was used for determination of particle size distributions. Results of periodic balance checks are as follows:

	Zero Check	Calibration Check (200mg)	Reference Filter Checks			
			Ref #1	Ref #2	Ref. #3	Ref. #4
Av. (mg)	-0.001	199.995	76.219	75.97	136.67	135.681
S. D. (mg)	0.002	0.003	0.002	0.004	0.003	0.005

Blanks

Three PTFE filter/trip blanks were supplied to DRI. These were used as matrix blanks. I.e., X-ray spectral backgrounds were subtracted using average spectra from the three filter/trip blanks.

One quartz filter/trip blank was supplied to DRI. This was used as a matrix blank,i.e., concentrations for ion and carbon analyzes were blank subtracted using the filter/trip blank.

Tunnel Backgrounds

Two PTFE and three quartz fiber tunnel background samples were collected and analyzed. The results of these analyses after matrix blank subtraction are summarized below and compared with the lower detection limits in units of mg/bhp-hr.

	Detection Limit	*Average Tunnel Background*
	mg/bhp-hr	*mg/bhp--hr*
Chloride	0.124	0.083
Nitrate	0.124	0.029
Sulfate	0.124	0.015
Ammonium	0.124	0.000
Organic Carbon	0.248	1.769
Elemental Carbon	0.248	0.189
Na	0.025	0.079
Mg	0.025	0.027
Al	0.025	0.017
Si	0.015	0.017
P	0.015	0.014
S	0.010	0.003
Cl	0.025	0.003
K	0.015	0.002

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Ca	0.010	0.006
Ti	0.010	0.000
V	0.005	0.000
Cr	0.005	0.000
Mn	0.004	0.000
Fe	0.004	0.002
Co	0.002	0.000
Ni	0.002	0.000
Cu	0.003	0.000
Zn	0.005	0.001
Ga	0.005	0.000
As	0.005	0.000
Se	0.003	0.000
Br	0.003	0.000
Rb	0.003	0.000
Sr	0.003	0.000
Y	0.003	0.000
Zr	0.005	0.000
Mo	0.005	0.000
Pd	0.025	0.000
Ag	0.030	0.000
Cd	0.030	0.005
In	0.030	0.006
Sn	0.040	0.010
Sb	0.045	0.013
Ba	0.125	0.033
La	0.130	0.006
Au	0.015	0.000
Hg	0.005	0.001
Tl	0.005	0.000
Pb	0.005	0.000
Ur	0.005	0.000

Only organic carbon, Na, and Mg were found in the tunnel background samples at levels higher than the detection limits. The sum of all species identified in the tunnel background samples is less than 1.5% of that found in the engine exhaust samples. Engine analysis results were corrected for tunnel backgrounds.

Estimation of Accuracy , Precision, and Detection Limit

The accuracies shown in Table 1-3 for Total PM are based upon meeting the audit flow rate tolerances of 2%. Balance errors were assumed to be negligible. Total PM requires two flow rates (sample flow and CVS flow), thus accuracy is given as 2%*sqrt(2). Particle size fractions are relative measurements and do not depend on flow rates; on the basis of balance data alone,

accuracy is better than 1% of total mass. Accuracy data for elements, ions, and EC/OC have not been determined.

The precisions for all particle species measurements are based upon replicate test variability.

The detection limits for Total PM and for particle size fractions are results for tunnel blanks. For particle size fractions these are conservative compared to the detection limit determined from microbalance QC data. The detection limits for elements, ions, and EC/OC are calculated as two times the average analytical uncertainties reported by DRI. These are consistent with the analytical results from analysis of tunnel blank samples.

3.6 Speciated hydrocarbons

Hydrocarbons were analyzed by gas chromatography: one for C1-C4 and one for C4-C12 species. The systems were calibrated using propane in a 23-component mixture and the response was checked against the component in the mixture. Response factors for a selection of species was routinely monitored during the course of the study. Table 3-1 shows the mean response, standard deviation, bias, and coefficient of variation for those species. Propane is included twice because it was measured on both the light end and heavy end GC. Precision and accuracy were within tolerance throughout the range.

Table 3-1 Speciated HC Analytical Precision

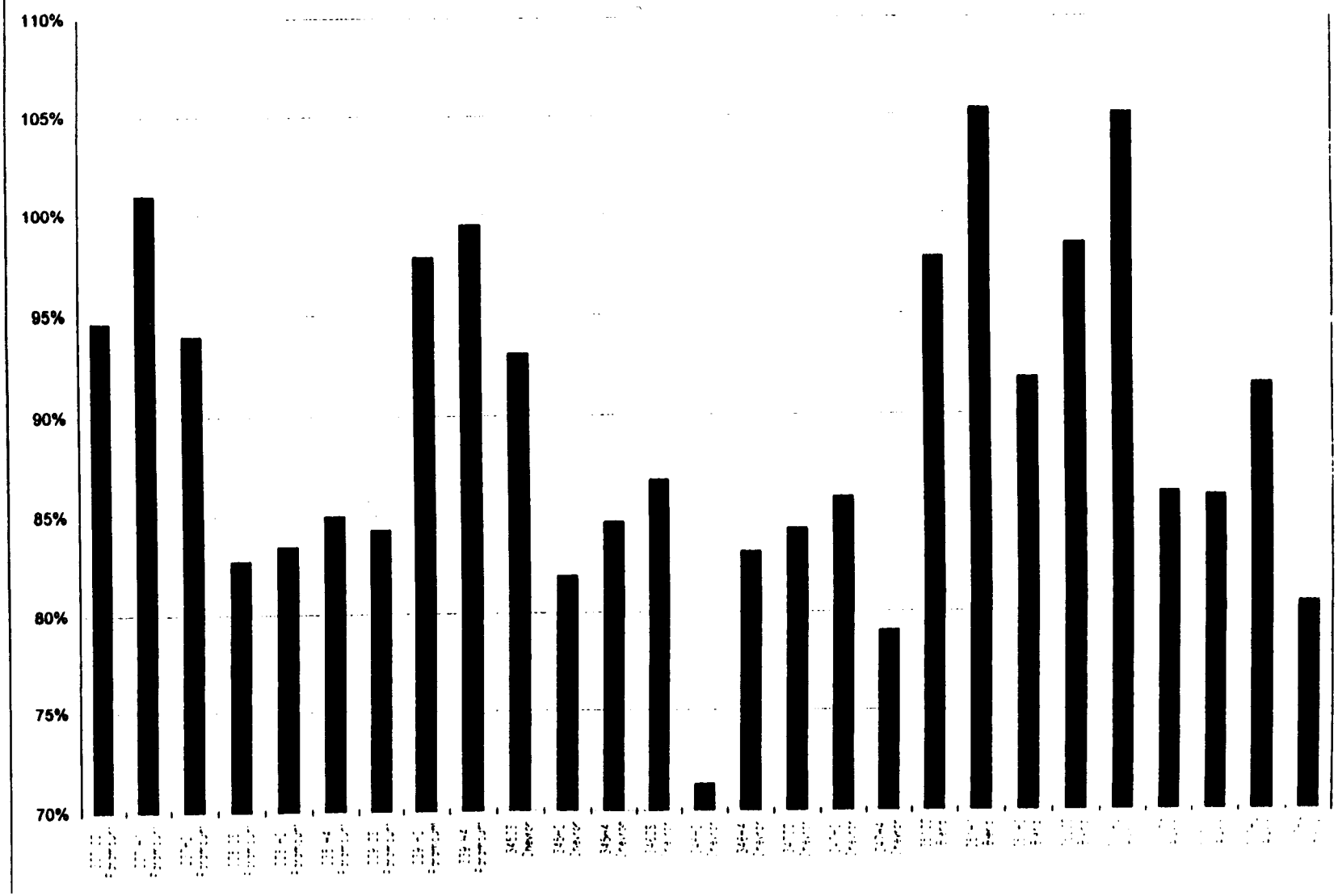
Species	True ppm	Mean Response ppm	Std. Dev ppm	Bias %	CV %
methane	5.16	5.16	0.01	-0.1%	0.1%
ethane	5.05	5.19	0.06	2.8%	1.1%
propane	9.18	9.18	0.00	0.0%	0.0%
13-butadiene	4.70	4.54	0.10	-3.4%	2.1%
propane	9.18	9.18	0.01	0.0%	0.1%
butane	5.08	4.98	0.10	-2.0%	1.9%
benzene	4.93	5.05	0.12	2.4%	2.4%
224tmp	4.98	4.92	0.07	-1.2%	1.4%
toluene	5.00	4.93	0.09	-1.5%	1.9%
decane	5.38	5.08	0.19	-5.6%	3.5%

The method employed for speciated hydrocarbon sampling specifies a tolerance of 80% recovery for the sum of hydrocarbon species as compared with the total hydrocarbons measured by FID analysis of the integrated emissions bag sample. Results for this study are shown in Figure 3-1. Two samples had recoveries of about 79% and 71 %. The sample with 71% had a GC-derived methane value that was suspiciously low. It was less than half the methane value observed for other samples in the same category. All other recoveries were >80%.

Estimation of Accuracy, Precision, and Detection Limit

The accuracies shown in Table 1-3 for speciated HC are based upon the mean bias observed for the response to the 23-component standard. The precisions are calculated as the standard deviation of the responses to the 23 component species. Detection limits are based upon the minimum peak area (minimum concentration) registered by the GC peak integration software, which is less than 0.01 ppmC.

Figure 3-1. MTA FID and CE-CERT GC Recovery



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3.7 Carbonyls

Carbonyls were collected at 1 LPM onto Sep-pak cartridges, extracted into acetonitrile, and analyzed by HPLC. Precisions are estimated from calibration standard data. These precisions are estimated from data at a concentration of 3.0 µg/ml (about 60 mg/bhp-hr). This is appropriate for formaldehyde, but provides conservative upper limits for the remaining species in this study.

An analytical blank and a two-point calibration (3.0 µg/ml and 30.0 µg/ml) were performed at the beginning of each analytical run, and a calibration curve generated for each species. Analytical blanks were below detection limits (i.e., no HPLC peak) in all cases. To estimate bias and precision, peak areas for the 3.0 µg/ml calibration standard were then converted to µg/ml based on the calibration equation obtained. The mean and standard deviations of these data are shown in Table 3-2. Bias is calculated as mean minus 3.0 and CV, coefficient of variation, is the standard deviation divided by the mean.

Table 3-2 Carbonyl Analytical Precision

Calibration Precision					
x	Mean	Std. Dev.	Bias	CV	$CV_{Mulliday}$
x	µg/ml	µg/ml	%	%	%
formaldehyde	2.97	0.037	-0.9%	1.2%	1.1%
acetaldehyde	2.97	0.023	-0.9%	0.8%	1.3%
acrolein	3.00	0.039	0.1%	1.3%	1.9%
acetone	3.03	0.084	1.0%	2.8%	2.8%
propionaldehyde	2.93	0.035	-2.2%	1.2%	2.4%
crotonaldehyde	2.97	0.113	-0.9%	3.8%	4.7%
methacrolein	3.02	0.090	0.7%	3.0%	2.0%
MEK	3.05	0.149	1.6%	4.9%	4.6%
butyraldehyde	2.87	0.173	-4.5%	6.0%	4.9%
benzaldehyde	2.92	0.020	-2.8%	0.7%	1.4%
valeraldehyde	2.83	0.078	-5.6%	2.7%	3.7%
tolualdehyde	2.96	0.031	-1.4%	1.0%	1.4%
hexaldehyde	2.82	0.145	-6.0%	5.1%	6.2%

Calibration performance during the course of an analytical run was also checked in a second way, based on the stability of the HPLC response factors from day to day. Based on the response factors for each of the six analytical run days, an average response factor was calculated. Response to injection of the calibration standards for each of these six days were then calculated using the overall average response factor. These data represent the variability in response that would occur if the analyzer were not recalibrated each day. In this way the calibration standards injected each day can be considered QC controls having a variability that will place an upper limit on the variability within a given day. These results are labeled $CV_{Mulitday}$ in Table 3-2. They demonstrate that the precision calculated from the initial calibration is reasonable, and that it is representative of the entire analytical run.

The analytical precisions were converted to emission units (mg/bhp-hr) and compared with typical concentrations in Table 3-3. Carbonyl emissions are calculated as the difference between a tunnel sample and a background sample. Thus, in Table 1-6, the precisions shown in Table 3-2 were multiplied by the square root of 2, to represent the precision of the net difference. For formaldehyde and acetaldehyde, the precisions are comparable with the variability of replicate testing. For the species measured at low concentrations, the precisions tend to be overestimates for two reasons. First, the precisions were estimated at 3.0 µg/ml; lower concentrations would yield smaller precisions. Second, the net carbonyl is a difference between sample and background samples; precisions for both samples were taken into account, but in fact the background samples were generally near zero and do not contribute to imprecision. The replicate test data show smaller precisions, and thus support the assertion that the relative precision estimates derived above are too large.

Table 3-3. Carbonyl Emission Rate Precisions

Background Corrected Sample Precision			
	Typical Emissions	Std. Dev. for Background Corrected Data	
	mg/bhp-hr	mg/bhp-hr	% of typical
formaldehyde	58.72	1.01	1.7%
acetaldehyde	19.17	0.64	3.3%
acrolein	3.43	1.07	31.2%
acetone	6.43	2.30	35.8%
propionaldehyde	4.04	0.96	23.7%
crotonaldehyde	1.71	3.07	179.4%
methacrolein	0.09	2.45	-

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MEK	0.00	4.06	-
butyraldehyde	4.08	4.73	116.0%
benzaldehyde	1.74	0.54	30.9%
valeraldehyde	0.82	2.13	-
tolualdehyde	3.38	0.84	24.7%
hexaldehyde	0.47	3.95	-

Estimation of Accuracy , Precision, and Detection Limit

The accuracies shown and precisions shown in Table 1-3 for speciated carbonyls are for the four toxic species of interest: formaldehyde, acetaldehyde, acrolein, and propionaldehyde. The accuracy is based upon the mean bias observed for the response to the 13-component standard. The precisions are calculated as the standard deviation of the responses to the 13-component species. Detection limits are based upon the minimum peak area (minimum concentration) registered by the HPLC peak integration software, which is less than 0.02 µg/ml.

3.8 Particulate-bound PAH and Nitro-PAH

Introduction

A sampling system consisting of a high volume filter backed by PUF plugs was used to collect samples for PAH and nitro-PAH analysis by GC-MS at SAPRC. Lists of toxic particle-bound and gas-phase PAH and nitro-PAH to be targeted for analysis were developed by the California Air Resources Board. Of the 20 PAH targeted for analysis in the particulate matter, 19 have been quantified. Only picene was not quantified, due to the lack of an available standard. Of the 19 semi-volatile PAH targeted for analysis, 15 were quantified in the filter and PUF plug samples. The four remaining semi-volatile PAH, acenaphthene, acenaphthylene and 1- and 2-methylnaphthalene, were not collected quantitatively on the high volume filter backed by PUF plugs sampling system. These last PAH were, however, quantitatively collected by the UCD XAD-backed sampling system.

Six nitro-PAH were targeted for analysis in the particulate matter and two (1-nitropyrene and 6-nitrobenzo[a]pyrene) were detected and quantified. Upper limits (nitro-PAH < specified value) were provided for the remaining four particle-associated nitro-PAH on the target list. Seven semi-volatile nitro-PAH and the methynitronaphthalenes were targeted for analysis. 9-

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Nitroanthracene (although listed as a semi-volatile nitro-PAH) was detected and quantified in the filter samples and 1- and 2-nitronaphthalene were detected and quantified in the PUF samples. Upper limits for the remaining semi-volatile nitro-PAH based on the estimated detectable levels were provided.

The collection and storage of samples followed specifically defined procedures. All testing conditions were recorded on Field Data Sheets while sampling at the LACMTA facility. For each sampling run, the date, time, flow rate, temperature and pressure of the sampling system was recorded. All samples were identified in a Master Log.
Transfer of the intercomparison samples and HPLC fractions for mutagenicity analysis between SAPRC and UCD were tracked with Chain of Custody forms. Samples were shipped by overnight carrier and were cooled by blue ice during shipment.

Blanks and Spike Recovery

A cleaned filter and a trip blank filter were spiked with the deuterated IS in similar µg levels to the emission sample filters. No non-deuterated PAH were detected in these samples, verifying both the trip blank and the absence of any interferences from the deuterated standards.
A cleaned filter was also spiked with the deuterated internal standards and SRM 1491 to verify the quantification of the PAH targeted present in NIST SRM 1491 (aromatic hydrocarbons in hexane/toluene). The filter was treated as if it were a sample and was Soxhlet extracted, concentrated and analyzed by GC-MS with SIM. The internal standards and quantitation ions were as listed in Table 10 of the main report. Table 3-4 lists the measured PAH on the filter and the % difference values from the amounts spiked.

Frequent GC-MS blank runs in which only solvent was injected were run. These blanks occurred between fuel types and before and after standard solutions were run. In no case was detectable carry over between runs observed.

Calibration Standards

Analysis of the screening samples (see Table 5 of the main report) allowed the deuterated PAH spikes to be added to the filter and PUF samples at levels comparable to those of the analytes. Calibration standards were designed to bracket the amounts present in the samples. For PAH quantification, calibration curve and response factor standards of 5-10 ng/µl were prepared from NIST SRM 1491 (aromatic hydrocarbons in hexane/toluene) and a master stock solution of

deuterated PAH and nitro-PAH in methylene chloride. Concentration ratios of 0.5:1, 1:1, and 2:1 were used for the calibration curve solutions. Milligram amounts of deuterated PAH and nitro-PAH standards were weighed on a small pan in a Cahn Model 25 Electrobalance and master stock solutions were prepared in 50 and 100 ml volumetric flasks. The solutions were wrapped with aluminum foil, sealed with teflon tape and stored in a freezer at -20 C. Calibration curve solutions were prepared from the SRM and the stock solutions using a Hamilton Gastight syringe. The solutions were stored in 2 ml amber vials with teflon-backed septa. Aliquots were transferred as needed into 2 ml autosampler vials for use in the Hewlett-Packard 7673A Autosampler. Standard solutions were prepared periodically as needed and to ensure the integrity of the solution concentration.

Deuterated compounds used as standards are: naphthalene-d_8, acenaphthene-d_{10}, anthracene-d_{10}, benzo[a]pyrene-d_{12}, chrysene-d_{12}, dibenz[a,h]anthracene-d_{14}, fluoranthene-d_{10}, perylene-d_{10}, phenanthrene-d_{10}, pyrene-d_{10}, 1-nitronaphthalene-d_7, 1-nitropyrene-d_9, and 2-nitrofluorene-d_9.

Table 3-4. PAH Recovery from Spiked Filter.

Polycyclic Aromatic Hydrocarbon	Spike (µg)	Recovered (µg)	% Difference[a]
phenanthrene	7.01	6.69	-4.6
anthracene	7.82	7.89	0.8
1-methylphenanthrene	7.00	6.99	-0.2
fluoranthene	5.91	5.90	-0.3
pyrene	5.89	6.11	3.7
benz[a]anthracene	3.59	2.69	-25.2
chrysene	7.03	7.61	8.3
benzo[b]fluoranthene	5.25	5.62	7.0
benzo[k]fluoranthene	5.57	7.45	33.8
benzo[e]pyrene	5.62	7.20	28.1
benzo[a]pyrene	6.79	7.91	16.4
perylene	7.12	8.03	12.8
indeno[1,2,3-cd]pyrene	6.29	6.09	-3.3
dibenz[a,h]anthracene	5.18	5.68	9.7
benzo[ghi]perylene	5.29	5.71	7.8

[a]Calculated as [(Recovered - Spiked)/Spiked] x 100.

Three PAH response factor standards were prepared in 50 ml volumetric flasks for the quantification of higher molecular weight PAH. Solutions were made using a Cahn Electrobalance, sealed and stored using the same procedure as the above volumetric solutions. Each solution in methylene chloride contained 5-10 ng/µl of chrysene-d_{12}, benzo[a]pyrene-d_{12}, and dibenz[a,h]anthracene-d_{14} plus the following PAH: solution #1, cyclopenta[cd]pyrene, benzo[c]phenanthrene, indeno[1,2,3-cd]pyrene, coronene, dibenzo[a,e]pyrene, and benzo[b]chrysene; solution #2, benzo[c]chrysene, dibenzo[a,h]pyrene; solution #3, dibenzo[a,i]pyrene, dibenzo[a,l]pyrene, dibenz[a,c]anthracene, and dibenz[a,j]anthracene.

The deuterated nitro-PAH spikes were added at levels expected based upon the amount of PAH present in the screening samples and the relative amount of nitro-PAH/PAH present in the NBS SRM 1650, Diesel Particulate. The actual nitro-PAH present in the samples were at levels lower than the expected values based on the SRM. Therefore, for quantification of nitro-PAH, two stock solutions were prepared of SRM 1587 (nitro-PAH in methanol) and 7.8 ng/µl 1-nitropyrene-d_9. One solution contained a 10-fold dilution of SRM 1587 (approximately 0.7 ng/µl) and the other solution a 50-fold dilution of the SRM (approximately 0.14 ng/µl). Solutions were stored in 2 ml amber vials as above. In addition a calibration solution containing approximately 3 ng/µl each 1-nitronaphthalene-d_7 and 2-nitrofluorene-d_9, 0.15 ng/µl each 1-nitronaphthalene and 2-nitronaphthalene plus a 100-fold dilution of SRM 1587 (~0.07 ng/µl) was prepared for quantification of nitro-PAH on the PUFs.

Instrument Control and Maintenance

Prior to running each group of samples and standards, the instrument was Autotuned and if the tune parameters were not satisfactory, the instrument source was cleaned.

If the GC peak shapes broadened and/or the column resolution decreased for the standard or sample peaks, inlet maintenance was performed, generally including changing the pre-column and the silylated glass-wool in the split/splitless injector.

Calibration standards were run prior to beginning the sample injections and periodically throughout the sample analysis. Any changes in the measured response factors [(area/ng PAH)/(area/ng deuterated PAH)] were generally associated with changes in the peak shapes and were corrected by inlet and pre-column maintenance.

Occasionally, the HP 7673A Automatic Sampler would not inject properly (perhaps an air bubble in the syringe, etc.) and less than the specified amount was injected. If no peaks were detected, the sample was re-run. However, in a few instances the more abundant analytes were detected and the sample was not repeated. In no case were fewer than replicate injections and peak areas used. Triplicate area counts were obtained and averaged for >99% of the analyte quantifications.

Fifty percent of each filter and front PUF and 37.5% of each back PUF extract was fractionated by HPLC and the appropriate fraction was analyzed by GC-MS for nitro-PAH. Again, all GC-MS injections were made in triplicate. For nitro-PAH analysis, on-column injection was necessary to achieve good compound response. Previously it was found that the autosampler run in the on-column mode would often result in carry-over between injections. All nitro-PAH analysis were, therefore, performed by manual cool, on-column injection using a syringe fitted with an approximately 6 in. fused silica needle that allowed the sample to be directly deposited into the deactivated fused-silica pre-column. Triplicate area counts were obtained and averaged for 100% of the nitro-PAH quantifications.

Replicates

For each of the three fuel types three independent replicate samples, as noted in Table 1, were collected and analyzed. Each replicate sample consisted of a filter, a front PUF and a back PUF to be analyzed. Analysis of PAH by GC-MS was conducted utilizing a 25% aliquot of each of the 9 filter, 9 front PUF and 9 back PUF extracts. All GC-MS injections were made in triplicate. For the filter samples, two series of GC-MS analyses were conducted to quantify the full molecular weight range of targeted PAH. The calibration standards used for these quantifications are detailed above.

Analysis of nitro-PAH by GC-MS was conducted on HPLC fraction #4 in which the nitro-PAH have been shown to elute. The nine filter HPLC fraction #4's and 9 front PUF HPLC fraction #4's were analyzed by triplicate GC-MS injections. The 9 back PUF HPLC fraction #4's were only injected once each, because no nitro-PAH were detected.

Table 3-5 lists the results of the PAH analyses for the three replicate two-cycle filter with PUF samples collected for each of the three fuel types. Table 3-6 lists the results of the nitro-PAH analyses. Tables 30 and 31 in the main report give the average emission rate and standard

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deviations based on the three replicate 2-cycle sample collections for each fuel type. Figures 14-20 in the main report show the means and 95% confidence intervals for each of the analytes.

Summary of Departures

No standardized test methods were available for the analysis of PAH and nitro-PAH in diesel samples. Methods previously successfully applied to ambient samples analyses (Final Report to CARB Contract No. A5-185-32; Atkinson *et al.*, 1988) were used. The procedures are summarized in the body of this report and no departures from these protocols were noted.

SAPRC/UC Davis PAH Intercomparison

In the October 1996 Pretest, three samples were taken: a single-cycle sample and two two-cycle samples. One of the two-cycle samples was allocated for a SAPRC-UCD intercomparison analysis. The other two samples were allocated to an exploratory analysis to determine how much sample would be required for the main study.

The two filters (front and back) for the intercomparison sample were cut in half and SAPRC retained half of each filter and the remaining halves were shipped to UCD. First, the total weight of the particulate matter was determined by weighing. Immediately before cutting each filter was weighed and after cutting the two halves were weighed to determine the amount of particulate matter represented by each half.

The results of this intercomparison are given in Table 3-7 and show good agreement between the two laboratories for the PAH quantified. Further intercomparisons of results where individual semi-volatile PAH were measured independently by the two laboratories are discussed in the body of the report.

Table 3-5. Emission Rates for Polycyclic Aromatic Hydrocarbons.

PAH	PRE-1993 FUEL			LOW AROMATIC FUEL			REFORMULATED FUEL		
	338H2,H3	338H4,H5	338H6,H7	346H5,H6	347H3,H4	347H5,H6	351H3,H4	352H3,H4	353H5,H6
	µg/bhp-hr	µg/bhp-hr	µg/bhp-hr	µg/bhp-hr	µg/bhp-hr	µg/bhp-hr	µg/bhp-hr	µg/bhp-hr	µg/bhp-hr
2,3,5-trimethylnaphthalene[a,b]	289.12	278.60	283.31	15.49	12.07	16.74	58.94	56.40	53.31
phenanthrene[c]	332.81	347.09	330.23	152.05	178.86	151.84	173.66	210.89	277.64
anthracene[d]	37.26	39.50	39.92	16.73	20.89	18.01	20.33	24.43	33.72
Me-phenanthrenes/anthracenes[c,e]	313.02	343.10	337.86	26.76	24.70	24.05	90.01	101.44	144.50
fluoranthene[d]	137.03	122.55	125.77	124.29	153.31	119.49	95.31	126.50	147.40
pyrene[d]	210.44	177.60	191.05	195.57	253.81	184.18	163.44	217.87	239.15
benzo[c]phenanthrene	3.26	3.05	2.78	1.65	1.89	1.67	1.31	1.49	1.82
benzo[ghi]fluoranthene[f]	27.93	23.40	23.20	17.14	21.30	18.35	14.61	16.98	19.22
cyclopenta[cd]pyrene	25.71	17.51	21.11	24.04	29.74	24.67	17.99	20.87	24.89
benz[a]anthracene	16.19	14.87	18.19	10.74	11.62	9.34	8.17	12.51	12.19
chrysene + triphenylene[g]	17.14	15.82	19.11	9.94	10.98	10.21	9.08	14.11	13.41
benzo[b+j+k]fluoranthene[g]	30.93	26.95	35.28	21.09	23.37	25.04	20.94	36.76	29.85
benzo[e]pyrene	17.07	13.83	19.22	13.57	16.08	14.00	13.54	24.69	18.73
benzo[a]pyrene	21.39	16.82	23.15	14.90	18.02	16.53	14.59	26.05	21.14
perylene	4.55	3.35	5.05	2.92	4.38	3.82	2.95	5.25	4.36
indeno[1,2,3-cd]fluoranthene	0.41	0.33	0.28	0.24	0.19	0.22	0.17	0.17	0.17
benzo[c]chrysene	0.28	0.24	0.34	0.21	0.13	0.22	0.11	0.13	0.19
dibenz[a,j]anthracene	0.89	0.99	0.92	0.65	0.45	0.56	0.57	0.69	0.75
indeno[1,2,3-cd]pyrene	19.99	16.51	21.84	16.23	12.33	13.57	14.26	32.12	20.10
dibenz[a,h + a,c]anthracene[g]	1.53	1.40	1.70	0.94	0.73	0.93	0.90	2.22	1.34
benzo[b]chrysene	0.39	0.41	0.39	0.21	0.13	0.12	0.22	0.28	0.32
benzo[ghi]perylene	50.47	38.97	58.09	48.15	35.51	35.77	39.09	90.44	52.70
coronene	13.04	8.33	7.10	5.04	4.42	5.33	5.98	9.14	7.32
dibenzo[a,l]pyrene	3.28	2.84	2.39	1.42	1.24	1.11	1.81	2.35	2.77
dibenzo[a,e]pyrene	1.40	1.08	0.83	0.68	0.60	0.56	0.96	1.25	1.19
dibenzo[a,i]pyrene	1.14	0.85	0.73	0.18	0.34	0.31	0.55	0.76	0.83
dibenzo[a,h]pyrene	1.62	1.22	1.15	0.83	0.75	0.68	0.61	0.91	1.00

Table 3-7. Emission Rates for Polycyclic Aromatic Hydrocarbons (cont.).

[a] Lower limit based on summing amounts on front PUF and back PUF (amount on filter negligible).

[b] The area of the molecular ion peak (m/z 170) and the response factor for 2,3,5-trimethylnaphthalene relative to deuterated phenanthrene were used to quantify 2,3,5-trimethylnaphthalene and a co-eluting isomer.

[c] Sum of amounts on filter, front PUF and back PUF.

[d] Sum of amounts on filter and front PUF; negligible amount found on back PUF.

[e] The areas of the molecular ion of the five isomers present were summed and the response factor for 1-methylphenanthrene relative to deuterated phenanthrene was used to quantify all isomers.

[f] Standard not available, response factor for cyclopenta[cd]pyrene relative to deuterated chrysene used for quantification.

[g] Co-eluting isomers.

Table 3.6. Emission Rates for Nitro-Polycyclic Aromatic Hydrocarbons.

Nitro-PAH	PRE-1993 FUEL			LOW AROMATIC FUEL			REFORMULATED FUEL		
	338H2,H3 µg/bhp-hr	338H4,H5 µg/bhp-hr	338H6,H7 µg/bhp-hr	346H5,H6 µg/bhp-hr	347H3,H4 µg/bhp-hr	347H5,H6 µg/bhp-hr	351H3,H4 µg/bhp-hr	352H3,H4 µg/bhp-hr	353H5,H6 µg/bhp-hr
1-nitronaphthalene	0.53	0.53	0.50	0.34	0.31	0.31	0.44	0.48	1.07
2-nitronaphthalene	1.50	1.53	1.51	0.64	0.68	0.74	1.13	1.17	1.80
methylnitronaphthalenes	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2-nitrobiphenyl	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
4-nitrobiphenyl	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
5-nitroacenaphthene	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2-nitrofluorene	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
9-nitroanthracene[a]	0.56	0.62	0.50	0.56	0.54	0.53	0.30	0.28	0.44
1-nitropyrene	2.10	2.13	1.64	2.00	2.20	2.01	1.23	2.08	1.61
3-nitrofluoranthene	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
4-nitropyrene	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
7-nitrobenz[a]anthracene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-nitrochrysene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-nitrobenzo[a]pyrene	0.32	0.39	0.22	0.47	0.41	0.39	0.31	0.45	0.43

[a]For the Pre-1993 Fuel and the Reformulated Blend, interferences prevented quantification using the molecular ion at m/z 223 and the $[M-NO]^+$ fragment ion was used.

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Table 3-7. PAH Measured on Intercomparison Filter.

Polycylic Aromatic Hydrocarbon	SAPRC ng/mg	UCD ng/mg	% Difference[a]
phenanthrene	90	110	19
anthracene	18	26	35
Me-phenanthrenes/anthracenes	133	169	24
fluoranthene	231	262	13
pyrene	448	556	21
benz[a]anthracene	97	-	-
chrysene + triphenylene	75	-	-
sum of 228 dalton species[b]	172	189	9
benzo[b+j+k]fluoranthene	160	179	11

[a]Calculated as [(UCD value - SAPRC value)/ Average value] x 100.

[b]At SAPRC separate values determined for 228 Dalton species benz[a]anthracene and chrysene + triphenylene.

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3.9 NITROSAMINE QUALITY ASSURANCE

Introduction

A screening test for nitrosamine was conducted at the MTA facility. Nitrosamine analysis was performed by Lancaster Laboratories. A summary of the QA procedures are given below.

Blanks

Trip blank. One trip blank was collected. A capped Thermosorb-N cartridge was taken to the MTA facility. The cartridge remained at the facility until Nitrosamine sampling was completed. The trip blank was sent along with the samples to Lancaster laboratories for analysis. Listed in Table 3-8 are tunnel and trip blank results.

Table 3-8. Tunnel and Trip Blanks Results

Nitrosamine	Trip Blank (ng/cart)	Tunnel Blank (ng/cart)
NDMA	<20	<20
NDEA	<20	<20
NDPA	<20	<20
NDBA	<30	<30
NPIP	<20	<20
NPYR	<20	<20
NMOR	<20	<20

Calibration Standards

All nitrosamine certified standards were obtained from Chem Services.

Laboratory control spikes

Laboratory control spikes LC1 and LC2 were run with each batch of samples. Two Thremosorb-N samples were each spiked with 50 ppb of nitrosamines. The relative percent difference between the two samples must be within 20%. Analysis of samples could be done when laboratory check samples were within 20%. If the difference is outside the control range

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the problem must be corrected before the samples are run. All samples that were reported were within the 20% cutoff criteria.

Replicates

Duplicate exhaust samples from the reformulated fuel and pre-1993 fuel were taken. Results are presented in Table 3 of the Results section in the main body of the report. Duplicate values in the study were near or at the detection limit and were below CARB's Monitoring Laboratory Division Quality Assurance section recommended levels for comparision. Standard laboratory practices as recommended by CARB requires the comparision of duplicate when values are greater or equal to five times the LOD.

Limit of Detection (LOD) and Calibration Curve.

The limit of detection was defined as 3:1 signal to noise.

The five point calibration curve ranged from 25 ppb to 500 ppb.

To ensure the instrument was in control the following procedure was run prior to the analysis of each batch of samples.

A 5 point calibration curve must be run prior to analysis of a batch of samples.

laboratory control spikes LC1 and LC2 must be within 20% prior to the analysis of samples.

Instrument Maintenance and Modification Summary

The laboratory did not report any major maintence or modification during the study.

Summary of Departures from Current Method and SOP

OSHA method 27 was used to analyze nitrosamines. One departure from the method was to replace the column specified in the method with a Restek Stablewax .53 ID 30 meter column to improve chromatography.

3.10 VAPOR PHASE PAH QUALITY ASSURANCE

Introduction

A test for vapor-phase PAHs was conducted at the MTA facility. Vapor phase PAH sampling and analysis was performed by UCD. Both high volume and low volume samplers were used to collect PAHs. Analysis of samples was performed by UCD. A summary of the QA procedures are given below.

Trip Blanks.

Two trip blank trains were collected, one for the high volume sampler and one for the low volume sampler. The train consisted of two filters and a sorbant containing both PUF and XAD. Prior to sampling the high volume sorbant cartridges and filters were wrapped in aluminum foil. Prior to sampling the low volume sorbant cartridges were sealed in Teflon containers with screw caps and the filters were placed between glassine paper and stored in a box. The filters and sorbant modules were taken to the MTA facility. The cartridge remained at the facility until PAH sampling was completed. The trip blank along with the samples were shipped and stored at ^{0}C at UCD until analysis.

Tunnel Blanks.

Three low volume and three high volume tunnel blanks were collected from the tunnel while the CVS fan on the tunnel was turned on and the engine turned off. One low volume and one high volume tunnel blank was taken prior to the start of the exhaust sampling with the diesel engine running on a new fuel. Given in Tables 3-9 and 3-10is the analysis of the tunnel and trip blanks.

Table 3-9. Blank levels in XAD Samples

Sample ID	Tr157	UL100	UL120	UL134	TR1PV	UL2PV	UL3PV	UL4PV
Type	trip	tunnel	tunnel	tunnel	trip	tunnel	tunnel	tunnel
	mass ug*	mass ug	mass ug	mass ug	mass ug	mass ug	mass ug	mass ug
naphthalene	19.5	17.7	25.7	29.3	30.5	37.5	38.6	15.1
2-methyl naphthalene	0.2	0.3	0.4	0.4	0.2	1.7	2.2	2.3
1-methyl naphthalene	0.2	0.3	0.4	0.4	0.2	1.0	1.3	1.3
biphenyl	0.1	0.1	0.1	0.1	0.4	0.4	0.7	0.7
2,6-dimethyl naphthalene	0.3	0.5	0.5	0.4	0.3	0.8	0.9	1.1
acenaphthylene	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0
acenaphthene	0.7	0.8	0.7	0.7	0.9	1.3	1.2	1.1
2,3,5-trimethyl naphthalene	1.9	1.9	1.5	1.4	1.4	1.5	1.6	1.6
fluorene	0.6	0.7	0.6	0.5	0.8	0.9	0.8	0.7
1-methyl phenanthrene	0.7	0.3	0.2	0.2	0.2	0.2	0.4	0.2
phenanthrene	3.1	2.0	1.6	1.2	2.3	1.6	2.1	1.8
anthracene	0.6	0.3	0.2	0.2	0.4	0.3	0.4	0.3
fluoranthene	0.2	0.1	0.1	0.0	0.2	0.1	0.1	0.1
pyrene	0.4	0.3	0.1	0.0	0.4	0.2	0.3	0.1

* µg = micrograms per sample

Table 3-10. Blank levels in PUF Samples.

Sample ID:	TR157	UL101	Ul120	UL134	TR1PV	UL2PV	UL3PV	UL4PV
Type:	trip	tunnel	tunnel	tunnel	trip	tunnel	tunnel	tunnel
	mass ug*	mass ug	mass ug	mass ug	mass ug	mass ug	mass ug	mass ug
naphthalene	0.0	0.2	0.2	0.2	0.1	0.1	0.2	0.2
2-methyl naphthalene	0.0	0.3	0.2	0.3	0.1	0.1	0.2	0.2
1-methyl naphthalene	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.1
biphenyl	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.1
2,6-dimethyl naphthalene	0.0	0.1	0.1	0.1	0.1	0.1	0.2	0.2
acenaphthylene	0.0	0.0	0.1	0.1	0.0	0.1	0.2	0.1
acenaphthene	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.0
2,3,5-trimethyl naphthalene	0.0	0.1	0.1	0.1	0.0	0.1	0.2	0.1
fluorene	0.0	0.1	0.1	0.0	0.0	0.1	0.1	0.1
1-methyl phenanthrene	0.0	0.2	0.3	0.1	0.0	0.2	0.3	0.1
phenanthrene	0.1	1.0	1.2	0.7	0.1	0.6	1.0	0.4
anthracene	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.1
fluoranthene	0.0	0.2	0.2	0.1	0.0	0.2	0.5	0.6
pyrene	0.0	0.2	0.2	0.2	0.0	0.2	0.8	1.0

* µg = micrograms per sample

Trip and tunnel blank effects are discussed in the main body of the report. Any sample where the tunnel or trip blank exceeds 20% of the sample values are highlighted in bold.

Calibration standards.

PAH NIST standard reference material 2260 was used for calibration. Deuterated standard were obtained from Cambridge Isotope Laboratories and Accustandards.

Instrument tune

The MS is tuned (calibrated) prior to running a batch of samples.

Multi-point calibration and limit of detection

A 5 point multi-point calibration curve was performed prior to the analysis of each batch of samples. The calibration range was from 25 pg/ul to 1000 pg/ul. R values were .99 or better. The reporting limit was based on the lowest level calibration standard (25 pg/ul) run during the calibration curve.

Reagent Blank

Prior to analysis of a batch of samples a reagent blank is performed to determine PAH background levels in the solvent.

Control

A midpoint calibration standard was run after every 10 samples to determine the instrument drift. If calibration checks differed from the initial calibration by more than 30% the samples were reanalyzed. If the drift exceeded 30% the samples were rerun and analyzed. Sample set run on 6/7/97 exceeded control limit and were reanalyzed. H110X1, H127XL, H145X, H150X, H170 were rerun on 8/28/97 and UL100X, Ul120X, UL134X, and TR157 were reun on 12/22/87.

Sample replicates

For the low volume sampler two diesel exhaust samples were taken for the reformulated and pre-1993 fuel. For the low aromatic fuel one diesel exhaust sample was collected.

For the high volume sampler one diesel exhaust sample per fuel was taken.

Analytical replicates

All samples were analyzed in duplicate except diesel particulate samples H170 and H127 results were based on single analysis.

Instrument Maintenance and Modification summary

Listed in the materials and methods section is the protocol for the analysis of the samples were not run unless the instrument passed tune and was calibrated with a 5 point calibration curve. Columns were clipped when tailing affected calibration or when there was target analytes were not adequately resolved. When tailing did not significantly improve after clipping the column or when the column was to short to adequately separate benz[a]anthracene from chrysene then the column was replaced. Septa and liners and gold seals in the injector were replace routinely during the study.

Summary of Departures

No standardized test method were available for the analysis of diesel samples. Basic test methods were developed by UCD in previous contracts. Protocols are summarized in the materials and methods section and no departures of these protocols were noted. Typically particulate samples are run with a multipoint calibration but since there was only 3 samples a single mid-point calibration standard was run for particulate filter samples H3, H4, H6. Since the multi-point calibration curves are quite stable a mid-point calibration was considered adequate.

Audits and Round Robin

Two laboratories were to conduct PAH analysis. Two determine comparability of the two labs a diesel particulate filter collect by SAPRC during the pre-test was divided in half with one-half sent to UCD for analysis and the other half analyzed by SAPRC. The comparison between the

analysis show good agreement. Results presented in Table 3-11 are in microgram per milligram of diesel particulate matter.

Table 3-11. SAPRC and UCD PAH results of a split diesel particulate filter

PAH	SAPRC (ng/mg)	UCD (ng/mg)
phenanthrene	90	110
anthracene	18	26
Me-phenanthrnes/anthracenes	133	169
fluoranthene	231	262
pyrene	446	556
benz[a]anthracene	97	
chrysene + triphenylene	76	
sum of 228 dalton species*	172	189
benzo[b+j+k] fluoranthene	180	179

* UCD analysis of chrysene, triphenylene, and benz[a]anthracene were not chromatographically resolved and are reported as one number.

UCD and SAPRC interlaboratory comparison High volume sampler. Two laboratories were involved in this study. SAPRC conducted PAH sampling using a high volume sampler consisting of a two filters and PUF sorbant. The sampling was designed to trap PAHs of three rings or more. UCD conducted PAH sampling using both high volume and low volume samplers consisting of two filters, a PUF sorbant and XAD sorbant. UCD was responsible for sampling for volatile PAHs (2-4 ring). The results of the comparison are given in the discussion section in the main body of the report.

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3.11 DIOXIN QUALITY ASSURANCE PROCEDURES

Introduction

A screening test for PCDDs and PCDFs was conducted at the MTA facility. PCDD and PCDF analysis was performed by Alta Laboratories. A summary of the QA procedures are given below.

Blanks and Spikes

Laboratory Solvent Blank Prior to analysis of a batch of samples a laboratory solvent blank is performed to determine PCDF and PCDF background levels in the solvent.

Laboratory Method Blanks. Prior to the analysis of a batch of samples a laboratory method blank is analyzed. The method blank is used to determine background levels in the analytical procedure. A suitable matrix is selected for the blank. The blank is then prepped identically to the samples and the blank is analyzed for background contamination. Listed in Table 3-12 is the summary of the matrix used for the method blanks.

Table 3-12. Summary of method blank matrixes for each sample type.

Sample Type	Matrix
Emission	PUF
Tunnel Particulate Matter	Ottawa Sand
Diesel Fuel	Extraction solvent (DCM)
Diesel Oil	Extraction solvent (DCM)

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Presented in Table 3-13 are the method blank results. All compound in the method blanks were below the detection with the exception of OCDD. The method and tunnel blanks are discussed in Table IV-7 and are discussed in the body of the report. Concentrations and detection limits are given in picograms per sample.

Table 3-13. Summary of method blank results

Method Blanks

Sample ID:	2950		3160		3214		3257	
Date Analyzed:	10/10/96		12/17/96		12/30/96		1/13/97	
Compound	Conc.	D.L.	Conc.	D.L.	Conc.	D.L.	Conc.	D.L.
2,3,7,8-TCDD	ND	2.2	ND	1.9	ND	2.1	ND	4.5
Total TCDD1	ND	2.2	ND	1.9	ND	3.5	ND	4.5
1,2,3,7,8-PeCDD	ND	2.6	ND	0.68	ND	1.5	ND	5
Total PeCDD	ND	2.6	ND	0.68	ND	1.5	ND	5
1,2,3,4,7,8-HxCDD	ND	2.5	ND	1.1	ND	1.8	ND	5.2
1,2,3,6,7,8-HxCDD	ND	2.2	ND	1	ND	1.8	ND	5
1,2,3,7,8,9-HxCDD	ND	2.4	ND	0.94	ND	1.6	ND	4.7
Total HxCDD	ND	2.5	ND	1.1	ND	1.8	ND	5.2
1,2,3,4,6,7,8-HpCDD	ND	4.9	ND	2.8	ND	1.9	ND	20
Total HpCDD	ND	4.9	ND	2.8	ND	1.9	ND	20
OCDD	10		14		5.7		57	
2,3,7,8-TCDF	ND	4.3	ND	1.5	ND	1.4	ND	6.9
Total TCDF	ND	4.3	ND	1.5	ND	1.4	ND	6.9
1,2,3,7,8-PeCDF	ND	2.9	ND	0.73	ND	1.7	ND	6
2,3,4,7,8-PeCDF	ND	2.9	ND	0.71	ND	1.7	ND	6
Total PeCDF	ND	2.9	ND	0.73	ND	1.7	ND	6
1,2,3,4,7,8-HxCDF	ND	1.2	ND	0.4	ND	0.69	ND	3.2
1,2,3,6,7,8-HxCDF	ND	1	ND	0.35	ND	0.6	ND	2.7
2,3,4,6,7,8-HxCDF	ND	0.86	ND	0.41	ND	0.72	ND	3.2
1,2,3,7,8,9-HxCDF	ND	1	ND	0.47	ND	0.82	ND	3.6
Total HxCDF	ND	1.2	ND	0.47	ND	0.82	ND	3.6
1,2,3,4,6,7,8-HpCDF	ND	3.2	ND	0.87	ND	0.87	ND	4.1
1,2,3,4,7,8,9-HpCDF	ND	4.2	ND	0.67	ND	1.1	ND	5
Total HpCDF	ND	4.2	ND	0.87	ND	1.1	ND	5
OCDF	ND	4.5	ND	2.1	ND	3.2	ND	25

Table 3-13. cont.

