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Project Summary

Environmental Assessment of a Reciprocating Engine Retrofitted with Nonselective Catalytic Reduction

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This report describes emission results obtained from field testing of a rich-burn reciprocating internal combustion (IC) engine retrofitted with a nonselective catalytic reduction (NSCR) system for NO_x reduction. Two series of tests were performed: a comprehensive test program to characterize catalyst inlet and outlet organic and inorganic emissions at optimum catalyst NO_x reduction performance; and a 15-day exhaust emission monitoring program to measure the catalyst performance under typical engine operating conditions.

Emission measurements during the comprehensive test program included: (1) continuous monitoring of flue gas emissions; (2) source assessment sampling system (SASS) sampling of the exhaust gas with subsequent laboratory analysis of samples to give solid particulate emissions, total organics in two boiling point ranges, compound category information within these ranges, specific quantitation of the semivolatile organic priority pollutants, and exhaust gas concentrations of 73 trace elements; (3) Modified Method 6 sampling for NH_3 and total cyanides; and (4) exhaust gas grab sampling from N_2O analysis by gas chromatography. Emission measurements during the 15-day monitoring program were limited to continuous monitoring of exhaust gas species.

Comprehensive test results indicated that over the 1-day test period the NO_x reduction performance of the catalyst ranged between 54 and 81 percent with an average of 70 percent. NO_x emissions at the catalyst inlet ranged between 1,650 and 1,850 ppm as measured at 0.1 percent O_2 (1,700 ppm average). At the catalyst outlet NO_x ranged between 300 and 800 ppm, also at 0.1 percent O_2 (550 ppm average).

Catalyst inlet CO concentrations averaged 14,600 ppm as measured and total unburned hydrocarbons (TUHC) averaged 215 ppm. High catalyst inlet combustible concentrations are necessary to ensure sufficient reducing agent to allow the catalytic NO_x reduction reactions to occur. This required that the engine operate with an air/fuel ratio (A/F) near or slightly below the stoichiometric A/F of 16.35 (dry weight basis). TUHC concentrations were reduced to 125 ppm, and CO levels were reduced to an average of 13,200 ppm by the catalyst. Total organic (C_{6+}) emissions were also reduced by the catalyst from 15.5 to 2.1 mg/dscm (36 to 4.7 mg/Bhp-hr) in parallel with corresponding TUHC and CO reductions. Emissions of 14 polynuclear aromatic hydrocarbon (PAH) species were quantitated in both catalyst inlet and outlet exhaust. Again, inlet levels were generally higher than outlet levels, except for naphthalene and phenol emissions, which increased.

During the 15-day performance test, the NO_x reduction performance was mostly in the 0 to 40 percent range. Only occasionally did NO_x reduction exceed 90 percent. During the periods of higher reduction performance, CO and TUHC emissions at the inlet were as high as 1 and 0.1 percent, respectively.

This Project Summary was developed by EPA's Industrial Environmental 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

In California, the South Coast Air Quality Management District (SCAQMD) continues to be in nonattainment of both federal and state NO_2 standards. Stationary reciprocating IC engines are estimated to contribute about 14 percent of the NO_x (about 59 mg/day (64 tons/day)) from all stationary sources and 5.1 percent of total NO_x emissions in the basin. In 1979, the California Air Resources Board (CARB) proposed a control strategy for IC engines in the SCAQMD that called for retrofit of these sources with nonselective and selective gas treatment catalysts (NSCR and SCR, respectively). The proposed SCAQMD rule 1110 calls for demonstration of 90 percent reduction or an emissions limit of 0.28 μg/J (0.75 g/Bhp-hr) of heat output. Following this proposed rule, there has been a sustained R&D effort to demonstrate the capability of commercially available NSCR and SCR catalysts and identify problems in their application.

This report gives results of comprehensive emission tests and long-term catalyst performance tests of a rich-burn reciprocating engine retrofitted with an NSCR system. Emissions were measured at both inlet (muffler outlet) and outlet of the catalyst to quantitate both NO_x reduction performance and the impact of the catalyst on other inorganic and organic pollutants.

