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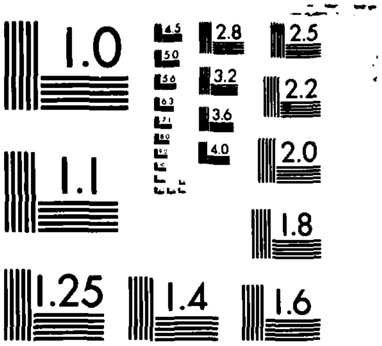
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ESL-TR-84-61

Composition and Photochemical Reactivity of Turbine Engine Exhaust

C. W. SPICER
M. W. HOLDREN
F. F. LYON
R. M. RIGGIN

JUNE 1985

FINAL REPORT

MARCH 1983 - SEPTEMBER 1984

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This study was carried out to augment the results of an earlier investigation of turbine engine emissions ~~(Reference 2)~~. Experiments were conducted to investigate the photochemical reactivity and biological activity of exhaust from a full-scale 60° sector combustor from a TF-39 turbine engine. All experiments were carried out at idle power setting. The study utilized exhaust from two conventional petroleum fuels (JP-4 and JP-5) and a shale fuel meeting JP-4 specifications. Photochemical reactivity was studied with two large ($8m^3$)n Teflon outdoor environmental chambers. Photochemical reactivity is defined for purposes of this study as the maximum ozone concentration produced during a one day irradiation in natural sunlight.

Experiments were undertaken with a TF-39 combustor operating on JP-4 and JP-5 fuels, for comparison with previous studies of a full-scale TF-39 engine ~~(Reference 2)~~. The combustor exhaust was more reactive than exhaust from the full-scale engine, regardless of which fuel

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Reactivity of Turbine Engine Exhaust. (Further Investigations of Reactivity and Bioactivity)

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was burned. The combustor exhaust was 60 percent more reactive than engine exhaust for JP-5 fuel, and between 30 and 100 percent more reactive for JP-4 fuel.

The photochemical reactivity of exhaust generated from a shale oil-derived fuel meeting JP-4 specifications was studied. Exhaust from the shale fuel was no more reactive than exhaust from petroleum fuels, and under some circumstances was actually less reactive. The shale fuel exhaust also generated less secondary aerosol than exhaust from the petroleum fuels. The use of shale-derived fuel in turbine engines should provide mutual benefits in reducing both the photochemical production of ozone and secondary aerosol in the exhaust.

Experiments were undertaken to permit estimation of the photochemical reactivity of equal volumes of exhaust from two full-scale engines studied previously (Reference 2). The results suggest that the reactivity of equivalent volumes of exhaust from the two engines is similar, even though organic emissions from one of the engines is 2-3 fold lower.

Large volume (30 m^3) samples of exhaust from JP-4, JP 5, and shale-derived JP-4 fuels were collected for assessment of biological activity. The exhaust was sampled through heated (150°C), tared, quartz fiber filters and then XAD-2 adsorptive resin, to collect nonvolatile and volatile compounds, respectively. Results of the bioassay experiments are not yet available and will be reported separately.

PREFACE

This report was prepared by Battelle, Columbus Laboratories, Columbus, Ohio 43201, under Contract Number F08635-82-C-0131 for the Air Force Engineering and Services Center, Engineering and Services Laboratory (AFESC/RD), Tyndall Air Force Base, Florida 32403. Co-sponsors of the study include the Naval Air Propulsion Center of the U.S. Navy, and the Federal Aviation Administration.

An earlier interim report (ESL-TR-82-42) described the preliminary studies and the final report (ESL-TR-84-28) described the experimental aspects of the research on composition and photochemical reactivity of turbine engine exhaust. This supplement to the final report describes additional experiments carried out to address the following three areas: (1) comparative photochemical reactivity of combustor rig, (2) effects of exhaust organic concentration on measured photochemical reactivity, and, (3) photochemical reactivity of exhaust from production shale-derived fuel. This work was performed between March 1984 and September 1984. AFESC/RDV project officer was Major Richard E. Padgett.

Principal research staff at Battelle included Mr. M.W. Holdren, Dr. R.M. Riggin, and Dr. C.W. Spicer. Assistance in conducting the program was provided by Mrs. D.L. Smith, Mr. R.N. Smith, Mr. G.F. Ward, Mr. J.R. Koetz, Dr. M.R. Kuhlman, Mr. C. Bridges, Mr. L.W. Miga, and Mrs. M.A. Roberts. Engine and combustor testing were conducted with assistance from personnel at the GE Evendale Combustion Laboratory and the GE Peebles Test Operation. Mr. T.F. Lyon and Mr. E. Rogala provided technical direction and program management for the General Electric subcontract. Battelle Program Manager was Dr. C.W. Spicer.

This report has been reviewed by the Public Affairs Officer (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication.

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Robert E. Boyer
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Laboratory

ROBERT F. OLFENBUTTEL, Lt Col, USAF, BSC
Chief, Environics Division

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SECTION I

INTRODUCTION

Emissions from jet aircraft engines may pose a threat to the health and well-being of flight line personnel, and to the air quality downwind of airports. To gain a better understanding of the impact of jet engine exhaust, the U.S. Air Force, U.S. Navy, and Federal Aviation Administration sponsored a study of the detailed composition, photochemical reactivity, and bioactivity of turbine engine emissions. The study involved the development and validation of sampling and analysis methods, preliminary experiments with a full-scale 60^{o}-sector combustor rig, and extensive experiments with two different full-scale turbine engines. These latter experiments investigated the detailed composition, atmospheric photochemical reactivity, and bioactivity of emissions from two conventional petroleum-based fuels and a shale-derived fuel. The results of this study have been reported in two volumes; "Turbine Engine Exhaust Hydrocarbon Analysis--Interim Report on Task 1 and 2" (Reference 1) and "Composition and Photochemical Reactivity of Turbine Engine Exhaust" (Reference 2).

Analysis of the results from the full-scale engine experiments raised some questions which could not be addressed with the available data. These questions fall into four categories:

(1) comparative photochemical reactivity of combustor rig and turbine engine exhaust

(2) effects of exhaust organic concentration on measured photochemical reactivity

(3) photochemical reactivity of exhaust from production shale-derived fuel

(4) relative bioactivity of exhaust from conventional fuels and shale-derived fuels.

The purpose of this report is to describe additional experiments carried out to address the above questions using a full-scale 60^{o}-sector combustor from a TF-39 engine.

SECTION II

EXPERIMENTAL

Experiments were conducted using a full-scale 60°-sector combustor from a General Electric TF-39 engine. All experiments were run at idle power setting. The combustor rig facility, combustor, and associated monitoring instruments have been described previously (Reference 1). Exhaust was sampled by four gas-sampling rakes connected to a manifold. The exhaust stream used for photochemical reactivity studies and bioassay sample collection passed from the manifold through a steam-cooled stainless steel tube to a heated, large-bore, stainless steel Whitey ball valve. This valve was used to meter the exhaust flow to the photochemical reaction chambers and the bioassay sample-collection system. After passing through the valve, the exhaust stream was filtered through a 14 cm diameter preweighed quartz fiber filter in a stainless steel filter holder, and then transferred through a flexible 100-foot by 1/2-inch heated Teflon® sample tube. The entire sampling line, including the valve, filter, and Teflon® tubing, was maintained at 150°C. For photochemical reactivity experiments, the exhaust was introduced into 8 m^3 Teflon® environmental chambers using this sampling scheme. It required 5-8 minutes at an exhaust stream flow rate of approximately 40 lpm to attain a chamber hydrocarbon concentration of 10 ppmC. With one exception, the environmental chambers were filled before sunrise and the photochemical reactivity monitored from dawn through midafternoon. The exception occurred on a day when the combustor rig was unavailable until late morning. In this case, the chambers were loaded just prior to noon, and the reactions were monitored through the afternoon hours. Exhaust aldehyde and dialdehyde levels were estimated from measurements made after the exhaust was diluted with ultraclean air in the environmental chamber. Immediately after the chambers were loaded, a 40-liter sample was collected at 2 lpm in a solution of dinitrophenyl hydrazine in acetonitrile. These samples were subsequently analyzed by HPLC for aldehydes and dialdehydes, as described in Reference 2. Dilution factors derived from total hydrocarbon levels in the exhaust and the chamber were used in conjunction with the chamber aldehyde measurements to estimate the levels of aldehydes in the exhaust. The photochemical reaction chambers, monitoring instrumentation, reference mixture composition, and procedures were identical to those employed in the full-scale engine experiments, and may be found in Reference 2.

Collection of samples for biological assay made use of the exhaust-handling apparatus described above. The exhaust stream passed through a clean preweighed quartz fiber filter at 150°C and then to a water-cooled condenser and a glass trap containing 150 grams of XAD-2 resin. The temperature of the XAD-2 resin was maintained below 38°C to avoid decomposition of the resin. After leaving the XAD-2 trap, the exhaust stream passed through a dry test meter used to monitor flow and total sample volume. The volume of exhaust sampled for each biological assay collection was 30 m^3, at a flow rate of 0.14 m^3-min^{-1} (~5 cfm).

