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Project Summary

Characterization of Emissions from Advanced Automotive Power Plant Concepts

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Emissions from three diesel cars using two fuel formulations were assessed. The three diesel cars included a prototype naturally aspirated Fiat 131, a prototype turbocharged Fiat 131, and a 1981 Oldsmobile Cutlass Supreme. Each Fiat was tested with and without a prototype catalytic trap. Vehicle operating procedures used for test purposes included the 1981 Federal Test Procedures, as well as the Highway Fuel Economy Test, the New York City Cycle, and an 85-km/h steady-state cruise. Both regulated and unregulated gaseous and particulate emissions were measured. Organic solubles in particulate were analyzed for various constituents and characteristics, including fractionation by relative polarity, benzo(a)pyrene, and mutagenic activity by Ames bioassay.

Application of the catalytic trap oxidizer system to the Fiat prototypes resulted in significant reductions of organic and carbon monoxide emissions under all transient driving conditions examined. Total particulate emissions were reduced an average of 55 percent with the turbocharged engine and 65 percent with the naturally aspirated engine. The Ames assay mutagenic response (revertants/μg) of the particulate phase organics was elevated by the catalytic exhaust aftertreatment device; however, the emission rates (revertants/km) were reduced an average of 66 percent with the turbocharged and 73 percent with the naturally aspirated engines.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Continuing concern for diminishing worldwide petroleum supplies has prompted a renewed interest in more efficient engine designs as alternates to gasoline engines now in wide use. Advanced-concept engines initially considered for emissions and fuel economy studies in this program were gas turbines Stirling cycle, turbocharged (TC) and naturally aspirated (NA) diesels, Rankine cycle, stratified charge, and advanced Otto-cycle. Actual engine availability permitted evaluation of only a prototype NA diesel, a prototype TC diesel, and a 1981 production NA diesel. Each prototype diesel was also evaluated with a prototype catalytic trap oxidizer system for particulate emissions control A "National Average" No. 2 fuel served as the "primary fuel" or base fuel. Although a "wide boiler" was initially considered as a "second" fuel,it became apparent that the test vehicles would need a higher-cetane distillate to run properly. Consequently, a "second" fuel which is basically a No. 2 home heating oil was chosen to provide a "worst case" comparison.

Because many emissions have potential impact on the public health, this study examined a substantial number of unregulated tailpipe emissions along with the regulated emissions (HC, CO, NO_x and particulate) The dynamometer driving schedules used included the 1981 Federal Test Procedure (three-bag FTP), four-bag FTP (cold 23-min FTP plus hot

23-min FTP), Highway Fuel Economy Test (HFET), New York City Cycle (NYCC), 85-km/h steady-state, and the "cold 505" (first 505 s of a cold-start FTP, used for smoke evaluation only).

Procedure

Vehicles

Three diesel-powered passenger cars were examined in this program. The automobiles included a prototype NA Fiat, a prototype TC Fiat, and a regular production 1981 Oldsmobile Cutlass coupe. The Oldsmobile Cutlass coupe was a low-mileage (less than 3,000 mi) rental vehicle, equipped with optional equipment, including automatic transmission, air conditioning, power steering, and power brakes. The prototype diesels were obtained from the Federal Department of Transportation, Research and Special Programs Administration, Cambridge, Mass.

Pretest vehicle preparations included draining of its fuel tank and fuel filter, and refilling them with the base-line fuel used in the program. The crankcase oil was also changed to new Quaker State SAE 30 SE/CC grade oil, and the oil filter was replaced with a new filter. Before actual testing began, each car was conditioned on the dynamometer at alternating speeds of 48, 64, and 80 km/h for approximately 80 km.

The Fiats were initially studied without exhaust aftertreatment, and subsequently with catalytic trap oxidizers. The injector pump timings were one degree before top dead center (TDC) on the NA Fiat, and three degrees after TDC on the TC Fiat at the manufacturer's specified pump lift. The timing was not altered with the addition of the particulate trap so as to not cloud or bias the emission results between the two different exhaust configurations. No significant operating difficulties were experienced with the three test vehicles during this project.