The tests were performed on a Waukesha 610 kW (818-hp) L7042 GU four-stroke naturally aspirated electric generator engine owned and operated by Southern California Gas Company (SoCal). In November 1982, the engine was retrofitted with a DuPont PR-5 NSCR catalyst having about 6,000 operating hours on another SoCal engine. This catalyst was previously tested and found capable of 90 percent NO_x reduction on the larger compressor engine. The PR-5 catalyst is based on a platinum/rhodium formulation and has an upper temperature limit of 1,450°F (788°C). Previous tests by SoCal had shown that 90 percent NO_x reduction was achieved over a narrow A/F range, with A/F rich enough that catalyst inlet CO and TUHC concentrations exceeded 4,000 and 1,000 ppm respectively. This A/F is richer than the engine would normally be operated, resulting in a fuel penalty of 11 percent.

Summary and Conclusions

Engine Operation

The tests called for evaluating NO_x reduction performance of the catalyst and its effect on organic and inorganic pollutants during 1 day of comprehensive tests with the engine A/F adjusted for optimum NO_x reduction at constant power output. In addition, the program called for continuous 15-day emission monitoring to evaluate the long-term NO_x control capability with the engine operating under typical conditions with varying load and A/F.

Table 1 summarizes engine operating characteristics during the comprehensive tests. Engine load was maintained relatively constant throughout this portion of the test program. Generator output varied from 415 to 455 kWe, corresponding to about 450 - 490 kW (600 - 660 bhp) engine shaft output. Brake specific fuel consumption was 12.3 MJ/kWh (8,660 Btu/bhp-hr) based on fuel lower heating value. This represents a loss in fuel efficiency of about 15 percent, based on the manufacturer's specification for full load operation.

Emission Measurements and Results — Comprehensive Tests

The sampling and analysis procedures used in this test conformed to a modified EPA Level 1 protocol. The exhaust gas measurements at both the catalyst inlet and outlet included:

- Continuous monitoring for O_2, CO_2, CO, NO/NO_x, and TUHC
- SASS sampling
- Modified Method 6 train sampling for NH_3 and total cyanide
- Gas grab sample for N_2O determination

Table 1. Engine Operation — Comprehensive Tests

Parameter	Range	Average
Ambient		
Dry bulb temperature, °C (°F)	*26 to 29 (79 to 85)*	*29 (84)*
Wet bulb temperature, °C (°F)	*20 to 22 (68 to 71)*	*22 (71)*
Relative humidity, percent	--	*52*
Barometric pressure, kPa (in. Hg)	--	*96.4 (28.55)*
Engine Operation		
Generator output, kW_e	*415 to 455*	*425*
Engine load, kW_t (bhp)[a]	*448 to 492 (601 to 660)*	*459 (616)*
Fuel flow, m^3/hr (scfh)	--	*156 (5,569)*
Heat input, MW (10^6 Btu/hr)[b]	--	*1.56 (5.33)*
Specific fuel consumption, kJ/kWhr (Btu/bhp-hr)[b]	--	*12,300 (8,660)*
Air manifold pressure		
● *L, kPa (in. Hg vac)*	*14 to 16 (4.1 to 4.6)*	*15 (4.4)*
● *R, kPa (in. Hg vac)*	*14 to 16 (4.1 to 4.8)*	*15 (4.5)*
Speed, rpm	*900 to 910*	*905*
Catalyst inlet temperature, °C (°F)	*533 to 536 (991 to 997)*	*535 (995)*
Catalyst output temperature, °C (°F)	*534 to 561 (994 to 1,042)*	*552 (1,025)*
Gas Analysis, percent volume[c]		
O_2	--	*0.073*
N_2	--	*1.119*
CO_2	--	*0.890*
CH_4	--	*90.119*
C_2H_6	--	*6.294*
C_3H_8	--	*1.247*
iso-C_4H_{10}	--	*0.094*
h-C_4H_{10}	--	*0.106*
iso-C_5H_{12}	--	*0.029*
h-C_5H_{12}	-	*0.029*
C_{6+}	--	*0.003*
HHV, MJ/m^3 (Btu/ft^3)[d]		*39.9 (1,072)*
LHV, MJ/m^3 (Btu/ft^3)[d]		*36.0 (968)*