SECTION III

RESULTS

Combustor rig experiments were conducted at General Electric's Evendale, H facility from August 23 to October 2, 1984. Six outdoor smog chamber xperiments were carried out during this period to investigate atmospheric hotochemical reactivity issues. The dates and conditions of the chamber xperiments are noted in Table 1. The weather on the days of the outdoor hamber experiments was clear, sunny, and warm, except for the September 6, 1984 experiment, which had cool, partly cloudy weather in the morning. his experiment was repeated under clear skies on October 2, 1984. Three ifferent fuels were used to generate the exhaust employed in these experients. Conventional petroleum-based fuels JP-4 and JP-5 were used, along ith a shale-derived fuel meeting JP-4 specifications. The shale JP-4 uel was provided by the Air Force from a preproduction refinery run. he final production run shale fuel was not available at the time of hese experiments, but the preproduction fuel used here is within the pecifications of the final production run fuel (Reference 3).[1]

Large volume (30 m^3) samples of exhaust from each of the three fuels ere collected through quartz fiber filters and XAD-2 traps for biological ssay. Dilute samples of exhaust from each fuel also were collected for ubsequent aldehyde and dialdehyde determination.

It is convenient to present the results of these experiments in hree parts: photochemical reactivity, aldehyde composition, and biological ssay.

. RESULTS OF PHOTOCHEMICAL REACTIVITY EXPERIMENTS

Photochemical reactivity is defined for purposes of this study as he maximum ozone concentration produced during a 1-day irradiation in atural sunlight (Reference 2). The conditions and results from the six hotochemical reactivity experiments are summarized in Table 1. As noted bove, the weather was clear, sunny, and warm for all experiments except R-5. All experiments were performed with exhaust generated at engine dle. Four of the six experiments employed a reference mixture of organic

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[1] Personal communication from T. Dues, Wright-Patterson AFB, OH, 1984.