Laboratory ID:	3404		3404		3605	
Matrix:	Fuel oil		Carbon		Carbon	
Date Analyzed:	3/5/97		3/5/97		3/5/97	
Compound	Conc (pg/L)	D.L. (pg/L)	Conc (pg/L)	D.L. (pg/L)	Conc. (pg/g)	D.L. (pg/g)
2,3,7,8-TCDD	ND	6.4	ND	2.9	ND	7.9
Total TCDD1	ND	6.4	ND	2.9	ND	27
1,2,3,7,8-PeCDD	ND	3.7	ND	2.6	ND	12
Total PeCDD	ND	3.7	ND	2.6	ND	12
1,2,3,4,7,8-HxCDD	ND	3.7	ND	2.1	ND	21
1,2,3,6,7,8-HxCDD	ND	4.1	ND	2.3	ND	23
1,2,3,7,8,9-HxCDD	ND	3.5	ND	2	ND	21
Total HxCDD	ND	4.1	ND	2.3	ND	23
1,2,3,4,6,7,8-HpCDD	ND	9.4	6.5		ND	26
Total HpCDD	ND	9.4	11		ND	26
OCDD	66		88		150	
2,3,7,8-TCDF	ND	5.1	ND	1.6	ND	9.7
Total TCDF	ND	5.1	ND	1.6	ND	9.7
1,2,3,7,8-PeCDF	ND	6	ND	1.8	ND	15
2,3,4,7,8-PeCDF	ND	5.7	ND	1.7	ND	15
Total PeCDF	ND	6	ND	1.8	ND	15
1,2,3,4,7,8-HxCDF	ND	1.6	ND	2.4	ND	10
1,2,3,6,7,8-HxCDF	ND	1.5	ND	2.2	ND	10
2,3,4,6,7,8-HxCDF	ND	17	17		49	
1,2,3,7,8,9-HxCDF	ND	2	ND	2.6	ND	12
Total HxCDF	ND	17	17		49	
1,2,3,4,6,7,8-HpCDF	ND	2.4	ND	0.95	ND	14
1,2,3,4,7,8,9-HpCDF	ND	3.4	ND	1.3	ND	15
Total HpCDF	ND	3.4	ND	1.3	ND	15
OCDF	ND	6.4	ND	2.9	ND	39

Concentrations and detection limits are given in picograms per liter of sample.

Tunnel Blanks. Two tunnel blanks were collected from the primary dilution tunnel while the CVS fan on the tunnel was turned on and the engine was not running. A tunnel blank was collected prior to diesel exhaust sampling of the reformulated and pre-1993 fuels. Discussion of tunnel blanks is given in IV- 5 of the Results section.

Recovery Spikes. Prior to sampling each sample and tunnel blank is spiked with a mix of isotopically label standards. Recovery of internal standards are considered in perfomance if recoveries are between 60-140%. If recovery of spiked internal standards are low this may indicate some problem in sampling such as breakthrough. Listed in Table IV-12 are the spike recoveries.

Calibration

Certified PCDD and PCDF standards and istopically labeled PCDF and PCDD standards obtained from Cambride Isotope Laboratories were used for calibration and spiking.

To ensure that the GC/HRMS is in control the following procedure is run with each batch of samples.

Initial calibration. Once every six month a 5 point calibration curve is performed to demonstrate linearity and to update the calibration.

Instrument tune. The HRMS is tuned (calibrated) prior to running a batch of samples.

Column performance standard/window define mix. A mix of PCDDs and PCDDs is injected to GC/HRMS to determine if the 2,3,7,8 TCDD peak is adequately resolved (25% valley) from other peaks. The mix also contains the first and last eluting isomer in each MS window to determine that the MS windows are properly set.

Continuing mid-point calibration. A mid-point calibration is performed daily. If the average response factor is within 25% of the initial multipoint average response factor the analysis can begin. If it is outside of the range the problem must be

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resolved and the daily calibration must be repeated. If the problem cannot be resolve a new 5 point calibration curve must be conducted.

Method blank. A method blank is run prior to the analysis of a batch of samples.

Laboratory Control Samples. Laboratory control samples like the method blank use a representative matrix similar to the sample analyzed. The matrix is spiked with native PCDDs and PCDFs and the control samples undergo the same analytical procedure as the sample. The relative percent difference between the two control are reported. Listed in Table 3 are the results of the LC samples conducted for these samples.

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Control

Presented in Table 3-14 are the laboratory control samples results.

Table 3-14. Summary of Laboratory Control Samples

Laboratory Control Spikes

	10/10/96			12/16/96		
Laboratory ID:	2950			3214		
	LCS1 %R	LCS2 %R	%RLP	LCS1 %R	LCS2 %R	%RLP
2,3,7,8-TCDD	97	95	2.1	90	88	2.2
1,2,3,7,8-PeCDD	100	98	2	98	95	3.1
1,2,3,4,7,8-HxCDD	97	101	4	94	95	1.1
1,2,3,6,7,8-HxCDD	113	106	6.4	97	97	
1,2,3,7,8,9-HxDCC	108	103	4.7	96	97	1
1,2,3,4,6,7,8-HpCDD	98	96	2.1	92	90	2.2
OCDD	102	99	3	94	93	1.1
2,3,7,8-TCDF	93	92	1.1	87	85	2.3
1,2,3,7,8-PeCDF	97	95	2.1	92	91	1.1
2,3,4,7,8-PeCDF	96	95	1	91	87	4.5
1,2,3,4,7,8-HxCDF	96	96	0	99	97	2
1,2,3,6,7,8-HxCDF	108	104	3.8	98	97	1
2,3,4,6,7,8-HxCDF	102	102	0	99	97	2
1,2,3,7,8,9-HxCDF	114	114	0	106	103	2.9
1,2,3,4,6,7,8-HpCDF	99	97	2	91	89	2.2
1,2,3,4,7,8,9-HpCDF	108	110	1.8	95	90	5.4
OCDF	104	101	2.9	92	91	1.1

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Table 3-14 cont.

Laboratory Control Spikes

	12/30/96			1/13/97		
Laboratory ID	3214			3257		
	LCS1 %R	LCS2 %R	RPD% %RLP	LCS1 %R	LCS2 %R	RPD% %RLP
2,3,7,8-TCDD	93	92	1.1	86	89	3.4
1,2,3,7,8-PeCDD	96	95	1	93	89	4.4
1,2,3,4,7,8-HxCDD	92	91	1.1	88	81	8.0
1,2,3,6,7,8-HxCDD	119	109	8.8	93	96	3.2
1,2,3,7,8,9-HxDCC	102	102	0	74	79	6.5
1,2,3,4,6,7,8-HpCDD	97	97	0	95	96	1
OCDD	100	99	0	100	100	0
2,3,7,8-TCDF	90	93	3.3	84	87	3.5
1,2,3,7,8-PeCDF	99	98	1	92	91	1.1
2,3,4,7,8-PeCDF	101	99	2	86	88	2.3
1,2,3,4,7,8-HxCDF	95	99	4.1	91	90	1.1
1,2,3,6,7,8-HxCDF	110	113	2.7	93	94	1.1
2,3,4,6,7,8-HxCDF	106	106	0	69	74	7
1,2,3,7,8,9-HxCDF	110	112	1.8	77	80	3.8
1,2,3,4,6,7,8-HpCDF	101	105	3.9	94	94	0
1,2,3,4,7,8,9-HpCDF	103	109	5.7	90	98	8.5
OCDF	111	118	6.1	111	109	1.8

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Table 3-14 cont.

Laboratory Control Spikes

	3/5/97			3/4/97		
Laboratory ID:	3404			3404		
	LCS1 %R	LCS2 %R	%RLP	LCS1 %R	LCS2 %R	%RLP
2,3,7,8-TCDD	85	88	3.5	86	89	3.4
1,2,3,7,8-PeCDD	100	104	2	94	100	6.2
1,2,3,4,7,8-HxCDD	92	96	4.3	93	95	2.1
1,2,3,6,7,8-HxCDD	93	95	2.1	91	95	4.3
1,2,3,7,8,9-HxDCC	91	93	2.2	89	92	3.3
1,2,3,4,6,7,8-HpCDD	96	99	3.1	93	96	3.2
OCDD	91	95	4.3	91	95	4.3
2,3,7,8-TCDF	89	89	0	89	92	3.3
1,2,3,7,8-PeCDF	95	99	4.1	94	98	4.2
2,3,4,7,8-PeCDF	96	102	6.1	97	100	3
1,2,3,4,7,8-HxCDF	91	93	2.2	90	92	2.2
1,2,3,6,7,8-HxCDF	92	95	3.2	89	93	4.4
2,3,4,6,7,8-HxCDF	88	92	4.4	86	91	5.6
1,2,3,7,8,9-HxCDF	92	95	3.2	90	93	3.3
1,2,3,4,6,7,8-HpCDF	90	93	3.3	88	91	3.4
1,2,3,4,7,8,9-HpCDF	89	92	3.3	88	90	2.2
OCDF	103	108	4.7	108	113	4.5

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Table 3-14 cont.

Laboratory Control Spikes

	4/25/97		
Laboratory ID:	3605		
	LCS1	LCS2	RPD%
	%R	%R	%RPD
2,3,7,8-TCDD	92	98	6.3
1,2,3,7,8-PeCDD	104	110	5.6
1,2,3,4,7,8-HxCDD	90	98	8.5
1,2,3,6,7,8-HxCDD	89	93	4.4
1,2,3,7,8,9-HxDCC	83	93	11
1,2,3,4,6,7,8-HpCDD	96	102	6.1
OCDD	92	98	6.3
2,3,7,8-TCDF	94	99	5.2
1,2,3,7,8-PeCDF	93	100	7.3
2,3,4,7,8-PeCDF	94	99	5.2
1,2,3,4,7,8-HxCDF	96	101	5.1
1,2,3,6,7,8-HxCDF	97	103	6
2,3,4,6,7,8-HxCDF	94	98	4.2
1,2,3,7,8,9-HxCDF	97	105	7.9
1,2,3,4,6,7,8-HpCDF	97	103	6
1,2,3,4,7,8,9-HpCDF	97	104	7
OCDF	102	107	4.8

PRELIMINARY DRAFT

Replicates

No laboratory replicates were performed however three replicates diesel exhaust samples were collected for the engine using both reformulated and pre-1993 fuel.

Limit of Detection

LODs are based on signal to noise ratio 2.5:1 of the analyte to background noise. LODs are performed on all the analytes for every analysis.

Instrument Maintenance and Modification Summary

No modifications to the methods given in the Chemical Analysis (section C) were made during the study.

Summary of Departure

No departures from methods and protocols listed in the materials and methods section were noted by the Alta Laboratory

3.12 Bioassy Analyses

Introduction

Bioassay analyses were conducted on emission samples from all fuels tested. The bioassay uses bacteria as an indicator organism and detects damage to DNA (genotoxicity) by chemical compounds and complex environmental mixtures. The amount of damage to DNA is reported as the number of mutant organisms, referred to as "revertants".

Blanks

There were a number of blank samples incorporated into the analyses. These were measured to determine any background levels of genotoxic compounds present. The total number of blank samples represented at 1 blank sample for every 3 fuel samples collected and extracted.

PRELIMINARY DRAFT

Trip blanks -- pre-cleaned filters and sorbents that were identical to those used to collect sample were extracted, handled, stored and tested in bioassay exactly as the samples. There were 2 trip blanks extracted.

Field blanks -- pre-cleaned filters and sorbents were used to collect blank dilution tunnel samples. Samples were extracted, handled, stored and tested in bioassay exactly as the samples. There were 2 field blanks collected and extracted.

Bioassay method blanks -- solvent controls are incorporated into the analyses to determine any background level of genotoxic activity. These are incorporated for each experiment and for every tester organism (TA98 and TA100) tested and for every metabolic enzyme condition tested (with and without S9). A statistical summary of these are provided in the "Controls" section below.

The blanks were handled and tested in an identical procedure as the samples. The trip and tunnel blanks for the particulate matter had activity similar to the negative control values compared to the samples. The trip and field blanks for the vapor-phase samples had little or no activity above that detected in the background samples. Trip and field blank samples for the fractionated PUF samples had measurable levels of activity in certain fractions, due possibly to compounds present in the tunnel, or present in the pre-cleaned C18 or silica SPE columns used.

Calibration

The bioassay is checked for reproducible responsiveness at each analyses by examining a number of factors. The test organisms used are also checked routinely for maintaining specific genes necessary for detecting genotoxic compounds.

Background level of genotoxic activity -- is measured with the solvent that is used to dissolve the extract from the filter or sorbent. This is usually dimethyl sulfoxide (DMSO). Each tester strain used has a historical background level of revertants (mutant) organisms.

Level of genotoxic activity with positive controls. -- is measured for each tester organism with known genotoxic compounds such as benzo(a)pyrene.

Test of specific genes present in the tester organisms. Known genes called genetic markers are routinely tested with every bioassay. These genes are important for the sensitivity and specificity of the strains.

Compounds or complex mixtures are considered genotoxic if there is a linear dose response curve and if the level of activity is elevated at least 2 times over the background level of genotoxic activity.

Linear dose-response curves were observed for particle and vapor-phase samples. All gene markers for all experiments were normal.

Controls

There are a number of controls used routinely in the bioassay.

Negative control -- or solvent control. As mentioned above, the solvent used to dissolve the genotoxic compounds is tested without additional compounds added to measure the background level of genotoxic activity. Mean (± SD) negative control values for each strain with and without metabolic enzymes added (± S9 added) were:

TA98 (+S9):	16 (± 6), DMSO, n = 10 separate experiments, triplicate plates for each experiment.
TA98 (-S9):	15 (±7), DMSO, n = 9 separate experiments, triplicate plates for each experiment.
TA100 (+S9):	71 (±9), DMSO, n = 7 separate experiments, triplicate plates for each experiment.
TA100 (-S9):	63 (±6), DMSO, n = 8 separate experiments, triplicate plates for each experiment.

Positive control -- or genotoxic compound control. The positive control is routinely tested with each experiment. The positive control is an indicator of the response of the tester strain.

TA98 (+S9):	414 (±41), benzo(a)pyrene, n = 10 separate experiments, triplicate plates for each experiment.
TA98 (-S9):	940 (±43), 2-nitrofluorene, n = 9 separate experiments, triplicate plates for each experiment.
TA100 (+S9):	776 (±99), benzo(a)pyrene, n = 7 separate experiments, triplicate plates for each experiment.
TA100 (-S9):	712 (±13), nitroquinoline-n-oxide, n = 8 separate experiments, triplicate plates for each experiment.

All positive and negative controls were within historical values for this laboratory. The positive controls had standard deviations of 15% or less. The negative controls for TA98 are historically lower than TA100 and were within values normally observed in this laboratory. For example, TA98 (+ S9) had an average background of 16 with SD of 6 (n=10 separate experiments), while TA100 had an average background of 71(+S9) with a standard deviation of 9 for 7 separate experiments. There was one experiment where the background on TA98 was many fold higher than the average. This experiment was repeated and the levels of the background genotoxic activity returned to the average value.

Replicates

Filter and sorbent samples for each fuel were fractionated and each fraction tested in duplicate. All high volume samples represented two consecutive cycles were extracted and tested. Where there is adequate sample for dose-response relationships, at least three doses in duplicate were tested. Positive and negative controls were tested in triplicate for each experiment.

4 Replicate Test Variability

Standard deviations calculated from replicate test data are shown with the emission results data in Chapter 3.0. Table 4-1 shows the pooled estimate of the standard deviations within fuel-type / cycle-type combinations in units of mg/bhp-hr and as a percentage of mean emission rates. The mean rates in this table were obtained by averaging the means of each fuel-type / cycle type combination. The means in this table therefore give equal weight to Cold-Start and Hot-Start emission rates

The table shows that replicate test variability was generally quite low. For species with emission rates above 10 mg/bhp-hr the variabilities range from about 1 to 10%. For the criteria pollutants, the variabilities are slightly larger than the 2% expected based on CFR tolerances, probably indicating small but real variability from run to run. For the remaining species, the run to run variability is about the same or smaller than the variability to be expected from flow rate and analytical precisions, indicating that within the capabilities of the test methods, the runs within a given fuel/cycle type are essentially equivalent.

Table 4-1. Replicate Test Variability

	Mean Rate	Pooled Std. Dev	
Species	mg/bhp-hr	mg/bhp-hr	%
NOx	4692	90	1.9%
THC	490	20	4.0%
CO	2355	111	4.7%
CO2	530567	4828	0.9%
PM	208	11	5.5%
1,3-Butadiene	2.02	0.25	13%
Benzene	6.69	0.72	11%
Toluene	2.08	0.32	15%
Ethylbenzene	0.92	0.53	58%
o-xylene	0.78	0.14	18%
m&p-xylene	1.76	0.39	22%
Styrene	1.45	0.56	39%
Naphthalene	1.48	0.34	23%
Nitrate	0.21	0.05	22%
Sulfate	0.70	0.39	55%
Ammonium	0.44	0.11	25%
Organic Carbon	62.10	6.68	11%
Elemental Carbon	117.69	10.78	9%
Mg	0.07	0.04	55%
Si	0.64	0.10	16%
P	0.08	0.02	29%

S	0.89	0.12	14%
Cl	0.03	0.02	46%
Ca	0.07	0.03	52%
Fe	0.27	0.16	59%
Cu	0.01	0.01	111%
Zn	0.16	0.05	29%
formaldehyde	58.72	3.11	5%
acetaldehyde	19.17	0.97	5%
acrolein	3.43	1.10	32%
acetone	6.43	0.76	12%
propionaldehyde	4.04	0.48	12%
crotonaldehyde	1.71	0.38	22%
methacrolein	0.09	0.27	-
MEK	0.00	0.00	-
butyraldehyde	4.08	1.32	32%
benzaldehyde	1.74	0.83	48%
valeraldehyde	0.82	0.18	23%
tolualdehyde	3.38	0.99	29%
hexaldehyde	0.47	0.14	30%

5 Adequacy of Data for Intended Purpose

All data capture criteria were met. External audits for criteria gases found one problem, but the cause of the problem was identified, corrective actions were taken, and corrected data met audit tolerances. External audits for flow rates were satisfied. Accuracies and precisions met goals. Within fuel/cycle type, variability was low. Computerized data calculations were checked and agreed with results using manual calculations. Raw data to support the results of the study are archived.

No problems have been identified that would affect the adequacy of the data for its intended purpose.

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FUEL PROPERTY TRENDS OF U.S. DIESEL FUELS AND THEIR EFFECTS ON PARTICULATE MATTER IN DIESEL ENGINE EXHAUSTS

SwRI 01-6645-350

Prepared For:

American Petroleum Institute
Washington, D.C.

Prepared By:

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May 1998

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1 EXECUTIVE SUMMARY

The American Petroleum Institute (API) requested a review of fuel property trends in diesel fuels. Of particular interest are the effects of fuel properties on particulate emissions in the exhaust from diesel engines, both for highway use and off-road applications. This paper presents timelines of important variables and gives an outline and brief summary of the literature on particulates. Perhaps as important as the information presented, is the identification of the gap in historical continuity of knowledge about the factors affecting diesel particulates.

The review was based on published information in the technical literature and data in the public domain. The first action was to initiate a literature search at the Southwest Research Institute (SwRI) library. The database search included Chem Abstracts, National Technical Information Service, Engineering Index, and Society of Automotive Engineers databases. The search produced a list of titles which were reviewed, and a selection of the most useful was then converted into a list with more complete information on authors and dates. From that list, the selection considered documents that were available in the library, departmental files, and nearby interlibrary loans. Then the references were obtained and reviewed for inclusion of material for this report.

It would have been desirable to make a review of specific engine types such as low, medium, and high speed engines because emissions are affected by engine variables more than any other variables. Low speed engines are typically used in marine applications. Heavy duty equipment such as trucks and railroad locomotives operate at medium speeds. Light duty vehicles such as automobiles and light trucks have high speed engines. The papers used in the review were limited to light and heavy duty, on-highway engines. Off-road equipment such as construction and power generation could be evaluated along with the relative diesel fuel consumption in a more complete study. The contribution of lubricating oil to particulates should also be of interest; it was mentioned in only one paper reviewed.

The total particulate emissions from all light duty diesel engines is much smaller than from all heavy duty diesel engines. Because of this fact, less research has been done on light duty engines. Three applicable papers were found concerning particulate emissions from light duty engines. The major findings of the review of light duty engine literature were:

• The greatest contributing factor of particulate emissions was the fuel sulfur content. The higher the sulfur content, the higher the particulate emissions.

• Polyaromatic hydrocarbons also contributed to the particulate matter in diesel exhaust. An increase of polyaromatic hydrocarbons in the fuel also increased the particulate emissions.

• Lubricant consumption effects were briefly explored in one paper. The results found that increasing the consumption of lubricating oil helped decrease the particulate emissions.

• The cetane number has a slight effect on particulate emissions. An increase in cetane number slightly decreased particulate emissions.

• The magnitude of change in particulates caused by the above factors depended on the engine operating mode, the load on the engine, and the aromatic structures in the fuel.

Six papers concerning particulate emissions from heavy duty engines were reviewed. The major findings of the review of heavy duty engine literature were:

• Developments in new engine technology have kept pace with several reductions in federal emissions standards for nitrogen oxides and particulate matter in EPA regulations from 1983 to 1993 and the Clean Air Act Amendments from 1994 to 1998.

• Particulate emissions tend to increase with higher sulfur content of diesel fuel. The requirement for maximum 0.05 percent sulfur in highway diesel fuel in both federal and California regulations since 1993 has been a major step in reducing this source of particulates.

• Aromatics also contribute to particulate matter in diesel exhaust by producing sulfur oxides which combine with water in the atmosphere. For this reason, California adopted a maximum of 10 volume percent aromatics content in diesel fuel in 1993. However, the California regulation allowed other fuel formulations if they could show low emissions in a specified engine test. As a result, average California 2-D diesel fuel contains 15-21 volume percent aromatics and is over 50 cetane number.

• Polyaromatic hydrocarbons (PAH) in diesel exhaust are a direct function of the amount of PAH in the diesel fuel.

• Distillation temperature at 90 percent (T_{90}) contributes to particulate matter in the exhaust by addition of higher molecular weight (and sometimes more aromatic) hydrocarbons.

• Soluble organic fractions in particulate emissions increases as a function of sulfur and polyaromatics in diesel fuel.

• Certain oxygen compounds in diesel fuel can significantly reduce particulate emissions.

• Cetane number of the fuel has little or no effect on particulate emissions.

The longer term trend is for reducing diesel particulate emissions by vehicle replacements using new technology engines and the Urban Transit Retrofit Program for city buses.

2 TRENDS IN DIESEL FUEL QUALITY

Periodic surveys of diesel fuel properties are made by organizations which monitor national trends or offer a subscription service. Data from surveys reported by the American Automobile Manufacturers Association (AAMA) were used in this report. Sulfur content and aromatics content are the two properties in the surveys which relate most strongly to particulates in diesel exhaust.

Figure 2-1 shows a plot of the national average values of sulfur and aromatics for No. 2-D Regular diesel fuel from the biannual reports, summer and winter, from 1989 to the end of 1997. Sulfur content ranged from about 0.3 weight percent down to 0.24 weight percent at the end of 1993. The sharp decline in 1994 to about 0.03 weight percent was the result of the change in EPA regulations which required a maximum 0.05 weight percent sulfur content effective October 1, 1993. The regulation was aimed at reducing the sulfur oxides portion of particulates in diesel exhaust. That reduction in sulfur oxides particulates would be proportional to the 88 to 90 percentage reduction in average sulfur fuel content from the previous year.

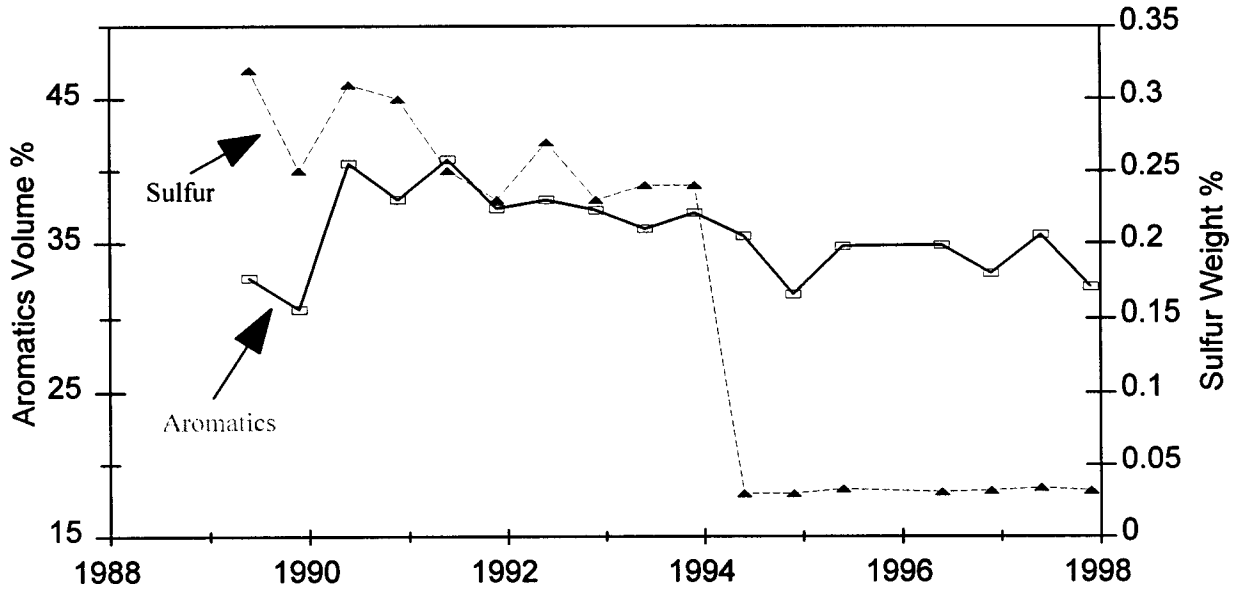


Figure 2-1. National Fuel Survey (2-D Regular) from 1988 to 1997

The EPA regulation included another requirement to equal or exceed 40.0 cetane index. The objective was to put a "cap" on aromatics content at about 35 volume percent. Aromatics are another contributor to particulate emissions. Figure 2-1 shows that the average aromatics in No. 2-D Regular diesel declined from 35-40 volume percent aromatics to 32-35 volume percent after 1993.

Figure 2-2 contains similar data for average No. 2-D Premium diesel fuel. Premium grade differs from Regular grade in having slightly lower sulfur and aromatics contents, lower 90 percent distillation temperature, and a small increase in cetane number. Sulfur content ranged from 0.2 to 0.3 weight percent through 1993 and then dropped to about 0.03 percent in 1994. Aromatic content stayed at approximately 35 volume percent.

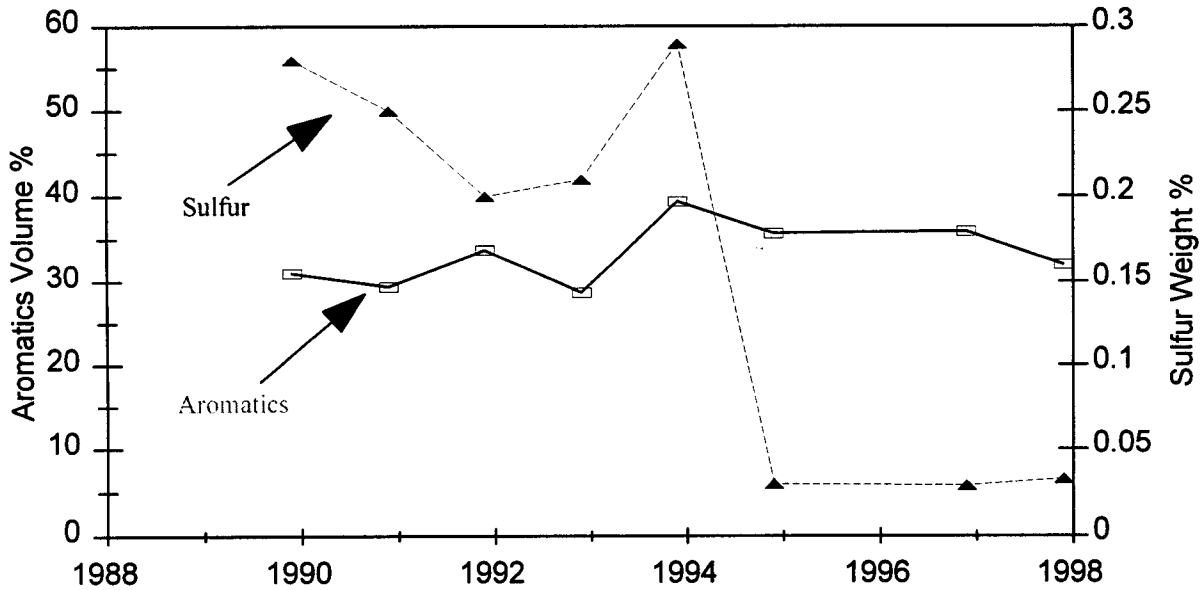


Figure 2-2. National Fuel Survey (2-D Premium) From 1989 to 1997

Figure 2-3 presents analogous data for No. 1-D Regular diesel fuel. No. 1-D diesel has lower distillation temperatures than either grade of No. 2-D and thereby contains less sulfur and aromatics typical of the higher boiling fractions. Cetane number was slightly higher than No. 2-D Regular and is comparable to No. 2-D Premium. No. 1-D Regular prices are usually higher than either No. 2-D grade, and it is used mostly in cold climates and by urban transit buses to reduce exhaust smoke and odor from existing equipment. Demand increases for winter use in colder northern regions, because of better cold flow properties of the No. 1-D grade. Sulfur content dropped to about 0.025 weight percent after 1993. Aromatic content remained at approximately 20 volume percent.

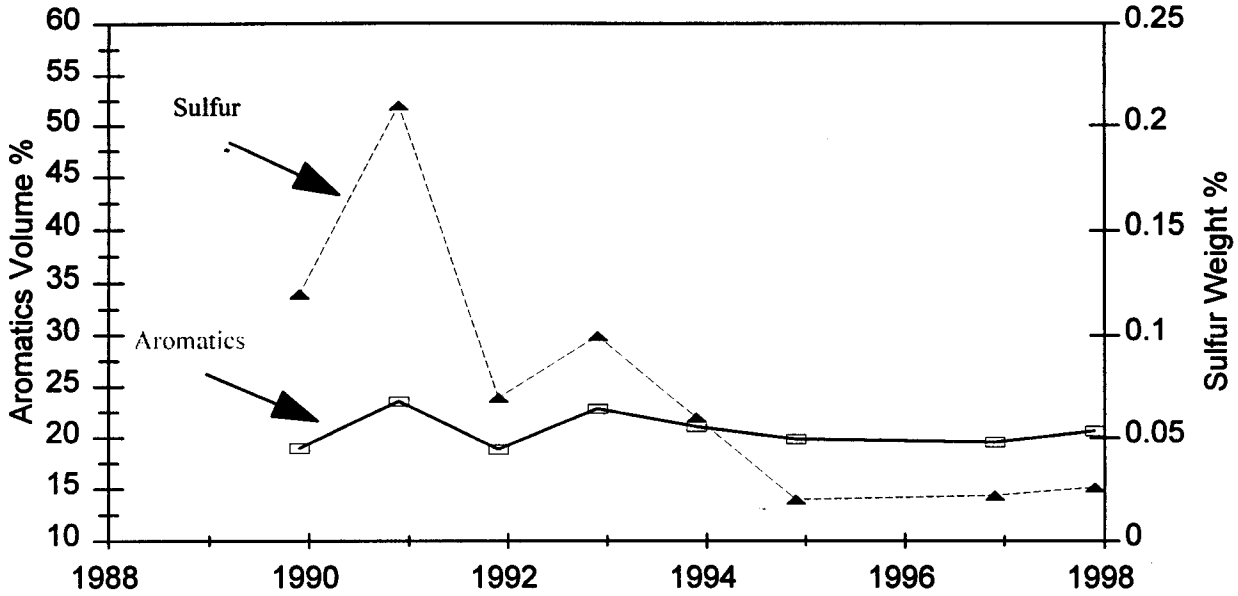


Figure 2-3. National Fuel Survey (1-D Regular) From 1989 to 1997

In Figure 2-4, average survey data for Southern California are shown for sulfur and aromatics contents of No. 2-D Regular diesel fuel. During the period shown, the California Air Resources Board (CARB) regulations underwent a change requiring maximum values of 0.05 weight percent sulfur and 10.0 volume percent aromatics or certified equivalent. The effective date was October 1, 1993, which was the same date as EPA regulations for the rest of the U.S.

Figure 2-4 shows that the average sulfur content, which was already fairly low, less than 0.10 weight percent, did drop to the range 0.005-0.025 weight percent after 1993. However, the average aromatics content reduced to 20-25 volume percent after 1993. The reason for this seemingly high aromatics level was the flexibility in the CARB regulation, which provided alternative aromatic specifications. If a fuel formulation could be demonstrated to produce equivalent or lower emissions than a "California reference fuel," it would be "certified" for sale in California.[1*] The basis for certification was testing the proposed fuel formulation and a California reference fuel in a 1991 Detroit Diesel DDC Series 60 engine.

* Numbers in parentheses in the text refer to references in Section 6.

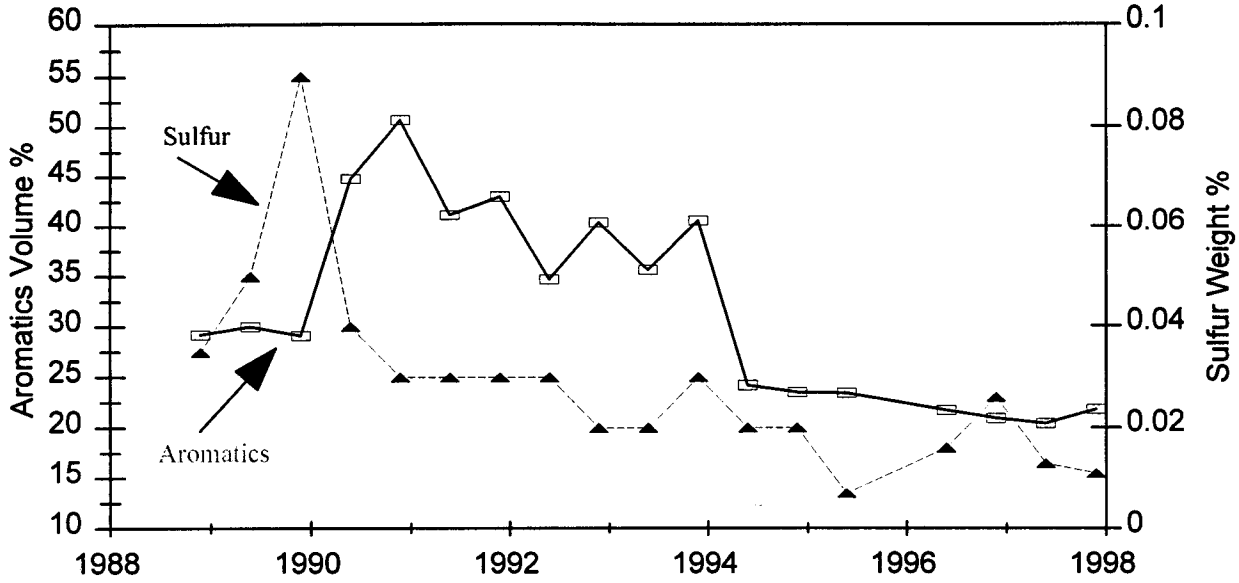


Figure 2-4. California [L.A.] Fuel Survey (2-D Regular) From 1988 to 1997

Most of the major California refiners have obtained CARB certification for their diesel fuel formulations. A review of individual refinery fuels in the AAMA surveys for Los Angeles showed that most of the No. 2-D fuels range from 18-25 volume percent aromatics and ignition quality from 50-60 cetane number.

Figures 2-5 and 2-6 are the data presented for the three grades of national diesel fuel and one grade of California fuel plotted another way. They are intended to allow visual comparisons of sulfur content (Figure 2-5) and aromatics contents (Figure 2-6) on one figure.

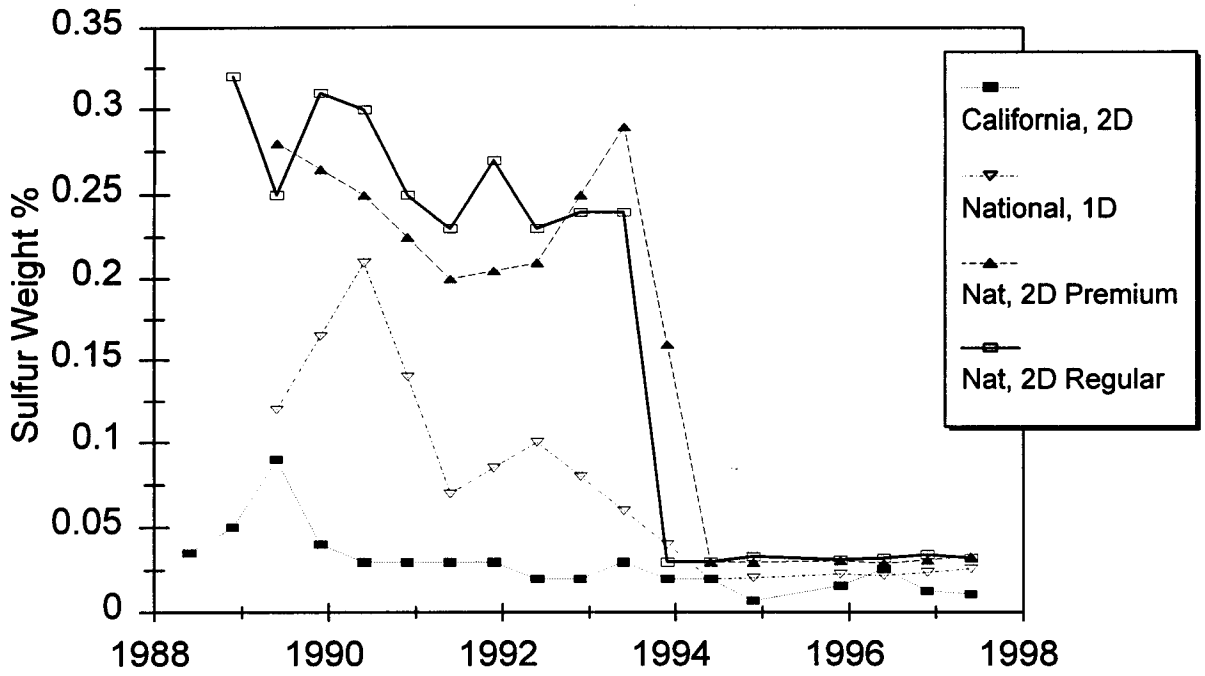


Figure 2-5. Percent Sulfur, National and California (Los Angeles) Averages

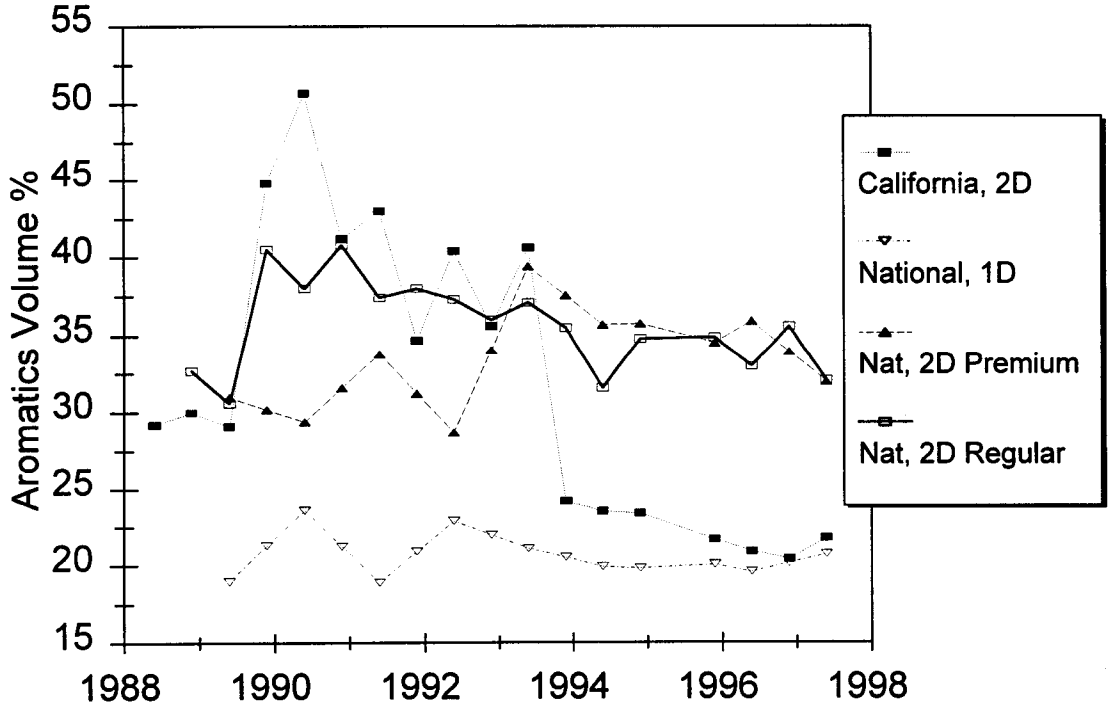


Figure 2-6. Percent Aromatics, National and California [Los Angeles] Averages

Cetane numbers and cetane index data from the fuel surveys are plotted on Figures 2-7, 2-8, 2-9 and 2-10. Figure 2-7 shows the national average cetane number and cetane index values for 2-D Regular diesel fuel from the AAMA reports. After 1993 the cetane number of the fuels stayed at approximately 45. On the other hand, after 1993 cetane index improved from 45.4 to 46.7.

Figure 2-8 shows the national average cetane values for 2-D Premium diesel fuel from the AAMA reports. Both cetane number and cetane index actually dropped from 1993 to the 1996, but rose back up in 1997.

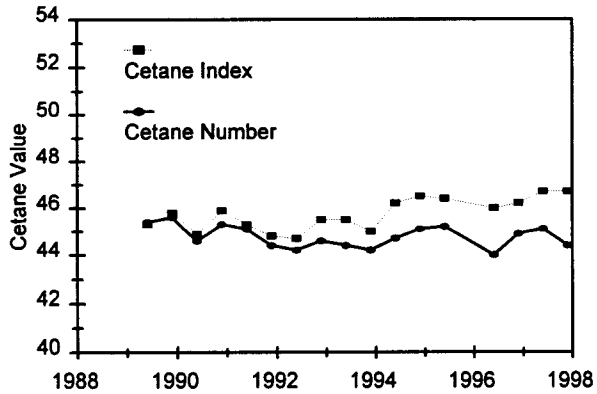


Figure 2-7. National 2-D Regular Ignition Quality (AAMA)

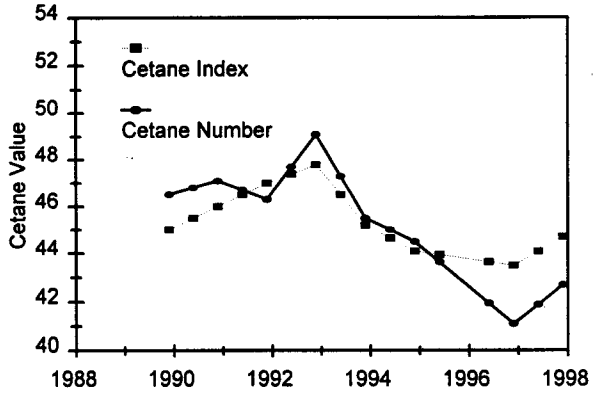


Figure 2-8. National 2-D Premium Ignition Quality (AAMA)

Figure 2-9 shows the national average cetane values for 1-D Regular diesel fuel from the AAMA reports. As in the 2-D Premium data, the 1-D diesel fuel cetane values have decreased since 1993; however, unlike 2-D Premium diesel fuel, 1-D cetane number has not gone back up yet.

Figure 2-10 shows the cetane values for California 2-D Regular diesel fuel. After 1993 the cetane number and the cetane index increased from 44 to at least 51 and from 46.5 to at least 48.5, respectively.