[a] *Horsepower not a measured value — calculated from generator output times 1.45.*
[b] *Based on low heating value.*
[c] *Based on data supplied by SoCal.*
[d] *Calulated heating value.*

The analysis protocol included:

- Analyzing SASS train samples for 73 trace elements using spark source mass spectrometry (SSMS), supplemented by atomic absorption spectrometry (AAS)
- Analyzing SASS train samples for total organic content in two boiling point ranges: 100° to 300°C by total chromatographable organics (TCO) analyses, and greater than 300°C by gravimetry (GRAV)
- Analyzing the SASS train sorbent module for 58 semivolatile organic species including many of the PAH compounds
- Performing infrared (IR) spectrometry analysis of organic sample extracts
- Performing liquid chromatography (LC) separation of selected sample extracts with subsequent TCO, GRAV, and IR analysis of LC fractions
- Performing mutagenicity and toxicity health effects bioassays of SASS samples

Table 2 summarizes emissions measured at the engine muffler outlet (catalyst inlet) and the catalyst outlet. Emissions are presented in milligrams per dry standard cubic meter (mg/dscm), nanograms per Joule heat input (ng/J), and milligrams per brake horsepower-hour shaft output (mg/bhp-hr). As a measure of the relative potential significance of the emissions, an occupational exposure guideline concentration for each species is also noted in the table. The guideline noted is generally either the time-weighted-average Threshold Limit Value (TLV) or the 8-hr time-weighted-average exposure limit established by the Occupational Safety and Health Administration (OSHA). These are noted only to aid in ranking the potential significance of pollutant species emissions. Conclusions regarding the absolute risk associated with emission levels compared to occupational exposure guidelines are not, and should not, be drawn. With respect to ranking, however, species emitted at levels several orders of magnitude higher than their occupational exposure guidelines might warrant further consideration. Species emitted at levels significantly lower than their occupational exposure guidelines could be considered of little potential concern. Only species emitted at levels exceeding 10 percent of their occupational exposure guidelines are noted in Table 2.

As shown in the table, NO_x emissions were reduced about 70 percent on the average from 770 to 250 ng/J (7.8 to 2.5 g/bhp-hr). Actually, NO_x reduction ranged from about 50 to 80 percent. This variation was probably caused by small perturbations in engine load accompanied by small changes in A/F. This degree of NO_x reduction is not sufficient to meet SCAQMD proposed NO_x reduction rules of 90 percent or 280 ng/J heat output (0.75 g/bhp-hr).

Both ammonia and total cyanide increased significantly across the catalyst. Catalyst outlet ammonia levels

Table 2. *Summary of Exhaust Gas Emissions*

Specie	Catalyst inlet[a]			Catalyst outlet[a]			Occupational exposure guideline[b]
	mg/dscm	ng/J	mg/bhp-hr	mg/dscm	ng/J	mg/bhp-hr	(mg/m^3)
Criteria and other gaseous pollutants and total organic emissions							
CO	5,350	1,210	1.22×10^4	4,840	1,030	10,400	55
NO_x (as NO_2)	3,410	770	7,790	1,180	250	2,530	6.0
NH_3	23	5.2	53	390	82	820	18
Total cyanide (as CN)	0.022	0.005	0.051	10	2.2	22	5.0
N_2O[c]	270	60	600	170	36	360	--[d]
Solid particulate	1.3	0.30	3.0	1.4	0.30	3.0	10[e]
Total chromatographable organics (C_7 to C_{16})	8.1	1.8	19	1.8	0.40	4.1	--
Total GRAV organics (C_{16+})	7.4	1.7	17	0.30	0.055	0.56	--
Trace elements							
Barium, Ba	0.049	0.011	0.11	0.064	0.014	0.14	0.50
Calcium, Ca	0.450	0.10	1.1	0.16	0.034	0.34	2.0
Chromium, Cr	0.0007	1.5×10^{-4}	0.0015	0.78	0.17	1.7	0.050
Copper, Cu	0.015	0.0035	0.035	1.2	0.25	2.5	0.10[f]
Iron, Fe	0.039	0.0090	0.091	0.41	0.088	0.88	1.0
Nickel, Ni	0.0008	1.8×10^{-4}	0.0018	0.69	0.15	1.5	0.10
Phosphorus, P	0.005	0.0012	0.012	0.03	0.0064	0.064	0.10
Potassium, K	0.17	0.040	0.41	0.36	0.076	0.76	2.0[g]
Silicon, Si	0.12	0.028	0.28	1.4	0.31	3.1	10
Silver, Ag	0.0015	3.4×10^{-4}	0.0034	0.22	0.046	0.46	0.010
Sodium, Na	150	34	340	160	35	350	2.0[g]
Zinc, Zn	0.024	0.0055	0.056	0.46	0.089	0.89	1.0

