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COMBUSTION SOURCES OF UNREGULATED GAS PHASE  
NITROGENOUS SPECIES

Ronald D. Matthews and Robert F. Sawyer

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COMBUSTION SOURCES OF UNREGULATED GAS PHASE  
NITROGENOUS SPECIES

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COMBUSTION SOURCES OF UNREGULATED  
GAS PHASE NITROGENOUS SPECIES

ABSTRACT

Published reports which have shown that a wide variety of unregulated nitrogenous species are produced by combustion systems are reviewed and discussed. The total nationwide production is estimated for those species for which sufficient data are available. It is concluded that several noncriteria nitrogen containing species are emitted in significant amounts and that this phenomenon merits further consideration. The emission of gaseous nitrogen compounds from combustion sources is estimated to consist of 76.27% NO, 8.09% NO<sub>2</sub>, 15.49% N<sub>2</sub>O, 0.10% NH<sub>3</sub> and other amines, 0.03% HCN and other nitriles, and 0.02% other nitrogenous species on a mass basis.

INTRODUCTION

Nitric oxide (NO) is generally recognized as being one of the most important combustion generated air pollutants. In fact, more than 95% of the 1970 nationwide emissions of NO were attributable to combustion sources (1), and it has traditionally been thought that NO is the only significant nitrogen-containing air pollutant which is emitted from combustion systems. However,

it has recently been shown that a wide variety of other nitrogenous species (N-species) are also emitted from combustion systems. Production of these other nitrogenous species is a cause for concern because molecular nitrogen ( $N_2$ ) is the only clearly innocuous N-species. Other members of the family of gas phase nitrogenous species are odorants or lacrymators at low concentrations, affect visibility, play a role in the formation of photochemical smog, take part in atmospheric reactions which threaten the ozone layer, are capable of shifting the energy balance of the earth, are toxic at low levels, are precursors of carcinogens, or are directly carcinogenic (2-4). This paper reviews the investigations which have demonstrated that many N-species are emitted from combustion systems.

Nitrogen containing species may be produced in combustion systems via several mechanisms. As shown in Table I, a wide variety of N-species may be produced by the combustion process. In general, the initial source of the nitrogen is the  $N_2$  in air, and the production of these N-species is affected by fuel/air ratio, mixing intensity, temperature, and other combustion parameters. The formation of N-species will be enhanced if the fuel contains organically bound nitrogen. This "fuel-nitrogen" is much more reactive than is the  $N_2$  in air. Emission of noncriteria N-species may also be promoted by some exhaust purification techniques which are designed to reduce emissions of NO. However, it is not the intention of this paper to propose



chemical mechanisms. Rather, it is desired to review the evidence which indicates that gaseous N-species other than NO and N<sub>2</sub> are emitted from combustion sources.

The species of interest may be categorized as oxides of nitrogen, cyanides, amines, and other gaseous N-species. The investigations which have demonstrated that these pollutants are emitted from combustion systems will be reviewed and discussed in the following sections.

#### THE OXIDES OF NITROGEN

Until recently, nitric oxide was considered to be the only nitrogen containing pollutant (and therefore the only oxide of nitrogen) that was produced during combustion. However, current investigations have demonstrated that two other oxides of nitrogen, nitrogen dioxide and nitrous oxide, can be emitted from combustion systems.

##### Nitrogen Dioxide (NO<sub>2</sub>)

Although NO<sub>2</sub> is indirectly regulated as part of the total NO<sub>x</sub> standard, it is covered in this context because of growing concern about its direct emission from combustion systems. In the past, the only significant source of NO<sub>2</sub> was thought to be atmospheric oxidation of NO. However, recent investigations have measured NO<sub>2</sub> directly in products of combustion. This finding is

significant because emission of  $\text{NO}_2$  rather than  $\text{NO}$  will affect local  $\text{NO}_2$  concentrations and will shorten the induction period for photochemical smog formation.  $\text{NO}_2$  is a significant atmospheric pollutant because it can decrease visibility through two separate mechanisms, because it is an important intermediary in the photochemical smog formation process, because it contributes directly to property and plant damage, and because it may react in the atmosphere to form aerosols, peroxyacyl nitrates, nitric acid, nitrous acid, nitro-olefins, and the highly carcinogenic nitrosamines.

Until the early 1970's, it was generally accepted that  $\text{NO}_2$  constituted, at most, 5% of the total oxides of nitrogen ( $\text{NO}_x$ ) in the emissions from gas turbines (5-7). In late 1971, Airesearch Manufacturing Company reported measuring significant concentrations of  $\text{NO}_2$  in the exhaust of gas turbines of their manufacture (8). As shown in Figure 1, they measured  $\text{NO}_2/\text{NO}_x$  fractions as high as 80% under idling conditions. Tuttle, et al. (9) have reviewed other investigations which have also reported significant  $\text{NO}_2$  emissions from commercial and military aircraft. Levels well above previously reported results and equilibrium predictions have been detected. There was much concern that the  $\text{NO}_2$  was an artifact of the sample transfer system. However, it is now fairly widely acknowledged that high  $\text{NO}_2/\text{NO}_x$  ratios may be a characteristic of gas turbines and many other lean turbulent diffusion combustion systems (10,11). Mellor (10) points out that  $\text{NO}_2$  emissions from gas turbines appear to be highest for

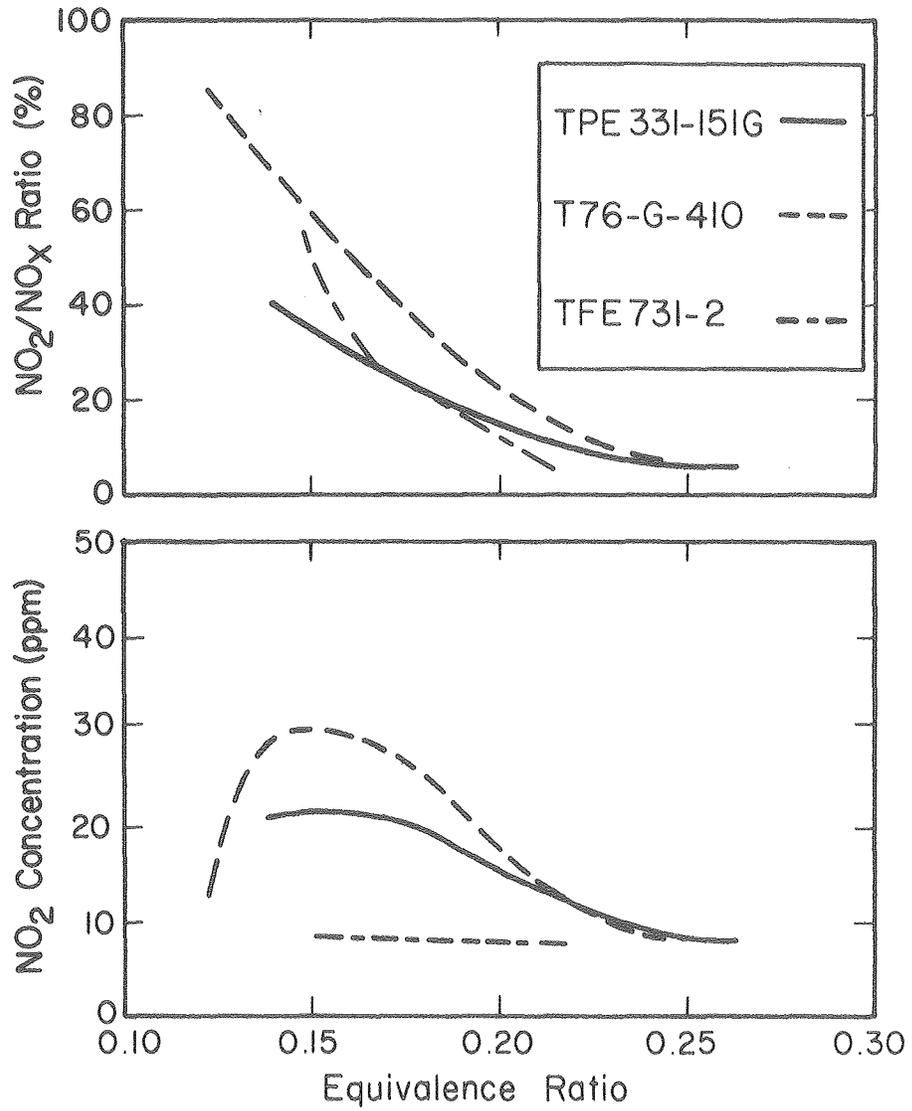


Figure I. Emissions of nitrogen dioxide from gas turbines (from the data presented by AiResearch (8)).

high compressor pressure ratio engines operating at low power settings such as idle. Furthermore, because idle conditions constitute 79% (in time) of the EPA Landing and Takeoff cycle, the  $\text{NO}_2/\text{NO}_x$  ratio as well as total  $\text{NO}_x$  may be significant in determining the contribution of aircraft to urban air pollution. Coppersmith, et al. (12) demonstrated that  $\text{NO}_2$  emissions from stationary gas turbines are also significant. They measured  $\text{NO}_2/\text{NO}_x$  ratios in the products of gas turbine power plant peaking units. Some units exhibited fractions as high as 76% at 25% of peak load, with the ratio decreasing as the load increased. Johnson and Smith (13) confirmed these findings in a natural gas fired power plant consisting of three stationary turbine units rated at 50 MW each. As shown in Figure 2, the  $\text{NO}_2$  concentration peaked at about half load and the  $\text{NO}_2/\text{NO}_x$  ratio decreased from 100% at idle (approximately 15 MW) to 22% at full load (about 45 MW). Therefore,  $\text{NO}_2$  emissions from both stationary and aircraft gas turbines may be important.

High levels of  $\text{NO}_2$  have also been detected in the emissions from spark ignition engines. Adelman, et al. (14) found that 180-190 mg/mi were produced by a methanol fueled vehicle. This corresponded to an  $\text{NO}_2/\text{NO}_x$  ratio of approximately 50%. The fraction was reduced to 10-20% (50-70 mg of  $\text{NO}_2$  per mile) when an exhaust catalyst was used. Noguchi, et al. (11) report that the  $\text{NO}_2/\text{NO}_x$  fraction for a prototype Toyota lean-burn engine increased from zero for fuel rich combustion to 25% at stoichiometric and 65% at a fuel/air equivalence ratio of 0.85.