Fuels

Two distillate fuels were used in this program, a national average No. 2D (coded EM-329-F) and a higher aromatic No. 2 distillate, which is marketed as home heater oil. Detailed specifications are presented in Table 1.

Table 1. Properties of Test Fuels

Fuel Code Description	EM-329-F "Nat'l. Avg." No. 2	EM-469-F Couch No. 2 Fuel SWRI Analysis	EM-469-F Couch No. 2 Fuel EPA 6/80
Cetane Number	50.1		48.0
Cetane Index	52.1	48.1	48.1
Gravity, °API	37.5	35.2	35.2
Density, g/mL	0.837	0.849	0.849
Cloud point, °C (°F)	-8 (18)		
Flash point, °C (°F)	65 (149)		
Viscosity, cs	2.36		
Gum, mg/100 mL	14.3	12.9	
Total solids, mg/L	7.4		
Metals in fuel, x-ray	0		
Carbon, %	85.8		84.60
Hydrogen, %	13.0		14.81
Nitrogen, ppm	48		<100[a]
Sulfur, %	0.24	0.18	0.30
Aromatics, %	21.3		39.1
Olefins, %	1.7		0.9
Saturates, %	77.0		60.0
D86, IBP	191 (377)	172 (342)	182 (360)
°C, 5% point	211 (412)	206 (402)	
(°F) 10% point	219 (427)	219 (426)	218 (424)
20% point	231 (448)	231 (448)	
40% point	251 (484)	252 (486)	
50% point		262 (504)	262 (504)
60% point	269 (517)	272 (522)	
80% point	290 (554)	297 (567)	
90% point	307 (585)	315 (599)	309 (588)
95% point	323 (613)	332 (629)	
EP	340 (644)	344 (651)	337 (638)

In all emission tests conducted during this project, the vehicle was fueled directly out of a 18.9-L (5-gal) can through auxiliary fuel lines installed in the vehicle. At each fuel change, the vehicle fuel filter was removed and purged with test fuel. Afterwards, the vehicle was conditioned on the dynamometer for 48 km (30 mi) at alternating speeds of 48 km/h (30 mph), 64 km/h (40 mph), and 80 km/h (50 mph). At the start of the conditioning, the auxiliary fuel return line from the vehicle was removed from the test fuel can and directed to fill a separate waste-fuel 2000-mL container. Upon filling the container, the fuel return line was reconnected to the test fuel can to continue the conditioning and subsequent 23-min FTP prep prior to testing. In this manner, an effective conditioning of the exhaust system and proper flush of the engine fuel filter and lines were assured each time a fuel was changed in a vehicle.

Other Equipment

All emissions tests were conducted in accordance with procedures specified for Federal emission certification. A 50-hp Clayton ECE-50 passenger car dynamometer was used for all tests. The dynamometer has a direct-drive variable inertia system for simulation of vehicle mass from 454 kg (1000 lb) to 4082 kg (9000 lb) in 57-kg (125 lb) increments. The constant volume sampler (CVS) used for these studies included a 460-mm (18-in) diameter by 5-m (16-ft)-long dilution tunnel, which operated at a nominal flow rate of 12.9 m^3/min (455 ft^3/min). The dilution tunnel is shown schematically in Figure 1, along with sampling stations for the varied exhaust analyses conducted in this project. In addition to measurement of the regulated emissions total hydrocarbon, carbon monoxide, oxides of nitrogen, and total particulate, many unregulated emissions were examined. The specific compounds and analytical procedures are described in Table 2. The category "individual hydrocarbons" included the lower molecular weight compounds methane, ethane, ethylene, acetylene, propane, propylene, and benzene.

Driving Schedules

Emissions were examined using three transient driving schedules and one steady-state condition. The transient schedules included the FTP simulation of urban driving with an average speed of 31.4 km/h (19.5 mph), the HWFET simulation of expressway driving with an average speed of 77.6 km/h (48.2 mph), and the NYCC simulation of congested city central core driving with an average speed of 11.5 km/h (7.1 mph). The steady-state condition examined was 85.0 km/h (52.8 mph). The transient driving schedules are graphically illustrated in Figure 2.