[a] *Average exhaust gas O_2 and CO_2 were 0.1 and 10.2 percent at both inlet and outlet.*
[b] *Time-weighted average Threshold Limit Value (TLV), unless noted.*
[c] *N_2O emissions were measured during low catalyst NO_x reduction efficiency following completion of the comprehensive tests. N_2O emissions are averages of two tests during which NO_x emissions were about 2,700 ppm.*
[d] *—denotes no occupational exposure guideline applicable.*
[e] *For nuisance particulate.*
[f] *8-hr time-weighted average OSHA exposure limit.*
[g] *Ceiling limit.*

exceeded inlet levels by an order of magnitude, 23 to 390 mg/dscm (31 to 490 ppm). Although much lower than ammonia, total cyanides showed a much greater percentage increase across the catalyst, from 0.022 to 10 mg/dscm. These results agree with previous studies on the effect of NSCR catalyst on NH_3 and CN emissions. Solid particulate showed no noticeable change due to the catalyst. In line with a reduction in combustible emissions (TUHC—as CH_4—and CO). TCO was reduced by the catalyst by about 75 percent, and GRAV organics were reduced by about 95 percent.

Table 2 shows that several trace elements (chromium, copper, nickel, silver, and sodium) were present in the engine exhaust at levels exceeding their respective occupational exposure guidelines. Except for sodium, these elements were present at levels exceeding their respective guidelines only at the catalyst outlet, which suggests that the catalyst system itself introduces some of each element. Both ammonia and cyanide were present in the catalyst outlet exhaust at levels exceeding their guidelines. CO emissions were at levels almost 90 times its occupational exposure guideline, and NO_x emissions at the catalyst outlet were at levels almost 200 times its guideline.

Table 3 summarizes the PAH and other organic compounds detected by GC/MS analysis of the catalyst inlet and outlet sample extracts. Consistent with the overall reduction in total combustible emissions, these compounds were present at significantly lower concentrations in the catalyst outlet exhaust than in the inlet exhaust. Interestingly, all three-ring fused aromatics were destroyed by passage through the reactor. Levels of phenol and naphthalene, one- and two-ring aromatics, instead were increased at the outlet, suggesting that these lower molecular weight aromatics were being formed from higher ring number compounds.

Bioassay tests were performed on the organic module extract (XAD-2 and organic module condensate) from both SASS trains (inlet and outlet). Only health effects tests were performed: the Ames mutagenicity assay and the CHO cytotoxicity assay. Table 4 summarizes the results of these assays. The data suggest that the XAD-2 extract from the inlet was of high mutagenicity and moderate to high toxicity. The catalyst outlet XAD-2 extract was of moderate mutagenicity and toxicity. These are typical bioassay responses for combustion source XAD-2 extract.

