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CHARACTERIZATION OF EXHAUST EMISSIONS FROM TRAP-EQUIPPED LIGHT-DUTY DIESELS

By

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FINAL REPORT

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FOREWORD

This project was conducted for the California Air Resources Board by the Department of Emissions Research, Southwest Research Institute. The program, authorized by Contract No. A5-159-32, was initiated August 12, 1986 and completed September 30, 1988. It was identified within Southwest Research Institute as Project 08-1280. The CARB Contract Manager for the program was Mr. Jack Paskind of the Research Division, Sacramento, California. The CARB Project Technical Monitor was initially Ms. Yolanda Garza and finally Mr. Ramon Cabrera, both of the Mobile Source Division, El Monte, California. SwRI Project Manager and principal researcher for the project was Dr. Lawrence R. Smith. Dr. Jong-Pyng Hsu of the Chemistry and Chemical Engineering Division, SwRI, was responsible for the mass spectral analyses. The Ames Bioassay analyses were conducted under a separate CARB Contract (No. A5-130-33) by the Department of Community and Environmental Medicine, University of California, Irvine, California under the direction of Dr. Ronald E. Rasmussen.

Mercedes-Benz of North America, Inc. and Volkswagen of America, Inc. provided the test vehicles that were evaluated in the program. Mr. Harald Polz, Manager of the Emission Control Department, Montvale, New Jersey, was the primary contact for Mercedes Benz, and provided valuable technical assistance to SwRI for test work related to the Mercedes vehicle. Mr. Bernd Herrbrick, Mercedes Benz of North America, Carson, California also provided technical assistance and was responsible for the delivery of the Mercedes test vehicle to SwRI. Mr.Wolfgang Groth, Manager Emission Regulations and Certification, and Mr. Ken Parker, Senior Product Engineer, both of Volkswagen of America, Troy, Michigan, were the primary contacts for Volkswagen of America, and both provided valuable technical assistance to SwRI for test work related to the Volkswagen vehicle. Dr. Mike Ingham of Chevron provided the low-aromatic test fuel used in the program.

This report is submitted in fulfillment of CARB Contract Number A5-159-32, "Characterization of Exhaust Emissions from Trap-Equipped Light-Duty Diesels" by Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas under the sponsorship of the California Air Resources Board. Work was completed as of September 30, 1988.

ABSTRACT

This program involved characterization and quantification of emissions from two different types of trap-equipped light-duty diesel vehicles. One vehicle was equipped with a catalyzed trap system and the other with an additive-regenerated trap system. The vehicles were tested using a chassis dynamometer, a dilution tunnel, and a constant volume sampler. Exhaust emissions were evaluated as to driving cycle, presence of trap, engine condition, trap condition, and fuel aromatic content. Emissions evaluated included the regulated exhaust emissions (total hydrocarbons, carbon monoxide, oxides of nitrogen, and particulate) and a number of unregulated emissions including: aldehydes and ketones, sulfate, metals and other trace elements, volatile organics, semivolatile organics, and 1,3-butadiene. Additional evaluations included the determination of the particulate soluble organic fraction, fuel economy by the carbon balance method, and the collection of particulate for mutagenesis testing in another program.

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SUMMARY

The objective of this program was to characterize and quantify the emissions from two different types of trap-equipped light-duty diesel vehicles. The two test vehicles evaluated included a 1986 Mercedes-Benz 300 SDL and a prototype Volkswagen Jetta. The Mercedes utilized a catalyzed trap system and the Volkswagen utilized an additive-regenerated trap system. Two low-sulfur fuels were used in the evaluations, a baseline fuel containing 36.2 percent aromatics and a low-aromatic fuel containing 16.2 percent aromatics. The vehicles were tested both with and without particulate traps using a chassis dynamometer, a dilution tunnel and a constant volume sampler. The vehicles were evaluated while operating over the Federal Test Procedure, the Highway Fuel Economy Test, and the low speed New York City Cycle. Additional evaluations included malfunction operation (failed or worn injectors and retarded injection timing), trap regeneration, and operation with a heavily-loaded trap.

Exhaust emissions evaluated in this program included: the currently regulated exhaust emissions (total hydrocarbons, carbon monoxide, oxides of nitrogen and particulate), aldehydes and ketones, sulfate, metals and other elements, volatile organics (gas phase and particulate-associated), semivolatile organics (gas phase and particulate-associated), and 1,3-butadiene. The organic soluble fraction of particulate was determined by Soxhlet extractions with methylene chloride. Particulate samples were also collected for subsequent extraction and mutagenesis testing by another contractor.

A number of observations were made about the data generated in this project. The observations are summarized (not necessarily in order) as follow:

- The Volkswagen had higher total hydrocarbon emissions, but lower carbon monoxide, oxides of nitrogen, and particulate emissions than the larger Mercedes vehicle. The Volkswagen also had better fuel economy than the Mercedes.

- The particulate traps reduced the engine-out particulate emissions from 79 to 93 percent for the two vehicles operating over the three test cycles.

- In general, the test vehicles gave lower total hydrocarbon emissions, higher carbon monoxide emissions, and lower fuel economy when the traps were installed on the vehicles.

- The low-speed New York City Cycle (NYCC) gave the highest regulated emissions and the lowest fuel economy of the three test cycles. The Highway Fuel Economy Test (HFET), which had the highest average speed of the three test cycles, gave the lowest regulated emission rates and the highest fuel economy results.

- Worn injectors supplied by Mercedes and supposedly failed injectors supplied by Volkswagen did not produce significant changes in the regulated emissions when installed in the vehicles.

- Retarding the injection timing by 3° crank angle in general gave higher total hydrocarbon, carbon monoxide, and particulate emissions, and lower

oxides of nitrogen emissions than the baseline tests. The fuel economy results were not consistent and varied with test cycle and presence of trap for the two vehicles.

- In general, the test vehicles gave lower total hydrocarbon, carbon monoxide, and particulate emissions, and lower fuel economy, when operating on the low-aromatic fuel as compared to the baseline fuel. Particulate emissions were 10 to 37 percent lower with the low-aromatic fuel.

- Regeneration testing (burning of trap-retained particulates in the trap) using the HFET test gave lower or equivalent total hydrocarbon emissions and higher carbon monoxide and particulate emissions than the HFET test without regeneration.

- Heavily-loaded trap tests (utilizing the NYCC test) gave lower fuel economy results and carbon monoxide emissions than tests with nominally loaded traps.

- Of the 33 metals and trace elements investigated in this study, only 13 were found routinely and at quantifiable levels on the filters used to collect the particulate matter. These 13 elements included: magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, potassium, calcium, chromium, iron, nickel, copper, and zinc.

- The trace metals and elements were detected at higher levels without the traps on the vehicles than with the traps in place. These results indicate that these elements may be retained in the trap and as a result could cause increased engine backpressure over a period of time. Regeneration tests gave higher levels of sulfur, calcium (for the Volkswagen), and copper than tests without regeneration. This observation suggests that these elements are first stored in the traps and then purged from the traps at the high temperatures experienced by the traps during regeneration.

- Formaldehyde and acetaldehyde were found to constitute 70 to 85 percent of the total aldehydes and ketones measured, and were the only aldehydes detected consistently throughout the program. In general, the aldehyde and ketone emission rates showed trends similar to those observed for the total hydrocarbons.

- Gas phase semivolatile organics detected in the exhaust of the test vehicles included phenol, 3-methylphenol, 4-methylphenol, N-nitrosodiphenylamine, naphthalene, 2-methylnaphthalene, acenaphthalene, dibenzofuran and phenanthrene. Particulate-associated semivolatiles detected included fluorene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, naphthalene, 2-methylnaphthalene, acenaphthalene, dibenzofuran, and phenanthrene. These compounds were detected in exhaust at levels ranging from 1 μg/mi to 4 mg/mi. The gas phase polynuclear compounds were typically C_{10} to C_{14} compounds, while the particulate-associated compounds, were C_{13} and larger compounds.

- The gas phase semivolatile data were generally too variable to draw any definite conclusions, however, there was not a definite decrease in emission levels of the compounds when the particulate traps were installed in the test vehicles. In contrast, the particulate-associated semivolatiles showed a definite decrease for the "with trap" tests as compared to the "without trap" tests. While this decrease could be real, it is also possible that it may be the result of the higher molecular weight semivolatiles not having elemental carbon sites at which to condense and therefore remaining in the gaseous state in the cleaner exhaust downstream of the trap. Many of these high molecular weight polynuclear aromatics are present in the "without trap" tests at levels below the detection limit of the gas phase semivolatile collection procedure.

- 1,3-butadiene was detected in the exhaust of both test vehicles both with and without the trap in place on the vehicles. The 1,3-butadiene percentage of the total hydrocarbons was similar for the two vehicles, 1.3 to 1.8 percent. For gasoline vehicles, 1,3-butadiene emissions occur primarily in the cold-start portion of the FTP. In this diesel study, the 1,3-butadiene emissions were similar for all three segments of the FTP.

- Benzene, toluene, and total xylenes were detected in the exhaust of both vehicles, with and without trap, and while operating over all three test cycles. Benzene and toluene were also found at lower levels in the background dilution air.

- On a revertants per mile basis, the tests with particulate traps gave lower mutagenic activity than the tests without traps for both vehicles operating over the three test cycles.

- The Mercedes loaded trap and regeneration tests gave mutagenic activity results comparable to the baseline results with trap. The Volkswagen, on the other hand, gave mutagenic activity results for these tests that were similar to the baseline results "without" trap.

- The tests with the low aromatic fuel gave lower average mutagenic activity than the comparable tests with the baseline fuel. However, there were considerable variations in the data and when these variations were taken into account, there were no significant differences in the mutagenic data for the two fuels. Additional analyses should be conducted before any conclusions are drawn.

Both the Mercedes catalyzed trap system and the Volkswagen additive-regenerated trap system were effective in reducing particulate emissions. With the exceptions of increased carbon monoxide and higher aldehyde and ketone (Volkswagen) emission rates, both vehicles with particulate trap exhibited equivalent or lower regulated and unregulated exhaust emissions than when operating without a trap. Mutagenesis testing using the Ames Bioassay indicated a reduction in mutagenic activity on a per mile basis when using the particulate traps. While some increase in mutagenic activity over baseline trap levels was noted in the regeneration and heavily loaded trap tests, these levels did not exceed levels observed without the particulate trap on the vehicle. Engine malfunctions (failed/worn injectors and retarded timing) influenced exhaust emissions in a similar

way for both the with and with trap tests. The low-aromatic test fuel gave lower hydrocarbons, carbon monoxide, and particulate emissions, and possibly lower mutagenic activity than the baseline fuel. The use of particulate traps and the low-sulfur fuel both caused a decrease in fuel economy for the test vehicles.

I. INTRODUCTION

Exhaust particulate matter emitted from diesel-powered vehicles is respirable, contains mutagenic and carcinogenic substances, and contributes to visibility degradation in the atmosphere. As a result, federal and state agencies have adopted particulate exhaust emission standards. To meet these standards, manufacturers have developed particulate traps to control the exhaust particulate matter. While these traps have demonstrated control of particulate matter, little information has been available concerning their impact on currently unregulated emissions. This program attempts to quantify the emissions from two different types of production trap-equipped light-duty vehicles.

A. Project Objective

The objective of this program was to develop and publish the most comprehensive body of data on emission effects of production light-duty diesel catalytic trap and additive-activated trap systems possible within existing time and budget constraints. The specific objectives included procurement and complete emission characterization of one Mercedes-Benz diesel automobile equipped with catalytic trap system and one Volkswagen diesel automobile equipped with an additive-assisted trap system. Another objective was to provide particulate and vapor phase samples for genotoxicity testing under another contract.

B. Test Vehicles and Fuels

The two test vehicles evaluated in this program were a 1986 Mercedes-Benz 300 SDL and a prototype Volkswagen Jetta. The Mercedes was equipped with a particulate trap oxidizer located between the exhaust manifold and the turbocharger. The Volkswagen came equipped with an underbody particulate trap and a system to inject an organometallic iron additive into the fuel prior to combustion. Two test fuels were also used in the study. The baseline fuel was a commercial low-sulfur No. 2 diesel fuel with an aromatic content of 36.2 percent. The second fuel was also a low-sulfur fuel, but with an aromatic content of 16.2 percent.

C. Test Procedures

The test vehicles were evaluated on a chassis dynamometer both with and without particulate traps, over test sequences consisting of the Federal Test Procedure, the Highway Fuel Economy Test, and the New York City Cycle. Additional testing included the evaluation of emissions during malfunction operation (failed or worn injectors and retarded injection timing), trap regeneration (burning of stored particulates), and with a heavily loaded particulate trap.

D. Emissions Measurement Procedures

The compounds or groups of compounds evaluated, along with the sampling methods used, were as follows:

Sampling Methods	Compounds Evaluated
Bags	Carbon monoxide, carbon dioxide, oxides of nitrogen, 1,3-butadiene
Continuous	Hydrocarbons
Impingers	Aldehydes and ketones, water soluble trace metals, methanol soluble trace metals
Filters	Particulates, sulfate, metals and other elements, organic soluble fraction of particulates, semivolatile organics, volatile organics, Ames bioassay
Traps	Vapor phase semivolatiles, vapor phase volatiles

The analytical procedures used to evaluate the emissions are discussed in a following section of this report.

II. GENERAL EQUIPMENT, INSTRUMENTS, PREPARATIONS AND PROCEDURES

This section describes the test vehicles, the test fuels, the facilities, and the general instrumentation and procedures utilized in this project. The overall sampling systems for the unregulated emissions are also discussed.

A. Test Vehicles

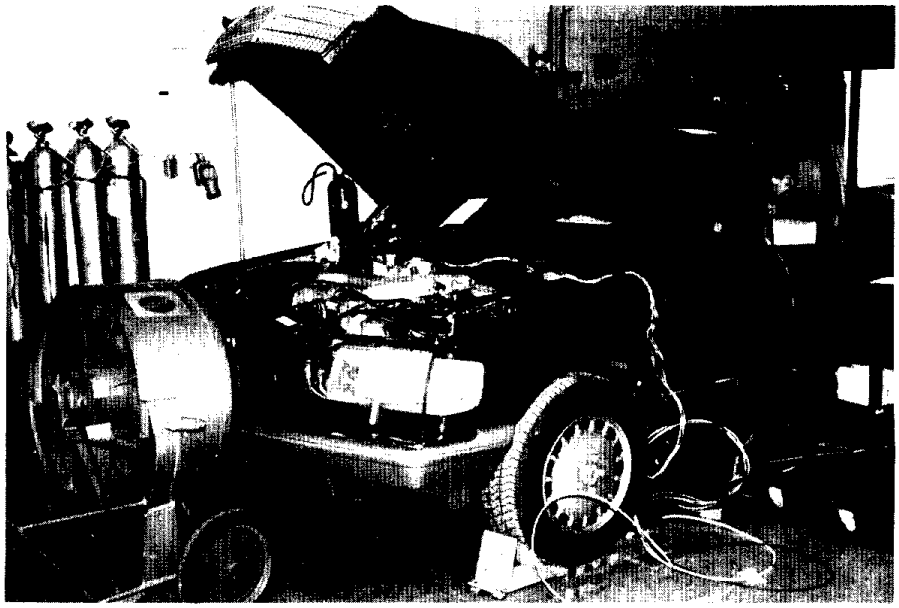
Originally the test vehicles for the program were to be leased commercially. The California air Resources Board had requested that the Mercedes trap-equipped test vehicle have from 10,000 to 50,000 miles on the odometer. At the time the vehicle procurement was underway, available trap-equipped Mercedes vehicles had less than 4,000 miles on their odometers. Trap-equipped Volkswagen vehicles were still under development and were not commercially available. Due to the unavailability of the trap-equipped Volkswagen and insufficient mileage on available Mercedes-Benz vehicles, the two test vehicles used in the program were provided by the manufacturers, Mercedes-Benz and Volkswagen. The two test vehicles are described in Table 1 and are shown in Figure 1.

The Mercedes Benz 300 SDL was provided by Mercedes-Benz of North America. Mr. Bernd Herrbrick of Mercedes-Benz delivered the vehicle to Southwest Research Institute on November 17, 1986. The test vehicle had originated from a Mercedes-Benz fleet in California and had 11,000 miles on the odometer. The vehicle came equipped with a particulate trap oxidizer located between the exhaust manifold and the turbocharger. The trap was of monolithic construction and housed

TABLE 1. VEHICLES EVALUATED

	Mercedes-Benz 300 SDL	Prototype Volkswagen Jetta
Model Year	1986	Prototype
Body Type	4-door	4-door
Transmission Type	A-4	M-5
Cylinders	I 6	I 4
Displacement, L	3.0	1.6
Odometer Miles	11,040	12,400
Engine Family	GMB3.0D9KC17	--
ID Number	WDBCB25D2GA241866	WVWGG0168GW729819
Chassis Dynamometer		
Inertia Setting, lbs	4250	2625
Power Setting, Horsepower	10.6	7.0

in a steel cylinder. The surface area of the monolithic structure was electroplated with a silver alloy. The catalyzed surface and the location of the trap near the exhaust manifold provided conditions suitable for trap regeneration (burning of collected particulates). The equivalent test weight, 4,250 lbs, and actual road load setting of 10.6 hp for the chassis dynamometer testing were provided by Ms. Yolanda Garza, Air Resources Engineer, El Monte California.



1986 Mercedes 300 SDL

Prototype Volkswagen Jetta

FIGURE 1. TEST VEHICLES

The trap-equipped prototype Volkswagen Jetta was provided by Volkswagen AG through Volkswagen of America. The vehicle originated from a test fleet in Germany and was flown from Germany to San Antonio for testing in this program. Mr. Wolfgang Groth and Mr. K. R. Parker of Volkswagen of America, and Mr. Werner Engeler of Volkswagen AG visited Southwest Research Institute on August 20, 1987 to officially present the vehicle to SwRI for testing. The vehicle came equipped with an underbody particulate trap and a system to inject an organometallic iron additive into the fuel prior to combustion. The organometallic iron additive was used to provide more suitable conditions for the burning of collected particulates in the trap. The equivalent test weight, 2,625 lbs, and actual road load setting, 7.0 hp, for the chassis dynamometer testing were once again obtained through Ms. Yolanda Garza of the Air Resources Board.

B. Test Fuels and Oil

The properties of the two test fuels that were used in this study are given in Table 2. The Baseline fuel, EM-619-F, was a commercial low-sulfur No. 2 diesel fuel with an aromatic content of 36.2 percent. The second fuel, EM-752-F, was a low-aromatic fuel (16.2 percent) and was provided by Dr. Mike Ingham of Chevron. This second fuel was also a low-sulfur fuel. The engine oil used in both vehicles was Quaker State SAE 30.

The fuel, EM-619-F, and oil, Quaker State SAE 30, were analyzed by x-ray fluorescence for metals and other elements. A total of 17 elements were examined in the analyses. Of these 17, only zinc (0.16%), calcium (0.16%), and sulfur (0.4%) were detected in the oil and none were detected in the fuel. Table 3 lists the elements and their fuel/oil concentration. If the elements were not detected, a less than (<) sign precedes the detection limit.

C. Dynamometer and CVS System

A Clayton Model ECE-50 passenger car dynamometer with a direct drive variable inertia system was utilized for all testing. This inertia system simulates equivalent weight of vehicles from 1,000 lbs to 8,875 lbs in 125 lbs increments. A nominal 18 inch diameter by 16 foot length dilution tunnel was used in conjunction with a constant volume sampler (CVS). The CVS used for these evaluations was SwRI CVS Number 17. This unit has a nominal capacity of 11.8 m^3/min. A cooling fan of 5,000 CFM capacity was used in front of the test vehicles during all tests. Vehicle hoods were maintained fully open during the tests and were closed during the soak periods. Partial views of the dynamometer, dilution tunnel, and the intake of the CVS can be seen in Figure 2. Both the dynamometer and the CVS were calibrated, maintained, and operated in accordance with the manufacturer's instructions and the appropriate sections of the code of Federal Regulations applicable to light-duty vehicles.(1)*

D. Exhaust Sampling and Analysis

A schematic of the exhaust and sampling system is shown in Figure 3. The primary features of this system are the sampling probes and the multiple 20 x 20

*Numbers in parentheses designate references at the end of the report.

TABLE 2. TEST FUEL PROPERTIES

	Baseline Fuel EM-619-F	Low Aromatic Fuel EM-752-F
Density	0.8473	0.8193
API Gravity, 60°F	35.5	41.2
Sulfur, % by Weight	0.05	0.05
Cetane No.	45[a]	55[b]
Aromatics, FIA%	36.2	16.2
Olefins, FIA %	--	--
Saturates, FIA %	63.8	83.8
Distillation, °F D-86		
IBP	339	434
10%	394	459
20%	421	472
30%	445	486
40%	467	500
50%	487	514
60%	509	528
70%	531	552
80%	560	570
90%	598	600
EP	650	651
Carbon, wt %	86.53	85.72
Hydrogen, wt %	13.06	14.00

[a]Calculated.
[b]Provided by Chevron.