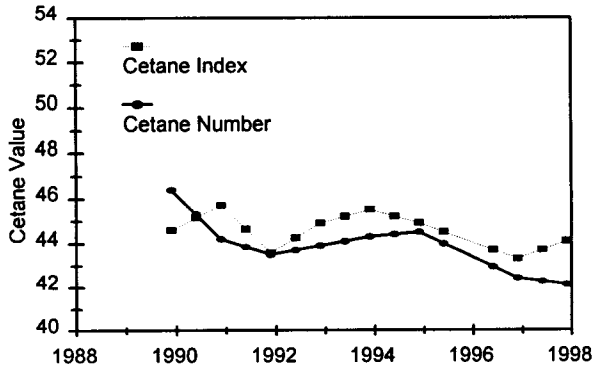


Figure 2-9. National 1-D Regular Ignition Quality (AAMA)

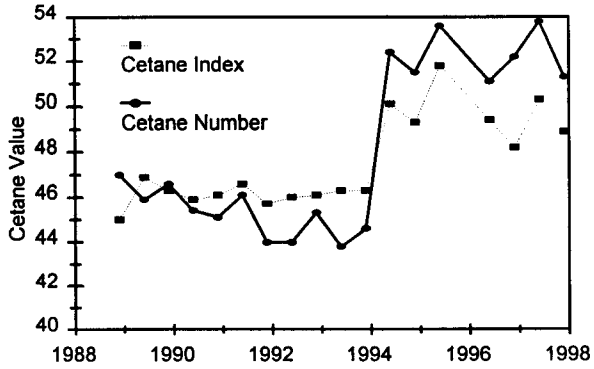


Figure 2-10. California 2-D Regular Ignition Quality (AAMA)

The final plot in this section is from a survey by the National Institute for Petroleum Energy Research (NIPER) in Bartlesville, Oklahoma. Figure 2-11 shows U.S. average Cetane Index for diesel grades 1-D and 2-D.

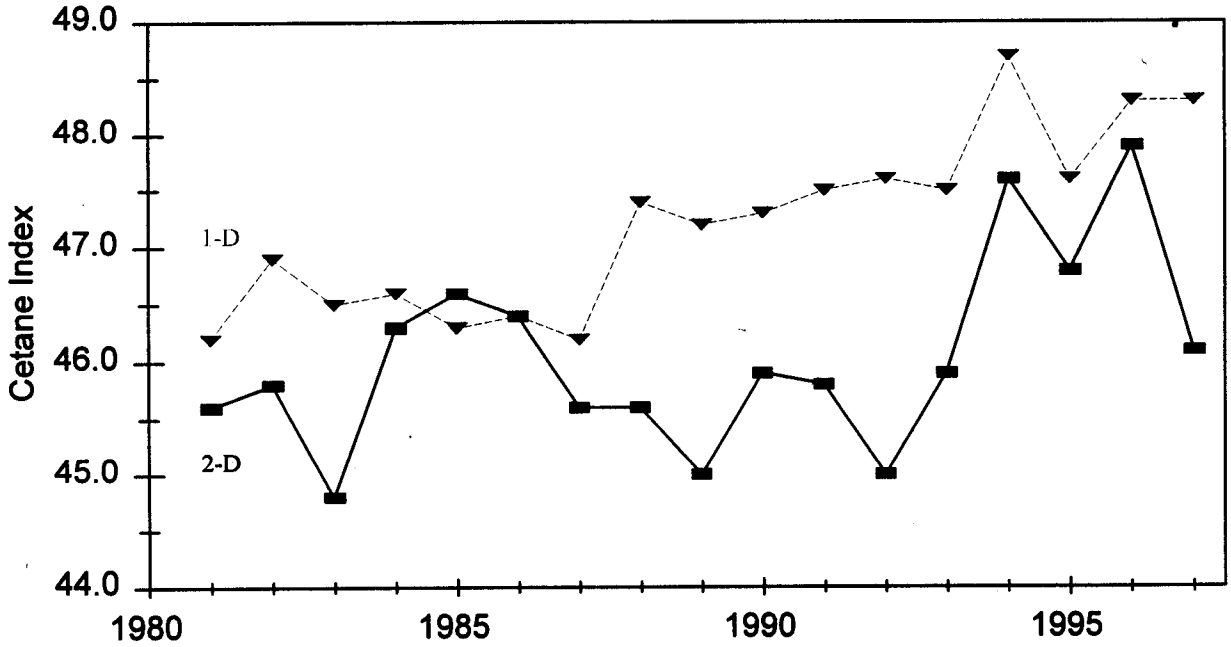


Figure 2-11. U.S. Average Cetane Index for Grades 1-D and 2-D (NIPER)

3 Light Duty Diesel Engine Emissions

3.1 EPA Regulations

Federal emission control requirements are different for light duty and heavy duty diesel engines because of different operating factors such as engine speed, expected load, etc. Light duty diesel engines such as automobiles and light trucks operate at high engine speeds 1800-3600 rpm. Table 3-1 lists the federal emission control requirements for light duty diesel automobiles and trucks from 1968 to 1995.[2] Note that after 1995 the standards for light trucks and automobiles became identical. The most stringent changes from 1982 onward were the nitrogen oxides and particulate emission levels.

Table 3-1. Federal Emission Control Requirements for Automobiles and Light Trucks, 1968-95 [a] (grams per mile)

Model Year	Automobiles				Light trucks[b]			
	Hydro-carbons (HC)	Carbon monoxide (CO)	Nitrogen oxides (NO_x)	Particulates[c]	Hydro-carbons (HC)	Carbon monoxide (CO)	Nitrogen oxides (NO_x)	Particulates[c]
1968-71	4.10	34.0	[d]	[d]	8.0	102.0	3.6	[d]
1972-74	3.00	28.0	3.1	[d]	8.0	102.0	3.6	[d]
1975-76	1.50	15.0	3.1	[d]	2.0	20.0	3.1	[d]
1977-78	1.50	15.0	2.0	[d]	2.0	20.0	3.1	[d]
1979	1.50	15.0	2.0	[d]	1.7	18.0	2.3	[d]
1980	0.41	7.0	2.0	[d]	1.7	18.0	2.3	[d]
1981	0.41	3.4	1.0	[d]	1.7	18.0	2.3	[d]
1982-83	0.41	3.4	1.0	0.60	1.7	18.0	2.3	0.60
1984-86	0.41	3.4	1.0	0.60	0.8	10.0	2.3	0.60
1987	0.41	3.4	1.0	0.20	0.8	10.0	2.3	0.26
1988-93	0.41	3.4	1.0	0.20	0.8	10.0	1.2[e]	0.26
1994	0.25	3.4	0.4	0.08	0.25	3.4[e]	1.2[e]	0.26
1995-on	0.25	3.4	0.4	0.08	0.25	3.4[e]	0.4[f]	0.08

Source:
1968-75: Motor Vehicle Manufacturers Association, Motor Vehicle Facts & Figures '85, 1985, p. 88.
1976-93: Code of Federal Regulations, 40CFR86, "Control of Air Pollution from New Motor Vehicles and New Vehicle Engines: Certification and Testing Procedures," July 1, 1987, p. 264.
1994-on: Clean Air Act Amendments of 1990.

[a] California standards not included.
[b] Applies to trucks under 6,000 pounds gross vehicle weight through model year 1978 and under 8,500 pounds GVWR beginning in model year 1979.
[c] Applies to diesel engines only.
[d] No standard was set for this year.
[e] Applies to light trucks up to and including 3,750 pounds loaded vehicle weight (LVW).
[f] Applies to light trucks up to and including 3,750 pounds LVW. Does not apply to diesel-fueled light trucks.

Figures 3-1 and 3-2 are graphical representations of the effect of tightening particulates and nitrogen oxides standards for light duty diesel automobiles and light trucks. New engine designs have decreased the particulates and nitrogen oxides, but to meet the ever-smaller, allowable "boxes" of NO_x vs particulate levels, diesel fuels have also been "re-designed," as was seen in Figures 2-5 and 2-6.

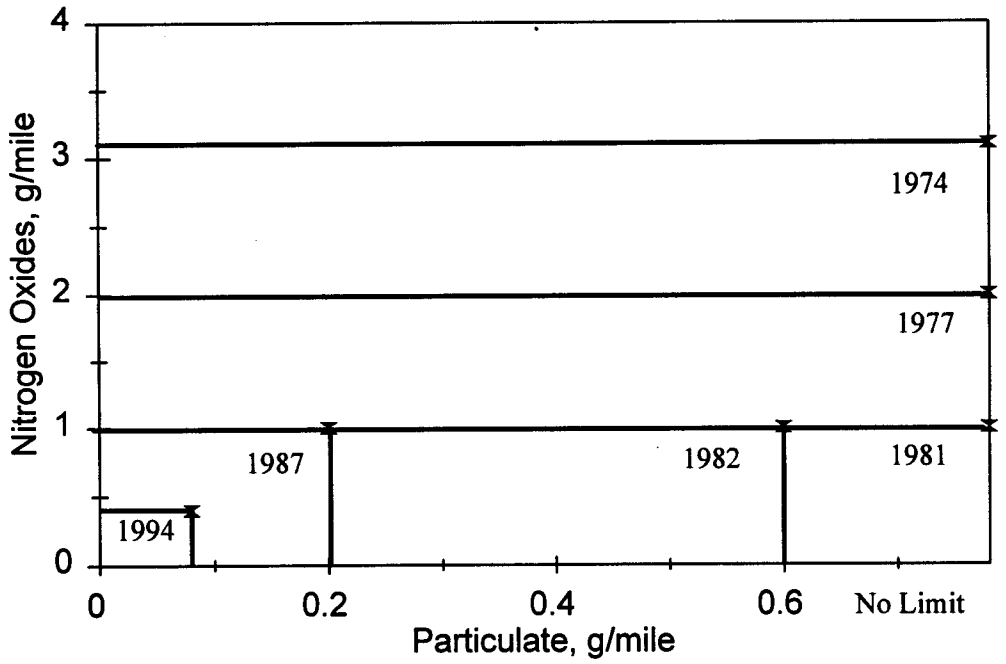


Figure 3-1. Automobile Diesel Engine Emission Standards

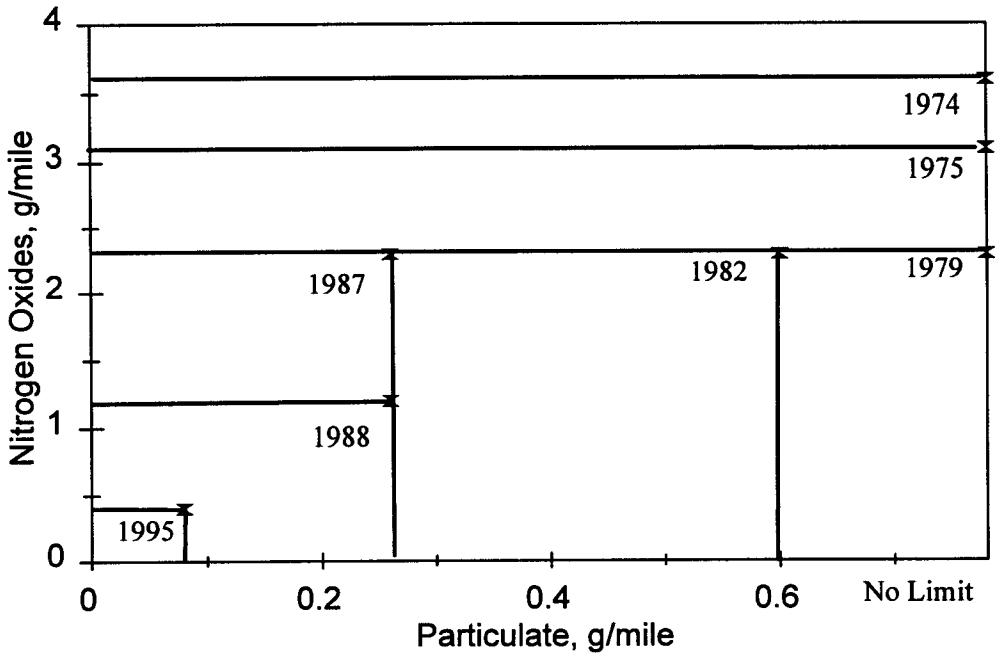


Figure 3-2. Light Truck Diesel Engine Emission Standards

3.2 Discussion of Light Duty Engine Literature

Although the continuously tightening regulations have had an effect on emissions, no identified survey provided a consistent record of the change. To report the fuel effect on particulate emissions, individual articles with commentary on this topic were consulted. This section summarizes the prominent trends.

1. Arai determined that cetane numbers and aromatics were strongly correlated in the fuel matrix as shown in Figure 3-3.[3] The relationship is linear with the slope and intercept depending on the sulfur weight percentage.

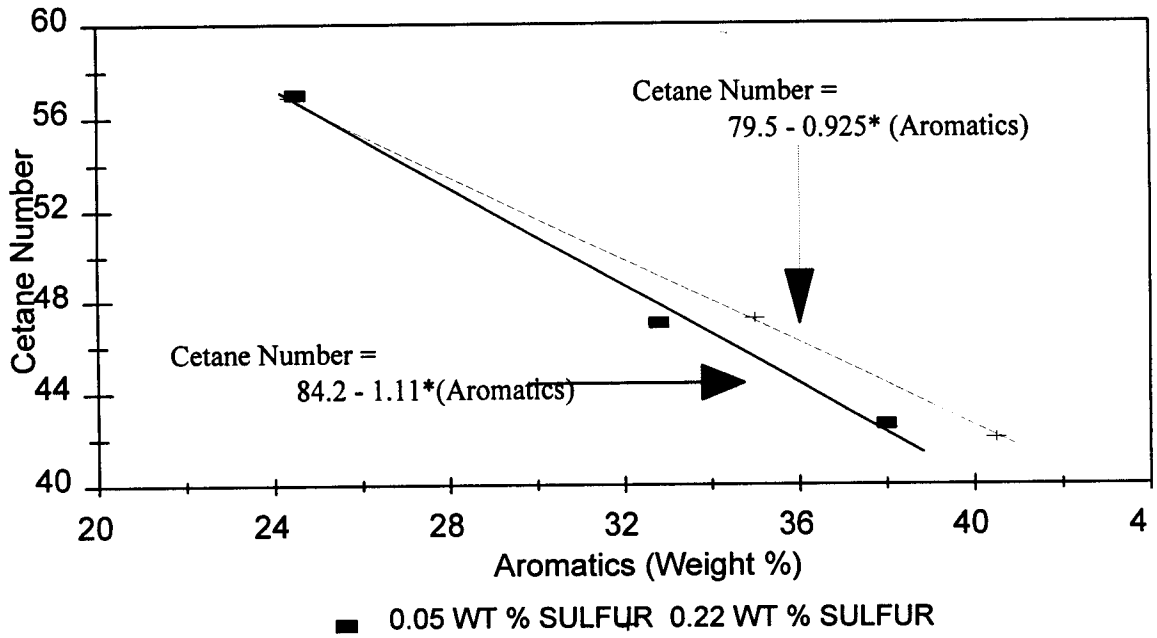


Figure 3-3. Cetane Number Variation with Aromatics Content Source: Ref.3, Arai

Arai used a 4 cylinder, 2.8 L, turbocharged direct-injection diesel engine to test 6 fuels with varying cetane numbers (aromatics) and sulfur content. The engine ran at five conditions, of which only two have data that showed any effect of fuel properties: the 2200 rpm 25% load and the 2200 rpm full load conditions. In the other three (LA-4, New Japan Mode, and Highway Fuel Econ Test) the soot and soluble organic fraction (SOF) of particulates were not sensitive to cetane number or aromatics. Figures 3-4 shows that SOF in particulates decreased slightly at higher cetane numbers (i.e., lower aromatics content) at 2200 rpm. Figure 3-5 shows that soot in particulates manifests a similar trend at full load, but remained constant at 25% load.

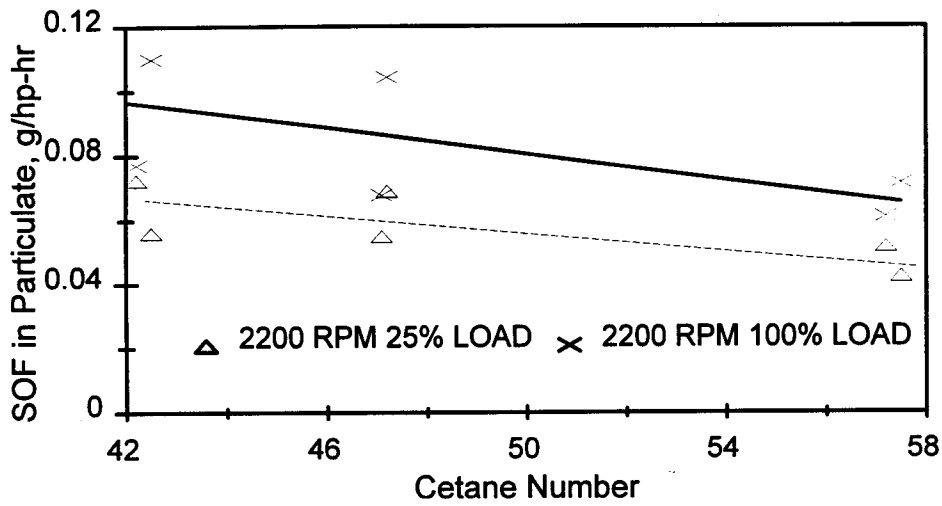


Figure 3-4. SOF in Particulate vs Cetane No. Source: Ref 3, Arai

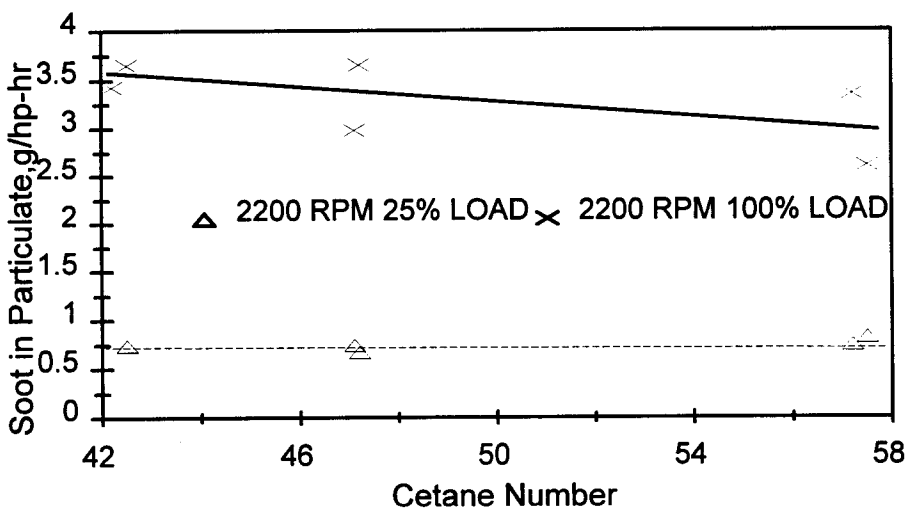


Figure 3-5. Particulate Soot vs Cetane No. Source: Ref 3, Arai

Lubricant consumption effects on particulate emissions were explored briefly by Arai with seven lubricating oils, two samples of SAE 30 and 5 samples of SAE 10W/30. Results are shown in Figure 3.8 for operation at 2200 rpm, full load with one fuel at 47.2 cetane number and 0.22 weight percent sulfur. The independent variable was lubricant viscosity at 100°C. The author's opinion was that the higher viscosity oil in piston blow-by is more likely to burn at high temperature (100% load) than to appear in the total particulates.

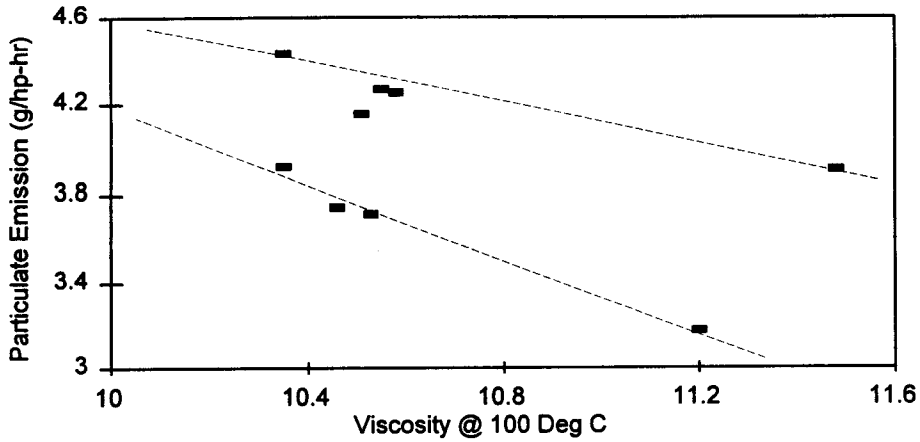


Figure 3-6. Effect of Lubricant Viscosity on Particulate Emissions
Source: Ref 3, Arai

2. Another light duty study was conducted at the Advanced Technology & Research Institute Petroleum Energy Center by Tamanouchi.[4] He used two 1992 vehicles on the same four fuels to evaluate the effects of increasing 90 percent distillation temperature and polyaromatic hydrocarbons (PAH). Vehicle J showed a marked increase in particulates and soluble organic fraction (SOF). Vehicle K exhibited a much smaller increase in particulates and no change in soluble oil fraction. These effects are illustrated in Figures 3-7, 3-8, 3-9, and 3-10. These results contrast with the previous study by Arai that found soot and SOF in particulates were not sensitive to aromatic volume percent.

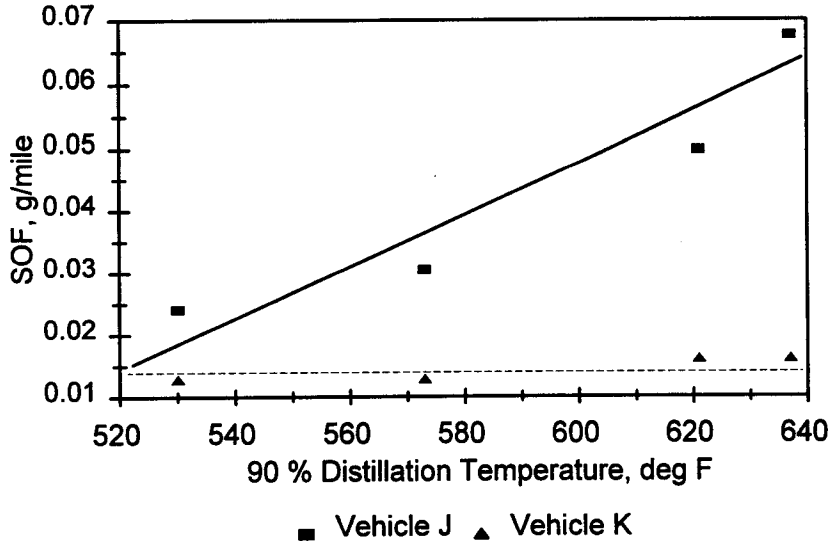


Figure 3-7. SOF vs T_{90}
Source: Ref 4, Tamanouchi

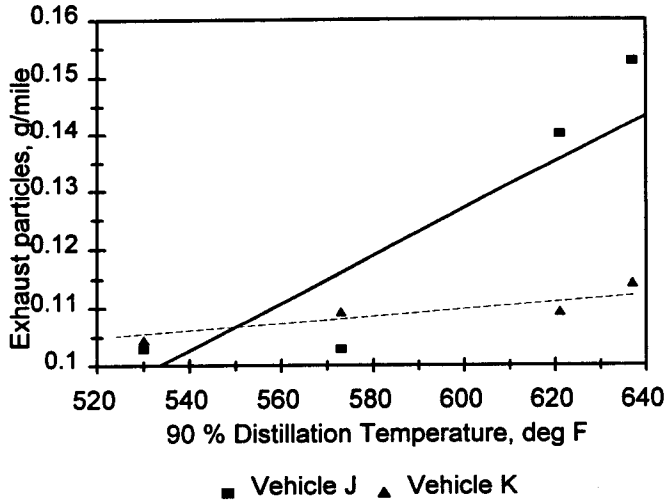


Figure 3-8 Exhaust Particulates vs T_{90}
Source: Ref 4, Tamanouchi

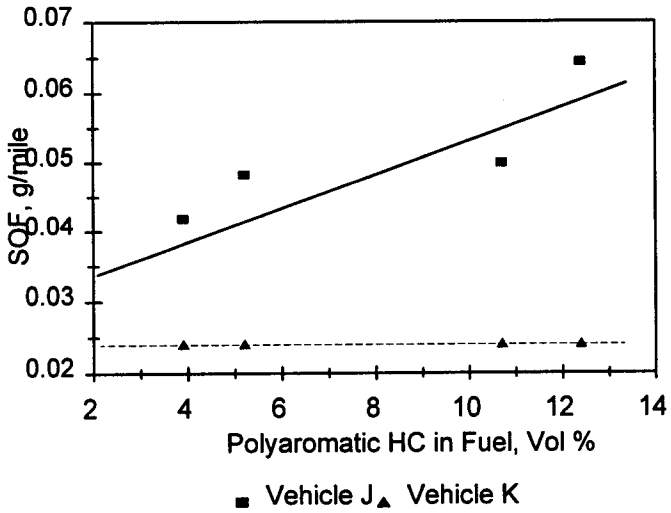


Figure 3-9. SOF vs PAH
Source: Ref 4, Tamanouchi

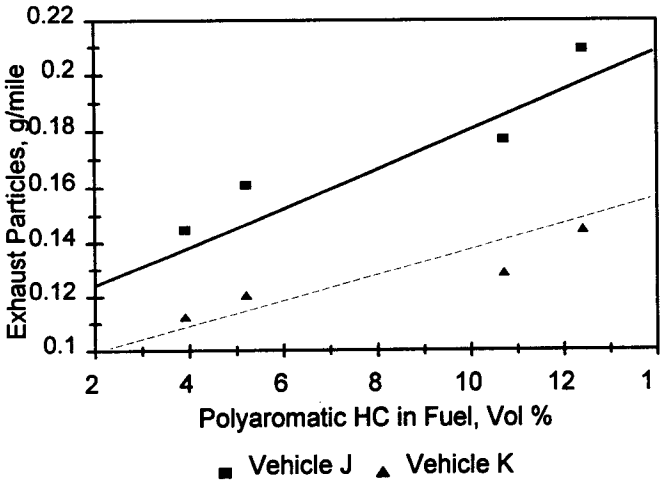


Figure 3-10. Exhaust Particulates vs PAH
Source: Ref 4, Tamanouchi

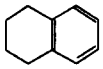
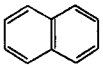
3. An applicable paper from Tsuyama College of Technology and the University of Wisconsin at Madison studied the effects of different fuel aromatic structures on diesel engine particulates [5]. They used a single cylinder, direct-injection, 2.34 L diesel engine to test three fuels with differing aromatic structures. The three fuels were a baseline low-sulfur Chevron fuel (designated STD), single aromatic (tetralin)  doped baseline fuel (SAT), and dicyclic aromatic (naphthalene)  doped baseline fuel (DAN). The properties of the test fuels are shown in Table 3-2.

Table 3-2. Properties of Test Fuels[a]

Name	STD	SAT	DAN
Aromatic content, volume %	21.0	28.9	28.9
Cetane number	49.8	48.0	48.1
Lower heating value MJ/kg	42.72	42.59	42.30

[a] Source: Ref 5, Fukuda

The researchers found that gaseous emissions of unburned hydrocarbons and nitrogen oxides are directly proportional to the aromatic content, regardless of the operating conditions. On the other hand, the relationship between particulate matter production and aromatic content in light duty engines was dependent on the operating conditions. The results of their research are summarized in Table 3-3. At high intake pressure and high temperature, the particulate matter was not measurably different in the three test fuels. At low intake pressure, the total particulates from the double aromatic doped fuel decreased compared to the baseline fuel. Also at intake low pressure, the total particulates from the single aromatic doped fuel increased or decreased compared to the baseline fuel depending on the temperature. Thus, the particulate emissions depended not only on the operating conditions, but also on the aromatic structures in the fuel.

Table 3-3. Particulate Emissions of the Three Fuels at Various Operating Conditions

Operating Conditions	Total Particulates (mg/m^3)			SOF in Particulates (mg/m^3)		
	STD	SAT	DAN	STD	SAT	DAN
27.0 psig, 62.9°C	10.5	11.5	12.0	2.1	1.5	1.5
17.0 psig, 62.9°C	52	56	50	7	5	6
17.0 psig, 33.9°C	48	46	44	6	6	6

4 Heavy Duty Diesel Engine Emissions

4.1 EPA Regulations for Heavy Duty Trucks

Table 4.1 lists the federal emission control requirements for heavy duty diesel trucks from 1976 to 1998 (2). Note that from 1984 onward the hydrocarbons and carbon monoxide limits were constant, but the footnote requires further reduction later using available technology. In distinction to hydrocarbon and carbon monoxide, the particulates and nitrogen oxide limits became increasingly more stringent. These two pollutants are in a trade-off position; that is, a decrease in particulates may cause an increase in nitrogen oxides, or vice versa. These requirements have caused continuing efforts at improving engine technology. Meeting the particulates emissions was aided by diesel fuel modification after highway diesel sulfur content was reduced to 0.05 weight percent maximum in late 1993.

Table 4.1 Federal Emission Control Requirements for Heavy-Duty Diesel Trucks, 1976-98[c] (grams per brake horsepower hour)

Model Year	Hydrocarbons (HC)	Carbon monoxide (CO)	Nitrogen oxides (NO_x)	Hydrocarbons + nitrogen oxides ($HC + NO_x$)	Particulates
1976-78	[a]	40.0	[a]	16.0	[a]
1979-83	1.5	25.0	[a]	10.0	[a]
1984	1.3	15.5	10.7	5.0	[a]
1985-87	1.3	15.5	10.7	[a]	[a]
1988-89	1.3	15.5	10.7	[a]	0.60
1990	1.3	15.5	6.0	[a]	0.60
1991-93	1.3	15.5	5.0	[a]	0.25
1994-97	1.3[b]	15.5	5.0	[a]	0.10
1998-on	1.3[b]	15.5[b]	4.0[b]	[a]	0.10[b]

Source:
1976-93: Code of Federal Regulations, 40CFR86, "Control of Air Pollution from New Motor Vehicles and New Vehicle Engines: Certification and Testing Procedures," July 1, 1987, p. 264.
1994-on: Clean Air Act Amendments of 1990.

[a] No standard was set for this year.
[b] Heavy-duty trucks must meet these standards or standards which reflect the greatest degree of emission reduction achievable through the application of the technology available.
[c] Applies to trucks greater than 6,000 pounds gross vehicle weight through model year 1978 and to trucks greater than 8,500 pounds gross vehicle weight beginning in model year 1979.

Figure 4-1 shows the effect of tightening particulates and nitrogen oxides standards with the allowable "boxes" becoming increasingly smaller. This effect shows the continuing efforts of

industries making engines, vehicles, and diesel fuels to comply with the needs for lower particulates and nitrogen oxides enunciated by the EPA.

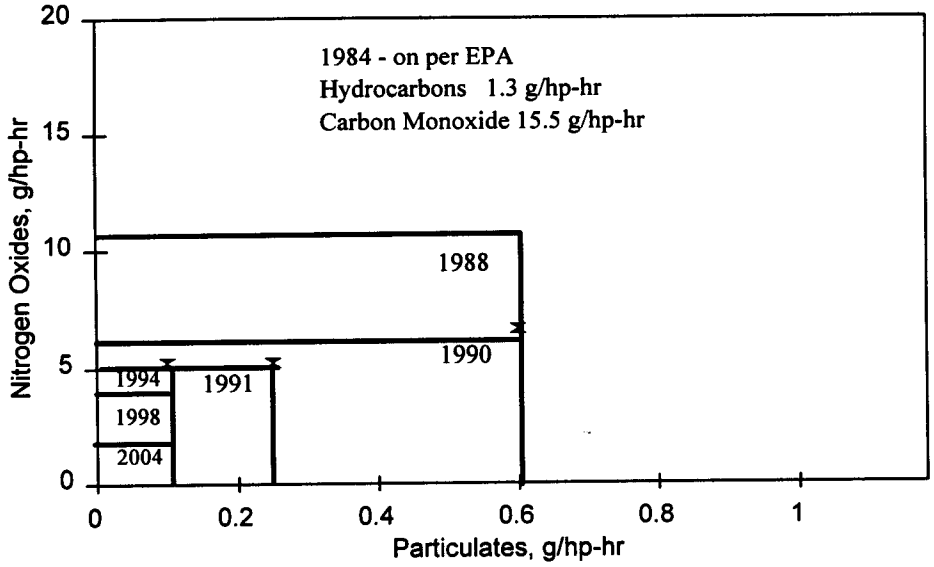


Figure 4-1. Heavy Duty Diesel Engine Emission Standards

Figure 4-1 goes one step beyond Table 4.1 to the box labeled 2004. The figure reflects the Statement of Principles agreement signed by EPA, CARB, API, and the Engine Manufacturers Association (EMA) to reduce emission limits by 2004 for heavy duty engines to:

- 2.0 g/hp-hr NO_x
- 2.4 g/hp-hr NO_x + HC and hold at
- 0.1 g/hp-hr particulates

These limits are contingent on a tentative revision to the diesel fuel specification to continue at the CARB limit of 10 volume percent aromatics and raise ignition quality to 60 cetane number. This new "clean diesel fuel" will require necessary processing revisions for U.S. refiners to meet the new fuel quality requirements expected in 1999. If there is not a clean fuel required, the sum of NO_x+HC would be 3.4 g/hp-hr.

4.2 Discussion of Heavy Duty Literature

1. A 1990 paper prepared at Navistar presented thorough evaluation of fuel property effects on particulate emissions.[6] The test engine was a Navistar DTA-466 prototype tuned to meet 1991 emission standards. A matrix of eleven fuels covered a range of cetane numbers, total aromatics, polyaromatics, sulfur contents, and 90 percent distillation temperatures.

Particulate emissions correlated best with sulfur content, aromatics content, 90 percent distillation temperature, and polyaromatic hydrocarbons (PAH) in the fuel. Cetane number changes did not affect particulate emissions. These effects are illustrated in Figures 4-2, 4-3, and 4-4.

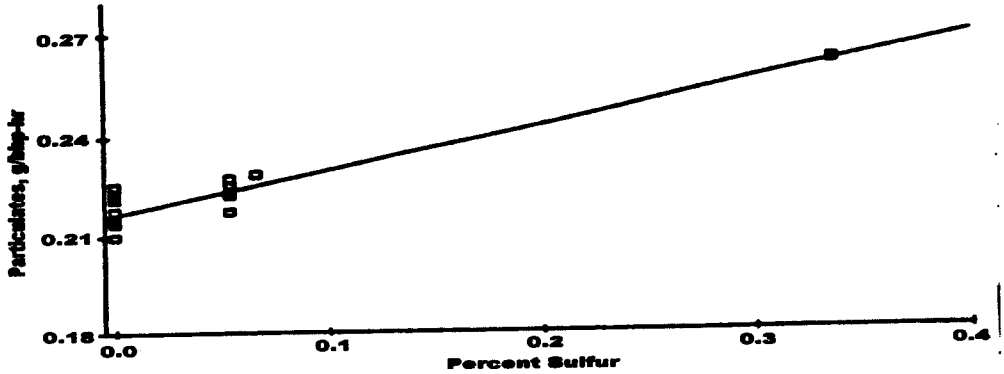


Figure 4-2. Particulates vs Sulfur Adjusted for Polyaromatic and T90
Source: Ref 6, Sienicki

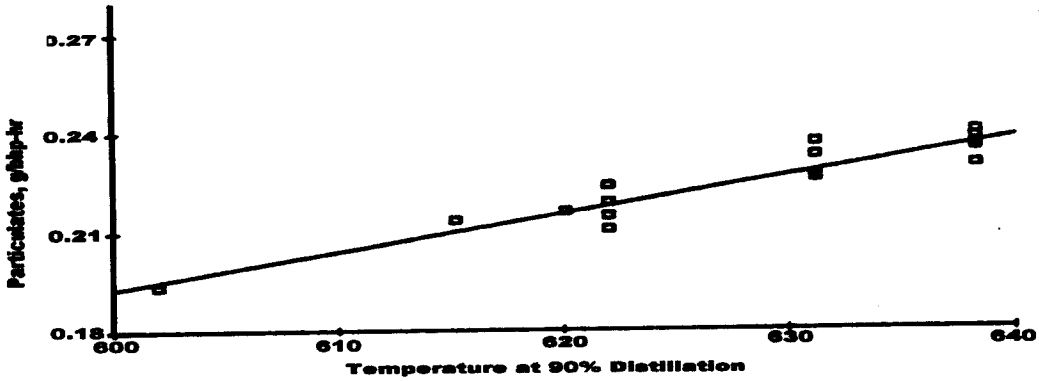


Figure 4-3. Particulates vs T90 Adjusted for Sulfur and Polyaromatics
Source: Ref 6, Sienicki

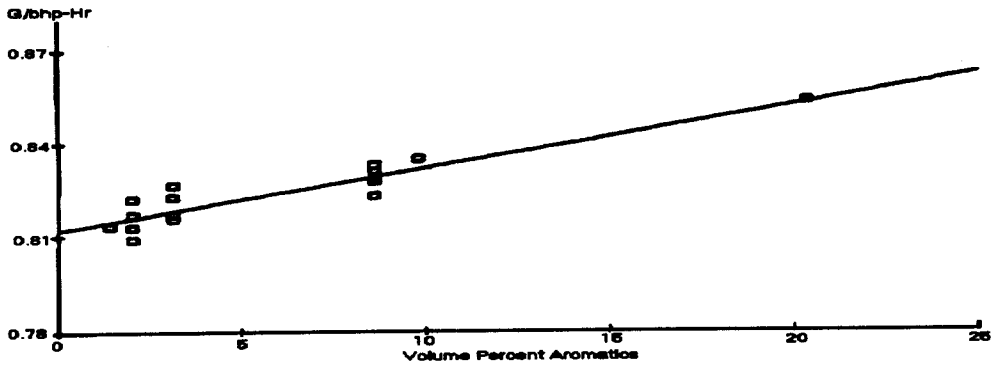


Figure 4-4. Particulates vs Polyaromatics Adjusted for Sulfur and T90
Source: Ref 6, Sienicki

Soluble oil fractions in the particulate increased as a function of sulfur and polyaromatics in the fuels. These trends are shown in Figures 4-5, 4-6, and 4-7.

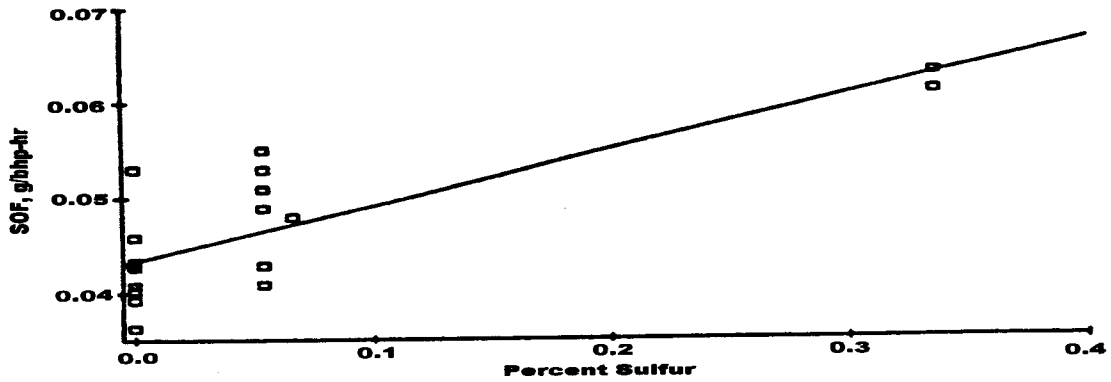


Figure 4-5. Soluble Organic Fraction vs Sulfur Adjusted for Mass Spectrometry Aromatics Source: Ref 6, Sienicki

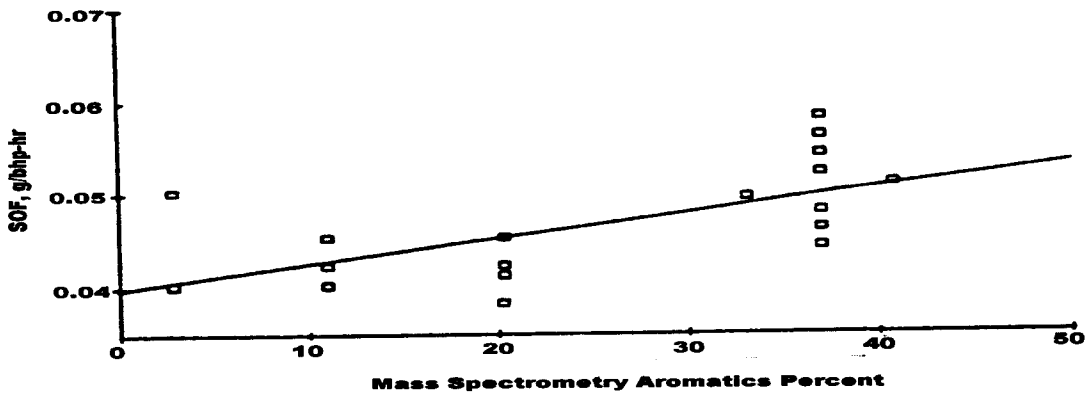


Figure 4-6. Soluble Organic Fraction vs Mass Spec Aromatics Adjusted for Sulfur Source: Ref 6, Sienicki

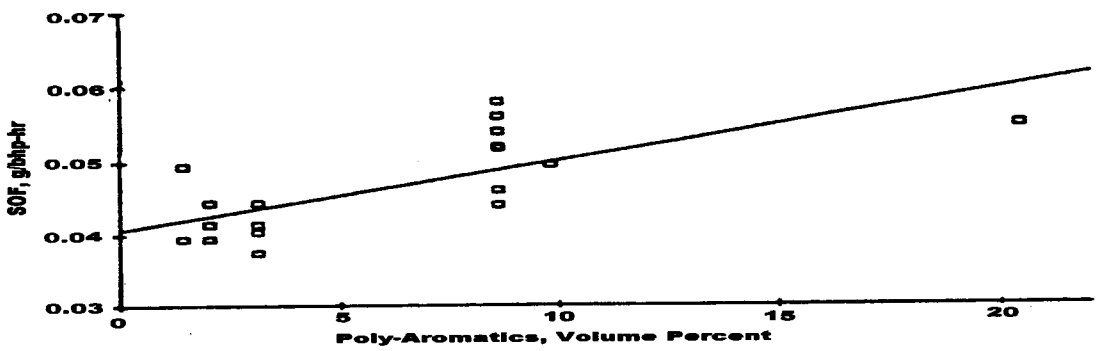


Figure 4-7. Soluble Organic Fraction vs Polyaromatics Adjusted for Sulfur
Source: Ref 6, Sienicki

2. A Canadian study was done to examine polyaromatic hydrocarbons (PAH) in the exhaust[7]. Four fuels were blended with varying amounts of 1-, 2- and 3+ (3 or more) ring PAH compounds measured by supercritical fluid chromatography (SFC). All fuels were low sulfur (less than 0.05 weight percent). One fuel met California standards (less than 10 volume percent aromatics). The other three fuels met Canadian and U.S. EPA standards (less than 35 volume percent aromatics) and contained varying amounts of cetane improver (to assure over 40 cetane number).

Two test engines were used. The first was a 1991 heavy duty Detroit Diesel DDC Series 60 production engine modified to target 1994 emission standards. The second engine was a 1991 Navistar DTA-466 engine also designed to comply with 1994 emission regulations. This engine is classified as medium duty and is used in pickup and delivery type trucks. Both engines were tested using the EPA federal test procedure (FTP).

Figures 4-8 and 4-9 show how 2 and 3+ ring aromatics in the exhaust relate to the same compounds in the fuels. Figure 4-8 for the DDC Series 60 engine shows similar slopes and correlation coefficients (R^2 values of 0.99 and 0.87 for both the 2- and 3+ ring PAH.) The intercept values of about 50 μg/hp-hr at zero amount of 2- and 3+ ring value in the fuel represent PAH compounds that come from the engine oil or are formed in the combustion process.

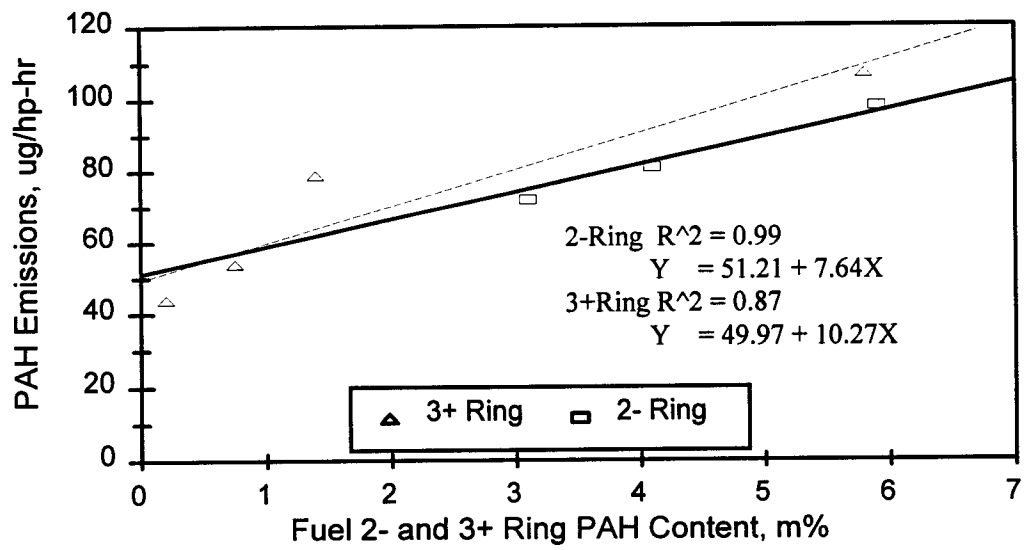


Figure 4-8 PAH Emissions Correlated with Fuel PAH Content, DDC Engine
Source: Ref 7, Mitchell

Figure 4-9 shows results for the Navistar DTA-466 engine. The correlation coefficient ($R^2 = 0.99$) shows good correlation with the 3+ ring PAH compounds and an intercept value of 44 μg/hp-hr. Results for 2-ring compounds did not correlate well ($R^2 = 0.16$) in this engine and the intercept value is about 70 μg/hp-hr.