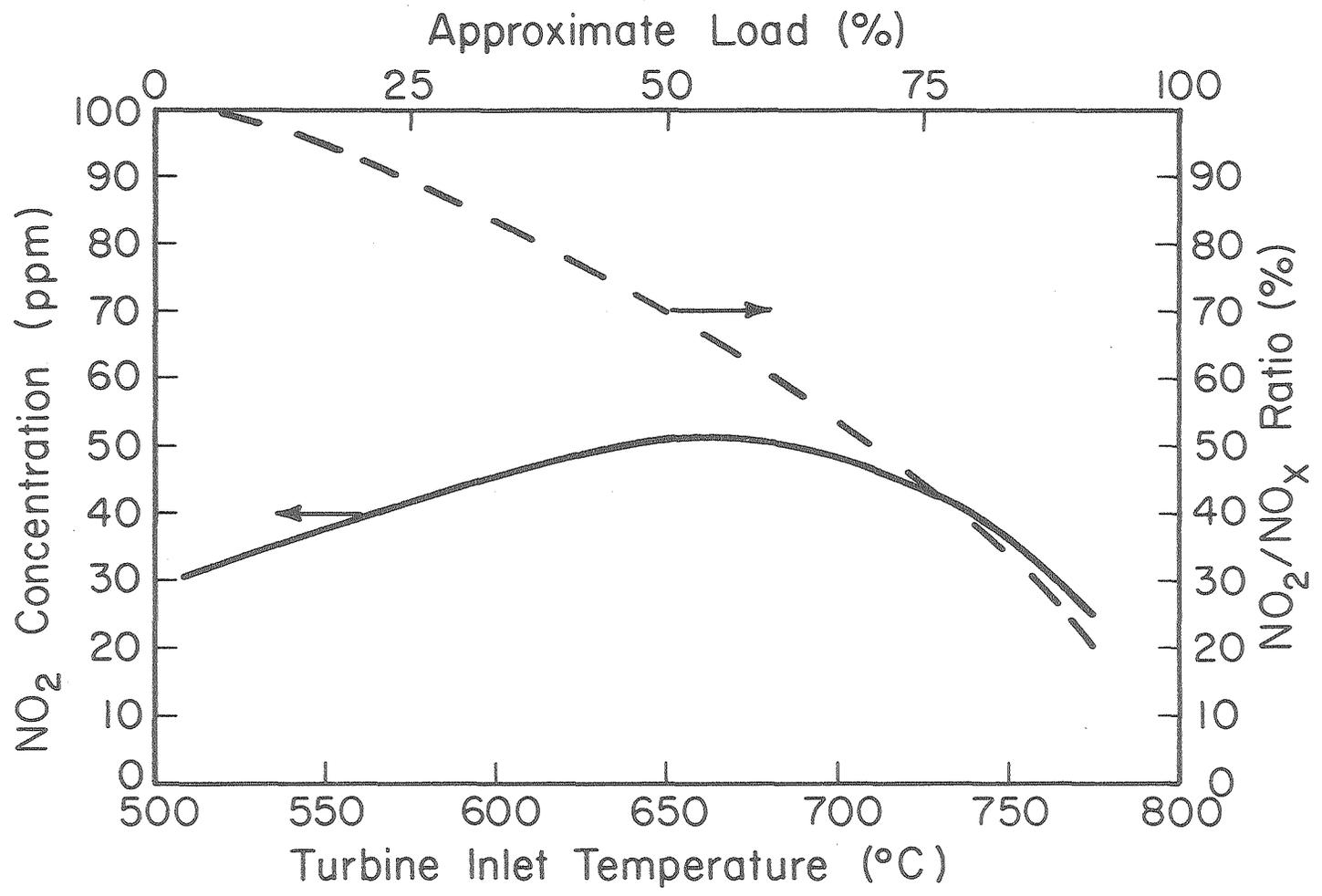


Figure 2. Nitrogen dioxide emissions from a stationary gas turbine (13).

However, Campau and Neerman (15) found only small percentages in spark ignition engine exhaust. The experiments of Hilliard and Wheeler (16,17) tend to unify these various results. They found that  $\text{NO}_2$  production by commercial engines increased with load up to a maximum at full load. These engines were operated with approximately stoichiometric mixtures. However, tests on a high  $\text{NO}_x$  single cylinder engine showed that  $\text{NO}_2$  production peaked at the lean air/fuel ratio of 17:1. A platinum catalyst decreased the  $\text{NO}_2$  emissions for rich and stoichiometric mixtures but increased them by as much as a factor of four for lean mixtures to almost 370 ppm (17%  $\text{NO}_2/\text{NO}_x$ ). CO was observed to inhibit the catalytic oxidation of NO to  $\text{NO}_2$ . Cadle, et al. (104) report that the average  $\text{NO}_2/\text{NO}_x$  ratio for cars operating over the 1975 FTP cycle was 12% before the oxidation catalyst and 5% after the catalyst with a maximum post-catalyst ratio of over 35% observed. However a prototype dual catalyst vehicle emitted 0.14 g/mi with an  $\text{NO}_2/\text{NO}_x$  fraction of over 25%. Therefore, the available evidence indicates that  $\text{NO}_2$  production by spark ignition engines is promoted by use of a stratified charge or other means of attaining lean combustion, low CO levels, low temperatures, use of methanol and possibly other alternative fuels, and is generally increased by use of exhaust purification catalysts.

Production of  $\text{NO}_2$  by compression-ignition engines has been investigated for normally aspirated and supercharged, direct and indirect injection diesels. Braddock and Bradow (18) found that the  $\text{NO}_2/\text{NO}_x$  ratio in the emissions from a light duty indirect

injection diesel was as high as 27.6% at idle (2.1 ppm NO<sub>2</sub>), 16.3% at 30 mph (5.7 ppm), and 9.1% at 50 mph (5.0 ppm). Hilliard and Wheeler (16) found that the maximum level produced by a direct injection diesel was three times that of an indirect injection engine, at approximately 9.3 g NO<sub>2</sub>/bhp-hr as compared to 3.4 g/bhp-hr for indirect injection. Their data have been used to construct Figures 3 and 4 which show the effect of speed and load on NO<sub>2</sub> production and the NO<sub>2</sub>/NO<sub>x</sub> fraction for a direct injection diesel. Formation of NO<sub>2</sub> reaches a maximum at moderate load while the NO<sub>2</sub>/NO<sub>x</sub> ratio decreases with load except at the highest engine speed. The NO<sub>2</sub> concentration and the NO<sub>2</sub>/NO<sub>x</sub> fraction both decrease with increasing engine speed. Figures 5 and 6 are graphical representations of data presented by Linnell and Scott (19) for a supercharged diesel. The NO<sub>2</sub> emission characteristics appear to be significantly different from those for unsupercharged diesels. Concentrations of NO<sub>2</sub> as high as 500 ppm were noted and NO<sub>2</sub>/NO<sub>x</sub> fractions varied in the range of 20-50%. The NO<sub>2</sub>/NO<sub>x</sub> ratio generally decreased with speed and peaked at about half load. Nitrogen dioxide concentrations peaked at medium speed, medium load but there was a general increase with load. Their data agree with those of other researchers (20-23). However, Harkins and Goodwine (24) report maximum NO<sub>2</sub> emissions of less than 60 ppm but more recent investigations of NO<sub>x</sub> analysis techniques indicate that the method they used may have led to NO<sub>2</sub> removal before analysis. Thus, the available data indicate that NO<sub>2</sub> production by diesels

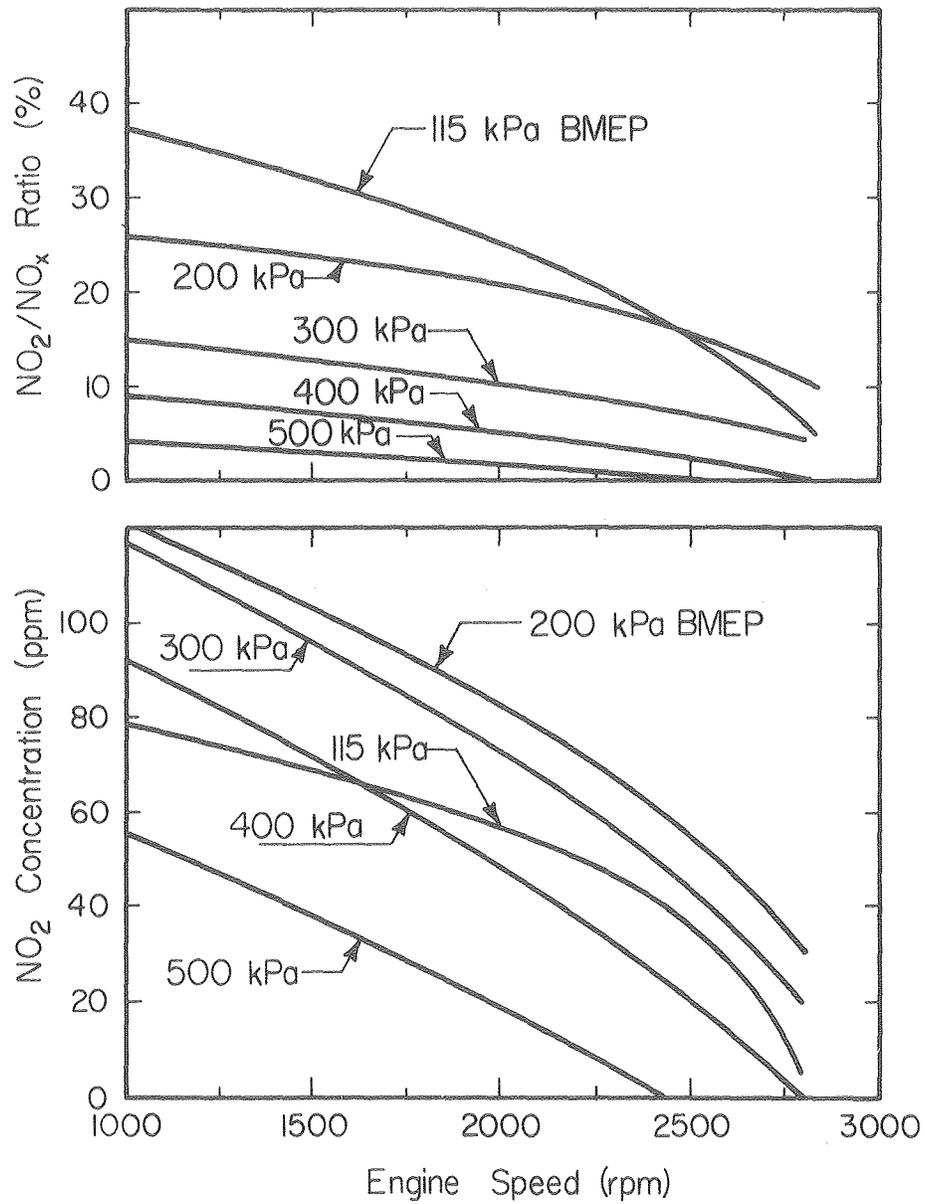


Figure 3. Effect of engine speed on NO<sub>2</sub> production by a direct injection diesel for various loads (from the data of Hilliard and Wheeler (16)).

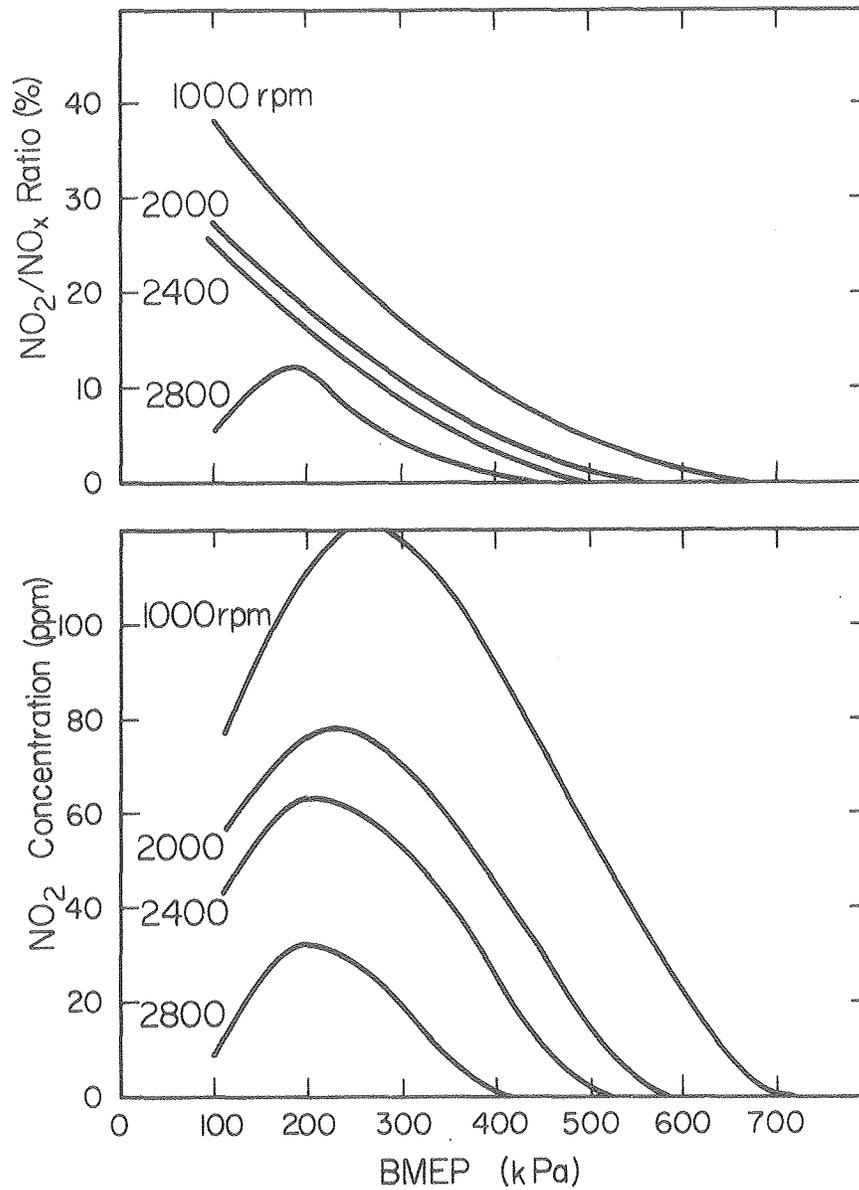


Figure 4. Effect of load on  $\text{NO}_2$  production by a direct injection diesel for various engine speeds (16).