TABLE 3. X-RAY FLUORESCENCE ANALYSES OF TEST FUEL AND OIL

Element	Concentration in ppm, except as noted	
	Fuel EM-619-F	Quaker State SAE 30
Aluminum	<250	<250
Silicon	<250	<250
Magnesium	<5000	<5000
Titanium	<20	<20
Chromium	<10	<10
Manganese	<5	<5
Nickel	<5	<5
Cobalt	<5	<5
Tin	<50	<50
Silver	<20	<20
Lead	<60	<60
Copper	<10	<10
Zinc	<10	0.16%
Calcium	<20	0.16%
Sulfur	<0.05%	0.4%
Iron	<5	<5
Arsenic	<50	<50

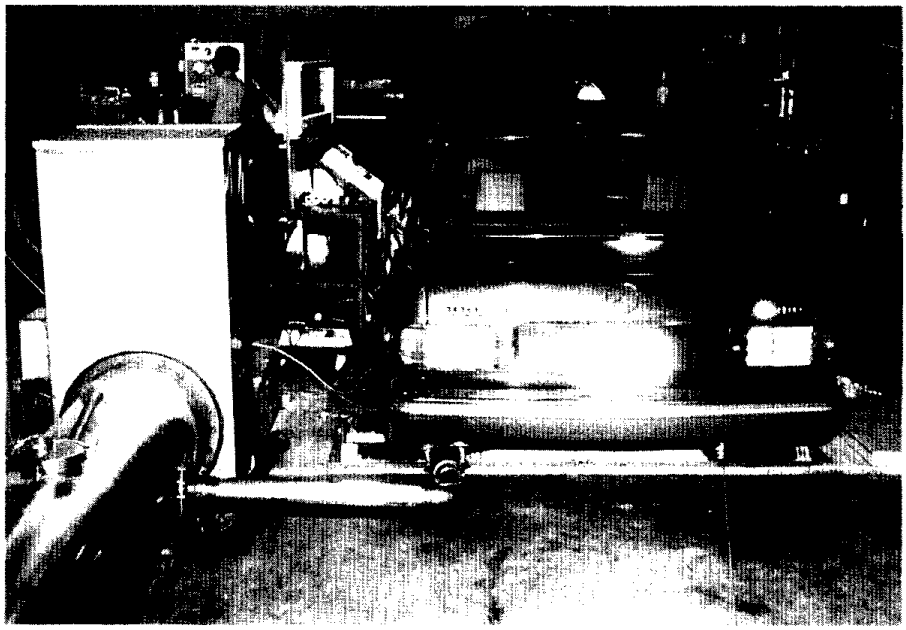


FIGURE 2. PARTIAL VIEWS OF THE DYNAMOMETER, DILUTION TUNNEL, AND THE INTAKE TO THE CVS

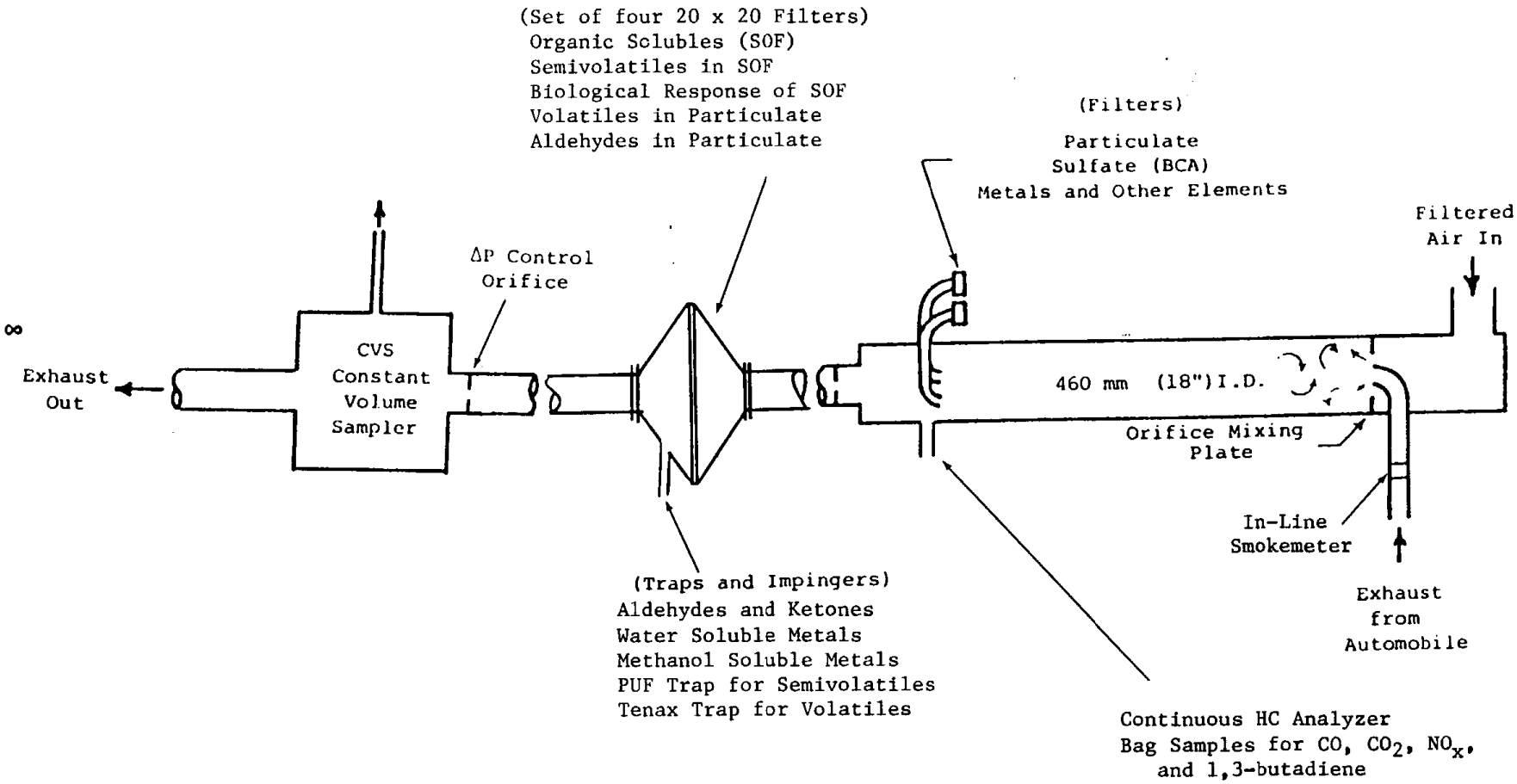


FIGURE 3. EMISSIONS SAMPLING SYSTEM

inch filter system required to collect unregulated emission samples. This complexity is illustrated in the views of the system shown in Figure 4. The regulated gaseous and particulate systems are discussed in more detail in the following section. To obtain multiple particulate samples for Soxhlet extraction and subsequent analyses, a set of four 20 x 20 inch filters were placed between the dilution tunnel and the CVS. These four filters collected all the particulate generated by the test vehicles during each test cycle. The filters, made of Teflon-coated glass fiber (Pallflex), each collected approximately one fourth of the total particulate (24 to 26 percent each) for a test cycle. Smoke opacity of undiluted exhaust was also measured and recorded continuously using a modified EPA heavy-duty certification type smokemeter mounted in-line. This meter has a 3.73 inch optical path length.

E. Instrumentation for Regulated Emissions

Bagged samples of the dilute exhaust were evaluated for carbon dioxide, carbon monoxide, and oxides of nitrogen using SwRI Bag Carts No. 1 and No. 2. these carts were designed, calibrated and operated in accordance with the appropriate sections of the code of Federal Regulations applicable to light-duty vehicles. Hydrocarbon analysis of the gaseous sample was continuous using a heated flame ionization detector (HFID). Electronic signal integration used with the HFID provided dilute hydrocarbon concentrations for each test run. Both the bagged sample and the continuous hydrocarbon sample were taken directly from the diluted exhaust stream through probes in the dilution tunnel (heated probe for hydrocarbons). Figure 5 shows the continuous HC analyzer.

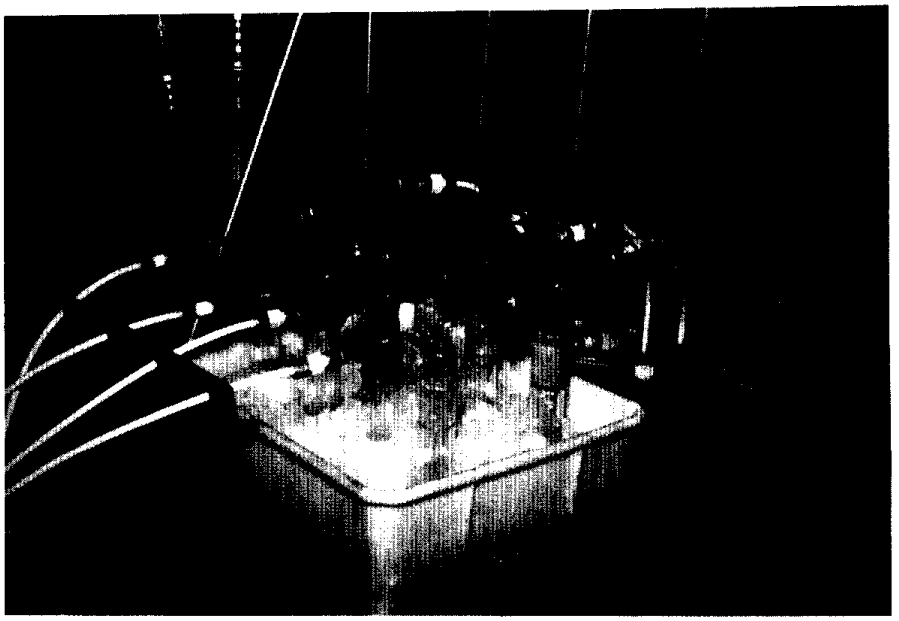
A particulate sampling system, connected to the dilution tunnel and meeting the basic design requirements of the Federal Register, was used to collect particulate on 47 mm fluorocarbon-coated glass fiber filters. Along with the usual filter holders, pumps, rotameters, temperature sensor, and dry gas meters, the system also employed an electropneumatically-controlled valve that enables remote and fast switching between two sets of paired primary test and back-up filters. In this manner, the particulate in the different cycles of the test sequence was sampled easily and separately, especially at the point of rapid transitions between the cold 505 and stabilized phases of the FTP. This sampling system is shown in Figure 6.

The commercially available 47 mm Pallflex filters (designated type T60A20) used in this study for particulate collection are made of glass fiber coated with fluorocarbon. The filters were weighed before and after use on a microbalance of one μg sensitivity. Before weighing, the filters were conditioned in a temperature- and humidity-controlled chamber which also houses the microbalance. The controlled air flow, temperature, and humidity provided an absolute humidity of 75 $\pm$ 5 grains water per pound of dry air in the chamber.

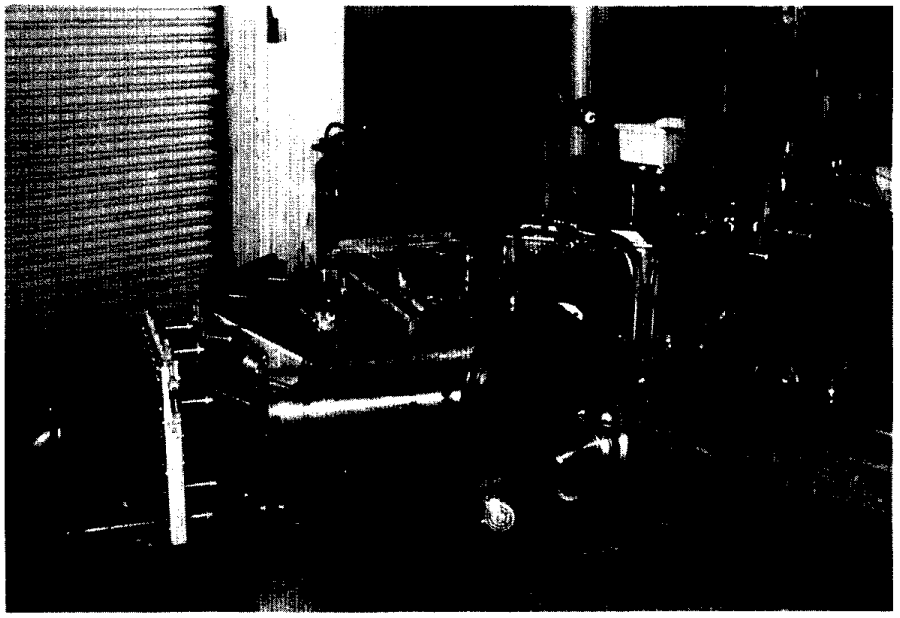
F. Emissions Test Procedures

The emissions test procedures utilized in this project are defined as follows:

FTP - Federal Test procedure [1] (uses the Urban Dynamometer Driving Schedule).
HFET - Highway Fuel Economy Driving Schedule.[2]
NYCC - New York City Cycle.[3]

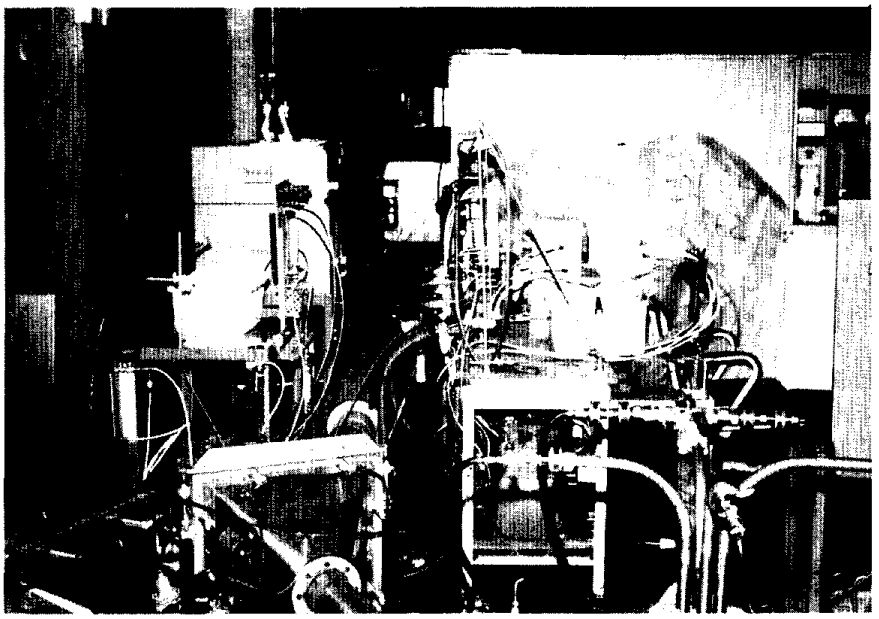


Impinger Sampling

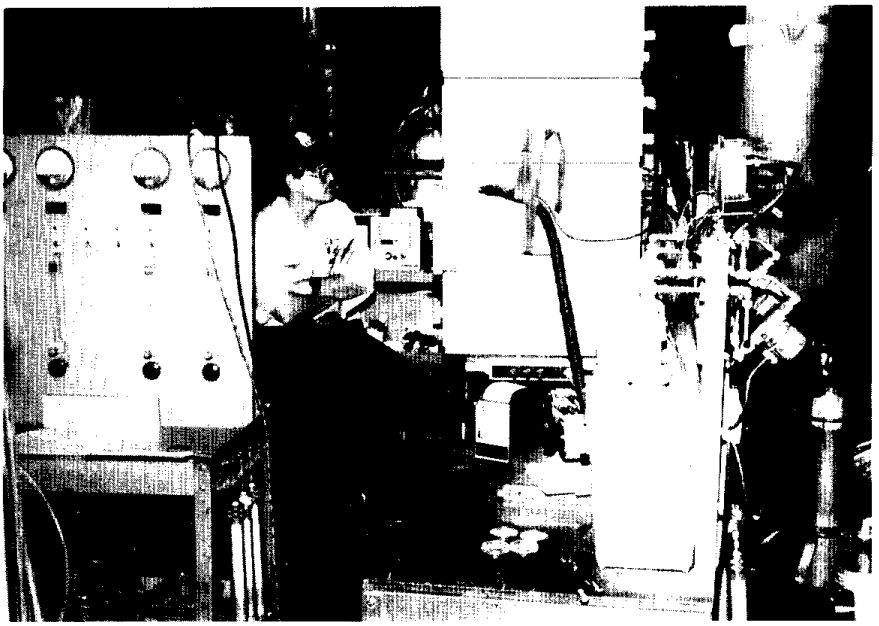


Set of Four 20 X 20 Filters in Series with
Tunnel and CVS

FIGURE 4 . VIEWS OF THE EMISSIONS SAMPLING SYSTEM



Sampling Equipment



Sampling Equipment

FIGURE 4 (CONT'D). VIEWS OF THE EMISSIONS SAMPLING SYSTEM

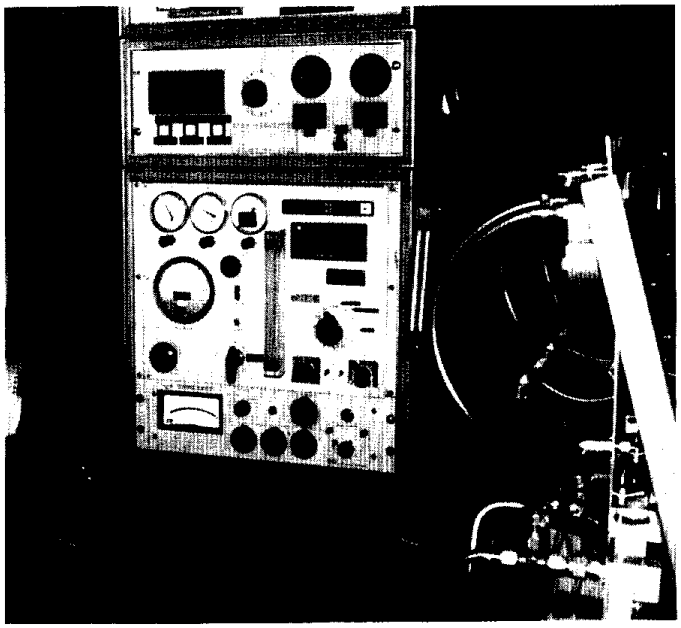


FIGURE 5. CONTINUOUS HC ANALYZER

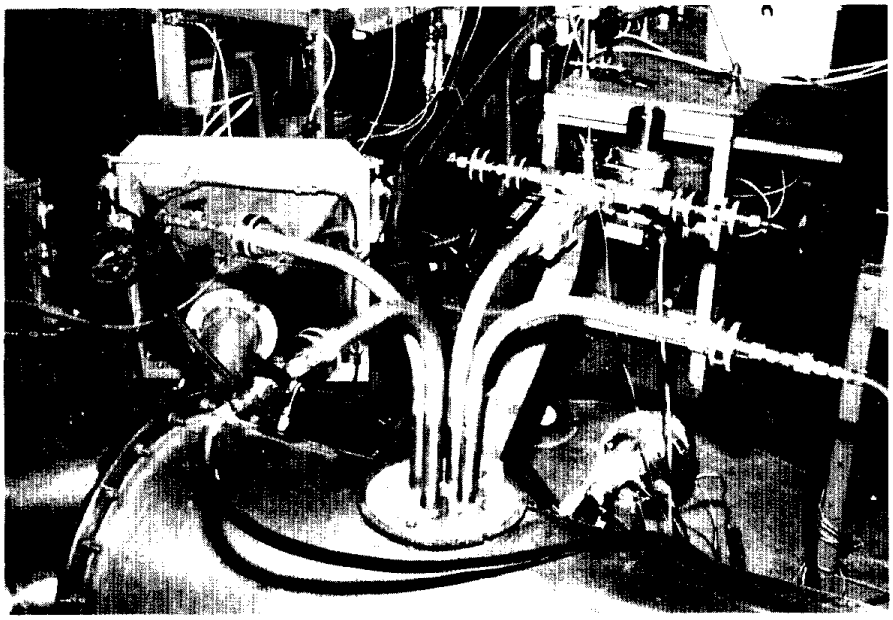


FIGURE 6. 47 MM FILTER HOLDERS WITH SWITCHING SOLENOID

The sequence of testing for each series of tests including the soak periods is given in Table 4. Each of the three emissions test procedures in this project (FTP, HFET, and NYCC) utilized bagged samples for determination of carbon monoxide and oxides of nitrogen as well as fuel consumption.

The HFET and NYCC are hot-start, single-segment driving cycles. The FTP, however, involved cold-start and hot-start, multi-cycle with multi-segment operation. The FTP, HFET, and NYCC schedules are summarized in Table 5 and illustrated in Figure 7. In addition, in this project, a four-bag FTP was utilized for the unregulated emissions; rather than the three-bag FTP specified in the Federal Test Procedure. Therefore, before proceeding, it is important to clarify the meaning of FTP as used in this program:

FTP- The FTP uses the Urban Dynamometer Driving Schedule (UDDS) which is 1372 seconds in duration. The UDDS, in turn, is divided into two segments; the first having 505 seconds and the second having 867 seconds. The FTP consists of a cold-start 505 and a stabilized 867 followed by a ten minute soak and then a hot-start 505. In this project, the hot-start 505 was followed by another 867 segment. The four-cycle FTP is therefore identified as follows:

	Four-Cycle FTP			
	Cold	UDDS	Hot	UDDS
Duration, seconds	505	867	505	867
Regulated Emissions, 3-bag	X	X	X	
Regulated Emissions, 4-bag	X	X	X	X
Unregulated Emissions:				
Impinger	--- X ---		--- X ---	
47 mm filter, sulfate	--- X ---		--- X ---	
47 mm filter, metals	--- X ---		--- X ---	
20 x 20 inch filters	--- X ---		--- X ---	
Tenax Trap	--- X ---		--- X ---	
PUF Trap (initial samples)	--- X ---		--- X ---	
PUF Trap	--- X ---		--- X ---	

NOTE: X designates a sample taken

TABLE 4. LABORATORY TEST SEQUENCE

1. Prepare vehicle with proper test equipment and fuel.
2. Condition vehicle with 50 miles of transient dynamometer operation (alternating UDDS and HFET cycles).
3. Precondition vehicle for emissions testing with two UDDS cycles, an HFET, and an NYCC.
4. Soak vehicle 12 to 20 hours.
5. Run test to include:
   - Cold-start UDDS (Cold 505 + stabilized) - Sample all regulated and unregulated emissions.
   - 10-minute soak
   - Hot-start UDDS (hot 505 + stabilized) - Sample all regulated and unregulated emissions.
   - HFET - Sample all regulated and unregulated emissions.
   - 10-minute soak
   - NYCC
6. Repeat steps 4 and 5.
7. Prepare vehicle for next series of tests.