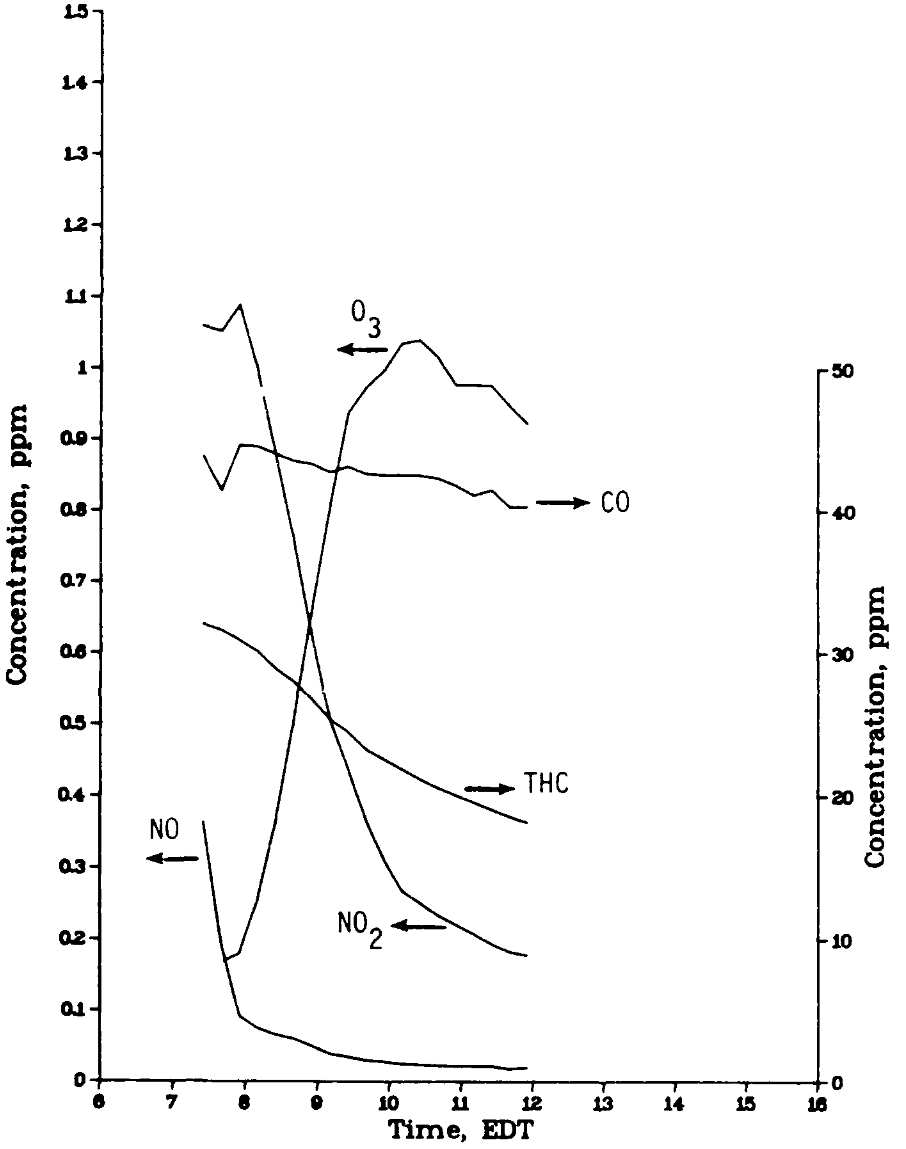

Figure 12. Smog Chamber Profiles From CR-4, Chamber B

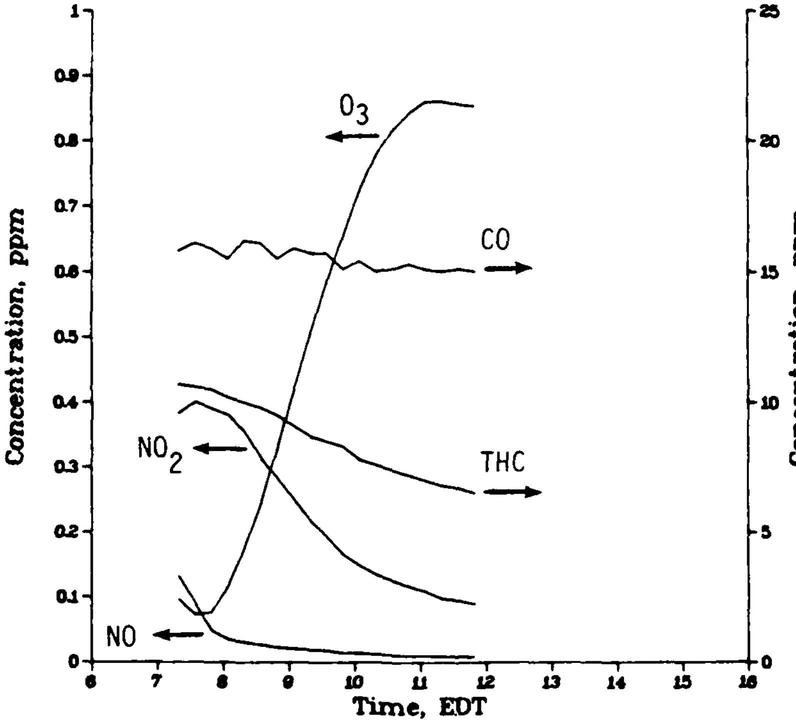

Figure 11. Smog Chamber Profiles From CR-4, Chamber A

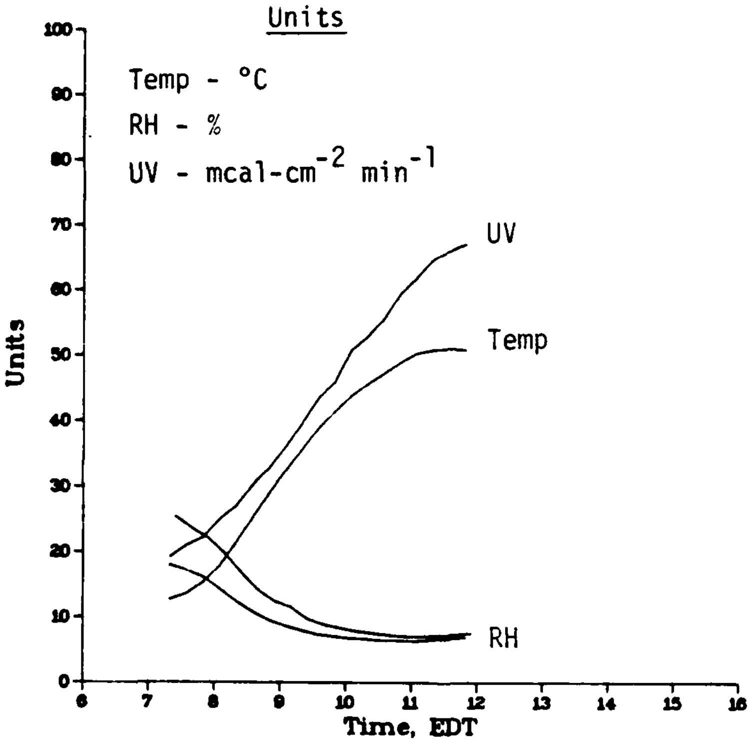

Figure 10. Profiles From Chamber Experiment CR-4

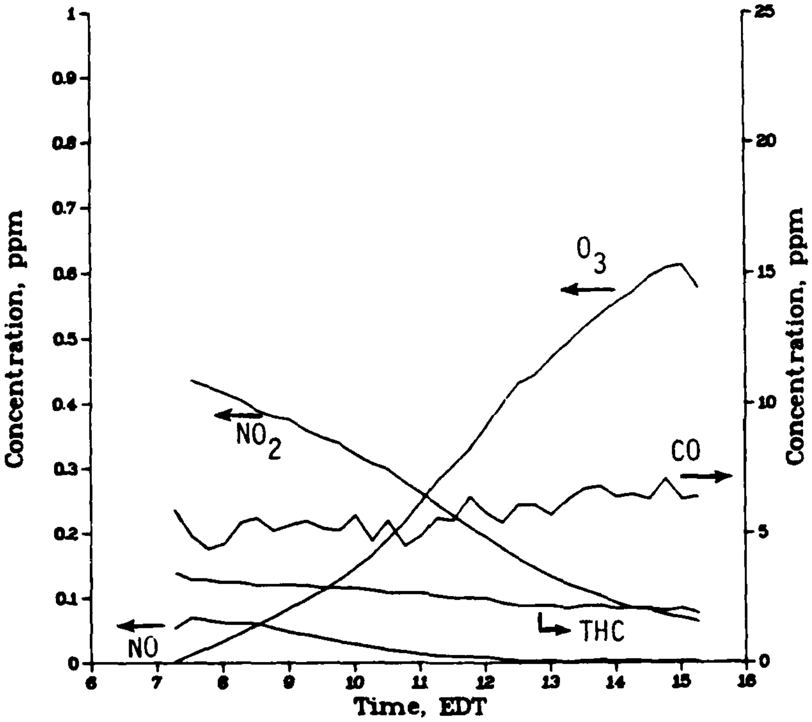

Figure 9. Smog Chamber Profiles From CR-3, Chamber B

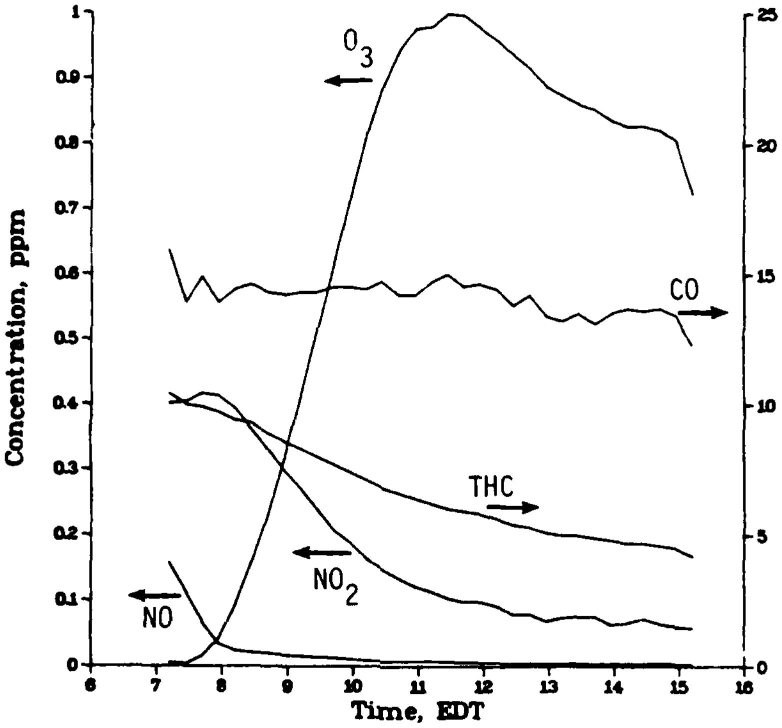

Figure 8. Smog Chamber Profiles From CR-3, Chamber A

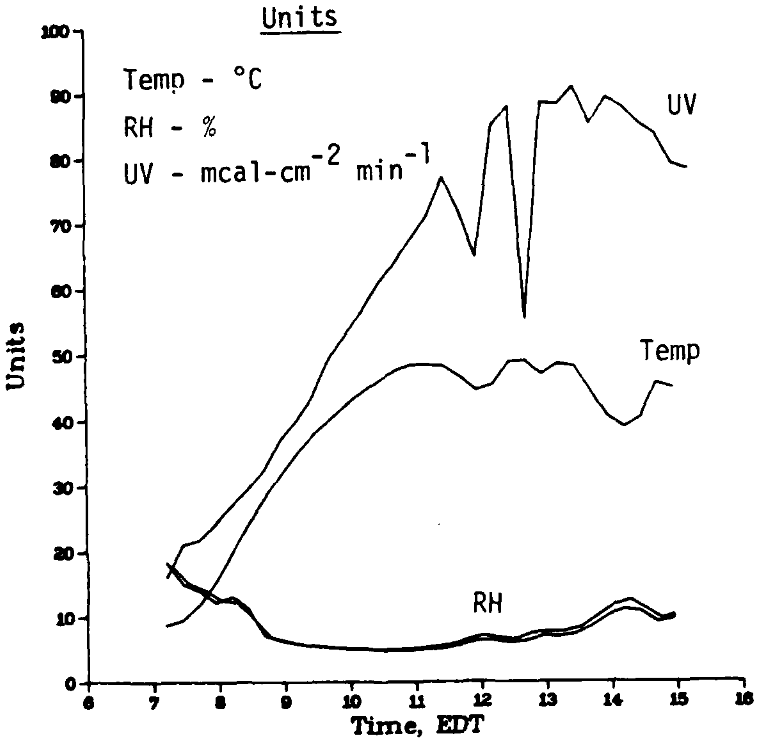

Figure 7. Profiles From Chamber Experiment CR-3

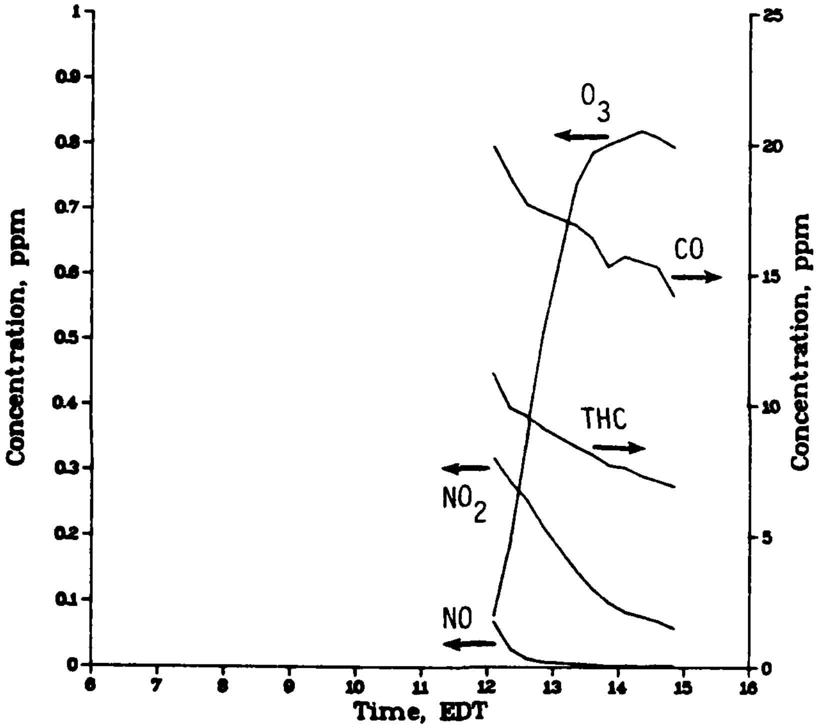

Figure 6. Smog Chamber Profiles From CR-2, Chamber B

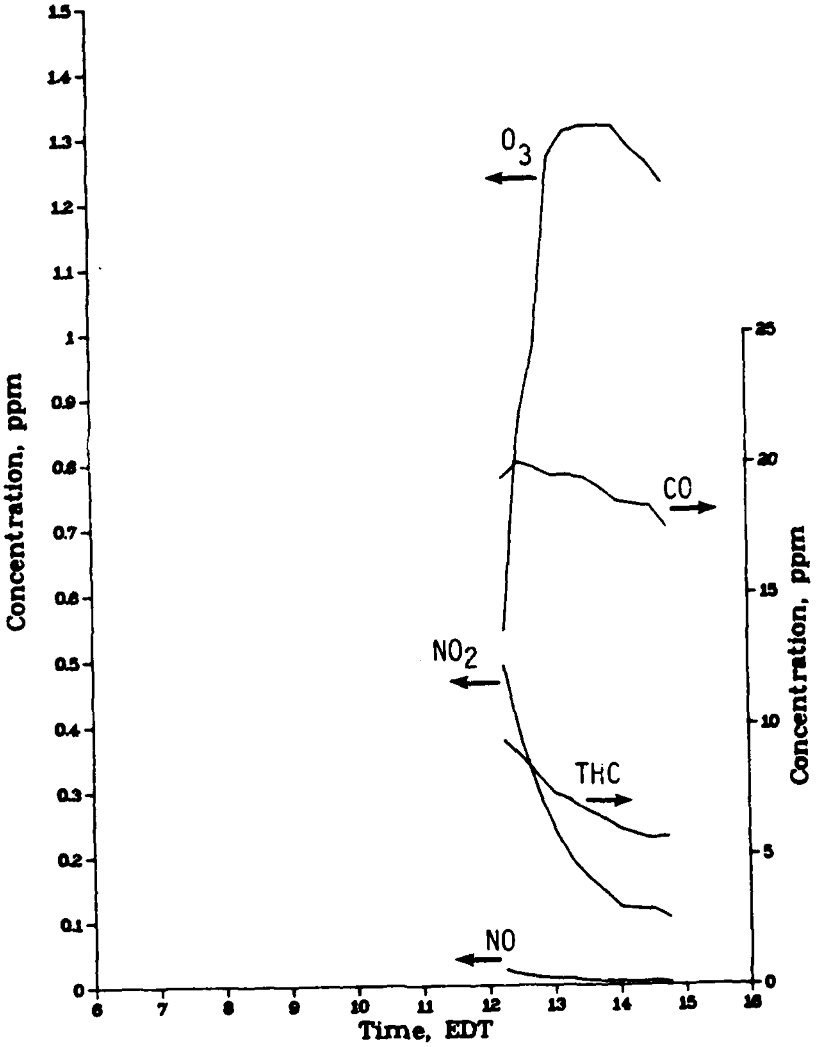

Figure 5. Smog Chamber Profiles From CR-2, Chamber A

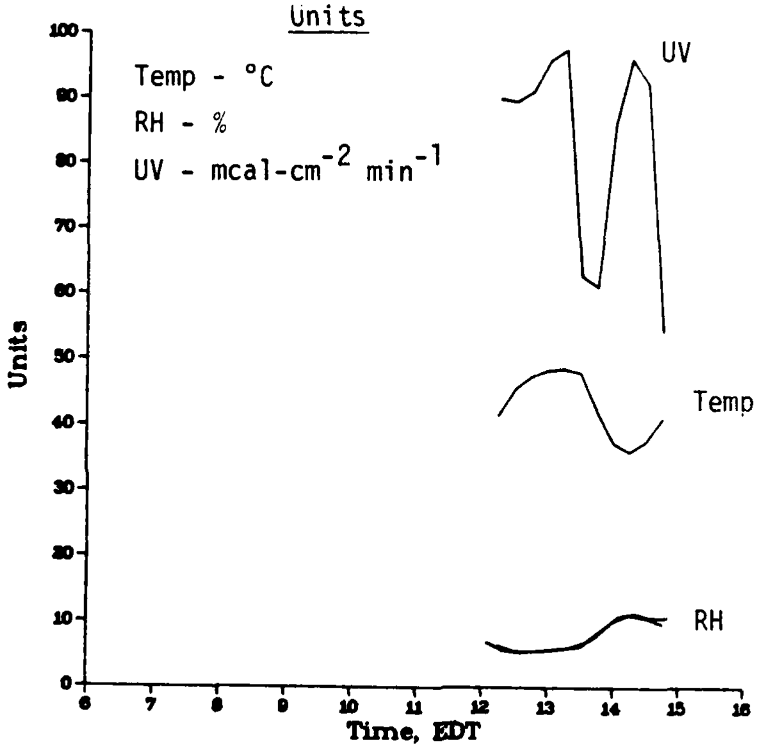

Figure 4. Profiles From Chamber Experiment CR-2

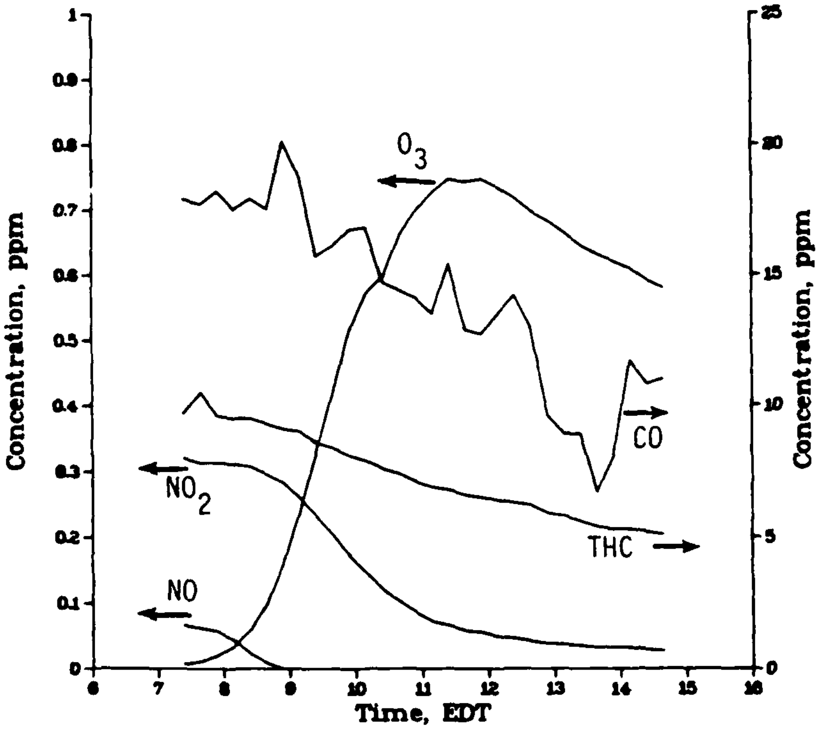

Figure 3. Smog Chamber Profiles From CR-1, Chamber B

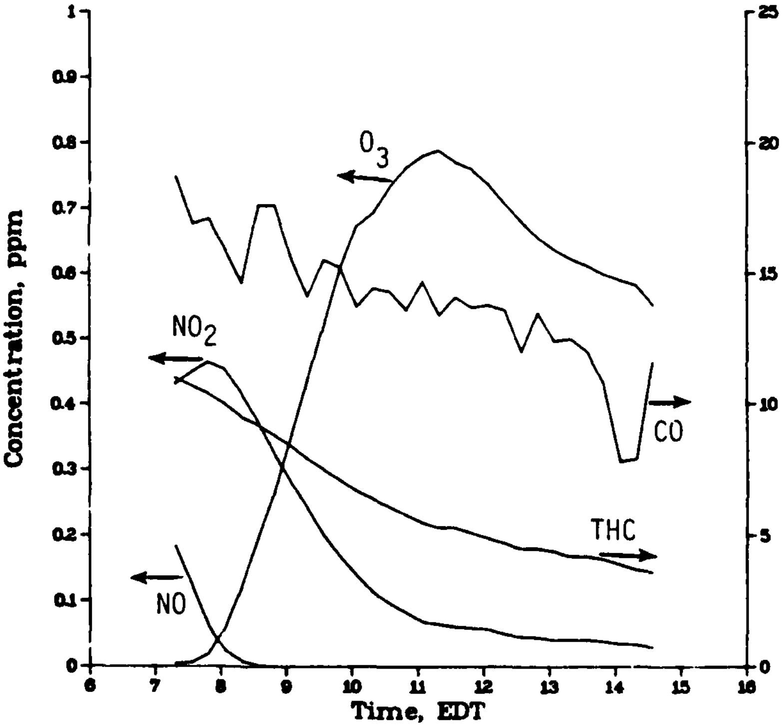

Figure 2. Smog Chamber Profiles From CR-1, Chamber A

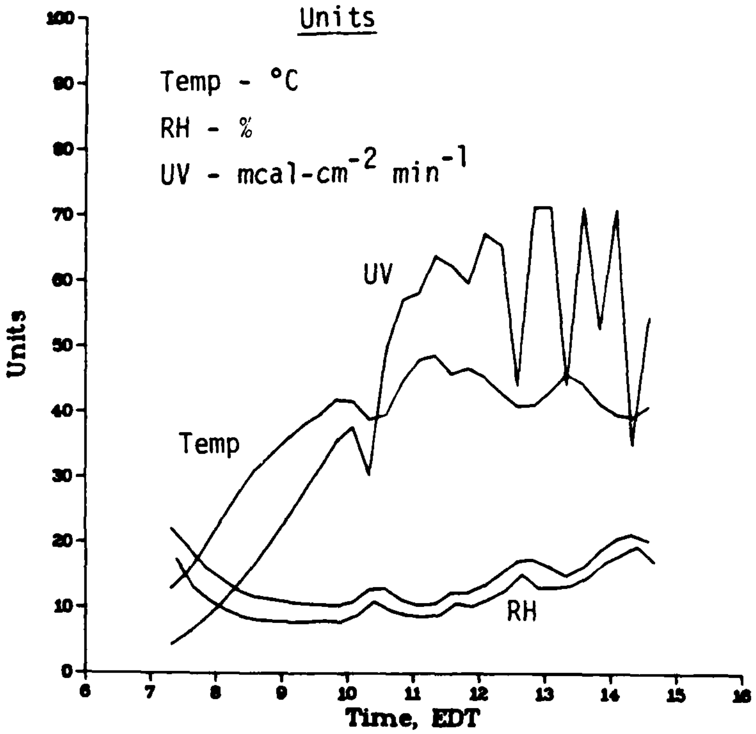

Figure 1. Profiles From Chamber Experiment CR-1

compounds, NO_x, and CO in one of the 8 m^3 chambers, to normalize the exhaust reactivity results with respect to daily variations in weather. The same reference mixture was used in the earlier full-scale engine experiments (Reference 2), providing a means of comparing the reactivity of the exhaust from the full-scale engines and the combustor rig. The remaining two experiments employed different levels of exhaust in each chamber to investigate the influence of organic concentration on