Table 3. *PAH and Other Organic Species Emission Summary*

Semivolatile and nonvolatile organics	*Inlet*[a]	*Outlet*[a,b]
Acenapthene	*16.5*	*<0.4*
Acenaphthylene	*62.3*	*1.2*
Benz(a)anthracene	*5.1*	*<0.4*
Benzofluoranthenes	*1.9*	*<0.4*
Bis(2-chloroethyl)ether	*2.1*	*<0.4*
Bis(2-ethylhexyl)phthalate	*54.9*	*1.2*
Butyl benzyl phthalate	*0.7*	*<0.4*
Chrysene	*1.9*	*<0.4*
Fluoranthene	*0.5*	*<0.4*
Fluorene	*17.9*	*<0.4*
Naphthalene	*<0.4*	*28.5*
Phenanthrene	*40.3*	*1.4*
Phenol	*<0.4*	*1.8*
Pyrene	*2.2*	*<0.4*

[a] *µg/dscm.*
[b] *Outlet results are based on the average of replicate analyses.*

Table 4. *Bioassay Results*

	Assay	
Sample	*Ames*[a]	*CHO*[b]
Catalyst Inlet, XAD-2 Extract	*H*	*H/M*
Catalyst Outlet, XAD-2 Extract	*M*	*M*

[a] *Mutagenicity assay.*
[b] *Toxicity assay.*
H = high; M = moderate; H/M = high to moderate.

Emission Measurements and Results — 15-Day Monitoring

The sampling and analysis protocol for this portion of the test program consisted of continuous monitoring of inlet and outlet exhaust gas for O_2, CO_2, CO, NO/NO_x, and TUHC with certification of NO_x analyzer readings using EPA Method 7. Since both engine power output and A/F were not restricted to specified ranges, the date obtained can be considered reflective of typical operating practice. Figures 1 through 5 summarize emission results. Each data point in these figures represents an hourly average. Therefore, frequent emission fluctuations are dampened by this hourly average reporting method.

Comprehensive tests were performed on June 7. This test period is indicated in Figure 1 by exhaust O_2 being near zero at both locations. Following these tests, the engine assumed a more typical operating condition which resulted in exhaust O_2 being in the range of 2 to 5 percent. (The difference between the inlet and outlet O_2 levels is considered suspect. Inlet concentrations of 2 percent are considered more accurate.) The result of the increase in A/F during the 15-day test period was an increase in inlet NO_x as well as a reduction in catalyst performance. In fact, NO_x reduction by the catalyst generally ranged between 0 and 40 percent. Only once was NO_x reduced by more than 90 percent. This reduction, which occurred early on June 18, was accompanied by a rapid increase in both CO and TUHC.

Summary

Emission tests of a rich-burn reciprocating IC engine retrofitted with a NSCR NO_x control system suggest that significant NO_x reduction (>80 percent) cannot be maintained without tight control of A/F within a narrow range. This range spans A/F near or below stoichiometry. The data suggest that corresponding CO and TUHC engine emissions required for optimum catalytic performance are in excess of 3,000 ppm and 400 ppm, respectively, at 15 percent O_2. Long-term (15-day) continuous monitoring indicates the inability of the engine tested to be maintained at the necessary conditions of A/F, CO, and TUHC to achieve controlled NO_x emissions at or below the proposed SCAQMD level. The catalyst was found to significantly reduce all combustible emissions including most PAH. This agrees with the oxidation reaction process of the NSCR reactor. Significant