TABLE 5. SUMMARY OF DRIVING SCHEDULE PARAMETERS

	Duration, Seconds	Distance, Miles	Average Speed km/hr	Average Speed mph
FTP:				
505	505	3.60	41.3	25.7
867	867	3.85	25.8	16.2
UDDS	1372	7.45	31.4	19.5
HFET	765	10.25	77.6	48.2
NYCC	599	1.19	11.5	7.1

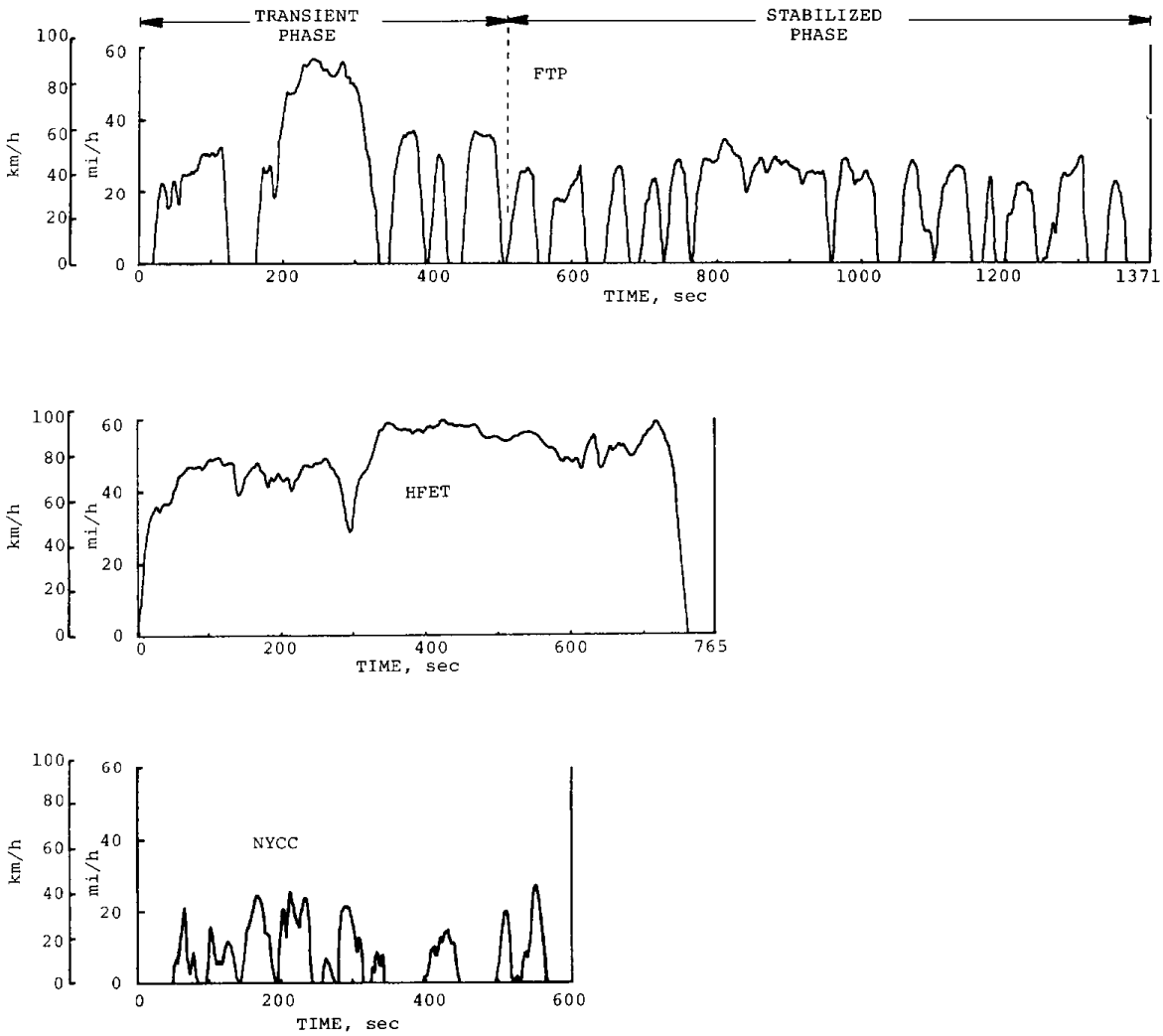


FIGURE 7. FTP, HFET, AND NYCC DRIVING CYCLES VS TIME TRACES

A composite value in mass per distance for the three-cycle, three-sample FTP regulated emissions is calculated using the following formula:

$$\frac{\text{MASS}}{\text{DISTANCE}} = \frac{0.43 \times (\text{MASS 1} + \text{MASS 2})}{(\text{DIST. 1} + \text{DIST. 2})} + \frac{0.57 \times (\text{MASS 3} + \text{MASS 2})}{(\text{DIST. 3} + \text{DIST. 2})}$$

Assuming Distance 3 is equal to Distance 1, this equation can be reduced to:

$$\text{3-FTP M/D} = \frac{0.43 \times (\text{M1} + \text{M2}) + 0.57 \times (\text{M3} + \text{M2})}{\text{D1} + \text{D2}}$$

For the four cycle, two sample FTP composite values determined in this project, the following formula was used:

$$\frac{\text{MASS}}{\text{DISTANCE}} = \frac{0.43 \times \text{M}(1 + 2)}{(\text{D1} + \text{D2})} + \frac{0.57 \times \text{M}(3 + 4)}{(\text{D3} + \text{D4})}$$

Assuming Distance 3 is equal to Distance 1 and Distance 4 is equal to Distance 2, then this equation can be reduced to:

$$\text{4-FTP M/D} = \frac{0.43 \times \text{M}(1 + 2) + 0.57 \times \text{M}(3 + 4)}{\text{D1} + \text{D2}}$$

Therefore, with the assumption that the changes in distance traveled are negligible, the composite results with the four-cycle FTP relative to results with the three-cycle FTP will differ only as the mass emissions emitted during Cycle 4 differ from those emitted during Cycle 2.

For a single sample 4-Bag FTP (PUF trap for semivolatiles) obtained in this study, a composite value (not weighted) was obtained using the following formula:

$$\text{4-Bag FTP Composite} = \frac{\text{Total Mass}}{\text{Total Distance Driven}}$$

III. ANALYTICAL PROCEDURES FOR UNREGULATED EMISSIONS

The analytical procedures used to measure the unregulated emissions are summarized in this section. Detailed descriptions of some of the procedures including sulfate, aldehydes and ketones, and 1,3-butadiene along with discussions of their development, validation, and qualification are available in the following EPA and Coordinating Research Council Reports: "Analytical Procedures for Characterizing Unregulated Emissions from Vehicles Using Middle-Distillate Fuels," EPA Report EPA-600/2-80-068[4]; "Characterization of Exhaust Emissions from Alcohol-Fueled Vehicles", CRC Final Report for Project CAPE-30-81[5]; and "Butadiene Measurement Technology", EPA Report EPA 460/3-88-005.[6]

The unregulated emissions evaluated in this project, along with the methods of sampling and the procedures used in the analysis, are listed in Table 6. The analytical procedures involved in this project are briefly described as follows:

Aldehydes and Ketones - The aldehydes and ketones that are included in this analysis are: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, isobutyraldehyde/methylethylketone (not resolved from each other under normal operating conditions and so reported together), benzaldehyde, and hexanaldehyde. The measurement of the aldehydes and ketones in exhaust is accomplished by bubbling the exhaust through glass impingers containing an acetonitrile solution of 2,4-dinitrophenylhydrazine (DNPH) and perchloric acid. The exhaust sample is collected continuously during the test cycle. For analysis, a portion of the acetonitrile solution is injected into a liquid chromatograph equipped with a UV detector. External standards of the aldehyde and ketone DNPH derivatives are used to quantify the results. Detection limits for this procedures are on the order of 0.005 ppm aldehyde and ketone in dilute exhaust.

A limited number of particulate samples (collected on 20 x 20 Pallflex filters) were analyzed for aldehydes and ketones by washing a particulate laden filter with an acetonitrile solution of 2,4-dinitrophenylhydrazine (DNPH) and perchloric acid. A portion of the resulting acetonitrile solution was injected into the liquid chromatograph for analysis.

Sulfate - Automotive exhaust is vented into a dilution tunnel where it is mixed with a flowing stream of filtered room air. In the tunnel, the SO_3 reacts rapidly with water in the exhaust to form sulfuric acid aerosols. The aerosols grow to a filterable size range within the tunnel and are collected on a fluorocarbon membrane filter. Particulate sulfate salts are also collected on the filter.

Sulfuric acid collected on the filter is then converted to ammonium sulfate by exposure to ammonia vapor. The soluble sulfates are leached from the filter with a measured volume of an isopropyl alcohol - water solution (60% IPA). A fixed volume of the sample extract is injected into a high pressure liquid chromatograph (HPLC) and pumped through a column of strong cation exchange resin in Ag^+ form to scrub out the halides (Cl^-, Br^-) and then through a column of strong cation exchange resin in H^+ form to scrub out the cations and convert the sulfate to sulfuric acid. Passage through a reactor column of barium chloranilate crystals precipitates out barium sulfate and releases the highly UV absorbing chloranilate ions. The amount of

TABLE 6. SAMPLING AND ANALYSIS METHODOLOGY FOR UNREGULATED EMISSIONS

Compound(s)	Sampling	Method of Analysis
Aldehydes & Ketones	Impinger and/or 20 x 20 inch Pallflex Filter	Dinitrophenylhydrazone derivative. Liquid chromatograph with ultraviolet detector.
Sulfate	Fluoropore Filter (47 mm)	Barium chloranilate derivative (BCA). Liquid chromatograph with ultraviolet detector.
Organic Solubles	20 x 20 inch Pallflex Filter	Soxhlet extraction with methylene chloride, dry, weigh.
1,3-Butadiene	Bag	Gas chromatograph with flame ionization detector.
Metals and other element	Fluoropore Filter (47 mm)	Weighed using microbalance. Spectral x-ray analysis at EPA-RTP.
	Impinger (toluene/methanol)	ICP-6000 atomic emission spectrometer.
Beryllium	Fluoropore Filter (47 mm)	Acid digestion with nitric and sulfuric acids. AAS-graphite furnace.
Iron	Impingers (methanol/water)	Concentration by evaporation. AAS-graphite furnace.
Volatile Organics	Tenax Trap	Thermal desorption. Gas chromatograph with mass spectrometer.
Volatile Organics	20 x 20 inch Pallflex Filter	Thermal desorption. Gas chromatograph with mass spectrometer.
Semivolatile organics	PUF Trap	Soxhlet extraction with methylene chloride. Concentration by evaporation. Gas chromatograph with mass spectrometer.
Semivolatile Organics	20 x 20 inch Pallflex Filters	Soxhlet extraction with methylene chloride. Concentration by evaporation. Gas chromatograph with mass spectrometer.
Biological Response	20 x 20 inch	Shipment of filters to University of California, Irvine. Extraction with methylene chloride. Mutagenesis testing of extract with tester strains TA98 and TA100.
Smoke	Optical	EPA Smokemeter (continuous)

chloranilate ions released is proportional to the sulfate in the sample and is measured by a sensitive liquid chromatograph UV detector at 310-313 nanometers. All the reactions and measurements take place in a flowing stream of 60% IPA. The scrubber and reactor columns also function as efficient filter media for any solid reaction products formed during passage of the sample through the column system.

Organic Solubles - Pallflex filters (20 x 20 inch) were used to collect particulate samples from dilute exhaust for each driving cycle or driving cycle segment. These particulate-loaded filters were then extracted in a Soxhlet apparatus with methylene chloride as a solvent. The extracts were filtered, concentrated under vacuum, transferred to preweighed glass vials, and weighed. The percent organic solubles for each filter was determined by dividing the extract weight by the weight of particulate collected on the filter and multiplying the resulting fraction by 100.

1,3-Butadiene - The analysis of 1,3-butadiene is accomplished by collecting dilute exhaust in Tedlar bags and analyzing the samples with a gas chromatograph equipped with a 9 ft x 1/8 inch stainless steel column containing 80/100 Carbopack C with 0.19% picric acid and a flame ionization detector (FID). In addition to 1,3-butadiene, the procedure provides separation and relative exhaust concentrations for six other C_4 hydrocarbons including: isobutane, butane, 1-butene, isobutylene, cis-2-butene, and trans-2-butene. External 1,3-butadiene standards in zero air are used to quantify the results. Detection limits for the procedure are on the order of 0.03 ppmC in dilute exhaust for 1,3-butadiene.

Metals and Other Elements (Filter) - The metals are collected as particulate on a 47 mm Fluoropore filter, which is then sent to the EPA Research Triangle Park (RTP) laboratory for analysis by x-ray fluorescence spectroscopy. The diluted exhaust sample is taken from within the dilution tunnel. Weight gain on the filter is determined by weighing the filter on a microbalance before and after sampling. Emission rates for a total of 32 metals and other elements are determined with the analysis.

Metals and Other Elements (Impinger) - During baseline testing of the Mercedes, CVS-diluted exhaust gas was pulled through impingers containing a hydrocarbon solvent (toluene for the "with trap" tests and methanol for the "without trap" tests). The resulting samples were concentrated by evaporation and analyzed for selected metals (beryllium, cadmium, chromium, manganese, nickel, lead, and tin) using a Perkin Elmer ICP-6000 inductively coupled argon plasma atomic emission spectrometer.

Beryllium - Beryllium is collected as particulate on 47 mm Fluoropore filters. The filters are analyzed using NIOSH method 7102, which utilizes acid digestion of the filters with nitric/sulfuric acid and analysis by AAS-graphite furnace. Detection limits for the instrument are on the order of 0.5 $\mu g/L$ of digested solution.

Iron (Impingers) - Filtered dilute exhaust is bubbled through either methanol or water solutions for the collection of possible gas phase iron organometallic compounds. The solutions are concentrated by evaporation and analyzed by AAS - graphite furnace.

Volatile Organics (Tenax Trap) - Gas phase volatile organics are collected by passing dilute filtered exhaust through Tenax tubes (5 inch long x 1/4 inch diameter) at a flow rate of 200 mL per minute. The volatile organics are thermally desorbed (180°) from the trap directly into a GC/MS system for analysis. The GC/MS system consists of a Finnigan 9500 gas chromatograph interfaced to a Finnigan 3000 electron impact mass spectrometer with mass range of 4 to 800. This instrument is also equipped with a Grob-type capillary inlet system, a jet separator, and a Tekmar 4000 purge and trap unit for the volatile organic analysis. The data system is equipped with a Nova 3/12 computer, a 70-megabyte Winchester disk drive, a Priam 20-megabyte cartridge-type streaming tape drive, and a Versatec 800 printer. The GC analytical column is a 6 ft by 2 mm glass column packed with 1% SP1000 on 60/80 Carbopack. The flow rate for the carrier gas, helium, is 20 mL per minute. Volatile compounds analyzed in the program included: benzene, toluene, total xylenes, 1,3-butadiene, chloroform, 1,4-dioxane, and phosgene.

Volatile Organics (20 x 20 Inch Filters) - Particulate-associated volatile organics are collected as particulate on 20 x 20 inch Pallflex filters. A 4 x 4 inch square is cut from the appropriate 20 x 20 inch Pallflex filter and heated at 40°C under a stream of helium. The resulting desorbed materials are collected in an 8 inch long x 1/4 inch diameter Tenax tube for subsequent thermal desorption (180°C) into a GC/MS for analysis. The GC/MS system is the same unit that is used for the gas phase volatile organic analyses.

Semivolatile Organics (PUF Traps) - Gas phase semivolatile organics are collected by passing filtered dilute exhaust gas through glass traps containng polyurethane foam. These traps are Soxhlet extracted (16 hours) with methylene chloride; and the resulting solution is concentrated to either 1 mL or to 200 μL (for improved detection limits). One μL of this solution is then injected into a Finnigan 9611 gas chromatograph interfaced to a Finnigan 4610B electron impact/chemical ionization quadrapole mass spectrometer with mass range of 4 to 1800. The instrument is also equipped with a pulsed positive ion/negative ion chemical ionization device (PPINICI) and a Grob-type capillary inlet system. The fused silica capillary column is connected directly to the mass spectrometer. The GC carrier, helium, flows at 1 mL/min. The temperature program includes isothermal operation at 40°C for two minutes followed by a temperature program to 295°C at a rate of 10°C/minute. Semivolatiles included in the analyses are polynuclear aromatics, nitrated polynuclear aromatics, phenols, dialkylnitrosamines, and nitrobenzene.

Semivolatile Organics (20 x 20 Inch Filters) - Particulate-associated semivolatile organics are collected as particulate on 20 x 20 inch Pallflex filters. Filters are extracted in a Soxhlet apparatus with a methylene chloride solvent. The resulting extract is concentrated to 500 μL to 1,000 mL (dependent on concentration), and 1 μL of the extract is injected into a GC/MS for analysis. This GC/MS system is the same unit that was used for the gas phase semivolatile organic analyses.

Biological Response - Samples are collected as particulate on 20 x 20 inch Pallflex filters. After collection the filters are carefully folded, weighed, sealed in Tedlar bags under a nitrogen atmosphere, and stored in the dark at -20°C until transfer to the University of California, Irvine. The samples are shipped on dry ice by air freight to the University of California at Irvine for subsequent methylene

chloride extraction and mutagenesis testing. Two tester strains; TA98 and TA100, are used in the testing, both in the presence and absence of metabolic activation with aroclor-induced Sprague Dawley rat liver homogenate(S9).

Smoke - Exhaust smoke was measured using an in-line optical light-extinction smokemeter of the type specified in Federal Regulations for heavy-duty diesel smoke certification. The control/readout unit for the smokemeter was mounted remote from the vehicle under test, and continuous recordings of smoke opacity were recorded for the FTP, HFET and NYCC tests.

IV. VEHICLE TESTING

Regulated and unregulated exhaust emissions were evaluated for a 1986 Mercedes 300 SDL and a prototype Volkswagen Jetta on two test fuels, with and without a particulate trap in place, and with two engine malfunctions (failed or worn injectors, and retarded timing). Three test cycles were used in the evaluations; the Federal Test Procedure (FTP), the Highway Fuel Economy Test (HFET), and the New York City Cycle (NYCC). The HFET test was utilized in conducting additional tests to determine the effect of particulate trap regeneration (burning of stored particulate) on emissions. A limited number of NYCC tests were also conducted to determine the effect of a heavily loaded trap on emissions. The two test fuels consisted of a baseline fuel with an aromatic content of 36.2 percent, and a low-aromatic fuel with an aromatic content of 16.2 percent. The test work conducted on the two test vehicles is summarized in Tables 7 and 8 for the Mercedes and Volkswagen, respectively. The test numbers listed in the two tables are used to identify emission results throughout the remainder of the report. A discussion of the tests listed in Tables 7 and 8 follows.

A. Mercedes Testing

Emissions tests conducted on the Mercedes 300 SDL vehicle are described in this section. Computer printouts of the regulated emission results for these tests can be found in Appendix B. Unregulated emissions data for the tests are summarized in Appendices D, F, H, J, L, M, O, and P. These emission results will be discussed in more detail in a following section of the report.

1. Initial Vehicle Testing and Definition of Regeneration Cycle

Upon receipt of the Mercedes test vehicle, a preliminary 3-bag FTP test (regulated emissions only) was conducted to establish relative emission levels. The regulated emission results (total hydrocarbons, 0.10 g/mi; carbon monoxide, 2.86 g/mi; oxides of nitrogen, 0.76 g/mi; and particulates, 0.080 g/mi) appeared acceptable and the program was continued. To determine the relative condition of the particulate trap on the vehicle, the engine backpressure was monitored at 4,000 rpm with the vehicle in "park" and found to be 28.5 psi (1.97 bar). The Service Manual for the 300 SDL lists a nominal 2.0 bar for the backpressure. From these values it appeared that the trap was in good operating condition and typical of traps in service.

To load the particulate trap for investigation of regeneration conditions, the 300 SDL was operated on the dynamometer over replicate NYCC cycles. The NYCC is 599 seconds in duration and has an average speed of 7.1 mph. The highest speed during the cycle in on the order of 28 mph. During the series of NYCC cycles, the maximum trap inlet temperatures for the cycle ranged from 430 to 490°C, depending on the trap loading. Similarly, the maximum trap outlet temperatures did not exceed 285 to 330°C (depending on trap loading). Trap loadings which gave engine backpressures of less than 10 psi (275 in. water) at 30 mph resulted only in "slow burn" regenerations when the vehicle was accelerated to 55 mph. A decrease in engine backpressure and pressure drop across the trap were noted when the trap inlet and outlet temperatures reached approximately 490°C. Despite the drop in engine backpressure, the inlet and outlet temperatures remained almost equal. At a

TABLE 7. MERCEDES TESTING

Test Condition	Trap Installed	Test Fuel Aromatics	Driving Cycles/with Emissions			Test Number
			FTP	HFET	NYCC	
Definition of Regeneration Cycle	Yes	Baseline	--	XX[a]	XX[a]	--
Initial Baseline	Yes	Baseline	2	2	2	1-1, 1-2, 1-3 (FTP)
	No	Baseline	2	2	2	2-1, 2-2
Regeneration[b]	Yes	Baseline	--	2	--	R-1, R-2
Heavily Loaded Trap	Yes	Baseline	--	--	1	L-1
Baseline 2[c]	No	Baseline	1	--	--	2-3
Baseline (Low Aromatic)	No	Low	2	--	--	4-1, 4-2
Re-establish Baseline	Yes	Baseline	2	--	--	11-1, 11-2
Baseline (Low Aromatic)	Yes	Low	2	--	--	13-1, 13-2
Regeneration	Yes	Low	--	3	--	R-1, R-2, R-3
Baseline 2[c]	Yes	Baseline	1	--	--	11-3
Worn Injectors[d]	Yes	Baseline	1	1	1	15-1
Baseline 3[c]	Yes	Baseline	1	--	--	11-4
	No	Baseline	1	--	--	2-4
Retarded Timing	Yes	Baseline	2	2	2	17-1, 17-2
Malfunction	No	Baseline	2	2	2	8-1, 8-2
Retarded Timing	Yes	Low	1	--	--	19-1
Malfunction	No	Low	1	--	--	10-1

TABLE 7 (CONT'D). MERCEDES TESTING

Test Condition	Trap Installed	Test Fuel Aromatics	Driving Cycles/with Emissions			Test Number
			FTP	HFET	NYCC	
Baseline 4[c]	Yes	Baseline	1	--	--	11-5
	No	Baseline	1	--	--	2-5

[a]A number of HFET and NYCC cycles were used to define the regeneration process used in this study.
[b]While regeneration is occurring to some degree at many points during vehicle operation, the regeneration cycle is defined as follows for this study: operation of the vehicle with a heavily-loaded trap (obtained by repetitive operation over low-speed NYCC cycle) over a cycle for which at some point during the cycle the trap exit temperature exceeds the inlet trap temperature and which is accompanied by a significant reduction in trap ΔP and engine backpressure.
[c]Regulated emissions only.
[d]Injectors removed from a vehicle operated 57,000 miles in Germany were used for testing. The wear on these injectors was not sufficient to obtain a noticeable effect in the emission results. Since little change was observed with these "worn" injectors, the duplicate test and the tests without trap were omitted.