Table 2. Sampling and Analysis Methodology for Unregulated Emissions

Exhaust Emissions Sampled	Constituent(s) Analyzed	Sampling Method	Analysis Method
gases	individual hydrocarbons	sample bag (CVS)	injection, GC/FID
	aldehydes	impinger	DNPH, GC/FID
	phenols	impinger	extraction, GC/FID
	hydrogen sulfide	impinger	methylene blue derivative, spectrophotometer
	total cyanide	impinger	cyanogen chloride derivative, GC/ECD
	ammonia	impinger	ion chromatograph
	organic sulfides	trap	injection, GC/FPD
	organic amines	impinger	GC/NPD with ascarite pre-column
	N-nitrosamines	ThermoSorb/N trap	GC coupled to TEA analyzer*
	gaseous hydrocarbons	trap	extraction, GC/FID
particulate	size distribution	impactor-filter	gravimetric
	trace elements	filter, 47 mm Fluoropore	x-ray fluorescence
	carbon, hydrogen, and nitrogen	filter, 47 mm glass	combustion/TC analyzer
	sulfate	filter, 47 mm Fluoropore	barium, chloranilate derivative (BCA), HPLC/UV
particulate organic solubles	organic solubles	500 x 500 mm filter	Soxhlet extraction, gravimetric
	benzo(a)pyrene (BaP)	---- ----	HPLC/fluorescence detection
	boiling point	---- ----	GC/FID
	carbon and hydrogen	---- ----	combustion/TC analyzer
	nitrogen	---- ----	oxidation pyrolysis/chemiluminescence
	biological response	---- ----	Ames bioassay
	polarity profile	---- ----	HPLC/fluorescence and UV detection
smoke	smoke (visible)	optical	EPA smokemeter (continuous)

If interferences occurred with GC/TEA analysis, a further analysis using HPLC/TEA was required.