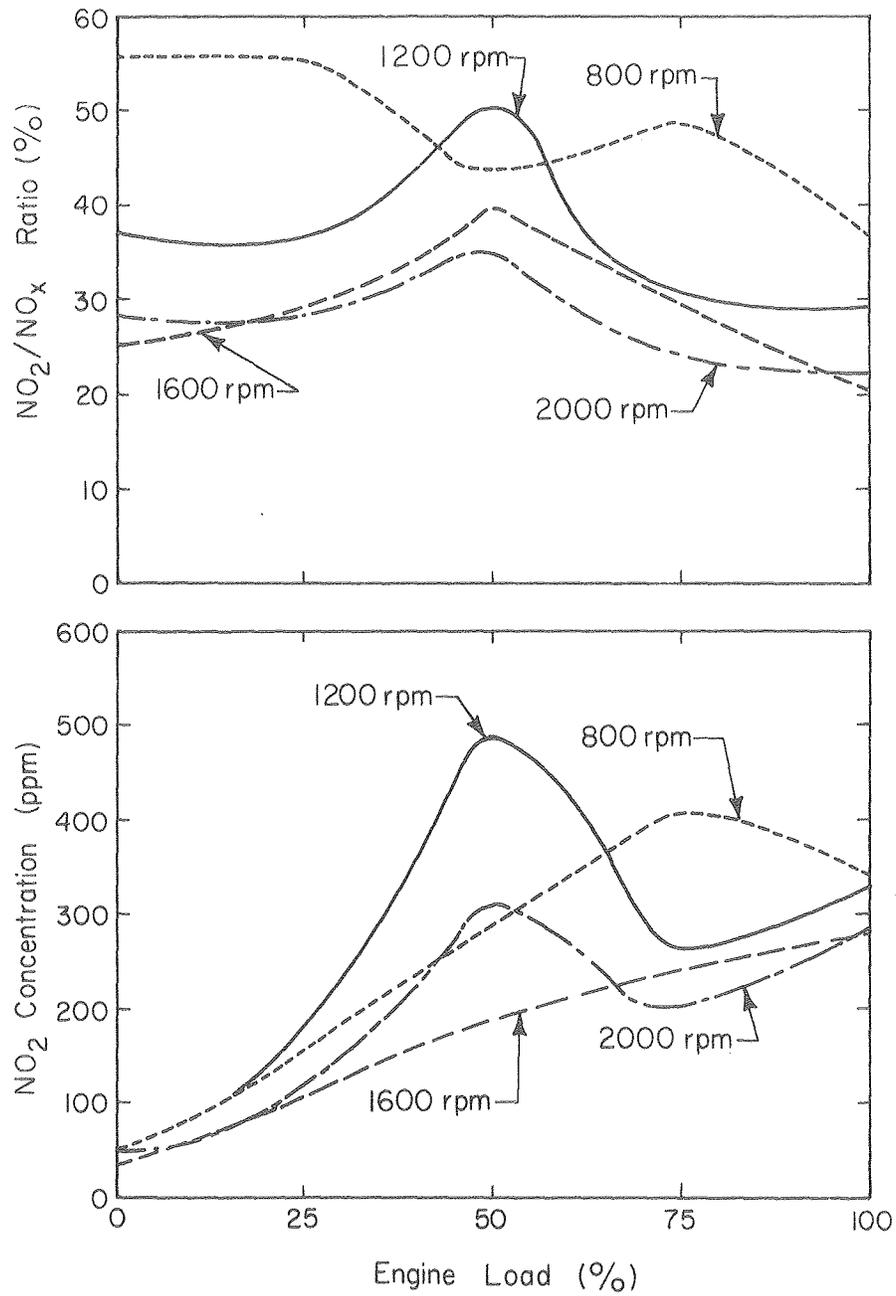


Figure 5. Effect of load on  $\text{NO}_2$  production by a supercharged diesel (from the data presented by Linnell and Scott (19)).

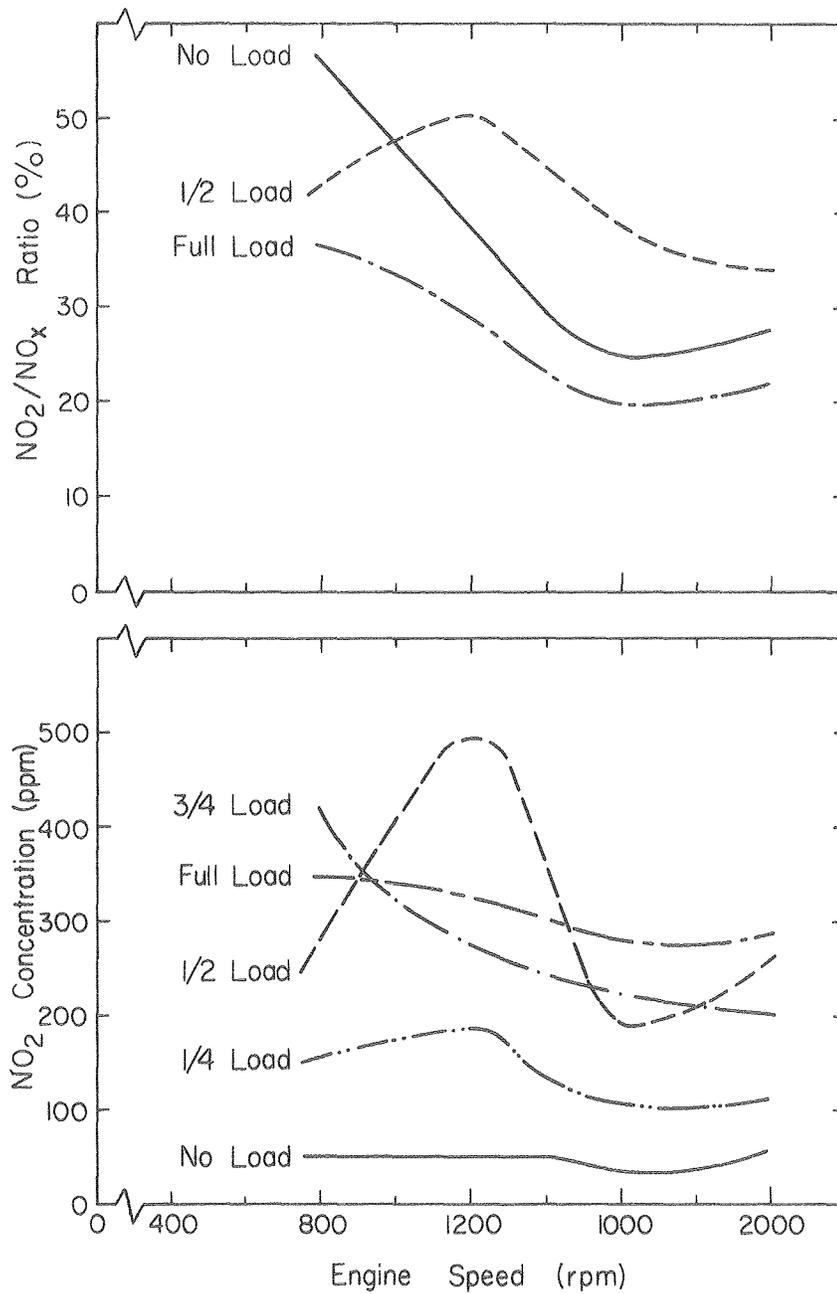


Figure 6. Effect of engine speed on NO<sub>2</sub> production by a supercharged diesel (from the data presented by Linnell and Scott (19)).

is much higher for direct injection than for indirect injection diesels and that supercharging significantly increases emissions.

Mason, et al. (107) report typical  $\text{NO}_2$  emissions of 100 ppm from coal, oil, and gas fired stationary power plants compared to more than 1000 ppm  $\text{NO}$ . They also report total  $\text{NO}_x$  emissions in 1974 from utility boilers, package boilers, warm air furnaces, and incinerators of 8.9 Mtons/yr.

$\text{NO}_2$  has also been measured in many laboratory combustion systems including turbulent diffusion combustors (25), jet stirred reactors (26), low pressure premixed flames (27-29), and swirl-stabilized combustors (30). In general, it has been observed that  $\text{NO}_2$  is formed in fuel lean premixed flames or in the cooler regions of turbulent diffusion flames. Survival of  $\text{NO}_2$  into the post flame gases depends on several factors such as residence time and temperature history.

It has now become fairly widely acknowledged that significant concentrations of  $\text{NO}_2$  may be emitted from practical combustion devices. The nationwide production of  $\text{NO}_2$  may be roughly approximated from the available information. Cavender, et al. (1) estimated that the  $\text{NO}_x$  emissions in 1970 were 8.2 MTons/yr for motor vehicles and 0.36 MTons/yr for aircraft. (1 MTon =  $10^6$  Tonnes (metric) =  $10^9$  kg). Assuming that 25% of the  $\text{NO}_x$  produced by aircraft is in the form of  $\text{NO}_2$  yields an estimated contribution of approximately 0.1 Mtons of  $\text{NO}_2$  per year. An estimate of 15% of the motor vehicle  $\text{NO}_x$  as  $\text{NO}_2$  yields a value of 1.2 MTons/yr from cars and trucks. This value agrees

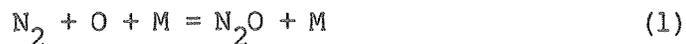
fairly well with the value obtained by using the 1979 motor vehicle  $\text{NO}_x$  emissions factor of 3.9 g/mi (31) which yields an estimate of 0.6 MTons/yr assuming  $10^{12}$  total miles per year. Stationary gas turbines produce 0.44 MTons/yr of  $\text{NO}_x$  and stationary IC engines produce 1.86 Mtons/yr (107). If the  $\text{NO}_2/\text{NO}_x$  fractions for these systems are assumed to be 25% and 15% respectively, these sources would produce 0.1 Mtons/yr and 0.3 Mtons/yr of  $\text{NO}_2$ . If 5% of the  $\text{NO}_x$  emissions from boilers, furnaces, incinerators, and process heating systems are emitted in the form of  $\text{NO}_2$ , they would constitute a source of about 0.5 Mtons/yr. It should be noted that although total  $\text{NO}_x$  emissions are predicted to decrease because of emissions regulations,  $\text{NO}_2$  production may increase with increasing use of lean combustion and other  $\text{NO}_x$  control techniques.

#### Nitrous Oxide ( $\text{N}_2\text{O}$ )

The major source of atmospheric  $\text{N}_2\text{O}$  is the bacterial denitrification of agricultural fertilizers. Estimates of production of  $\text{N}_2\text{O}$  from the soil range from 24 MTons/yr (32,33) to 55 MTons/yr (34). In addition, the ocean may be a major source, at 134 MTons/yr (32,33), or it may be a major sink, taking up 39 MTons/yr (34). Because of these uncertainties in the understanding of  $\text{N}_2\text{O}$ , estimates of its atmospheric lifetime vary from 5 years (32,33) to 170 years (35). Craig, et al. (36) have found that  $\text{N}_2\text{O}$  levels over the Pacific Ocean have increased 1.5% over the last decade. This is significant because increasing

levels of atmospheric  $N_2O$  could cause the surface temperature of the earth to increase through two separate mechanisms (37-39).

Pierotti and Rasmussen (40) have recently measured  $N_2O$  in the stack gases from power plants burning coal and natural gas. They detected  $N_2O$  concentrations of 3.1 and 11.0 ppm in the exhaust of two power plants operating on natural gas. The  $N_2O$  formation mechanism was previously suggested by Pratt and Malte (41). They propose that the reaction:



is important in combustion processes for temperatures which are lower than 1800 K.