TABLE 8. VOLKSWAGEN TESTING

Test Condition	Trap Installed	Test Fuel Aromatics	Driving Cycles/with Emissions			Test Number
			FTP	HFET	NYCC	
Definition of Regeneration Cycle	Yes	Baseline		XX[a]	XX[a]	--
Initial Baseline	Yes	Baseline	2	2	2	1-1, 1-2
	No	Baseline	2	2	2	2-1, 2-2
Regeneration[b]	Yes	Baseline	--	3	--	R-1, R-2, R-3
Heavily Loaded Trap	Yes	Baseline	--	--	1	L-1
Baseline 2[c]	Yes	Baseline	1	--	--	1-3
	No	Baseline	1	--	--	2-3
Baseline	Yes	Low	2	--	--	3-1, 3-2
	No	Low	2	--	--	4-1, 4-2
Regeneration	Yes	Low	--	2	--	R-1, R-2
No additive[d]	Yes	Baseline	1	--	--	L-2
Baseline 3[c]	Yes	Baseline	1	--	--	1-4
	No	Baseline	1	--	--	2-4
Failed Injectors[e]	Yes	Baseline	2	2	2	5-1, 5-2, 5-3 (FTP)
	No	Baseline	2	2	2	6-1, 6-2
Baseline 4[c]	Yes	Baseline	2	--	--	1-5, 1-6
	No	Baseline	1	--	--	2-5
Retarded Injection Timing	Yes	Baseline	2	2	2	7-1, 7-2
Malfunction	No	Baseline	2	2	2	8-1, 8-2
Retarded Injection Timing	Yes	Low	1	--	--	9-1
Malfunction	No	Low	1	--	--	10-1

TABLE 8 (CONT'D). VOLKSWAGEN TESTING

Test Condition	Trap Installed	Test Fuel Aromatics	Driving Cycles/with Emissions			Test Number
			FTP	HFET	NYCC	
Baseline 5[c]	Yes	Baseline	1	--	--	1-7
	No	Baseline	1	--	--	2-6

[a]A number of HFET and NYCC cycles were used to define the regeneration process used in this study.
[b]While regeneration is occurring to some degree at many points during vehicle operation, the regeneration cycle is defined as follows for this study: operation of the vehicle with a heavily-loaded trap (obtained by repetitive operation over low-speed NYCC cycle) over a cycle for which at some point during the cycle the trap exit temperature exceeds the inlet trap temperature and which is accompanied by a significant reduction in trap ΔP and engine backpressure.
[c]Regulated emissions only.
[d]A previously unused trap was loaded with particulate by operation over NYCC cycles followed by HFET cycles. The additive system was not connected during this operation. The vehicle was then operated over an FTP cycle and emissions were recorded. The additive system was reconnected and the trap regenerated with NYCC cycles followed by an HFET cycle.
[e]Mr. Ken Parker of Volkswagen provided SwRI with eight injectors that had been diagnosed as being damaged or worn to such a degree as to affect performance. He also indicated that one faulty injector is a "normal" failure, and that multiple faulty injectors could prevent the vehicle from starting. The replacement of one original injector with a "failed" injector did not produce a noticeable effect in vehicle emissions or performance. For testing in this program, three of the original injectors were replaced with the "failed" injectors.

loading of 11.7 psi (325 in. water), a discernable regeneration occurred as the vehicle was accelerated slowly to 55 mph, with regeneration first noted at approximately 45 mph and an inlet/outlet temperature of 460°C. Increase in speed and operation at 55 mph for six minutes resulted in a decrease in engine backpressure to 5.1 psi (140 in. H_2O). Outlet trap temperatures exceeded inlet trap temperatures by approximately 15 to 20° for four minutes during the regeneration.

Based on the above data, the NYCC cycle was selected as a well defined means of loading a particulate trap without regeneration occurring. The HFET cycle was selected to provide the exhaust temperatures and the engine backpressures necessary to induce the regeneration of a heavily loaded trap. Emission results from the HFET baseline testing of the Mercedes would also be available for comparison with the HFET regeneration results to determine the extent of the emissions effects of the regeneration process. Regeneration testing of the Mercedes is discussed in more detail later in this section.

2. Baseline Testing

Before baseline testing of the Mercedes was initiated, both the oil and oil filter were changed and approximately 100 miles of expressway driving were accumulated on the vehicle to condition it with the new oil (Quaker State SAE 30). Duplicate test series (FTP, HFET, NYCC) were run with the particulate trap in place on the vehicle. All of the unregulated emissions discussed in Section II were evaluated during these initial baseline tests. The results of the tests will be discussed in a following section of the report. The initial FTP test (Test 1-1) was voided due to slippage of the driver's aid trace during testing, and was repeated as FTP Test 1-3. All samples, regulated and unregulated, were discarded for Test 1-1 and were repeated for Test 1-3. After the prep sequence and before the first series of tests, the engine backpressure at 30 mph was 83 in. water. After Test 1-3, the engine backpressure at 30 mph was 137 in. water.

Early in the program an attempt was made to fabricate a replacement piece for the Mercedes particulate trap in order to duplicate pressure drops across the trap for baseline testing without a trap on the vehicle. Mr. Harald Polz of Mercedes-Benz of North America cautioned that any replacement part would not fully simulate the influence of the trap on the engine. Mr. Polz expressed his concerns in a March 18, 1987 letter to Dr. Lawrence Smith of SwRI (Appendix A-1). In this letter, Mr. Polz suggested that the baseline tests without the particulate trap be conducted by converting the vehicle to an actual 49-state non-trap production vehicle. After a discussion of this approach among Dr. Smith, Mr. Jerry Wendt (CARB, El Monte) and Ms. Yolanda Garza (CARB, El Monte), it was decided that the approach suggested by Mr. Polz would be the best approach for conducting the baseline tests without the trap installed on the vehicle.

The test vehicle was modified by replacing the trap with an exhaust manifold (provided by Mercedes-Benz), replacing the California version of the ECU unit with a 49-state version (also provided by Mercedes-Benz), and disconnecting and plugging the vacuum line to the air-bypass valve. Duplicate test series (FTP, HFET, NYCC) were then run on the vehicle in the "without trap" baseline configuration with sampling for all unregulated emissions.

After a series of regeneration tests and during the testing of the Volkswagen Jetta, the Mercedes at one point was allowed to stand for approximately three weeks without starting. When the vehicle was started, it was impossible to operate the vehicle at speeds over 5 mph on the dynamometer without the engine dying. Subsequent investigations revealed that the particulate trap was plugged. The nature of this plugging was uncertain, because the vehicle was parked with neither an unusually high nor low engine backpressure having been measured with the trap in place. Attempts to unplug the trap were unsuccessful (reverse flow, high pressure pulsed air in reverse direction, and acetylene torch). Two options for continuing the tests with the Mercedes and trap included replacing the plugged trap with a new trap, or thermally regenerating the plugged trap in a oven.

An attempt was made to regenerate (clean) the Mercedes trap by heating to 500°C, followed by immediately cooling the trap to room temperature (that is, not holding temperature at 500°C). The test vehicle would not start when the trap was reinstalled onto the vehicle. A second attempt was made to clean the trap by heating the trap in the oven and holding the temperature at 500°C for 15 minutes before cooling to room temperature. While the vehicle would start and could be operated at low speeds after this second cleaning attempt, the maximum speed that could be attained was 8 mph, and further regeneration on the vehicle was impossible. A third attempt to clean the plugged Mercedes trap by heating the trap at 500°C for a full 30 minutes was also unsuccessful.

In a telephone conversation among Mr. Mike Bogdanoff, Ms. Yolanda Garza, and Mr. Ramon Cabrera (all of CARB, El Monte) and Dr. Lawrence Smith of SwRI, it was decided that the best course of action would be to obtain a second used particulate trap from Mercedes. Mr. Harald Polz of Mercedes-Benz was contacted by Dr. Smith to see if Mercedes would be able to supply a used trap for the completion of the program. Mr. Polz agreed to obtain a used trap, and asked that the original trap be sent to Daimler-Benz for analysis. At this point the original trap was returned to Germany. Daimler-Benz reported at a later date that they were successful in regenerating this trap on an engine test stand under carefully controlled conditions.

After the replacement trap was received from Mr. Polz, it was installed on the test vehicle and duplicate FTP tests with a complete set of unregulated emissions were conducted to re-establish the baseline. Table 9 summarizes the regulated emissions and fuel economy for the baseline FTP testing with the replacement trap (computer printouts of the regulated emissions are included in Appendix B) along with the baseline data for the original trap. In general, the emissions were slightly higher (except for NO_x) and the fuel economy slightly lower with the replacement trap. Based on these results, the program was continued with the replacement trap. Tests are designated in the tables using two numbers separated by a dash (N_1-N_2). The first number is the test number and the second number is the run number (1, 2, or 3) and is used for multiple tests with the same vehicle test configuration. It should be noted that odd test numbers refer to tests with the trap on the vehicle, and that even test numbers refer to tests without the trap. A double digit odd test number indicates that the test was conducted with the replacement trap, while a single digit odd number indicates that the test was conducted with the original trap.

TABLE 9. MERCEDES FTP REGULATED EMISSIONS RESULTS, BASELINE WITH ORIGINAL AND REPLACEMENT TRAPS

	FTP Emissions in g/mi, except as noted					
	Original Trap			Replacement Trap		
	Test 1-3	Test 1-2	Avg.	Test 11-1	Test 11-2	Avg.
Hydrocarbons	0.13	0.16	0.15	0.21	0.18	0.20
Carbon Monoxide	2.46	3.01	2.74	3.03	3.10	3.07
Oxides of Nitrogen	0.87	0.90	0.89	0.78	0.82	0.80
Particulates	0.049	0.046	0.048	0.075	0.056	0.066
Fuel Economy, mpg	20.57	21.21	20.89	20.53	19.77	20.15

TABLE 10. FTP BASELINE EMISSIONS AND FUEL ECONOMY RESULTS FOR THE MERCEDES - WITH AND WITHOUT TRAP

	With Trap Emissions in g/mi, except as noted				
	Original Baseline Average Two Tests Test 1-3, 1-2	Replacement Trap Baseline Average Two Tests Test 11-1, 11-2	Baseline 2 Test 11-3	Baseline 3 Test 11-4	Baseline 4 Test 11-5
Hydrocarbons	0.15	0.20	0.23	0.27	0.17
Carbon Monoxide	2.74	3.07	3.24	3.23	3.51
Oxides of Nitrogen	0.89	0.80	0.84	0.90	0.94
Particulates	0.048	0.066	0.025	0.025	0.075
Fuel Economy, mi/gal	20.89	20.15	20.76	21.35	20.38

	Without Trap Emissions in g/mi, except as noted			
	Original Baseline Average Two Tests Test 2-1, 2-2	Baseline 2 Test 2-3	Baseline 3 Test 2-4	Baseline 4 Test 2-5
Hydrocarbons	0.23	0.27	0.23	0.19
Carbon Monoxide	1.19	1.11	1.07	1.06
Oxides of Nitrogen	0.92	0.90	0.94	1.03
Particulates	0.396	0.338	0.368	0.365
Fuel Economy, mi/gal	23.33	23.47	23.06	22.42

Throughout the course of the program additional baseline FTP tests (regulated emissions only) were conducted both with and without trap to monitor baseline consistency in the program. The results of these baseline tests are presented in Table 10.

Without the trap on the vehicle, the FTP regulated emissions appear to be relatively constant throughout the program, with the most significant emission changes occurring after the retarded timing tests (i.e., a noticeable decrease in hydrocarbon emissions and a corresponding increase in oxides of nitrogen emissions). A decrease in fuel economy was also evident after the retarded timing tests. With the trap, a gradual increase in hydrocarbons and carbon monoxide was noted, however, the other regulated emissions and the fuel economy did not show established trends.

3. Regeneration and Heavily-Loaded Trap Tests

Before any regeneration or heavily-loaded trap tests were conducted for record, it was necessary to operate the vehicle over several FTP and HFET tests to purge particulate retained during tests from the exhaust system. As a check, the Mercedes was operated over an HFET cycle and regulated emissions were recorded. The results for this additional HFET cycle (HC, 0.09 g/mi; CO, 2.00 g/mi; NO_x, 0.50 g/mi; particulates 0.026 g/mi; and fuel economy, 27.8 mi/gal) were used in the evaluation of the regeneration HFET cycles.

The Mercedes was then operated over 17 consecutive NYCC cycles to load approximately 11 grams of particulate into the trap. The NYCC cycles increased the pressure drop across the trap from 4 psi to 15.9 psi at 30 mph vehicle operation. A complete set of emissions were sampled during the next NYCC cycle (18th) for the heavily-loaded trap test. This test was followed by an HFET test with all emissions being sampled to evaluate regeneration emissions. At the conclusion of the HFET test, the pressure drop across the trap (ΔP) had decreased to 3.9 psi. While there was a gradual decrease in ΔP across the trap during the initial segment of the HFET, indicating partial trap regeneration, the regeneration process appeared to accelerate at the point in the cycle where the vehicle speed dropped below 30 mph (296 seconds into the test) followed by an acceleration to 59 mph (350 seconds into the test). At one point (at 355 seconds), the exhaust temperature at the exit of the trap exceeded the inlet temperature by 120°C. During the baseline HFET testing, the temperature difference at this point was 30°C. The vehicle was then operated over an additional 16 NYCC cycles to give a trap ΔP of 15.9 psi, followed by a second HFET regeneration test with a complete set of emissions. The computer printouts for the "heavily-loaded" trap test, NYCC test L-1, and the HFET regeneration tests, HFET R-1 and HFET R-2, are included in Appendix B. The regulated emissions and fuel consumption for these tests are summarized in Table 11, along with the results for the HFET test preceding the NYCC loading and average baseline HFET and NYCC results for the Mercedes "with trap."

The regeneration HFET gave lower hydrocarbon emission rates and higher carbon monoxide, oxides of nitrogen, and particulate emission rates than the baseline tests. The fuel economy for the regeneration HFET was higher than the baseline value, but lower than the fuel economy for the HFET immediately

TABLE 11. REGULATED EMISSIONS AND FUEL ECONOMY RESULTS FOR THE MERCEDES HEAVILY-LOADED TRAP AND REGENERATION TESTS

	Emissions in g/mi, except as noted					
	HFET Avg. Baseline With Trap Tests 1-1, 1-2	HFET Before Loading	HFET Regen-eration R-1	HFET Regen-eration R-2	NYCC Avg. Baseline With Trap Tests 1-1, 1-2	NYCC Loaded Trap L-1
Hydrocarbons	0.11	0.09	0.06	0.06	0.20	0.08
Carbon Monoxide	2.22	2.00	3.17	2.66	3.79	7.20
Oxides of Nitrogen	0.55	0.50	0.62	0.58	2.09	2.23
Particulates	0.025	0.026	0.073	0.064	0.107	0.019
Fuel Economy, mpg	24.8	27.8	26.0	25.7	13.2	10.4

preceding the trap loading. The loaded-trap NYCC gave lower hydrocarbon and particulate emission rates, and a higher carbon monoxide emission rate than the baseline NYCC tests. Fuel economy for the loaded-trap NYCC was 2.8 mpg lower than the NYCC baseline. Results for the unregulated emissions from the "heavily-loaded" trap NYCC and regeneration HFET tests are discussed in subsequent sections of the report.

4. Engine Malfunction Tests

The program included the evaluation of both vehicles with two engine malfunctions. Criteria for the malfunctions were that the malfunctions be likely to occur in consumer service, likely to cause measurable emission changes, and be reversible. The two engine malfunctions selected for the program included fuel injector deterioration and retarded injection timing. The former can be simulated with worn injectors (75,000 to 100,000 miles of use). Worn injectors were expected to produce higher hydrocarbons and particulate mass emissions. Retarded timing generally produces higher hydrocarbons, lower NO_x, and causes higher fuel consumption. It can occur due to normal wear in the injection pump.

For the worn injector testing, Mercedes-Benz provided SwRI with injectors removed from a vehicle operated 57,000 miles in Germany. Injectors with 75,000 to 100,000 miles of operation were not available for the engine model. After replacement of the injectors, the test vehicle was operated for 50 miles on the dynamometer to condition both vehicle and trap with the "worn injectors." A full series of tests including FTP, HFET, and NYCC were then run on the vehicle for both regulated and unregulated emissions. After reviewing the regulated emission results of the first test series (Appendix Tables B-27, -28, -29) with Mr. Ramon Cabrera and Mr. Mike Bogdanoff of CARB - El Monte, it was decided that the emission rates were similar (except for slightly higher carbon monoxide emission rates with the worn injectors) for the worn injector and baseline tests, and that the remainder of the testing with the worn injectors would be dropped from the test plan. At this point the worn injectors were replaced with the original injectors, and the test series continued.

The second malfunction included retarding the timing 3° CA from its original setting. Mr. Cabrera of CARB - El Monte indicated that both advanced and retarded timings for in-service vehicles had been observed, and that a 3°CA retarded setting was in the range of timing settings noted in the field. The Mercedes was retarded 3° CA from its original setting by a local Mercedes dealer and a full series of tests were conducted on the vehicle, both with and without the trap in place on the vehicle.

5. Testing with Low Aromatic Fuel

Failed trap testing was originally planned for both the Mercedes and Volkswagen, however, these tests were dropped from the program and replaced with testing on a low-aromatic fuel. Dr. Mike Ingham of Chevron provided SwRI with a low-aromatic test fuel (16.2 percent aromatics as compared to a 36.2 percent aromatics in the baseline fuel) for use in the program. Duplicate FTP tests, with regulated and unregulated emissions, were conducted on the Mercedes with and without the trap on the vehicle. Additional testing with the low-aromatic fuel included replicate regeneration HFET tests and single FTP tests, both with and without trap, and with retarded timing.

For regeneration testing with the low-aromatic fuel the Mercedes was then operated over 30 NYCC cycles to load the trap with particulate. This operation gave a pressure drop across the trap of only 8 psi at 30 mph. Similar operation with the baseline fuel and with the original trap oxidizer had given loadings up to 16 psi with 18 NYCC cycles. An HFET regeneration test (R-1) with emissions was then conducted. At the conclusion of this test the pressure drop across the trap (ΔP) had decreased to 3.7 psi at 30 mph. The loading sequence was repeated with 18 NYCC cycles and a much higher ΔP, ~ 16 psi, was obtained. This loading sequence compared favorably with the earlier work. A second HFET regeneration test was then conducted (R-2). At the conclusion of the test the ΔP at 30 mph was 3.9 psi. The trap was again loaded to a ΔP of 16 psi with multiple NYCC cycles (16), and a third HFET regeneration test was conducted (R-3). As was the case for the earlier work with the baseline fuel, the regeneration process appeared to accelerate at the point in the cycle where the vehicle speed dropped below 30 mph (296 seconds into the test) followed by an acceleration to 59 mph (350 seconds into the test). Immediately after this acceleration, there was a noticeable drop in trap ΔP and engine backpressure.

B. Volkswagen Testing

Emission tests conducted on the Volkswagen Jetta are described in this section. Computer printouts of the regulated emission results for these tests can be found in Appendix C. Unregulated emissions data for the tests are summarized in Appendices E, G, I, K, L, N, and P. These emissions will be discussed in more detail in a following section of the report.

1. Initial Vehicle Testing and Definition of Regeneration Cycle

Upon receipt of the Volkswagen Jetta from Germany, the fuel tank was filled with the test fuel, the oil and oil filter were changed, and a preliminary 3-bag FTP test (regulated emissions only) was conducted to establish relative emission

levels. The shift schedule for operating the vehicle over the FTP cycle was provided by Mr. Ken Parker of Volkswagen of America, Inc. and is included as Appendix A-2 of this report. The regulated emissions (total hydrocarbons, 0.37 g/mi; carbon monoxide, 1.25 g/mi; oxides of nitrogen, 0.82 g/mi; and particulates, 0.087 g/mi) appeared acceptable and the program was continued.

To investigate regeneration conditions for the Volkswagen Jetta, replicate NYCC cycles were used to load particulate into the trap and HFET cycles were used to regenerate the trap. With a clean trap (20 in. H_2O at 30 mph in 4th gear), the maximum trap inlet and outlet temperatures during an HFET cycle were 475°C and 390°C, respectively. The maximum trap inlet temperatures ranged from 285°C to 305°C for the NYCC cycles. A trap loaded to give a minimum engine backpressure of 80 in. of water was found to be required before a discernable regeneration was noted during the HFET cycle (trap outlet temperature exceeding trap inlet temperature and significant drop in engine backpressure after the test). Trap loading to 69 in. of water gave a maximum trap inlet temperature of 465°C and a maximum trap outlet temperature of 410°C. The engine backpressure at the end of the test was 68 in. of water (30 mph in 4th gear) indicating only a partial "slow burn" regeneration. When the trap was loaded to give an engine backpressure of 89 in. of water, the HFET cycle gave a maximum trap inlet temperature of 475°C and a maximum trap outlet temperature of 565°C. At one point in the cycle the outlet trap temperature exceeded the inlet temperature by 170°C (at 345 seconds into the test cycle). The engine backpressure at the conclusion of the test was 29 in. of water, indicating a significant regeneration. As was the case with the Mercedes, the regeneration process appeared to accelerate at the point in the cycle where the vehicle speed dropped below 30 mph (296 seconds into the test) followed by an acceleration to 59 mph (350 seconds into the test). The maximum trap inlet temperature is reached during this acceleration period. During one HFET regeneration test, a noticeable regeneration was noted earlier in the cycle (beginning at 250 seconds into the cycle) with a trap inlet temperature of 370°C (vehicle speed of 49 mph). At 286 seconds into the cycle the trap outlet temperature exceeded the inlet temperature by 100°C. Due to this earlier regeneration, the trap outlet temperature did not exceed the inlet temperature at 345 seconds into the test. This regeneration only lowered the engine backpressure to 38 in. of water at the completion of the test.

After the conclusion of the preliminary test work, Mr. Wolfgang Groth and Mr. K. R. Parker of Volkswagen of America and Mr. Werner Engeler of Volkswagen AG visited Southwest Research Institute to officially present the trap-equipped Jetta to SwRI for testing and to discuss the proposed testing. In general they were satisfied with the preliminary FTP test results, however, they thought that the particulate emission rate was a little high (0.087 g/mile). The planned regeneration sequence was also discussed (loading with NYCC cycle and regeneration with HFET cycle). Mr. Engeler thought that the hydrocarbon emissions during the HFET cycle were too low for a proper regeneration, and that a lower and more variable speed test would be more appropriate. This topic was concluded with a discussion of the necessity of having a regeneration cycle for which the results could be directly compared to a cycle in which little or no regeneration took place, and to the results obtained for the Mercedes. No alternate test cycle was suggested to replace the HFET.