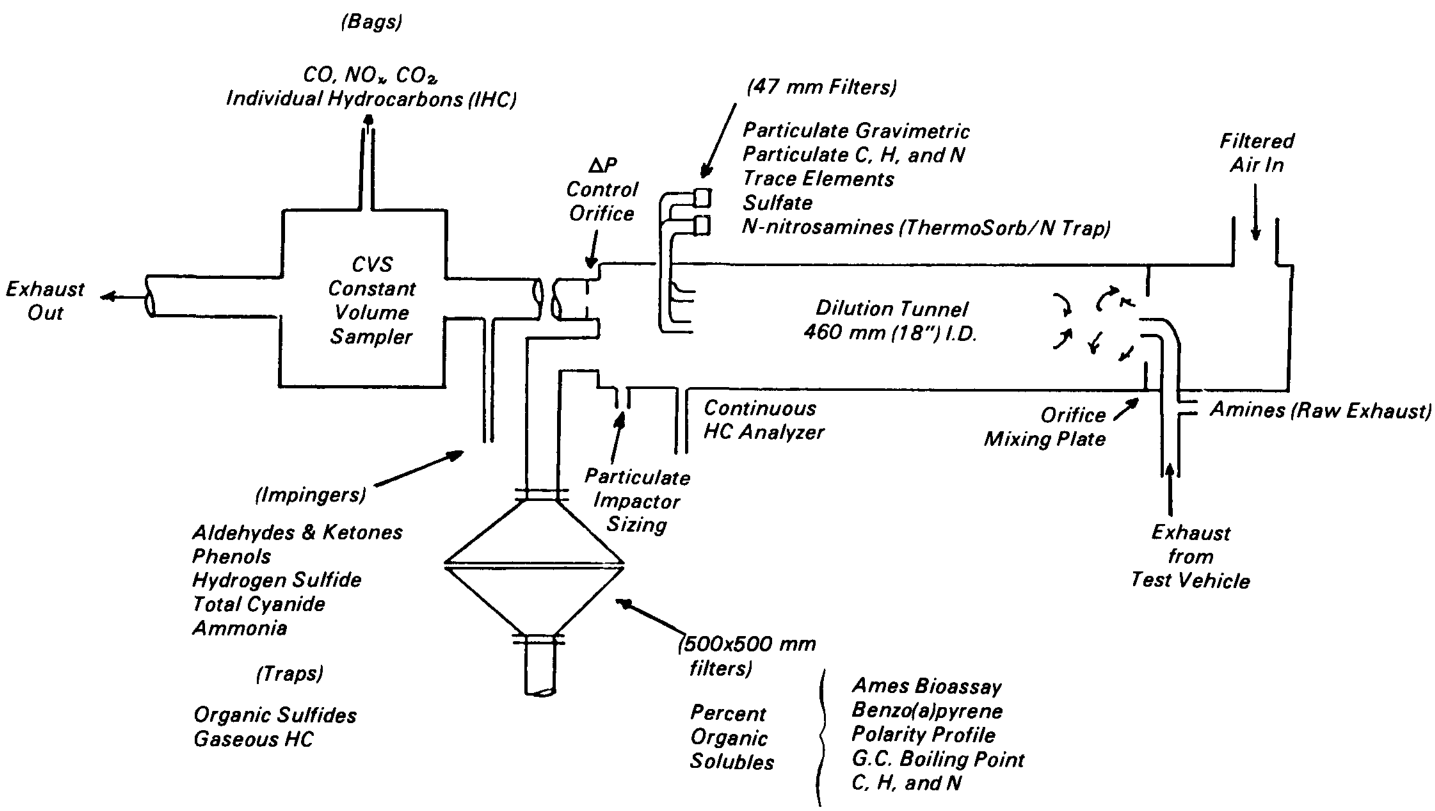

Figure 1. *Emissions sampling system.*

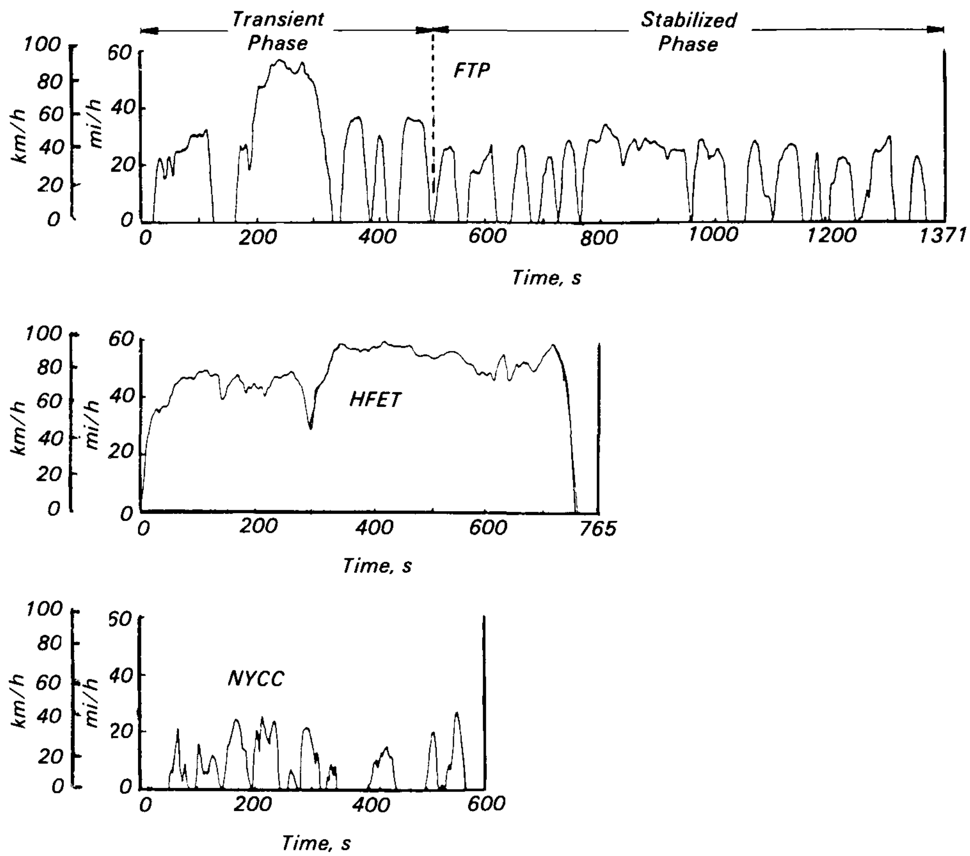

Figure 2. *FTP, HFET, and NYCC driving cycles vs time traces.*

Results and Discussion

The major purpose of this project was to evaluate many different emissions during dynamometer operation of a prototype NA Fiat 131 diesel with and without a catalytic particulate trap, a prototype TC Fiat 131 diesel with and without a catalytic particulate trap, and a 1981 production Oldsmobile Cutlass diesel, under varied transient and steady-state driving conditions. All test vehicles were operated using a "National Average" No. 2 fuel (EM-329-F) and a second No.2 fuel (EM-469-F), which was basically a home heating oil.

The project plan was organized to provide a substantial amount of information on regulated and unregulated emissions, with minimum repetitive testing. The total number of tests completed included 36 sequences consisting of a four-bag FTP, HFET, NYCC, and 85-km/h cycle each. In addition, more than 138 supplementary tests were completed consisting of 10 four-bag FTP, 30 hot-FTP, 17 HFET, 39 NYCC, 25 85-km/h, and 17 cold 505 cycles, and various trap regeneration tests.

An important finding in this project was the success of the catalytic traps in significantly reducing the various regulated and unregulated organic emissions from the NA and TC Fiats. An illustration of the trap oxidizer effectiveness in organic emissions control is provided in Figure 3, where HFID total hydrocarbon, soluble particulate phase organic (SOF), individual hydrocarbon (IHC), aldehyde and ketone, and phenol emissions are indicated for the FTP driving schedule. Similar observations were made with the other driving schedules.

The FTP emissions shown in Figure 3 were generally higher with EM-469-F than with EM-329-F, but not by substantial amounts. The highest emissions of HC, SOF, IHC, and aldehydes and ketones were from the Fiats without aftertreatment. The SOF was the largest portion of the total HC measured with the Fiats without aftertreatment, ranging from 25 th 46 percent of the total HC. Catalytic trap use on the two Fiats significantly reduced emissions of total HC, SOF, IHC, and aldehydes. Total hydrocarbons alone were reduced by an average of 83 percent on the NA Fiat, and by an average of 64 percent on the TC Fiat. Average reductions of SOF with catalytic traps were 96 and 88 percent for the Fiat NA and TC diesels, respectively.