reactivity. The maximum ozone concentrations reported in Table 1 represent the highest 3-minute average obtained during an experiment. The light-scattering coefficient, b_{scat}, is a measure of the amount of particulate matter present in the chamber. This measurement was always made at the end of the experiments, after ozone concentration had peaked. The exhaust was filtered before it was introduced into the chambers, so any aerosol found at the end of the experiment is secondary in nature; i.e., it was produced by chemical reactions during the experiment.

The results of the individual experiments are shown graphically in Figures 1-18.

B. RESULTS OF ALDEHYDE MEASUREMENTS

Samples of dilute exhaust were collected from the chambers before sunrise to determine aldehyde concentrations. Forty-liter samples were collected in DNPH/acetonitrile solution, as described in Reference 2. The aldehyde concentrations measured in the chambers were used to calculate exhaust aldehyde levels. The ratio of total hydrocarbon concentration in the exhaust and in the chamber was used to adjust the chamber aldehyde concentrations for dilution. Aldehyde measurements were made with exhaust from JP-4, JP-5, and shale-derived JP-4 fuels. The results of these measurements are given in Table 2.

C. RESULTS OF BIOLOGICAL ASSAY COLLECTIONS

Exhaust samples were collected for biological assay with the combustor operating at idle power. Exhaust was generated,using each of the three fuels, JP-4, JP-5, and shale-derived JP-4. The nominal flow rate was 0.14 $m^3\text{-}min^{-1}$ over a period of 3.5 hours, for a total volume of 30 m^3.