2. Baseline Testing

Initial baseline testing of the Volkswagen Jetta was conducted both with the particulate trap in place on the vehicle and with the trap having been replaced by exhaust tubing. For the testing without the particulate trap on the vehicle, the only additional modification required to convert the Volkswagen to a non-trap configuration included removing the relay that controlled the addition of the organometallic iron additive to the fuel. This removal stopped the supply of additive to the fuel. Duplicate test series were conducted with sampling for both regulated and unregulated emissions.

As was the case with the Mercedes, additional baseline FTP tests (both with and without trap) were conducted throughout the course of the program to monitor baseline consistency in the program. The results of these baseline tests are presented in Table 12. The hydrocarbon emission rates were found to consistently decrease from the initial baseline tests to the Baseline 4 tests. The Baseline 5 hydrocarbon emissions returned to the Baseline 3 levels. The other regulated emissions and the fuel economy values showed no definite trends throughout the program.

TABLE 12. FTP BASELINE EMISSIONS AND FUEL ECONOMY RESULTS FOR THE VOLKSWAGEN - WITH AND WITHOUT TRAP

	With Trap Emissions in g/mi, except as noted				
	Initial Baseline Average Two Tests Tests 1-1, 1-2	Baseline 2 Test 1-3	Baseline 3 Test 1-4	Baseline 4 Average Two Tests Tests 1-5, 1-6	Baseline 5 Test 1-7
Hydrocarbons	0.39	0.33	0.21	0.13	0.20
Carbon Monoxide	1.28	1.13	1.26	1.06	1.05
Oxides of Nitrogen	0.79	0.69	0.84	0.76	0.79
Particulates	0.037	0.054	0.045	0.039	0.045
Fuel Economy, mi/gal	34.07	34.15	33.14	35.01	35.24

	Without Trap Emissions in, g/mi, except as noted				
	Initial Baseline Average Two Tests Tests 2-1, 2-2	Baseline 2 Test 2-3	Baseline 3 Test 1-4	Baseline 4 Test 1-5	Baseline 5 Test 1-6
Hydrocarbons	0.38	0.43	0.30	0.28	0.29
Carbon Monoxide	1.11	1.10	1.05	1.05	1.08
Oxides of Nitrogen	0.83	0.75	0.72	0.74	0.80
Particulates	0.187	0.211	0.193	0.204	0.201
Fuel Economy, mi/gal	35.53	36.18	37.03	36.71	34.93

3. Regeneration and Heavily-Loaded Trap Tests

For these tests, the particulate trap and the relay controlling the addition of the organometallic additive were in place on the vehicle. Before any tests were conducted, the vehicle was operated over HFET cycles to purge any particulate that may have been retained during previous tests from the exhaust system. At this point, the Volkswagen was operated over multiple NYCC cycles to load particulate into the particulate trap. During the 15th NYCC loading cycle, the trap underwent a partial regeneration, with the engine backpressure dropping from approximately 85 in. of water to 65 in. of water (30 MPH in 4th gear). The NYCC regeneration was noted a second time in an attempt to load the trap to give an engine backpressure greater than 85 in. of water. At this point it was decided that it would be necessary to limit the trap loading to approximately 80 in. of water for the engine backpressure in order to conduct the planned regeneration and loaded trap tests.

To evaluate loaded trap emissions, a complete set of emissions were sampled for the Volkswagen during an NYCC cycle with an initial engine backpressure of 76 in. of water. The backpressure at the end of the NYCC test was 82 in. of water. This test was followed by an HFET test (R-1) with all emissions being sampled to evaluate regeneration emissions. At the conclusion of the HFET test, the engine backpressure had decreased to 36 in. of water at 30 mph in 4th gear. As was the case for the Mercedes, the regeneration process appeared to accelerate at the point in the cycle where the vehicle speed dropped below 30 mph, followed by an acceleration to 59 mph (350 seconds into the test). At one point (310 seconds into the test) the exhaust temperature at the trap outlet exceeded the inlet temperature by 85°C. The highest trap outlet temperature (495°C) occurred at 340 seconds into the test. The vehicle was again operated over additional NYCC cycles to give an engine backpressure of 77 in. of water, followed by a second HFET regeneration test (R-2). However, no discernable regeneration was noted at any point during the test. The engine backpressure at the end of the test was 54 in. of water. The trap outlet temperature did not exceed 390°C for the entire test. Sampling problems occurred during the cycle to prevent a complete set of emissions, but the regulated gaseous emissions were obtained for the test. The vehicle was then loaded with an additional 9 NYCC cycles to give an engine backpressure of 82 in. of water. All exhaust emissions were measured during the following HFET cycle (R-3). The engine backpressure at the end of the cycle was 35 in. of water. The noticeable regeneration for this test occurred later into the test than in the first regeneration test, with the trap exit temperature exceeding the inlet temperature by 100°C at 350 seconds into the test. The highest trap outlet temperature, 520°C, also occurred at this point. The regulated emissions and fuel consumption for the above tests are summarized in Table 13, along with baseline HFET and NYCC results for the Volkswagen. Computer printouts for the tests are included in Appendix C.

The regeneration HFET gave higher carbon monoxide, particulate, and carbon dioxide emission rates than the baseline tests. The fuel economy for the regeneration HFET was consistently lower than the baseline HFET. The success of the regeneration test is indicated by the higher carbon dioxide emission rates (and lower fuel economy calculated by the carbon balance method) for Tests R-1 and R-3 (231 and 229 g/mi) as compared to the attempted regeneration Test R-2 (219 g/mi)

TABLE 13. REGULATED EMISSIONS AND FUEL ECONOMY RESULTS FOR THE VOLKSWAGEN HEAVILY-LOADED TRAP AND REGENERATION TESTS

	Emissions, g/mi					
	HFET Baseline With Trap Tests 1-1, 1-2	HFET Regeneration R-1	HFET Attempted Regeneration R-2	HFET Regeneration R-3	NYCC Baseline With Trap	NYCC Loaded Trap L-1
Hydrocarbons	0.16	0.18	0.11	0.15	0.75	1.00
Carbon Monoxide	0.59	1.18	0.86	1.06	2.37	2.55
Oxides of Nitrogen	0.52	0.50	0.49	0.57	1.32	1.16
Particulates	0.014	0.073	--	0.030	0.060	0.078
Carbon Dioxide	198	231	219	229	485	524
Fuel Economy,mpg	51.1	43.5	46.0	43.9	20.7	19.1

and the baseline tests (198 g/mi). The additional carbon dioxide emissions during regeneration are a result of the combustion of previously "trapped" particulate. The loaded-trap NYCC gave emissions and fuel consumption values similar to the baseline tests. Unregulated emission results for these tests will be discussed in a following section of the report.

An evaluation of trap behavior without the fuel additive was also conducted with the Volkswagen Jetta. To conduct the evaluation of the trap behavior without the fuel additive, the Jetta's fuel tank was drained and filled with baseline fuel, the additive relay was removed, and the particulate trap was replaced with a previously unused trap. The Jetta was then operated over repetitive cycles of ten NYCC tests and one HFET test to load particulate into the trap. Trap regeneration had previously been noted during NYCC cycles when the pressure drop across the trap (ΔP) exceeded 85 in. H_2O. In this evaluation the trap was steadily loaded to 110 in. H_2O without a discernable regeneration taking place. A 3-bag FTP test (regulated emissions only) was conducted to document emission rates with the higher trap loading. The regulated emissions and fuel economy for this test are compared to the average of three previous baseline tests in Table 14. The higher trap loading did not appear to have a detrimental effect on the regulated emissions.

TABLE 14. A COMPARISON OF THE REGULATED EMISSIONS AND FUEL ECONOMY FOR THE VOLKSWAGEN AT BASELINE AND HIGH TRAP LOADINGS

	FTP Emissions, g/mi	
	Avg. Three Baseline Tests	110 in. H_2O Test
Hydrocarbons	0.37	0.16
Carbon Monoxide	1.23	1.05
Oxides of Nitrogen	0.75	0.79
Particulate	0.042	0.022
Fuel Economy, mi/gal	34.10	33.45

Trap loading was continued with cycles of ten NYCC and one HFET tests until a loading in excess of 150 in. H_2O was reached. When the HFET test in the sequence was run, a partial trap regeneration was noted (decrease to 110 in. H_2O in trap ΔP). It is possible that traces of additive in the combustion system could have aided in this regeneration. At this point the additive relay was reinstalled into the vehicle and an additional cycle of ten NYCC and one HFET was run. Regeneration of the trap occurred during the HFET (none noted during the NYCC tests) with the ΔP dropping to 45 in. H_2O. These tests indicate that if the additive system fails, the vehicle can be operated for a number of hours without excessive trap loading occurring; and when the additive is reintroduced into the system, the trap will regenerate without trap failure.

4. Engine Malfunction Tests

The two engine malfunctions selected for the Volkswagen were "failed injectors" and retarded timing. The Volkswagen was tested over a full series of emissions tests with three "failed" injectors that had been provided by Mr. Ken Parker of Volkswagen of America.

Mr. Parker sent eight injectors which had been returned to their Parts Investigation group by Volkswagen dealers. These injectors had been diagnosed by dealership personnel as being damaged or worn to a degree sufficient to affect performance. (Refer to December 18, 1987 letter to Dr. Smith, Appendix A-3). Mr. Parker also indicated that one faulty injector is a "normal" failure, and that multiple faulty injectors could prevent the vehicle from starting. The injectors were partially evaluated at SwRI as to opening pressure and leakage. One of the injectors, which would not close even in the absence of fuel pressure, was diagnosed to be too severe of a failure and not used in the program. One injector which exhibited some leakage before and after opening was selected as the failed injector. After installing the failed injector, the Jetta was operated over the hot-start 505 segment of the FTP cycle. There were no performance problems and the emissions were not significantly different from the previous baseline results. At this point, two additional failed injectors were installed, and the Jetta was again operated over the hot-start 505 segment of the FTP. Once again no performance problems were noted; however, a noticeable increase in carbon monoxide emissions and a decrease in fuel economy were noted. The vehicle was then prepared for a full series of tests (regulated and unregulated emissions and with and without trap) with the three failed injectors.

The second malfunction included retarding the injection timing $3^{o}CA$ from its original setting. This malfunction was accomplished by rotating the injection pump 1 1/2 degrees beyond its standard setting. A full series of emission tests were then conducted on the vehicle.

5. Testing with Low Aromatic Fuel

Duplicate FTP tests were conducted on the Volkswagen with the low aromatic fuel both with and without the trap on the vehicle. Additional testing with the low aromatic fuel included duplicate regeneration HFET tests and single FTP tests both with and without trap and with retarded timing.

For the regeneration tests with the low-aromatic fuel, the Volkswagen was driven over repetitive NYCC cycles to load particulate into the trap for the regeneration tests. Initially, a trap loading of 85 in. H_2O ΔP at 30 mph did not produce a significant regeneration during the HFET test. It was necessary to load the trap to 120 in. H_2O before a significant regeneration occurred during the HFET. The first regeneration HFET cycle (R-1) was run at this loading. The ΔP after the test had decreased to 35 in. H_2O. The maximum trap outlet temperature, 515°C, occurred at 345 seconds into the test cycle. The vehicle was again operated over additional NYCC cycles, however a trap ΔP of 95 in. H_2O could not be obtained without partial regeneration during the NYCC loading cycle. For the second regeneration test, R-2, the trap was loaded to a trap ΔP of 93 in. H_2O and the vehicle operated over the HFET test with sampling for all emissions. The engine backpressure at the end of the cycle was 55 in. H_2O. While a discernable drop in the trap ΔP was noted during the cycle (~40 in. H_2O), the trap outlet temperature did not exceed 400°C. The less complete regeneration in R-2 as compared to R-1 was also reflected by lower carbon monoxide emissions (R-1, 3.17 g/mi; R-2, 0.69 g/mi) and higher fuel economy (R-1, 48.3 mi/gal; R-2, 51.1 mi/gal).

V. RESULTS

This section reports the analysis performed on the emissions data generated in this project. The analysis involved averaging and reformatting the data to enable making various comparisons. Due to the limited number of data points for each pollutant at each specific condition, advanced statistical analyses were judged to be inapplicable.

A. Regulated Emissions and Fuel Economy

The initial analysis of the data involved averaging the results for the baseline emissions tests. Individual test data can be found in Appendix B for the Mercedes and Appendix C for the Volkswagen. The data have been compared as to vehicle, presence of trap, test cycle, engine malfunction, condition of trap, and fuel aromatic content.

Average baseline regulated emission and fuel economy results for the Mercedes and Volkswagen are presented in Table 15. The Volkswagen had higher hydrocarbon emissions, but lower carbon monoxide, oxides of nitrogen, and particulate emissions than the larger Mercedes vehicle. The fuel economy was also higher for the Volkswagen than the Mercedes. With the particulate traps on the vehicles, the particulate emissions were reduced from 79 to 89 percent over the three test cycles when compared with the results for the vehicles without traps. In general, the hydrocarbon emissions and fuel economy increased and the carbon monoxide emissions decreased when the particulate traps were removed from the test vehicles. The low speed NYCC test cycle gave the highest regulated emissions and the lowest fuel economy of the three test cycles. The HFET, the test cycle with the highest average vehicle speed, gave the lowest regulated emissions and the highest fuel economy results.

Table 16 compares the baseline emission and fuel economy results with the failed/worn injectors and the retarded timing results. These comparisons include the two test vehicles operating over the three test cycles with and without particulate traps. The Mercedes was not tested with worn injectors and without a particulate trap. With the exception of slightly higher carbon monoxide emission rates for both vehicles and lower fuel economy for the Volkswagen, the worn or failed injector tests gave results similar to those obtained in the baseline tests. The retarded timing tests, however, gave higher hydrocarbons, carbon monoxide, and particulate (except for the Mercedes without trap) emissions, and lower oxides of nitrogen emissions than the baseline tests. For the retarded timing tests the use of particulate traps on the vehicles was not as efficient as for the baseline tests, with reductions in particulate ranging from 63 to 82 percent when compared to the without trap tests. The fuel economy results were not consistent, and varied with test cycle and presence of trap for the two test vehicles.

A comparison of the FTP emission rates and fuel economy for the two test vehicles operating on the two test fuels (baseline with 36.2 percent aromatics and low aromatic with 16.2 percent aromatics) is presented in Table 17. With the exception of the Mercedes baseline HFET tests with trap, both vehicles gave lower hydrocarbon, carbon monoxide, and particulate emissions, and lower fuel economy results, with the low aromatic fuel than with the baseline fuel. This trend held for

TABLE 15. AVERAGE BASELINE REGULATED EMISSIONS AND FUEL ECONOMY, MERCEDES AND VOLKSWAGEN

	Mercedes Emissions in g/mi, except as noted					
	FTP		HFET		NYCC	
	With Trap[a]	Without Trap[b]	With Trap[c]	Without Trap[c]	With Trap[c]	Without Trap[c]
Hydrocarbons	0.19	0.23	0.11	0.17	0.20	0.31
Carbon Monoxide	3.08	1.12	2.22	0.72	3.79	2.41
Oxides of Nitrogen	0.89	0.94	0.55	0.49	2.09	2.21
Particulates	0.050	0.372	0.025	0.208	0.107	0.703
Fuel Economy, mi/gal	20.65	23.12	24.8	34.0	13.2	13.1
	Volkswagen					
Hydrocarbons	0.25	0.34	0.16	0.18	0.75	0.73
Carbon Monoxide	1.16	1.08	0.59	0.51	2.37	2.22
Oxides of Nitrogen	0.77	0.78	0.52	0.56	1.32	1.33
Particulates	0.042	0.197	0.014	0.106	0.060	0.294
Fuel Economy, mi/gal	34.38	35.98	51.1	49.6	20.7	22.1

[a]Data is average for seven tests.
[b]Data is average for six tests.
[c]Data is average for two tests.

TABLE 16. AVERAGE REGULATED EMISSIONS AND FUEL ECONOMY RESULTS, BASELINE, FAILED/WORN INJECTORS, AND RETARDED TIMING TESTS

	Mercedes with Trap Emissions in g/mi, except as noted								
	FTP			HFET			NYCC		
	Baseline	Worn Injectors	Retarded Timing	Baseline	Worn Injectors	Retarded Timing	Baseline	Worn Injectors	Retarded Timing
Hydrocarbons	0.19	0.19	0.44	0.11	0.09	0.16	0.20	0.39	0.57
Carbon Monoxide	3.08	3.72	3.25	2.22	2.96	2.40	3.79	4.97	4.76
Oxides of Nitrogen	0.89	0.86	0.74	0.55	0.59	0.46	2.09	2.02	1.66
Particulates	0.050	0.041	0.078	0.025	0.026	0.036	0.107	0.059	0.206
Fuel Economy, mi/gal	20.65	19.64	22.09	24.8	24.6	27.3	13.2	13.3	13.9
	Mercedes without Trap								
Hydrocarbons	0.23	--	0.40	0.17	--	0.18	0.31	--	0.67
Carbon Monoxide	1.12	--	1.30	0.72	--	0.74	2.41	--	2.32
Oxides of Nitrogen	0.94	--	0.88	0.49	--	0.60	2.21	--	1.81
Particulates	0.372	--	0.338	0.208	--	0.180	0.703	--	0.553
Fuel Economy, mi/gal	23.12	--	22.89	34.0	-	29.6	13.1	--	14.5

TABLE 16 (CONT'D). AVERAGE REGULATED EMISSIONS AND FUEL ECONOMY RESULTS, BASELINE, FAILED/WORN INJECTORS, AND RETARDED TIMING TESTS

	Volkswagen with Trap Emissions in g/mi, except as noted								
	FTP			HFET			NYCC		
	Baseline	Worn Injectors	Retarded Timing	Baseline	Worn Injectors	Retarded Timing	Baseline	Worn Injectors	Retarded Timing
Hydrocarbons	0.25	0.25	0.54	0.16	0.10	0.17	0.75	0.42	1.07
Carbon Monoxide	1.16	1.67	1.64	0.59	0.96	0.81	2.37	2.76	3.53
Oxides of Nitrogen	0.77	0.68	0.74	0.52	0.52	0.54	1.32	1.15	1.14
Particulates	0.042	0.023	0.059	0.014	0.010	0.030	0.060	0.070	0.093
Fuel Economy, mi/gal	34.38	33.93	34.47	51.1	46.2	44.7	20.7	20.6	21.2
	Volkswagen without Trap								
Hydrocarbons	0.34	0.34	0.62	0.18	0.77	0.22	0.73	0.57	1.49
Carbon Monoxide	1.08	1.38	1.62	0.51	0.54	0.64	2.22	2.58	3.58
Oxides of Nitrogen	0.78	0.74	0.68	0.56	0.53	0.52	1.33	1.08	1.02
Particulates	0.197	0.231	0.239	0.106	0.100	0.111	0.294	0.387	0.365
Fuel Economy, mi/gal	35.98	34.10	34.58	49.6	47.7	46.5	22.1	21.6	21.5

TABLE 17. AVERAGE REGULATED EMISSION AND FUEL ECONOMY RESULTS, BASELINE AND LOW AROMATIC FUELS

	Mercedes FTP Emissions in g/mi, except as noted							
	Baseline Configuration				Retarded Timing			
	With Trap		Without Trap		With Trap		Without Trap	
	Baseline Fuel	Low Aromatic Fuel	Baseline Fuel	Low Aromatic Fuel	Baseline Fuel	Low Aromatic Fuel	Baseline Fuel	Low Aromatic Fuel
Hydrocarbons	0.19	0.11	0.23	0.23	0.44	0.25	0.40	0.26
Carbon Monoxide	3.08	1.95	1.12	1.08	3.25	2.90	1.30	1.13
Oxides of Nitrogen	0.89	0.76	0.94	0.88	0.74	0.75	0.88	0.93
Particulates	0.050	0.045	0.372	0.299	0.078	0.049	0.338	0.265
Fuel Economy, mi/gal	20.65	20.06	23.12	22.79	22.09	21.37	22.89	22.71
	Volkswagen							
Hydrocarbons	0.25	0.20	0.34	0.23	0.54	0.38	0.62	0.38
Carbon Monoxide	1.16	0.81	1.08	0.78	1.64	1.14	1.62	1.08
Oxides of Nitrogen	0.77	0.82	0.78	0.72	0.74	0.62	0.68	0.65
Particulates	0.042	0.032	0.197	0.151	0.059	0.045	0.239	0.163
Fuel Economy, mi/gal	34.38	32.85	35.98	35.82	34.47	33.58	34.58	32.79

the three test cycles, both with and without particulate trap, and in both the baseline and retarded timing configurations. The Mercedes baseline HFET hydrocarbon emissions with trap were equivalent for both fuels, 0.23 g/mi. Particulate emissions were 10 to 37 percent lower, carbon monoxide emissions 4 to 37 percent lower, and hydrocarbon emissions 0 to 43 percent lower with the low aromatic fuel as compared to the baseline fuel.

The regulated emissions and fuel economy results for the regeneration HFET and heavily-loaded trap NYCC tests are presented in Table 18. The heavily-loaded trap NYCC tests for the Mercedes and Volkswagen both gave lower fuel economy and carbon monoxide emissions than the baseline tests. While the Mercedes heavily-loaded trap gave lower hydrocarbon and particulate emissions and higher oxides of nitrogen emissions than the baseline test, the Volkswagen heavily-loaded trap gave the opposite results with higher hydrocarbon and particulate emissions and lower oxides of nitrogen emissions than the baseline test.

Lower or equivalent hydrocarbons, higher carbon monoxide and particulate, and equivalent oxides of nitrogen emissions are observed for the regeneration tests (tests which include burning of particulate in the trap) when compared to the baseline test. There also appeared to be some evidence of lower computed fuel economy for these tests; however, the comparisons were difficult to make for the low-aromatic fuel tests because no HFET baseline testing was conducted with the low aromatic fuel, and because in general, the low-aromatic fuel gave lower fuel economies than the baseline fuel for the FTP tests. In many of the tests the degree of regeneration (increases in trap outlet temperature and decrease in trap backpressure) was proportional to the carbon monoxide emission rate, with higher carbon monoxide emissions resulting from more complete regenerations.