This study identified many of the PAH compounds as well as nitro-PAH and aldehyde emissions in the exhaust. The paper also reports a reduction in emissions with the use of two different catalysts on the Navistar engine exhaust.

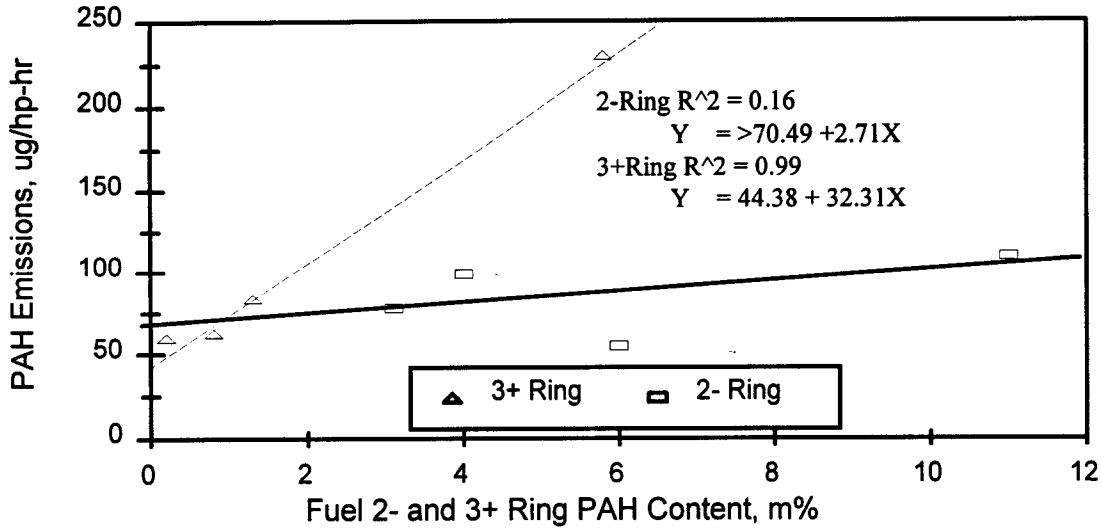


Figure 4-9 PAH Emissions Correlated with Fuel PAH Content, Navistar Engine
Source: Ref 7, Mitchell

3. As engine technology was developed to meet lower emission standards for NO_x andparticulates, additional heavy duty engine studies were made to evaluate effects of fuel properties. A study was reported in early 1994 on the effects of cetane number, cetane improver, aromatics and oxygenates in diesel fuel[8]. The engine used was a Detroit Diesel 1994 DDC Series 6 tuned for NO_x at 5 or 4 g/hp-hr. Eleven fuels were blended to cover the four major variables, including one ignition improver and two oxygenate compounds which also increased cetane number.

Statistical analysis of FTP test cycles showed cetane numbers were not significant variables for particulate emissions. Particulate emissions varied primarily with changes in oxygen content and sulfur content. Regarding fuel oxygen and sulfur content, the study concluded:

> "Increasing fuel oxygen independently by one weight percent is predicted to reduce transient composite particulate by 7 and 6 percent for the 5 and 4 g NO_x calibrations, respectively. Reducing fuel sulfur independently by 100 ppm was predicted to reduce particulate by 5 and 3 percent for the 5 and 4 g NO_x calibrations, respectively."

Figures 4-10 and 4-11 show these effects graphically. The symbols representing the data points are the letter designations of the test fuels used in the study.

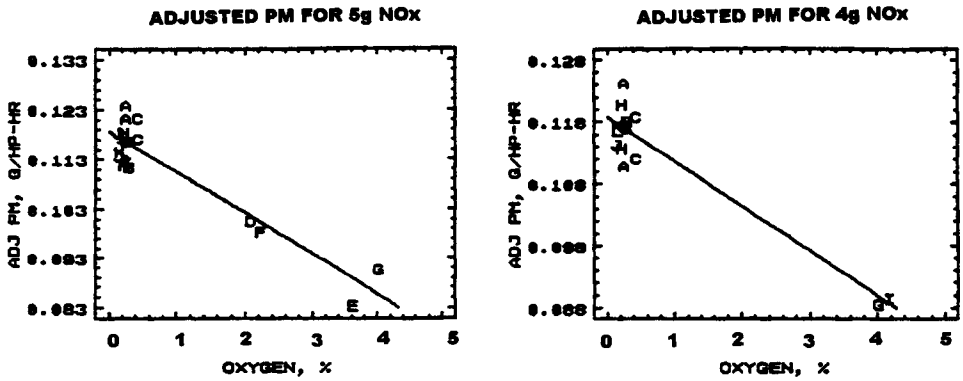


Figure 4-10. Variation of PM Emissions with Oxygen Adjusted for Sulfur
Source: Ref 8, Ullman

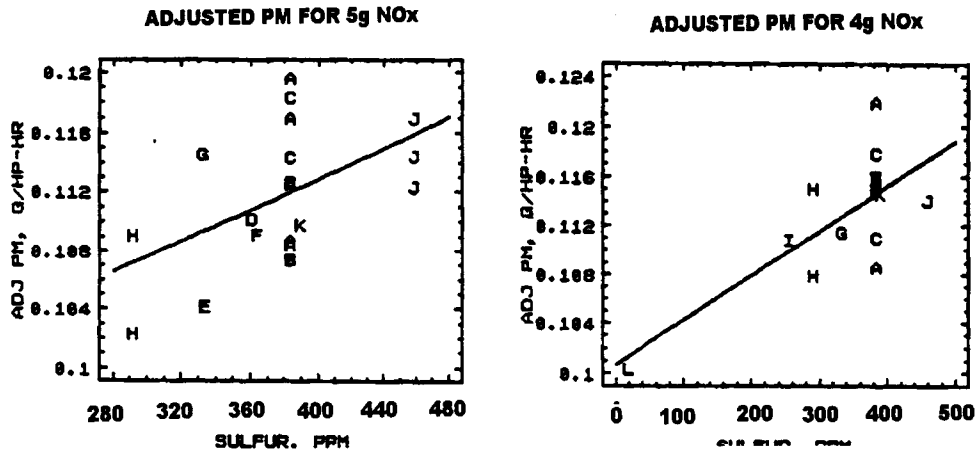


Figure 4-11. Variation of PM Emissions with Sulfur Adjusted for Oxygen
Source: Ref 8, Ullman

4. A study was made using a 1994 Navistar DTA-466 prototype engine to evaluate the effects of cetane number, aromatics, and oxygenates in emissions[9]. The set of ten fuels was the same as ten of the eleven fuels used with the DDC Series 60 engine in Reference 8. The report included the following conclusion about particulate emissions (PM):

> "Increasing only cetane number decreased PM emissions for the 4 gram NO_x calibration, but it did not change PM emissions for the 5 gram calibration. To compensate for the nonlinear response of emissions to cetane number, the cetane variable used in the prediction equations was a log transformation of the original cetane variable.

"Fuel aromatics significantly affected PM emissions for both NO_x calibrations. Aromatic content was a significant variable for emissions of HC and NO_x for the 5 gram but not the 4 gram NO_x calibration. Aromatic content was not found to be significant for HC and NO_x for the 4 gram NO_x calibration, perhaps in part due to the limited size of the experimental data set for that calibration.

"Oxygen content was a significant variable in the equations for estimating PM emissions for both NO_x calibrations. The decrease in PM emissions resulting from a 2 percent increase of oxygen was equivalent for both calibrations."

Figures 4-12, 4-13, and 4-14 portray these results graphically.

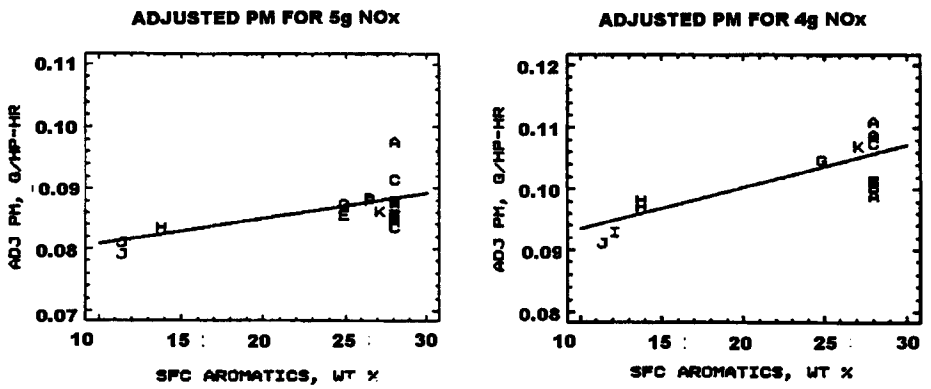


Figure 4-12. Variation of PM Emissions with SFC Aromatics Adjusted for Oxygen and Cetane Number Source: Ref 9, Spreen

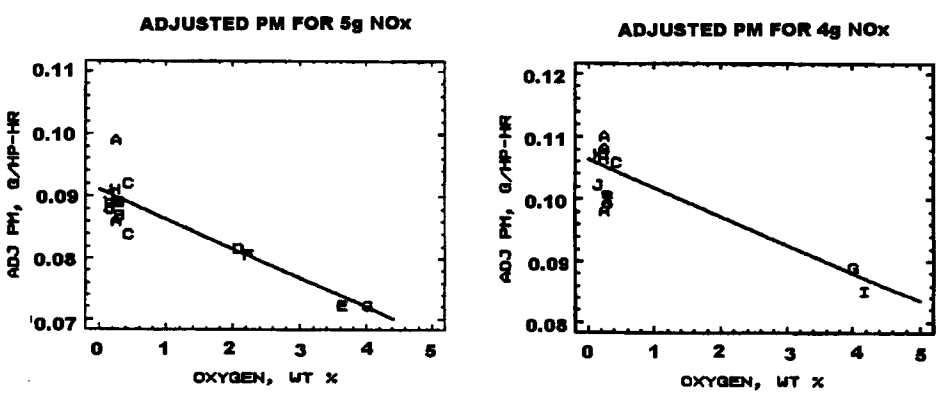


Figure 4-13. Variation of PM Emissions with Oxygen Adjusted for SFC Aromatics with Cetane Number Source: Ref 9, Spreen

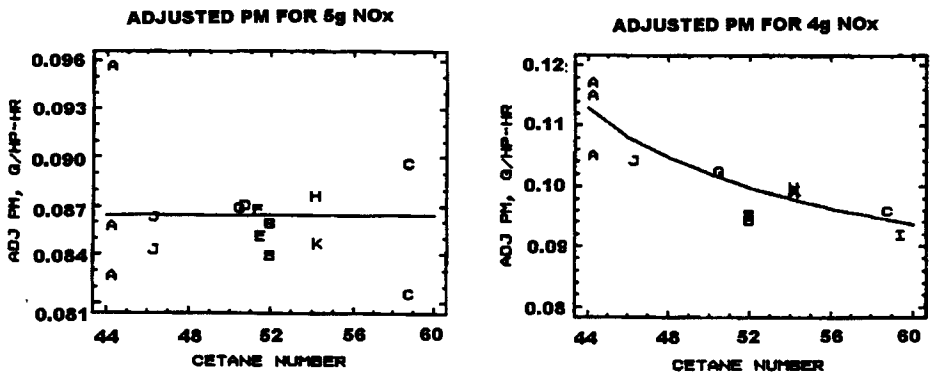


Figure 4-14. Variation of PM Emissions with Cetane Number Adjusted for SFC Aromatics and Oxygen Source: Ref 9, Spreen

5. The Clean Air Act Amendments of 1990 require 0.1 g/hp-hr particulate matter (PM) and 4.0 g/hp-hr nitrogen oxides (NO_x) in 1998 until EPA makes a further reduction in NO_x in 2004. A study was conducted that evaluated the effect of increasing cetane number on all emissions[10]. The engine used was a 1998 Detroit Diesel DDC Series 60 prototype engine. Three base fuels were used with different natural cetane numbers. Two of these base fuels (low and middle cetane numbers) were modified to increase their cetane numbers by addition of ethylhexyl nitrate (EHN). The middle cetane fuel was also modified with di-tertiary-butyl peroxide (DTBP) to its increase cetane number. The final matrix of eleven fuels was then tested in the EPA FTP modes.

In general, higher cetane numbers reduced all gaseous emissions. Figure 4-15 presents a plot of the three base fuels and their cetane numbers showing the small effect on PM of higher natural cetane numbers. The nonlinear regression curves show that the effect of cetane improver is less effective at higher cetane numbers.

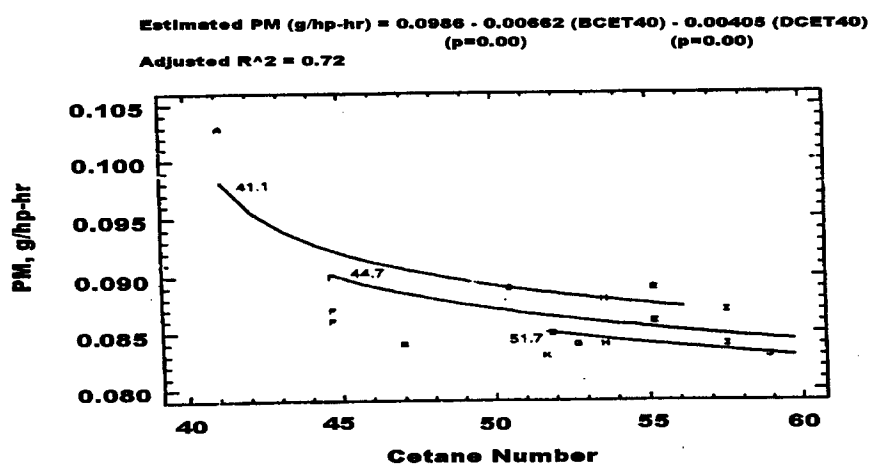


Figure 4-15. Model Predicted Composite PM Emissions for Base Cetane Number and Chemically Induced Cetane Number Increase
Source: Ref 10, Ullman

6. The Urban Bus Retrofit Program is aimed at reducing particulate emissions from transit buses. The Clean Air Act Amendments of 1990 established urban bus standards that were more severe than the emissions standards for other heavy duty trucks. The result was the bus companies began to retain the older buses for longer times, using rebuilding as a means to maintain the aging fleets. Most of the buses in the U.S. are equipped with Detroit Diesel 2-stroke engines that produce very high HC and PM emissions. The current retrofit rules require all rebuilt engines of this type to meet the current on-road PM standard of 0.1 g/hp-hr over the transient Federal test procedure. The requirements specify that the "retrofit kit" must be certified for each engine type. These "kits" can include fuels, injection system modifications, and exhaust aftertreatment devices, as long as the incremental life cycle costs associated with the emissions controls, including any incremental fuel costs, do not increase by more than approximately $11,000.

5 SUMMARY

The objective of this study was to identify diesel fuel quality trends related to particulate matter in diesel engine exhaust before and after specification changes which were made effective October 1, 1993. The changes were to limit diesel fuel to 0.05 weight percent sulfur maximum. In addition, California required aromatics reduction to 10 volume percent maximum. The U.S. EPA imposed a cetane quality requirement to limit aromatics compounds in diesel fuel in the other 49 states.

Fuel survey data provided general trends of some of the controlling variables indicators for particulates production such as sulfur and aromatics. The 90 percent distillation temperature is a factor for inclusion of heavier hydrocarbons in the fuel which may mean more polyaromatic hydrocarbons. The fuel survey data reviewed in Section 2 showed that sulfur content was sharply reduced after 1993, and average aromatics in 49 states leveled off at concentrations lower than previous amounts. In California, average aromatics did not fall to less than 10 volume percent, but leveled off at 20-25 volume percent because their regulation allowed alternate fuel formulations if emissions were shown to do as well as a California reference fuel in a specified engine test. The cetane numbers of grade 2-D fuels rose from the low 40's to well over 50.

Aromatics content is an important controlling factor for particulates in diesel exhaust. Aromatics are usually measured by a relatively simple method called fluorescent indicator adsorption (FIA). The literature reported that a better predictor was use of supercritical fluid chromatography (SFC) to measure aromatics. Mass spectroscopy (MS) is even more useful because it can identify specific PAH concentration in the fuel, which will appear as a portion of the exhaust particulates as PAH or soluble organic fraction (SOF). These methods are too expensive to use in routine surveys and are applied in laboratory research programs. The AAMA national surveys do include aromatics by SFC starting in the report for summer 1993.[11] It is important to note which aromatics measurement method a particular report is using and to realize that there are discrepancies among the methods.

Particulate matter collected in engine tests has several components that can be measured. Total particulates collected on a weighed filter pad is the simplest. The filter pad or multiple pads may be extracted with a solvent to separate the SOF containing PAH. The transient FTP actually collects one cold start filter and six hot start filters. Another set of filters may be extracted to recover sulfuric acid mist in an aqueous solution to measure sulfur oxides. The weight of sulfuric acid mist and other sulfur oxides may actually double with the weight of bound water and hydrocarbons; the amount depends on the relative humidity so the filters are stored in a controlled atmosphere before weighing. Finally, other filters can be used to collect samples of unregulated emissions such as aldehydes or nitro-PAH compounds for separate analysis.

The references collected and reviewed in this study included studies covering all of the above variations. It should also be noted that particulates from steady state tests are usually higher than from transient testing with a simulated driving cycle. This fact makes comparisons difficult, and generalizations are even more tenuous.

There are many pitfalls for measuring and correlating particulates with fuel factors. Wall and Hoekman from Chevron described a careful study of 42 test fuels in which special care was taken to control or account for many of the known variables of interest.[11] The specific conclusions relate to the prevailing engine technology in 1984, but the approach to measuring fuel effects have continuing relevance. Self correlation of variables such as sulfur with aromatics or aromatics with T_{90} was avoided in the choice of the experimental matrix of variables. Furthermore, correlations and representations of the particulate measurements took care to account for the effects of other variables as the effect of a given variable was being discussed. This was particularly important for the effect of sulfur content of the fuel. Methods sought to distinguish the effects of fuel from lubricating oil. Effect of humidity on sulfate-related particulate weight was considered. This approach acknowledged te importance of combinations of variables when discussing particulates formation.

Additionally, they pointed out the weak relation between PAH measured in the collected particulates from the PAH of total aromatics of the original test fuels. The PAH in the exhaust responded nonlinearly to fuel aromatics and T_{90}. This led them to observe that interpolating PAH level in particulates from data derived from fuels of extremely low and high aromatics contents could "greatly overestimate the PAH content of mid-range fuels".

One study (Reference 7) used all of the combinations mentioned above. They tested eleven fuels in a 1991 Navistar engine operated over the FTP transient test cycle. Their major findings are given below and are contrasted with other studies reviewed:

1. Particulates did not change with variations in cetane number. Another study (Reference 10) also over the FTP cycle found a very small reduction in PM for a 15 number increase in cetane number. The same investigators (Reference 11) reported small decreases in PM for increases in natural cetane number and declining PM reductions for cetane increases with additives. In the latter two studies, PM was at or below the 0.1 g/hp-hr limit for 1998.

2. Total particulates correlated positively with sulfur content, 90 percent distillation temperature, and polyaromatics in the fuel. Statistical analysis separated the contributions from these interrelated properties for good linear correlation plots. Another study (Reference 9) found similar trends with fuel sulfur concentration in a 1994 DDC Series 60 engine. A later project (Reference 10) using the same fuel set as Reference 9, but in a 1994 Navistar engine, reported small PM increases versus SFC aromatics at very low PM levels (0.08 to 0.108 g/hp-hr).

3. Soluble organic fraction showed linear increases with increased sulfur content, mass spectroscopy aromatics, and mass spectroscopy polyaromatics in the fuel. Another study (Reference 8) reported an increase of similar magnitude with mass spectroscopy aromatics but inconsistent trends with the other two parameters, sulfur and mass spectroscopy polyaromatics.

The current situation on PM emission standards is that the heavy duty diesel engine requirement has moved downward since 1982 from 0.60 g/hp-hr to 0.1 g/hp-hr for 1998, an 83 percent reduction. No further reduction is planned, even under the Statement of Principles Agreement, unless the planned engine testing results in a requirement for reduction in aromatic content of fuels.

The emission standard now in place eventually will reduce particulate emissions for on-highway use. It may take 16 years of vehicle replacements by age or accidents to supplant 50 percent of the trucks on the road, based on 1990 estimates[(2)]. The Urban Transit Retrofit Program will approach the 0.10 g/hp-hr PM limit with time. The general trend will be a continued decline in particulates in heavy duty emissions.

Heavy duty vehicles consume much more diesel fuel than light duty cars or trucks, so they will show the majority of the reduction. However, the light duty vehicle PM emission standard has decreased from 0.6 g/mile in 1982 to 0.08 g/mile in 1998, an 87 percent reduction. The light duty vehicle has a shorter replacement time than heavy duty vehicles.

The general conclusion is that there has been a continuing reduction in vehicle particulate emissions since 1982, with a small acceleration of the reduction in late 1993 attributable to changes in fuel quality. Taking a fairly long term view, this trend should continue into the future.

6 REFERENCES

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3. Arai, Minoru. Isuzu Advanced Engineering Center, Ltd., "Impact of Changes in Fuel Properties and Lubrication Oil on Particulate Emissions and SOF," SAE Paper 920556, February, 1992.

4. Tamanouchi, Mitsuo et al. Advanced Technology & Research Institute Petroleum Energy Center, "Effects of Fuel Properties and Oxidation Catalyst on Exhaust Emissions for Heavy Duty Diesel Engines and Diesel Passenger Cars," SAE Paper 980530, February 1998.

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8. Ullman, Terry L. et al. Southwest Research Institute, "Effects of Cetane Number, Cetane Improver, Aromatics, and Oxygenates on 1994 Heavy-Duty Diesel Engine Emissions," SAE Paper 941020, February 1994.

9. Spreen, Kent B. et al. Southwest Research Institute, "Effects of Cetane Number, Aromatics, and Oxygenates on Emissions From a 1994 Heavy-Duty Diesel Engine With Exhaust Catalyst," SAE Paper 950250, February 1995.

10. Ullman, Terry L. et al. Southwest Research Institute, "Effects of Cetane Number on Emissions From a Prototype 1998 Heavy-Duty Diesel Engine," SAE Paper 950251, February 1995.

11. Wall, J.C. and S.K. Hoekman Chevron Research Company, "Fuel Composition Effects on Heavy-Duty Diesel Particulate Emissions," SAE Paper 841364, 1984.

Glossary of Terms and Abbreviations

AAMA	American Automotive Manufacturers Association.
ASTM	American Society for Testing and Materials.
Aromatics	Cyclic organic compounds, e.g., benzene and naphthalene, having the formula C_nH_{2n-6r}, where n = # carbon atoms and r = # rings. The most common method of measuring diesel aromatics concentration is ASTM D 1319.
CARB	California Air Resources Board.
Cetane index	An estimate of a diesel fuel's ignition quality as expressed by the cetane number per ASTM D4737. The formula calculates the value using the fuel's density, 10% distillation temperature, 50% distillation temperature, and 90% distillation temperature.
Cetane number	A measure of a diesel engine's ignition quality per ASTM D613 on a scale of 0 to 100, but typical testing values are between 30 and 65.
EPA	Environmental Protection Agency.
HC	Hydrocarbon compounds, i.e., molecules containing carbon and hydrogen.
NIPER	National Institute of Petroleum Energy Research.
NO_x	Nitrogen oxides. Toxic compounds formed in the high temperature plasma of the combustion chamber of reaction between nitrogen-containing compounds and oxygen.
PAH	Polyaromatic hydrocarbons, e.g., naphthalene, anthracene and their adducts.
Particulates	Solid materials formed in the engine from the combustion of fuels, comprised of soot, ash, and soluble organic fractions.
PM emissions	Particulate matter emissions.
SOF	Soluble organic fraction, i.e., the fraction of particulate soluble in solvent.
Soot	Carbonaceous high molecular weight solids formed from combustion of fuel.
Sulfur oxides	Reaction species formed from the high temperature reaction between fuel borne sulfur and oxygen, typically SO_2 and SO_3.
SFC	Supercritical fluid chromatography per ASTM D5186, in which fuel sample is injected onto a silica analytical column. Carbon dioxide is used to separate aromatic and other components for registering on a flame ionization detector.
T_{90}	Ninety percent distillation temperature, ie, the temperature at which ninety percent of the material has been distilled per ASTM D86.

SwRI 8271

LITERATURE REVIEW OF TIER 1 REQUIREMENTS OF THE CLEAN AIR ACT 211(b) REGULATIONS

By

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FINAL LETTER REPORT

Prepared for

AMERICAN PETROLEUM INSTITUTE
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December 1996

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December 9, 1996

To: *American Petroleum Institute*
1220 L Street Northwest
Washington, DC 20005-4070

Attention: Mr. David H. Lax, Senior Environmental Scientist

Subject: Final Report, SwRI Project No. 08-8271, "Literature Review of Tier 1 Requirements of the Clean Air Act 211(b) Regulations"

I. INTRODUCTION

Tier 1 of the final rule on Fuels and Fuel Additives Regulations of the Clean Air Act, section 211(b), requires manufacturers to submit data which characterize the emissions of vehicles operated on various categories of fuels and fuel additives to the Environmental Protection Agency (EPA). Manufacturers are permitted to utilize data from test programs that have already been conducted, with the caveat that the test program, fuels, etc., are relevant and meet all requirements set forth in section 211(b). The 211(b) Research Group of the American Petroleum Institute (API) has contracted with the Department of Emissions Research to perform an in-depth literature search to determine if sufficient data exist in the public domain to meet the Tier 1 requirements for the characterization of exhaust emissions from heavy-duty diesel vehicles, under the final rule on Fuels and Fuel Additives Registration Regulations in *40 CFR Part 79, §79.52.* API requested data from studies performed with heavy heavy-duty engines, which are defined as those engines with horsepower ratings generally in excess of 250, with sleeves to permit multiple rebuilds, and which are normally used in inter-city, long-haul trucks, tractors, and buses (vehicles which normally exceed 33,000 lbs GVWR.[1] Some of the studies reviewed made reference to medium-duty engines in addition to heavy heavy-duty engines. The *CFR* defines medium heavy-duty engines as those with power ranges generally from 170 to 250 horsepower, normally used in school buses, tandem axle straight trucks, and city tractors (vehicles whose GVWR varies from 19,500 - 33,000 lbs). EPA requires three measurements for each constituent listed in Table 1.

This report concludes Task 3, which was to compile a summary of the findings reported in Tasks 1 and 2, namely, to determine whether "sufficient" (as defined in section 211(b)) data exist to satisfy the minimum reporting requirements for all the categories listed in Table 1. A synopsis of each study reviewed was also to be included as a part of Task 3.

---

[1] *40 CFR 86, Subpart A §86.085-2*

TABLE 1. EMISSIONS CONSTITUENTS FOR WHICH TIER 1 CHARACTERIZATION DATA ARE REQUIRED

VAPOR PHASE	SEMI-VOLATILE PHASE	PARTICULATE PHASE
Total hydrocarbons (HC) Carbon monoxide (CO) Oxides of Nitrogen (NO_x) Speciated HC (C_1 - C_{12}) Aldehydes & Ketones Alcohols & Ethers	Polynuclear aromatic hydrocarbons (PAH) Nitrated PAH (NPAH)	Total Particulate PAH NPAH

II. RESULTS

An in-depth electronic search was performed to locate data for all categories in Table 1 for heavy-duty diesel exhaust. Searches were conducted using the following electronic databases:

- SAE MOVE -- features all technical publications of the Society of Automotive Engineers (technical papers, books, conference proceedings, international publications) from 1906 to the present -- over 104,000 entries.

- Ei Compendex Plus -- machine-readable version of *The Engineering Index*, providing abstracted information from the world's significant literature of engineering and technology. Approximately 2,600 journals and selected government reports are included.

- Aerospace Database, American Institute of Aeronautics and Astronautics -- features scientific and technical documents, books, reports, and conferences covering R&D in over 40 countries.

- CA SEARCH -- includes over 10 million citations to the literature of chemistry and its applications, an expanded database of information that appears in print in *Chemical Abstracts*.

- NTIS -- provides access to the results of U.S. government-sponsored research, development, and engineering, plus work performed by federal agencies, their contractors, or grantees. Includes reports from National Advisory Council (NAC), Defense Documentation Center (DDC), Departments of Commerce, Energy, Transportation, Housing and Urban Development, and some 600 other agencies. Some state and local government agencies contribute their reports to the database. Also included are reports contributed by the Japan Ministry of International Trade and Industry (MITI), the United Kingdom Department of

Industry, the German Federal Ministry of Research and Technology (BMFT), and the French National Center for Scientific Research (CNRS).

- Enviroline -- features indexing and abstracting coverage of more than 5,000 international primary and secondary source publications reporting on all aspects of the environment. Literature covered includes periodicals, government documents, industry reports, proceedings of meetings, newspaper articles, films, and monographs.

- Environmental Bibliography -- covers atmospheric studies, energy, ecology, land and water resources, health, etc. Includes more than 300 periodicals.

These searches resulted in over 300 citations. Each citation was reviewed to see what information about the study could be gained from the title, or abstract (if supplied). Culling from this list yielded thirty-four studies that were considered promising. Each of those documents was reviewed, rated for adequacy (whether or not it meets the requirements for an acceptable study as defined by the 211 (b) rules, listed below), and summarized.

Eight papers were found that adequately address *all* the requirements for acceptable study parameters as defined in section 211 (b). Summaries of the acceptable studies are presented in Appendix A. Purchased copies of these reports are included in this transmittal. A summary of the 211 (b) requirements for acceptable studies is as follows:

- test must be run with and without aftertreatment, if aftertreatment was used
- type I or II diesel fuel must be used
- the test engine should be representative of those used in Class 8 trucks
- the EPA new engine certification procedure (heavy duty transient test) should be used.

In addition, it was requested by the 211(b) Research Group that information on the engine, fuel(s), test cycle, temperatures tested, analytical methods used, and laboratory name be reported when available (these data are not required by EPA). This information has been provided, when available, in the summaries presented in Appendices A, C, and D.

Only two of all the papers reviewed made any mention of alcohols, and no reference has been found to ethers. However, it is important to note that our study focused on exhaust emissions programs associated with baseline diesel fuel. Because alcohols and ethers are not components of baseline diesel fuel (in *40 CFR Part 79, §79.55(c)(1)*), we do not feel it is important or required to report measurements on these two classes of compounds. Correspondence received from your office on September 13, 1996, indicated that the 211 (b) Research Group is in agreement with this position concerning measurements of alcohols and ethers in the exhaust emissions associated with baseline diesel fuel.

In addition, no studies reporting separate measurements for particulate vs semi-volatile fractions for the *complete* list of PAH/NPAH compounds were found. Eight studies did report separate measurements for

PAH/NPAH between particulate and semivolatile fractions; however, none reported the complete list of compounds called for in the 211(b) rules. Of these, all had some deficiency, such as using steady-state operation instead of transient operation, which excluded them from the "acceptable study" category. Two studies, Nos. 1 and 2 in the following paragraph, cover the complete list of PAH/NPAH compounds *and* meet acceptability requirements, but report results as a composite for the semi-volatile and particulate-associated phases.

Three studies, from the group of eight which meet all the criteria for acceptability, provide coverage for all the analysis categories listed in Table 1, with the exceptions noted above. Those studies are identified below. Please note that references 1 and 2 below report the same data. Appendix B contains a table which presents three measurements for each constituent listed in Table 1.

1. K. Mitchell, et al. *Impact of Diesel Fuel Aromatics on Particulate, PAH and Nitro-PAH Emissions*, SAE 942053, Fuels & Lubricants Meeting and Exposition, Baltimore, MD, Oct 17-20, 1994.

2. *Impact of Diesel Fuel Aromatics on Particulate, PAH and Nitro-PAH Emissions*, Ortech International, for Efficiency and Alternative Energy Technology Branch, CANMET, Natural Resources Canada, Ottawa, Ontario, Canada, Catalogue No. M91-7/290-1994E, April, 1994.

3. Edward A. Bass and Matthew S. Newkirk, *Reactivity Comparison of Exhaust Emissions from Heavy-Duty Engines Operating on Gasoline, Diesel, and Alternative Fuels*, Southwest Research Institute internal document SwRI 9856, December, 1995.

Twelve additional reports were located which met the above criteria for acceptability to varying degrees. There are some excellent studies in this group; however, because they do not meet *all* the criteria, they are presented separately in Appendix C. In general, the studies summarized in Appendix C were run under steady-state operating conditions.

Fourteen other reports, found in the database searches and reviewed, fell so short of the acceptance criteria that they are presented separately from the group in Appendix C. These unacceptable papers are summarized in Appendix D. *Please note that this is no reflection on the quality of the work performed or on the validity of the conclusions.* Rather, it only implies that the studies in this group do not come close to meeting the criteria for acceptable studies for the purposes of data submission under part 211 (b). Finally, search criteria and "positive hits" (the output from the database searches) are presented in Appendix E.

III. CLOSURE

Several studies evaluated in this literature review, and summarized in Appendix A, provide satisfactory coverage for the Tier I requirements for baseline diesel fuel. A number of programs summarized in Appendix C come close to meeting the requirements of 211(b), and could be included in the submission to EPA. We believe that the 211 (b) Research Committee can submit the information summarized in Appendix B to the EPA to fulfill the data requirements of the Clean Air Act 211 (b) Tier I rules for baseline diesel fuel.

This report fulfills the requirements for Task 3, as described in our proposal dated June 17, 1996. Please contact Patrick Merritt at 210-522-5422 (fax 210-522-3950) if you have any questions or comments. It has been a pleasure to be of service to the 211 (b) Research Group of the American Petroleum Institute.

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APPENDIX A

ACCEPTABLE STUDIES FOR SUBMISSION OF DATA UNDER THE REQUIREMENTS OF TIER I REGULATIONS OF SECTION 211(B) OF THE CLEAN AIR ACT

Title	Impact of Diesel Fuel Aromatics on Particulate, PAH and Nitro-PAH Emissions
Author(s)	K. Mitchell, D.E. Steer, and J.A. Taylor, Canadian Petroleum Products Institute; B. Manicom, ORTECH Corp.; J.E. Fisher and E. J. Sienicki, Engine Manufacturers Association; C. Chiu, Environment Canada; P. Williams, Natural Resources Canada
Bibliographic Information	SAE Technical Paper No. 942053, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001, Fuel & Lubricants Meeting and Exposition, Balitimore, MD., October 17-20, 1994.
Abstract	Two state-of-the-art diesel engines were used. One, a heavy heavy-duty DDC Series 60, is representative of those used in highway trucks. The second, a medium heavy-duty Navistar DTA-466, is used in delivery type vehicles. The Navistar was tested with and without an aftertreatment catalyst. Each was tested according to the US EPA transient emissions test on a series of diesel fuels. Fuels were all of low sulfur content (<0.05%). Particulate and vapor phase PAH and nitro-PAH samples were collected and analyzed. Regulated emissions and aldehydes were also measured. Comparisons were made of PAH and nitro-PAH levels with aromatic content of the four test fuels.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	✔[1]
	CO	✔		NPAH	✔[2]
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	✔[1]
	Carbonyls	✔		NPAH	✔[2]
Test performed with and without aftertreatment?		✔[3]	Engine Representative of Class 8 Trucks?		✔
Type I or II Diesel Fuel Used?		✔	New Engine Cert Procedure (EDDS) Used?		✔

Number, type, year of engine	Detroit Diesel Series 60, heavy heavy-duty, modified to meet 1994 emissions regulations, 246 kW, 1722 Nm, direct injection, turbo, 11.1 L; Navistar DTA 466 (medium heavy-duty), 1991 prototype targeting 1994 emissions regulations, 149 kW, direct injection, turbo, 7.6 L
Number, type, specs of fuel used	Four diesel fuels, low sulfur (<0.05%), Type II; Fuel specs given in Table 1 on page 4
Engine cycle, temps tested	US EPA Heavy Duty Transient Test Cycle, 40 CFR, Part 86, Subpart N
Analytical methods	NDIR, FID, CL, gravimetric, GC/MS[4]
Laboratory Name	ORTECH Corporation and Environment Canada

1 Semi-volatile and particulate-associated PAH reported together as a composite

2 Semi-volatile and particulate-associated NPAH reported together as a composite

3 Applies only to the Navistar engine.

4 NDIR = non-dispersive infra red, for CO, CO_2
CL = chemiluminescence, for oxides of nitrogen
FID = flame ionization detector, for hydrocarbons
GC/MS = gas chromatography/mass spectroscopy, for PAH & NPAH

Title	Impact of Diesel Fuel Aromatics on Particulate, PAH and Nitro-PAH Emissions
Author(s)	ORTECH Corporation (No Author(s) or Editor Credited)
Bibliographic Information	NIST document no. 95-01082; ISBN 0-662-22311-X; Catalog No. M91-7/290-1994E, Minister of Supply and Services Canada, 1994
Abstract	Two state-of-the-art diesel engines were used. One, a heavy heavy-duty DDC Series 60, is representative of those used in highway trucks. The second, a medium heavy-duty Navistar DTA-466, is used in delivery type vehicles. The Navistar was tested with and without an aftertreatment catalyst. Each was tested according to the US EPA transient emissions test on a series of diesel fuels. Fuels were all of low sulfur content (<0.05%). Particulate and vapor phase PAH and nitro-PAH samples were collected and analyzed. Regulated emissions and aldehydes were also measured. Comparisons were made of PAH and nitro-PAH levels with aromatic content of the four test fuels.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	✔[1]
	CO	✔		NPAH	✔[2]
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	✔[1]
	Carbonyls	✔		NPAH	✔[2]
Test performed with and without aftertreatment?		✔[3]	Engine Representative of Class 8 Trucks?		✔
Type I or II Diesel Fuel Used?		✔	New Engine Cert Procedure (EDDS) Used?		✔

Number, type, year of engine	Detroit Diesel Series 60, heavy heavy-duty, 1991 modified to meet 1994 emissions regulations, 246 kW, 1722 Nm, direct injection, turbo, 11.1 L; Navistar DTA 466, medium heavy-duty, 1991 prototype targeting 1994 emissions regulations, 149 kW, direct injection, turbo, 7.6 L
Number, type, specs of fuel used	Four diesel fuels, low sulfur (<0.05%), Type II; Fuel specs given in Appendix A
Engine cycle, temps tested	US EPA Heavy Duty Transient Test Cycle, 40 CFR, Part 86, Subpart N
Analytical methods	NDIR, FID, CL, gravimetric, GC/MS[4]
Laboratory Name	ORTECH Corporation and Environment Canada
Note: this data is the same as that reported in the previous reference, SAE 942053	

1 Semi-volatile and particulate-associated PAH reported together as a composite

2 Semi-volatile and particulate-associated NPAH reported together as a composite

3 Applies only to the Navistar engine.

4 NDIR = non-dispersive infra red, for CO, CO_2
CL = chemiluminescence, for oxides of nitrogen
FID = flame ionization detector, for hydrocarbons
GC/MS = gas chromatography/mass spectroscopy, for PAH & NPAH

Title	Reactivity Comparison of Exhaust Emissions from Heavy-Duty Engines operating on Gasoline, Diesel, and Alternative Fuels
Author(s)	Edward A. Bass and Matthew S. Newkirk, Southwest Research Institute
Bibliographic Information	Final Report, to the Advisory Committee for Research, SwRI 9856, Southwest Research Institute, San Antonio, Texas, December 1995
Abstract	Five engines were tested using five different fuels (each engine was optimized to run on one type of fuel). Fuels examined were LPG, CNG, "industry average" gasoline (RF-A), California Phase 2 gasoline (CP2), and diesel fuel. Each engine/fuel combination was tested in triplicate using the US EPA heavy-duty transient cold- and hot-start test protocol. Regulated emissions and hydrocarbon speciation were measured for all tests to allow determination of ozone-forming potentials, using the California Air Resources Board (CARB) maximum incremental reactivity factors, as well as determination of Clean Air Act "toxic" emissions.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO	✔		NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC	✔		PAH	
	Carbonyls	✔		NPAH	
Test performed with and without aftertreatment?		✔	Engine Representative of Class 8 Trucks?		✔
Type I or II Diesel Fuel Used?		✔	New Engine Cert Procedure (EDDS) Used?		✔

Number, type, year of engine	Detroit Diesel Series 60 , heavy heavy-duty diesel, 1991
Number, type, specs of fuel used	2D diesel fuel, low sulfur (330 ppm) Properties reported in Table 3, p.4
Engine cycle, temps tested	US EPA Heavy Duty Transient Test Cycle, 40 CFR, Part 86, Subpart N
Analytical methods	NDIR, FID, CL, gravimetric, GC-FID, HPLC-UV[1]
Laboratory Name	Department of Emissions Research, Southwest Research Institute

[1] GC-FID = gas chromatography/flame ionization detector, for speciated hydrocarbons
HPLC-UV = high performance liquid chromatography/ultraviolet detector, for carbonyls
NDIR = non-dispersive infra red, for CO, CO_2
CL = chemiluminescence, for oxides of nitrogen
FID = flame ionization detector, for hydrocarbons

Title	Effects of Fuel Oxygenates, Cetane Number, and Aromatic Content on Emissions From 1994 and 1998 Prototype Heavy-Duty Diesel Engines
Author(s)	Kent B. Spreen, Terry L. Ullman, and Robert L. Mason, Southwest Research Institute
Bibliographic Information	Final Report, SwRI 4127, Southwest Research Institute, San Antonio, Texas, December 1995 Performed for the Coordinating Research Council
Abstract	In part one, the effects of cetane number, aromatic level, and oxygen content of diesel fuel were examined. In part two, cetane number effects on emissions from a prototype 1998 heavy-duty engine were examined. Testing was performed according to the US EPA Heavy Duty Transient Test. Regulated emissions and speciated hydrocarbons were measured.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO	✔		NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC	✔		PAH	
	Carbonyls	✔		NPAH	
Test performed with and without aftertreatment?		✔	Engine Representative of Class 8 Trucks?		✔
Type I or II Diesel Fuel Used?		✔	New Engine Cert Procedure (EDDS) Used?		✔

Number, type, year of engine	Detroit Diesel Series 60 , heavy heavy-duty diesel, 1994 Navistar DTA-466, medium heavy-duty diesel, 1994
Number, type, specs of fuel used	Eleven diesel fuels, with base fuel meeting type II specs, low sulfur (<500 ppm), 27.5 ± 2.5 volume percent aromatics. Properties for all fuels reported in Tables 9 & 10, p.24
Engine cycle, temps tested	US EPA Heavy Duty Transient Test Cycle, 40 CFR, Part 86, Subpart N
Analytical methods	NDIR, FID, CL, gravimetric, GC-FID, HPLC-UV, FIA[1]
Laboratory Name	Department of Emissions Research, Southwest Research Institute

[1] GC-FID = gas chromatography/flame ionization detector, for speciated hydrocarbons
HPLC-UV = high performance liquid chromatography/ultraviolet detector, for carbonyls
FIA = fluorescent indicator adsorption
NDIR = non-dispersive infra red, for CO, CO_2
CL = chemiluminescence, for oxides of nitrogen
FID = flame ionization detector, for hydrocarbons

Title	The Effect of Oxygenated Fuels on Emissions from a Modern Heavy-Duty Diesel Engine
Author(s)	Frank J. Liotta, Jr., ARCO Chemical Co. and Daniel A. Montalvo, Southwest Research Institute
Bibliographic Information	SAE 932734, Society of Automotive Engineers, Warrendale, PA Fuels and Lubricants Meeting and Exposition, Philadelphia, PA, October 18-21, 1993
Abstract	Oxygenates of varying molecular structure were evaluated for their effect on emissions from a modern, heavy-duty diesel engine. Transient, hot-start emissions were measured using the US EPA Heavy Duty Transient Test cycle. Regulated emissions and carbonyl compounds were measured.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO	✔		NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	
	Carbonyls	✔		NPAH	
Test performed with and without aftertreatment?		N/A	Engine Representative of Class 8 Trucks?		✔
Type I or II Diesel Fuel Used?		✔	New Engine Cert Procedure (EDDS) Used?		✔

Number, type, year of engine	Detroit Diesel Series 60 , heavy heavy-duty diesel, 1991
Number, type, specs of fuel used	2D diesel fuel, low sulfur (330 ppm). Properties reported in Table 3, p.4
Engine cycle, temps tested	US EPA Heavy Duty Transient Test Cycle, 40 CFR, Part 86, Subpart N
Analytical methods	NDIR, FID, CL, gravimetric, GC-FID, HPLC-UV[1]
Laboratory Name	Department of Emissions Research, Southwest Research Institute

[1] GC-FID = gas chromatography/flame ionization detector, for speciated hydrocarbons
HPLC-UV = high performance liquid chromatography/ultraviolet detector, for carbonyls
NDIR = non-dispersive infra red, for CO, CO_2
CL = chemiluminescence, for oxides of nitrogen
FID = flame ionization detector, for hydrocarbons

Title	Effects of Fuel Aromatics, Cetane Number, and Cetane Improver on Emissions from a 1991 Prototype Heavy-Duty Diesel Engine
Author(s)	Terry L. Ullman, Robert L. Mason, and Daniel A. Montalvo, Southwest Research Institute
Bibliographic Information	SAE 902171, Society of Automotive Engineers, Warrendale, PA International Fuels and Lubricants Meeting and Exposition, Tulsa, OK, October 22-25, 1990
Abstract	To separate the effects of aromatics and cetane number, a fuel set with controlled variation in aromatics and cetane number was developed, including the use of an ignition improver to increase the cetane number of selected fuels. Results indicate that cetane number was the key fuel property affecting transient HC and CO emissions. Cetane number was the principal fuel property affecting composite particulate emissions, but aromatic effects were also significant. Both cetane number and aromatic content affect transient NO_x emissions.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO	✔		NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	✔
Type I or II Diesel Fuel Used?	✔	New Engine Cert Procedure (EDDS) Used?	✔

Number, type, year of engine	Detroit Diesel Series 60 , heavy heavy-duty diesel, 1991 Prototype
Number, type, specs of fuel used	Thirteen diesel fuels, Base fuel meets type II, low sulfur (<0.05 %). Properties reported in Table A-1, p. 13
Engine cycle, temps tested	1984 and 1988 US EPA Heavy Duty Transient Test Cycle, 40 CFR, Part 86, Subpart N
Analytical methods	NDIR, FID, CL, gravimetric[1]
Laboratory Name	Department of Emissions Research, Southwest Research Institute

[1] NDIR = non-dispersive infra red, for CO, CO_2
CL = chemiluminescence, for oxides of nitrogen
FID = flame ionization detector, for hydrocarbons

Title	Study of Fuel Cetane Number and Aromatic Content Effects on Regulated Emissions from a Heavy-Duty Diesel Engine
Author(s)	Terry L. Ullman, Robert L. Mason, and Daniel A. Montalvo, Southwest Research Institute
Bibliographic Information	Final Report, SwRI 08-2940, Southwest Research Institute, September 1990 Prepared for the Coordinating Research Council
Abstract	Cetane number and aromatic content were varied systematically in eight fuels. Replicate cold- and hot-start transient tests using the US EPA Heavy Duty Transient Test Procedure were used to produce measurements of regulated emissions.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO	✔		NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	✔
Type I or II Diesel Fuel Used?	✔	New Engine Cert Procedure (EDDS) Used?	✔

Number, type, year of engine	Detroit Diesel Series 60 , heavy heavy-duty diesel, 1991 Prototype
Number, type, specs of fuel used	Thirteen diesel fuels, Base fuel meets type II, low sulfur (<0.05 %) Properties reported in Table A-1, p. 13
Engine cycle, temps tested	1984 and 1988 US EPA Heavy Duty Transient Test Cycle, 40 CFR, Part 86, Subpart N
Analytical methods	NDIR, FID, CL, gravimetric[1]
Laboratory Name	Department of Emissions Research, Southwest Research Institute

Note: this data is the same as that reported in the previous reference, SAE 902171.