TABLE 1. SUMMARY OF COMBUSTOR RIG PHOTOCHEMISTRY EXPERIMENTS

			Chamber A			Chamber B		
Experiment	Date	Fuel	Initial Concentration/ Source of Total Hydrocarbon ppmC	Max. Ozone, ppb	b_{scat}[a], 10^{-4} m^{-1}	Initial Concentration/ Source of Total Hydrocarbon, ppmC	Max. Ozone, ppb	b_{scat}[a], 10^{-4} m^{-1}
CR-1	8-23-84	JP-5	10/exhaust	788	18.0	10/reference	746	0.2
CR-2	8-24-84	JP-4[b]	10/exhaust	1315[b]	12.0	10/reference	821[b]	0.5
CR-3	8-25-84	JP-4	10/exhaust	992	8.3	3.3/exhaust	612	0.5
CR-4	8-27-84	JP-4	10/exhaust	859	12.0	30/exhaust	1040	84.0
CR-5	9-26-84	Shale JP-4[c]	10/exhaust	437[c]	2.3	10/reference	416[c]	0.5
CR-6	10-2-84	Shale JP-4	10/reference	749	0.5	10/exhaust	631	3.9

[a] Light scattering aerosol coefficient.

[b] Experiment initiated at 1145 EDT.

[c] Partly cloudy.