Emissions of  $N_2O$  from coal-fired power plants were found to be an order of magnitude higher, at 32.7, 32.8, and 37.6 ppm, because of the fuel nitrogen. Weiss and Craig (42) confirmed these findings, reporting 25.8 ppm in the exhaust of a coal fired power plant and 25.0 ppm in the emissions from a power plant which used fuel oil. They calculated that combustion of coal and fuel oil could contribute 2.0 MTons/yr of  $N_2O$  to the atmosphere worldwide, and that combustion sources could then account for 50% of the observed increase in atmospheric nitrous oxide. However, combustion sources could be even more significant. Pierotti and Rasmussen estimate that coal combustion alone could contribute 3.5 MTons/yr. Furthermore,  $N_2O$  may be emitted from other

combustion devices, as will be discussed in the subsequent paragraphs.

Reaction (1) may be important in other commercial combustion devices, but measurements have only been attempted on one other combustion system, the spark ignition engine. Pierotti and Rasmussen (40) report measuring 100-200 ppb of  $N_2O$  in auto exhaust. Urban and Garbe (105) measured 5-6 mg/mi in the exhaust of a noncatalyst car with EGR and an air pump. This value was not significantly affected by mixture setting or engine misfire. Gray, et al. (44) monitored the  $N_2O$  concentrations in the exhaust and blowby of a single cylinder engine which was fueled with ammonia. The blowby contained 3-18 ppm, depending on the engine operating conditions. Figure 7 is a graphical representation of their exhaust  $N_2O$  data, showing that the concentration increases with air/fuel ratio and speed, is almost independent of compression ratio, and shows a general decrease with increasing spark advance. These levels are expected to be higher than for gasoline engines because of the nature of the fuel.

Furthermore, it has been shown (42) that automotive exhaust purification catalysts may promote the emission of  $N_2O$ . Several types of automotive catalytic converters are currently being used or have been proposed. Oxidation catalysts remove CO and UHC's from auto exhaust and reduction catalysts remove NO. These may be combined into "dual-catalyst" or "three way catalyst" systems. Seinfeld (45) suggests that  $N_2O$  may be formed over oxidation

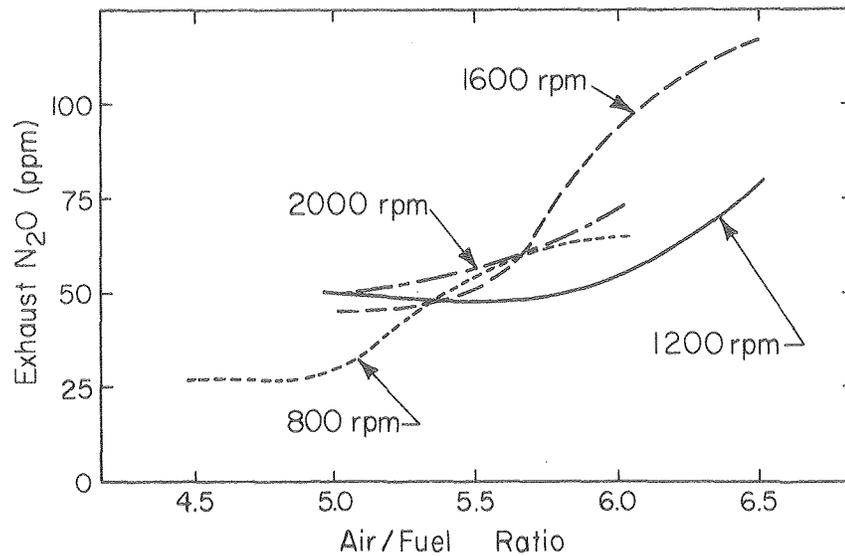
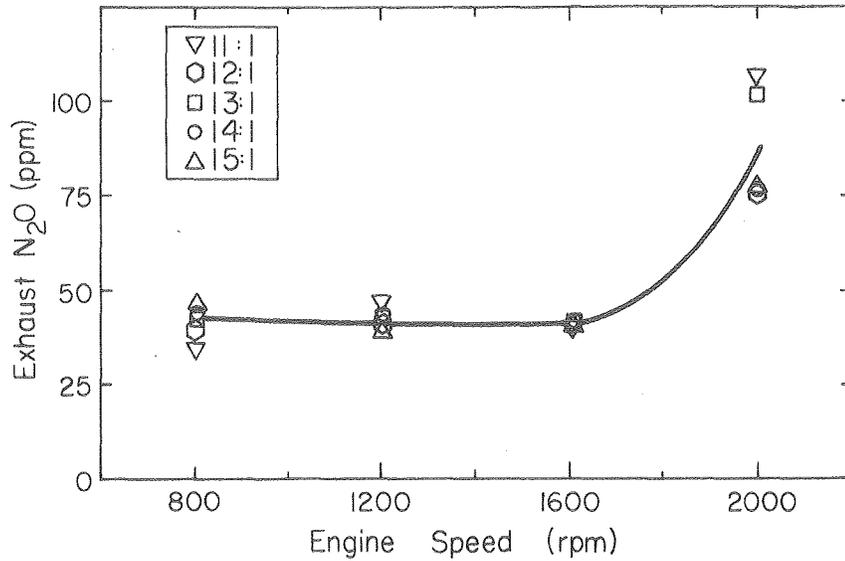
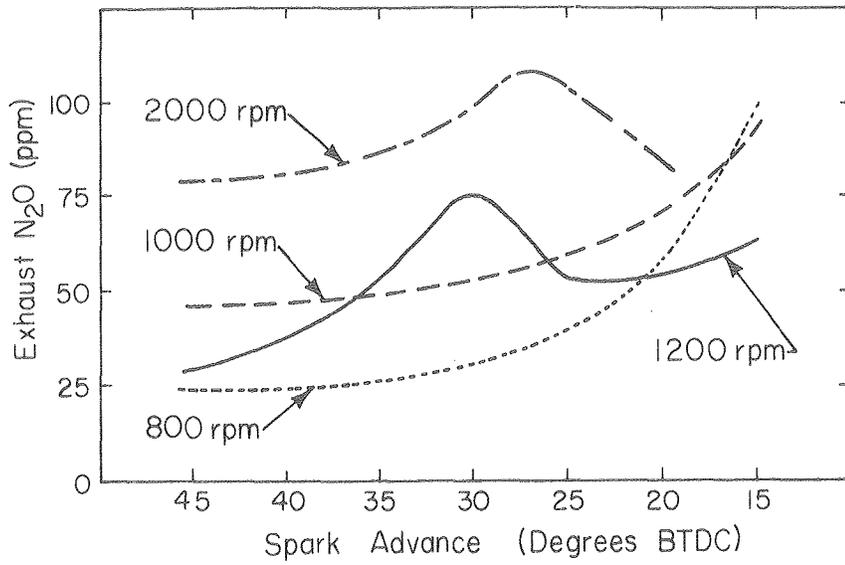
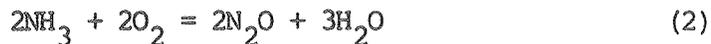
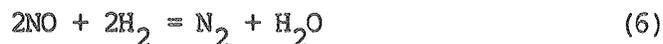
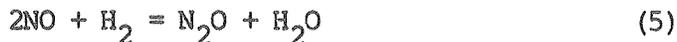
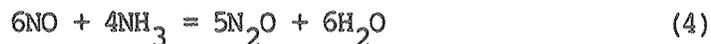
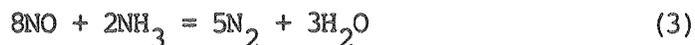


Figure 7. Nitrous oxide production by an ammonia fueled spark ignition engine for various operating and design conditions (from the data of Gray, et al.(44)).

catalysts via the overall reaction.



Otto, et al. (46,47) used four overall reactions to describe the operation of reduction catalysts:



They report that platinum catalysts which are the type being used commercially exhibit a 45% conversion of NO to  $\text{N}_2\text{O}$ . Voorhoeve, et al. (48) have studied the effect of catalyst material on NO reduction. Of the 13 rare-earth manganites studied only one demonstrated 100% conversion of NO to  $\text{N}_2$ . The rest evidenced the production of either  $\text{NH}_3$  (up to 50% of the inlet NO) or  $\text{N}_2\text{O}$  (up to 70%). Pierotti and Rasmussen (40) found that a catalytic converter could increase  $\text{N}_2\text{O}$  emissions by as much as a factor of

10 with levels up to 1 ppm being observed. Weiss and Craig (42) report a personal communication from Cicerone who measured  $N_2O$  emissions up to 10 ppm from 1976 cars equipped with platinum-palladium catalysts. Cadle, et al. (104) report an increase of from less than 3 ppm to more than 7 ppm over the catalyst for a 1977 production vehicle at 48 km/h. No increase was observed at 72 km/h. Weiss and Craig predict that emissions as high as 400 ppm are possible from reduction catalysts. Using this value they calculate that  $N_2O$  emissions from catalytic converters could reach 3.3 MTons/yr. Urban and Garbe (105) found that two cars equipped with catalysts and air pumps produced 8 and 34 mg/mi while two catalyst vehicles which did not have air pumps emitted 43 and 66 mg/mi during normal operation. System malfunctions were capable of increasing the average emission rate to 113 mg/mi. Woolsey (49) reports preliminary findings that average  $N_2O$  emissions from vehicles passing through the tunnel under Boston Harbor are less than 60 ppb or 64 mg/mi. However, the traffic mix in this study did not contain many catalyst-equipped vehicles. Assuming an average emission rate of 30 mg/mi yields an estimated production of  $N_2O$  by motor vehicles of 30000 Tonnes/yr, two orders of magnitude less than the initial estimate by Weiss and Craig.

In a recently developed  $NO_x$  control technique for stationary sources (50,91,92,93),  $NH_3$  is injected into the stack gases and reacts with the NO. Between 1 and 2 moles of  $N_2O$  may be formed for every 100 moles of NO removed. This would constitute a

source of  $N_2O$  of 0.3 MTons/yr for the application of this process to all stationary sources.

These investigations have shown that  $N_2O$  is present in the emissions of power plants and automobiles. The levels produced by power plants may be increased when fuels containing bound nitrogen are used or when secondary ammonia injection is employed. Automotive exhaust purification catalysts may also promote the formation of nitrous oxide. Although production by combustion systems does not appear to be as significant as previously believed, combustion sources could contribute 2-4 MTons/yr and may account for a portion of the observed increase in atmospheric levels of  $N_2O$ .

#### THE CYANIDES

Organic cyanides (nitriles) have been detected in the emissions from a variety of combustion systems. Of the various nitriles which have been measured, hydrogen cyanide appears to be the most prevalent.

##### Hydrogen Cyanide (HCN)

Hydrogen cyanide is a highly toxic protoplasmic poison. Little is known of its role as an atmospheric contaminant, and no ambient measurements have been reported. Stationary noncombustion sources discharge 2100 Tonnes/yr into the

atmosphere (51).

Several studies have reported measuring HCN emissions from spark ignition engines. Schuchmann and Laidler (52) found slightly less than 1 ppm of HCN in the exhaust of a 1963 Ford Anglia which was operated under both rich and slightly rich conditions. Myerson and Blair (53) found up to 8 ppm in the exhaust of a 1972 Ford 302 V8. Using a specific ion electrode, Kaneko (54) measured cyanide concentrations (as HCN) ranging from 2 ppm at idle, to 5 ppm at 40 km/hr, 10 ppm at 60 km/hr, and 15 ppm at 80 km/hr. Hurn, et al. (55) detected 1 to 1.5 ppm of HCN in the exhaust of 3 1972 Chevrolet vehicles and 2 stationary 1972 Chevrolet engines.