In summary, the following observations were made during this study:

- Catalytic trap use on the NA and TC Fiats provided acceptable engine operation on all cycles and with each test fuel. Over its 1686 km (1048 mi) of use, the catalytic trap on the NA Fiat required regeneration every 422 km (261 mi) on the average, while the trap on the TC Fiat required no regeneration over the entire 1141 km (877 mi) of its use.
- Emissions of CO by the Fiat NA and TC vehicles were reduced by an average of 91 percent on the Fiat NA diesel and 80 percent on the Fiat TC diesel when the catalytic traps were used.
- With the trap the NO_x emissions from the NA Fiat were increased by an average of 17 percent. Trap operation on the TC Fiat reduced NO_x emissions slightly with EM-329-F and increased them slightly with EMF-469-F. The effect of trap back-pressure on the NO_x emission changes observed is not known, since trap backpressure was not monitored continuously during emissions testing performed on the Fiats.
- Regulated particulate emissions from the Fiats were lower for every cycle and fuel combination with catalytic trap than without, by an average of 65 and 55 percent on the Fiat NA and TC diesels, respectively. No major differences in particulate emissions were observed as a function of the test fuel for either vehicle or with any driving cycle examined.
- Methylene chloride soluble organics were significantly lower with the catalytic traps on the Fiat NA and TC diesels than without. Over the five cycles and two fuels, the average percent by weight of solubles decreased from 58 percent with no aftertreatment to 9 percent with trap for the NA Fiat, and from 34 percent with no aftertreatment to 10 percent with trap for the TC Fiat.
- Weak to strong positive mutagenic responses were obtained on all

organic solubles from particulate emitted by the five vehicle configurations and two fuels. Highest overall mutagenic response in revertants/μg was obtained with the trap-equipped Fiats. On the basis of revertants/km,however, the trap-equipped Fiats generally indicated the lowest mutagenic activity. Revertants/km of the Fiats with traps were reduced by an average of 73 percent on the NA Fiat and by an average of 66 percent on the TC Fiat as compared to corresponding cases without aftertreatment.