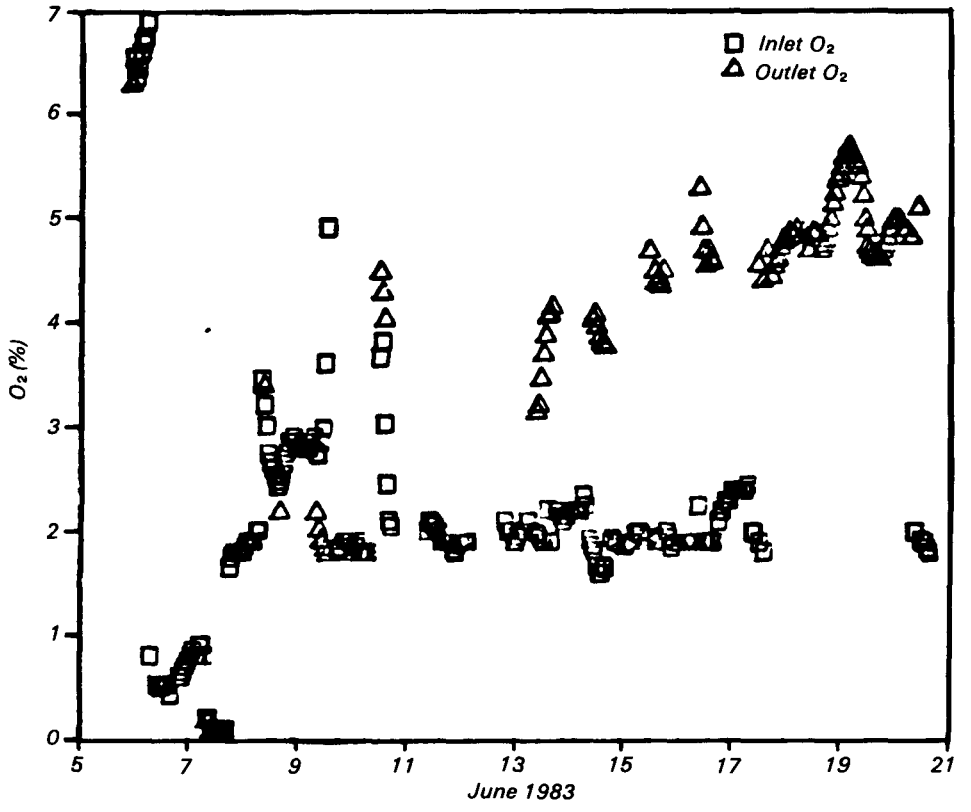

Figure 1. Exhaust O_2 during the 15-day continuous monitoring period.

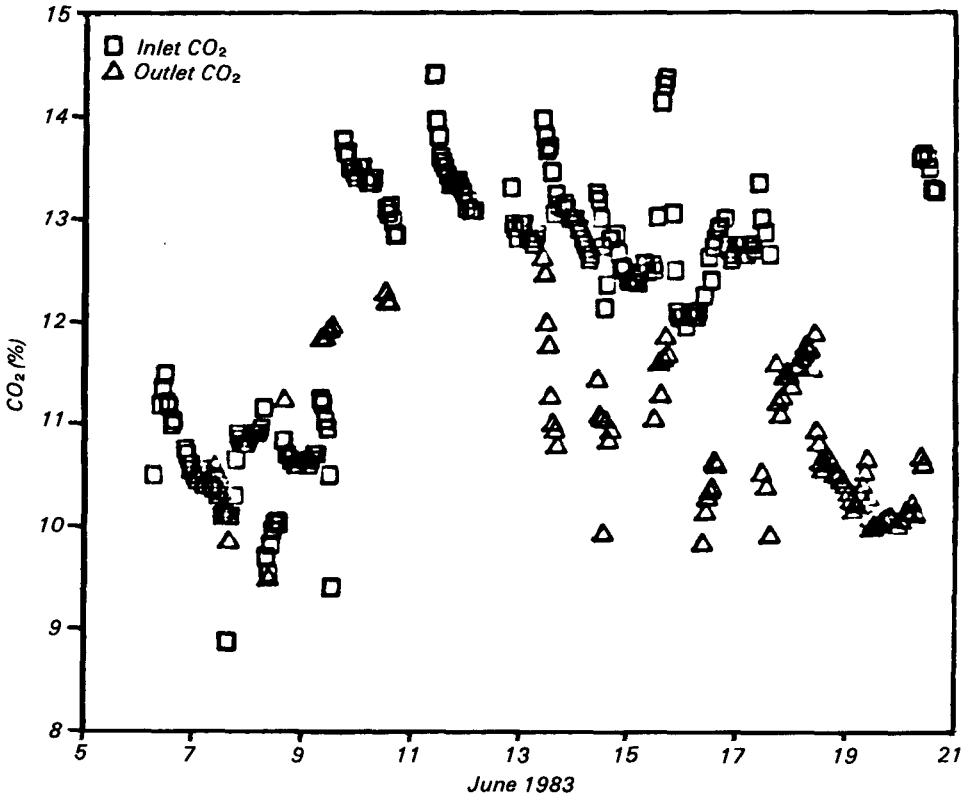

Figure 2. Exhaust CO_2 during the 15-day continuous monitoring period.

increases in NH_3 and total cyanide emissions were recorded, confirming anticipated and previously discovered trends. Exhaust levels of many inorganic trace elements also increased across the catalyst. Major elements of potential concern are chromium, copper, nickel, silver, and sodium.