As shown in Table II, hydrogen cyanide emissions have also been measured using cars operated over test driving cycles. Gabele, et al. (56) report average HCN emissions from a Honda CVCC as 11.5 mg/mi and a Chrysler vehicle with a lean-burn engine emitted 10.7 mg/mi. Urban and Garbe (105) measured 3.9 mg/mi from a 1977 Pacer with EGR and air pump. Oetting (106) measured 10.1 mg/mi from a Volkswagen Rabbit without EGR operating over the Urban Driving Cycle. Hurn, et al. (55) have made extensive measurements of HCN emissions from automobiles. Emissions from a Volkswagen varied from 9-33 mg/mi. A Ford V8 emitted levels in the range 5-39 mg/mi and a Chevrolet V8 emitted 2-24 mg/mi. A Mazda rotary exhibited the lowest values, between 1 and 14 mg/mi. These measurements were made on new cars using various fuel additives during 9000 miles of tests (23000 for the Mazda). The

Table II HCN Emissions from Motor Vehicles over the FTP Cycle  
(except as noted)

Year	Make & Model	CID	CYL	EGR	AIR	CAT*	Rate (mg/mi)	Ref.	Comments
UNCONVENTIONAL									
1974	Mazda Rotary		2R	Y	Y	N	6.3	55	Range 1-14, simulated FTP
1976	Chrys. Lean Burn	440	V8				10.7	56	
1975	Honda CVCC	91	4	N	N	N	11.5	56	
"Avg"	Stratified Charge					N	7	104	Avg. of 2 cars
1975	Peugeot Diesel	129	4	N	N	N	0.9-1.9	64	Dependence on fuel
-	GM Diesel			N	N	N	2	104	
CONVENTIONAL NONCATALYST									
1977	AMC Pacer	258	6	Y	Y	N	3.9	105	
1974	Chev.	350	V8			N	7.6	55	Simulated FTP, range 3-16
1977	Chev. Nova	250	6	Y	N	N	8-14	43	
1974	Chev. Vega	140	4	N	N	N	7-10	43	Normal or rich
1974	Ford	351	V8			N	12.5	55	Simulated FTP, range 5-39
1974	VW		4	N	N	N	20.8	55	Simulated FTP, range 9-33
-	VW Rabbit	97	4	N	N	N	10.1	106	UDC
"Avg"	Noncatalyst					N	12	57	
"Avg"	Noncatalyst					N	11	104	Avg. of 7 cars
CATALYST VEHICLE									
Prot	AMC	230	6			D	4.44	58	
1974	Chev. Vega	140	4	N	N	3	10	43	
1978	Chev. Malibu	305	V8	Y	N	P	1.0	105	
1978	Chev. Malibu	305	V8	Y	Y	P	0.2	105	
1978	Ford Granada	302	V8	Y	Y	M	0.3	105	
1978	Ford Mustang II	302	V8	Y	N	M	0.8	105	
1977	Chrysler	440	V8			O	0.4	56	
-	VW Rabbit	97	4	N	Y	O	12.5	106	3" catalyst, UDC
-	VW Rabbit	97	4	Y	Y	O	5.4	106	6" catalyst, UDC
-	VW Rabbit	97	4	N	Y	3	3.3	106	UDC
"Avg"	Oxidation					O	1	57, 104	Avg. of 8 cars (104)
"Avg"	Three-way					3	3	57	
"Avg"	Dual and 3-way					B	5	104	Avg. of 6 cars
RICH MALFUNCTION									
1977	AMC Pacer	258	6	Y	Y	N	2.7	105	Rich best idle
1974	Chev. Vega	140	4	N	N	N	7-10	43	
1974	Chev. Vega	140	4	N	N	3	23	43	
1978	Chev. Malibu	305	V8	Y	N	P	4.5	105	Rich best idle
1978	Chev. Malibu	305	V8	Y	Y	P	2.6	105	High oil consumption
1978	Ford Granada	302	V8	Y	Y	M	2.4	105	Disabled EGR
1978	Ford Mustang II	302	V8	Y	N	M	9.9	105	Rich best idle
1977	Volvo 244 DL	130	4	-	N	3	66.3	60	
1977	Volvo	-	-	-	-	N	15.3	109	O <sub>2</sub> sensor off, correct idle
1977	Volvo	-	-	-	-	3	8.4	109	O <sub>2</sub> sensor off, rich idle
"Avg"	Three-way					3	50	57	
"Avg"	Dual and 3-way					B	13	104	Avg. of 3 cars

\*B-dual and 3-way, D-dual, M-monolithic oxidation, N-none, O-oxidation, P-pelleted oxidation, 3-three way.

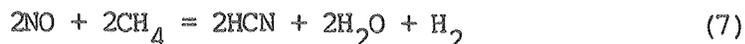
emission of HCN appeared to be independent of fuel additive usage and was not greatly affected by the accumulation of mileage on the vehicle. Preliminary tests conducted by the Environmental Science Department at General Motors (43) tentatively found that HCN emissions from a fuel injected four cylinder Chevrolet ranged from 7-10 mg/mi. These emissions appeared to be independent of whether the fuel injection system was operating normally or was in a fuel rich mode which was used to simulate failure of the oxygen sensor. Cadle and coworkers (57,104) have summarized the final GM data, reporting that the typical emission rate from noncatalyst cars is 11-12 mg/mi.

Exhaust purification catalysts have been shown to either decrease or have no effect on HCN emissions under normal conditions but may promote production of HCN during fuel rich operation (deceleration, downhill coasting, air pump malfunction, etc.). Kaneko (54) reports that a catalytic converter can remove 50-90% of the cyanide emissions normally found in auto exhaust. Gabele, et al. (58) found that HCN emissions from a prototype dual catalyst car were 4.44 mg/mi. This is approximately half the level reported for lean-burn, stratified charge, or uncontrolled engines. A Chrysler V8 with a conventional oxidation catalyst and air injection emitted only 0.4 mg/mi (56). Oetting (106) found that a Rabbit driven over the Urban Driving Cycle emitted 12.5 mg/mi with an 8 cm oxidation catalyst and air injection, 5.4 mg/mi with a 15 cm oxidation catalyst, air and EGR, and 3.3 mg/mi with an air injected three-way catalyst.

Urban and Garbe (105) measured about 0.8 mg/mi in the exhaust of two cars with oxidation catalysts and EGR while two other cars with oxidation catalysts, EGR, and air injection emitted 0.3 mg/mi. Tentative experiments at GM (43) found that a 3-way catalyst which had been aged for 50,000 miles had no effect on HCN emissions from a fuel injected four cylinder engine during normal operation. But, under fuel rich conditions the catalyst more than doubled HCN emissions to 22-24 mg/mi. The final GM data has been summarized by Cadle and coworkers (57,104). They report that the typical emissions from vehicles not equipped with catalysts are 11-12 mg/mi while vehicles equipped with an oxidation catalyst emit only 1 mg/mi and those with a three-way catalyst emit 3 mg/mi. The highest emission rate for any normally operating dual or three-way catalyst vehicle tested was 10 mg/mi. Under rich malfunction conditions, the three-way catalyst increases HCN emissions to between 13 mg/mi (104) and 50 mg/mi (57). These findings were confirmed by Bradow and Stump (60) who measured emission levels as high as 66.3 mg/mi for a vehicle with a malfunctioning (fuel-rich) three-way catalyst system. This result was predicted by Voorhoeve, et al. (59) who found that between 5 ppm and 700 ppm of HCN could be produced over a Pt oxidation catalyst under reducing conditions. HCN production was maximized at 700 C in the absence of H<sub>2</sub>O and SO<sub>2</sub> in the reactants. More recently, Voorhoeve, et al. (61) found that intermittent O<sub>2</sub> admission counteracted the inhibitory effect of SO<sub>2</sub> on catalytic HCN formation. Such a state is

expected to occur on cars equipped with dual or three-way catalysts which rapidly cycle from slightly rich to slightly lean. Keirns and Holt (109) found that a 3-way catalyst could remove HCN from the exhaust even under 13% misfire, rich idle, or disconnected oxygen sensor modes when a fuel containing 305 ppm S was used. The HCN levels under these conditions were up to a factor of 4 higher than for normal operation. There was a slight effect of the relative concentrations of platinum and rhodium in the catalyst. Also, Cadle, et al. (104) believe that the pelleted oxidation catalyst may be much less prone to HCN formation than monolithic catalysts.

Two studies aimed at promoting the conversion of  $\text{NO}_x$  to  $\text{N}_2$  found that injection of a hydrocarbon-oxygen mixture into auto exhaust worked well under optimum conditions. However, one of the studies found that retarding the spark timing by just  $4^\circ$  could increase the HCN emission by an order of magnitude to 125 ppm (53,63). The other investigation revealed a heterogeneous reaction between NO and hydrocarbons on the metallic components of the exhaust system to form HCN (62). Myerson (63) points out that hydrocarbon injection could proceed through reactions such as:



These investigations emphasize the wisdom of monitoring

unregulated species when developing novel pollution control techniques.

Braddock and Gabele (64) measured HCN emissions from a diesel powered passenger car. The levels ranged from 0.37-1.91 mg/mi, depending on the fuel (Jet A, Local No. 1, national average No. 2, or NO. 2-D) and the test cycle (1975 Federal Test Procedure, Highway Fuel Economy Test, or Sulfate Emissions Test). Cadle, et al. (104) found that the average emission rate from diesel powered GM cars was 2 mg/mi. Notably, HCN emissions from diesels appear to be 2 to 10 times lower than for stratified charge, lean-burn, dual catalyst, or uncontrolled cars over the same cycle.

Hydrogen cyanide and other N-species are produced by fires involving plastics and cellulose, primarily because these materials contain bound nitrogen (65-68). This probably explains the results of a recent study which found small concentrations of cyanide in the flue gas of a municipal incinerator (69). Kaneko (54) also found low concentrations in incinerator emissions and showed that the levels could increase to 5-8 ppm under imperfect combustion conditions.

Mason, et al. (107) report "small" concentrations of HCN in the flue gas of coal, oil, and gas fired power plants under normal operating conditions. A few ppm may also be formed with  $\text{NH}_3$  stack gas injection for  $\text{NO}_x$  control (50).

HCN formation has also been studied using laboratory combustion systems, including jet stirred reactors (70), two stage combustors (71), flat flame burners (72), Meker burners (73-76), and catalytic combustion systems (77,78). The results of these studies indicate that HCN production increases with increasing fuel/air ratio, increasing fuel nitrogen concentration, decreasing mixing intensity, and decreasing temperature.

In summary, it has been shown that significant levels of HCN may be emitted in automobile exhaust. These emissions may be halved through the proper use of exhaust purification catalysts but may be more than doubled on cars equipped with malfunctioning catalyst systems. Assuming that the average car emits 5 mg/mi allows estimation of the total contribution of HCN by automobiles at 5000 Tonnes/yr or 2 to 3 times that attributed to stationary noncombustion sources. Emissions of HCN should decrease as more catalyst equipped vehicles are absorbed into the nationwide fleet. Emissions from diesel engines appear to be significantly lower than for spark-ignition engines. Low levels are given off by municipal incineration and it is expected that HCN may also be produced by other combustion systems. The importance of HCN emissions is not clear because little is known about the background levels and atmospheric chemistry of this species.

### Other Nitriles (RCN)

Many nitriles have been identified in the emissions from various combustion systems. As is the case for HCN, little is known of the atmospheric chemistry of the cyanides and no ambient measurements have been reported. Noncombustion stationary sources emit 400 Tonnes of methyl cyanide and 500 Tonnes of vinyl cyanide annually (51). Similar information for the other nitriles of interest is not available.

The nitriles identified in automotive exhaust are cyanogen, phenyl cyanide, methyl cyanide, vinyl cyanide, and ethyl cyanide. Cyanogen was measured by Hurn, et al. (55) in studies aimed at determining the effect of use of gasoline additives on gaseous emissions from automobiles. A 1500 cc VW was found to emit up to 7 mg/mi of  $C_2N_2$ , a Ford V8 emitted up to 5 mg/mi, and the levels exhausted from a Chevrolet V8 and a Mazda were less than 1 mg/mi. Seizinger and Dimitriades (79) identified but did not quantify phenyl cyanide in the exhaust of a 1970 Ford 6 cylinder. Methyl cyanide, ethyl cyanide, and vinyl cyanide were detected by Bellar and Sigsby (80). Methyl cyanide was also detected by Schuchmann and Laidler (52).