[1] NDIR = non-dispersive infra red, for CO, CO_2
CL = chemiluminescence, for oxides of nitrogen
FID = flame ionization detector, for hydrocarbons

Title	Emissions Evaluation of Two Heavy-Duty Diesel Engines on Two Low-Sulfur Fuels with Variation in Aromatics
Author(s)	Terry L. Ullman, Southwest Research Institute
Bibliographic Information	Final Report, SwRI 08-8707, Southwest Research Institute, April, 1988 Prepared for the California Air Resources Board
Abstract	Fuels having low sulfur with high and low levels of aromatic content were evaluated with the US EPA Transient Test for heavy duty engines to determine effects on regulated emissions.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO	✔		NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	
	Carbonyls			NPAH	
Test performed with and without aftertreatment?		N/A	Engine Representative of Class 8 Trucks?		✔
Type I or II Diesel Fuel Used?		✔	New Engine Cert Procedure (EDDS) Used?		✔

Number, type, year of engine	Detroit Diesel Series 60, heavy heavy-duty diesel Cummins NTCC 400, heavy heavy-duty diesel
Number, type, specs of fuel used	Two diesel fuels, low sulfur and low aromatics
Engine cycle, temps tested	US EPA Heavy Duty Transient Test Cycle, 40 CFR, Part 86, Subpart N
Analytical methods	NDIR, FID, CL, gravimetric[1]
Laboratory Name	Department of Emissions Research, Southwest Research Institute

[1] NDIR = non-dispersive infra red, for CO, CO_2
CL = chemiluminescence, for oxides of nitrogen
FID = flame ionization detector, for hydrocarbons

APPENDIX B

Summary of representative data

TABLE C-1 SUMMARY OF DATA CALLED FOR IN SECTION 211 (B)

		Measurement Result[a]		
		1	2	3
Vapor Phase	HC, g/bhp-hr	0.19	0.20	0.17
	CO, g/bhp-hr	2.13	2.05	2.06
	NO_x, g/bhp-hr	4.63	4.57	4.46
	Speciated HC	Please see Tables B-16, B-17, and B-18 in Appendix B of reference A-3, *Reactivity Comparison of Exhaust Emissions from Heavy-Duty Engines operating on Gasoline, Diesel, and Alternative Fuels*, Edward A. Bass and Matthew S. Newkirk (Copy Provided)		
	Carbonyls, mg/bhp-hr	36.5	35.0	33.8
Composite of Semi-volatile and Particulate-Associated Phases, µg/bhp-hr	Benzo [a] anthracene	0.20	0.06	ND
	Benzo [ ][b] fluoranthene	0.12	ND	ND
	Benzo [a] pyrene	ND	ND	ND
	Chrysene	0.82	0.17	0.17
	Dibenzo [a,h] anthracene	ND	ND	ND
	Ideno [1,2,3-c,d] pyrene	ND	ND	ND
	7-Nitrobenzo [a] anthracene	ND	ND	ND
	6-Nitrobenzo [a] pyrene	ND	ND	ND
	6-Nitrochrysene	ND	ND	ND
	2-Nitrofluorene	ND	ND	ND
	1-Nitropyrene	0.061	0.043	0.067
	Particulate, (g/hp-hr)	0.127	0.128	0.110

ND - not detected
[a] Data from reference A-1, *Impact of Diesel Fuel Aromatics on Particulate, PAH and Nitro-PAH Emissions*, K. Mitchell, et al.
[b] Composite of [b], [k], [j] isomers

APPENDIX C

Studies which meet most of the acceptance criteria in section 211 (b)

Title	Measurement of PAH and Nitro-PAH From a Heavy-Duty Diesel Engine
Author(s)	S.K. Hoekman and M.C. Ingham, Chevron Research Co.
Bibliographic Information	Proceedings of the 80th Annual Meeting of the Air Pollution Control Association, June 21-26, 1987, New York ILL 8299531
Abstract	Procedures for the measurement of PAH and Nitro-PAH from a heavy-duty diesel engine were developed and validated. The variability of PAH and N-PAH production was compared with the variability of analytical procedures.

Vapor Phase	HC		Semi-volatile Phase	PAH	
	CO			NPAH	
	NOx		Particulate Phase	Particulate matter	
	Speciated HC			PAH	✔
	Carbonyls			NPAH	✔

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Cummins NTCC-350, 14L
Number, type, specs of fuel used	Commercial No. 2 diesel
Engine cycle, temps tested	Steady-state
Analytical methods	HPLC-F, GC-ECD[1]
Laboratory Name	Chevron Research Co.

[1] HPLC-F = high performance liquid chromatography with fluorescence detector
GC-ECD = gas chromatograph with electron capture detector

Title	A Review of Diesel Particulate Control Technology and Emissions Effects - 1992 Horning Memorial Award Lecture
Author(s)	John H. Johnson, Susan T. Bagley, Linda D. Gratz, and David G. Leddy, Michigan Technological University
Bibliographic Information	SAE 940233, Society of Automotive Engineers, Warrendale, PA, 1994
Abstract	This paper is a review of 1) modern emission control technologies, 2) emissions sampling and chemical, physical, and biological characterization methods, and 3) summary results from a study conducted at Michigan Technical University on heavy-duty diesel engines with a trap and an oxidation catalytic converter (OCC) operated on three different fuels.

Vapor Phase	HC		Semi-volatile Phase	PAH	✔[1]
	CO			NPAH	✔[1]
	NOx		Particulate Phase	Particulate matter	
	Speciated HC			PAH	✔[1]
	Carbonyls			NPAH	✔[1]

Test performed with and without aftertreatment?	Yes	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	1988 Cummins L10-300
Number, type, specs of fuel used	No. 2 diesel, 0.26% sulfur No. 1 diesel, 0.04% sulfur
Engine cycle, temps tested	steady-state mode 9
Analytical methods	HPLC-F, GC/MS[2]
Laboratory Name	Michigan Technical University

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] HPLC-F = high performance liquid chromatography with fluorescence detector
GC/MS = gas chromatography/mass spectroscopy

Title	Polycyclic Aromatic Hydrocarbons in Diesel Exhaust -- Final Report for the Period January 1984 to May 1985
Author(s)	IIT Research Institute
Bibliographic Information	NTIS PB86-216314
Abstract	Chemical transformations of PAH were conducted as they pass down the exhaust system of a heavy-duty diesel engine. Initial work was done with a mini-dilution tunnel. Particulate and vapor phase PAH were sampled.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	✔[1]
	CO	✔		NPAH	✔[1]
	NOx	✔	Particulate Phase	Particulate matter	
	Speciated HC			PAH	✔[1]
	Carbonyls			NPAH	✔[1]

Test performed with and without aftertreatment?	No	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	1983 Caterpillar 3204 DINA
Number, type, specs of fuel used	DOE reference fuel D-2, lot C504 Phillips Chemical Co. fuel specs given in Table 3 on page 6
Engine cycle, temps tested	Two steady-states: 75% & 25% load-rated speed
Analytical methods	HPLC-F[2]
Laboratory Name	Caterpillar, Peoria; IIT Research Institute - Chicago

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] HPLC-F = high performance liquid chromatography with fluorescence detector

Title	The Influence of Low Sulfur Fuel and a Ceramic Particle Trap on the Physical, Chemical, and Biological Character of Heavy-Duty Diesel Emissions
Author(s)	Troy C. Kantola, Susan T. Bagley, Linda D. Gratz, David G. Leddy, and John H. Johnson, Michigan Technological University
Bibliographic Information	SAE 920565, Society of Automotive Engineers, Warrendale, PA, 1992
Abstract	This study was conducted to assess the effects of a low sulfur fuel and an uncatalyzed ceramic particle trap on heavy-duty diesel emissions during both steady-state operation and during periods of electrically assisted trap regeneration.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	✔[1]
	CO			NPAH	
	NOx	✔	Particulate Phase	Particulate matter	
	Speciated HC			PAH	✔[1]
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	Yes	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Cummins LTA 10-300, 1988, 224 kW
Number, type, specs of fuel used	fuel specs given in Table 1 on p. 192
Engine cycle, temps tested	steady-state, modes 9 & 11
Analytical methods	HPLC-F[2]
Laboratory Name	Michigan Technological University

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] HPLC-F = high performance liquid chromatography with fluorescence detector

Title	Effect of Fuel on the Regulated, Unregulated and Mutagenic Emissions of DI Diesel Engines
Author(s)	Leena Rantanen, Seppo Mikkonen, NESTE Oy; Lars Nylund, Pirkko Kociba, Intitute of Occupational Health; Maija Lappi, and Nils-Olof Nylund, Technical Research Center of Finland
Bibliographic Information	SAE 932686, Society of Automotive Engineers, Warrendale, PA, 1993
Abstract	Emissions of heavy duty engines using hydrocarbon fuels and rape seed methyl ester were measured according to the ECE R49 test procedure. Particulates were measured in a AVL mini dilution tunnel and gaseous unregulated hydrocarbons by FTIR.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO	✔		NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC	✔[1]		PAH	✔[2]
	Carbonyls	✔		NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Scania DS952, Valmet 634 DS, Volvo THD101GC, Volvo THD 103KB
Number, type, specs of fuel used	6 fuels, reference fuel low sulfur No. 2 diesel
Engine cycle, temps tested	ECE R49
Analytical methods	FTIR, gravimetric, GC-FID[3]
Laboratory Name	NESTE Oy, Institute of Occupational Health, Technical Research Centre of Finland

[1] Not full speciation

[2] All PAH compounds reported together as a composite result.

[3] FTIR = Fourier transform infrared spectroscopy
GC-FID = gas chromatography with flame ionization detector

Title	Characterization of Particulate- and Vapor-Phase Organic Fraction Emissions from Heavy-Duty Diesel Engine Equipped with Particulate Trap & Regeneration
Author(s)	Susan Bagley, et al, Michigan Technological University
Bibliographic Information	Health Effects Institute Research Report No. 56, July 1993
Abstract	Investigations of particulate- and vapor-phase organic fraction emissions from heavy duty diesel engines operating on steady state (13 mode, mainly modes 9 & 11) dynamometer tests. Particulate trap with regeneration was evaluated.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	✔[1]
	CO			NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	✔[1]
	Carbonyls	✔		NPAH	

Test performed with and without aftertreatment?	Yes	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Caterpillar 3208 Direct Injection 10.4L, 157 kW, 1979 Cummins LTA-300
Number, type, specs of fuel used	Amoco Premier No. 2 - no other specs given
Engine cycle, temps tested	US EPA 13 mode, primarily 9 & 11
Analytical methods	CL, FID, HPLC-F[2]
Laboratory Name	Department of Biological Sciences, Michigan Technical University

[1] Does not cover the complete list of compounds called for in section 211 (b) rules

[2] FID = flame ionization detector, for hydrocarbons
HPLC-F = high performance liquid chromatography/fluorescence detector, for PAH/NPAH
CL = chemiluminescence, for oxides of nitrogen

Title	The Effects of Fuel Sulfur Concentration on Regulated and Unregulated Heavy-Duty Diesel Emissions
Author(s)	Cornelius N. Opris, Linda D. Gratz, Susan T. Bagley, Kirby J. Baumgard, David G. Leddy, and John H. Johnson, Michigan Technological University
Bibliographic Information	SAE 930730, Society of Automotive Engineers, Warrendale, PA, 1993 International Congress and Exposition, Detroit, MI, March 1-5, 1993
Abstract	The effects of fuel sulfur concentration on regulated and unregulated heavy-duty diesel emissions were studied at two EPA steady-state operating conditions, Mode 9 and Mode 11. Effects on soluble organic fraction (SOF), NO_x, Organic component, HC, total particulate matter (TPM), and sulfate (SO_4) were studied. Particle size distribution was also studied. Partitioning of PAH compounds and mutagenic activity was reviewed.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO			NPAH	
	NOx	✔	Particulate Phase	Particulate matter	
	Speciated HC			PAH	✔[1]
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Cummins LTA-10-300 10L I-6 1988
Number, type, specs of fuel used	Two low sulfur fuels: 0.01 and 0.29 wt%
Engine cycle, temps tested	EPA steady state modes 9 & 11
Analytical methods	HPLC-F[2]
Laboratory Name	Michigan Technological University

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] HPLC-F = high performance liquid chromatography/fluorescence detector, for PAH/NPAH

Title	Heavy-Duty Diesel Engine/Fuels Combustion Performance and Emissions — A Cooperative Research Program
Author(s)	E.G. Barry, L.J. McCabe, Mobil Research & Development Corp.; D.H. Gerke, and J.M. Perez, Caterpillar Tractor Co.
Bibliographic Information	SAE 852078, Society of Automotive Engineers, Warrendale, PA, 1985 International Fuels and Lubricants Meeting and Exposition, Tulsa, OK, October 21-24, 1985
Abstract	An evalutation of the impact of fuel composition (volatility, aromatics, and sulfur) on the combustion and emissions performance of a Caterpillar 3406B turbocharged diesel engine. Tests included steady-state and transient operation.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO	✔		NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	✔[1]
	Carbonyls	✔		NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Caterpillar 3406B, 261 kW
Number, type, specs of fuel used	10 fuels, base fuel representative of No. 2 diesel
Engine cycle, temps tested	US EPA 13-mode steady-state, transient smoke test, and heavy-duty transient test.
Analytical methods	Mini-dilution tunnel & shared double dilution tunnel used for sample collection
Laboratory Name	Mobil R & D, Caterpillar Tractor Co.

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

Title	Effects of a Ceramic Particle Trap and Copper Fuel Additive on Heavy-Duty Diesel Emissions
Author(s)	George D. Harvey, Kirby J. Baumgard, John H. Johnson, Linda D. Gratz, Susan T. Bagley, and David G. Leddy, Michigan Technological University
Bibliographic Information	SAE 942068, Society of Automotive Engineers, Warrendale, PA, 1994
Abstract	The effects of a copper fuel additive on the regulated and unregulated (SOF, XOC, PAH, NPAH) emissions from a 1988 Cummins LTA10 diesel engine using low sulfur fuel were studied.

Vapor Phase	HC		Semi-volatile Phase	PAH	✔[1]
	CO			NPAH	✔[1]
	NOx		Particulate Phase	Particulate matter	
	Speciated HC			PAH	✔[1]
	Carbonyls			NPAH	✔[1]

Test performed with and without aftertreatment?	Yes	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	1988 Cummins LTA10
Number, type, specs of fuel used	low sulfur No. 2 diesel, 28.8% aromatic; specs in Table 1 on p. 208
Engine cycle, temps tested	Steady-state, Modes 9 & 11
Analytical methods	HPLC-F[2]
Laboratory Name	Michigan Technological University

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] HPLC-F = high performance liquid chromatography with fluorescence detector

Title	The Effect of a Ceramic Particulate Trap on the Particulate and Vapor Phase Emissions of a Heavy-Duty Diesel Engine
Author(s)	L.D. Gratz, S.T. Bagley, Michigan Technological University; K.S. King, Caterpillar, Inc.; K.J. Baumgard, D.G. Leddy, and J.H. Johnson, Michigan Technological University
Bibliographic Information	SAE 910609, Society of Automotive Engineers, Warrendale, PA, 1991
Abstract	Exhaust emissions were characterized from a Cummins LTA 10 heavy-duty diesel engine operated at two EPA steady-state modes with and without an uncatalyzed Corning ceramic particulate trap.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	✔[1]
	CO			NPAH	✔[1]
	NOx	✔	Particulate Phase	Particulate matter	
	Speciated HC			PAH	✔[1]
	Carbonyls			NPAH	✔[1]

Test performed with and without aftertreatment?	Yes	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Cummins LTA 10-300, 10L, 224 kW
Number, type, specs of fuel used	Amoco Premier No. 2
Engine cycle, temps tested	Steady-state, modes 9 & 11
Analytical methods	HPLC-F[2]
Laboratory Name	Michigan Technological University, Caterpillar, Inc.

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] HPLC-F = high performance liquid chromatography with fluorescence detector

Title	Chemical Analysis and Biological Testing of Emissions from a Heavy-Duty Diesel Truck With and Without Two Different Particulate Traps
Author(s)	Roger Westerholm, Tomas Alsberg, et al, University of Stockholm
Bibliographic Information	SAE 860014, Society of Automotive Engineers, Warrendale, PA, 1986 from Advances in Diesel Particulate Control, P-172, February, 1986
Abstract	Thirteen mode emissions tests were performed to evaluate the performance of particulate traps. Regulated emissions and PAH, and mutagenicity by Ames test were performed. Emissions were also measured under a transient bus driving cycle on a chassis dynamometer.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO	✔		NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	✔[1]
	Carbonyls	✔		NPAH	✔[1]

Test performed with and without aftertreatment?	Yes	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Scania DS115, 11L, 232 kW
Number, type, specs of fuel used	two low-sulfur fuels used
Engine cycle, temps tested	US EPA 13-mode; German Bus Transient Driving Cycle
Analytical methods	NDIR, FID, CL, Gravimetric, HPLC-F[2]
Laboratory Name	University of Stockholm, Stockholm, Sweden The National Swedish Environment Protection Board, Nyköping, Sweden

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] NDIR = non-dispersive infra red spectroscopy
FID = flame ionization detector, for hydrocarbons
HPLC-F = high performance liquid chromatography/fluorescence detector, for PAH/NPAH
CL = chemiluminescence, for oxides of nitrogen

Title	Fuel Composition Effects on Heavy-Duty Diesel Particulate Emissions
Author(s)	J.C. Wall and S.K. Hoekman, Chevron Research Co.
Bibliographic Information	SAE 841364, Society of Automotive Engineers, Warrendale, PA, 1984 Fuels and Lubricants Meeting and Exposition, Baltimore, MD, October 8-11, 1984
Abstract	The effects of mid-distillate fuel properties on particulate emissions from a heavy-duty diesel engine were reported. Forty-two test fuels in 155 engine tests, over a two year period were studied to determine the sensitivity of particulate emissions to each of the key fuel variables at different engine operating conditions.

Vapor Phase	HC		Semi-volatile Phase	PAH	
	CO			NPAH	
	NOx		Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	✔[1]
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Cummins NTC 290, DI, Turbocharged 6 cylinder, 14L, 216 kW
Number, type, specs of fuel used	42 different fuels, Several No. 2 commercial fuels used
Engine cycle, temps tested	Steady state at three conditions: 1100 rpm @ 5 kW; 1400 hp @ 84 kW; 2100 rpm @ 183 kW
Analytical methods	HPLC-F[2]
Laboratory Name	Chevron Research Company

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] HPLC-F = high performance liquid chromatography with fluorescence detector

APPENDIX D

Studies which do not meet the
acceptance criteria in section 211 (b):

- heavy heavy-duty engine was not used, or
- Type I or II diesel fuel was not used, or
- no relevant data was reported

Title	Diesel Fuel Aromatic and Cetane Number Effects on Combustion and Emissions from a Prototype 1991 Diesel Engine
Author(s)	Edward J. Sienicki, Richard E. Jass, Warren J. Slodowske, Navistar International Transportation Corporation; Christopher I. McCarthy, Allen L. Krodel, Amoco Oil Company
Bibliographic Information	SAE 902172, Society of Automotive Engineers, Warrendale, PA International Fuels and Lubricants Meeting and Exposition, Tulsa, OK, October 22-25, 1990
Abstract	US EPA transient test emissions were used to determine the effect of fuel properties on combustion characteristics and exhaust emissions. Eleven test fuels with varying aromatic content, cetane number, and other variables were studied.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO			NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	No
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	Yes

Number, type, year of engine	Navistar DTA 466, medium-heavy duty diesel, 1991 Prototype
Number, type, specs of fuel used	Eleven diesel fuels, Base fuel meets type II, low sulfur (<0.05%) Properties reported in Table I, p. 2
Engine cycle, temps tested	US EPA Heavy Duty Transient Test Cycle, 40 CFR, Part 86, Subpart N
Analytical methods	NDIR, FID, gravimetric[1]
Laboratory Name	Navistar International Transportation Corp., Amoco Oil Company

[1] CL = chemiluminescence, for oxides of nitrogen
FID = flame ionization detector, for hydrocarbons

Title	Measurement of Unregulated Exhaust Emissions from Heavy Duty Diesel Engines with Mini-Dilution Tunnel
Author(s)	Nobuyoshi Hirakouchi, Izumi Fuano, and Hayami Nagano, Mitsubishi Motors
Bibliographic Information	SAE 900643, Society of Automotive Engineers, Warrendale, PA, 1990
Abstract	Study examines the use of a mini-tunnel as compared to full flow dilution tunnel specified by US EPA. Regulated exhaust emissions, speciated hydrocarbons, alcohols, carbonyls, and selected PAH and NPAH were measured.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO	✔		NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC	✔		PAH	✔[1]
	Carbonyls	✔		NPAH	✔[1]

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	[2]
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Not reported
Number, type, specs of fuel used	No. 2 diesel fuel; specs given in table 4, p1452.
Engine cycle, temps tested	US EPA Transient Test (with mini-dilution tunnel)
Analytical methods	mini-tunnel used for dilution; Refers to Smith, et al, *Analytical Procedures for Characterizing Unregulated Emissions from Vehicle Using Middle-Distillate Fuels*, Interim Report of US EPA, April 1980
Laboratory Name	Mitsubishi Motors Corporation

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] Not reported

Title	Final Report on Development of Species Profiles for Selected Organic Emission Sources -- Volume II: Engine Exhaust Emissions
Author(s)	Albert C. Censullo, California Polytechnic State University
Bibliographic Information	NTIS PB92157972, California Air Resources Board ARB-R-92/483-vol-2, California Polytechnic State University, San Luis Obispo, CA, April, 1991
Abstract	Fugitive emissions were characterized from utility and heavy-duty engines. A portable exhaust dilution system was fabricated and its use discussed. Speciated hydrocarbons, including aldehydes and ketones were measured.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO	✔		NPAH	
	NOx		Particulate Phase	Particulate matter	
	Speciated HC	✔		PAH	
	Carbonyls	✔		NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	No
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Various farm utility engines
Number, type, specs of fuel used	ARCO commercial No. 2 diesel
Engine cycle, temps tested	Steady-state full load
Analytical methods	HPLC-UV, GC-FID, GC-MSD, mini-tunnel was used[1]
Laboratory Name	California Polytechnic University

[1] HPLC-UV = high performance liquid chromatography with ultra-violet detector
GC-FID = gas chromatography with flame ionization detector
GC-MSD = gc with mass selective detector

Title	Gaseous and Particulate Emissions from Gasoline- and Diesel-Powered Heavy-Duty Trucks
Author(s)	James N. Braddock, Atmospheric Sciences Research Laboratory
Bibliographic Information	SAE 860617, Society of Automotive Engineers, Warrendale, PA, 1986
Abstract	Gaseous and particulate emissions from seven class 2B, one class 5, and six class 6 heavy-duty gasoline- and diesel-powered trucks were determined using transient chassis dynamometer test procedures. Regulated emissions, SOF, particle size, lead, bromine, and chlorine were analyzed.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO	✔		NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	No
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No[1]

Number, type, year of engine	Gasolline: Three 5.4 L V-8's, 5.7 L V-8, 5.9 L V-8 Diesel: 6.2 L V-8, two 6.9 L V-8, four 8.2 L V-8, 10.4 L V-8
Number, type, specs of fuel used	Type 2-D diesel Leaded regular gasoline
Engine cycle, temps tested	HD Transient Chassis Dyno Test
Analytical methods	FID, NDIR, CL, gravimetric[2]
Laboratory Name	Mobil Source Emission Research Branch, USEPA
Note: Not class 8 engines and most had far too much mileage accumulated	

[1] Heavy-duty Transient *Chassis* Dynamometer test was used

[2] FID = flame ionization detector, for hydrocarbons
NDIR = non-dispersive infra-red spectroscopy
CL = chemiluminescence, for oxides of nitrogen

Title	Reduction of NO_x and Particulate Emissions in the Diesel Combustion Process
Author(s)	W.R. Wade, C.E. Hunter, F.H. Trinker, H.A. Cikanek, Ford Motor Co.
Bibliographic Information	Transactions of the ASME, **426** Vol. 109, October 1987
Abstract	A model of the combustion and emission formation processes was formulated to identify modifications to combustion process parameters with potential for reducing NO_x and particulate emissions in a diesel engine.

Vapor Phase	HC		Semi-volatile Phase	PAH	
	CO			NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	No
Type I or II Diesel Fuel Used?	[1]	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Single cylinder test engine
Number, type, specs of fuel used	Not reported
Engine cycle, temps tested	Steady-state
Analytical methods	
Laboratory Name	Ford Motor Co.

Note: This is a parametric study to perform modeling.

[1] Not Reported

Title	Characterization of Polar Polycyclic Aromatic Compounds in a Heavy-Duty Diesel Exhaust Particulate by Capillary Column Gas Chromatography and High-Resolution Mass Spectroscopy
Author(s)	Jose M. Bayona, Karin E. Markides, and Milton L. Lee, Dept of Chemistry, Brigham Young University
Bibliographic Information	**1440**, Environmental Science and Technology, Vol. 22, No. 12, 1988
Abstract	Polar, normal-phase HPLC fraction of a heavy-duty diesel exhaust particulate of a NIST stardard reference material were analyzed by GC-HRMS. Over 80 compounds were tentatively identified. Cyclic imides and their alkylated derivatives were tentatively identified for the first time.

Vapor Phase	HC		Semi-volatile Phase	PAH	
	CO			NPAH	
	NOx		Particulate Phase	Particulate matter	
	Speciated HC			PAH	✔[1]
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	N/A
Type I or II Diesel Fuel Used?	N/A	New Engine Cert Procedure (EDDS) Used?	N/A

Number, type, year of engine	N/A
Number, type, specs of fuel used	N/A
Engine cycle, temps tested	N/A
Analytical methods	Gas chromatography/high resolution mass spectrometry
Laboratory Name	Department of Chemistry, Brigham Young University

This paper covers analysis of an NIST standard reference material only.
No exhaust emissions were generated.

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

Title	Characterization of Heavy-Duty Diesel Vehicle Emissions
Author(s)	Douglas H. Lowenthal, Barbara Zielinska, et al, Desert Research Institute; Mridul Gautam and Donald H. Ferguson, West Virginia University Gary R. Neuroth and Kathy D. Stevens, Arizona Department of Environmental Quality, Office of Air Quality
Bibliographic Information	Atmospheric Environment, Vol 28, No. 4, pp 731-743, 1994
Abstract	Emissions were measured using a transportable heavy-duty vehicle emissions testing laboratory. Thirteen heavy-duty trucks and buses were tested at the Phoenix Transit Yard. Vehicles were operated on No. 2 diesel and Jet A fuels, with and without a fuel additive, and with and without particulate control traps.

Vapor Phase	HC	[1]	Semi-volatile Phase	PAH	✔[2]
	CO	[1]		NPAH	
	NOx	[1]	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	✔[2]
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	Yes	Engine Representative of Class 8 Trucks?	[3]
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No[4]

Number, type, year of engine	not reported
Number, type, specs of fuel used	No. 2 diesel Jet A
Engine cycle, temps tested	Urban Bus Cycle
Analytical methods	AA, XRF, GC-MS[5]
Laboratory Name	Desert Research Institute

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[1] Discussed, but not reported in tabular form.

[2] Does not cover the complete list of compounds called for in section 211 (b) rules.

[3] Not reported

[4] Heavy-duty chassis dynamometer test was used. for central business district cycle.

[5] AA= atomic absorption spectroscopy
XRF = X-ray fluorescence
GC-MS = gas chromatography / mass spectroscopy

Title	The Role of Exhaust Pipe and In cylinder Deposits on Diesel Particulate Composition
Author(s)	G.E. Andrews, S. Abdelhalim, M.K. Abbass, H.R. Asadi-Aghdam, P.T. Williams, and K.D. Bartle, University of Leeds
Bibliographic Information	SAE 921648, Society of Automotive Engineers, Warrendale, PA, 1992
Abstract	Diesel engine exhaust pipe and in-cylinder deposits were analyzed for the global fuel, lube oil, carbon and ash fractions for a range of diesel engines. These deposits were shown to contain significant PAH levels, and hence contain a source of diesel PAH emissions and possible sites for in-cylinder pyrosynthesis of high molecular weight PAH.

Vapor Phase	HC		Semi-volatile Phase	PAH	
	CO			NPAH	
	NOx		Particulate Phase	Particulate matter	
	Speciated HC			PAH	✔[1]
	Carbonyls			NPAH	✔[1]

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	No
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	[2]

Number, type, year of engine	Perkins 4-236, Pelter AV1, Ford 1600cc
Number, type, specs of fuel used	Diesel and kerosene
Engine cycle, temps tested	not reported
Analytical methods	GC-LC-MS[3]
Laboratory Name	University of Leeds
Note: only exhaust pipe deposits were analyzed.	

[1] Does not cover the complete list of compounds called for in section 211 (b) rules; Pipe deposits were analyzed - no analysis on gaseous emissions

[2] Not reported

[3] GC-LC-MS = gas chromatography/liquid chromatography/mass spectroscopy

Title	Sampling Strategies for Characterization of the Reactive Components of Heavy Duty Diesel Exhaust Emissions
Author(s)	Mridul Gautam, Brian Kelly, Deepak Gupta, Nigel Clark, Richard Atkinson, Laila El-Gazzar, and Donald W. Lyons, West Virginia University
Bibliographic Information	SAE 942262, Society of Automotive Engineers, Warrendale, PA, 1994
Abstract	Techniques have been developed to sample and speciate dilute heavy-duty diesel exhaust to determine the specific reactivities and the ozone forming potential.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	
	CO			NPAH	
	NOx		Particulate Phase	Particulate matter	✔
	Speciated HC	✔		PAH	
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	No
Type I or II Diesel Fuel Used?	[1]	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Deutz MWM 916-6 (medium duty diesel)
Number, type, specs of fuel used	not reported
Engine cycle, temps tested	steady state
Analytical methods	GC-FID[2]
Laboratory Name	West Virginia University

[1] Not reported

[2] GC-FID = gas chromatography with flame ionization detector

Title	Investigation of the CTA Emission Control System Applied to Heavy-duty Diesel Engines Used in Underground Mining Equipment
Author(s)	J.P. Mogan, E.D. Dainty, CANMET, Energy, Mines & Resources Canada; K.C. Westaway, Laurentian University; H.C. Vergeer, A. Lawson, Ontario Research Foundation; J.K. Weglo, Falconbridge Nickel Mines Ltd.; L.R. Thomas, Engine Control Systems Ltd.
Bibliographic Information	SAE 850151, Society of Automotive Engineers, Warrendale, PA, 1985
Abstract	This paper describes the application of a catalytic trap oxidizer (CTO) system for particulate emission control to a test-bed engine and a mining vehicle in service. Gaseous and particulate emissions are compared to baseline results. Carbonyls, PAH, and particulate matter are measured.

Vapor Phase	HC		Semi-volatile Phase	PAH	
	CO			NPAH	
	NOx		Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	✔[1]
	Carbonyls	✔		NPAH	

Test performed with and without aftertreatment?	Yes	Engine Representative of Class 8 Trucks?	No
Type I or II Diesel Fuel Used?	[2]	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Deutz F8L-413 F/W 135 kW
Number, type, specs of fuel used	not reported
Engine cycle, temps tested	Michigan Technical University load-haul-dump cycle
Analytical methods	HPLC-UV
Laboratory Name	CANMET, Energy, Mines, & Resources Canada

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] Not reported

Title	Impact of a Barium Fuel Additive on the Mutagenicity and Polycyclic Aromatic Hydrocarbon Content of Diesel Exhaust Particulate Emissions
Author(s)	William M. Draper, Jane Phillips, California Public Health Foundation; H. William Zeller, US Department of Interior, Bureau of Mines
Bibliographic Information	SAE 881651, Society of Automotive Engineers, Warrendale, PA, 1988 Fuels and Lubricants Meeting and Exposition, Portland, OR, October 10-13, 1988
Abstract	The impact of a barium fuel additive on the Ames test mutagenicity and polycyclic aromatic hydrocarbon content of diesel exhaust particulate emissions is reviewed.

Vapor Phase	HC		Semi-volatile Phase	PAH	
	CO			NPAH	
	NOx		Particulate Phase	Particulate matter	
	Speciated HC			PAH	✔[1]
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	No
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Deutz F6L 912W
Number, type, specs of fuel used	No. 2 diesel fuel
Engine cycle, temps tested	light duty, 8 minute transient
Analytical methods	HPLC-F[2]
Laboratory Name	California Public Health Foundation, U.S. Department of Interior Bureau of Mines

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] HPLC-F = high performance liquid chromatography with fluorescence detector

Title	Ways Toward the Clean Heavy-Duty Diesel
Author(s)	P. Zelenka, W. Kriegler, P.L. Herzog, W. P. Cartellieri, AVL LIST Gmbh
Bibliographic Information	SAE 900602, Society of Automotive Engineers, Warrendale, PA, 1990
Abstract	A review of the current status of development of heavy-duty direct injection diesel ingines to meet 1994 US-EPA heavy duty diesel emission standards is made. **No data is presented.**

Vapor Phase	HC		Semi-volatile Phase	PAH	
	CO			NPAH	
	NOx		Particulate Phase	Particulate matter	
	Speciated HC			PAH	
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	N/A
Type I or II Diesel Fuel Used?	N/A	New Engine Cert Procedure (EDDS) Used?	N/A

Number, type, year of engine	N/A
Number, type, specs of fuel used	N/A
Engine cycle, temps tested	N/A
Analytical methods	N/A
Laboratory Name	AVL LIST GmbH, Graz, Austria

No data is presented.

Title	Chemical and Biological Characterization of Particulate-, Semivolatile-, and Gas-phase-associated Compounds in Diluted Heavy-duty Diesel Exhausts: a Comparison of Three Different Semivolatile-phase Samplers
Author(s)	Roger N. Westerholm, Jacob Almén, Hang Li, J. Ulf Rannug, Stockholm University; Karl-Erik Egebäck, and Kerstin Grägg, National Environmental Protection Board, Nyköping, Sweden
Bibliographic Information	SAE 841364, Society of Automotive Engineers, Warrendale, PA, 1984 Fuels and Lubricants Meeting and Exposition, Baltimore, MD, October 8-11, 1984
Abstract	Cryo-condensation, XAD-2 adsorbent, and PUF sampling methods are compared for suitability for sampling PAH emissions.

Vapor Phase	HC	✔	Semi-volatile Phase	PAH	✔[1]
	CO	✔		NPAH	
	NOx	✔	Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	✔[1]
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	Yes	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	Yes	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	Scania DSC 1403, 331 kW, 14.2L **odometer 200,000 km**
Number, type, specs of fuel used	Commercial diesel fuel - specs in Table 1
Engine cycle, temps tested	Urban bus cycle
Analytical methods	NDIR, FID, CL, gravimetric, GC-FID, HPLC-UV, GC-MS[2]
Laboratory Name	University of Stockholm
Note: High usage level on this engine precludes its use for 211(b) purposes.	

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] FID = flame ionization detector, for hydrocarbons
NDIR = non-dispersive infra-red spectroscopy
CL = chemiluminescence, for oxides of nitrogen
GC-FID = gas chromatography with flame ionization detector
HPLC-UV = high performance liquid chromatography, ultra-violet detector
GC-MS = gas chromatography - mass spectroscopy

Title	A Review of Sampling Condition Effects on Polynuclear Aromatic Hydrocarbons (PNA) from Heavy-duty Diesel Engines
Author(s)	Ronald L. Williams, General Motors Research Laboratories; Joseph M. Perez, Caterpillar Tractor Co.; Margaret E. Griffing, Coordinating Research Council
Bibliographic Information	SAE 852081, Society of Automotive Engineers, Warrendale, PA, 1985 Special Publication SP-639, Diesel *Fuel Quality and Trends*, October 1985
Abstract	Reports issued by Gulf R&D Co. and Battelle Columbus Laboratories were reviewed. Both studies failed to verify the accuracy of PAH emission measurements from heavy-duty diesel engines.

Vapor Phase	HC		Semi-volatile Phase	PAH	✔[1]
	CO			NPAH	
	NOx		Particulate Phase	Particulate matter	✔
	Speciated HC			PAH	✔[1]
	Carbonyls			NPAH	

Test performed with and without aftertreatment?	N/A	Engine Representative of Class 8 Trucks?	Yes
Type I or II Diesel Fuel Used?	[2]	New Engine Cert Procedure (EDDS) Used?	No

Number, type, year of engine	swirl chamber D1 prototype Caterpillar 3406, DI, TC, 325 hp
Number, type, specs of fuel used	not reported
Engine cycle, temps tested	steady-state
Analytical methods	GC-MS[3]
Laboratory Name	General Motors Research Laboratories, Caterpillar Tractor Co., Coordinating Research Council, Gulf R&D Co., Battelle Columbus Laboratories

[1] Does not cover the complete list of compounds called for in section 211 (b) rules.

[2] Not reported

[3] GC-MS = gas chromatography/mass spectroscopy

APPENDIX E

SEARCH CRITERIA AND POSITIVE HITS
(OUTPUT FROM THE DATABASE SEARCHES)

```
********
Welcome to DIALOG

Dialog level 42.07.03D

Last logoff:  15aug96 07:16:37
Logon file001 15aug96 10:24:02
** Please Note: Scheduled Dialog down time will be extended on
   August 17 by five hours. Down time on August 16 will begin
   as scheduled at 23:00 PDT (1:00 EST). Dialog will be available
   again by 11:00 PDT (13:00 EST).


File   1:ERIC  1966-1996/Jul
     (c) format only 1996 Knight-Ridder Info

     Set  Items  Description
     ---  -----  -----------
?b108;set select short

      15aug96 10:24:08 User004031 Session D4718.1
          $0.06    0.002 Hrs File1
    $0.06  Estimated cost File1
    $0.02  TYMNET
    $0.08  Estimated cost this search
    $0.08  Estimated total session cost   0.002 Hrs.

File 108:Aerospace Database  1962-1996/Jul
     (c) 1996 AIAA
*File 108: RELOAD!  DIALOG Accession Numbers have changed.

     Set  Items  Description
     ---  -----  -----------
SELECT response set to SHORT.
?s heavy()duty and diesel? ?;s emission? ? or exhaust? ?[illegible];s regulated()emission? ?b

     S1     104  HEAVY()DUTY AND DIESEL? ?
     S2  106462  EMISSION? ? OR EXHAUST
     S3       0  REGULATED()EMISSION? ?B.
?s reguoa[illegible]lated(_)em[illegible])emiswsion[illegible]sion? ?

     S4      14  REGULATED()EMISSION? ?
?s tot[illegible]hydrocarbon? ? or hc or thc;s carbon()monoxide;s [illegible] or co;s nitrogen()oxide? ?

     S5   12437  HYDROCARBON? ? OR HC OR THC
     S6   23256  CARBON()MONOXIDE OR CO
     S7    4836  NITROGEN()OXIDE? ?
?s nitrous()oxc[illegible]xide;[illegible]ide;s mtrric[illegible]nitric()oxide;s nitrogen()dioxide;s oxides of nitrogen

     S8     756  NITROUS()OXIDE
     S9    3256  NITRIC()OXIDE
    S10    1817  NITROGEN()DIOXIDE
    S11       0  OXIDES OF NITROGEN
?s ns[illegible]20 or no2 or n2o3

    S12    2493  N20 OR NO2 OR N2O3
?s aldehyudr[illegible]de or formaldehyde or acetaldehyde;s ketone;s carbonyl

    S13    1823  ALDEHYDE OR FORMALDEHYDE OR ACETALDEHYDE
```

```
   S14    334  KETONE
   S15    951  CARBONYL
?s alcohol or methanol or ethanol;s ether;s particulate? ? or tpm

   S16   5222  ALCOHOL OR METHANOL OR ETHANOL
   S17   1175  ETHER
   S18   7793  PARTICULATE? ? OR TPM
?c1and4

   S19      2  1AND4
?c1and2and(5or6or7or8or9or10or11or12or13or14or15or16or17or18or19or[illegible]9)[illegible])

   S20     36  1AND2AND(5OR6OR7OR8OR9OR10OR11OR12OR13OR14OR15OR16OR17OR-
             18)
?c19or20

   S21     36  19OR20
?en[illegible]end/savetemp

Temp SearchSave "TD834" stored
?b8,399,108,6,40,68;exs td834

     15aug96 10:32:58 User004031 Session D4718.2
        $9.00    0.150 Hrs File108
   $9.00  Estimated cost File108
   $1.80  TYMNET
  $10.80  Estimated cost this search
  $10.88  Estimated total session cost   0.152 Hrs.

SYSTEM:OS  - DIALOG OneSearch
  File   8:Ei Compendex*Plus(TM)  1970-1996/Sep W3
       (c) 1996 Engineering Info. Inc.
  File 399:CA SEARCH(R)  1967-1996/UD=12508
       (c) 1996 American Chemical Society
*File 399: Use is subject to the terms of your user/customer agreement.
For format prices, including formats 6 & 8, see HELP RATES 399.
  File 108:Aerospace Database  1962-1996/Jul
       (c) 1996 AIAA
*File 108: RELOAD!  DIALOG Accession Numbers have changed.
  File   6:NTIS  64-1996/Sep W5
       Comp & dist by NTIS, Intl Copyright All Rights Res
  File  40:Enviroline(R)  1975-1996/Jul
       (c) 1996 Congressional Information Service
  File  68:Env.Bib.  1974-1996/Oct
       (c) 1996 Internl Academy at Santa Barbara

     Set  Items  Description
     ---  -----  ----------
SELECT response set to SHORT.
     S1    1350  HEAVY()DUTY AND DIESEL? ?
     S2  454972  EMISSION? ? OR EXHAUST
     S3       0  REGULATED()EMISSION? ?B.
     S4     131  REGULATED()EMISSION? ?
     S5  258018  HYDROCARBON? ? OR HC OR THC
     S6  452026  CARBON()MONOXIDE OR CO
Processing
     S7   64937  NITROGEN()OXIDE? ?
     S8   11438  NITROUS()OXIDE
     S9   30423  NITRIC()OXIDE
    S10   15390  NITROGEN()DIOXIDE
    S11      32  OXIDES OF NITROGEN
```

```
   S12    6810  N20 OR NO2 OR N2O3
   S13  158071  ALDEHYDE OR FORMALDEHYDE OR ACETALDEHYDE
   S14   56126  KETONE
   S15  108564  CARBONYL
   S16  239814  ALCOHOL OR METHANOL OR ETHANOL
   S17  137745  ETHER
   S18   76262  PARTICULATE? ? OR TPM
   S19      20  S1ANDS4
   S20     523  S1ANDS2AND(S5ORS6ORS7ORS8ORS9ORS10ORS11ORS12ORS13ORS14OR-
                S15ORS16ORS17ORS18)
   S21     523  S19ORS20
?sx [redacted]s s1 and s2 and nox

   S22      81  S1 AND S2 AND NOX
?c21or22

   S23     528  21OR22
?s s23/eng

>>>Term "ENG" is not defined in one or more files
   S24     518  S23/ENG
?rd s24

...examined 50 records  (50)
...examined 50 records  (100)
...examined 50 records  (150)
...examined 50 records  (200)
...examined 50 records  (250)
...examined 50 records  (300)
...examined 50 records  (350)
...examined 50 records  (400)
...examined 50 records  (450)
...examined 50 records  (500)
...completed examining records
   S25     391  RD S24 (unique items)
?s s25/1985:1996

Processing
   S26     259  S25/1985:1996
?s s26 from 8;s s26 from 399;s s26 from 108;s s26 from 6;s s26 from 40

   S27     135  S26 FROM 8
   S28      36  S26 FROM 399
   S29      11  S26 FROM 108
   S30      62  S26 FROM 6
   S31      14  S26 FROM 40
?s s26 from 68

   S32       1  S26 FROM 68
?end/savetemp

Temp SearchSave "TD835" stored
?t 26/6/1-100[redacted]/1-135


 26/6/1     (Item 1 from file: 8)
04412061
  Title: Real-world emissions and calculated reactivities of organic
species from motor vehicles
  Conference Title: Proceedings of the 1993 A&WMA International Specialty
Conference on Regional Photochemical Measurements and Modeling
```

26/6/2 (Item 2 from file: 8)
04412060
Title: Volatile organic compounds up to C//2//0 emitted from motor vehicles; measurement methods
Conference Title: Proceedings of the 1993 A&WMA International Specialty Conference on Regional Photochemical Measurements and Modeling

26/6/3 (Item 3 from file: 8)
04383164
Title: Transient testing of soy methyl ester fuels in an indirect injection, compression ignition engine

26/6/4 (Item 4 from file: 8)
04329180
Title: LNG - technology on the edge

26/6/5 (Item 5 from file: 8)
04260804
Title: Effects of injection pressure and nozzle geometry on D.I. diesel emissions and performance
Conference Title: Proceedings of the 1995 SAE International Congress & Exposition

26/6/6 (Item 6 from file: 8)
04258921
Title: Effect of sulfur dioxide in recirculated exhaust gas on wear within diesel engines (Relationship between wear and amount of SO//2 absorbed by lubricating oil film)

26/6/7 (Item 7 from file: 8)
04247586
Title: Low emission stoichiometric CNG engine with EGR
Conference Title: Proceedings of the ASME Internal Combustion Engine Division Spring Meeting

26/6/8 (Item 8 from file: 8)
04211315
Title: New fuel filtration demands for electronically-controlled diesel engines

26/6/9 (Item 9 from file: 8)
04207749
Title: Giga: new heavy-duty truck series

26/6/10 (Item 10 from file: 8)
04053810
Title: Proceedings of the 16th Annual Fall Technical Conference on the Internal Combustion Engine Division, ASME
Conference Title: Proceedings of the 16th Annual Fall Technical Conference on the Internal Combustion Engine Division, ASME

26/6/11 (Item 11 from file: 8)
04045312
Title: Focus on industry solutions for exhaust pollution control

26/6/12 (Item 12 from file: 8)
03941570
Title: Multivariate statistical analysis of fuel-related polycyclic aromatic hydrocarbon emissions from heavy-duty diesel vehicles

26/6/13 (Item 13 from file: 8)
03934677
Title: Characterization of heavy-duty diesel vehicle emissions

26/6/14 (Item 14 from file: 8)
03897017
Title: Fluid-dynamic investigation and optical characterization of particulate to reduce diesel emissions

26/6/15 (Item 15 from file: 8)
03775119
Title: High turbulence combustion chamber for lean-burn heavy-duty CNG engines
Conference Title: Proceedings of the 15th Annual Fall Technical Conference of the ASME Internal Combustion Engine Division

26/6/16 (Item 16 from file: 8)
03775117
Title: Alternate Fuels, Engine Performance and Emmissions
Conference Title: Proceedings of the 15th Annual Fall Technical Conference of the ASME Internal Combustion Engine Division

26/6/17 (Item 17 from file: 8)
03772973
Title: Carbonyl compounds and PAH emissions from CNG heavy-duty engine

26/6/18 (Item 18 from file: 8)
03746518
Title: Status report on South Coast Air Quality Management District alternative fuels demonstrations
Conference Title: 1993 Future Transportation Technology Conference

26/6/19 (Item 19 from file: 8)
03728643
Title: Heavy-duty diesel emissions using California reference fuel and military grade JP-8
Conference Title: Energy-Sources Technology Conference and Exhibition

26/6/20 (Item 20 from file: 8)
03650593
Title: Contribution of fuel flow improvement in nozzle to spray formation
Conference Title: International Congress and Exposition

26/6/21 (Item 21 from file: 8)
03634244
Title: In-use emissions and performance monitoring of heavy duty vehicles using a transportable transient chassis test facility
Conference Title: International Off-Highway and Powerplant Congress and Exposition

26/6/22 (Item 22 from file: 8)
03634187
Title: Design and development of catalytic converters for diesels
Conference Title: International Off-Highway and Powerplant Congress and Exposition

26/6/23 (Item 23 from file: 8)
03634183
Title: Development of an ammonia/SCR NO//x reduction system for a heavy duty natural gas engine
Conference Title: International Off-Highway and Powerplant Congress and Exposition

26/6/24 (Item 24 from file: 8)
03591349
Title: Fleet-site measurements of exhaust gas emissions from urban buses.
Conference Title: 14th Annual Fall Technical Conference of the ASME Internal Combustion Engine Division

26/6/25 (Item 25 from file: 8)
03591270
Title: Development of a heavy duty on-highway natural gas-fueled engine.
Conference Title: International Fuels and Lubricants Meeting and Exposition

26/6/26 (Item 26 from file: 8)
03584891
Title: Alternative fuels for mobile transport.