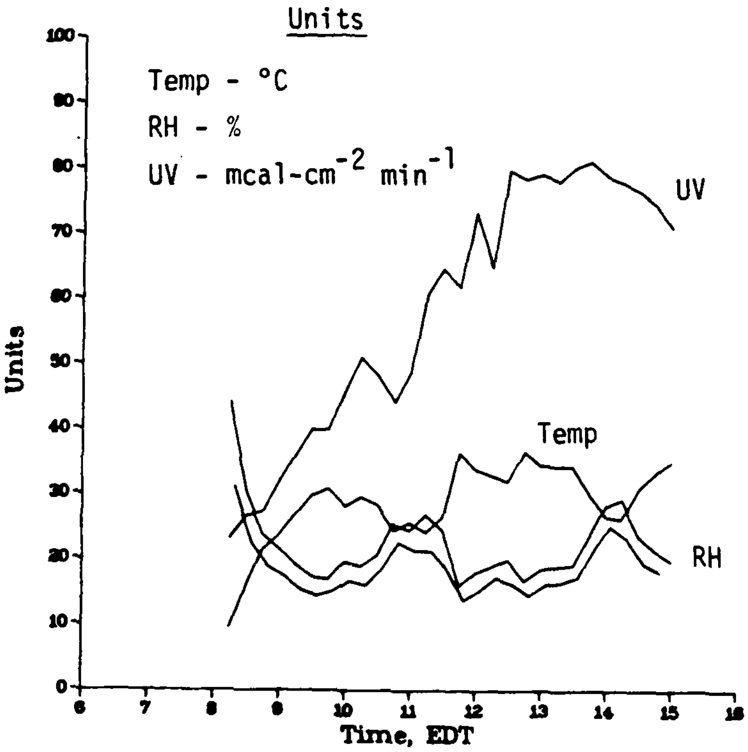

Figure 13. Profiles From Chamber Experiment CR-5

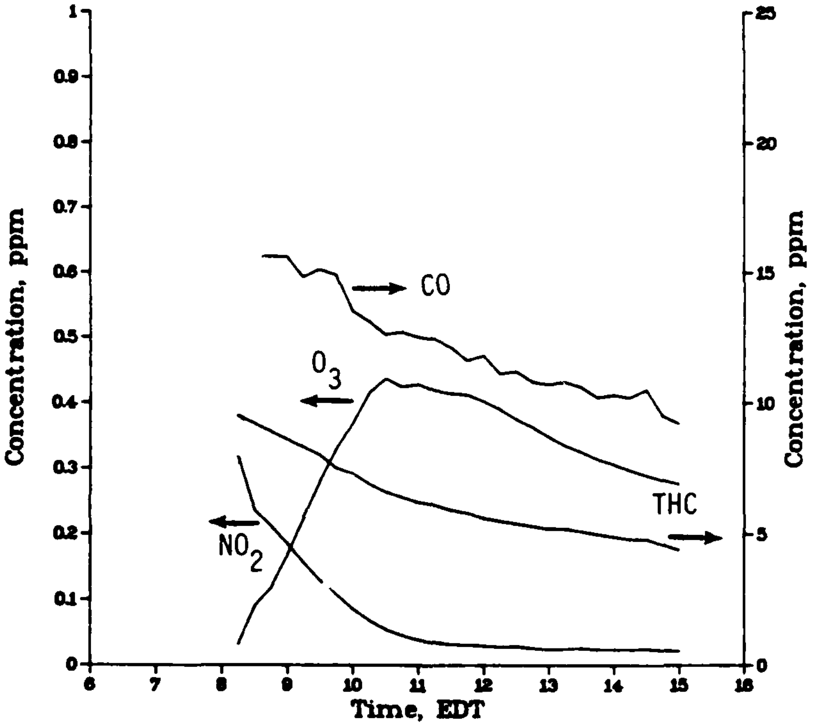

Figure 14. Smog Chamber Profiles From CR-5, Chamber A

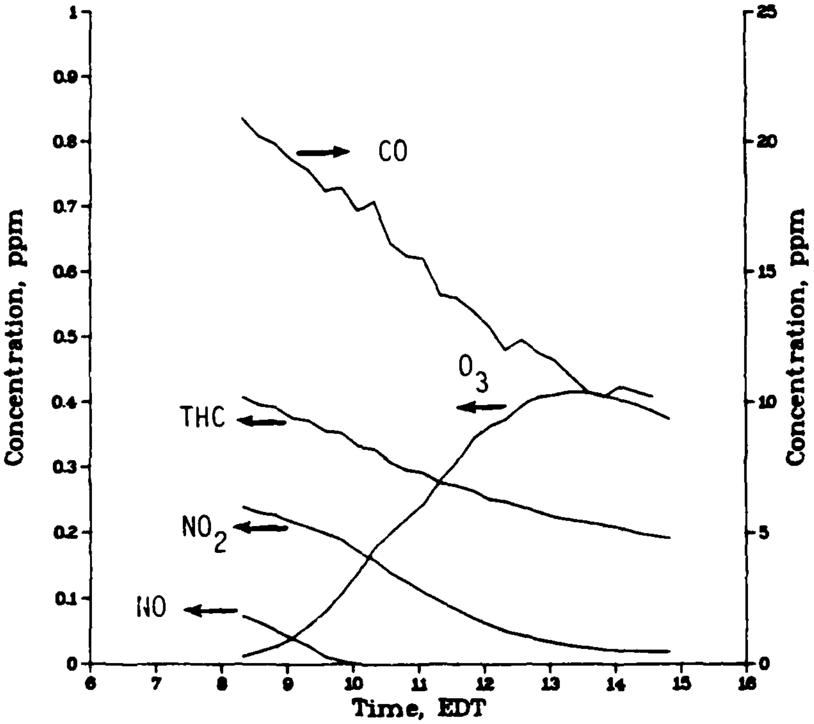

Figure 15. Smog Chamber Profiles From CR-5, Chamber B

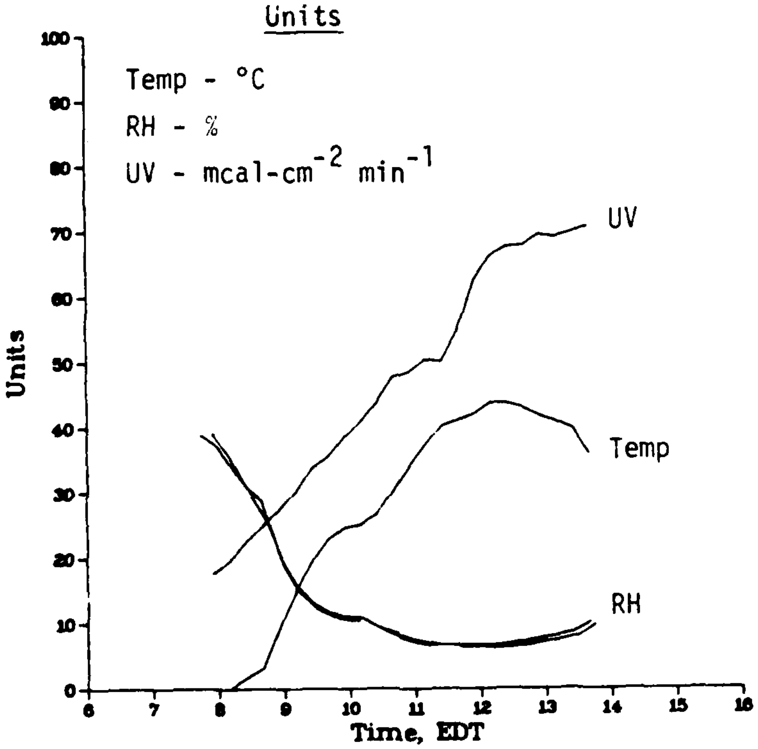

Figure 16. Profiles From Chamber Experiment CR-6

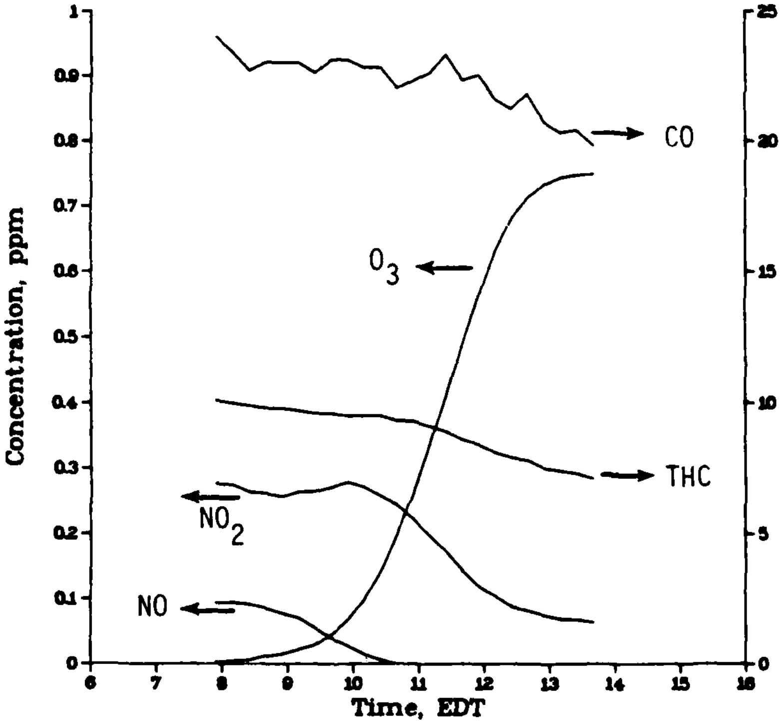

Figure 17. Smog Chamber Profiles From CR-6, Chamber A

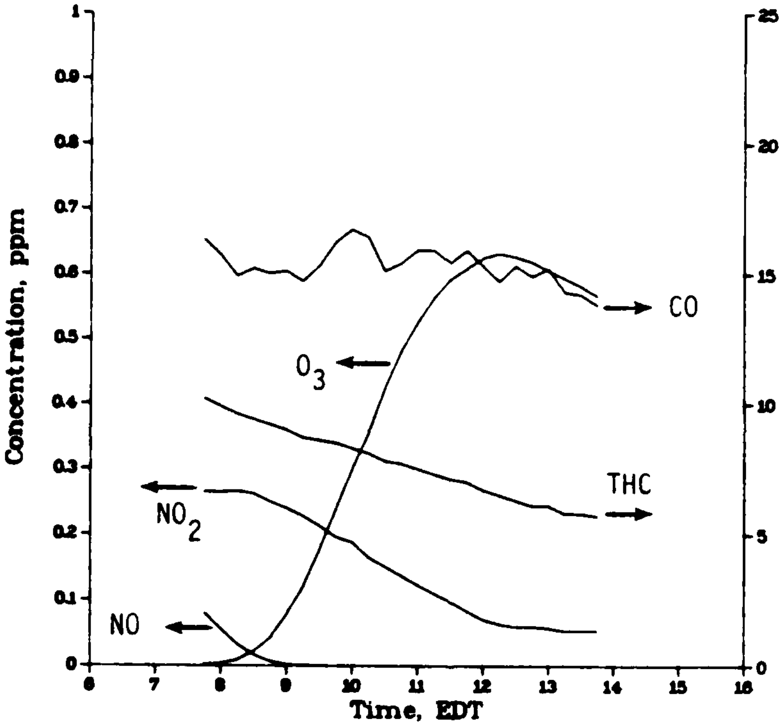

Figure 18. Smog Chamber Profiles From CR-6, Chamber B

TABLE 2. ALDEHYDE AND DIALDEHYDE CONCENTRATIONS IN COMBUSTOR RIG EXHAUST (ppmV)

Compound	Fuel: Experiment:	JP-5 CR-1	JP-4 CR-3	Shale JP-4 CR-5
Formaldehyde		28.4	20.7	14.1
Acetaldehyde		5.5	3.3	ND[a]
Acrolein		3.1	0.8	ND[a]
Propanal		1.3	ND[a]	ND[a]
Benzaldehyde		0.3	ND[a]	ND[a]
Glyoxal		0.41	0.60	1.06
Methylglyoxal		0.14	0.10	0.45

[a] ND = not determined.

The mass of material collected on the particle filter, and the mass of extractable material collected on the filters and in the XAD-2 traps are reported in Table 3. The biological assays will be performed by the Health Effects Research Laboratory, U.S. EPA, under a separate agreement with the Air Force. The results of the bioassay experiments are not yet available, and will be reported separately at a later date.

TABLE 3. CHARACTERIZATION OF EXHAUST SAMPLES COLLECTED FOR BIOLOGICAL ASSAY

Fuel: Date: Total Hydrocarbon in Exhaust (ppmC):	JP-5 9-26-84 643	JP-4 8-24-84 360	Shale JP-4 9-26-84 508
Exhaust Volume Collected, m^3	30.2	30.8	29.6
Change in Filter Mass, mg	41.7	21.9	12.0
$MeCl_2$ Extractable Filter Mass, mg	5.1	2.5	3.0
MeOH Extractable Filter Mass, mg	6.4	5.5	5.9
Extractable Mass from XAD-2, mg	2,179	1,275	1,379

SECTION IV

DISCUSSION

For convenience the discussion of the combustor rig experiments can be broken into three categories. The main focus of the experiments was on photochemical reactivity, and this topic will be covered first. The reactivity discussion will be followed by sections on aldehyde and dialdehyde levels in the exhaust, and the biological assay experiments. This latter section is merely a brief status report, because the bioassay experiments have not been completed, and the final results will be reported elsewhere.

A. PHOTOCHEMICAL REACTIVITY EXPERIMENTS

All photochemical reactivity experiments were carried out with exhaust generated by the TF-39 combustor operating at idle power. The photochemistry experiments were designed to investigate three issues: (1) the comparative reactivity of combustor exhaust and full-scale turbine engine exhaust, (2) the photochemical reactivity of exhaust from production shale fuel, and (3) the effect of exhaust organic concentration on photochemical reactivity. These issues are discussed below.

1. Comparison of the Reactivity of Combustor Rig Exhaust and Turbine Engine Exhaust

Our previous studies showed the organic composition of exhaust from a TF-39 combustor as very similar to the composition of that from a full-scale TF-39 engine (Reference 2). This finding suggests that the combustor rig is an adequate surrogate for the engine, at least with respect to organic composition. As a consequence, future studies of exhaust composition may be able to make use of combustor rigs, rather than carry out full-scale engine experiments.

One of the goals of the present task is to examine the photochemical reactivity of combustor rig exhaust, and compare combustor exhaust reactivity with engine exhaust reactivity. If the combustor is found to be a good surrogate for the engine in terms of exhaust reactivity, then future reactivity experiments can use the more convenient combustor facilities.

The combustor used in these experiments is a full-scale 60^{o}-sector from a General Electric TF-39 engine.

The photochemical reactivity runs were carried out in the same manner as the previous full-scale engine experiments (Reference 2). In both the combustor rig and engine experiments, two 8 m^3 outdoor smog chambers were employed for all irradiations. Exhaust was introduced into one chamber until a total hydrocarbon concentration of 10 ppmC was attained. The other chamber was loaded with a reference mixture consisting of a binary hydrocarbon system, NO, NO_2, and CO. The composition and concentration in the "reference" chamber were the same for all combustor rig and earlier TF-39 engine experiments. The purpose of the reference chamber is to determine the effects on photochemical reactivity of daily variations in meteorological conditions, so the exhaust chamber results can be normalized with respect to such variations. The reference mixture consisted of propene and butane (25 percent propene/75 percent butane), NO, NO_2, and CO. The nominal reference chamber concentrations of these constituents were:

10 ppmC	total hydrocarbon (propene/butane mix)
18 ppm	CO
0.08 ppm	NO
0.34 ppm	NO_2.

The derivation of this mixture is described in Reference 2.

The results of the photochemical reactivity experiments were summarized in Table 1 and shown graphically in Figures 1-18. The four experiments which address the engine/combustor comparison most directly are CR-1, CR-2, CR-5, and CR-6. Each of these experiments employed 10 ppmC of exhaust from one of the three study fuels in one chamber, and the reference mixture in the other chamber. The full-scale engine experiments to which these combustor data are to be compared were reported in Reference 2.

A comparison of several features of exhaust composition between the combustor and the engine operating on JP-5 fuel is included in Table 4. The combustor produced higher concentrations of total hydrocarbons, NO_x, and CO. However, the ratio of total hydrocarbons to NO_x, which is of great importance with respect to photochemical reactivity, is similar

TABLE 4. COMPARISON OF EXHAUST COMPOSITION FROM TF-39 ENGINE AND COMBUSTOR RIG FOR JP-5 FUEL

	Combustor Rig	TF-39 Engine
Total Hydrocarbon, ppmC	483	350
NO_x, ppm	33	19.9
CO, ppm	808	542
Total Hydrocarbon/NO_x	14.6	17.6
NO/NO_x	0.38	0.61

for the two exhaust sources. The NO/NO_x ratio influences the initial rate of O_3 formation, and this ratio is significantly lower in the combustor exhaust.

On an absolute basis, JP-5 combustor exhaust produced 788 ppb of O_3 on a day when the reference mixture generated 746 ppb. In comparison, JP-5 exhaust from the full-scale TF-39 engine generated 574 ppb of O_3, while the reference mixture yielded 863 ppb. This comparison shows that the combustor exhaust is more reactive; i.e., generates higher concentrations of ozone, than the engine exhaust. The ratios of exhaust/reference ozone maxima were 1.1 for JP-5 combustor exhaust, and 0.7 for JP-5 engine exhaust.

The exhaust composition of the combustor and engine for JP-4 fuel are compared in Table 5. There are two engine experiments with which to compare, and these are designated as AF-3 and AF-4 in Table 5, following the numbering scheme of Reference 2. The greatest difference in exhaust composition is the twofold higher NO_x concentration in the combustor exhaust. This leads to a significant difference in the total hydrocarbon/NO_x ratio. The combustor exhaust NO/NO_x ratio is considerably lower than the ratio in engine exhaust, as was observed for JP-5 fuel.