B. Trace Metals and Other Elements

Analyses were conducted for 33 metals and other elements during the course of this program. Analyses for 32 of the elements were conducted by x-ray fluorescence of particulate-laden fluoropore filters at the EPA-RTP laboratory. Complete emission results for these analyses can be found in Appendices D and E for the Mercedes and Volkswagen, respectively. Analyses for the remaining element, beryllium, were conducted at SwRI on a limited number of filter samples by acid digestion with nitric and sulfuric acids and detection with a graphite furnace-atomic absorption spectrophotometer (AAS). Analyses were also conducted on a limited number of impinger samples for the elements beryllium, cadmium, chromium, manganese, nickel, lead, and tin using a Perkin-Elmer ICP-6000 inductively coupled argon plasma atomic emission spectrometer, and for iron using a graphite furnace - AAS.

Of the 32 elements for which analyses were conducted by x-ray fluorescence spectroscopy, sixteen were found on 25 percent or less of the 120 sample filters. These sixteen elements included sodium (19 filters), vanadium (4 filters), cobalt (5 filters), arsenic (26 filters), selenium (27 filters), bromine (6 filters), strontium (28 filters), molybdenum (9 filters), cadmium (2 filters), tin (6 filters), antimony (4 filters), cesium (3 filters), iodine (1 filter), barium (7 filters), mercury (8 filters), and lead (21 filters). Of these sixteen elements, only sodium, vanadium, arsenic, selenium, and lead were detected at quantifiable levels (three times the detection limit). Bromine, strontium, molybdenum, and lead were also detected in one of

TABLE 18. REGULATED EMISSIONS AND FUEL ECONOMY, REGENERATION AND, HEAVILY-LOADED TRAP TESTS, MERCEDES AND VOLKSWAGEN

Mercedes

	HFET Emissions in g/mi, except as noted						
	Baseline Fuel				Low Aromatic Fuel		
	Baseline Tests		Regeneration		Regeneration		
	Average 1-1,1-2	6/3/87 Test	R-1	R-2	R-1	R-2	R-3
Hydrocarbons	0.11	0.09	0.06	0.06	0.12	0.11	0.09
Carbon Monoxide	2.22	2.00	3.17	2.66	1.77	2.53	2.21
Oxides of Nitrogen	0.55	0.50	0.62	0.58	0.52	0.60	0.58
Particulates	0.025	0.026	0.073	0.064	0.031	0.037	0.026
Fuel Economy, mi/gal	24.8	27.8	26.0	25.7	24.9	24.5	24.4

	NYCC Emissions in g/mi, except as noted	
	Baseline Fuel	
	Baseline Tests	Heavily Loaded Trap
Hydrocarbons	0.20	0.08
Carbon Monoxide	3.79	7.20
Oxides of Nitrogen	2.09	2.23
Particulates	0.107	0.019
Fuel Economy, mi/gal	13.2	10.4

Volkswagen

	HFET Emissions in g/mi, except as noted					
	Baseline Fuel				Low-Aromatic Fuel	
	Baseline Tests	Regeneration			Regeneration	
		R-1	R-2	R-3	R-1	R-2
Hydrocarbons	0.16	0.18	0.11	0.15	0.10	0.11
Carbon Monoxide	0.59	1.18	0.86	1.06	3.17	0.69
Oxides of Nitrogen	0.52	0.50	0.49	0.57	0.51	0.50
Particulates	0.014	0.073	--	0.030	0.033	0.028
Fuel Economy, mi/gal	51.1	43.5	46.0	43.9	48.3	51.1

	NYCC Emissions in g/mi, except as noted	
	Baseline Fuel	
	Baseline Tests	Heavily Loaded Trap
Hydrocarbons	0.75	1.00
Carbon Monoxide	2.37	2.55
Oxides of Nitrogen	1.32	1.16
Particulates	0.060	0.078
Fuel Economy, mi/gal	20.7	19.1

three background samples (samples collected from the dilution tunnel without a vehicle in place. For sodium, uncorrectable systematic biases were suspected during many of the analyses and the results for this element must be interpreted with caution. Vanadium was present at quantifiable levels only during the regeneration testing of the Mercedes (0.10 mg/mi, R-1, and 0.08 mg/mi, R-2 with baseline fuel. Emission rates for arsenic and selenium were quantified only for one of the two tests on the Mercedes with the replacement trap at baseline conditions (0.16 mg/mi arsenic and 0.24 mg/mi selenium). Lead was quantified on filters from three tests on the Mercedes, including the two regeneration tests with the baseline fuel (1.73 and 1.75 mg/mi) and the loaded trap test with the baseline fuel (14.6 mg/mi).

Three elements, titanium (25 filters), manganese (41 filters), and platinum (33 filters) appeared on a larger number of filters, however only two filters gave quantifiable levels of titanium (0.01 mg/mi - Volkswagen with failed injectors and trap, and 0.04 mg/mi - Mercedes with retarded timing and trap) and only one gave quantifiable levels of manganese (0.10 mg/mi - Mercedes baseline without trap). Platinum was not detected at quantifiable levels, and uncorrectable systematic biases were suspected during a number of the analyses for platinum.

Each of the remaining 13 elements was detected on 40 percent or more of the filters analyzed at EPA-RTP. Manganese, aluminum, silicon, sulfur, potassium, iron, and copper were also detected at trace levels on one or more of three filters collected from the dilution tunnel without a vehicle in-place. Calcium and chromium were detected at quantifiable levels on one or more of these background filters. Since these background samples could not be collected simultaneously with the exhaust samples, no background corrections have been made in the emission rates. The emission rates for the 13 elements have been summarized in Tables 19-22 to permit comparisons as to vehicle, test cycle, presence of trap, engine condition, test fuel, and regeneration. Background results are presented in Appendices D and E.

In general, trace element emissions were found to be higher for the Mercedes than the Volkswagen; higher for the without trap than for the with trap tests; and when present at detectable levels, higher for the NYCC cycle than for the FTP and HFET cycles. The higher emission rates without the traps indicate that many of the elements are retained in the particulate trap during vehicle operation, and as a result could cause increased engine backpressure over a period of time. The sulfur emission rates increased 6 to 9 fold when the traps were removed from the test vehicles (Table 19). Calcium emission rates for the Mercedes appear not to be affected by the presence of a trap, while the calcium emission rates from the Volkswagen increase when the trap is removed. Calcium may be in a form that is not retained in the higher temperature Mercedes trap (located near the manifold) but collected in the lower temperature Volkswagen trap (in an underbody location). Engine condition (Table 20) and aromatic content in the fuel (Table 21) appear to have little or no effect on the trace elements. The regeneration HFET cycle (Table 22) gave higher phosphorus, sulfur (4 to 7 fold higher), calcium, and copper emission rates than the baseline HFET cycle. These data indicate that these elements may be purged from the particulate traps when the traps reach higher operating temperatures during regeneration.

Beryllium, collected on 47mm filters during the baseline operation of the Mercedes and Volkswagen (both with traps in place), was analyzed using a graphite

TABLE 19. AVERAGE BASELINE METALS AND OTHER ELEMENTS, MERCEDES AND VOLKSWAGEN

	Mercedes Emissions in mg/mi, except as noted					
	FTP		HFET		NYCC	
	With Trap[a]	Without Trap	With Trap	Without Trap	With Trap	Without Trap
Magnesium	T2[b]	0.05	ND[c]	0.02	ND	T1
Aluminum	0.02	T1	ND	ND	ND	ND
Silicon	0.02	0.11	T1	ND	ND	ND
Phosphorus	0.01	0.15	ND	0.08	ND	0.23
Sulfur	0.26	1.77	0.13	0.86	0.30	2.80
Chlorine	0.02	0.02	T1	ND	ND	ND
Potassium	0.01	0.05	ND	T2	ND	ND
Calcium	0.11	0.11	0.03	0.04	0.31	0.22
Chromium	0.03	0.26	T2	0.10	1.69	0.82
Iron	2.06	4.10	0.55	0.60	3.12	4.72
Nickel	0.17	0.50	0.08	0.19	T2	1.51
Copper	0.08	T2	T2	T2	T1	T1
Zinc	T3	0.12	T1	0.07	ND	T2
	Volkswagen					
Magnesium	T1	0.01	T1	T2	T1	ND
Aluminum	0.01	0.01	T1	ND	T1	ND
Silicon	0.01	T2	T1	T1	ND	ND
Phosphorus	ND	0.05	ND	0.03	ND	T2
Sulfur	0.11	0.72	0.06	0.52	0.11	1.03
Chlorine	0.01	0.02	0.01	T1	T1	T2
Potassium	T2	ND	ND	ND	ND	T1
Calcium	0.03	0.08	0.01	0.04	T2	0.09
Chromium	0.06	T2	0.10	T2	1.30	T2
Iron	0.90	1.10	0.53	0.50	3.19	2.62
Nickel	T2	0.03	T2	T2	0.51	T2
Copper	T1	T2	T1	T1	T1	T1
Zinc	ND	T2	0.07	T2	ND	T1

[a]Mercedes FTP data with trap is the average of four tests (with original and replacement traps), all other data are the average of two tests.
[b]T - Signifies that the element was detected but below the limits of quantification, detection limit <T <3 times detection limit. The number 1, 2, 3 signifies the number of tests in which trace levels of the element were detected.
[c]ND - None detected.

TABLE 20. AVERAGE METALS AND OTHER ELEMENTS, BASELINE, FAILED/WORN INJECTORS, AND RETARDED TIMING TESTS

	With Trap FTP Emissions in mg/mi					
	Mercedes			Volkswagen		
	Baseline[a]	Worn Injectors[b]	Retarded Timing	Baseline	Worn Injectors	Retarded Timing
Magnesium	T2	T	T2	T1	ND[d]	T2
Aluminum	0.02	0.02	T1	0.01	0.01	T2
Silicon	0.02	T	0.01	0.01	0.01	T1
Phosphorus	0.01	0.01	ND	ND	T2	T1
Sulfur	0.26	0.31	0.18	0.11	0.04	0.02
Chlorine	0.02	T	ND	0.01	T1	ND
Potassium	0.01	T	0.01	T2	0.04	T2
Calcium	0.11	0.06	0.10	0.03	0.08	0.04
Chromium	0.03	0.14	0.13	0.06	0.14	T2
Iron	2.06	0.52	0.41	0.90	0.47	0.12
Nickel	0.17	T	T2	T2	T1	ND
Copper	0.08	T	ND	T1	0.10	ND
Zinc	T3	ND	T2	ND	T1	ND
	Without Trap FTP Emissions in mg/mi					
Magnesium	0.05	--[e]	0.04	0.01	T2	0.01
Aluminum	T1	--	0.03	0.01	0.02	0.01
Silicon	0.11	--	0.05	T2	0.03	0.08
Phosphorus	0.15	--	0.10	0.05	0.04	0.03
Sulfur	1.77	--	1.52	0.72	0.54	0.37
Chlorine	0.02	--	T1	0.02	0.02	0.01
Potassium	0.05	--	T1	ND	T2	T2
Calcium	0.11	--	0.07	0.08	0.17	0.07
Chromium	0.26	--	T2	T2	0.17	0.07
Iron	4.19	--	1.38	1.10	0.87	0.43
Nickel	0.50	--	0.21	0.03	ND	ND
Copper	T2	--	ND	T2	0.22	ND
Zinc	0.12	--	0.06	T2	T2	T1

[a]Mercedes baseline data with trap is the average of four tests.
[b]Mercedes worn injectors data is only one test point.
[c]T - Signifies that the element was detected but below the limits of quantification, detection limit <T <3 times detection limit. Number 1, 2 or 3 signifies the number of tests in which trace quantities of the element were detected.
[d]ND - None detected.
[e]Test was not conducted.

TABLE 21. AVERAGE METALS AND OTHER ELEMENTS, BASELINE AND LOW AROMATIC FUELS

	Mercedes FTP Emissions in mg/mi							
	Baseline Configuration				Retarded Timing			
	With Trap		Without Trap		With Trap		Without Trap	
	Baseline[a] Fuel	Low Aromatic Fuel	Baseline Fuel	Low Aromatic Fuel	Baseline Fuel	Low[b] Aromatic Fuel	Baseline Fuel	Low[b] Aromatic Fuel
Magnesium	T2	0.02	0.05	0.03	T2	T	0.04	0.03
Aluminum	0.02	0.02	T1	0.05	T1	ND[d]	0.03	0.02
Silicon	0.02	0.03	0.11	0.11	0.01	ND	0.05	0.02
Phosphorus	0.01	0.01	0.15	0.13	ND	ND	0.10	0.08
Sulfur	0.26	0.21	1.77	1.15	0.18	0.05	1.52	0.80
Chlorine	0.02	0.01	0.02	0.09	ND	ND	T1	T
Potassium	0.01	0.01	0.05	T1	0.01	ND	T1	T
Calcium	0.11	0.06	0.11	0.07	0.10	0.01	0.07	0.05
Chromium	0.03	0.13	0.26	0.19	0.13	T	T2	T
Iron	2.06	1.53	4.10	3.45	0.41	0.10	1.38	0.90
Nickel	0.17	0.06	0.50	0.59	T2	ND	0.21	0.12
Copper	0.08	0.12	T2	0.07	ND	ND	ND	ND
Zinc	T3	ND	0.12	0.10	T2	ND	0.06	T
	Volkswagen							
Magnesium	T1	ND	0.01	T2	T2	T	0.01	0.01
Aluminum	0.01	0.04	0.01	0.04	T2	T	0.01	0.01
Silicon	0.01	T2	T2	0.02	T1	ND	0.08	T
Phosphorus	ND	T2	0.05	0.04	T1	ND	0.03	0.04
Sulfur	0.11	0.11	0.72	0.20	0.02	0.03	0.37	0.36
Chlorine	0.01	0.01	0.02	0.01	ND	ND	0.01	ND
Potassium	T2	0.01	ND	0.01	T2	T	T2	T
Calcium	0.03	0.10	0.08	0.09	0.04	T	0.07	0.07
Chromium	0.06	0.05	T2	0.06	T2	T	0.07	0.11
Iron	0.90	0.90	1.10	0.69	0.12	T	0.43	0.23
Nickel	T2	T1	0.03	ND	ND	ND	ND	ND
Copper	T1	0.10	T2	T2	ND	ND	ND	ND
Zinc	ND	T1	T2	T2	ND	ND	T1	T

[a]Mercedes baseline data with trap is the average of four tests.
[b]Mercedes and Volkswagen data with retarded timing and low aromatic fuel is for one test only.
[c]T - Signifies that the element was detected but below the limits of quantification, detection limits <T<3 times detection limit. The number 1, 2, or 3 signifies the number of tests in which trace levels of the element were detected.
[d]ND - None detected.

TABLE 22. METALS AND OTHER ELEMENTS, REGENERATION TESTS

	HFET Emissions in mg/mi					
	Mercedes			Volkswagen		
	Baseline Configuration	Regeneration Baseline Fuel	Regeneration Low Aromatic Fuel	Baseline Configuration	Regeneration Baseline Fuel	Regeneration Low Aromatic Fuel
Magnesium	ND[a]	0.02	T1[b]	T1	--	T1
Aluminum	ND	T1	T3	T1	--	0.06
Silicon	T1	0.10	T1	T1	--	0.03
Phosphorus	ND	T1	0.03	ND	--	0.01
Sulfur	0.13	0.85	0.56	0.06	--	0.25
Chlorine	T1	0.08	ND	0.01	--	T2
Potassium	ND	ND	T3	ND	--	T2
Calcium	0.03	0.04	0.16	0.01	--	0.11
Chromium	T2	0.15	0.12	0.10	--	T2
Iron	0.55	7.42	0.54	0.53	--	1.04
Nickel	0.08	1.20	T1	T2	--	T1
Copper	T2	0.21	0.10	T1	--	0.18
Zinc	T1	T1	T1	0.07	--	ND

[a]ND - None detected.
[b]T - Signifies that the element was detected but below the limits of quantification, detection limit <T <3 times detection limit. The number 1, 2, or 3 signifies the number of test points in which trace levels of the element were detected.
[c]Data not available.

furnace atomic absorption spectrophotometer. None of the sixteen filters analyzed were found to contain detectable levels of beryllium. Detection limits for the analyses, expressed on a per mile basis, are 1 μg/mile for the FTP and HFET cycles and 7 μg/mile for the NYCC cycle.

During the baseline testing of the Mercedes, filtered exhaust gas was pulled through impingers containing a hydrocarbon solvent (toluene for the with trap tests and methanol for the without trap tests). The resulting samples are analyzed for selected metals (beryllium, cadmium, chromium, manganese, nickel, lead, and tin) using a Perkin-Elmer ICP-6000 inductively coupled argon plasma atomic emission spectrometer. None of the selected metals were detected in the samples and the analyses were discontinued. Detection limits for the analyses have been listed for reference in Table 23.

A limited number of methanol and water impinger samples were analyzed for iron using a graphite furnace-atomic absorption spectrophotometer. The results of these analyses are presented in Table 24. These impinger samples were collected downstream of the 20 x 20 inch particulate filters in an attempt to determine if any gas phase organometallic iron compounds were present in the Volkswagen exhaust. While iron was detected in both the methanol and water samples collected during the operation of the Volkswagen test vehicle, the results were erratic and complicated by the detection of iron in the samples collected during the operation of the Mercedes. Iron was not detected in blank methanol or water samples.

C. Aldehyde and Ketone Emissions, Sulfate Emissions, and Particulate Soluble Organic Fractions

Aldehyde and ketone emission rates (including formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, isobutyraldehyde/methylethylketone, benzaldehyde and hexanaldehyde), sulfate emission rates, and the particulate soluble organic fractions are listed in Appendices F and G for the Mercedes and Volkswagen, respectively. These results have been averaged and grouped in Tables 25 - 28 to allow comparisons as to vehicle, presence of trap, test cycle, engine condition, aromatic content in fuel, and trap condition. Of the aldehydes and ketones analyzed, only formaldehyde, acetaldehyde, and total aldehydes and ketones are presented in the tables. Formaldehyde and acetaldehyde constitute 70 to 85 percent of the aldehydes measured, and were the only aldehydes detected consistently throughout the program.

The Volkswagen typically gave higher aldehyde and ketone emission rates (including formaldehyde and acetaldehyde) than the Mercedes. As was the case for the regulated emissions and trace elements, the low speed NYCC tests gave the highest aldehyde and ketone emission rates. With the exception of the original trap data for the Mercedes which appeared to give unusually low formaldehyde emission rates, the two test vehicles gave similar aldehyde and ketone emission rates both with and without the particulate traps on the vehicles.

The worn or failed injector tests gave aldehyde and ketone emission rates similar to the baseline tests, while the retarding timing tests gave higher formaldehyde, acetaldehyde, and total aldehydes and ketones than the baseline tests. The tests with low-aromatic fuel appeared to give lower aldehyde and ketone emissions than the baseline test fuel for both vehicles with and without particulate

TABLE 23. DETECTION LIMITS FOR ATOMIC EMISSION ANALYSES, MERCEDES WITH AND WITHOUT TRAP

	Detection limit mg/mi		
	Mercedes, with trap		
	FTP	HFET	NYCC
Beryllium	0.5	0.4	3.2
Cadmium	1.0	0.7	6.3
Chromium	1.0	0.7	6.3
Manganese	1.0	0.7	6.3
Nickel	5.0	3.7	32
Lead	5.0	3.7	32
Tin	5.0	3.7	32
	Mercedes, without trap		
	FTP	HFET	NYCC
Beryllium	0.7	0.5	4.7
Cadmium	0.7	0.5	4.7
Chromium	0.7	0.5	4.7
Manganese	0.7	0.5	4.7
Nickel	1.9	1.4	12
Lead	3.7	2.7	23
Tin	3.7	2.7	23

TABLE 24. METHANOL AND WATER SOLUBLE IRON EMISSION RATES

Vehicle	Test Number	Test Cycle	Solvent	Iron Emissions in μg/mi
Volkswagen	Test 1-1,-2	FTP	Methanol	220
Volkswagen	Test 2-1,-2	FTP	Methanol	460
Volkswagen	Test R-1,-2,-3	Regeneration	Methanol	20
Volkswagen	Test 7-1,-2	FTP	Methanol	6
Mercedes	Test 1-2	FTP	Methanol	310
Volkswagen	Test 1-1,-2	FTP	Water	3400
Volkswagen	Test 2-1,-2	FTP	Water	2600
Volkswagen	Test R-1,-2,-3	Regeneration	Water	530
Volkswagen	Test 7-1,-2	FTP	Water	38
Mercedes	Test 11-1	FTP	Water	310

TABLE 25. AVERAGE ALDEHYDE AND KETONE AND SULFATE EMISSIONS, AND PARTICULATE SOLUBLE ORGANIC FRACTIONS, BASELINE TESTS

Mercedes
Emissions in mg/mi except as noted

	FTP			HFET		NYCC	
	Original Trap	Replacement Trap	Without Trap	Original Trap	Without Trap	Original Trap	Without Trap
Formaldehyde	10.7	22.3	20.8	6.9	15.6	45.1	43.9
Acetaldehyde	7.7	6.0	6.9	5.4	5.3	18.9	9.8
Total Aldehydes & Ketones	26.9	34.3	33.4	16.4	26.1	89.5	66.4
Sulfate	0.8	1.9	6.1	0.1	2.8	0.3	13.7
Particulate Soluble Organic Fraction, Percent	13.1	11.8	8.0	10.8	12.5	7.9	8.2

Volkswagen
Emissions in mg/mi except as noted

	FTP		HFET		NYCC	
	With Trap	Without Trap	With Trap	Without Trap	With Trap	Without Trap
Formaldehyde	33.5	31.4	16.3	12.0	86.5	73.4
Acetaldehyde	10.6	8.9	5.5	3.9	24.8	20.3
Total Aldehydes & Ketones	54.1	49.4	25.6	19.2	128.9	110.2
Sulfate	1.9	3.2	1.7	2.8	5.9	17.9
Particulate Soluble Organic Fraction, Percent	46.5	22.5	48.0	22.7	57.1	19.5

TABLE 26. AVERAGE ALDEHYDE AND KETONE AND SULFATE EMISSIONS AND PARTICULATE SOLUBLE ORGANIC FRACTIONS, BASELINE, FAILED/WORN INJECTORS, AND RETARDED TIMING

	With Trap FTP Emissions in mg/mi, except as noted					
	Mercedes			Volkswagen		
	Baseline[a]	Worn Injectors[b]	Retarded Timing	Baseline	Worn Injectors	Retarded Timing
Formaldehyde	22.3	19.2	38.1	33.5	32.3	40.1
Acetaldehyde	6.0	5.5	11.1	10.6	11.6	11.6
Total Aldehydes & Ketones	34.3	31.2	72.6	54.1	62.4	70.5
Sulfate	1.9	1.6	2.2	1.9	0.8	1.2
Particulate Soluble Organic Fraction, Percent	11.8	14.8	37.3	46.5	69.9	69.6
	Without Trap FTP Emissions in mg/mi, except as noted					
Formaldehyde	20.8	--[a]	28.3	31.4	29.2	NA[b]
Acetaldehyde	6.9	--	7.2	8.9	9.0	NA
Total Aldehydes & Ketones	33.4	--	45.7	49.4	48.8	NA
Sulfate	6.1	--	4.0	3.2	2.1	2.6
Particulate Soluble Organic Fraction, Percent	8.0	--	15.4	22.6	17.6	30.6

[a]Tests not conducted.
[b]NA - not available.