Cyanides have also been detected in gas turbine exhaust. Table III lists the N-species measured in a series of studies by Stumpf and Blazowski (81), Conkle, et al. (82), Sievers, et al. (83), and Roquemore and Hodgeson (84). Several fuels and two additives were tested in a T56 Series III A single combustor. Six of these combustors, annularly arranged, form the basis of

Table III Distribution of Nitrogenous Species in Gas Turbine Exhaust, from Conkle, et al. (82)

Fuel Additive Pressure, psig	JP4	JP4	JP4	C <sub>8</sub> H <sub>18</sub>	C <sub>8</sub> H <sub>18</sub>	JP4 Pyridine	JP4 Pyridine	JP8	JP5**	JP5 Ferrocene	JP5 Ferrocene
	15	33	50	33	33	33	33	33	75	75	75
Total N-species, ppm as Hexane	0.0319	0.0743	0.0328	0.005	0.0103	0.0374	.0407	0.0119		.0008	0.039
Distribution, % of Total N											
Methyl Cyanide	43.89	98.25	14.63		25.24	5.61	5.16	17.65	37.78		10.26
Glycolonitrile			3.05								
n-Valeronitrile			0.61								
Nitromethane	15.36		8.54	100.0	33.01	29.41	41.77	72.27	18.41	100.0	89.74
Imidazole	40.75					56.15					
Neo-Pentyl Nitrate			73.17								
B-Keto-1-Nitro Octane		1.75									
2,4-Dimethyl Inidazoline							46.68				
3,6-Dipropyl 1-1,2,4,5-Tetrazine					41.75	6.42					
2-Methyl-2-Nitro Propane (Ethyl Cyanide)* (Pryazole) (2-Ethyl-1-Diazridine)						2.41	6.39		43.81		
								10.08			

\*Tentative identification.

\*\*Average of three points.

the T56 turboprop engine which is used in the C-131 aircraft. The test facility allowed the simulation of high power operation and the attainment of idle at several different pressure ratios to simulate the operating conditions of other engines. Stumpf and Blazowski state that the "data do not include significant amounts of HCN, contrary to expectations." This may be due to HCN adsorbing on the Porapak Q gas chromatograph column, a difficulty which has been indicated by other investigations. Table IV shows the experimental conditions which were investigated and how they affected the fraction of the organic emissions which were attributable to nitrogenous species. The most obvious trend is that the fraction increases markedly with increasing combustor inlet pressure (pressure ratio). Secondly, the fuel type can affect the fraction when all other conditions remain constant. Results for JP4, JP5, and iso-octane are comparable under mid-pressure ratio idle conditions, but are down by a factor of 5-6 for JP8 under the same conditions. Fuel additives also have an impact on the fraction which is nitrogenous. Addition of 0.042 wt. % of ferrocene (an iron containing smoke suppressant additive) to JP5 at 75 psig can decrease the fraction which is nitrogenous by more than 50%. Addition of 1.68% pyridine (yielding a fuel-N concentration of 0.3 wt. %) to JP4 at 33 psig increases the fraction which is nitrogenous by more than a factor of 3. Therefore, the fraction of the organics (other than HCN) which is attributable to N-species increases with increasing pressure and is affected by

Table IV Percent of Organic Gas Turbine Emissions which contain Nitrogen\*

Fuel	JP4	JP4	JP4	JP4	JP8	C <sub>8</sub> H <sub>18</sub>	JP5	JP5
Additive	---	---	---	1.68 wt% pyridine	---	---	---	0.042 wt% Ferrocene
Pressure, psig	15	33	50	33	33	33	75	75
Combustor Inlet Temperature, °K	367	439	478	489	438	439	627	627
Combustor Inlet Pressure, psig	2.0	3.2	4.4	3.2	3.2	3.2	6.0	6.0
Fuel/Air wt ratio	0.0078	0.0076	0.0080	0.0075	0.0075	0.0078	0.0179- 0.0188	0.0183- 0.0191
Condition**	LPR Idle	MPR Idle	HPR Idle	MPR Idle	MPR Idle	MPR Idle	High Power	High Power
RN/HC, %	0.1	2.0	5.5	6.5	0.4	2.5	5.4	2.1

\*From the data of Stumpf and Blazowski (81).

\*\*LPR-low pressure ratio; MPR-mid pressure ratio; HPR-high pressure ratio.

fuel and additive type. Table III details the distribution of nitrogenous organics among the various N-species which were measured. Methyl cyanide and nitromethane were the most prevalent species, although other species were important in some instances. It should be noted that the actual concentrations of these species are very low, partially due to the diluent effect of the secondary cooling air in gas turbines. The main significance of this series of studies is that it emphasizes that complex nitrogenous species can be formed in commercial combustion systems, even those that are operated under very fuel lean conditions. This is attributable to the nature of the turbulent diffusion flame, and the same emissions characteristics may not be expected for premixed, fuel-lean combustion systems.

Fuel nitrogen studies using laboratory combustion systems have also revealed the production of cyanides. Dubay and Hites (85) report measuring several cyano-arenes in the combustion products from an alcohol lamp and a Meker burner. In both cases, the fuel was doped with pyridine (a nitrogenous additive) and the combustion process was fuel rich. Both isomers of cyanonaphthalene and four isomers of cyanacenaphthylene were identified and several isomers of cyanophenanthrene were tentatively identified. Some of these species are potentially carcinogenic. Malte, et al. (70) measured significant production of HCN in the combustion of stoichiometric and fuel rich mixtures in a jet stirred reactor. They also noted the formation of  $\text{CH}_3\text{CN}$  (methyl cyanide or ethane nitrite) and  $\text{CH}_2\text{CHCN}$

(vinyl cyanide or propene nitrite). The production of these species increased with increasing equivalence ratio and was independent of additive type.

The available data are not sufficient to allow extensive assessment of the production of nitriles by combustion systems. Automobiles may account for 1000 Tonnes/yr or more of cyanogen. Additionally, they have been shown to produce ethyl cyanide, methyl cyanide, phenyl cyanide, and vinyl cyanide. The effect of air pollution control systems on emission of these species has not been determined. Methyl cyanide is also emitted by gas turbines. Cavender, et al. (1) report that aircraft emitted 0.38 MTons of hydrocarbons in 1970 and Mason, et al. (107) estimate that stationary gas turbines emitted 13700 Tonnes in 1974. If it is assumed that the emissions characteristics of stationary gas turbines are similar to those of aircraft gas turbines, and if it is estimated (from Table IV) that 1% of the hydrocarbon emissions are nitrogenous and (from Table III) that 20% of the nitrogenous hydrocarbons are methyl cyanide, then it may be estimated that stationary gas turbines produce 30 Tonnes/yr and aircraft produce 760 Tonnes/yr of methyl cyanide. Therefore, these two sources may emit twice the amount attributed to stationary noncombustion sources. The significance of emission of the nitriles is not clear because little is known about the atmospheric chemistry and background levels of these species.

## THE AMINES

Ammonia, nitrosamines, and alkylamines have been detected as products of combustion. Ammonia is the most prevalent, but the nitrosamines, because they are highly carcinogenic, may prove to be the most significant amines emitted by combustion systems.

Ammonia (NH<sub>3</sub>)

Ammonia is not a highly toxic species but measured urban levels are approaching the theoretically safe level for continuous exposure of the general populace (3). Also, Wang, et al. (37) predict that atmospheric levels of NH<sub>3</sub> could double within the next half century. They report that this could have a significant climatic impact, increasing the surface temperature of the earth. Ammonia may also play an important role in the photochemical smog mechanism, especially in aerosol nitrate formation. Noncombustion stationary sources emit 89000 Tonnes/yr and stationary combustion sources emit 15000 Tonnes/yr. Recent investigations indicate that NH<sub>3</sub> may be emitted from more combustion systems than those listed by Eimutis and Quill (51). Therefore, combustion sources may be more important than previously realized.

As shown in Table V, NH<sub>3</sub> has been reported in the emissions of a wide variety of automobiles. Dietzman and Bradow (86) and Myerson and Blair (53) failed to detect NH<sub>3</sub> in the exhaust of V8 engines, and Hurn and coworkers (55) only tentatively detected it

Table V Ammonia Emissions from Motor Vehicles over the FTP Cycle  
(except as noted)

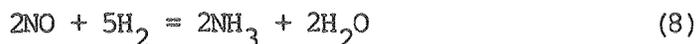
Year	Make & Model	CID	CYL	EGR	AIR	CAT*	Rate, mg/mi (ppm)	Ref.	Comments
UNCONVENTIONAL									
	Mazda Rotaries		2R	Y	Y	N	(32-90)	88	Thermal reactor, 60 mph
Prot	Honda CVCC	91	4	-	-	N	(9)	88	60 mph
1974	Ford Proco	-	-	-	-	-	(14)	88	60 mph
	EPA Gas Turbine	-	-	N	N	N	(28)	88	60 mph
	Peugeot Diesel	129	4	N	N	N	(7)	88	60 mph
1973	Opel Diesel	-	-	-	-	N	(39)	88	60 mph
	GM Diesels			N	N	N	1-2	104	
CONVENTIONAL NONCATALYST									
1977	AMC Pacer	258	6	Y	Y	N	5.0	105	
1974	Chev. Vega	140	4	N	N	N	7-10	43	
1977	Chev. Nova	250	6	Y	N	N	3-18	43	Lean Carb.
1973	Ford	-	-	-	-	N	(7)	88	60 mph
1956	Oldsmobile	-	V8	N	N	N	(1-6)	87	CMVPCB Cycle
1972	Pontiac	-	-	-	-	N	(17)	88	75 Hardware, 60 mph
"Avg"	Noncatalyst					N	3	57	
"Avg"	Noncatalyst					N	4	104	Average of 6 cars
CATALYST VEHICLE									
1974	Chev. Vega	140	4	N	N	3	19-24	43	
1977	Chev. Nova	250	6	Y	N	0	2-4	43	Lean Carb.
Other	GM					0	0.2-23	43	Cal. Emissions Pkg.
1978	Chev. Malibu	305	V8	Y	N	P	5.0	105	
1978	Chev. Malibu	305	V8	Y	Y	P	8.6	105	
1978	Ford Granada	302	V8	Y	Y	M	3.0	105	
1978	Ford Mustang II	302	V8	Y	N	M	5.0	105	
1972	Ford	-	-	-	-	0	(1)	88	60 mph
	EPA Cricket	-	-	-	-	0	(1)	88	60 mph
1976	Oldsmobile	231	6	N	N	0	7.2	43	
1978	Olds Cutlass	305	V8	Y	N	0	2.7	105	
1977	Volvo	-	-	-	-	3	10-25	109	Dep. on Cat. Mat'l.
"Avg"	Oxidation					0	4	57	
"Avg"	Oxidation					0	33	103	Avg. of 22 cars
"Avg"	Three-way					3	7	57	
"Avg"	Dual and 3-way					B	8	104	Avg. of 7 cars
RICH MALFUNCTION									
1974	Chev. Vega	140	4	N	N	N	0.3	43	
1974	Chev. Vega	140	4	N	N	3	108	43	Slightly rich
1974	Chev. Vega	140	4	N	N	3	268	43	Richer
1978	Chev. Malibu	305	V8	Y	N	P	29.3	105	Rich best idle
1978	Chev. Malibu	305	V8	Y	Y	P	20.0	105	High oil consumption
1978	Ford Granada	302	V8	Y	Y	M	34.2	105	Rich best idle
1978	Ford Mustang II	302	V8	Y	N	M	90.6	105	Rich best idle
1963	Ford Anglia			N	N	N	(to 180)	52	Not FTP
1978	Olds Cutlass	305	V8	Y	N	0	14.9	105	Rich best idle
1977	Volvo	-	-	-	-	N	80.5	109	O <sub>2</sub> sensor off
1977	Volvo	-	-	-	-	3	344.3	109	13 percent misfire
"Avg"	three-way					3	200	57	
"Avg"	Dual and 3-way					B	184	104	Avg. of 3 cars

\*B-dual and 3-way, D-dual, M-monolithic oxidation, N-none, O-oxidation, P-pelleted oxidation, 3-three way.