- Benzo(a)pyrene (BaP) emission rates ranged from "not detected" to 30.8 μg/km with most BaP emission rates less than 7.8 μg/km. Highest BaP emissions on each cycle and with each fuel were associated with the two Fiats without aftertreatment. Employing the catalytic trap, however, generally reduced BaP emissions by more than 82 percent on the NA Fiat, and by more than 53 percent on the TC Fiat.

- Fractionation of organic solubles by HPLC indicated that normalized relative response was generally lowest in the transitional region and highest in the polar region. There were no correlations between the normalized peak areas and the Ames abd BaP results.

- Aldehyde emissions were low and considerably scattered. Formaldehyde was generally the most abundant of the "total" aldehydes evaluated, and at times the only aldehyde detected. Highest formaldehyde emissions were from the Fiats without aftertreatment. Formaldehyde was reduced by more than 53 percent with the catalytic trap on the NA Fiat and by more than 43 percent on the TC Fiat. The FTP formaldehyde emissions from the trap-equipped Fiats were low (from "none detected" to 2.4 mg/km), and comparable to those obtained in a separate EPA study using low-mileage 1978 gasoline cars equipped with an oxidation-catalyst.

- Ammonia emission rates ranged from 0.43 to 118 mg/km, with most emissions measuring under 10 mg/km. Both cold- and hot- FTP ammonia emissions were reduced with the catalytic trap on the Fiat NA diesel.

- The phenol compound appearing most consistently and found in largest quantities throughout the study was 2,3,5,6-tetramethylphenol. Although "total" phenol emissions indicated considerable variation overall, the results did indicate some reduction of phenols with the trap-equipped Fiat.

- Carbonyl sulfide and methyl sulfide were present in the exhaust with all vehicle configurations, fuels, and test cycles examined. Emission rates ranged from 1.5 to 206 mg/km, and from 0.15 to 43 mg/km, respectively.

- The use of catalytic traps on both Fiats generally reduced their visible smoke. Overall, the lowest and highest smoke emitters were the NA Fiat with catalytic trap and the TC Fiat without aftertreatment, respectively.

- Particle aerodynamic size generally increased with trap use on the Fiat diesels. The largest particles were observed with the trap-equipped Fiat NA diesel with about 60 percent of the particle diameters measuring more than 0.1 μm.

- Elemental analysis indicated low hydrogen content in most of the particulate matter examined, suggestive of dry soot-like particulate material rather than oily material. There