26/6/27 (Item 27 from file: 8)
03574260
Title: Advanced nitrogen oxides reduction technology.
Conference Title: Proceedings of the Annual Automotive Technology Development Contractors' Coordination Meeting

26/6/28 (Item 28 from file: 8)
03574245
Title: Advanced component development and emissions reduction for heavy duty Diesel Engines.
Conference Title: Proceedings of the Annual Automotive Technology Development Contractors' Coordination Meeting

26/6/29 (Item 29 from file: 8)
03571533
Title: Diesel Combustion, Emissions, and Exhaust Aftertreatment.
Conference Title: International Off-Highway and Powerplant Congress and

Exposition

26/6/30 (Item 30 from file: 8)
03558126
Title: Effects of EGR with a supplemental manifold water injection to control exhaust emissions from heavy-duty diesel powered vehicles.
Conference Title: International Congress and Exposition

26/6/31 (Item 31 from file: 8)
03536958
Title: Application of methods for determining total organic contribution to diesel particulates.

26/6/32 (Item 32 from file: 8)
03536957
Title: Progress in diesel engine emissions control.

26/6/33 (Item 33 from file: 8)
03536956
Title: Emissions from heavy-duty trucks converted to CNG.

26/6/34 (Item 34 from file: 8)
03528586
Title: California's heavy-duty vehicle smoke and tampering inspection program.
Conference Title: Future Transportation Technology Conference and Exposition

26/6/35 (Item 35 from file: 8)
03528582
Title: Natural gas conversion systems for heavy duty truck engines.
Conference Title: Future Transportation Technology Conference and Exposition

26/6/36 (Item 36 from file: 8)
03522563
Title: Strategies to meet worldwide heavy-duty diesel emission standards.

26/6/37 (Item 37 from file: 8)
03511305
Title: Development of a turbocharger system with variable area turbine nozzle for heavy-duty trucks.
Conference Title: International Congress and Exposition

26/6/38 (Item 38 from file: 8)
03499821
Title: Optimizing control of NOx and smoke emissions from DI engine with EGR and methanol fumigation.
Conference Title: International Congress and Exposition

26/6/39 (Item 39 from file: 8)

03499753
Title: Preliminary investigation on genotoxic potential of diesel exhaust.
Conference Title: International Congress and Exposition

26/6/40 (Item 40 from file: 8)
03499725
Title: Role of the through flow oxidation catalyst in the development of a low emissions specification HD diesel engine.
Conference Title: International Congress and Exposition

26/6/41 (Item 41 from file: 8)
03499724
Title: Performance testing and field evaluation of an in-line full-flow particulate trap system for the DDC 6V-92TA two stroke engine.
Conference Title: International Congress and Exposition

26/6/42 (Item 42 from file: 8)
03498371
Title: Effects of sulfate adsorption on performance of diesel oxidation catalysts.
Conference Title: International Congress and Exposition

26/6/43 (Item 43 from file: 8)
03498367
Title: Effect of low sulfur fuel and a ceramic particle filter on diesel exhaust particle size distributions.
Conference Title: International Congress and Exposition

26/6/44 (Item 44 from file: 8)
03498366
Title: Influence of a low sulfur fuel and a ceramic particle trap on the physical, chemical, and biological character of heavy-duty diesel emissions.
Conference Title: International Congress and Exposition

26/6/45 (Item 45 from file: 8)
03497252
Title: Diesel Particulate Control, Trap, and Filtration Systems.
Conference Title: International Congress and Exposition

26/6/46 (Item 46 from file: 8)
03472752
Title: In-cylinder fluid motion and emissions of a conventional and re-entrant diesel combustion systems.
Conference Title: International Off-Highway and Powerplant Congress and Expostion

26/6/47 (Item 47 from file: 8)
03472722
Title: Present and future European exhaust emission regulations for off-road diesel engines.
Conference Title: International Off-Highway and Powerplant Congress and

Expostion

26/6/48 (Item 48 from file: 8)
03446184
Title: Development of a multipurpose utility D.I. diesel engine for low emissions.
Conference Title: 1991 Small Engine Technology Conference Proceedings

26/6/49 (Item 49 from file: 8)
03444255
Title: Gaseous Fuels For Engines.
Conference Title: International Fuels and Lubricants Meeting and Exposition

26/6/50 (Item 50 from file: 8)
03431789
Title: Application of a low emission methanol engine to a heavy-duty truck. Vehicle installation and operating experience.
Conference Title: International Truck & Bus Meeting and Exposition

26/6/51 (Item 51 from file: 8)
03431525
Title: Performance and emissions of a DDC 8V-71 transit bus engine using ignition-improved methanol and ethanol.
Conference Title: International Fuels and Lubricants Meeting and Exposition

26/6/52 (Item 52 from file: 8)
03431497
Title: Additive approaches to reduced diesel emissions.
Conference Title: International Fuels and Lubricants Meeting and Exposition

26/6/53 (Item 53 from file: 8)
03429436
Title: Application of heavy duty diesel engine to future emission standards.
Conference Title: International Congress and Exposition

26/6/54 (Item 54 from file: 8)
03429362
Title: Application of a high flexible electronic injection system to a heavy duty diesel engine.
Conference Title: International Congress and Exposition

26/6/55 (Item 55 from file: 8)
03427376
Title: Truck Engine Design and Emissions.
Conference Title: International Truck and Bus Meeting and Exposition

26/6/56 (Item 56 from file: 8)
03403426

Title: Effects of diesel ignition improvers in low-sulfur fuels on heavy-duty diesel emissions.

26/6/57 (Item 57 from file: 8)
03403425
Title: Effects of fuel aromatics, cetane number, and cetane improver on emissions from a 1991 prototype heavy-duty diesel engine.

26/6/58 (Item 58 from file: 8)
03403421
Title: Methanol-fueled caterpillar 3406 engine experience in on-highway trucks.

26/6/59 (Item 59 from file: 8)
03403401
Title: Catalyst considerations for diesel converters.

26/6/60 (Item 60 from file: 8)
03403306
Title: Simulation of high altitude effects on heavy-duty diesel emissions.

26/6/61 (Item 61 from file: 8)
03403305
Title: Injection timing and rate control. A solution for low emissions.

26/6/62 (Item 62 from file: 8)
03403279
Title: Measurement of unregulated exhaust emissions from heavy duty diesel engines with mini-dilution tunnel.

26/6/63 (Item 63 from file: 8)
03403265
Title: Ways toward the clean heavy-duty diesel.

26/6/64 (Item 64 from file: 8)
03403259
Title: Aspects of influencing oil consumption in diesel engines for low emission.

26/6/65 (Item 65 from file: 8)
03389670
Title: Technology for meeting the 1991 U.S.A. exhaust emission regulations on heavy duty diesel engine.

26/6/66 (Item 66 from file: 8)
03389626
Title: Cummins A3.4-125. A charge cooled IDI turbo diesel for the 1991 US light-heavy duty market.

26/6/67 (Item 67 from file: 8)
03389598
Title: Durability studies of trap oxidizer systems.

26/6/68 (Item 68 from file: 8)
03383871
Title: Environmental impact of heavy-duty natural gas vehicles.
Conference Title: International Mechanical Engineering Congress and Exhibition - MECH 91

26/6/69 (Item 69 from file: 8)
03378505
Title: Heavy-duty spark ignition engines fueled with methane.

26/6/70 (Item 70 from file: 8)
03376635
Title: EGR control method for heavy-duty diesel engines under transient operations.

26/6/71 (Item 71 from file: 8)
03340375
Title: Chemical and biological characterization of particulate-, semivolatile-, and gas-phase-associated compounds in diluted heavy-duty diesel exhausts. A comparison of three different semivolatile-phase samplers.

26/6/72 (Item 72 from file: 8)
03304079
Title: Early engine emission reduction test results with RAPRENOX.
Conference Title: Proceedings of the Annual Automotive Technology Development Contractors' Meeting

26/6/73 (Item 73 from file: 8)
03304075
Title: Ignition enhancement of the DDC methanol engine - results.
Conference Title: Proceedings of the Annual Automotive Technology Development Contractors' Meeting

26/6/74 (Item 74 from file: 8)
03304072
Title: 3-D modeling of diesel engine intake flow, combustion and emissions.
Conference Title: Proceedings of the Annual Automotive Technology Development Contractors' Meeting

26/6/75 (Item 75 from file: 8)
03304030
Title: Effects of fuel properties on diesel engine emissions. A review of information available to the EEC-MVEG group.
Conference Title: 1991 SAE International Congress and Exposition

26/6/76 (Item 76 from file: 8)

03304019
Title: New developments of ceramic foam as a Diesel Particulate Filter.
Conference Title: 1991 SAE International Congress and Exposition

26/6/77 (Item 77 from file: 8)
03106179
Title: Dynamic measurement of particulate matter. A valuable tool to approach US 1994 HD diesel emission standards.
Conference Title: Proceedings of the 23rd International Symposium on Automotive Technology and Automation

26/6/78 (Item 78 from file: 8)
03106178
Title: Future particulate measurement techniques of the ECE-R49 test with partial-flow dilution systems.
Conference Title: Proceedings of the 23rd International Symposium on Automotive Technology and Automation

26/6/79 (Item 79 from file: 8)
03102187
Title: Influence of decreasing vehicle exhaust emissions on the standards for ventilation systems for urban road tunnels.

26/6/80 (Item 80 from file: 8)
03092296
Title: Engine performance and NOx emission characteristics of direct-injection methanol engines fueled with near-neat methanol.
Conference Title: Eighteenth FISITA Congress - The Promise of New Technology in the Automotive Industry

26/6/81 (Item 81 from file: 8)
03029151
Title: Effect of fuel properties on mutagenic activity in extracts of heavy-duty diesel exhaust particulate.

26/6/82 (Item 82 from file: 8)
03022856
Title: New Cummins C series diesel engine.
Conference Title: International Off-Highway and Powerplant Congress and Exposition

26/6/83 (Item 83 from file: 8)
03012202
Title: Emissions and fuel economy test results for methanol- and diesel-fueled buses.
Conference Title: Proceedings - 82nd A&WMA Annual Meeting

26/6/84 (Item 84 from file: 8)
02971648
Title: Particulate regeneration improvements on actual vehicle under various conditions.
Conference Title: Advances in Diesel Particulate Control - Papers presented at the 1990 SAE International Congress and Exposition

26/6/85 (Item 85 from file: 8)
02930243
Title: Analysis of transient emission data of a modelyear 1991 heavy duty diesel engine.
Conference Title: SAE International Congress and Exposition

26/6/86 (Item 86 from file: 8)
02930036
Title: Particulate emissions from diesel engines. Influence of in-cylinder surface.
Conference Title: SAE International Congress and Exposition

26/6/87 (Item 87 from file: 8)
02887905
Title: Particulate emissions from 'in-use' motor vehicles. II. Diesel vehicles.

26/6/88 (Item 88 from file: 8)
02852613
Title: Mobile sources of atmospheric polycyclic aromatic hydrocarbons: a roadway tunnel study.

26/6/89 (Item 89 from file: 8)
02838851
Title: Study of the feasibility and possible impact of reduced emission level from diesel engined vehicles.

26/6/90 (Item 90 from file: 8)
02801840
Title: Strategic review of heavy-duty engine emission regulations and alternate fuels.

26/6/91 (Item 91 from file: 8)
02801837
Title: Technical problems and policy issues associated with the 1991 bus emissions standards.

26/6/92 (Item 92 from file: 8)
02801836
Title: Introduction to diesel particulate emission, alternative fuels, and the transit industry.

26/6/93 (Item 93 from file: 8)
02799053
Title: Diesel lube oils - fourth dimension of diesel particulate control.

26/6/94 (Item 94 from file: 8)
02716236
Title: Characterization of polar polycyclic aromatic compounds in a heavy-duty diesel exhaust particulate by capillary column gas chromatography and high-resolution mass spectrometry.

26/6/95 (Item 95 from file: 8)
02561112
Title: EXPERIENCES OF HEAVY-DUTY ALCOHOL-FUELLED DIESEL-IGNITION ENGINES.
Conference Title: Papers Presented at the SAE International Off-Highway & Powerplant Congress & Exposition.

26/6/96 (Item 96 from file: 8)
02559399
Title: DIRECT ANALYSIS OF DIESEL PARTICULATE-BOUND HYDROCARBONS BY GAS CHROMATOGRAPHY WITH SOLID SAMPLE INJECTION.
Conference Title: Papers Presented at the SAE International Congress and Exposition.

26/6/97 (Item 97 from file: 8)
02537942
Title: HEAVY-DUTY DIESEL ENGINE FUELS COMBUSTION PERFORMANCE AND EMISSIONS - A COOPERATIVE RESEARCH PROGRAM.
Conference Title: National Petroleum Refiners Association Technical Papers. (Presented at the 1985 Fuels & Lubricants Meeting.)

26/6/98 (Item 98 from file: 8)
02523701
Title: PERFORMANCE OF A CERAMIC DIESEL PARTICULATE TRAP OVER TYPICAL MINING DUTY CYCLES USING FUEL ADDITIVES.
Conference Title: Heavy-Duty Diesel Emission Control: A Review of Technology. (Presented at the 1986 Annual General Meeting of the Canadian Institute of Mining & Metallurgy.)

26/6/99 (Item 99 from file: 8)
02523700
Title: INVESTIGATION OF THE CTO EMISSION CONTROL SYSTEM APPLIED TO HEAVY-DUTY DIESEL ENGINES USED IN UNDERGROUND MINING EQUIPMENT.
Conference Title: Heavy-Duty Diesel Emission Control: A Review of Technology. (Presented at the 1986 Annual General Meeting of the Canadian Institute of Mining & Metallurgy.)

26/6/100 (Item 100 from file: 8)
02523697
Title: DIESEL EXHAUST EMISSIONS CONTROL USING EGR AND PARTICULATE FILTERS.
Conference Title: Heavy-Duty Diesel Emission Control: A Review of Technology. (Presented at the 1986 Annual General Meeting of the Canadian Institute of Mining & Metallurgy.)

26/6/101 (Item 101 from file: 8)
02523676
Title: HEAVY-DUTY DIESEL EMISSION CONTROL: A REVIEW OF TECHNOLOGY.
Conference Title: Heavy-Duty Diesel Emission Control: A Review of Technology. (Presented at the 1986 Annual General Meeting of the Canadian Institute of Mining & Metallurgy.)

26/6/102 (Item 102 from file: 8)
02509410

Title: REDUCTION OF NO//x AND PARTICULATE EMISSIONS IN THE DIESEL COMBUSTION PROCESS.

26/6/103 (Item 103 from file: 8)
02357624
Title: IMPACT OF PROJECTED CANADIAN 1990'S FUEL QUALITY ON EXHAUST EMISSIONS FROM HEAVY DUTY DIESEL ENGINES.
Conference Title: Papers Presented at the Energy Sources Technology Conference and Exhibition.

26/6/104 (Item 104 from file: 8)
02350825
Title: RELATIONSHIP BETWEEN NITRIC OXIDE AND WORK AS INFLUENCED BY ENGINE OPERATING CONDITIONS AND COMBUSTION SYSTEM PARAMETERS FOR A DIRECT INJECTION DIESEL ENGINE.
Conference Title: SAE International Congress and Exposition.

26/6/105 (Item 105 from file: 8)
02329991
Title: CHARACTERIZATION OF MUTAGENIC SUBFRACTIONS OF DIESEL EXHAUST MODIFIED BY CERAMIC PARTICULATE TRAPS.

26/6/106 (Item 106 from file: 8)
02306590
Title: WAYS TO CONTROL DIESEL EMISSIONS.

26/6/107 (Item 107 from file: 8)
02282124
Title: PAH - EMISSION OF TWO HEAVY DUTY DIESEL ENGINES.
Conference Title: Aerosols: Formation and Reactivity, Proceedings - Second International Aerosol Conference.

26/6/108 (Item 108 from file: 8)
02279497
Title: STATUS REPORT ON A PRELIMINARY SURVEY OF STRATEGIES TO MEET US-1991 HD DIESEL EMISSION STANDARDS WITHOUT EXHAUST GAS AFTERTREATMENT.
Conference Title: SAE International Congress and Exposition.

26/6/109 (Item 109 from file: 8)
02261349
Title: EXPERIENCES IN THE DEVELOPMENT OF CERAMIC FIBER COIL PARTICULATE TRAPS.
Conference Title: Diesel Particulates: An Update. (Papers Presented at the SAE International Congress and Exposition.)

26/6/110 (Item 110 from file: 8)
02261346
Title: DEVELOPMENT AND SELECTION OF DIESEL PARTICULATE TRAP REGENERATION SYSTEM.
Conference Title: Diesel Particulates: An Update. (Papers Presented at the SAE International Congress and Exposition.)

26/6/111 (Item 111 from file: 8)
02247541
Title: SIMPLIFIED DILUTION TUNNEL SYSTEM INTENDED FOR HEAVY DUTY DIESEL DEVELOPMENT.
Conference Title: Combustion, Heat Transfer and Analysis. (Papers Presented at the SAE International Off-Highway & Powerplant Congress & Exposition.)

26/6/112 (Item 112 from file: 8)
02234800
Title: METHANOL AS A FUEL FOR COMMERCIAL VEHICLES.
Conference Title: International Fuels and Lubricants Meeting and Exposition.

26/6/113 (Item 113 from file: 8)
02234761
Title: SYNTHETIC FUEL OPERATION IN A HEAVY DUTY DIESEL ENGINE.
Conference Title: International Fuels and Lubricants Meeting and Exposition.

26/6/114 (Item 114 from file: 8)
02231451
Title: EMISSION CONTROL OPTIONS FOR HEAVY-DUTY ENGINES.
Conference Title: SAE West Coast International Meeting.

26/6/115 (Item 115 from file: 8)
02225639
Title: TRANSIENT EMISSIONS FROM AN UNCOOLED DIESEL ENGINE.
Conference Title: International Congress and Exhibition - Society of Automotive Engineers.

26/6/116 (Item 116 from file: 8)
02222136
Title: INTERNATIONAL OFF-HIGHWAY & POWERPLANT CONGRESS & EXPOSITION.
Conference Title: International Off-Highway & Powerplant Congress & Exposition.

26/6/117 (Item 117 from file: 8)
02126503
Title: FEASIBILITY OF RETROFIT TECHNOLOGIES FOR DIESEL EMISSIONS CONTROL.
Conference Title: Advances in Diesel Particulate Control. (Papers presented at the SAE International Congress and Exposition.)

26/6/118 (Item 118 from file: 8)
02126488
Title: CHEMICAL ANALYSIS AND BIOLOGICAL TESTING OF EMISSIONS FROM A HEAVY DUTY DIESEL TRUCK WITH AND WITHOUT TWO DIFFERENT PARTICULATE TRAPS.
Conference Title: Advances in Diesel Particulate Control. (Papers presented at the SAE International Congress and Exposition.)

26/6/119 (Item 119 from file: 8)
02126481
Title: CATALYTICALLY ACTIVATED DIESEL PARTICULATE TRAPS - NEW DEVELOPMENT

AND APPLICATIONS.
Conference Title: Advances in Diesel Particulate Control. (Papers presented at the SAE International Congress and Exposition.)

26/6/120 (Item 120 from file: 8)
02096911
Title: DEVELOPMENT OF A VARIABLE CONTROLLED INERTIA CHARGING SYSTEM FOR NATURALLY ASPIRATED DIESEL ENGINES FOR HEAVY DUTY TRUCKS.
Conference Title: Second IAVD Congress on Vehicle Design and Components.

26/6/121 (Item 121 from file: 8)
02090804
Title: REDUCING THE SULFUR AND AROMATIC CONTENT OF DIESEL FUEL: COSTS, BENEFITS, AND EFFECTIVENESS FOR EMISSIONS CONTROL.
Conference Title: International Congress and Exposition - Society of Automotive Engineers.

26/6/122 (Item 122 from file: 8)
02090799
Title: GASEOUS AND PARTICULATE EMISSIONS FROM GASOLINE- AND DIESEL-POWERED HEAVY-DUTY TRUCKS.
Conference Title: International Congress and Exposition - Society of Automotive Engineers.

26/6/123 (Item 123 from file: 8)
02090708
Title: TRANSIENT CYCLE EMISSIONS REDUCTION AT RICARDO - 1988 AND BEYOND.
Conference Title: International Congress and Exposition - Society of Automotive Engineers.

26/6/124 (Item 124 from file: 8)
02090638
Title: ALDEHYDE AND UNBURNED FUEL EMISSIONS FROM METHANOL-FUELED HEAVY-DUTY DIESEL ENGINES.
Conference Title: International Congress and Exposition - Society of Automotive Engineers.

26/6/125 (Item 125 from file: 8)
02079946
Title: REVIEW OF SAMPLING CONDITION EFFECTS ON POLYNUCLEAR AROMATIC HYDROCARBONS (PNA) FROM HEAVY-DUTY DIESEL ENGINES.
Conference Title: Diesel Fuel Quality and Trends. (Papers presented at the International Fuels and Lubricants Meeting and Exposition.)

26/6/126 (Item 126 from file: 8)
02072505
Title: ANALYSIS OF THE ENVIRONMENTAL NEED FOR NOx CONTROLS ON LIGHT DUTY TRUCKS AND HEAVY DUTY VEHICLES.
Conference Title: Proceedings - 78th APCA Annual Meeting.

26/6/127 (Item 127 from file: 8)
02066764
Title: PARTICULATE CONTROL TECHNOLOGY FOR LIGHT AND HEAVY DUTY DIESEL

POWERED VEHICLES.
Conference Title: Winter Annual Meeting - American Society of Mechanical Engineers.

26/6/128 (Item 128 from file: 8)
02065919
Title: HEAVY-DUTY DIESEL EMISSIONS FROM OPERATION ON CRUDE AND MINIMALLY-PROCESSED SHALE OILS.
Conference Title: Combustion, Emission and Analysis. (Papers presented at the 1985 SAE International Congress & Exposition. Papers presented at the 1985 SAE International Congress & Exposition.)

26/6/129 (Item 129 from file: 8)
02065917
Title: REDUCTION OF PARTICULATE EMISSION FROM THE BREAK-IN FACILITIES OF A HEAVY-DUTY ENGINE PLANT BY MEANS OF CERAMIC MONOLITH TRAPS.
Conference Title: Combustion, Emission and Analysis. (Papers presented at the 1985 SAE International Congress & Exposition. Papers presented at the 1985 SAE International Congress & Exposition.)

26/6/130 (Item 130 from file: 8)
01979593
Title: ARE STRINGENT EMISSION STANDARDS FOR HEAVY-DUTY TRUCKS WORTH THE COST?

26/6/131 (Item 131 from file: 8)
01889208
Title: COLORADO DIESEL EMISSIONS CONTROL PROGRAM - STAGE 1.
Conference Title: Diesel Particulate Control. (Papers presented at the 1985 SAE International Congress & Exposition. Papers presented at the 1985 SAE International Congress & Exposition.)

26/6/132 (Item 132 from file: 8)
01889206
Title: EVALUATION OF HEAVY-DUTY ENGINE EXHAUST PARTICULATE TRAPS.
Conference Title: Diesel Particulate Control. (Papers presented at the 1985 SAE International Congress & Exposition. Papers presented at the 1985 SAE International Congress & Exposition.)

26/6/133 (Item 133 from file: 8)
01876025
Title: APPLICATION OF A TAPERED ELEMENT OSCILLATING MICROBALANCE TO CONTINUOUS DIESEL PARTICULATE MEASUREMENT.
Conference Title: International Congress & Exposition - Society of Automotive Engineers.

26/6/134 (Item 134 from file: 8)
01813267
Title: POLAR POLYNUCLEAR AROMATIC HYDROCARBON DERIVATIVES IN EXTRACTS OF PARTICULATES: BIOLOGICAL CHARACTERIZATION AND TECHNIQUES FOR CHEMICAL ANALYSIS.

26/6/135 (Item 135 from file: 8)

01745832
Title: AMES ASSAY CHROMATOGRAMS OF EXTRACTS OF DIESEL EXHAUST PARTICLES FROM HEAVY-DUTY TRUCKS ON THE ROAD AND FROM PASSENGER CARS ON A DYNAMOMETER.
?ds

Set	Items	Description
S1	1350	HEAVY()DUTY AND DIESEL? ?
S2	454972	EMISSION? ? OR EXHAUST
S3	0	REGULATED()EMISSION? ?B.
S4	131	REGULATED()EMISSION? ?
S5	258018	HYDROCARBON? ? OR HC OR THC
S6	452026	CARBON()MONOXIDE OR CO
S7	64937	NITROGEN()OXIDE? ?
S8	11438	NITROUS()OXIDE
S9	30423	NITRIC()OXIDE
S10	15390	NITROGEN()DIOXIDE
S11	32	OXIDES OF NITROGEN
S12	6810	N20 OR NO2 OR N2O3
S13	158071	ALDEHYDE OR FORMALDEHYDE OR ACETALDEHYDE
S14	56126	KETONE
S15	108564	CARBONYL
S16	239814	ALCOHOL OR METHANOL OR ETHANOL
S17	137745	ETHER
S18	76262	PARTICULATE? ? OR TPM
S19	20	S1ANDS4
S20	523	S1ANDS2AND(S5ORS6ORS7ORS8ORS9ORS10ORS11ORS12ORS13ORS14ORS1-5ORS16ORS17ORS18)
S21	523	S19ORS20
S22	81	S1 AND S2 AND NOX
S23	528	21OR22
S24	518	S23/ENG
S25	391	RD S24 (unique items)
S26	259	S25/1985:1996
S27	135	S26 FROM 8
S28	36	S26 FROM 399
S29	11	S26 FROM 108
S30	62	S26 FROM 6
S31	14	S26 FROM 40
S32	1	S26 FROM 68

?c29-32/or

S33 88 29-32/OR

?→

28/3/1 (Item 1 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

125017643 CA: 125(2)17643j TECHNICAL REPORT
Effects of fuel oxygenates, cetane number, and aromatic content on emissions from 1994 and 1998 prototype heavy-duty diesel engines
AUTHOR(S): Spreen, K. B.; Ullman, T. L.; Mason, R. L.
LOCATION: Automotive Products Emissions Res. Div., Southwest Res. Inst., San Antonio, TX, USA
JOURNAL: Report DATE: 1995 NUMBER: SWRI-4127; Order No. PB96-139456GAR
PAGES: 257 pp. CODEN: D8REP4 LANGUAGE: English CITATION: Gov. Rep. Announce. Index (U. S.) 1996, 96(8), Abstr. No. 08-01,018 AVAIL: NTIS

28/3/2 (Item 2 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

124268840 CA: 124(20)268840v JOURNAL
Urban driving cycle results of retrofitted diesel oxidation catalysts on heavy duty vehicles

AUTHOR(S): Brown, Kevin F.; Rideout, Greg
LOCATION: Engine Control Systems Ltd., Can.,
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1996 VOLUME: SP-1140 NUMBER: Diesel Exhaust Aftertreatment 1996 PAGES: 57-70 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/3 (Item 3 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

124184155 CA: 124(14)184155n CONFERENCE PROCEEDING
Chassis dynamometer emissions testing results for diesel and alternative-fueled transit buses
AUTHOR(S): Dunlap, Lauren S.; Pellegrin, Vince; Ikeda, Randal; Wilson, Ray; Stanley, Sylvia; Porter, Harvey
LOCATION: Los Angeles Metropolitan Transportation Authority, USA
JOURNAL: Alternate Fuels: Decade Success Promise EDITOR: Bata, Reda Mohamed (Ed), DATE: 1994 PAGES: 65-92 CODEN: 62KQAI LANGUAGE: English
PUBLISHER: Society of Automotive Engineers,Warrendale, Pa

28/3/4 (Item 4 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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124095905 CA: 124(8)95905q JOURNAL
The effect of fuel processes on heavy duty automotive diesel engine emissions
AUTHOR(S): Reynolds, E. G.
LOCATION: BP Oil International, USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1995 VOLUME: SP-1119, PAGES: 13-20 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English
MEETING DATE: 950000

28/3/5 (Item 5 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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124065005 CA: 124(6)65005d JOURNAL
Performance of oxidation catalysts for heavy-duty diesel engines
AUTHOR(S): Stein, H. J.; Huethwohl, G.; Lepperhoff, G.
LOCATION: Dept. EN/MGA, Mercedes-Benz AG, Stuttgart, Germany, D-70322
JOURNAL: Stud. Surf. Sci. Catal. DATE: 1995 VOLUME: 96 NUMBER: Catalysis and Automotive Pollution Control III PAGES: 517-28 CODEN: SSCTDM ISSN: 0167-2991 LANGUAGE: English

28/3/6 (Item 6 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

123348710 CA: 123(26)348710x JOURNAL
Multivariate Analysis of Exhaust Emissions from Heavy-Duty Diesel Fuels
AUTHOR(S): Sjoegren, Michael; Li, Hang; Rannug, Ulf; Westerholm, Roger
LOCATION: Department of Genetic and Cellular Toxicology, Stockholm University, S-106 91, Stockholm, Swed.
JOURNAL: Environ. Sci. Technol. DATE: 1995 VOLUME: 30 NUMBER: 1
PAGES: 38-49 CODEN: ESTHAG ISSN: 0013-936X LANGUAGE: English

28/3/7 (Item 7 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

123178055 CA: 123(14)178055t JOURNAL
Effects of a ceramic particle trap and copper fuel additive on heavy-duty diesel emissions
AUTHOR(S): Harvey, George D.; Baumgard, Kirby J.; Johnson, John H.; Gratz, Linda D.; Bagley, Susan T.; Leddy, David G.
LOCATION: Michigan Technological Univ., MI, USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1994 VOLUME: SP-1053 PAGES: 207-25 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/8 (Item 8 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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123178054 CA: 123(14)178054s JOURNAL
Effect of cerium fuel additive on the emissions characteristics of a heavy-duty diesel engine
AUTHOR(S): Lemaire, Jacques; Khair, Magdi
LOCATION: Rhone-Poulenc, Fr.
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1994 VOLUME: SP-1053 PAGES: 189-205 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/9 (Item 9 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

122243657 CA: 122(20)243657m JOURNAL
Effects of oxygenated fuel and cetane improver on exhaust emission from heavy-duty DI diesel engines
AUTHOR(S): Akasaka, Yukio; Sakurai, Yoshihito
LOCATION: JOMO Technical Research Co. Ltd., USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1994 VOLUME: SP-1056 NUMBER: Diesel Fuel PAGES: 181-8 CODEN: SAESA2 ISSN: 0099-5908
LANGUAGE: English

28/3/10 (Item 10 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

122218126 CA: 122(18)218126e JOURNAL
Fuel quality effects on particulate matter emissions from light- and heavy-duty diesel engines
AUTHOR(S): Ouden, C. J. J. Den; Clark, R. H.; Cowley, L. T.; Stradling, R. J.; Lange, W. W.; Maillard, C.
LOCATION: Shell Research Ltd., USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1994 VOLUME: SP-1056 NUMBER: Diesel Fuel PAGES: 159-80 CODEN: SAESA2 ISSN: 0099-5908
LANGUAGE: English

28/3/11 (Item 11 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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122062935 CA: 122(6)62935e JOURNAL

The contribution of the lube oil to particulate emissions of heavy duty diesel engines
AUTHOR(S): Tritthart, P.; Ruhri, F.; Cartellieri, W.
LOCATION: AVL-List Ges.m.b.H., Graz, Austria
JOURNAL: Mech. Eng. (Marcel Dekker) DATE: 1993 VOLUME: 80 NUMBER: Engine Oils and Automotive Lubrication PAGES: 535-52 CODEN: MCLEEF
ISSN: 0899-3858 LANGUAGE: English

28/3/12 (Item 12 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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122037710 CA: 122(4)37710v JOURNAL
Exhaust emissions from light- and heavy-duty vehicles: chemical composition, impact of exhaust after treatment, and fuel parameters
AUTHOR(S): Westerholm, Roger; Egebaeck, Karl-Erik
LOCATION: Department of Analytical Chemistry, University of Stockholm, S-106 91, Stockholm, Swed.
JOURNAL: Environ. Health Perspect. Suppl. DATE: 1994 VOLUME: 102
NUMBER: Suppl. 4 PAGES: 13-23 CODEN: EHPSEO ISSN: 1078-0475
LANGUAGE: English

28/3/13 (Item 13 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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122013428 CA: 122(2)13428h JOURNAL
Reducing particulate and NOx emissions by using multiple injections in a heavy duty D.I. diesel engine
AUTHOR(S): Tow, T. C.; Pierpont, D. A.; Reitz, R. D.
LOCATION: University of Wisconsin, Madison, WI, USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1994 VOLUME: SP-1028 NUMBER: Diesel Combustion Processes and Emission Control PAGES: 201-15 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/14 (Item 14 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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121087299 CA: 121(8)87299t JOURNAL
Emissions comparisons of twenty-six heavy-duty vehicles operated on conventional and alternative fuels
AUTHOR(S): Wang, Wenguang; Gautam, Mridul; Sun, Xiaobo; Bata, Reda; Clark, Nigel; Palmer, Michael; Lyons, Donald
LOCATION: West Virginia Univ., WV, USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1993 VOLUME: SP-1001 NUMBER: Truck Alternative Fuels and Exhaust Gas Emission PAGES: 31-40 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/15 (Item 15 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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121038901 CA: 121(4)38901z JOURNAL
The influence of composition and properties of diesel fuel on particulate emissions from heavy-duty engines
AUTHOR(S): Cowley, L. T.; Stradling, R. J.; Doyon, J.

LOCATION: Shell Res. Ltd., UK,
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1993 VOLUME: SP-994
NUMBER: DIESEL FUELS FOR THE NINETIES: COMPOSITION AND ADDITIVES TO MEET EMISSIONS AND PERFORMANCE NEEDS PAGES: 13-48 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/16 (Item 16 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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121038898 CA: 121(4)38898d JOURNAL
A study of emissions from CNG and diesel fueled heavy-duty vehicles
AUTHOR(S): Wang, Wenguang; Sun, Xiaobo; Bata, Reda; Gautam, Mridul; Clark, Nigel; Palmer, G. Michael; Lyons, Donald
LOCATION: West Virginia Univ., USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1993 VOLUME: SP-993
NUMBER: GASEOUS FUEL TECHNOLOGY FOR THE NINETIES PAGES: 99-108 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/17 (Item 17 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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121038892 CA: 121(4)38892x JOURNAL
Development of a heavy-duty turbocharged and aftercooled CNG-fueled lean-burn engine - conversion of a naturally-aspirated diesel engine into Otto-type CNG engine
AUTHOR(S): Takada, Yutaka; Matsuda, Hiroshi; Notsu, Ikurou; Niimura, Keiichi; Hamazaki, Nobuo; Watanabe, Yoshito
LOCATION: Nissan Diesel Mot. Co., Ltd., Japan,
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1993 VOLUME: SP-993
NUMBER: GASEOUS FUEL TECHNOLOGY FOR THE NINETIES PAGES: 23-9 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/18 (Item 18 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

121038861 CA: 121(4)38861m JOURNAL
The effect of oxygenated fuels on emissions from a modern heavy-duty diesel engine
AUTHOR(S): Liotta, Frank J. Jr.; Montalvo, Daniel M.
LOCATION: ARCO Chem. Co., USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1993 VOLUME: SP-994
NUMBER: DIESEL FUELS FOR THE NINETIES: COMPOSITION AND ADDITIVES TO MEET EMISSIONS AND PERFORMANCE NEEDS PAGES: 59-75 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/19 (Item 19 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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120195495 CA: 120(16)195495s JOURNAL
Effect of fuel composition including aromatics content on emissions from a range of heavy-duty diesel engines
AUTHOR(S): Cowley, L. T.; Le Juene, A.; Lange, W. W.
LOCATION: Shell Res. Ltd., Chester, UK,

JOURNAL: IMechE Semin. DATE: 1993 NUMBER: 5, Worldwide Engine Emission Standards and How to Meet Them PAGES: 225-44 CODEN: ISEME4 LANGUAGE: English

28/3/20 (Item 20 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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120195340 CA: 120(16)195340n JOURNAL
Fuel efficient and green - the future heavy duty diesel
AUTHOR(S): Needham, J. R.; Such, C. H.; Nicol, A. J.
LOCATION: Ricardo Consult. Eng. Ltd., Shoreham-by-Sea, West Sussex, UK,
JOURNAL: IMechE Semin. DATE: 1993 NUMBER: 5, Worldwide Engine Emission Standards and How to Meet Them PAGES: 197-207 CODEN: ISEME4 LANGUAGE: English

28/3/21 (Item 21 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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120168356 CA: 120(14)168356r JOURNAL
Optimizing control of nitrogen oxides (NOx) and smoke emissions from DI engine with EGR and methanol fumigation
AUTHOR(S): Odaka, Matsuo; Koike, Noriyuki; Tsukamoto, Yujirou; Narusawa, Kazuyuki
LOCATION: Minist. Transport, Japan,
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1992 VOLUME: SP-895
NUMBER: Reducing Emissions from Diesel Combustion PAGES: 121-9 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/22 (Item 22 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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120037157 CA: 120(4)37157d JOURNAL
Characterization of particle- and vapor-phase organic fraction emissions from a heavy-duty diesel engine equipped with a particle trap and regeneration controls
AUTHOR(S): Bagley, Susan T.; Gratz, Linda D.; Leddy, David G.; Johnson, John H.
LOCATION: Dep. Biol. Sci., Michigan Technol. Univ., Houghton, MI, USA
JOURNAL: Res. Rep. - Health Eff. Inst. DATE: 1993 VOLUME: 56, PAGES: 136 pp. CODEN: RRHIEV ISSN: 1041-5505 LANGUAGE: English

28/3/23 (Item 23 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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119078864 CA: 119(8)78864e JOURNAL
Performance related exhaust emissions from heavy duty diesel engines
AUTHOR(S): Hickman, A. J.; Graham, M. A.
LOCATION: Transp. Road Res. Lab., Crowthorne/Berkshire, UK, RG11 6AU
JOURNAL: Sci. Total Environ. DATE: 1993 VOLUME: 134, PAGES: 211-23
CODEN: STENDL ISSN: 0048-9697 LANGUAGE: English

28/3/24 (Item 24 from file: 399)

DIALOG(R)File 399:CA SEARCH(R)
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116155163 CA: 116(16)155163t TECHNICAL REPORT
Efficient optimization of heavy-duty diesel in compliance with emission standards
AUTHOR(S): Cornetti, G. M.; Pidello, F.
LOCATION: Iveco Fiat - Eng. Res., I-10156, Turin, Italy
JOURNAL: Comm. Eur. Communities, (Rep.) EUR DATE: 1992 NUMBER: EUR 13867 PAGES: 72 pp. CODEN: CECED9 ISSN: 0303-755X LANGUAGE: English

28/3/25 (Item 25 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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116132487 CA: 116(14)132487n JOURNAL
Characterization of exhaust emissions from two heavy duty vehicles fueled with eight different diesel fuels
AUTHOR(S): Egebaeck, K. E.; Mason, G.; Rannug, U.; Westerholm, R.
LOCATION: Environ. Sect., Swed. Mot. Veh. Insp. Co., S-162 15, Vaellingby , Swed.
JOURNAL: Stud. Surf. Sci. Catal. DATE: 1991 VOLUME: 71 NUMBER: Catal. Automot. Pollut. Control 2 PAGES: 75-91 CODEN: SSCTDM ISSN: 0167-2991
LANGUAGE: English

28/3/26 (Item 26 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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116132472 CA: 116(14)132472d TECHNICAL REPORT
Study of fuel cetane number and aromatic content effects on regulated emissions from a heavy-duty diesel engine
AUTHOR(S): Ullman, T. L.; Mason, R. L.; Montalvo, D. A.
LOCATION: Southwest Res. Inst., San Antonio, TX, USA
JOURNAL: Report DATE: 1990 NUMBER: SWRI-08-2940, CRC-APRAC-VE-1; Order No. PB91-170050 PAGES: 186 pp. CODEN: D8REP4 LANGUAGE: English
CITATION: Gov. Rep. Announce. Index (U. S.) 1991, 91(14), Abstr. No. 137,137 AVAIL: NTIS

28/3/27 (Item 27 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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115165503 CA: 115(16)165503x TECHNICAL REPORT
Exhaust emissions from heavy duty vehicles
CORPORATE AUTHOR(S): Sypher-Mueller International Inc.
LOCATION: Ottawa, ON, Can.,
JOURNAL: Report DATE: 1990 NUMBER: DOE/CE/50182-T1; Order No. DE91006798 PAGES: 46 pp. CODEN: D3REP3 LANGUAGE: English CITATION: Energy Res. Abstr. 1991, 16(4), Abstr. No. 10322 AVAIL: NTIS

28/3/28 (Item 28 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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115053085 CA: 115(6)53085f TECHNICAL REPORT
Heavy duty liquid and gaseous fuel emissions database test results from

four alternative fuel configurations of the Caterpillar 3406 engine
AUTHOR(S): Waldman, D. J.
LOCATION: Caterpillar, Inc., Peoria, IL, USA
JOURNAL: Report DATE: 1990 NUMBER: ORNL/Sub-86-SB195/1; Order No. DE90014783 PAGES: 68 pp. CODEN: D3REP3 LANGUAGE: English CITATION: Energy Res. Abstr. 1990, 15(20), Abstr. No. 44599 AVAIL: NTIS

28/3/29 (Item 29 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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115034728 CA: 115(4)34728b TECHNICAL REPORT
Trial of particulate traps for heavy duty vehicles with diesel engines. Final report
AUTHOR(S): Neppel, H. P.
LOCATION: Tech. Ueferwach.-Verein Bayern e.V., Munich, Fed. Rep. Ger.
JOURNAL: Report DATE: 1989 NUMBER: UBA-FB-89-135 PAGES: 254 pp.
CODEN: D3REP3 LANGUAGE: English CITATION: Energy Res. Abstr. 1990, 15(23), Abstr. No. 51111 AVAIL: UB/TIB, Hannover, Ger.