in the exhaust of various 1974 models. However, many other researchers have been able to quantify the ammonia produced by spark ignition engines. Harkins and Nicksic (87) measured between 1 and 6 ppm of  $\text{NH}_3$  in the exhaust of a 1956 Oldsmobile V8. The presence of nitrogen-containing detergent additives or lead antiknock compounds in the fuel did not affect the  $\text{NH}_3$  levels in the exhaust. Based on these measurements, they calculated that auto exhaust could account for 10% of urban atmospheric  $\text{NH}_3$ . The levels they reported appear to be at the lower end of the published measurements. At the other extreme, Schuchmann and Laidler (52) measured levels of  $\text{NH}_3$  and lower amines as high as 180 ppm for slightly rich combustion and 60 ppm for rich combustion in the exhaust from a 1963 Ford Anglia. The National Research Council (88) reports that  $\text{NH}_3$  was emitted from all seventeen engines tested at 60 mph. A prototype Honda CVCC emitted 9 ppm while rotary engines (Mazda RX2's and RX3's) equipped with thermal reactor, bypass, air pump, and EGR emitted 32.5-36.5 ppm. However, one rotary emitted 89.4 ppm, although its aldehyde emissions were not significantly different from those of the other rotary engined cars. A 1972 Pontiac emitted 17.4 ppm, a 1973 Ford emitted 7.3 ppm, and a 1974 Ford Capri with a PROCO engine emitted 13.7 ppm at 60 mph. Urban and Garbe (105) found that a noncatalyst Pacer with EGR and air injection emitted 5 mg/mi. Ammonia was tentatively quantified during preliminary experiments at GM (43). A 1974 Vega 4 cylinder with electronic fuel injection emitted 8.0 mg/mi for stoichiometric operation but

only 0.3 mg/mi with rich mixtures. A 1977 Nova 250 CID 6 cylinder with electronic EGR and a special lean carburetor emitted 3-18 mg/mi. The final results from this investigation indicate that typical  $\text{NH}_3$  emissions from a noncatalyst vehicle were 3-4 mg/mi (57,104).

Several studies have found that ammonia may be formed over exhaust purification catalysts. Lee and Makowskii (89) have demonstrated that  $\text{NH}_3$  is an active intermediate in NO removal over NO reduction catalysts. Substantial emission of  $\text{NH}_3$  may occur at high inlet NO, low inlet  $\text{O}_2$ , and high inlet  $\text{H}_2$ . In addition to reactions (3) and (6) they offer the global reactions:



Mequerian, et al. (90) also attribute  $\text{NH}_3$  formation to reaction (9), where the hydrogen may be present in the exhaust products or may be formed over the catalyst by the water-gas shift reaction. They found 29-100%  $\text{NO}_x$  conversion to  $\text{NH}_3$  over metal oxide catalysts, dependent upon catalyst material. Also, the conversion to  $\text{NH}_3$  was shown to decrease with increasing  $\text{O}_2/\text{CO}$  ratio and increasing catalyst temperature and could be minimized by the proper selection of promoters and support material.

Bernhardt and Hoffman (91) noted maximum production of 150-1000 ppm  $\text{NH}_3$  dependent upon catalyst material. High catalyst temperature and high space velocity inhibit ammonia formation but some catalysts lose effectiveness as the throughput rate increases. Cooper, et al. (108) found that the use of rhodium as a promotor for platinum catalysts improved  $\text{NO}_x$  control but resulted in higher  $\text{NH}_3$  production, especially under oxygen deficient conditions. Catalyst aging improved the  $\text{NH}_3$  production characteristics, but up to 1000 ppm was still noted. Voorhoeve, et al. (48) studied the use of thirteen rare earth manganites as exhaust catalysts and found that as much as 50% of the inlet NO could be converted to  $\text{NH}_3$ . In a later study (59), they found that  $\text{NH}_3$  was the primary product of NO reduction over platinum catalysts for temperatures less than 600 C. However, the National Research Council (88) reports that a 1972 Ford and a Cricket equipped with catalysts emitted only about 1 ppm at 60 mph, much less than the test cars which did not have catalysts. This apparent inconsistency is clarified by preliminary results from GM (43), which showed that a catalyst would lower or have no effect on  $\text{NH}_3$  for lean combustion but increase it for stoichiometric and rich combustion. A 1977 Nova 6 cylinder emitted 8 mg/mi without the converter and only 3 mg/mi with the converter. This car was equipped with a special lean carburetor and EGR. A fuel injected 1974 Vega was modified to run rich to simulate failure of the oxygen sensor. Without the catalyst, it emitted 8 mg/mi for stoichiometric combustion and 0.3 mg/mi for

rich conditions. With the converter,  $\text{NH}_3$  emissions increased to 19-24 mg/mi stoichiometric, 108 mg/mi slightly rich, and 268 mg/mi rich. Use of air injection in conjunction with the California emissions package and catalyst was seen to reduce  $\text{NH}_3$  emissions by a factor of between 2 and 30, with the lowest levels being 0.2 mg/mi. Cadle, et al. (57,104) summarize these results by reporting typical emissions to be 3-4 mg/mi for noncatalyst vehicles, 4-33 mg/mi for vehicles with oxidation catalysts, and 7-8 mg/mi for those with dual or three-way catalysts. Dual and three-way catalyst vehicles operating under rich malfunction conditions produced an average of 184-200 mg/mi with a maximum rate of 235 mg/mi emitted. Keirns and Holt (109) investigated a prototype 1977 Volvo with various 3-way catalysts over the FTP cycle. Under normal operating conditions, the catalysts emitted 10-25 mg/mi but the levels increased up to 344 mg/mi for various malfunction conditions. Urban and Garbe (105) found that a pelleted catalyst car with EGR emitted 5.0 mg/mi without air injection and a similar car with air injection emitted 3.0 mg/mi. These investigations indicate that in some cases automotive exhaust treatment systems may decrease emission of NO at the expense of increased production of  $\text{NH}_3$ .

It has also been shown that ammonia may be produced by diesels and gas turbines. A 1972 Opel diesel was found to emit 38.9 ppm and a Peugeot diesel emitted 7.28 ppm at 60 mph (88). Cadle, et al. (104) report that GM diesels emit 1-2 mg/mi. An EPA Williams automotive gas turbine was found to produce 28.20

ppm at 60 mph (88).

Mason, et al. (107) report ammonia concentrations of less than 100 ppm in the flue gas of coal, oil, and gas fired power plants. An investigation (92) which proposed secondary fuel injection to reduce  $\text{NO}_x$  emissions from power plants found that injection of methane could reduce  $\text{NO}_x$  by 50%, and injection of ammonia could decrease  $\text{NO}_x$  emissions by as much as 90%. Muzio, et al. (93) and Exxon (50) have confirmed these findings using  $\text{NH}_3$ ,  $\text{H}_2$ , and various hydrocarbons as secondary fuels. Ammonia was found to be the most effective secondary fuel. However,  $\text{H}_2$  or  $\text{CH}_4$  may be injected with the  $\text{NH}_3$  for temperature compensation (94). With  $\text{CH}_4/\text{NH}_3$  injection a few ppm of HCN can be emitted. Emissions of  $\text{NH}_3$  can be kept to about 10 ppm under optimum conditions, but exhaust  $\text{NH}_3$  may be much higher during off-design operation.

These investigations indicate that motor vehicles may produce significant amounts of  $\text{NH}_3$ . Automotive air pollution control systems may increase or decrease these emissions, dependent primarily upon the fuel/air ratio. Assuming a nationwide average emission of 10 mg/mi yields an estimated contribution from automobiles of 10000 Tonnes/yr. Stationary combustion systems are reported to produce 15000 Tonnes/yr (51). Additionally, power plant stack gas treatment systems may also contribute to atmospheric loadings of  $\text{NH}_3$ . Therefore, combustion systems may account for 20-25% of the anthropogenic production of ammonia.

Alkylamines (RNH<sub>i</sub>)

Monoethylamine (MEA, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>), monomethylamine (MMA, CH<sub>3</sub>NH<sub>2</sub>), dimethylamine (DMA, (CH<sub>3</sub>)<sub>2</sub>NH), and trimethylamine (TMA, (CH<sub>3</sub>)<sub>3</sub>N) are the alkylamines which have been identified as products of combustion. Of these, DMA and TMA are of the most significance because they may nitrosate to form the carcinogenic nitrosamines. Additionally, the Bay Area Air Pollution Control District in California has established a 0.05 ppm standard for TMA based on its strong odor.

A number of researchers have identified alkylamines in the exhaust from automobiles. Schuchmann and Laidler (52) report detecting but not quantifying lower amines in the exhaust of a 1963 Ford Anglia. They also report that Haagen-Smit detected alkylamines in auto exhaust. Urban and Garbe (105) found traces of MEA in the exhaust of a 1978 Oldsmobile with EGR and an oxidation catalyst. During preliminary tests, researchers at the GM Environmental Science Department (43) measured 40 ppb of MMA and 20 ppb of DMA in the exhaust of a 1974 Vega operating at the stoichiometric air/fuel ratio. These levels decreased to 3 ppb MMA and 2 ppb DMA for rich combustion. However, the exhaust concentrations were significantly higher after an exhaust purification catalyst was installed. For stoichiometric mixtures, the catalyst promoted the formation of 230 ppb MMA but did not significantly affect DMA. For slightly rich mixtures, the emissions increased to 1.35 ppm MMA and 110 ppb DMA. When running rich, the Vega produced 1.22 ppm MMA (an increase of a

factor of 400 over the level emitted without the catalyst) and 140 ppb DMA (an increase of a factor of 70). This result was foreseen by Voorhoeve, et al. (59) who noted the formation of DMA when simulated exhaust gas was passed through a model catalyst. As shown in Table VI, GM also measured MMA and DMA emissions from other catalyst equipped cars. A 1976 Olds 6 cylinder emitted the highest MMA levels at 300 ppb and a 1977 Vega 4 cylinder produced the highest concentrations of DMA at 90 ppb. Catalyst equipped cars which also had the California emission package and air injection emitted MMA and DMA levels which were much lower in most cases. A 1975 Buick V8 was a notable exception, emitting less than 0.05 mg/mi of MMA and DMA without air injection. This compares to 1975 Oldsmobile V8 without air injection which emitted 0.76 mg/mi MMA and 0.13 mg/mi DMA and a 1975 Chevrolet V8 with air injection which emitted 0.16 mg/mi MMA and 0.13 mg/mi DMA. Therefore, it appears that MMA and DMA are emitted from uncontrolled engines, with the exhaust concentrations decreasing for rich mixtures. A catalyst will increase emissions of alkylamines, but use of a catalyst in conjunction with air injection and the California emissions package may decrease emissions of these species.

Mason, et al. (107) report low concentrations of amines in the flue gas from coal and oil fired power plants. They also estimate that combustion sources account for less than 5% of total amine emissions.

TABLE VI. AMINE EMISSIONS FROM MOTOR VEHICLES (43)

YEAR	MAKE	ENGINE	CATALYST	NH <sub>3</sub> mg/mi	MMA mg/mi (ppm)	DMA mg/mi(ppm)	COMMENTS
74	Chev. Vega	140CID4	None	8.0	(0.4)	(0.02)	Stoichiometric
74	Chev. Vega	140CID4	None	0.3	(0.003)	(0.002)	Rich
74	Chev. Vega	140CID4	3-Way	19-24	(0.23)	(0.03)	Stoichiometric
74	Chev. Vega	140CID4	3-Way	108	(1.35)	(0.11)	Slightly rich
74	Chev. Vega	140CID4	3-Way	268	(1.22)	(0.14)	Rich
77	Chev. Vega	140CID4	Oxid.	5.9	(0.11)	(0.09)	CEP*, Rich Idle
76	Olds. Starfire	231CID6	Oxid.	7.2	(0.30)	(0.02)	
75	Chev. Impala	350CIDV8	Oxid.	0.2	(0.002)	(0.001)	CEP, Air
75	Chev. Impala	350CIDV8	Oxid.	0.6	0.16	0.13	CEP
75	Chev. Impala	350CIDV8	Oxid.	1.2	(0.11)	(0.009)	CEP
76	Chev. Caprice	350CIDV8	Oxid.	5.6	(0.27)	(0.005)	
75	Olds. Cutlass	350CIDV8	Oxid.	2.4	0.76	0.13	CEP
75	Pont. Bonneville	400CIDV8	Oxid.	1.4	(0.09)	(0.04)	
77	Olds. 88	403CIDV8	Oxid.	0.8-23.0	to .11	to .29	CEP, Air
75	Buick Electra	455CIDV8	Oxid.	5.9	(<.05)	(<.05)	CEP

A conservative estimate of a nationwide average of 0.1 mg/mi for both dimethylamine and trimethylamine yields an estimated production of 100 Tonnes/yr of each by automobiles. Other combustion systems may also emit alkylamines but this possibility has not been extensively investigated. The primary significance of emission of the alkylamines is that they are precursors of the carcinogenic nitrosamines. However, because there are significant natural sources of secondary amines, it is possible that control of atmospheric formation of nitrosamines may be most effectively obtained through restrictions of  $\text{NO}_x$ , nitrites, and nitrates rather than amines.