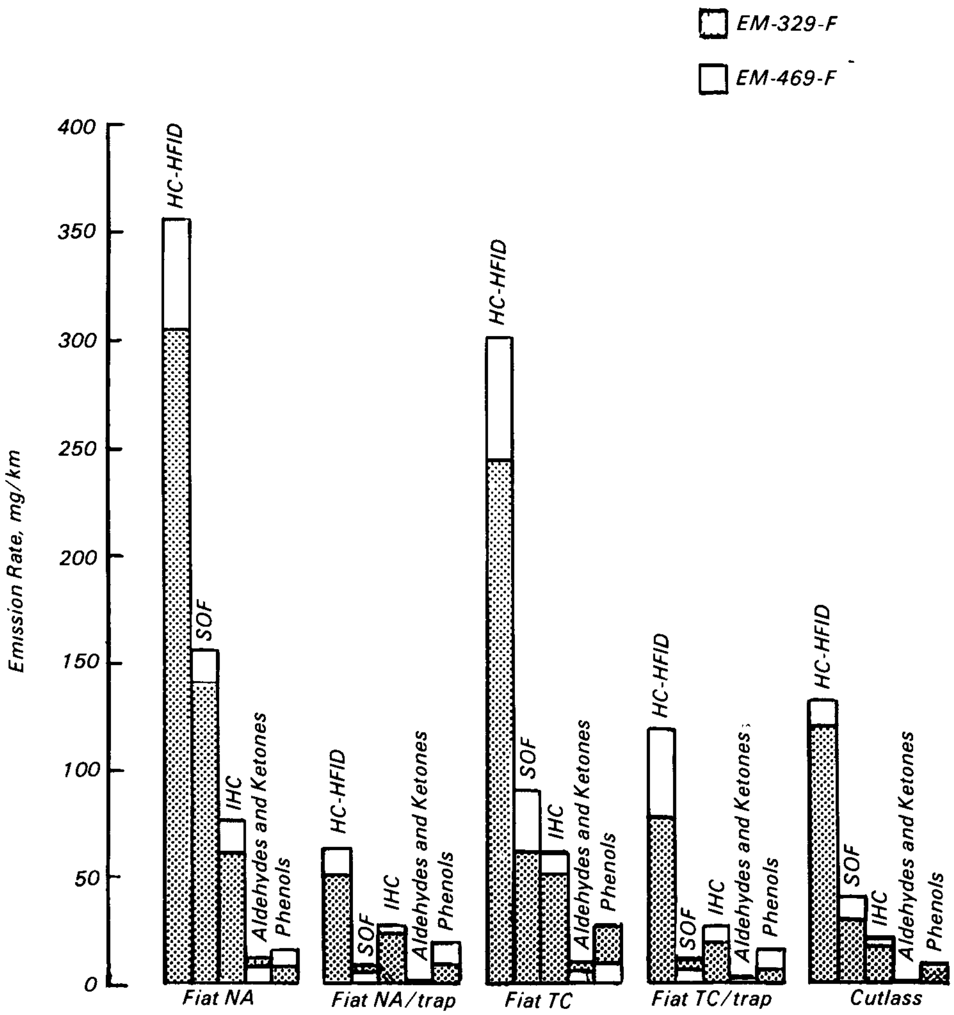

Figure 3. *FTP organic emissions of Fiat NA, Fiat TC, and 1981 Oldsmobile Cutlass diesel vehicles with EM-329-F and EM-469-F fuels.*

were no significant elemental content differences between fuels. Nitrogen in particulate matter averaged 0.5 percent overall.

- Sulfate emissions were increased by the catalytic trap in the HFET, NYCC, and 85-km/h sequences with the Fiat NA diesel, but were decreased in all cycles with the Fiat TC diesel. The largest trap-related increase in sulfate, as percent of particulate, occurred in the HFET and NYCC tests with the Fiat NA diesel (sulfate emissions were not examined during trap regeneration).

- Trace elements most commonly found in particulate matter from the test vehicles included sulfur, magnesium, aluminum, zinc, silicon, calcium, iron, barium, and phosphorus. Sulfur and iron generally accounted for more than 50 percent of the "total" trace element emissions in each cycle. Overall the emitted elements ranged from 1.2 to 11.8 percent of the total particulate emissions. Trace element emissions greater than 3 percent of the total particulate emission rate were observed only with the trap-equipped Fiats.

- Analysis for carbon, hydrogen, and nitrogen in the particulate organic solubles indicated the presence of hydrocarbon-like materials with numeric H/C ratios between 1.58 and 1.95. The lowest H/C ratios were observed with the catalytic-trap-equipped Fiats, which may indicate a higher content of unsaturated hydrocarbons with the trap than without the trap.

Conclusions and Recommendations

The potential for substantial reduction of organic, carbon monoxide, and particulate emissions from light-duty diesel motor vehicles by using catalytic trap oxidizer exhaust aftertreatment devices was demonstrated. The examined system required a modified engine operation schedule to achieve trap regeneration when necessary to avoid excessive engine backpressures. Emissions during trap regeneration were not examined. When production trap-equipped diesel motor vehicles become available, further emissions characterization, to include emissions during trap regeneration, should be undertaken. Emphasis should be directed to sulfate emissions.

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The complete report, entitled "Characterization of Emissions from Advanced Automotive Power Plant Concepts," (Order No. PB 85-126 126; Cost: $35.50, subject to change) will be available only from:
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