28/3/30 (Item 30 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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113011396 CA: 113(2)11396m JOURNAL
Exhaust emissions from heavy duty diesel engined vehicles
AUTHOR(S): Latham, S.; Hickman, A. J.
LOCATION: Veh. Environ. Div., Transp. Road Res. Lab., Crowthorne/Berkshire, UK, RG11 6AU
JOURNAL: Sci. Total Environ. DATE: 1990 VOLUME: 93, PAGES: 139-45
CODEN: STENDL ISSN: 0048-9697 LANGUAGE: English

28/3/31 (Item 31 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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111180001 CA: 111(20)180001t JOURNAL
Exhaust emission reduction from a heavy duty diesel truck, using a catalyst and a particulate trap
AUTHOR(S): Westerholm, Roger; Hang, Li; Egebaeck, Karl Erik; Graegg, Kerstin
LOCATION: Dep. Anal. Chem., Univ. Stockholm, S-106 91, Stockholm, Swed.
JOURNAL: Fuel DATE: 1989 VOLUME: 68 NUMBER: 7 PAGES: 856-60 CODEN: FUELAC ISSN: 0016-2361 LANGUAGE: English

28/3/32 (Item 32 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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109134277 CA: 109(16)134277y TECHNICAL REPORT
Control of heavy-duty diesel particulate emissions using catalyzed ceramic traps
AUTHOR(S): Ullman, T. C.
LOCATION: Southwest Res. Inst., San Antonio, TX, USA
JOURNAL: Report DATE: 1987 NUMBER: SWRI-8707, ARB-R-87/320; Order No. PB88-133020 PAGES: 88 pp. CODEN: D8REP4 LANGUAGE: English CITATION: Gov. Rep. Announce. Index (U. S.) 1988, 88(7), Abstr. No. 816,995 AVAIL:

NTIS

28/3/33 (Item 33 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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108137047 CA: 108(16)137047p JOURNAL
Measurement of PAH and nitro-PAH from a heavy-duty diesel engine
AUTHOR(S): Hoekman, S. K.; Ingham, M. C.
LOCATION: Chevron Res. Co., Richmond, CA, USA
JOURNAL: Proc. - APCA Annu. Meet. DATE: 1987 VOLUME: 80th NUMBER: Vol. 1 PAGES: 87/1.4, 22 pp. CODEN: PAAME3 ISSN: 0193-9688 LANGUAGE: English

28/3/34 (Item 34 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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107201980 CA: 107(22)201980w CONFERENCE PROCEEDING
Evaluation of ignition-improved methanol as an alternative fuel for heavy-duty diesel engines
AUTHOR(S): Myburgh, J. S.; Weiss, E. K. J.
LOCATION: Natl. Mech. Eng. Res. Inst., Counc. Sci. Ind. Res., Pretoria, S. Afr.
JOURNAL: Symp. Int. Carbur. Alcool., 7th DATE: 1986 PAGES: 278-83
CODEN: 56DWAI LANGUAGE: English PUBLISHER: Technip,Paris, Fr

28/3/35 (Item 35 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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107201687 CA: 107(22)201687f CONFERENCE PROCEEDING
Use of dissociated methanol in heavy duty DI engine with spark plug
AUTHOR(S): Yoshida, Y.; Yamaguchi, I.; Seko, T.; Suzuki, J.; Hori, M.; Kim, Y. K.
LOCATION: Japan Autom. Res. Inst., Inc., Tsukuba, Japan,
JOURNAL: Symp. Int. Carbur. Alcool., 7th DATE: 1986 PAGES: 285-9
CODEN: 56DWAI LANGUAGE: English PUBLISHER: Technip,Paris, Fr

28/3/36 (Item 36 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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106209249 CA: 106(25)209249q JOURNAL
Long-term inhalation studies on effects of exhaust from heavy and light duty diesel engines on F344 rats
AUTHOR(S): Ishinishi, Noburu; Kuwabara, Noriyuki; Nagase, Sumi; Suzuki, Tadao; Ishiwata, Shoji; Kohno, Toshiyuki
LOCATION: Fac. Med., Kyushu Univ., Fukuoka, Japan, 812
JOURNAL: Dev. Toxicol. Environ. Sci. DATE: 1986 VOLUME: 13 NUMBER: Carcinog. Mutagen. Eff. Diesel Engine Exhaust PAGES: 329-48 CODEN: DTESD7
ISSN: 0165-2214 LANGUAGE: English
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t33/6/all

33/6/1 (Item 1 from file: 108)
02244234 N96-18197

Alternative fuel transit buses: Interim results from the National Renewable Energy Laboratory (NREL) Vehicle Evaluation Program

33/6/2 (Item 2 from file: 108)
02229437 N96-10681
Future market for ceramics in vehicle engines and their impacts

33/6/3 (Item 3 from file: 108)
02229306 N96-10550
Atmospheric process evaluation of mobile source emissions

33/6/4 (Item 4 from file: 108)
02188165 N95-18041
Advanced diesel engine component development program, tasks 4-14
Final Report

33/6/5 (Item 5 from file: 108)
02139141 N94-24753
Development of high temperature liquid lubricants for low-heat rejection: Heavy duty diesel engines

33/6/6 (Item 6 from file: 108)
01964697 N91-19315
Alternative fuels for heavy duty engines: Status of fleet trials

33/6/7 (Item 7 from file: 108)
01896896 N90-18603
Alternative fuels R/D needs: Program directions

33/6/8 (Item 8 from file: 108)
01842072 N89-26930
Supercritical fluid chromatography of polar organic compounds in combustion particulates
Final Report

33/6/9 (Item 9 from file: 108)
01832522 N89-17359
Emission-reduction effects of methanol vehicles: State of knowledge

33/6/10 (Item 10 from file: 108)
01770381 N88-20645
Engine testing for synfuel operation

33/6/11 (Item 11 from file: 108)
01679865 N86-18742
Emission characterization of a 2-stroke heavy-duty diesel coach engine and vehicle with and without a particulate trap
Final Report, 20 Apr. 1982 - 28 May 1983

33/6/12 (Item 1 from file: 6)

1925335 NTIS Accession Number: PB96-181185/XAB
Application of Exhaust Gas Recirculation to the Navistar DT-466 Methanol Engine
(Final rept. 1990-92)
NTIS Prices: PC A05/MF A01

33/6/13 (Item 2 from file: 6)
1919729 NTIS Accession Number: PB96-174818/XAB
Real-World Automotive Emissions: Summary of Studies in the Fort McHenry and Tuscarora Mountain Tunnels
(Final rept)
NTIS Prices: PC A14/MF A03

33/6/14 (Item 3 from file: 6)
1910919 NTIS Accession Number: AD-A301 922/1/XAB
Comparison of Diesel Exhaust Emissions Using JP-8 and Low-Sulfur Diesel Fuel
(Interim rept. Mar 94-Mar 95)
NTIS Prices: PC A07/MF A02

33/6/15 (Item 4 from file: 6)
1894465 NTIS Accession Number: MIC-95-07634/XAB
Development and evaluation of a hydrocarbon reductant NOx reduction system for a heavy duty diesel engine
NTIS Prices: PC E12/MF E01

33/6/16 (Item 5 from file: 6)
1885661 NTIS Accession Number: DE95796332/XAB
Motorgasdrivna bussar i Sundsvall. Slutrapport fraan utveckling av och prov med gasoldrivna stadsbussar i Sundsvall 1990-1993. (Liquefied petroleum gas propelled buses. Final report from development and testing 1990-1993)
NTIS Prices: PC A03/MF A01

33/6/17 (Item 6 from file: 6)
1853232 NTIS Accession Number: MIC-95-02383/XAB
Development and evaluation of an ammonia NOx reduction system for a heavy duty diesel derived natural gas engine
NTIS Prices: PC E07/MF E01

33/6/18 (Item 7 from file: 6)
1836297 NTIS Accession Number: MIC-95-01082/XAB
Impact of diesel fuel aromatics on particulate, PAH and Nitro-PAH emissions
NTIS Prices: PC E17/MF E01

33/6/19 (Item 8 from file: 6)
1827772 NTIS Accession Number: PB95-169561/XAB
Retrofit of Buses to Meet Clean Air Regulations. A Synthesis of Transit Practice 8
NTIS Prices: PC A03/MF A01

33/6/20 (Item 9 from file: 6)

1824328 NTIS Accession Number: PB95-147567/XAB
Development of the Cummins L10 Engine to Operate on Natural Gas for Heavy Duty Transit Bus Applications. Final Report, August 1988-December 1991
NTIS Prices: PC A03/MF A01

33/6/21 (Item 10 from file: 6)
1775590 NTIS Accession Number: PB94-162450/XAB
Heavy-Duty Engine Testing Report Non-Road Engine Configuration Test Results, 1991
(Technical rept)
NTIS Prices: PC A04/MF A01

33/6/22 (Item 11 from file: 6)
1769877 NTIS Accession Number: PB94-158425/XAB
Technical Support Information for the Development of Heavy Duty Diesel Vehicle Rules for the California Federal Implementation Plans
(Technical memo)
NTIS Prices: PC A06/MF A02

33/6/23 (Item 12 from file: 6)
1739191 NTIS Accession Number: PB94-112158/XAB
Emissions Standards for Heavy-Duty Clean-Fuel Fleets. Regulatory Support Document
(Draft rept)
NTIS Prices: PC A04/MF A01

33/6/24 (Item 13 from file: 6)
1735929 NTIS Accession Number: PB94-109907/XAB
Measurement and Chemical Characterization of Vapor-Phase Mutagens in Diesel Exhaust
(Final rept)
NTIS Prices: PC A06/MF A02

33/6/25 (Item 14 from file: 6)
1735768 NTIS Accession Number: PB94-108016/XAB
Emissions Control Strategies for Heavy-Duty Diesel Engines
NTIS Prices: PC A06/MF A02

33/6/26 (Item 15 from file: 6)
1719149 NTIS Accession Number: PB93-236172/XAB
Heavy-Duty Engine Testing Report Cummins/EPA/Taiwan Correlation Test Results, 1993
(Technical rept)
NTIS Prices: PC A03/MF A01

33/6/27 (Item 16 from file: 6)
1700781 NTIS Accession Number: MIC-93-04650/XAB
Evaluation of a heavy duty methanol engine with glow plug ignition: Effect of combustion parameters on emissions: Final report
NTIS Prices: PC E17/MF E01

33/6/28 (Item 17 from file: 6)
1698567 NTIS Accession Number: PB93-504553/XAB

Emissions and Fuel Economy Results 1993 Car Models (for Microcomputers) (Software)
The software is on one 3 1/2 inch diskette, 1.44M high density. File format: ASCII.
NTIS Prices: CP D02

33/6/29 (Item 18 from file: 6)
1698566 NTIS Accession Number: PB93-504546/XAB
Emissions and Fuel Economy Results 1992 Car Models (for Microcomputers) (Software)
The software is on one 3 1/2 inch diskette, 1.44M high density. File format: ASCII text.
NTIS Prices: CP D02

33/6/30 (Item 19 from file: 6)
1673654 NTIS Accession Number: DE93752748/XAB
Individual and public transportation. Emissions and energy consumption models
NTIS Prices: PC A04/MF A01

33/6/31 (Item 20 from file: 6)
1650179 NTIS Accession Number: DE92563092/XAB
Natur- och biogasdrivna fordon. Aktuella projekt och aktiviteter under 1991. (Natural gas and biogas vehicles. Projects and activities during 1991)
NTIS Prices: PC A03/MF A01

33/6/32 (Item 21 from file: 6)
1648662 NTIS Accession Number: TIB/A92-02619/XAB
Entwicklung eines Verfahrens zur Messung der Partikelemission von Nfz-Motoren im Rahmen der ECE R49. (Development of a measuring procedure of particulate emissions of heavy duty diesel engines based on the ECE R49 regulations)
NTIS Prices: PC E14

33/6/33 (Item 22 from file: 6)
1601421 NTIS Accession Number: PB92-167972/XAB
Final Report on Development of Species Profiles for Selected Organic Emission Sources. Volume 2: Engine Exhaust Emissions
NTIS Prices: PC A06/MF A02

33/6/34 (Item 23 from file: 6)
1591827 NTIS Accession Number: MIC-92-01195/XAB
Novel design of an injector/ignitor unit for methanol fuel in a heavy-duty engine
NTIS Prices: PC E07/MF E01

33/6/35 (Item 24 from file: 6)
1543549 NTIS Accession Number: MIC-91-03198/XAB
Petroleum Association for Conservation of the Canadian Environment: Annual review 1988
NTIS Prices: PC E07/MF E01

33/6/36 (Item 25 from file: 6)
1537307 NTIS Accession Number: MIC-91-02585/XAB
Windsor Workshop on Alternative Fuels: Proceedings
NTIS Prices: PC E99/MF E01

33/6/37 (Item 26 from file: 6)
1537189 NTIS Accession Number: MIC-91-02407/XAB
Di-methyl ether as an ignition assistance source for a heavy-duty methanol engine
NTIS Prices: PC E12/MF E01

33/6/38 (Item 27 from file: 6)
1534010 NTIS Accession Number: DE91008995/XAB
Twelfth annual report to Congress on the Automotive Technology Development Program. Annex No. 2
(Progress rept)
NTIS Prices: PC A04/MF A01

33/6/39 (Item 28 from file: 6)
1531115 NTIS Accession Number: MIC-91-01247/XAB
Emission impact of current and possible future Canadian fuels on heavy duty diesel engines
NTIS Prices: PC E12/MF E01

33/6/40 (Item 29 from file: 6)
1507585 NTIS Accession Number: PB91-129106/XAB
Examination of the Sources of Variability in Particle Emission Measurements by the Transient Test Method for Heavy-Duty Diesel Engines. Phase 1. Final Report
NTIS Prices: PC A04/MF A01

33/6/41 (Item 30 from file: 6)
1497910 NTIS Accession Number: TIB/A90-82039/XAB
Erprobung von Russfiltern fuer schwere Dieselfahrzeuge. Schlussbericht. (Trial of particulate traps for heavy duty vehicles with diesel engines. Final report)
NTIS Prices: PC E07

33/6/42 (Item 31 from file: 6)
1450402 NTIS Accession Number: PB90-179136/XAB
Diesels in the Occupational Environment: An Environmental Perspective
NTIS Prices: PC A03/MF A01

33/6/43 (Item 32 from file: 6)
1449891 NTIS Accession Number: DE90728300/XAB
Emissions from Heavy Diesel Vehicles: Measurements 1980-1988
U.S. Sales Only. Paper copy only, copy does not permit microfiche production.
NTIS Prices: PC A03

33/6/44 (Item 33 from file: 6)
1449874 NTIS Accession Number: DE90728280/XAB
Emissions from Heavy Vehicle Engines: Development of Particle Traps for

Diesel Exhaust Gases
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NTIS Prices: PC A03/MF A01

33/6/45 (Item 34 from file: 6)
1442127 NTIS Accession Number: DE90000965/XAB
Navy Mobility Fuels Forecasting System Phase 5 Report: Impacts of Ultra Low Sulfur Diesel Fuel Production on Navy Fuel Availability
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NTIS Prices: PC A03/MF A01

33/6/46 (Item 35 from file: 6)
1440831 NTIS Accession Number: PB90-160938/XAB
Investigation of the Effects of Fuel Composition and Injection and Combustion System Type on Heavy-Duty Diesel Exhaust Emissions
(Final rept)
NTIS Prices: PC A14/MF A02

33/6/47 (Item 36 from file: 6)
1419163 NTIS Accession Number: PB89-229843/XAB
Feasibility and Cost-Effectiveness of Controlling Emissions from Diesel Engines in Rail, Marine, Construction, Farm, and Other Mobile Off-Highway Equipment
(Final rept)
NTIS Prices: PC A07/MF A01

33/6/48 (Item 37 from file: 6)
1380653 NTIS Accession Number: PB89-158208/XAB
Diesel Particulate Extract Study. Part 2
NTIS Prices: PC A04/MF A01

33/6/49 (Item 38 from file: 6)
1380323 NTIS Accession Number: PB89-152441/XAB
Supercritical Fluid Chromatography of Polar Organic Compounds in Combustion Particulates. Final Report
(Rept. for 28 Sep 84-31 Aug 87)
NTIS Prices: PC A05/MF A01

33/6/50 (Item 39 from file: 6)
1378946 NTIS Accession Number: DE88755860/XAB
Inorganic and Organic Compounds in Emissions from Diesel Powered Vehicles. A Literature Survey
U.S. Sales Only. Portions of this document are illegible in microfiche products.
NTIS Prices: PC A04/MF A01

33/6/51 (Item 40 from file: 6)
1372555 NTIS Accession Number: PB89-145429/XAB
Study of Excess Motor Vehicle Emissions: Causes and Control. Volume 1 (Sections 1-5). Volume 2 (Sections 6-10)
(Final rept)
NTIS Prices: PC A99/MF E06

33/6/52 (Item 41 from file: 6)
1369371 NTIS Accession Number: PB89-139497/XAB
Controlling Transit Bus Emissions and Improving Management
NTIS Prices: PC A04/MF A01

33/6/53 (Item 42 from file: 6)
1365215 NTIS Accession Number: DE89000239/XAB
Motor Vehicles in the 1990s: Emerging Environmental Constraints on Current Fuels, and Emissions and Energy Trade-Offs Related to Nonpetroleum Alternatives
Portions of this document are illegible in microfiche products.
NTIS Prices: PC A04/MF A01

33/6/54 (Item 43 from file: 6)
1350413 NTIS Accession Number: PB89-100382/XAB
Genotoxicity of Diesel Exhaust Particles and Vapors Collected from Engines with and without Particulate Trap Oxidizers
(Final rept. 30 May 86-1 Sep 88)
NTIS Prices: PC A06/MF A01

33/6/55 (Item 44 from file: 6)
1344194 NTIS Accession Number: PB88-240098/XAB
Heavy-Duty Diesel Vehicle Inspection and Maintenance Study. Volume 1. Summary Report; Volume 2. Quantifying the Problem; Volume 3. Development and Validation of I/M (Inspection and Maintenance) Test Procedures; Volume 4. I/M Program Design and Cost-Effectiveness Analysis
(Final rept. Jun 85-May 88)
NTIS Prices: PC A99/MF A01

33/6/56 (Item 45 from file: 6)
1323193 NTIS Accession Number: PB88-191846/XAB
Proceedings of the Diesel Particulate Control/Alternative Fuels Symposium Held at Chicago, Illinois on January 27-28, 1987
NTIS Prices: PC A11/MF A01

33/6/57 (Item 46 from file: 6)
1317339 NTIS Accession Number: PB88-180559/XAB
Regulatory Impact Analysis, Oxides of Nitrogen Pollutant Specific Study and Summary and Analysis of Comments
NTIS Prices: PC A14/MF A01

33/6/58 (Item 47 from file: 6)
1317336 NTIS Accession Number: PB88-180526/XAB
Diesel Fuel Quality Effects on Emissions, Durability, and Performance
(Draft rept. (Final))
NTIS Prices: PC A07/MF A01

33/6/59 (Item 48 from file: 6)
1317199 NTIS Accession Number: PB88-178421/XAB
Correlation Testing of the European EMA (Engine Manufacturers Association) Round Robin Engine (Daimler-Benz OM 366 A). Heavy-Duty Engine Testing Report
(Technical rept.)
NTIS Prices: PC A03/MF A01

33/6/60 (Item 49 from file: 6)
1314567 NTIS Accession Number: PB88-169115/XAB
Draft Regulatory Impact Analysis and Oxides of Nitrogen Pollutant Specific Study. Control of Air Pollution from New Motor Vehicles and New Motor Vehicle Engines: Gaseous Emission Regulations for 1987 and Later Model Year Light-Duty Vehicles, Light-Duty Trucks, and Heavy-Duty Engines; Particulate Emission Regulations for 1987 and Later Model Year Heavy-Duty Diesel Engines
NTIS Prices: PC A16/MF A01

33/6/61 (Item 50 from file: 6)
1311831 NTIS Accession Number: PB88-169891/XAB
Heavy-Duty Engine Testing Report - Correlation Testing of Isuzu 5.79L/JAMA Engine
(Technical rept.)
NTIS Prices: PC A04/MF A01

33/6/62 (Item 51 from file: 6)
1294906 NTIS Accession Number: PB88-122643/XAB
Survey of Heavy-Duty Diesel Engine Rebuilding, Reconditioning, and Remanufacturing Practices
(Final rept)
NTIS Prices: PC A08/MF A01

33/6/63 (Item 52 from file: 6)
1286767 NTIS Accession Number: PB88-100516/XAB
Heavy-Duty Engine Testing Report. Correlation Testing of Mack EM G-285
(Technical rept.)
NTIS Prices: PC A03/MF A01

33/6/64 (Item 53 from file: 6)
1268346 NTIS Accession Number: PB87-205266/XAB
Compilation of Air Pollutant Emission Factors. Volume 2. Mobile Sources (4th Edition)
NTIS Prices: PC A24/MF A01

33/6/65 (Item 54 from file: 6)
1262321 NTIS Accession Number: PB87-196481/XAB
Heavy-Duty Engine Testing Report: Correlation Testing of Cummins NTCC-400
(Technical rept.)
NTIS Prices: PC A04/MF A01

33/6/66 (Item 55 from file: 6)
1262249 NTIS Accession Number: PB87-195384/XAB
New York City Bus Terminal Diesel Emissions Study: Measurement and Collection of Diesel Exhaust for Chemical Characterization and Mutagenic Activity
NTIS Prices: PC A02/MF A01

33/6/67 (Item 56 from file: 6)
1233608 NTIS Accession Number: DE86015962/XAB
Cost Analysis of Particulate Emission Control Technology for Heavy-Duty Diesel Vehicles

NTIS Prices: PC A04/MF A01

33/6/68 (Item 57 from file: 6)
1227271 NTIS Accession Number: DE86014496/XAB
Analysis of the Costs of Particulate Trap-Oxidizer Systems for Heavy-Duty Diesel Vehicles
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NTIS Prices: PC A02/MF A01

33/6/69 (Item 58 from file: 6)
1207755 NTIS Accession Number: PB86-216314/XAB
Polycyclic Aromatic Hydrocarbons in Diesel Exhaust
(Final rept. Jan 84-May 85)
NTIS Prices: PC A07/MF A01

33/6/70 (Item 59 from file: 6)
1168683 NTIS Accession Number: PB86-124468/XAB
Emissions Characterization of a Heavy-Duty Diesel Truck Engine Operated on Crude and Minimally-Processed Shale Oils
(Final rept. 30 Sep 84-25 Apr 85)
NTIS Prices: PC A14/MF A01

33/6/71 (Item 60 from file: 6)
1162156 NTIS Accession Number: PB86-102548/XAB
Control of Heavy-Duty Diesel NOx Emissions by Exhaust Gas Recirculation
(Final rept. Apr-Aug 84)
NTIS Prices: PC A05/MF A01

33/6/72 (Item 61 from file: 6)
1149078 NTIS Accession Number: PB85-233658/XAB
Emissions Characterization of Heavy-Duty Diesel and Gasoline Engines and Vehicles
(Final rept. 20 Sep 78-20 Dec 84)
NTIS Prices: PC A15/MF A01

33/6/73 (Item 62 from file: 6)
1128079 NTIS Accession Number: PB85-183051/XAB
Motor Vehicle NOx Inventories
(Technical rept.)
NTIS Prices: PC A04/MF A01

33/6/74 (Item 1 from file: 40)
00432811 ENVIROLINE NUMBER: 96-06570
Multivariate Analysis of Exhaust Emissions from Heavy-Duty Diesel Fuels

33/6/75 (Item 2 from file: 40)
00426212 ENVIROLINE NUMBER: 95-15830
Emissions and Engine Performance from Blends of Soya and Canola Methyl Esters with ARB #2 Diesel in a DDC 6V92TA MUI Engine

33/6/76 (Item 3 from file: 40)
00422665 ENVIROLINE NUMBER: 95-12966

A New Method to Determine Exhaust Emission Factors for Heavy Duty Vehicles

33/6/77 (Item 4 from file: 40)
00420070 ENVIROLINE NUMBER: 95-10661
Amoco, Haldor Topsoe Develop Dimethyl Ether as Alternative Diesel Fuel

33/6/78 (Item 5 from file: 40)
00411305 ENVIROLINE NUMBER: 93-07248
Environmental Benefits of Natural Gas Vehicles

33/6/79 (Item 6 from file: 40)
00411282 ENVIROLINE NUMBER: 93-07224
Forecast of Road Traffic Emissions in the European Community up to the Year 2000

33/6/80 (Item 7 from file: 40)
00410146 ENVIROLINE NUMBER: 93-06086
Heavy-Duty Diesel Vehicles

33/6/81 (Item 8 from file: 40)
00408869 ENVIROLINE NUMBER: 93-04804
Sources of Fine Organic Aerosol. 2. Noncatalyst and Catalyst-Equipped Automobiles and Heavy-Duty Diesel Trucks

33/6/82 (Item 9 from file: 40)
00389574 ENVIROLINE NUMBER: 92-00107
Chemical Composition of Emissions from Urban Sources of Fine Organic Aerosol

33/6/83 (Item 10 from file: 40)
00374125 ENVIROLINE NUMBER: 90-00008
Low-Emission Diesel Fuel for 1991-1994

33/6/84 (Item 11 from file: 40)
00370347 ENVIROLINE NUMBER: 89-02830
Characterization of Polar Polycyclic Aromatic Compounds in a Heavy-Duty Diesel Exhaust Particulate by Capillary Gas Chromatography and High-Resolution Mass Spectrometry

33/6/85 (Item 12 from file: 40)
00367528 ENVIROLINE NUMBER: 89-00011
L.A. Air

33/6/86 (Item 13 from file: 40)
00357145 ENVIROLINE NUMBER: 86-68214
Environmental Protection Agency, 40 CFR Part 86 Control of Air Pollution from New Motor Vehicles and New Motor Vehicle Engines; Nonconformance Penalties for Heavy-Duty Engines and Heavy-Duty Vehicles, Including Light-Duty Trucks; Final Rule

33/6/87 (Item 14 from file: 40)
00353971 ENVIROLINE NUMBER: 86-41840
Highway Motor Vehicles as Sources of Atmospheric Particles: Projected Trends 1977 to 2000

33/6/88 (Item 1 from file: 68)
0367573 1800796
Characterization of polar polycyclic aromatic compounds in a heavy duty diesel exhaust particulate by capillary coumpound gas chromatography and high-resolution mass spectrometry
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Set	Items	Description
S1	1350	HEAVY()DUTY AND DIESEL? ?
S2	454972	EMISSION? ? OR EXHAUST
S3	0	REGULATED()EMISSION? ?B.
S4	131	REGULATED()EMISSION? ?
S5	258018	HYDROCARBON? ? OR HC OR THC
S6	452026	CARBON()MONOXIDE OR CO
S7	64937	NITROGEN()OXIDE? ?
S8	11438	NITROUS()OXIDE
S9	30423	NITRIC()OXIDE
S10	15390	NITROGEN()DIOXIDE
S11	32	OXIDES OF NITROGEN
S12	6810	N20 OR NO2 OR N2O3
S13	158071	ALDEHYDE OR FORMALDEHYDE OR ACETALDEHYDE
S14	56126	KETONE
S15	108564	CARBONYL
S16	239814	ALCOHOL OR METHANOL OR ETHANOL
S17	137745	ETHER
S18	76262	PARTICULATE? ? OR TPM
S19	20	S1ANDS4
S20	523	S1ANDS2AND(S5ORS6ORS7ORS8ORS9ORS10ORS11ORS12ORS13ORS14ORS1-5ORS16ORS17ORS18)
S21	523	S19ORS20
S22	81	S1 AND S2 AND NOX
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S31	14	S26 FROM 40
S32	1	S26 FROM 68
S33	88	29-32/OR

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$15.00 0.125 Hrs File399
$70.20 36 Type(s) in Format 3
$70.20 36 Types
$85.20 Estimated cost File399
$0.84 0.014 Hrs File108

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        $12.65  11 Type(s) in Format  3
         $0.00  11 Type(s) in Format  6
       $12.65  22 Types
  $13.49  Estimated cost File108
       $2.22    0.037 Hrs File6
         $0.00  62 Type(s) in Format  6
       $0.00  62 Types
   $2.22  Estimated cost File6
       $0.54    0.009 Hrs File40
         $0.00  14 Type(s) in Format  6
       $0.00  14 Types
   $0.54  Estimated cost File40
       $0.21    0.007 Hrs File68
         $0.00  1 Type(s) in Format  6
       $0.00  1 Types
   $0.21  Estimated cost File68
       OneSearch, 6 files,  0.233 Hrs FileOS
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  $107.88  Estimated cost this search
  $118.76  Estimated total session cost   0.385 Hrs.
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               Logoff: level 42.07.03 D  13:26:44
          $61.65  Estimated total session cost   0.240 Hrs.
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 File   8:Ei Compendex*Plus(TM)  1970-1996/Sep W2
 File 399:CA SEARCH(R)  1967-1996/UD=12506
 File   6:NTIS  64-1996/Sep W4
 File  40:Enviroline(R)  1975-1996/Jun
 File  68:Env.Bib.  1974-1996/Oct
    Set  Items  Description
    ---  -----  -----------
    SELECT response set to SHORT.
    S1     813  HEAVY()DUTY AND DIESEL? ? AND (EXHAUST OR EMISSION? ?)
    S2     245  (PAH OR POLYCYCLIC()AROMATIC()HYDROCARBON? ?) AND
                (NITRATED OR NITRO)
    S3      24  NITROPOLYCYCLIC()AROMATIC()HYDROCARBON? ?
    S4       1  POLYCYCLIC()NITROAROMATIC()HYDROCARBON? ?
    S5      95  (PNA OR POLYNUCLEAR()AROMATIC()HYDROCARBON? ?) AND
                (NITRATED OR NITRO)
    S6      16  NITRO()POLYNUCLEAR()AROMATIC()HYDROCARBON? ?
    S7       0  POLYNUCLEAR()NITROAROMATIC()HYDROCARBON? ?
    S8       0  SEMI()VOLATILE AND HYDROCARBON ? ?
    S9    5994  HYDROCARBON? ? AND (SPECIATION OR SPECIATED OR VOLATILE)
   S10      19  S1AND(S2ORS3ORS4ORS5ORS6ORS7ORS8ORS9)
   S11      19  S10/ENG
   S12      19  S11/NPT
   S13      16  RD S12 (unique items)
   S14       5  S13 FROM 399
   S15      11  13NOT14

                Temp SearchSave "TD820" stored

 15/5/1     (Item 1 from file: 8)
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DIALOG(R)File 8:Ei Compendex*Plus(TM)
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04412060 E.I. No: EIP96053198398
Title: Volatile organic compounds up to C//2//0 emitted from motor vehicles; measurement methods
Author: Zielinska, Barbara; Sagebiel, John C.; Harshfield, Gregory; Gertler, Alan W.; Pierson, William R.
Corporate Source: Desert Research Inst, Reno, NV, USA
Conference Title: Proceedings of the 1993 A&WMA International Specialty Conference on Regional Photochemical Measurements and Modeling
Conference Location: San Diego, CA, USA Conference Date: 19931108-19931112
E.I. Conference No.: 44705
Source: Atmospheric Environment v 30 n 12 pt 2 Jun 1996. p 2269-2286
Publication Year: 1996
CODEN: ATENBP ISSN: 1352-2310
Language: English
Document Type: JA!(Journal Article) Treatment: X!(Experimental)
Journal Announcement: 9607W3
Abstract: To understand better the sources of observed differences between on-road vehicle emissions and model estimates, and to evaluate the emission of ozone precursors from motor vehicles, a series of experiments was conducted in the Fort McHenry Tunnel, and in the Tuscarora Mountain Tunnel. Samples were collected and analyzed using several techniques. A custom-designed database management system was used to handle the large data sets generated by the analyses. Results show that hydrocarbons in the range of C//1//0-C//2//0 are important components of gas-phase hydrocarbons emitted from heavy-duty diesel vehicles and hence that solid absorbent should be used in addition to canister sampling in measurements of motor vehicle emissions. Refs.
Descriptors: *Volatile organic compounds; Gas emissions; Ground vehicles; Ozone; Gas chromatography; Fourier transform infrared spectroscopy; Mass spectrometry; High performance liquid chromatography; Sampling
Identifiers: Motor vehicles; Flame ionization detection; Hydrocarbon concentrations
Classification Codes:
451.1 |(Air Pollution Sources); 804.1 |(Organic Components); 802.3 |(Chemical Operations); 741.1 |(Light/Optics)
451 |(Air Pollution); 804 |(Chemical Products); 662 |(Automotive Design & Manufacture); 802 |(Chemical Apparatus & Plants); 741 |(Optics & Optical Devices)
45 |(POLLUTION & SANITARY ENGINEERING); 80 |(CHEMICAL ENGINEERING); 66 |(AUTOMOTIVE ENGINEERING); 74 |(OPTICAL TECHNOLOGY)

15/5/2 (Item 2 from file: 8)
DIALOG(R)File 8:Ei Compendex*Plus(TM)
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04383164 E.I. No: EIP96043142796
Title: Transient testing of soy methyl ester fuels in an indirect injection, compression ignition engine
Author: Purcell, D.L.; McClure, B.T.; McDonald, J.; Basu, Hemendra N.
Corporate Source: U.S. Bur of Mines, Minneapolis, MN, USA
Source: JAOCS, Journal of the American Oil Chemists' Society v 73 n 3 Mar 1996. p 381-388
Publication Year: 1996
CODEN: JJASDH ISSN: 0003-021X
Language: English
Document Type: JA; (Journal Article) Treatment: X; (Experimental)

Journal Announcement: 9606W3
Abstract: An evaluation of the exhaust emissions from a compression ignition engine for fuels composed of 100 and 30% methyl esters of soy oil (SME) is described. These fuels were compared with a low-sulfur, petroleum #2 diesel fuel in a Caterpillar 3304, prechamber, 75 kW diesel engine, operated over heavy- and light-duty transient test cycles developed by the United States Bureau of Mines. More than 60 h of testing was performed on each fuel. The objective was to determine the influence of the fuels upon diesel particulate matter (DPM) and gaseous emissions. The effect of a modern diesel oxidation catalyst (DOC) also was determined in an effort to minimize emissions. Neat SME produced a higher volatile fraction of the DPM, but much less carbon soot fraction, leading to overall DPM reductions of 23 to 30% for the light- and heavy-duty transients. The DOC further reduced the volatile fraction and the total DPM. The SME fuel reduced gaseous emissions of CO by 23% and hydrocarbons by over 30% without increasing NO//x. The DOC further reduced CO and hydrocarbon levels. Mutagenicity of the SME exhaust was low. Results indicate that SME fuel, used with a proper DOC, may be a feasible emission reduction technology for underground mines. (Author abstract) 29 Refs.
Descriptors: *Diesel fuels; Vegetable oils; Ignition systems; Esters; Synthetic fuels; Gas emissions; Particulate emissions; Oxidation; Catalysts ; Carbon monoxide
Identifiers: Soy methyl ester fuels; Compression ignition engine; Diesel particulate matter; Exhaust emissions; Volatile fraction; Underground mines
Classification Codes:
804.1 (Organic Components); 612.1 (Internal Combustion Engines, General); 521.1 (Fuel Combustion); 451.1 (Air Pollution Sources); 802.2 (Chemical Reactions)
523 (Liquid Fuels); 804 (Chemical Products); 612 (Combustion Engines); 521 (Combustion & Fuels); 451 (Air Pollution); 802 (Chemical Apparatus & Plants)
52 (FUEL TECHNOLOGY); 80 (CHEMICAL ENGINEERING); 61 (PLANT & POWER ENGINEERING); 45 (POLLUTION & SANITARY ENGINEERING)

15/5/3 (Item 3 from file: 8)
DIALOG(R)File 8:Ei Compendex*Plus(TM)
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03568910 E.I. Monthly No: EI9303029734
Title: Effect of a ceramic particulate trap on the particulate and vapor phase emissions of a heavy-duty diesel engine.
Author: Gratz, L. D.; Bagley, S. T.; King, K. S.; Baumgard, K. J.; Leddy, D. G.; Johnson, J. H.
Corporate Source: Michigan Technological Univ
Source: SAE (Society of Automotive Engineers) Transactions v 100 n Sect 3 1991, 910609 p 878-899
CODEN: SAETA5 ISSN: 0096-736X ISBN: 1-56091-274-X
Language: English
Document Type: JA; (Journal Article) Treatment: L; (Literature Review/Bibliography); X; (Experimental)
Journal Announcement: 9303
Abstract: Exhaust emissions were characterized from a Cummins LTA10 heavy-duty diesel engine operated at two EPA steady-state modes with and without an uncatalyzed Corning ceramic particulate trap. The regulated emissions of nitrogen oxides (NO//x), hydrocarbons (HC), and total particulate matter (TPM) and its components as well as the unregulated emissions of PAH, nitro-PAH, mutagenic activity and particle size distributions were measured. The consistently significant effects of the trap on regulated emissions included reductions of TPM and TPM-associated components. There were no changes in No//x and HC were reduced only at one

operating condition. Particle size distribution measurements showed that nuclei-mode particles were formed downstream of the trap, which effectively removed accumulation-mode particles. All of the mutagenicity was direct-acting and the mutagenic activity of the XOC was approximately equivalent to that of the SOF without the trap. When the trap was used, the particle-associated mutagenicity decreased mainly due to the reduction in the concentration of particles. The trap XOC showed no mutagenic activity. There was some shifting of PAH into the vapor phase when particle emissions were reduced with the use of the trap. Under the test conditions chosen for this engine, the ceramic particulate trap reduced the concentration of emitted particles without increasing the levels of particle-associated mutagenicity, PAH or nitro-PAH. (Author abstract) 60 Refs.

Descriptors: *DIESEL ENGINES; PARTICULATE EMISSIONS; CERAMIC MATERIALS

Identifiers: CERAMIC PARTICULATE TRAPS; VAPOR PHASE EMISSIONS; CUMMINS ENGINE EXHAUST SAMPLING; HEAVY DUTY DIESEL ENGINES; STEADY-STATE EXHAUST SAMPLING SYSTEM; TRAP PARTICLE EMISSIONS DATA

Classification Codes:

612 (Combustion Engines); 451 (Air Pollution); 812 (Ceramics & Refractories)

61 (PLANT & POWER ENGINEERING); 45 (POLLUTION & SANITARY ENGINEERING); 81 (CHEMICAL PROCESS INDUSTRIES)

15/5/4 (Item 4 from file: 8)
DIALOG(R)File 8:Ei Compendex*Plus(TM)
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03383871 E.I. Monthly No: EIM9202-008266

Title: Environmental impact of heavy-duty natural gas vehicles.

Author: Ly, K. H.; Saxby, W. H.; Armitage, W. R.

Corporate Source: AGL Gas Co

Conference Title: International Mechanical Engineering Congress and Exhibition - MECH 91

Conference Location: Sydney, Aust Conference Date: 19910708

E.I. Conference No.: 15606

Source: Resources, Usage, Conservation and the Environment National Conference Publication - Institution of Engineers, Australia n 91 pt 10. Publ by IE Aust, Barton, Aust. p 75-79

Publication Year: 1991

CODEN: NPIEDX ISSN: 0313-6922

Language: English

Document Type: PA; (Conference Paper) Treatment: A; (Applications); G; (General Review)

Journal Announcement: 9202

Abstract: The paper outlines vehicle emission standards for Australia and overseas and discusses emissions from the two types of heavy-duty natural gas vehicle engines: the dedicated gas engine and the dual fuel engine. Vehicle exhaust emissions have a wide ranging impact on the environment, both urban and global. Experimental work to date indicates that dedicated gas engines have the potential of producing significantly cleaner exhausts than equivalent diesel engines, particularly as a result of the Nordic Gas Bus project. On the other hand, the benefits are not so clear-cut in the case of dual fuel engines employing conventional low pressure admission, homogeneous gas-air mixtures. Substituting natural gas for petroleum as a transport fuel could reduce nitrogen oxides, volatile organics and particulates. Natural gas has potential greenhouse benefits compared to petroleum, because natural gas vehicles emit significantly less carbon dioxide. (Author abstract) 21 Refs.