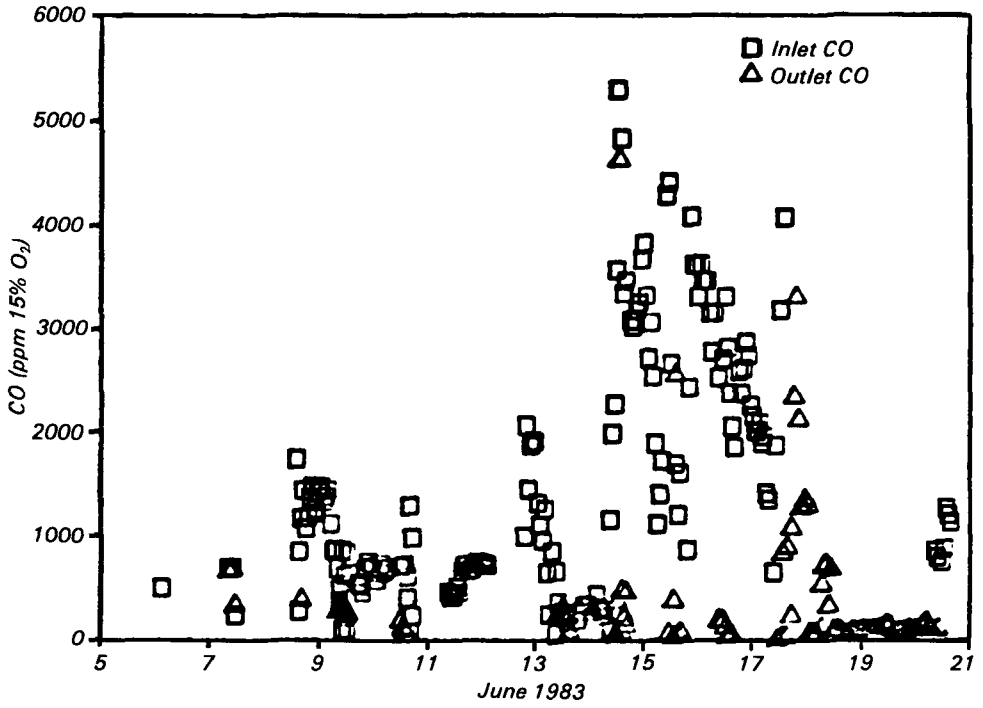

Figure 3. *CO emissions during the 15-day continuous monitoring period.*

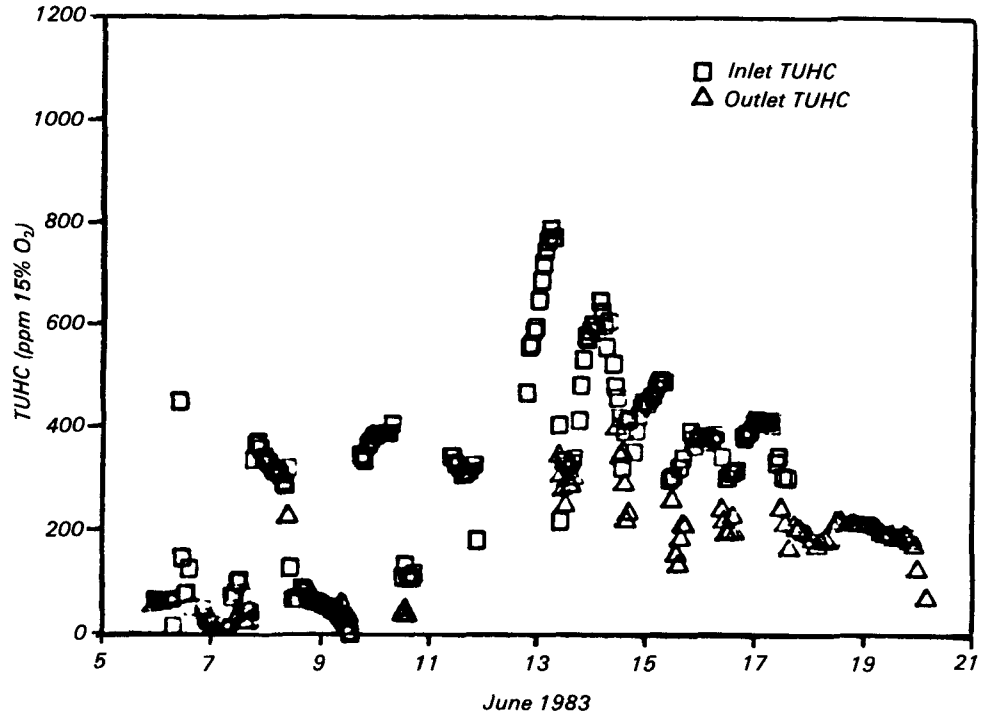

Figure 4. *TUHC emissions during the 15-day continuous monitoring period.*

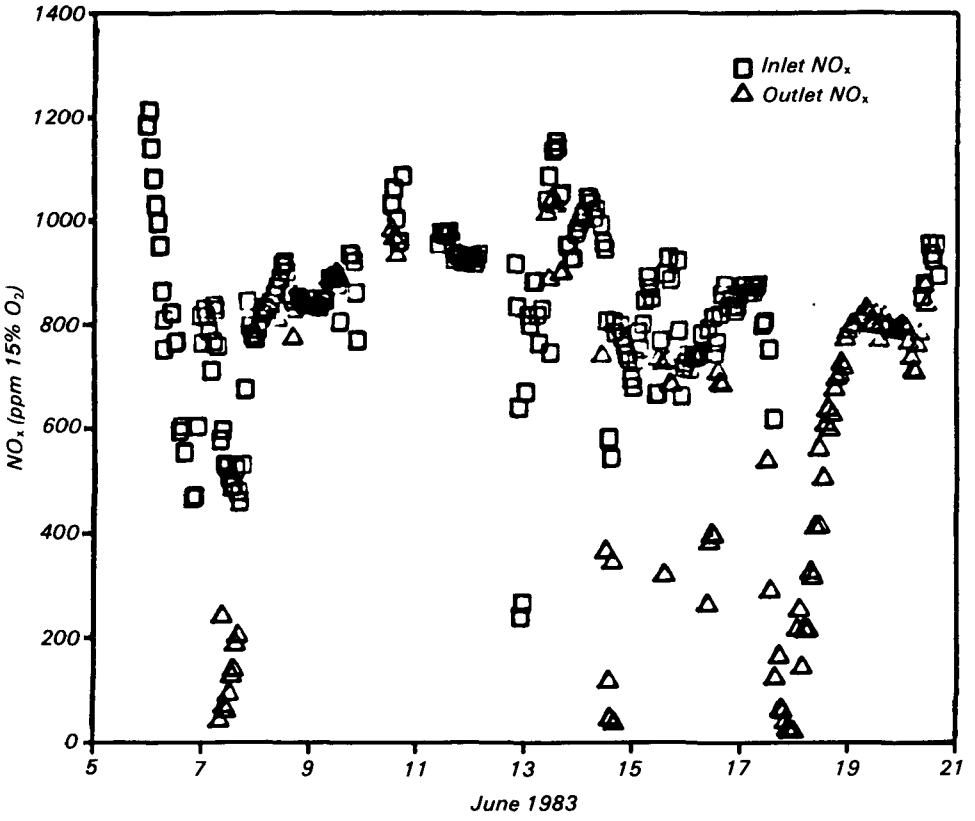

Figure 5. *NO_x emissions during the 15-day continuous monitoring period.*

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The complete report consists of two volumes, entitled "Environmental Assessment of a Reciprocating Engine Retrofitted with Nonselective Catalytic Reduction:"
"Volume I. Technical Results," (Order No. PB 84-224 351; Cost: $13.00)
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