The concentration of ozone produced by the JP-4 combustor exhaust was 1315 ppb, while 821 ppb was obtained in the reference chamber. Two experiments with the TF-39 engine burning JP-4 fuel yielded an average of 608 ppb O_3, with the reference mixture generating an average of 720 ppb. As noted in Table 1, the combustor rig experiment with JP-4 fuel, CR-2, was not initiated until 1145 EDT, due to unavailability of the combustor facility. This experiment was initiated in the middle of the day, when UV intensity is strong and temperature is already high, while all the other reactivity experiments were initiated before sunrise. Because this experiment was initiated under highly reactive sunlight and temperature conditions, both the exhaust and the reference mixture produced the highest ozone concentrations observed for each of these systems during the study. While both the exhaust and reference chamber O_3 levels were high, it is not certain that the late start of this experiment influenced the exhaust and the reference mixture to the same degree. It is possible that the

TABLE 5. COMPARISON OF EXHAUST COMPOSITION FROM THE TF-39 ENGINE AND COMBUSTOR RIG FOR JP-4 FUEL

	Combustor Rig	TF-39 Engine AF-3	 AF-4
Total Hydrocarbon, ppmC	370	412	394
NO_x, ppm	33	17.0	17.1
CO, ppm	658	552	543
Total Hydrocarbon/NO_x	11.2	24.2	23.0
NO/NO_x	0.32	0.66	0.55

latively higher concentration of O_3 in the exhaust is due in part to e late start, and that normalization using the reference chamber results ly partially accounts for the different initiating conditions. If ue, this argument suggests that the comparison of combustor and engine haust reactivities will be biased, probably on the high side, for the -4 experiments. However, two other experiments run with JP-4 exhaust R-3 and CR-4 in Table 1) also showed high O_3, and these runs were itiated before sunrise. These latter two experiments were run for a fferent purpose, so there is no reference mixture data. Nevertheless, en these three experiments are considered altogether, it is clear that -4 combustor exhaust is more reactive than the reference mixture (i.e.. produced from 10 ppmC hydrocarbon loading of the exhaust ranged from 9 to 1315 ppb, while O_3 from the reference mixture never exceeded 821 b in any of the experiments listed in Table 1). On the other hand, ference 2 shows that JP-4 exhaust from the full scale TF-39 engine was ss reactive than the reference mixture. Averaged over two experiments, e ratio of exhaust chamber O_3 maximum to reference chamber O_3 maximum om the TF-39 engine was 0.8. This comparison demonstrates quite clearly at exhaust generated by the combustor is more reactive than JP-4 exhaust oduced by the TF-39 engine. As noted earlier, higher reactivity was so observed for combustor-generated exhaust when both the combustor d engine were burning JP-5 fuel.

In summary, the relative reactivity of exhaust from the combustor d engine is shown in Table 6 for JP-4 and JP-5 fuels. The combustor haust was more reactive, regardless of which fuel was utilized. Our rlier studies showed the organic composition of exhaust from these two urces to be similar, so the difference in reactivity is most likely sociated with the relatively higher levels of NO_x and higher NO_2/NO tios in the combustor exhaust.

It is not possible to compare the reactivity of exhaust from e combustor and the engine for a specific shale-derived fuel, because e experiments with the two combustion sources used different shale els. The engine experiments reported in Reference 2 used a shale fuel eting JP-8 specifications, while the combustor experiments employed a

TABLE 6. COMPARISON OF NORMALIZED PHOTOCHEMICAL REACTIVITY OF EXHAUST FROM TF-39 ENGINE AND COMBUSTOR RIG

	Max. Exhaust Chamber $[O_3]$/Max. Reference Chamber $[O_3]$	
Fuel	TF-39 Engine Exhaust	Combustor Rig Exhaust
JP-4	0.8[a]	1.2-1.6[b]
JP-5	0.7	1.1

[a] Based on two experiments.

[b] Range based on three experiments; see text.

JP-4 shale fuel. The reactivity of exhaust from JP-4 shale fuel is assessed in the next section.

2. Photochemical Reactivity of Exhaust From Shale-Derived Fuel

In earlier experiments, the photochemical reactivity of exhaust generated with a shale-derived fuel was investigated using two different full-scale turbine engines (Reference 2). The shale fuel used in the engine studies was supplied by the Air Force and met the specifications for JP-8 fuels. In general, the reactivity of exhaust produced from the JP-8 shale fuel was similar to or slightly lower than JP-4 and JP-5 exhaust reactivities. The JP-8 shale fuel was an early version of the shale-derived fuel envisioned for wide spread Air Force use. The final "production run" shale fuel is expected to be available for widespread Air Force utilization in 1985. The purpose of this task was to investigate the photochemical reactivity of the production run shale fuel. Unfortunately, production fuel was not available in time for this study due to delays in refinery production start up. However, a "preproduction" version of the fuel was available. This preproduction shale fuel meets JP-4 specifications and is reported to fall within the specification range of the final production shale fuel (Reference 3).

Two experiments were carried out using shale-derived JP-4 fuel to generate exhaust with the combustor. The experiments are designated as CR-5 and CR-6, and the results are summarized in Table 1 and shown graphically in Figures 13-18. The exhaust composition for these two runs is shown in Table 7. Experiment CR-5 was run on a cool day with some midmorning cloudiness. The peak ozone concentrations in both the exhaust and reference chambers were quite a bit lower than observed for the previous combustor rig experiments. The exhaust produced a maximum concentration of 437 ppb of O_3, while the reference mixture yielded 416 ppb. This experiment with shale JP-4 exhaust was repeated on a warm, clear, sunny day (CR-6). Under these conditions, the ozone maximum produced by the exhaust was 631 ppb, while the reference mixture yielded 749 ppb. In contrast to the two petroleum-derived fuels, the shale-derived JP-4 produced an exhaust which was less reactive than the reference mixture

TABLE 7. COMBUSTOR EXHAUST COMPOSITION FOR SHALE-DERIVED FUEL (JP-4)

	Experiment No.	
	CR-5	CR-6
Fuel	Shale (JP-4)	
Total Hydrocarbon, ppmC	524	506
NO_x, ppm	24.6	24.7
CO, ppm	749	710
Total Hydrocarbon/NO_x	21.3	20.5
NO/NO_x	0.23	0.32

under comparable meteorological conditions (i.e., clear sunny weather) and similar in reactivity to the reference mixture under less favorable weather conditions. This observation corroborates the findings in Reference 2 that exhaust from shale-derived fuel is no more photochemically reactive than exhaust from conventional jet fuels and, under some circumstances, is actually less reactive.

Our previous studies with a JP-8 shale-derived fuel suggested the possibility of enhanced secondary aerosol formation in the exhaust from shale fuels. However, comparison of the Table 1 data on exhaust chamber b_{scat} levels for the preproduction shale fuel (JP-4), and standard JP-5 and JP-4 fuels, indicates that secondary aerosol formation is lowest for the shale fuel exhaust. The use of shale-derived fuel in turbine engines would appear to provide mutual benefits in reducing both the photochemical production of O_3 and secondary aerosol in the exhaust.

3. Effect of Exhaust Concentration On Photochemical Reactivity

The investigation of turbine engine exhaust photochemistry reported in Reference 2 involved two turbine engines. The TF-39 is a current generation engine and is not equipped with emission abatement features, while the CFM-56 represents an advanced engine specifically designed for low emissions. Our previous studies at engine idle showed that, although the concentration of organic species in the CFM-56 exhaust was 2-3 times less than the concentration in the TF-39 exhaust, the CFM-56 exhaust is more reactive when compared on an equal organic mass basis. This observation raises the possibility that the advanced engine may produce higher reactivity organic compounds which may partially offset the benefits of lower emissions from the CFM-56 engine, at least in terms of photochemical reactivity.

The photochemical reactivity experiments conducted with TF-39 and CFM-56 exhaust were run with an initial hydrocarbon concentration of 10 ppmC in the smog chambers. Because of the lower hydrocarbon concentration of CFM-56 exhaust, a larger volume of CFM-56 exhaust was injected into the chambers in order to obtain the design loading value of 10 ppmC. Thus, the exhausts were compared on the basis of equal mass concentration of organic emissions, although a much greater volume of CFM-56 exhaust was employed. What if equal volumes of the exhausts had been compared? That is, if a constant volume of exhaust had been introduced into the chambers, rather than a constant organic concentration, would the lower emissions of the CFM-56 engine provide correspondingly lower photochemical reactivity? These questions could not be addressed directly with the data from the engine experiments. Consequently, two experiments were carried out as part of this combustor rig study to investigate this issue. The most direct way to answer these questions of course, would be to conduct new experiments with the two full-scale engines, but financial considerations precluded this approach. However, much can be learned from an examination of the influence of chamber loading on reactivity. If equal volumes of exhaust from the two engines were introduced into the chambers, the chamber containing the TF-39 exhaust would have a 2-3 fold higher total hydrocarbon concentration. Therefore, a combustor rig experiment was conducted to determine the effects of a three-fold difference in chamber loading. Experiment CR-4 in Table 1 utilized JP-4 fuel to generate exhaust. One chamber was loaded to the standard 10 ppmC total hydrocarbon concentration, while the other was loaded with three times the exhaust volume to reach a concentration of 30 ppmC. Both exhaust mixtures reacted simultaneously under identical meteorological conditions. Table 1 shows that the chamber containing three times as much exhaust produced 21 percent more O_3. This suggests that part of the higher reactivity of the CFM-56 exhaust observed during the full-scale engine experiments was due to the two- to threefold greater volume of exhaust employed in the CFM-56 experiments. For experiments conducted with JP-4 fuel and normalized with respect to the reference mixture, the CFM-56 exhaust was about 1.7 times as reactive as the TF-39 exhaust (Reference 2). Thus, chamber loading can only partially explain the reactivity difference. Differences in organic composition may account for some of the reactivity difference, and indeed the CFM-56 exhaust was found to contain significantly higher concentrations of reactive aldehydes than the TF-39 exhaust (Reference 2). It is also possible that part of the reactivity difference may be attributable to the different organic/NO_x ratio of the exhaust from the two engines. The total hydrocarbon to NO_x