#### Nitrosamines ( $\text{R}_1\text{NNO}$ )

Nitrosamine emissions from combustion systems are significant because these species are powerful carcinogens. The World Health Organization (95) recognizes the N-nitroso compounds as the most powerful carcinogens yet tested against experimental animals. The EPA (96) states that the nitrosamines have no equals as a family of carcinogens.

Fine and coworkers (97) were the first researchers to report nitrosamines in auto and diesel exhaust. Urban and Garbe (105) tentatively detected up to 0.35 mg/mi of dimethylnitrosamine in auto exhaust. Several other researchers have unsuccessfully attempted to detect these carcinogens in the emissions from automobiles (55, 86, 98). There is concern that the nitrosamines were formed in the sample concentration process used by Fine, et

al., but even this would indicate the presence of precursors. The other investigators also failed to detect these precursor amines, which might indicate some difficulty with their sample transfer or analytical systems. Recall that several researchers have observed amines in auto exhaust (43, 52, 99). It is currently believed that nitrosamine formation in engine crankcases may be a more significant problem than exhaust emissions because of the longer residence times available for crankcase reactions.

The lack of agreement among these researchers emphasizes the difficulties in the quantitative analysis of amines in combustion products. Considering the significance of these species, further research is warranted.

#### MISCELLANEOUS N-SPECIES

##### Nitroparaffins ( $C_n H_{2n+1} NO_2$ )

Nitromethane and nitroethane have been measured in the emissions from combustion systems. These species are not very toxic and, therefore, probably are not a direct public health hazard. However, they may take part in atmospheric reactions and their atmospheric chemistry merits further investigation.

Cadle and Nebel (57) note the detection of nitromethane in the exhaust of a prototype GM catalyst car. Seizinger and Dimitriades (79) measured as much as 5 ppm of nitromethane in the exhaust of a 1970 Ford 6 cylinder. Dietzmann and Bradow (86) report nitromethane levels between 0.1 and 0.5 ppm. Fuel/additive combination, engine configuration, and exhaust treatment did not significantly affect exhaust nitromethane concentrations. Bellar and Sigsby (80) also detected nitromethane in auto exhaust. Hurn, et al. (55) measured 0.2-0.3 ppm of nitromethane in auto exhaust and found that exhaust levels were not affected by the use of a nitrogen containing gasoline additive. For the four vehicles tested, nitroethane concentrations were less than 3 mg/mi independent of fuel additive or mileage accumulation. Nitromethane emissions from a Mazda rotary, at 4-16 mg/mi, were 2-4 times higher than nitroethane or HCN emissions. A Chevrolet V8 also had high nitromethane emissions at 7-18 mg/mi. The VW and Ford V8 had lower exhaust concentrations at 1-7 mg/mi. Nitromethane emissions were approximately independent of additive type, but did appear to be linearly related to exhaust  $\text{NO}_x$  levels.

Nitromethane was also noted to be one of the primary non- $\text{NO}_x$  N-species emitted from gas turbines, as shown in Table III. In two cases, nitromethane was the only non- $\text{NO}_x$  N-species measured. It was not measured for only one operating condition.

Assuming that 40% of the nitrogenous hydrocarbon emissions from both stationary and aircraft gas turbines is emitted as nitromethane (Tables III and IV) yields the estimate that aircraft produce 1500 Tonnes/yr and stationary gas turbines produce 55 Tonnes/yr. A conservative assumption of 1 mg/mi for both nitromethane and nitroethane yields an estimate of production of 1000 Tonnes/yr of these nitroparaffins by motor vehicles. The effect of emission control systems on production of these species has not been investigated. Nitroparaffins may be produced by other combustion systems as well.

Nitro-olefins ( $C_nH_{2n-1}NO_2$ )

Nitro-olefins are significant because they are postulated as being one of the lacrymatory constituents of smog. Furthermore, 3-nitro-3-hexene has been identified as a potential carcinogen.

Nitro-olefins have been identified in engine exhaust by several different researchers. Wasserberger, et al. (100) identified 3-nitro-2-methyl-2-butene in the exhaust of a single cylinder four stroke engine which was fueled with 2-methyl-2-butene, the principal olefin in a premium grade gasoline. This same nitro-olefin was tentatively identified in the exhaust of a gasoline fueled, 36 horsepower Volkswagen engine during the same investigation. Lampe and Diechmann (101) investigated the combustion of isobutylene in a single cylinder engine. They detected both the conjugated nitro-olefin, 1-nitro-2-methyl-1-propene, and the nonconjugated nitro-olefin,

1-nitro-2-methyl-2-propane, in the engine exhaust. In a similar experiment, they found 3-nitro-3-hexene and its nonconjugated tautomer in the exhaust when 3-hexene (a normal constituent of gasoline) was the fuel (102). Stephens and Price (103) report the tentative identification of nitroethylene and 1-nitro-1-propane in the exhaust of a truck fueled with 1-nitro-1-propane.

The available data are not extensive enough to allow estimation of the total production of nitro-olefins by automobiles. It is possible that these species are also produced by other combustion systems.

#### SUMMARY

It has been shown that a wide variety of nitrogenous species other than NO may be produced by various combustion systems. Estimates of the total production of these species have been attempted. When sufficient data were available, a reasonably accurate assessment was made. Conservative estimates were made when fewer data were available. In some cases, the data were not sufficient to allow any assessment. Measurements of many of these nitrogenous species have not been reported for most combustion devices and it is possible that noncriteria N-species are produced by more combustion devices than those that have been covered in this paper.

Spark ignition engines have been shown to produce  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ , HCN and other nitriles,  $\text{NH}_3$  and various alkylamines, and various nitro-olefins and nitroparaffins. Nitrosamines may also be emitted in auto exhaust but crankcase emissions may be more significant. Exhaust purification catalysts generally decrease  $\text{NO}_2$  and HCN emissions and increase  $\text{N}_2\text{O}$  and  $\text{NH}_3$ . However, all of these species may be increased by the catalyst dependent upon stoichiometry, exhaust gas recirculation, catalyst material, catalyst configuration (pelletted or monolithic, oxidation or dual or three-way), speed, load, and the levels of other exhaust species, especially CO,  $\text{H}_2$ , and  $\text{O}_2$ . Vehicles may produce roughly 1 Mton/yr of  $\text{NO}_2$ , 30000 Tonnes/yr of  $\text{N}_2\text{O}$ , 5000 Tonnes/yr of HCN, 1000 Tonnes/yr of  $\text{C}_2\text{N}_2$ , 10000 Tonnes/yr of  $\text{NH}_3$ , 100 Tonnes/yr of dimethylamine, 100 Tonnes/yr of trimethylamine, 1000 Tonnes/yr of nitromethane, 1000 Tonnes/yr of nitroethane, and possibly several hundred Tonnes/yr of nitrosamines. Other species may also be emitted in significant concentrations. The effects of future technologies such as turbocharging and alternative fuels have not been documented.

Currently, diesels account for only about 1% of the total vehicle miles driven annually, at approximately  $10^{10}$  miles/yr. The current diesel fleet is a mix of direct injection, prechamber, and two-cycle engines, with and without supercharging. However, if a significant fraction of the automotive market becomes dieselized, the importance of diesel emissions will increase significantly. Automotive diesels will

probably be of the prechamber type and may possibly incorporate exhaust gas recirculation, turbocharging, oxidation catalysts, particulate traps, and other pollution control systems. Current automotive diesels appear to produce more  $\text{NO}_2$  and less HCN and  $\text{NH}_3$  than cars with spark ignition engines. Production of other nitrogenous species by prechamber diesels has not been investigated.

Aircraft gas turbines have been shown to produce  $\text{NO}_2$ , various nitriles, and a wide variety of nitro-olefins and nitroparaffins. They may produce roughly 0.1 Mtons/yr of  $\text{NO}_2$ , 760 Tonnes/yr of methyl cyanide, 1500 Tonnes/yr of nitromethane, and 1500 Tonnes/yr of other nitriles, nitro-olefins, and nitroparaffins.

Power may be generated at stationary sources by spark ignition engines, diesels, gas turbines, and boilers and furnaces. There is insufficient information to quantify emissions of most species from stationary diesel or spark ignition engines, but it is expected that the same species are generated by the stationary sources as by the mobile sources. Stationary IC engines may produce 0.3 Mtons/yr of  $\text{NO}_2$  and unquantifiable amounts of other nitrogenous compounds. Stationary gas turbines are a more significant source of power than stationary diesels or SI engines. The available data allows estimation of production of  $\text{NO}_2$  (0.1 Mtons/yr), nitromethane (55 Tonnes/yr), methyl cyanide (30 Tonnes/yr), and other nitriles, nitro-olefins, and nitroparaffins (55 Tonnes/yr). Boilers and

furnaces have been shown to produce  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ , HCN,  $\text{NH}_3$ , and amines. Production of  $\text{NO}_2$  is estimated to be 0.5 MTons/yr and 2-4 MTons/yr of  $\text{N}_2\text{O}$  could be produced by coal and oil combustion. Stationary combustion sources are reported to produce 15000 Tonnes/yr of ammonia (51). Secondary injection for stack gas  $\text{NO}_x$  control could result in the production of 0.3 MTons/yr of  $\text{N}_2\text{O}$  and unquantifiable emissions of HCN and  $\text{NH}_3$ .

Summing over all of the combustion systems discussed allows the observation that 2 MTons/yr of  $\text{NO}_2$ , up to 3.83 MTons/yr of  $\text{N}_2\text{O}$ , 8345 Tonnes/yr of HCN and other nitriles, 25200 Tonnes/yr of  $\text{NH}_3$  and other amines, 3555 Tonnes/yr of nitroparaffins, and several hundred Tonnes/yr of other N-species may be emitted by combustion sources. Therefore, the emission of gaseous nitrogen compounds from combustion sources is estimated to consist of 76.27%  $\text{NO}$ , 15.49%  $\text{N}_2\text{O}$ , 8.09%  $\text{NO}_2$ , 0.10%  $\text{NH}_3$  and other amines, 0.03% HCN and other nitriles, and 0.02% other nitrogenous species on a mass basis. Of course, these percentages will vary for any particular combustion system.

It should be noted that the data for motor vehicles is much more extensive than for stationary sources. Because of the higher fuel nitrogen content of residual fuel oil and coal, it is anticipated that the combustion of these fuels may result in the production of significant quantities of nitrogenous compounds which have not yet been measured. Also, the data for all of these sources has not been sufficient to allow rigorous analysis of total production. Therefore, factors such as vehicle mileage,

fleet mix, and deterioration have not been accounted for. Differences in use and operational characteristics of similar combustion systems have necessarily not been accounted for. The effects of future performance and emission control technologies and changes in fuel type and availability have been mentioned but not extensively analyzed.

This paper was intended to determine which nitrogenous species are emitted from combustion sources in sufficient concentrations to merit further investigation. The hazard posed by these species is also dependent on their environmental effects. The atmospheric chemistry and toxicology of many of these species have not been extensively investigated.

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