Descriptors: *VEHICLES--*Fuels; ENVIRONMENTAL IMPACT; NATURAL GAS--Applications; CARBON DIOXIDE; INTERNAL COMBUSTION ENGINES--Exhaust Gases

Identifiers: NATURAL GAS VEHICLES; GREENHOUSE GASES; FOREIGN EMISSION

LIMITS; HEAVY DUTY DIESELS; HYDROCARBON LIMIT; SMOG FORMATION
Classification Codes:
432 (Highway Transportation); 521 (Combustion & Fuels); 522 (Gas Fuels); 454 (Environmental Engineering); 512 (Petroleum & Related Deposits); 804 (Chemical Products)
43 (TRANSPORTATION); 52 (FUEL TECHNOLOGY); 45 (POLLUTION & SANITARY ENGINEERING); 51 (PETROLEUM ENGINEERING); 80 (CHEMICAL ENGINEERING)

15/5/5 (Item 5 from file: 8)
DIALOG(R)File 8:Ei Compendex*Plus(TM)
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02329991 E.I. Monthly No: EI8711110378
Title: CHARACTERIZATION OF MUTAGENIC SUBFRACTIONS OF DIESEL EXHAUST MODIFIED BY CERAMIC PARTICULATE TRAPS.
Author: Dorie, Linda D.; Bagley, Susan T.; Leddy, David G.; Johnson, John H.
Corporate Source: Michigan Technological Univ, Houghton, MI, USA
Source: Environmental Science and Technology v 21 n 8 Aug 1987 p 757-765
Publication Year: 1987
CODEN: ESTHAG ISSN: 0013-936X
Language: ENGLISH
Document Type: JA; (Journal Article) Treatment: X; (Experimental)
Journal Announcement: 8711
Abstract: Protocols were developed for collection and characterization of heavy-duty diesel exhaust hydrocarbons. Dichloromethane extracts of particulate and gaseous-phase samples were partitioned between hexane and methanol, and the highly mutagenic (Ames TA98) methanolic fractions were further separated with reverse-phase HPLC. Twenty-eight polycyclic aromatic hydrocarbons (PAH), including 4 nitro- and 13 oxy-PAH derivatives, were tentatively identified in the active (moderately polar) HPLC fractions with GC/MS. In terms of raw exhaust emissions (milligrams per cubic meter), the use of the ceramic traps caused reduced levels of particulate and associated organic compounds. Total mutagenic activity also decreased with the traps, but to a lesser extent than the decrease in particulate. Additional study results are discussed. (Edited author abstract) 46 refs.
Descriptors: *DIESEL ENGINES--*Exhaust Gases; MUTAGENS--Analysis; AIR POLLUTION--Particulate Emissions; CERAMIC MATERIALS
Identifiers: MUTAGENIC SUBFRACTIONS; CERAMIC PARTICULATE TRAPS
Classification Codes:
612 (Combustion Engines); 451 (Air Pollution); 461 (Biotechnology); 801 (Chemical Analysis & Physical Chemistry)
61 (PLANT & POWER ENGINEERING); 45 (POLLUTION & SANITARY ENGINEERING); 46 (BIOENGINEERING); 80 (CHEMICAL ENGINEERING)

15/5/6 (Item 6 from file: 8)
DIALOG(R)File 8:Ei Compendex*Plus(TM)
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01813267 E.I. Monthly No: EI8510085866 E.I. Yearly No: EI85002859
Title: POLAR POLYNUCLEAR AROMATIC HYDROCARBON DERIVATIVES IN EXTRACTS OF PARTICULATES: BIOLOGICAL CHARACTERIZATION AND TECHNIQUES FOR CHEMICAL ANALYSIS.
Author: Schuetzle, D.; Jensen, T. E.; Ball, J. C.
Corporate Source: Ford Motor Co, Scientific Research Lab, Dearborn, MI, USA
Source: Environment International v 11 n 2-4 1985, Pap from the Conf and Workshop on Genotoxic Air Pollut, Rougemont, NC, USA, Apr 24-27 1984 p 169-181

Publication Year: 1985
CODEN: ENVIDV ISSN: 0160-4120 ISBN: 0-08-033141-6
Language: ENGLISH
Document Type: JA; (Journal Article) Treatment: A; (Applications); X; (Experimental)
Journal Announcement: 8510
Abstract: A protocol incorporating the concept of 'bioassay directed chemical analysis' has been developed for the analysis of polar polynuclear aromatic hydrocarbon (polar-PAH) derivatives in particulate matter samples. As an example of the protocol, results and are presented for a National Bureau of Standards (NBS) candidate standard reference diesel particulate material (SRM 1650). Good recovery of mutagenicity and mass suggests that compound decomposition/conversion was minimized. Identification of polar-PAH derivatives was undertaken for liquid chromatographic fractions of a heavy-duty diesel particulate extract that were found to contain a large portion of the total extract mutagenicity. Hydroxy-PAH, hydroxy-nitro-PAH, PAH-quinones, and nitrated heterocyclics were tentatively identified in the polar fractions of the diesel extract. (Edited author abstract) Refs.
Descriptors: *AIR POLLUTION--*Particulate Emissions; HYDROCARBONS--Chemical Analysis; BACTERIOLOGY; BIOCHEMISTRY
Identifiers: POLYNUCLEAR AROMATIC HYDROCARBON DERIVATIVES; EXTRACTS OF PARTICULATES; BIOLOGICAL CHARACTERIZATION
Classification Codes:
451 (Air Pollution); 803 (Chemical Agents & Basic Industrial Chemicals); 804 (Chemical Products); 801 (Chemical Analysis & Physical Chemistry); 461 (Biotechnology)
45 (POLLUTION & SANITARY ENGINEERING); 80 (CHEMICAL ENGINEERING); 46 (BIOENGINEERING)

15/5/7 (Item 1 from file: 6)
DIALOG(R)File 6:NTIS
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1919729 NTIS Accession Number: PB96-174818/XAB
Real-World Automotive Emissions: Summary of Studies in the Fort McHenry and Tuscarora Mountain Tunnels
(Final rept)
Pierson, W. R. ; Gertler, A. W. ; Robinson, N. F. ; Sagebiel, J. C. ; Zielinska, B.
Nevada Univ. System, Reno. Desert Research Inst.
Corp. Source Codes: 050066003;
Sponsor: Denver Univ., CO. Dept. of Chemistry.; Coordinating Research Council, Inc., Atlanta, GA.; Environmental Protection Agency, Washington, DC.; National Renewable Energy Lab., Golden, CO.
Report No.: DRI-6480.1F1; CRC-VE-12-1-92
Aug 95 297p
Languages: English
Journal Announcement: GRAI9615
Prepared in cooperation with Denver Univ., CO. Dept. of Chemistry. Sponsored by Coordinating Research Council, Inc., Atlanta, GA., Environmental Protection Agency, Washington, DC. and National Renewable Energy Lab., Golden, CO.
NTIS Prices: PC A14/MF A03
Country of Publication: United States
Motor vehicles are the main source of carbon monoxide (CO). Under multiple sponsorship, two major vehicle emissions studies were conducted: one in Fort McHenry tunnel (under the Baltimore Harbor) in June 1992 and the other in the Tuscarora Mountain tunnel in south-central Pennsylvania (Pennsylvania Turnpike) in September 1992. The cars at both sites tended to

be newer than elsewhere (median age was < 4 years), and much better maintained as judged by low CO/CO2 ratios and other emissions characteristics. Measured CO/CO2 ratios agreed with concurrent roadside infrared remote sensing measurements on light-duty vehicles. Remote sensing measurements on heavy-duty diesels were obtained for the first time and were roughly in agreement with the regular (bag sampling) tunnel measurements in both CO/CO2 and HC/CO2 ratios.
Descriptors: *Air pollution in tunnels; *Exhaust emission measurement; Hydrocarbons; Carbon monoxide; Air pollution monitors; Emission factors; Ozone; Forecasting; Automobile exhaust; Air pollution sampling; Exhaust pipes; Remote sensing; Mathematical models; Computerized simulation; Maryland; Pennsylvania
Identifiers: *Fort McHenry Tunnel; *Tusarora Mountain Tunnel; Volatile organic compounds; Exhaust inventories; NTISCRC; NTISEPAG
Section Headings: 68A (Environmental Pollution and Control--Air Pollution and Control); 85H (Transportation--Road Transportation); 43F (Problem Solving Information for State and Local Governments--Environment); 91A (Urban and Regional Technology and Development--Environmental Management and Planning)

15/5/8 (Item 2 from file: 6)
DIALOG(R)File 6:NTIS
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1836297 NTIS Accession Number: MIC-95-01082/XAB
Impact of diesel fuel aromatics on particulate, PAH and Nitro-PAH emissions
ORTECH International, Ottawa (Ontario).
Corp. Source Codes: 888888888
Sponsor: Canada Centre for Mineral and Energy Technology. Efficiency and Alternative Energy Technology Branch, Ottawa (Ontario).
Report No.: SSC-M91-7/290-1994E; ISBN-0-662-22311-X
c1994 206p
Languages: English
Journal Announcement: GRAI9511
NTIS Prices: PC E17/MF E01
Country of Publication: Canada
Contract No.: CANMET-015SQ.23440-1-9524
Examination of the polynuclear aromatic hydrocarbon (PAH) emissions from two diesel engines representing state-of-the-art technology, one the DDC Series 60 heavy-duty engine used in highway trucks, and one a Navistar DTA-466 medium-duty engine used in pick-up and delivery type vehicles. The Navistar engine was tested for engine out emissions and with two different sized exhaust oxidation catalysts. Both of the catalysts were composed of a ceramic monolith coated with a palladium type catalyst. Both engines were tested according to the United States Environmental Protection Agency transient emissions test on a series of diesel fuels blended with varying aromatics and PAH contents to determine the impact of fuel quality on emissions. All diesel fuels had a low sulphur content to minimize the formation of sulphate. The particulate matter was collected on teflon-coated filters, backed up with polyurethane foam filters to capture the vapour phase PAH. The PAHs were extracted from both filters with dichloromethane and measured by high resolution gas chromatography (GC) coupled to a low resolution mass spectrometer. A number of nitro-PAHs were analyzed by GC coupled to a high resolution mass spectrometer.
Descriptors: *Polycyclic aromatic hydrocarbons; Diesel fuels
Identifiers: *Foreign technology; *CANMET; *Air pollution control; NTISTFCAN
Section Headings: 68A (Environmental Pollution and Control--Air Pollution and Control); 97R (Energy--Environmental Studies); 97L (Energy--Engine

Studies (Energy Related)); 97K (Energy--Fuels); 81J (Combustion, Engines, and Propellants--Reciprocating and Rotating Combustion Engines)

The following source appears to contain hydrocarbon speciation data which may satisfy Tier 1 requirements.

15/5/9 (Item 3 from file: 6)
DIALOG(R)File 6:NTIS
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1601421 NTIS Accession Number: PB92-167972/XAB
Final Report on Development of Species Profiles for Selected Organic Emission Sources. Volume 2: Engine Exhaust Emissions
Censullo, A. C.
California Polytechnic State Univ., San Luis Obispo. Dept. of Chemistry.
Corp. Source Codes: 045497015
Sponsor: **California State Air Resources Board, Sacramento.**
Report No.: ARB-R-92/483-VOL-2
30 Apr 91 110p
Languages: English
Journal Announcement: GRAI9213
See also PB92-170026. Sponsored by California State Air Resources Board, Sacramento.
NTIS Prices: PC A06/MF A02
Country of Publication: United States
Contract No.: ARB-A832-059
The project involved the characterization of fugitive emissions from three source categories. Category 1 sources, discussed in volume 1, comprised emissions from California oil production facilities. Category 2 and 3 sources, discussed in this volume, included exhaust from utility and **heavy-duty engines**. The selection of 21 samples, based on estimates of engine populations in California, was described. The design and fabrication of a portable exhaust dilution system was discussed. Diluted exhaust from selected engines was sampled simultaneously for hydrocarbons and aldehydes. **Diesel engines were additionally sampled for higher hydrocarbons.** Hydrocarbon species were collected into evacuated stainless steel canisters. Aldehydes were absorbed into midget impingers containing DNPH/acetonitrile. **High molecular weight hydrocarbons from Diesel exhaust were adsorbed in sorbent tubes filled with XAD-2 resin. Hydrocarbons were speciated by gas chromatographic techniques, as with Category 1 sources. Analysis of DNPH-aldehyde derivatives was performed using high performance liquid chromatography. Extracts from the XAD-2 resin were analyzed by gas chromatography, using a mass selective detector.**
Descriptors: *Pollution sources; *Organic compounds; *Air pollution sampling; *Air pollution detection; Exhaust emissions; Chemical analysis; Tables(Data); Gas chromatography; Concentration(Composition); Quality assurance; Hydrocarbons; Aldehydes; Heavy duty vehicles
Identifiers: Utility equipment; NTISCARBRA
Section Headings: 68A (Environmental Pollution and Control--Air Pollution and Control); 99A (Chemistry--Analytical Chemistry)

The following sources appears to contain PAH/NPAH data which may satisfy Tier 1 requirements.

15/5/10 (Item 4 from file: 6)
DIALOG(R)File 6:NTIS
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1207755 NTIS Accession Number: PB86-216314/XAB
Polycyclic Aromatic Hydrocarbons in Diesel Exhaust
(Final rept. Jan 84-May 85)
IIT Research Inst., Chicago, IL.
Corp. Source Codes: 009229000

Report No.: IITRI-C08759-F; CRC-APRAC-CAPE-33-83-01
Jun 85 148p
Languages: English
Journal Announcement: GRAI8621
Coordinating Research Council, Inc., Atlanta, GA.
NTIS Prices: PC A07/MF A01
Country of Publication: United States
Contract No.: APRAC-CAPE-33-83
A research program was supported by the CRC-APRAC-CAPE-33-83 Project Group to study chemical transformations of polycyclic aromatic hydrocarbons (PAH) as the gases pass down the exhaust system of heavy-duty diesel engine. The report discusses the development of the sampling system, including the use of a full-flow vapor phase sampling system using the PUF sampler; the development of analytical methods for benzo(e)pyrene, 9-fluorenone, and 1-nitropyrene; the characterization of the tunnel background; and the analysis of particulates and hydrocarbons at two engine load conditions, 25 and 75% load, rated speed.
Descriptors: ***Diesel engine exhaust; *Aromatic polycyclic hydrocarbons**; Exhaust systems; Air pollution; Hydrocarbons; Chemical analysis; Pyrenes
Identifiers: *Particulate sampling; Pyrene/nitro; Pyrene/benzo; Fluorenone; NTISCRC
Section Headings: 7B (Chemistry--Inorganic Chemistry); 99A (Chemistry--Analytical Chemistry); 68A (Environmental Pollution and Control--Air Pollution and Control)

15/5/11 (Item 1 from file: 40)
DIALOG(R)File 40:Enviroline(R)
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00341038 ENVIROLINE NUMBER: 84-00813
Factors Influencing the Emissions of Nitrated-Polynuclear Aromatic Hydrocarbons (Nitro-Pah) from Diesel Engines
Schuetzle, Dennis, Ford Motor Co, MI; Perez, Joseph M., Caterpillar Tractor Co, IL
J Air Pollut Control Assoc v33, n8, p751(5)
Aug 83
LANGUAGE: English
(Full text available from Congressional Information Service at 1-800-227-2477.)
ABSTRACT: The potential problem of 1-nitropyrene (1-Np) formation during filter sampling of diesel engine emissions from dilution tubes is assessed. A portion of the 1-Np found in particulates collected from light-duty and heavy-duty diesels was found to be due to formation on the filter under average sampling conditions of 10-15/1 dilution at 44 C with 3 ppm nitrogen dioxide for 23 minutes. The concentration of 1-Np in particulates emitted from heavy-duty engines averaged 16 times less than that found in light-duty diesels.
SPECIAL FEATURES: 1 graph(s); 36 reference(s); 4 table(s)
MAJOR DESCRIPTORS: NITRATES; PARTICULATES; AIR CHEMISTRY; MATHEMATIC MODELS, AIR; POLYNUCLEIC AROMATIC HYDROCARBON; DIESEL ENGINES, TRANSPORT; AUTOMOBILE EMISSIONS
REVIEW CLASSIFICATION: 00

14/3/1 (Item 1 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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123178055 CA: 123(14)178055t JOURNAL
Effects of a ceramic particle trap and copper fuel additive on heavy-duty

diesel emissions
AUTHOR(S): Harvey, George D.; Baumgard, Kirby J.; Johnson, John H.; Gratz. Linda D.; Bagley, Susan T.; Leddy, David G.
LOCATION: Michigan Technological Univ., MI, USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1994 VOLUME: SP-1053 PAGES: 207-25 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

14/3/2 (Item 2 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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123178054 CA: 123(14)178054s JOURNAL
Effect of cerium fuel additive on the emissions characteristics of a heavy-duty diesel engine
AUTHOR(S): Lemaire, Jacques; Khair, Magdi
LOCATION: Rhone-Poulenc, Fr.
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1994 VOLUME: SP-1053 PAGES: 189-205 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

14/3/3 (Item 3 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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120037157 CA: 120(4)37157d JOURNAL
Characterization of particle- and vapor-phase organic fraction emissions from a heavy-duty diesel engine equipped with a particle trap and regeneration controls
AUTHOR(S): Bagley, Susan T.; Gratz, Linda D.; Leddy, David G.; Johnson, John H.
LOCATION: Dep. Biol. Sci., Michigan Technol. Univ., Houghton, MI, USA
JOURNAL: Res. Rep. - Health Eff. Inst. DATE: 1993 VOLUME: 56, PAGES: 136 pp. CODEN: RRHIEV ISSN: 1041-5505 LANGUAGE: English

14/3/4 (Item 4 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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114048682 CA: 114(6)48682y JOURNAL
Chemical and biological characterization of particulate-, semivolatile-, and gas-phase-associated compounds in diluted heavy-duty diesel exhausts: a comparison of three different semivolatile-phase samplers
AUTHOR(S): Westerholm, Roger N.; Almen, Jacob; Li, Hang; Rannug, J. Ulf; Egebaeck, Karl Erik; Graegg, Kerstin
LOCATION: Dep. Anal. Chem., Stockholm Univ., S-106 91, Stockholm, Swed.
JOURNAL: Environ. Sci. Technol. DATE: 1991 VOLUME: 25 NUMBER: 2 PAGES: 332-8 CODEN: ESTHAG ISSN: 0013-936X LANGUAGE: English

14/3/5 (Item 5 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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108137047 CA: 108(16)137047p JOURNAL
Measurement of PAH and nitro-PAH from a heavy-duty diesel engine
AUTHOR(S): Hoekman, S. K.; Ingham, M. C.
LOCATION: Chevron Res. Co., Richmond, CA, USA
JOURNAL: Proc. - APCA Annu. Meet. DATE: 1987 VOLUME: 80th NUMBER: Vol. 1 PAGES: 87/1.4, 22 pp. CODEN: PAAME3 ISSN: 0193-9688 LANGUAGE: English

26/6/62 (Item 62 from file: 8)
03403279
Title: Measurement of unregulated exhaust emissions from heavy duty diesel engines with mini-dilution tunnel.

26/6/75 (Item 75 from file: 8)
03304030
Title: Effects of fuel properties on diesel engine emissions. A review of information available to the EEC-MVEG group.
Conference Title: 1991 SAE International Congress and Exposition

26/6/76 (Item 76 from file: 8)
03304019
Title: New developments of ceramic foam as a Diesel Particulate Filter.
Conference Title: 1991 SAE International Congress and Exposition

26/6/77 (Item 77 from file: 8)
03106179
Title: Dynamic measurement of particulate matter. A valuable tool to approach US 1994 HD diesel emission standards.
Conference Title: Proceedings of the 23rd International Symposium on Automotive Technology and Automation

26/6/78 (Item 78 from file: 8)
03106178
Title: Future particulate measurement techniques of the ECE-R49 test with partial-flow dilution systems.
Conference Title: Proceedings of the 23rd International Symposium on Automotive Technology and Automation

26/6/83 (Item 83 from file: 8)
03012202
Title: Emissions and fuel economy test results for methanol- and diesel-fueled buses.
Conference Title: Proceedings - 82nd A&WMA Annual Meeting

26/6/85 (Item 85 from file: 8)
02930243
Title: Analysis of transient emission data of a modelyear 1991 heavy duty diesel engine.
Conference Title: SAE International Congress and Exposition

26/6/86 (Item 86 from file: 8)
02930036
Title: Particulate emissions from diesel engines. Influence of in-cylinder surface.
Conference Title: SAE International Congress and Exposition

26/6/93 (Item 93 from file: 8)
02799053
Title: Diesel lube oils - fourth dimension of diesel particulate control.

26/6/94 (Item 94 from file: 8)

PATRICK MERRITT 08-8271-001 L-0221 D4718 X-5422

Logon file001 15aug96 10:24:02

Temp SearchSave "TD834" stored

File 8:Ei Compendex*Plus(TM) 1970-1996/Sep W3
File 399:CA SEARCH(R) 1967-1996/UD=12508
File 108:Aerospace Database 1962-1996/Jul
File 6:NTIS 64-1996/Sep W5
File 40:Enviroline(R) 1975-1996/Jul
File 68:Env.Bib. 1974-1996/Oct

Set	Items	Description
SELECT response set to SHORT.		
S1	1350	HEAVY()DUTY AND DIESEL? ?
S2	454972	EMISSION? ? OR EXHAUST
S3	0	REGULATED()EMISSION? ?B.
S4	131	REGULATED()EMISSION? ?
S5	258018	HYDROCARBON? ? OR HC OR THC
S6	452026	CARBON()MONOXIDE OR CO
S7	64937	NITROGEN()OXIDE? ?
S8	11438	NITROUS()OXIDE
S9	30423	NITRIC()OXIDE
S10	15390	NITROGEN()DIOXIDE
S11	32	OXIDES OF NITROGEN
S12	6810	N20 OR NO2 OR N2O3
S13	158071	ALDEHYDE OR FORMALDEHYDE OR ACETALDEHYDE
S14	56126	KETONE
S15	108564	CARBONYL
S16	239814	ALCOHOL OR METHANOL OR ETHANOL
S17	137745	ETHER
S18	76262	PARTICULATE? ? OR TPM
S19	20	S1ANDS4
S20	523	S1ANDS2AND(S5ORS6ORS7ORS8ORS9ORS10ORS11ORS12ORS13ORS14OR-S15ORS16ORS17ORS18)
S21	523	S19ORS20
S22	81	S1 AND S2 AND NOX
S23	528	21OR22
S24	518	S23/ENG
S25	391	RD S24 (unique items)
S26	259	S25/1985:1996
S27	135	S26 FROM 8
S28	36	S26 FROM 399
S29	11	S26 FROM 108
S30	62	S26 FROM 6
S31	14	S26 FROM 40
S32	1	S26 FROM 68

Temp SearchSave "TD835" stored

26/6/1 (Item 1 from file: 8)
04412061
Title: Real-world emissions and calculated reactivities of organic species from motor vehicles
Conference Title: Proceedings of the 1993 A&WMA International Specialty Conference on Regional Photochemical Measurements and Modeling

26/6/2 (Item 2 from file: 8)

04412060
Title: Volatile organic compounds up to C//2//0 emitted from motor vehicles; measurement methods
Conference Title: Proceedings of the 1993 A&WMA International Specialty Conference on Regional Photochemical Measurements and Modeling

26/6/5 (Item 5 from file: 8)
04260804
Title: Effects of injection pressure and nozzle geometry on D.I. diesel emissions and performance
Conference Title: Proceedings of the 1995 SAE International Congress & Exposition

26/6/13 (Item 13 from file: 8)
03934677
Title: Characterization of heavy-duty diesel vehicle emissions

26/6/19 (Item 19 from file: 8)
03728643
Title: Heavy-duty diesel emissions using California reference fuel and military grade JP-8
Conference Title: Energy-Sources Technology Conference and Exhibition

26/6/21 (Item 21 from file: 8)
03634244
Title: In-use emissions and performance monitoring of heavy duty vehicles using a transportable transient chassis test facility
Conference Title: International Off-Highway and Powerplant Congress and Exposition

26/6/27 (Item 27 from file: 8)
03574260
Title: Advanced nitrogen oxides reduction technology.
Conference Title: Proceedings of the Annual Automotive Technology Development Contractors' Coordination Meeting

26/6/28 (Item 28 from file: 8)
03574245
Title: Advanced component development and emissions reduction for heavy duty Diesel Engines.
Conference Title: Proceedings of the Annual Automotive Technology Development Contractors' Coordination Meeting

26/6/29 (Item 29 from file: 8)
03571533
Title: Diesel Combustion, Emissions, and Exhaust Aftertreatment.
Conference Title: International Off-Highway and Powerplant Congress and Exposition

26/6/52 (Item 52 from file: 8)
03431497
Title: Additive approaches to reduced diesel emissions.
Conference Title: International Fuels and Lubricants Meeting and

Exposition

26/6/62 (Item 62 from file: 8)
03403279
Title: Measurement of unregulated exhaust emissions from heavy duty diesel engines with mini-dilution tunnel.

26/6/75 (Item 75 from file: 8)
03304030
Title: Effects of fuel properties on diesel engine emissions. A review of information available to the EEC-MVEG group.
Conference Title: 1991 SAE International Congress and Exposition

26/6/76 (Item 76 from file: 8)
03304019
Title: New developments of ceramic foam as a Diesel Particulate Filter.
Conference Title: 1991 SAE International Congress and Exposition

26/6/77 (Item 77 from file: 8)
03106179
Title: Dynamic measurement of particulate matter. A valuable tool to approach US 1994 HD diesel emission standards.
Conference Title: Proceedings of the 23rd International Symposium on Automotive Technology and Automation

26/6/78 (Item 78 from file: 8)
03106178
Title: Future particulate measurement techniques of the ECE-R49 test with partial-flow dilution systems.
Conference Title: Proceedings of the 23rd International Symposium on Automotive Technology and Automation

26/6/83 (Item 83 from file: 8)
03012202
Title: Emissions and fuel economy test results for methanol- and diesel-fueled buses.
Conference Title: Proceedings - 82nd A&WMA Annual Meeting

26/6/85 (Item 85 from file: 8)
02930243
Title: Analysis of transient emission data of a modelyear 1991 heavy duty diesel engine.
Conference Title: SAE International Congress and Exposition

26/6/86 (Item 86 from file: 8)
02930036
Title: Particulate emissions from diesel engines. Influence of in-cylinder surface.
Conference Title: SAE International Congress and Exposition

26/6/93 (Item 93 from file: 8)
02799053

Title: Diesel lube oils - fourth dimension of diesel particulate control.

26/6/94 (Item 94 from file: 8)
02716236
Title: Characterization of polar polycyclic aromatic compounds in a heavy-duty diesel exhaust particulate by capillary column gas chromatography and high-resolution mass spectrometry.

26/6/97 (Item 97 from file: 8)
02537942
Title: HEAVY-DUTY DIESEL ENGINE FUELS COMBUSTION PERFORMANCE AND EMISSIONS - A COOPERATIVE RESEARCH PROGRAM.
Conference Title: National Petroleum Refiners Association Technical Papers. (Presented at the 1985 Fuels & Lubricants Meeting.)

26/6/101 (Item 101 from file: 8)
02523676
Title: HEAVY-DUTY DIESEL EMISSION CONTROL: A REVIEW OF TECHNOLOGY.
Conference Title: Heavy-Duty Diesel Emission Control: A Review of Technology. (Presented at the 1986 Annual General Meeting of the Canadian Institute of Mining & Metallurgy.)

26/6/102 (Item 102 from file: 8)
02509410
Title: REDUCTION OF NO//x AND PARTICULATE EMISSIONS IN THE DIESEL COMBUSTION PROCESS.

26/6/104 (Item 104 from file: 8)
02350825
Title: RELATIONSHIP BETWEEN NITRIC OXIDE AND WORK AS INFLUENCED BY ENGINE OPERATING CONDITIONS AND COMBUSTION SYSTEM PARAMETERS FOR A DIRECT INJECTION DIESEL ENGINE.
Conference Title: SAE International Congress and Exposition.

26/6/118 (Item 118 from file: 8)
02126488
Title: CHEMICAL ANALYSIS AND BIOLOGICAL TESTING OF EMISSIONS FROM A HEAVY DUTY DIESEL TRUCK WITH AND WITHOUT TWO DIFFERENT PARTICULATE TRAPS.
Conference Title: Advances in Diesel Particulate Control. (Papers presented at the SAE International Congress and Exposition.)

26/6/121 (Item 121 from file: 8)
02090804
Title: REDUCING THE SULFUR AND AROMATIC CONTENT OF DIESEL FUEL: COSTS, BENEFITS, AND EFFECTIVENESS FOR EMISSIONS CONTROL.
Conference Title: International Congress and Exposition - Society of Automotive Engineers.

26/6/122 (Item 122 from file: 8)
02090799
Title: GASEOUS AND PARTICULATE EMISSIONS FROM GASOLINE- AND DIESEL-POWERED HEAVY-DUTY TRUCKS.
Conference Title: International Congress and Exposition - Society of

Automotive Engineers.

26/6/125 (Item 125 from file: 8)
02079946
Title: REVIEW OF SAMPLING CONDITION EFFECTS ON POLYNUCLEAR AROMATIC HYDROCARBONS (PNA) FROM HEAVY-DUTY DIESEL ENGINES.
Conference Title: Diesel Fuel Quality and Trends. (Papers presented at the International Fuels and Lubricants Meeting and Exposition.)

Set	Items	Description
S1	1350	HEAVY()DUTY AND DIESEL? ?
S2	454972	EMISSION? ? OR EXHAUST
S3	0	REGULATED()EMISSION? ?B.
S4	131	REGULATED()EMISSION? ?
S5	258018	HYDROCARBON? ? OR HC OR THC
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S7	64937	NITROGEN()OXIDE? ?
S8	11438	NITROUS()OXIDE
S9	30423	NITRIC()OXIDE
S10	15390	NITROGEN()DIOXIDE
S11	32	OXIDES OF NITROGEN
S12	6810	N20 OR NO2 OR N2O3
S13	158071	ALDEHYDE OR FORMALDEHYDE OR ACETALDEHYDE
S14	56126	KETONE
S15	108564	CARBONYL
S16	239814	ALCOHOL OR METHANOL OR ETHANOL
S17	137745	ETHER
S18	76262	PARTICULATE? ? OR TPM
S19	20	S1ANDS4
S20	523	S1ANDS2AND(S5ORS6ORS7ORS8ORS9ORS10ORS11ORS12ORS13ORS14ORS1-5ORS16ORS17ORS18)
S21	523	S19ORS20
S22	81	S1 AND S2 AND NOX
S23	528	21OR22
S24	518	S23/ENG
S25	391	RD S24 (unique items)
S26	259	S25/1985:1996
S27	135	S26 FROM 8
S28	36	S26 FROM 399
S29	11	S26 FROM 108
S30	62	S26 FROM 6
S31	14	S26 FROM 40
S32	1	S26 FROM 68
S33	88	29-32/OR

28/3/1 (Item 1 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

125017643 CA: 125(2)17643j TECHNICAL REPORT
Effects of fuel oxygenates, cetane number, and aromatic content on emissions from 1994 and 1998 prototype heavy-duty diesel engines
AUTHOR(S): Spreen, K. B.; Ullman, T. L.; Mason, R. L.
LOCATION: Automotive Products Emissions Res. Div., Southwest Res. Inst., San Antonio, TX, USA
JOURNAL: Report DATE: 1995 NUMBER: SWRI-4127; Order No. PB96-139456GAR
PAGES: 257 pp. CODEN: D8REP4 LANGUAGE: English CITATION: Gov. Rep. Announce. Index (U. S.) 1996, 96(8), Abstr. No. 08-01,018 AVAIL: NTIS

28/3/3 (Item 3 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

124184155 CA: 124(14)184155n CONFERENCE PROCEEDING
Chassis dynamometer emissions testing results for diesel and alternative-fueled transit buses
AUTHOR(S): Dunlap, Lauren S.; Pellegrin, Vince; Ikeda, Randal; Wilson, Ray; Stanley, Sylvia; Porter, Harvey
LOCATION: Los Angeles Metropolitan Transportation Authority, USA
JOURNAL: Alternate Fuels: Decade Success Promise EDITOR: Bata, Reda Mohamed (Ed), DATE: 1994 PAGES: 65-92 CODEN: 62KQAI LANGUAGE: English
PUBLISHER: Society of Automotive Engineers,Warrendale, Pa

28/3/4 (Item 4 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

124095905 CA: 124(8)95905q JOURNAL
The effect of fuel processes on heavy duty automotive diesel engine emissions
AUTHOR(S): Reynolds, E. G.
LOCATION: BP Oil International, USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1995 VOLUME: SP-1119, PAGES: 13-20 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English
MEETING DATE: 950000

28/3/5 (Item 5 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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124065005 CA: 124(6)65005d JOURNAL
Performance of oxidation catalysts for heavy-duty diesel engines
AUTHOR(S): Stein, H. J.; Huethwohl, G.; Lepperhoff, G.
LOCATION: Dept. EN/MGA, Mercedes-Benz AG, Stuttgart, Germany, D-70322
JOURNAL: Stud. Surf. Sci. Catal. DATE: 1995 VOLUME: 96 NUMBER: Catalysis and Automotive Pollution Control III PAGES: 517-28 CODEN: SSCTDM ISSN: 0167-2991 LANGUAGE: English

28/3/9 (Item 9 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

122243657 CA: 122(20)243657m JOURNAL
Effects of oxygenated fuel and cetane improver on exhaust emission from heavy-duty DI diesel engines
AUTHOR(S): Akasaka, Yukio; Sakurai, Yoshihito
LOCATION: JOMO Technical Research Co. Ltd., USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1994 VOLUME: SP-1056 NUMBER: Diesel Fuel PAGES: 181-8 CODEN: SAESA2 ISSN: 0099-5908
LANGUAGE: English

28/3/10 (Item 10 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

122218126 CA: 122(18)218126e JOURNAL
Fuel quality effects on particulate matter emissions from light- and heavy-duty diesel engines
AUTHOR(S): Ouden, C. J. J. Den; Clark, R. H.; Cowley, L. T.; Stradling, R. J.; Lange, W. W.; Maillard, C.
LOCATION: Shell Research Ltd., USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1994 VOLUME: SP-1056 NUMBER: Diesel Fuel PAGES: 159-80 CODEN: SAESA2 ISSN: 0099-5908
LANGUAGE: English

28/3/11 (Item 11 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

122062935 CA: 122(6)62935e JOURNAL
The contribution of the lube oil to particulate emissions of heavy duty diesel engines
AUTHOR(S): Tritthart, P.; Ruhri, F.; Cartellieri, W.
LOCATION: AVL-List Ges.m.b.H., Graz, Austria
JOURNAL: Mech. Eng. (Marcel Dekker) DATE: 1993 VOLUME: 80 NUMBER: Engine Oils and Automotive Lubrication PAGES: 535-52 CODEN: MCLEEF
ISSN: 0899-3858 LANGUAGE: English

28/3/12 (Item 12 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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122037710 CA: 122(4)37710v JOURNAL
Exhaust emissions from light- and heavy-duty vehicles: chemical composition, impact of exhaust after treatment, and fuel parameters
AUTHOR(S): Westerholm, Roger; Egebaeck, Karl-Erik
LOCATION: Department of Analytical Chemistry, University of Stockholm, S-106 91, Stockholm, Swed.
JOURNAL: Environ. Health Perspect. Suppl. DATE: 1994 VOLUME: 102
NUMBER: Suppl. 4 PAGES: 13-23 CODEN: EHPSEO ISSN: 1078-0475
LANGUAGE: English

28/3/14 (Item 14 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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121087299 CA: 121(8)87299t JOURNAL
Emissions comparisons of twenty-six heavy-duty vehicles operated on conventional and alternative fuels
AUTHOR(S): Wang, Wenguang; Gautam, Mridul; Sun, Xiaobo; Bata, Reda; Clark, Nigel; Palmer, Michael; Lyons, Donald
LOCATION: West Virginia Univ., WV, USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1993 VOLUME: SP-1001 NUMBER: Truck Alternative Fuels and Exhaust Gas Emission PAGES: 31-40 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/15 (Item 15 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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121038901 CA: 121(4)38901z JOURNAL
The influence of composition and properties of diesel fuel on particulate

emissions from heavy-duty engines
AUTHOR(S): Cowley, L. T.; Stradling, R. J.; Doyon, J.
LOCATION: Shell Res. Ltd., UK,
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1993 VOLUME: SP-994
NUMBER: DIESEL FUELS FOR THE NINETIES: COMPOSITION AND ADDITIVES TO MEET EMISSIONS AND PERFORMANCE NEEDS PAGES: 13-48 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/16 (Item 16 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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121038898 CA: 121(4)38898d JOURNAL
A study of emissions from CNG and diesel fueled heavy-duty vehicles
AUTHOR(S): Wang, Wenguang; Sun, Xiaobo; Bata, Reda; Gautam, Mridul; Clark, Nigel; Palmer, G. Michael; Lyons, Donald
LOCATION: West Virginia Univ., USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1993 VOLUME: SP-993
NUMBER: GASEOUS FUEL TECHNOLOGY FOR THE NINETIES PAGES: 99-108 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/18 (Item 18 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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121038861 CA: 121(4)38861m JOURNAL
The effect of oxygenated fuels on emissions from a modern heavy-duty diesel engine
AUTHOR(S): Liotta, Frank J. Jr.; Montalvo, Daniel M.
LOCATION: ARCO Chem. Co., USA
JOURNAL: Soc. Automot. Eng., (Spec. Publ.) SP DATE: 1993 VOLUME: SP-994
NUMBER: DIESEL FUELS FOR THE NINETIES: COMPOSITION AND ADDITIVES TO MEET EMISSIONS AND PERFORMANCE NEEDS PAGES: 59-75 CODEN: SAESA2 ISSN: 0099-5908 LANGUAGE: English

28/3/19 (Item 19 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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120195495 CA: 120(16)195495s JOURNAL
Effect of fuel composition including aromatics content on emissions from a range of heavy-duty diesel engines
AUTHOR(S): Cowley, L. T.; Le Juene, A.; Lange, W. W.
LOCATION: Shell Res. Ltd., Chester, UK,
JOURNAL: IMechE Semin. DATE: 1993 NUMBER: 5, Worldwide Engine Emission Standards and How to Meet Them PAGES: 225-44 CODEN: ISEME4 LANGUAGE: English

28/3/22 (Item 22 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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120037157 CA: 120(4)37157d JOURNAL
Characterization of particle- and vapor-phase organic fraction emissions from a heavy-duty diesel engine equipped with a particle trap and regeneration controls
AUTHOR(S): Bagley, Susan T.; Gratz, Linda D.; Leddy, David G.; Johnson,

John H.
LOCATION: Dep. Biol. Sci., Michigan Technol. Univ., Houghton, MI, USA
JOURNAL: Res. Rep. - Health Eff. Inst. DATE: 1993 VOLUME: 56, PAGES: 136 pp. CODEN: RRHIEV ISSN: 1041-5505 LANGUAGE: English

28/3/23 (Item 23 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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119078864 CA: 119(8)78864e JOURNAL
Performance related exhaust emissions from heavy duty diesel engines
AUTHOR(S): Hickman, A. J.; Graham, M. A.
LOCATION: Transp. Road Res. Lab., Crowthorne/Berkshire, UK, RG11 6AU
JOURNAL: Sci. Total Environ. DATE: 1993 VOLUME: 134, PAGES: 211-23
CODEN: STENDL ISSN: 0048-9697 LANGUAGE: English

28/3/25 (Item 25 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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116132487 CA: 116(14)132487n JOURNAL
Characterization of exhaust emissions from two heavy duty vehicles fueled with eight different diesel fuels
AUTHOR(S): Egebaeck, K. E.; Mason, G.; Rannug, U.; Westerholm, R.
LOCATION: Environ. Sect., Swed. Mot. Veh. Insp. Co., S-162 15, Vaellingby , Swed.
JOURNAL: Stud. Surf. Sci. Catal. DATE: 1991 VOLUME: 71 NUMBER: Catal. Automot. Pollut. Control 2 PAGES: 75-91 CODEN: SSCTDM ISSN: 0167-2991
LANGUAGE: English

28/3/26 (Item 26 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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116132472 CA: 116(14)132472d TECHNICAL REPORT
Study of fuel cetane number and aromatic content effects on regulated emissions from a heavy-duty diesel engine
AUTHOR(S): Ullman, T. L.; Mason, R. L.; Montalvo, D. A.
LOCATION: Southwest Res. Inst., San Antonio, TX, USA
JOURNAL: Report DATE: 1990 NUMBER: SWRI-08-2940, CRC-APRAC-VE-1; Order No. PB91-170050 PAGES: 186 pp. CODEN: D8REP4 LANGUAGE: English
CITATION: Gov. Rep. Announce. Index (U. S.) 1991, 91(14), Abstr. No. 137,137 AVAIL: NTIS

28/3/27 (Item 27 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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115165503 CA: 115(16)165503x TECHNICAL REPORT
Exhaust emissions from heavy duty vehicles
CORPORATE AUTHOR(S): Sypher-Mueller International Inc.
LOCATION: Ottawa, ON, Can.,
JOURNAL: Report DATE: 1990 NUMBER: DOE/CE/50182-T1; Order No. DE91006798 PAGES: 46 pp. CODEN: D3REP3 LANGUAGE: English CITATION: Energy Res. Abstr. 1991, 16(4), Abstr. No. 10322 AVAIL: NTIS

28/3/30 (Item 30 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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113011396 CA: 113(2)11396m JOURNAL
Exhaust emissions from heavy duty diesel engined vehicles
AUTHOR(S): Latham, S.; Hickman, A. J.
LOCATION: Veh. Environ. Div., Transp. Road Res. Lab., Crowthorne/Berkshire, UK, RG11 6AU
JOURNAL: Sci. Total Environ. DATE: 1990 VOLUME: 93, PAGES: 139-45
CODEN: STENDL ISSN: 0048-9697 LANGUAGE: English

28/3/31 (Item 31 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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111180001 CA: 111(20)180001t JOURNAL
Exhaust emission reduction from a heavy duty diesel truck, using a catalyst and a particulate trap
AUTHOR(S): Westerholm, Roger; Hang, Li; Egebaeck, Karl Erik; Graegg, Kerstin
LOCATION: Dep. Anal. Chem., Univ. Stockholm, S-106 91, Stockholm, Swed.
JOURNAL: Fuel DATE: 1989 VOLUME: 68 NUMBER: 7 PAGES: 856-60 CODEN: FUELAC ISSN: 0016-2361 LANGUAGE: English

28/3/32 (Item 32 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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109134277 CA: 109(16)134277y TECHNICAL REPORT
Control of heavy-duty diesel particulate emissions using catalyzed ceramic traps
AUTHOR(S): Ullman, T. C.
LOCATION: Southwest Res. Inst., San Antonio, TX, USA
JOURNAL: Report DATE: 1987 NUMBER: SWRI-8707, ARB-R-87/320; Order No. PB88-133020 PAGES: 88 pp. CODEN: D8REP4 LANGUAGE: English CITATION: Gov. Rep. Announce. Index (U. S.) 1988, 88(7), Abstr. No. 816,995 AVAIL: NTIS

28/3/33 (Item 33 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
(c) 1996 American Chemical Society. All rts. reserv.

108137047 CA: 108(16)137047p JOURNAL
Measurement of PAH and nitro-PAH from a heavy-duty diesel engine
AUTHOR(S): Hoekman, S. K.; Ingham, M. C.
LOCATION: Chevron Res. Co., Richmond, CA, USA
JOURNAL: Proc. - APCA Annu. Meet. DATE: 1987 VOLUME: 80th NUMBER: Vol. 1 PAGES: 87/1.4, 22 pp. CODEN: PAAME3 ISSN: 0193-9688 LANGUAGE: English

28/3/36 (Item 36 from file: 399)
DIALOG(R)File 399:CA SEARCH(R)
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106209249 CA: 106(25)209249q JOURNAL
Long-term inhalation studies on effects of exhaust from heavy and light duty diesel engines on F344 rats

AUTHOR(S): Ishinishi, Noburu; Kuwabara, Noriyuki; Nagase, Sumi; Suzuki, Tadao; Ishiwata, Shoji; Kohno, Toshiyuki
LOCATION: Fac. Med., Kyushu Univ., Fukuoka, Japan, 812
JOURNAL: Dev. Toxicol. Environ. Sci. DATE: 1986 VOLUME: 13 NUMBER: Carcinog. Mutagen. Eff. Diesel Engine Exhaust PAGES: 329-48 CODEN: DTESD7
ISSN: 0165-2214 LANGUAGE: English

33/6/14 (Item 3 from file: 6)
1910919 NTIS Accession Number: AD-A301 922/1/XAB
Comparison of Diesel Exhaust Emissions Using JP-8 and Low-Sulfur Diesel Fuel
(Interim rept. Mar 94-Mar 95)
NTIS Prices: PC A07/MF A02

33/6/15 (Item 4 from file: 6)
1894465 NTIS Accession Number: MIC-95-07634/XAB
Development and evaluation of a hydrocarbon reductant NOx reduction system for a heavy duty diesel engine
NTIS Prices: PC E12/MF E01

33/6/17 (Item 6 from file: 6)
1853232 NTIS Accession Number: MIC-95-02383/XAB
Development and evaluation of an ammonia NOx reduction system for a heavy duty diesel derived natural gas engine
NTIS Prices: PC E07/MF E01

33/6/18 (Item 7 from file: 6)
1836297 NTIS Accession Number: MIC-95-01082/XAB
Impact of diesel fuel aromatics on particulate, PAH and Nitro-PAH emissions
NTIS Prices: PC E17/MF E01

33/6/24 (Item 13 from file: 6)
1735929 NTIS Accession Number: PB94-109907/XAB
Measurement and Chemical Characterization of Vapor-Phase Mutagens in Diesel Exhaust
(Final rept)
NTIS Prices: PC A06/MF A02

33/6/48 (Item 37 from file: 6)
1380653 NTIS Accession Number: PB89-158208/XAB
Diesel Particulate Extract Study. Part 2
NTIS Prices: PC A04/MF A01

33/6/54 (Item 43 from file: 6)
1350413 NTIS Accession Number: PB89-100382/XAB
Genotoxicity of Diesel Exhaust Particles and Vapors Collected from Engines with and without Particulate Trap Oxidizers
(Final rept. 30 May 86-1 Sep 88)
NTIS Prices: PC A06/MF A01

33/6/69 (Item 58 from file: 6)
1207755 NTIS Accession Number: PB86-216314/XAB

Polycyclic Aromatic Hydrocarbons in Diesel Exhaust
(Final rept. Jan 84-May 85)
NTIS Prices: PC A07/MF A01

33/6/72 (Item 61 from file: 6)
1149078 NTIS Accession Number: PB85-233658/XAB
Emissions Characterization of Heavy-Duty Diesel and Gasoline Engines and Vehicles
(Final rept. 20 Sep 78-20 Dec 84)
NTIS Prices: PC A15/MF A01

33/6/84 (Item 11 from file: 40)
00370347 ENVIROLINE NUMBER: 89-02830
Characterization of Polar Polycyclic Aromatic Compounds in a Heavy-Duty Diesel Exhaust Particulate by Capillary Gas Chromatography and High-Resolution Mass Spectrometry

33/6/88 (Item 1 from file: 68)
0367573 1800796
Characterization of polar polycyclic aromatic compounds in a heavy duty diesel exhaust particulate by capillary coumpound gas chromatography and high-resolution mass spectrometry

Set	Items	Description
S1	1350	HEAVY()DUTY AND DIESEL? ?
S2	454972	EMISSION? ? OR EXHAUST
S3	0	REGULATED()EMISSION? ?B.
S4	131	REGULATED()EMISSION? ?
S5	258018	HYDROCARBON? ? OR HC OR THC
S6	452026	CARBON()MONOXIDE OR CO
S7	64937	NITROGEN()OXIDE? ?
S8	11438	NITROUS()OXIDE
S9	30423	NITRIC()OXIDE
S10	15390	NITROGEN()DIOXIDE
S11	32	OXIDES OF NITROGEN
S12	6810	N20 OR NO2 OR N2O3
S13	158071	ALDEHYDE OR FORMALDEHYDE OR ACETALDEHYDE
S14	56126	KETONE
S15	108564	CARBONYL
S16	239814	ALCOHOL OR METHANOL OR ETHANOL
S17	137745	ETHER
S18	76262	PARTICULATE? ? OR TPM
S19	20	S1ANDS4
S20	523	S1ANDS2AND(S5ORS6ORS7ORS8ORS9ORS10ORS11ORS12ORS13ORS14ORS1-5ORS16ORS17ORS18)
S21	523	S19ORS20
S22	81	S1 AND S2 AND NOX
S23	528	21OR22
S24	518	S23/ENG
S25	391	RD S24 (unique items)
S26	259	S25/1985:1996
S27	135	S26 FROM 8
S28	36	S26 FROM 399
S29	11	S26 FROM 108
S30	62	S26 FROM 6
S31	14	S26 FROM 40
S32	1	S26 FROM 68

S33 88 29-32/OR

SearchSave "SD055" stored

Logoff: level 42.07.03 D 10:46:52
$118.76 Estimated total session cost 0.385 Hrs.