ratio (THC/NO_x) of TF-39 exhaust was about 23 for JP-4 fuel at engine idle, but only 5 for CFM-56 exhaust under the same conditions. Therefore, a separate combustor rig experiment was conducted to investigate the influence of this variable on reactivity. Experiment CR-3 was run with one chamber loaded to the conventional 10 ppmC of JP-4 combustor exhaust, while the second chamber was loaded to one-third of this concentration. Furthermore, NO_x was added to this latter chamber to simulate the lower initial THC/NO_x ratio of the CFM-56 engine. This experiment represents simultaneous experiments with equal volumes of TF-39 and CFM-56 exhaust and THC/NO_x ratios representative of the two different engines. Unlike experiments with exhaust from the two engines, however, the organic composition of the exhaust used in the two chambers was identical. The experiment may be thought of as simulating a full-scale engine experiment with equal volumes of exhaust from the two engines, but without the confounding influence of organic composition differences.

The data in Table 1 and Figures 7-9 show that the chamber with 10 ppmC of exhaust produced a maximum of 992 ppb of O_3, while the 3.3 ppmC chamber with added NO_x yielded 612 ppb. The combination of lower initial THC/NO_x and lower organic concentration in this latter chamber reduced maximum O_3 to 62 percent of the level in the 10 ppmC chamber. This observation suggests that the use of equal organic mass concentration as a basis for comparison in the engine studies is responsible for nearly all of the 1.7 fold difference in CFM-56 and TF-39 reactivity. Therefore, equal volumes of exhaust from the two engines are expected to produce nearly equal maximum O_3 concentrations. There are clearly many environmental benefits of reduced turbine engine emissions, including reduction in the concentration of potentially toxic substances; however, these experiments indicate that photochemical production of O_3 from turbine engine exhaust is largely unaffected by the organic emissions abatement strategies.

One aspect of photochemical reactivity that benefits from reduced emissions levels is secondary aerosol production. Secondary aerosol is particulate material produced from photochemically induced reactions of gaseous species. In these experiments, all primary aerosol (i.e., particulate matter emitted directly by the engine) was filtered out of the exhaust before the exhaust was introduced into the chambers. Thus, any aerosol observed was produced during the reaction. The light-scattering coefficient, b_{scat}, a function of particle concentration in the light-scattering range, was measured at the end of each chamber experiment. These results are shown in Table 1. Examination of the b_{scat} results for experiments CR-3 and CR-4, in which the initial concentration of exhaust organics was varied from 3.3 to 30 ppmC, reveals a dramatic effect of organic concentration on secondary aerosol production. As the exhaust organic loading of the chamber is reduced from 30 ppmC to 10 ppmC (CR-4) and from 10 ppmC to 3.3 ppmC (CR-3), the decrease in secondary aerosol is nearly exponential. Advanced design engines with emissions abatement features generate exhaust with lower organic concentrations, which should result in reduced levels of secondary aerosol being produced by photochemical reactions in the atmosphere.

B. EXHAUST CONCENTRATIONS OF ALDEHYDES AND DIALDEHYDES

Our studies of the exhaust composition of full-scale jet engines revealed high levels of monoaldehydes and the first reported observation of dialdehydes in turbine engine exhaust (Reference 2). There is little, if any, information in the literature on dialdehyde emissions from other types of combustion sources, so there is no baseline with which to compare jet engine emissions of these species. Dialdehydes are considered to be photochemically reactive, so their presence in an exhaust may influence overall exhaust reactivity. In order to determine whether dialdehyde emissions unduly affect the comparison of engine and combustor exhaust reactivity, the concentrations of these species were measured during the combustor rig experiments. The concentration data are included in Table 2. The results are further summarized in Table 8, where dialdehyde and total aldehyde concentrations are normalized with respect to exhaust total hydrocarbon concentration. The aldehyde concentrations in Table 8 are reported in ppmC for consistency with the total hydrocarbon measurements. When normalized to total hydrocarbon emissions, the dialdehydes are generally less abundant in the combustor exhaust relative to full-scale engine exhaust. The total aldehyde concentrations are roughly

TABLE 8. ALDEHYDE AND DIALDEHYDE LEVELS IN TURBINE ENGINE EXHAUST

Fuel	[Dialdehyde], ppmC	[Total Aldehyde], ppmC	$\frac{[\text{Dialdehyde}]}{[\text{Total Hydrocarbon}]}$	$\frac{[\text{Total Aldehyde}]}{[\text{Total Hydrocarbon}]}$
TF-39 Engine				
JP-4	4.7	40.3	0.01	0.09
CFM-56 Engine				
JP-4	2.7	20.2	0.02	0.14
JP-5	4.0	32.0	0.02	0.16
JP-5	2.6	16.6	0.02	0.15
JP-8 (shale)	3.5	30.9	0.02	0.15
TF-39 Combustor				
JP-4	1.5	31.2	0.004	0.09
JP-5	1.2	55.9	0.002	0.12
JP-4 (shale)	3.5	17.6	0.007	0.03

similar for the engines and combustor, but higher total hydrocarbon levels in the combustor exhaust result in lower total aldehyde/total hydrocarbon ratios for certain combustor-fuel combinations. Direct comparison of exhaust dialdehyde levels for the TF-39 engine and the TF-39 combustor is available only for JP-4 fuel. The full-scale engine produced three times as much of the two measured dialdehydes, glyoxal and methyl glyoxal, as the combustor. Overall, however, the combustor and engine yielded the same relative amounts of total aldehydes, with aldehydes accounting for 9 percent of the total hydrocarbon emissions for both sources. Overall, the influence of differences in aldehyde emissions on the comparison of engine and combustor exhaust reactivities is deemed to be minimal.

C. BIOLOGICAL ACTIVITY OF COMBUSTOR EXHAUST

The combustor exhaust samples collected during this study have been submitted to the Health Effects Research Laboratory of the U.S. EPA for biological assay. The main features of these samples were noted in Table 3. The bioassay experiments have not been completed; the results will be reported separately. It is probable that these samples will be further fractionated and characterized based on the bioassay results. The purpose of the bioassay-directed fractionation will be to identify the compounds or classes of compounds responsible for biological activity.

SECTION V

CONCLUSIONS

Experiments were conducted to investigate the photochemical reactivity and biological activity of exhaust from a full-scale 60^{o}-sector combustor from a TF-39 turbine engine. All experiments were carried out at idle power setting. The study used exhausts from two conventional petroleum fuels (JP-4 and JP-5) and a shale fuel meeting JP-4 specifications. Photochemical reactivity was studied with two large (8 m^3) Teflon® outdoor environmental chambers. Photochemical reactivity is defined for purposes of this study as the maximum ozone concentration produced during a 1-day irradiation in natural sunlight.

One of the objectives of this study was to determine whether exhaust from a combustor rig simulates the photochemical reactivity of exhaust from a full-scale jet engine. Experiments were undertaken with a TF-39 combustor operating on JP-4 and JP-5 fuels, for comparison with previous studies of a full-scale TF-39 engine (Reference 2). The combustor exhaust was more reactive than exhaust from the full-scale engine, regardless of which fuel was burned. The combustor exhaust was 60 percent more reactive than engine exhaust for JP-5 fuel, and between 30 and 100 percent more reactive for JP-4 fuel. The cause of the difference in reactivity between combustor and engine was not identified, but higher initial NO_x concentrations and higher NO_2/NO ratios in the combustor exhaust undoubtedly play a role.

The photochemical reactivity of exhaust generated from a shale oil-derived fuel meeting JP-4 specifications was studied. Exhaust from the shale fuel was no more reactive than exhaust from petroleum fuels, and, under conditions most conducive to photochemical reactions, was actually less reactive. The shale fuel exhaust also generated less secondary aerosol than exhaust from the petroleum fuels.

Experiments were undertaken to permit estimation of the photochemical reactivity of equal volumes of exhaust from two full-scale engines studied previously (Reference 2). The results suggest that the reactivity of equivalent volumes of exhaust from the two engines is similar, even though organic emissions from one of the engines is two- to threefold lower. Possible reasons for this behavior include differences in organic composition and organic/NO_x ratio for exhaust from the two engines (Reference 2).

The concentrations of aldehydes and dialdehydes in combustor exhaust were measured to extend the data base for these reactive species and to determine whether differences in emission rates of these compounds might influence the comparison of combustor and engine exhaust reactivity. The combustor emits less of the dialdehydes than the engine when burning JP-4 and JP-5 fuels, but overall, for a given fuel, emissions of aldehydes relative to total organic emissions are similar for the two combustion sources. It is unlikely that aldehyde emissions are the cause of the higher combustor exhaust reactivity.

Large volume (30 m^3) samples of exhaust from JP-4, JP-5, and shale-derived JP-4 fuels were collected for assessment of biological activity. The exhaust was sampled through heated (150°C), tared, quartz fiber filters and then XAD-2 adsorptive resin, to collect nonvolatile and volatile compounds respectively. The filter and XAD-2 samples were extracted, and the extracts forwarded to the Health Effects Research Laboratory of U.S. EPA for biological assay. Results of the bioassay experiments are not yet available and will be reported separately.

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