TABLE 27. AVERAGE ALDEHYDE AND KETONE AND SULFATE EMISSIONS AND PARTICULATE SOLUBLE ORGANIC FRACTIONS, BASELINE AND LOW AROMATIC FUELS

	Baseline FTP Emissions in mg/mi, except as noted							
	Mercedes				Volkswagen			
	With Replacement Trap		Without Trap		With Trap		Without Trap	
	Baseline Fuel	Low Aromatic Fuel	Baseline Fuel	Low Aromatic Fuel	Baseline Fuel	Low Aromatic Fuel	Baseline Fuel	Low Aromatic Fuel
Formaldehyde	22.3	15.2	20.8	19.9	33.5	21.1	31.4	19.6
Acetaldehyde	6.0	5.0	6.9	5.4	10.6	7.3	8.9	6.3
Total Aldehydes & Ketones	34.3	25.0	33.4	30.1	54.1	36.6	49.4	31.5
Sulfate	1.9	1.2	6.1	4.1	1.9	NA	3.2	1.4
Particulate Organic Fraction, Percent	11.8	11.6	8.0	7.7	46.5	45.3	22.6	24.6

TABLE 28. AVERAGE ALDEHYDE AND KETONE AND SULFATE EMISSIONS AND PARTICULATE SOLUBLE ORGANIC FRACTIONS, REGENERATION AND LOADED TRAP TESTS

	Mercedes Emissions in mg/mi, except as noted				
	NYCC Baseline Fuel		HFET		
			Baseline Fuel		Low Aromatic Fuel
	Baseline	Loaded Trap	Baseline	Regeneration	Regeneration
Formaldehyde	45.1	41.7	6.9	13.4	12.5
Acetaldehyde	18.9	11.2	5.4	3.7	6.4
Total Aldehydes & Ketones	89.5	70.0	16.4	18.7	23.7
Sulfate	0.3	NA[a]	0.1	NA	2.2
Particulate Soluble Organic Fraction, Percent	7.9	6.9	10.8	NA	24.2
	Volkswagen				
Formaldehyde	86.5	84.1	16.3	19.6	14.2
Acetaldehyde	24.8	22.6	5.5	6.2	6.8
Total Aldehdyes & Ketones	128.9	132.3	25.6	27.0	30.1
Sultate	5.9	11.7	1.7	3.1	3.3
Particulate Soluble Organic Fraction, Percent	57.1	42.4	48.0	39.1	30.3

[a]Not available.

traps. The heavily-loaded trap and regeneration tests did not give aldehyde and ketone emission rates significantly different from the baseline tests. As mentioned earlier, the Mercedes with original trap (the HFET baseline data used in Table 28) appeared to give unusually low formaldehyde emission rates, and the data should not be used to indicate an increase in formaldehyde emissions for the regeneration tests. In general, the aldehyde and ketone emission rates show trends similar to those observed for the total hydrocarbon emissions rates.

An attempt was made to analyze particulate samples (collected on 20 x 20 inch Pallflex filters) for aldehydes and ketones by extracting the filter samples with an acetonitrile DNPH solution and injecting a portion of the extract into a liquid chromotograph for separation and quantification. Filters collected during the baseline operation of the Mercedes (both with and without a particulate trap) were extracted for analysis. While no aldehydes or ketones were detected in the samples, a number of unknown compounds eluted from the analytical column over a long period of time. These unknown compounds interfered with the routine aldehyde and ketone analyses. At this point the analyses of the particulate filters were discontinued.

The test to test sulfate emission rates were variable, and meaningful observations were difficult to make when comparing the data for the various test conditions. As was the case for sulfur determined by x-ray, higher levels of sulfate were found in the tests without particulate traps on the test vehicles, as compared to those with the traps on the vehicles. Other relationships in the sulfate data were less apparent.

The Mercedes gave similar soluble organic fractions (SOF) of the particulate both with and without the particulate trap. In contrast, the Volkswagen with trap tests gave higher SOF levels than the Volkswagen without trap tests. Particulate SOF levels were higher for the Volkswagen than for the Mercedes both with and without trap and for all three test cycles. The retarded timing tests gave higher SOF levels than the baseline tests for both vehicles with and without trap. The aromatic content in the fuel did not appear to alter the SOF levels for either of the test vehicles. In the case of the Volkswagen NYCC tests with trap, the SOF levels were variable due to the low particulate and particulate extactable fractions. Extractable levels as low as 4 milligrams (1 milligram is obtained from a blank filter) per 20 x 20 inch filter were obtained.

D. Semivolatile Organics

Analyses were conducted for 37 semivolatile organic compounds both in the gas phase (collected from dilute filtered exhaust in polyurethane foam traps) and as particulate-associated material (collected on 20 x 20 inch Pallflex filters). The compounds analyzed included 18 polynuclear aromatics, 11 nitrated polynuclear aromatics, phenol, 3 methylphenols, 3 nitrosamines, and nitrobenzene. The polynuclear aromatics acenaphthene and dibenz(a,h)anthracene; the nitrated polynuclear aromatics 9-nitroanthracene, 9-methyl-10-nitroanthracene, 7-nitrobenz(a)anthracene, 6-nitro-benz(a)pyrene, 6-nitrochrysene, 3-nitrofluoranthrene, 2-nitrofluorene, 1-nitropyrene, 1,3-nitropyrene, 1,6-dinitropyrene, and 1,8-dinitropyrene; 2-methylphenol; the nitrosamines N-nitrosodimethylamine and N-nitrosodipropylamine; and nitrobenzene were not detected in any of the gas phase or particulate-associated samples analyzed in the program. Detection limits for the

gas phase analyses ranged from 40 to 2400 μg/mile depending on the test cycle and when the sample was run (before or after steps were taken to improve the detection limit). Detection limits for the particulate-associated samples were much lower and ranged from 0.4 μg/mile to 6.7 μg/mi.

1-Nitropyrene has been found in particulate-associated samples in previous studies[7], however, the levels found in exhaust were typically on the order of 2 μg/mi for the FTP cycle. The 1-nitropyrene emission rates in this program were apparently lower than this level and consequently below the 1.1 μg/mi FTP detection limit.

The emission rates for the 20 semivolatile organic compounds that were detected can be found in Appendices H and I for the gas phase semivolatiles and in Appendices J and K for the particulate-associated semivolatiles. Tables 29-31 summarize the emission rates for the 16 gas phase and particulate associated polynuclear aromatic compounds detected in this program. The emission rates for the remaining four compounds (phenol, 3-methylphenol, 4-methylphenol, and N-nitroso-diphenylamine) are discussed briefly in the text.

N-nitroso-diphenylamine was found in only nine gas phase samples: Mercedes baseline HFET test without trap (Test 2-1), 550 μg/mi; Mercedes regeneration tests with baseline fuel (Tests R-1 and R-2), 660 and 360 μg/mi; Volkswagen HFET baseline test with trap (Test 1-1), 390 μg/mi; Volkswagen baseline FTP tests without trap (Tests 2-1 and 2-2), 1,000 and 420 μg/mi; Volkswagen baseline HFET test (Test 2-2), 470 μg/mi; and Volkswagen NYCC tests without trap (Tests 2-1 and 2-2), 2,900 and 6,200 μg/mi. 3-Methylphenol was detected only in FTP gas phase samples collected during the retarded timing testing of the Volkswagen; 55 and 40 μg/mi for the with trap tests and 57 and 76 μg/mi for the without trap tests.

Phenol and 4-methylphenol were also only found in the gas phase samples, and were detected primarily during the retarded timing tests for both the Mercedes and the Volkswagen. Phenol emission rates ranged from 40 μg/mi for the Volkswagen HFET test with retarded timing and with trap to 480 μg/mi for the Volkswagen NYCC test with retarded timing and without trap. 4-methylphenol emission rates ranged from 30 μg/mi for the Mercedes HFET test to 1100 μg/mi for the Volkswagen NYCC test with retarded timing and with trap.

Of the 16 polynuclear aromatics detected in this study, only naphthalene, 2-methylnaphthalene, acenaphthalene, dibenzofuran, and phenanthrene were found in the gas phase samples at detectable levels. While all sixteen of the polynuclear aromatics listed in Tables 29-31 were found in one or more of the particulate-associated samples, the most consistently detected compounds were phenanthrene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(a)pyrene. Fluorene, anthracene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene were detected in only a limited number of samples.

The gas phase polynuclear aromatics detected in this study were typically C_{10} to C_{14} compounds, while the particulate-associated polynuclear aromatics were C_{13} and larger compounds. The gas phase data in Tables 29-31 were generally too variable to draw any conclusions as to the effect of trap, test cycle, fuel, or engine malfunction. The particulate-associated data indicated higher polynuclear aromatic emission rates in general for the Mercedes than for the Volkswagen, higher emission

TABLE 29. SEMIVOLATILE ORGANICS, MERCEDES AND VOLKSWAGEN BASELINE TESTS WITH AND WITHOUT TRAP

Mercedes

	Semivolative Organic Emissions in μg/mi[a]						
	FTP			HFET		NYCC	
	Original Trap	Replacement Trap	Without Trap	Original Trap	Without Trap	Original Trap	Without Trap
Naphthalene	4600	1300	2800	2500	1700	ND	2400
2-Methylnaphthalene	ND	110	1200	ND	690	ND	ND
Acenaphthalene	ND	ND	380	ND	140	ND	ND
Dibenzofuran	(0.3)	ND	ND	ND	ND	ND	ND
Phenanthrene	(6.8)	ND	(108)	(2.5)	(39)	(11)	(18.9)
Fluorene	ND	ND	ND	ND	ND	ND	ND
Anthracene	ND	NA[b]	(5.9)	ND	ND	ND	(17)
Fluoranthene	(15)	NA	(50)	(8.0)	(38)	(26)	(81)
Pyrene	(11)	NA	(66)	(7.1)	(46)	(28)	(112)
Benzo(a)anthracene	(0.3)	NA	ND	(0.5)	ND	ND	ND
Chrysene	(2.3)	NA	(5.8)	(2.0)	(4.8)	(3.6)	(6.8)
Benzo(b)fluorantheme	(1.8)	NA	ND	(2.3)	ND	ND	ND
Benzo(k)fluoranthene	ND	NA	ND	ND	ND	ND	ND
Benzo(a)pyrene	(1.2)	NA	ND	(1.7)	ND	ND	ND
Indeno(1,2,3-cd)pyrene	ND	NA	ND	ND	ND	ND	ND
Benzo(g,h,i)perylene	ND	NA	ND	ND	ND	ND	ND
Detection Limits for gas phase semivolatile analyses	380	40	380	280	280	2400	2400
Detection Limits for particulate-associated semivolatile analyses	0.6	--	1.1	0.4	0.8	38	6.7

TABLE 29 (CONT'D). SEMIVOLATILE ORGANICS, MERCEDES AND VOLKSWAGEN BASELINE TESTS WITH AND WITHOUT TRAP

	Volkswagen					
	Semivolatile Organic Emissions in $\mu g/mi$[a]					
	FTP		HFET		NYCC	
	With Trap	Without Trap	With Trap	Without Trap	With Trap	Without Trap
Naphthalene	1300	1200	530	610	3000	3600
2-Methylnaphthalene	650	820	260	360	850	1800
Acenaphthalene	ND	65	ND	ND	ND	ND
Dibenzofuran	ND	ND	ND	ND	ND	ND
Phenanthrene	(0.3)	55(13)	(0.5)	ND	(3.5)	ND
Fluorene	ND	ND	ND	ND	ND	ND
Anthracene	ND	ND	ND	ND	ND	ND
Fluoranthene	(1.4)	(20)	(0.8)	(9.8)	ND	(48)
Pyrene	(4.6)	(48)	(2.3)	(22)	(4.9)	(90)
Benzo(a)anthracene	(0.8)	(46)	(0.8)	(3.3)	ND	(8.7)
Chrysene	(2.7)	(3.5)	(3.5)	(2.8)	ND	(11)
Benzo(b)fluoranthene	(1.0)	(4.5)	(2.5)	(4.5)	ND	(15)
Benzo(k)fluoranthene	ND	ND	ND	ND	ND	ND
Benzo(a)pyrene	ND	(3.3)	ND	(2.4)	ND	(4.2)
Indeno(1,2,3-cd)pyrene	ND	(0.4)	ND	(1.0)	ND	ND
Benzo(g,h,i)perylene	ND	(2.5)	ND	(2.0)	ND	(12)
Detection Limits for gas semivolatiles analyses	80	80	60	60	480	480
Detection Limits for particulate-associated semivolatile analyses	1.1	1.1	0.8	0.8	6.7	6.7

[a]Numbers not in parenthesis are gas phase results, number in parentheses are particulate-associated results.
[b]Results not available.

TABLE 30. SEMIVOLATILE ORGANICS, MERCEDES AND VOLKSWAGEN WITH AND WITHOUT TRAP AND WITH LOW AROMATIC FUEL

	Semivolatile Organic FTP Emissions in μg/mi[a]			
	Mercedes		Volkswagen	
	With Trap	Without Trap	With Trap	Without Trap
Naphthalene	310	740(0.6)	760	860
2-Methylnaphthalene	20	290(0.3)	380	570
Acenaphthalene	ND	30(0.4)	ND	ND
Dibenzofuran	ND	(1.5)	ND	ND
Phenanthrene	20(5.9)	(129)	ND	(12)
Fluorene	ND	(1.6)	ND	ND
Anthracene	ND	ND	ND	ND
Fluoranthene	(4.3)	(33)	ND	(20)
Pyrene	(2.2)	(45)	ND	(20)
Benzo(a)anthracene	ND	(0.3)	ND	(2.2)
Chrysene	ND	(4.2)	ND	(3.2)
Benzo(b)fluoranthene	ND	(1.2)	ND	(2.7)
Benzo(k)fluoranthene	ND	ND	ND	ND
Benzo(a)pyrene	ND	(0.8)	ND	(2.2)
Indeno(1,2,3-cd)pyrene	ND	ND	ND	ND
Benzo(g,h,i)perylene	ND	ND	ND	ND
Detection Limits for gas phase semivolatile organics	40	40	40	40
Detection Limits for particulate-associated semivolatile organics	1.1	1.1	1.1	1.1

[a]Numbers not in parentheses are gas phase results, numbers in parentheses are particulate-associated results.

TABLE 31. SEMIVOLATILE ORGANICS, MERCEDES AND VOLKSWAGEN RETARDED TIMING TESTS WITH AND WITHOUT TRAPS

	FTP Retarded Timing Emissions in μg/mi[a]			
	Mercedes		Volkswagen	
	With Trap	Without Trap	With Trap	Without Trap
Naphthalene	1200	450	650	730
2-Methylnaphthalene	840	430	890	950
Acenaphthalene	310	160	180	230
Dibenzofuran	200	80	95	100
Phenanthrene	290(3.8)	170(25.8)	250(2.2)	260(17.2)
Fluorene	ND	ND	ND	ND
Anthracene	ND	ND	ND	ND
Fluoranthene	(7.5)	(46)	(4.3)	(32)
Pyrene	(10)	(39)	(8.1)	(9.7)
Benzo(a)anthracene	1.6)	(7.5)	(2.7)	(12)
Chrysene	(5.4)	(10.8)	(3.8)	(15)
Benzo(b)fluoranthene	(4.3)	(9.7)	(2.2)	(19)
Benzo(k)fluoranthene	(1.1)	ND	ND	ND
Benzo(a)pyrene	(2.7)	2.7)	ND	(6.5)
Indeno (1,2,3-cd)pyrene	ND	ND	ND	ND
Benzo(g,h,i)perylene	ND	ND	ND	ND
Detection Limits for gas phase semivolatile organics	40	40	40	40
Detection Limits for particulate-associated semivolatile organics	1.1	1.1	1.1	1.1

[a]Numbers not in parentheses are gas phase results, numbers in parentheses are particulate-associated results.

rates for the tests without traps than for the tests with traps for both vehicles, and higher emission rates for the NYCC test as compared to FTP and HFET tests. While the particulate-associated semivolatiles were lower for the with trap tests than for the without trap tests, there were no readily observed differences between the with and without trap emissions for the gas phase semivolatiles. This indicates the possibility that the particulate-associated semivolatiles could still be present in the exhaust of vehicles with traps at levels similar to levels found in the exhaust of vehicles without traps. The removal of the inorganic carbon from exhaust with the particulate trap could leave the higher molecular weight polynuclear aromatics in a more gaseous state which would not be collected on particulate filters. While many of these higher molecular weight compounds were not detected as gas phase compounds, their concentrations were typically below the detection limits of the gas phase procedure.

E. 1,3-Butadiene

In addition to the samples which were collected in Tenax traps and analyzed by GC/MS, a limited number of 1,3-butadiene samples were collected in Tedlar bags and analyzed by GC/FID. This supplemental procedure was developed at SwRI for the EPA and was not available for use early in the program. The results for the 1,3-butadiene analyses using the GC/FID procedure are presented in Appendix L of this report. Isobutylene and 1-butene emission rates were also quantified and are included with the data. The data have been averaged and summarized in Table 32. 1,3-Butadiene was found at comparable levels for both the Mercedes and Volkswagen with and without trap. The 1,3-butadiene percentage of the total hydrocarbons was similar for the two vehicles, 1.3 to 1.8 percent. For gasoline vehicles, 1,3-butadiene emissions occur for the most part in the cold-start 505 bag of the FTP. In this diesel study the 1,3-butadiene emissions were similar for all three segments of the FTP cycle.

TABLE 32. AVERAGE 1,3-BUTADIENE EMISSIONS

	FTP Emissions in mg/mi, except as noted			
	Mercedes		Volkswagen	
	With Trap	Without Trap	With Trap	Without Trap
Total Hydrocarbons	270	210	170	295
1,3-Butadiene	3.6	3.6	3.0	4.4
1,3-Butadiene Percent of Total Hydrocarbons	1.3	1.7	1.8	1.5
Other C_4 Hydrocarbons				
Isobutylene	1.0	0.7	1.1	1.5
1-Butene	2.5	2.5	3.0	3.4

F. Volatile Organic Hydrocarbons

Gas phase volatile organic hydrocarbons in dilute filtered exhaust were analyzed by collection with a Tenax trap and thermal desorption into a gas

chromatograph/mass spectrometer. In the initial tests with the Mercedes, analyses were conducted for a total of 37 compounds. The results of these tests have been included as Appendix M of this report. The compounds analyzed in these tests included:

Methylene Chloride	1,2-Dichloropropane	Styrene
Acetone	trans-1,3-dichloropropene	Tetrahydrofuran
Carbon Disulfide	Trichloroethene	Benzene
1,1-Dichloroethene	Dibromochloromethane	Toluene
1,1-Dichloroethane	1,1,2-Trichloroethane	Total Xylenes
trans-1,2-Dichloroethene	cis-1,3-Dichloropropene	1,3-Butadiene
1,2-Dichloroethane	2-Chloroethyl vinyl ether	Chloroform
Acrolein	Bromoform	1,4-Dioxane
Acrylonitrile	2-Hexanone	Phosgene
2-Butanone	4-Methly-2-pentanone	
1,1,1-Trichloroethane	Tetrachloroethene	
Carbon Tetrachloride	1,1,2,2-Tetrachloroethane	
Vinyl Acetate	Chlorobenzene	
Bromodichloromethane	Ethylbenzene	

Of these 37 compounds only methylene chloride, acetone, acrolein, 2-butanone, vinyl acetate, 2-hexanone, 4-methyl-2-pentanone, ethylbenzene, styrene, benzene, toluene, and total xylenes were detected in any of the samples analyzed. The ketones acetone, 2-butanone, 2-hexanone, and 4-methyl-2-pentanone were detected for the most part in the Mercedes without trap samples. Methylene chloride, acrolein, and vinyl acetate were detected sporadically and at levels near the detection limit of the procedure. Ethylbenzene and styrene were detected in several of the samples analyzed.

For the remainder of the Mercedes and Volkswagen testing, analyses were conducted for only seven of the volatile organic compounds: benzene, toluene, total xylenes, 1,3-butadiene, chloroform, 1,4-dioxane, and phosgene. Of these seven only benzene, toluene, and total xylenes were detected in the exhaust samples. The results for these analyses are included in Appendices M and N for the Mercedes and Volkswagen, respectively.

The detection of 1,3-butadiene in exhaust by GC-FID was not confirmed in the volatile organic analyses. The high volatility and the reactivity of 1,3-butadiene may make the trap collection and thermal desorption into a GC/MS an unacceptable method of analyses for exhaust samples. Therefore the lack of GC/MS confirmation should not be used to disregard or void the 1,3-butadiene results discussed in Section E. Benzene was found in the exhaust at concentrations ranging from none detected to 26.4 mg/mi, toluene at concentrations ranging from 0.7 to 44.9 mg/mi, and total xylenes at concentrations ranging from none detected to 14.8 mg/mi. Consistent trends and relationships in the data were not readily apparent. In general benzene emission levels were higher than toluene emission levels, which in turn were higher than xylene emission levels. Average FTP benzene, toluene, and xylene emission rates (for all test conditions) are presented in Table 33 for relative comparisons only.

TABLE 33. AVERAGE FTP BENZENE, TOLUENE, AND XYLENE EMISSION RATES

	FTP Emissions in mg/mi	
	Mercedes	Volkswagen
Benzene	8.4 ± 4.2	5.4 ± 2.7
Toluene	5.9 ± 3.8	5.3 ± 1.8
Xylene	2.0 ± 1.1	2.9 ± 2.0

No corrections for the background levels of benzene or toluene have been made for the data in Appendices M and N and in Table 33, because background traps were not analyzed in conjunction with the exhaust sampling. Benzene and toluene, however, have both been found in the background dilution air at levels equivalent to 0-2 mg/mi for both compounds in the exhaust. Xylenes have not been detected in the background air.

A limited number of 20 x 20 inch filters collected during initial Mercedes baseline testing were also analyzed for particulate-associated volatile organic compounds. The results of these analyses are included as Appendix O of this report. The list of compounds analyzed was similar to the list analyzed for the gas phase volatile organics. The volatile organics were thermally desorbed from the filter and concentrated in a Tenax trap. The Tenax trap was then desorbed into the GC/MS for analysis. Only acetone, toluene, and methylene chloride were detected in isolated samples. 1,1,1-Trichloroethane was detected in all of the particulate samples, however, it was also detected in blank filter samples at comparable levels. Because these particulate-associated volatile analyses gave only limited information, the analyses were discontinued for the remainder of the program.

G. Smoke

In their trap-equipped configurations, both test vehicles gave very low smoke opacity readings during all testing. With the exception of spikes (~1 sec. at half height) of up to 2 percent in the baseline loaded trap NYCC test and in the retarded timing tests, the smoke opacity for the trap-equipped Volkswagen did not exceed one percent during any of the tests. For the trap-equipped Mercedes, smoke opacity spikes did not typically exceed 6 percent. The number of smoke spikes with an opacity of greater than 1.5 percent was on the average 11 for the FTP, 9 for the HFET, and 3 for the NYCC. The baseline loaded trap NYCC test and the regeneration HFET tests for the Mercedes gave slightly higher smoke opacity spikes of 15 and 16 percent respectively. The loaded trap test had a total of five spikes that exceeded 6 percent opacity, while the regeneration test had 2 spikes exceeding 6 percent. The cold-start FTP testing of the Mercedes with worn injectors also gave one smoke opacity peak which exceeded 6 percent (13 percent at 200 seconds into the test). For most of the trap-equipped vehicle tests, instrument drift exceeded the height of the smoke spikes (1 to 3 percent) and prevented an accurate integration of the smoke opacity signal.

For the non-trap Volkswagen tests, the largest smoke opacity spikes were recorded at the start of each test (generally 15 to 40 percent) and at 200 seconds into each FTP test (10 to 35 percent). The remainder of the smoke spikes were generally less than 10 percent opacity. In the retarded timing tests, the Volkswagen gave opacity spikes of 70 to 80 percent during the cold-start of FTP tests. For the

non-trap Mercedes testing, the start of each test did not give a large smoke spike (generally <5 percent opacity). Major spikes in the FTP tests for the Mercedes occurred at 30 (12 to 22 percent), 200 (10 to 35 percent), 600 (5 to 10 percent) and 800 (20 to 30 percent) seconds into the test. As was the case for the Volkswagen testing, the retarded timing tests with the Mercedes gave more numerous and more intense opacity spikes than the baseline tests.

H. Literature Search for Mutagenic Health Impact of Diesel Particulate Traps

One task in this program was to conduct a literature search to assess available data on the mutagenic health impact of diesel particulate traps. This section presents the results of this effort. A computer-assisted literature search was conducted to locate studies that have been performed on the mutagenic health impact of diesel particulate traps. Orbit IV and Dialog Information Services were accessed to search several databases. They included SAE Global Mobility Pollution Abstracts, Biosis Previews, Chem Abstracts, Enviroline, Environmental Bibliography, Compendex Engineering Index, Cancerlit, Medline, and Toxline. Several articles were located which addressed the health impact issue. A summary of the research results follows.

The health effects of diesel particulate emissions (without a particulate trap) have been studied in detail. Diesel particulate has been found to contain a number of mutagenic and carcinogenic compounds. In addition, diesel particulate extract gives a positive response in the Ames test for mutagenicity, a test that indicates biological mutagenicity or toxicity. While particulate traps reduce the amount of particulate emitted by diesel vehicles and engines, it desirable to know the mutagenic character of the resulting particulate emissions.

Several studies have investigated the health impact of diesel particulate traps. In general, particulate traps reduced particulate emissions on average by 1 to 98 percent, depending upon engine speed and load and type of trap. Mutagenic response, as determined by the Ames bioassay, was likewise reduced by particulate traps by 11 to 100 percent. Scholl, et al determined the effect of uncatalyzed Corning ceramic traps on the emissions of the diesel powered Caterpillar 3208 operated over the 13-mode steady-state cycle.(7) Particulate sample filters were extracted with methylene chloride to obtain samples to test for biological activity. Reduction in particulate and Ames mutagenic response occurred at most modes relative to baseline (no trap) conditions, especially at the more heavily loaded modes as shown below. Tester strains TA98, TA100, TA1535, TA1537, and TA1538 were used to determine mutagenic response.

			Baseline		With Trap			
					Brake-Specific Particulate		Brake-Specific Mutagenic Response	
Mode	RPM	Load	Part., g/kW-hr	Mutagenic Response, KRev/kW-hr	g/kW-hr	Percent Change	KRev/ kW-hr	Percent Change
3	1680	25%	1.05	375	1.04	-1%	335	-11%
4	1680	50%	0.48	110	0.17	-65%	195	+77%
5	1680	75%	0.24	45	0.02	-92%	0	-100%
9	2800	75%	0.80	20	0.02	-98%	0	-100%
10	2800	50%	0.79	85	0.02	-97%	10	-88%
11	2800	25%	1.86	420	0.14	-92%	90	-79%

On a brake specific basis, mutagenic response was lower for most modes when a ceramic trap was used. Some of the subfractions of the soluble organic fraction, however, produced very high revertants per microgram of solubles, indicating that some of the compounds produced in the trap may be exhibiting toxic behavior.

In a study by Dorie, et al, a 1979 Caterpillar Model 3208 diesel engine was operated over modes 4 and 5 of the EPA steady-state 13 mode cycle.[8,9] The engine was tested with and without a Corning Ex-47 uncatalyzed ceramic trap. Both soluble organic fraction (SOF) samples and vapor phase organics were analyzed with the Ames bioassay. The SOF sample was obtained by methylene chloride extraction of particulate-sampled filters. The vapor phase organic (VPO) sample was collected in a trap positioned after the particulate filter. The trap, containing XAD-2 resin and polyurethane foam, was extracted with methylene chloride. Particulate (in mg/m^3) and mutagenicity levels (in revertants/$m^3 x 10^{-3}$ for both the SOF and VPO samples) typically decreased with use of the trap. The results are given below for total particulate and mutagenicity using tester strain TA98.

			Baseline			With Trap				
						Particulate Emissions		Mutagenic Response		
Mode	RPM	Load	Part., mg/m^3	Sample	Mutagenic Response, Rev/$m^3 x 10^{-3}$	mg/m^3	Percent Change	Sample	Rev/ $m^3 x 10^{-3}$	Percent Change
4	1680	50%	56.8	SOF	5.3, 8.0	16.8	-70%	SOF	3.0, 4.2	-43, -46%
5	1680	75%	42.7		4.5	5.8	-86%		3.4	-24%
4	1680	50%	--	VPO	1.8, 1.8	--	--	VPO	1.1, 2.4	-39, +33%[a]
5	1680	75%	--		1.2	--	--		0.4	-67%

[a]One sample showed a decrease in mutagen response and one an increase.

A qualitative analysis of a fraction of the mode 4 SOF and VPO trap samples for polynuclear aromatic hydrocarbons showed the presence of some known direct-acting mutagens, nitronapthalene and nitropyrene. These two compounds were found at trace levels, and are therefore not likely to be the source of all the mutagenicity of the samples. Quinoline/isoquinoline (unresolved peak) was also identified as a component of the trap sample. Quinoline is a mutagenic compound. Nitronapthalene, nitropyrene, and quinoline/isoquinoline were detected only in exhaust samples passed through the ceramic trap, not in baseline samples. Anthracenedione, a weak mutagen, was found in both baseline and trap samples. Overall, the ceramic trap appears to favor oxidation by providing surface area and increased residence time.

Dainty, et al tested two Corning Ex-47 ceramic wall-flow filters, one base metal-catalyzed and one base/noble-catalyzed.[10] In addition, a manganese-based fuel additive was used which provided 80 mg of manganese per liter of fuel. A Deutz F8L FW diesel engine was operated over the MTU mod 5 HD cycle (developed by Michigan Technological University) both with and without the trap. Particulate emissions (in mg/m^3) and Ames response with tester strain TA98 were reduced with

use of the traps. The results are shown below.

Baseline		With Trap				
			Particulate Emissions		Mutagen Concentration	
Part., mg/m³	Mutagenic Conc., Rev./m³	Trap	mg/m³	Percent Change	Rev/m³	Percent Change
75.1	36,350	Base Catalyzed Filter	1.97	-97%	2496	-93%
		Base/Noble Filter	1.91	-97%	1580	-96%

A portion of the solubles samples from the base/noble trap was analyzed for polynuclear aromatics. Reductions in levels of a known carcinogen, benzo(a)pyrene, were observed from use of the trap.

Westerholm, et al tested a Scania T112 heavy-duty diesel truck over a transient bus cycle with an average speed of 14.2 mph.[11] The vehicle was operated with two types of particulate trap, one a Degussa monolith type trap coated with a combination of noble and non-noble metals. The second trap was a Johnson-Matthey wire mesh trap coated with a noble metal. Both traps reduced particulate emissions and Ames mutagenic activity. Tester strains TA100, TA100 NR, and TA98 were used in the bioassay. The results are given below.

Baseline			With Trap				
				Particulate Emissions		Mutagenic Response	
Part. g/km	Strain	Avg. Mutagenic Response Rev./meter	Trap	g/km	Percent Change	Avg. Rev/ meter	Percent Change
0.71	TA100(-S9)	451	Monolith	0.10	-86%	128	-72%
	TA100(+S9)	464				197	-58%
	TA100NR(-S9)	223				107	-52%
	TA98(-S9)	196				98	-50%
	TA98(+S9)	228				106	-54%
			Wire Mesh	0.20	-72%	221	-51%
						201	-57%
						129	-42%
						67	-66%
						61	-73%

Emissions of several polycyclic aromatic hydrocarbons were measured. Levels of benzo(a)pyrene, a carcinogen, and 1-nitropyrene, a direct-acting mutagen, were reduced relative to baseline (no trap) levels. Average values are shown below. Ranges of values are also given in parentheses.

Compound	Baseline	Trap	
		Monolith	Wire Mesh
benzo(a)pyrene, μg/km	3.36(0.80-12)	0.17(ND-0.40)	0.20(0.20-0.20)
1-nitropyrene, μg/km	2.0(0.50-7.2)	0.35(0.10-0.58)	0.25(0.20-0.27)

A study by Ullman and Hare with a 1970 DDAD 6V71 coach engine and a 1980 GMC RTS-II bus with a DDAD 6V71 coach engine indicated slightly increased benzo(a)pyrene emissions with the use of an uncatalyzed Corning EX-47 ceramic trap.[12] Baseline emissions of benzo(a)pyrene were below detection limits while trap emissions were slightly higher. The engine was tested over a 7-mode steady-state cycle, a transient cycle, and a bus cycle. Chassis tests included a transient cycle and a bus cycle.

In addition to reducing particulate emissions and mutagenic activity of organic soluble material, particulate traps also affected regulated gaseous and sulfate emissions. Reductions in hydrocarbons, oxides of nitrogen, and sulfate emissions were observed by Scholl, et al[7] and Dorie, et al[8] with use of uncatalyzed ceramic traps. Dainty, et al[10] reported a reduction in carbon monoxide with the base/noble catalyzed ceramic trap.[11] Also noted was minimal conversion of sulfur dioxide to sulfuric acid, which had been a problem with other noble metal catalysts. Westerholm, et al observed decreased hydrocarbon emissions and slightly reduced oxides of nitrogen emissions from use of a catalyzed ceramic trap and a catalyzed wire mesh trap. The wire mesh trap also reduced carbon monoxide emissions relative to baseline. Ullman and Hare reported reduced carbon monoxide emissions and slightly increased oxides of nitrogen emissions from an uncatalyzed ceramic trap.[12]

In summary, diesel particulate traps have been found to reduce particulate emissions and mutagenic activity of organic solubles from particulate. Several carcinogenic or mutagenic compounds such as nitronapthalene, nitropyrene, quinoline/isoquinoline, and anthracenedione were decreased from use of traps. Both increases and decreases in benzo(a)pyrene were reported from particulate trap usage. Also reported were reductions in hydrocarbons, oxides of nitrogen, carbon monoxide, and sulfate for several traps.

I. Ames Bioassay Results

Samples were collected as particulate on 20 x 20 inch Pallflex filters. After particulate collection the filters were weighed, sealed in Tedlar bags under a nitrogen atmosphere, and stored in the dark at -20°C pending transfer to Dr. Ronald Rusmussen of the University of California, Irvine. The samples were shipped to Dr. Rasmussen on dry ice by air freight for subsequent methylene chloride extraction and mutagenesis testing using the Ames bioassay (Salmonella mutagenicity test). Vapor phase samples were also collected on polyurethane foam traps for both vehicles operating in the baseline configuration. While these traps collected sufficient material for GC/MS analysis, they did not provide enough material for the Ames mutagenesis tests, and consequently no studies of the mutagenic activity in the vapor phase were possible. Two tester strains, TA98 and TA100, were used in the Ames testing, both in the presence and absence of metabolic activation with

aroclor-induced Sprague Dawley rat liver homogenate (S9). The testing is described in detail in the CARB Final Report A-5-130-33, "Genotoxicity of Diesel Exhaust Particles and Vapor Collected from Engines with and without Particulate Trap Oxidizers," by Dr. Rasmussen.[13] Data tables taken directly from the report are included as Appendix P of this report. These appendix tables present the data as revertants per microgram of methylene chloride-soluble extract and as revertants per mile. It must be noted that the term equivalent revertants per vehicle mile does not imply that some number of revertants are emitted by a vehicle. This calculated value is used to permit a comparison of the Ames data from different fuels and vehicles and takes into account the vehicle particulate emission rate and the percent of organic soluble matter in the particulate. The data in Appendix P has been averaged and presented in Tables 34 (revertants/μg) and Table 35 (revertants/mile). The Ames response for the extract material from testing both the Mercedes and Volkswagen was comparable for the with and without trap tests, however, on a revertants per mile basis, the with trap tests were considerably lower than the without trap tests. These findings are consistent with the findings discussed in the literature search section (i.e., the use of traps decrease the mutagenic activity on a per mile or unit of work basis). The Mercedes loaded trap and regeneration test results were similar to the with trap baseline results. The Volkswagen, on the other hand, exhibited loaded trap and regeneration results similar to the baseline without trap results. The tests with the low aromatic fuels gave lower average revertants per mile results than the comparable baseline tests for the Mercedes and the Volkswagen. However, there were considerable variations in the data and when these variations were taken into account, there were no significant differences in the mutagenic data for the two fuels. Additional analyses should be conducted before any conclusions are drawn. Average revertants per mile results for a 1982 Mercedes 240D and a 1982 Volkswagen (1.6 liter) operating on nine different fuels[14] are presented in Table 35 for comparison purposes. The results for these two vehicles were intermediate between the with and without trap results obtained in this program.

TABLE 34. AVERAGE AMES BIOASSAY RESULTS, REVERTANTS PER MICROGRAM OF EXTRACT

	Mercedes Revertants/μg extract			
	TA98 + S9	TA98 - S9	TA100 + S9	TA100-S9
Baseline with Trap				
FTP	11.1 ± 7.1[a]	16.5 ± 10.9	8.9 ± 7.0	7.9 ± 4.8
HFET	12.8 ± 4.4	39.0 ± 28.4	14.0 ± 2.6	13.7 ± 3.1
NYCC	9.9 ± 6.1	18.0 ± 15.7	8.4 ± 5.4	7.2 ± 5.4
Baseline without Trap				
FTP	16.0 ± 5.5	16.8 ± 4.9	15.9 ± 4.3	8.0 ± 3.6
HFET	16.3 ± 7.1	19.7 ± 5.4	12.0 ± 4.7	11.1 ± 5.1
NYCC	8.4 ± 1.3	10.2 ± 1.8	5.8 ± 3.2	12.0 ± 2.9[b]
Loaded Trap				
NYCC	6.0 ± 1.0[b]	7.0 ± 1.2[b]	5.3 ± 1.3[b]	3.7 ± 1.6[b]
Regeneration				
HFET	11.4 ± 4.5	22.5 ± 9.3	16.1 ± 4.7	12.1 ± 2.7
Low Aromatic without Trap				
FTP	8.0 ± 2.4	12.7 ± 2.0	8.7 ± 1.8	8.9 ± 2.4
	Volkswagen			
Baseline with Trap				
FTP	8.6 ± 1.9	12.7 ± 3.0	7.5 ± 2.8	9.7 ± 3.3
HFET	16.3 ± 4.3	17.2 ± 2.9	10.1 ± 4.0	13.0 ± 4.2
NYCC	2.9 ± 1.5	3.7 ± 1.4	6.9 ± 5.7	3.7 ± 3.0
Baseline without Trap				
FTP	10.7 ± 3.2	13.0 ± 2.5	12.4 ± 3.8	10.6 ± 2.6
HFET	14.0 ± 3.4	18.3 ± 2.7	14.0 ± 2.9	13.3 ± 3.4
NYCC	8.5 ± 3.8	22.6 ± 12.3	13.3 ± 4.1	17.4 ± 11.4
Loaded Trap				
NYCC	18.4 ± 2.0[b]	25.8 ± 4.2[b]	15.5 ± 3.1[b]	18.5 ± 7.9[b]
Regeneration				
HFET	44.7 ± 12.0	66.2 ± 12.3	26.5 ± 7.5	20.3 ± 9.1
Low Aromatic with Trap				
FTP	15.0 ± 5.6	20.4 ± 7.7	9.7 ± 3.4	8.1 ± 2.8
Low Aromatic without Trap				
FTP	9.5 ± 1.8	15.1 ± 4.8	10.5 ± 3.4	9.8 ± 2.0

[a]Standard deviation reflects both the variability for three analyses of each sample and the variability for the analysis of two independent samples from different vehicle tests.
[b]Only one sample analyzed. Standard deviation for multiple analyses of same sample only.

TABLE 35. AVERAGE AMES BIOASSAY RESULTS, REVERTANTS PER VEHICLE MILE

	Mercedes Revertants/mile x 10^{-5}			
	TA98 + S9	TA98 - S9	TA100 + S9	TA100-S9
Baseline with Trap				
FTP	0.39 ± 0.27[a]	0.67 ± 0.52	0.31 ± 0.25	0.24 ± 0.16
HFET	0.31 ± 0.11	0.94 ± 0.68	0.33 ± 0.06	0.32 ± 0.07
NYCC	0.87 ± 0.54	1.59 ± 1.39	0.73 ± 0.64	0.63 ± 0.47
Baseline without Trap				
FTP	4.86 ± 1.66	4.90 ± 1.50	4.58 ± 1.29	2.34 ± 1.07
HFET	3.70 ± 1.61	4.54 ± 1.24	2.85 ± 1.12	2.67 ± 1.23
NYCC	4.18 ± 0.65	5.07 ± 0.89	2.87 ± 1.58	5.87 ± 1.42[b]
Loaded Trap				
NYCC	1.22 ± 0.22[b]	1.51 ± 0.26[b]	1.39 ± 0.25[b]	0.72 ± 0.31[b]
Regeneration				
HFET	0.68 ± 0.39	1.15 ± 0.41	0.81 ± 0.29	0.59 ± 0.13
Low Aromatic without Trap				
FTP	1.98 ± 0.50	3.13 ± 0.41	2.19 ± 0.53	1.74 ± 0.46
	Volkswagen			
Baseline with Trap				
FTP	0.71 ± 0.24	1.08 ± 0.48	0.63 ± 0.30	0.83 ± 0.43
HFET	0.96 ± 0.25	0.96 ± 0.16	0.58 ± 0.23	0.75 ± 0.24
NYCC	0.39 ± 0.20	0.49 ± 0.19	0.93 ± 0.77	0.49 ± 0.40
Baseline without Trap				
FTP	4.22 ± 1.22	5.21 ± 1.21	4.95 ± 1.71	4.22 ± 1.29
HFET	3.00 ± 0.73	3.95 ± 0.58	3.00 ± 0.62	2.87 ± 0.73
NYCC	5.08 ± 2.27	13.47 ± 7.33	7.90 ± 2.44	10.36 ± 6.79
Loaded Trap				
NYCC	8.45 ± 0.93[b]	11.90 ± 1.91[b]	7.16 ± 1.40[b]	8.54 ± 3.66[b]
Regeneration				
HFET	6.71 ± 1.80	10.32 ± 1.92	3.95 ± 1.12	2.98 ± 1.34
Low Aromatic with Trap				
FTP	0.70 ± 0.33	0.96 ± 0.43	0.45 ± 0.20	0.37 ± 0.08
Low Aromatic without Trap				
FTP	2.30 ± 0.34	3.53 ± 0.97	2.49 ± 0.77	2.18 ± 0.39
Mercedes 240D Average for 9 different Fuels[c]				
FTP	1.06 ± 0.46	1.87 ± 0.75	2.07 ± 1.05	2.26 ± 1.28
Volkswagen (1.6 liter)[c] Average for 9 Fuels				
FTP	1.39 ± 1.07	2.04 ± 1.93	3.24 ± 3.52	3.33 ± 4.79

[a]Standard deviation reflects both the variability for the three analyses of each sample and the variability for the analysis of two independent samples from different vehicle tests.
[b]Only one sample analyzed. Standard deviation for multiple analyses of the same sample only.
[c]Results from a CRC - Cape-33-83 study.[14]

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APPENDICES

A-1. March 18, 1987 Letter from Mr. Harald Polz, Mercedes-Benz of North America, Inc. to Dr. Lawrence R. Smith, Southwest Research Institute

A-2. Volkswagen Jetta Shift Points

A-3. Letter of Transmittal with Failed Injectors from Volkswagen of America, Inc.

B. Computer Printouts for the Regulated Emissions, Mercedes

C. Computer Printouts for the Regulated Emissions, Volkswagen

D. Metals and Other Elements, Mercedes

E. Metals and Other Elements, Volkswagen

F. Aldehydes and Ketones, Sulfate, and Particulate Soluble Organic Fraction Mercedes

G. Aldehydes and Ketones, Sulfate, and Particulate Soluble Organic Fraction, Volkswagen

H. Gas Phase Semivolatile Organics, Mercedes

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J. Particulate Associated Semivolatile Organics, Mercedes

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L. 1,3-Butadiene, Mercedes and Volkswagen

M. Gaseous Volatile Organics, Mercedes

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O. Particulate Associated Volatile Organics

P. Mutagenic Activity Results