



Project Summary

EPA Workshop on N₂O Emission from Combustion (Durham, NC, February 13-14, 1986)

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This report summarizes the dialogue and interaction which took place during an EPA sponsored workshop addressing nitrous oxide (N₂O) emissions from fossil fuel combustion. The workshop was held in Durham, NC, February 13-14, 1986. Prior research studies had identified N₂O as a trace gas potentially contributing to depletion of stratospheric ozone as well as being a contributor to global climate change through the greenhouse effect. Prior studies also suggested that fossil fuel combustion was a major anthropogenic source of N₂O emissions. The workshop was organized to assess the current understanding of combustion generated N₂O emission and to assist EPA in formulating combustion research activities. The four technical sessions addressed: (1) measurement of N₂O; (2) N₂O formation/destruction mechanisms during combustion; (3) emission source prioritization; and (4) emission control approaches. It appears that the most significant N₂O emitters are utility and industrial boilers firing coal and heavy fuel oil. Mobile sources are a minor contributor to atmospheric N₂O loading. Available field test data indicate a direct correlation between N₂O and nitrogen oxide (NO_x) emission rates, suggesting that combustion modifications for NO_x control may also reduce N₂O emission. The current data base and the understanding of N₂O formation processes are insufficient to identify control strategies. Workshop attendees suggested that further research be conducted to improve the data base and to better understand the chemical processes controlling N₂O formation and destruction.

This Project Summary was developed by EPA's Air and Energy Engineering 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

The U.S. EPA sponsored a workshop on nitrous oxide (N₂O) emissions from the combustion of fossil fuels, held in Durham, NC, February 13-14, 1986. The workshop was designed to help EPA identify critical issues related to combustion emission of N₂O which would serve as the basis for developing an N₂O research program plan. This report summarizes the dialogue and interaction which took place during the workshop.

Concern over N₂O emissions is based on three facts: (1) N₂O participates in reactions which deplete ozone in the stratosphere, (2) N₂O is a greenhouse gas, and (3) atmospheric N₂O concentration is increasing. N₂O is one of several trace gases which participate in ozone depletion reactions. Ozone strongly absorbs ultraviolet radiation from the sun at wavelengths of 240-320 nm. If the stratospheric ozone concentration is decreased, increased quantities of this radiation, referred to as UV-B, will reach the Earth's surface with potentially serious effects on human health, agricultural productivity, and fisheries.

In addition to participation in ozone depletion reactions, there is concern for the fact that N₂O absorbs infrared (IR)

radiation in wavelength ranges which are normally transparent in the atmosphere. This IR absorption process reduces cooling of the earth during the night. This is the greenhouse effect usually associated with CO₂.

The atmospheric concentration of N₂O was about 300 ppb in the late 1970s, but is increasing at a rate of approximately 0.25 percent per year. The increasing concentration is of particular concern since there are no known atmospheric sinks for N₂O. In fact, the stratospheric lifetime of N₂O is estimated to be in excess of 100 years.

N₂O is emitted to the atmosphere from both natural and anthropogenic sources. Figure 1 shows that soil denitrification and ocean release account for about two-thirds of the ambient N₂O loading. It is believed that one of the major sources of anthropogenic N₂O is the combustion of fossil fuel. Since combustion generated N₂O is potentially controllable, the EPA and others are examining methods which may be effective in reducing N₂O emissions from combustion sources. It should be emphasized that the scope of the current workshop was limited to examining combustion generated N₂O; it did not address the impact of potential control strategies on ozone layer protection, global climate change, or human health. The workshop was organized to assist EPA in defining critical combustion issues and in suggesting appropriate research actions.

The workshop was divided into five sessions: an introductory session containing an overview of the global N₂O situation, and four technical sessions (N₂O measurement techniques, N₂O formation/destruction mechanisms, source prioritization, and control approaches).

Introductory Session

The introductory session began with an overview of EPA's risk assessment studies relative to global climate change. With the current levels of trace gases in the atmosphere, modification of the global climate is inevitable, even if current emission levels are drastically reduced. With current emission rates it is projected that the global surface temperature could rise by as much as 5 °C over the next 50 years. This is as much as the temperature differential between the current level and that at the height of the Ice Age. The potential gravity of the situation is great, but is often overlooked by both researchers and the general public. It should be emphasized that N₂O is only one of the several gases contributing to the climate change phenomena and that the global warming pro-

Total Natural: ≈0.3 Tmol/yr (from stratospheric removal models assuming no other sinks)

Oceans: ≈0.1 Tmol/yr (from mean oceanic supersaturation of ≤4% and radon calibrated exchange models)

Terrestrial: ≈0.2 Tmol/yr (by difference, includes soil sources and sinks)

Anthropogenic: ≈0.14 Tmol/yr (from observed rate of increase and box model calculations)

Note: 1 Tmol = 10¹² g moles

Approx. Source Strength (Tmol/yr)

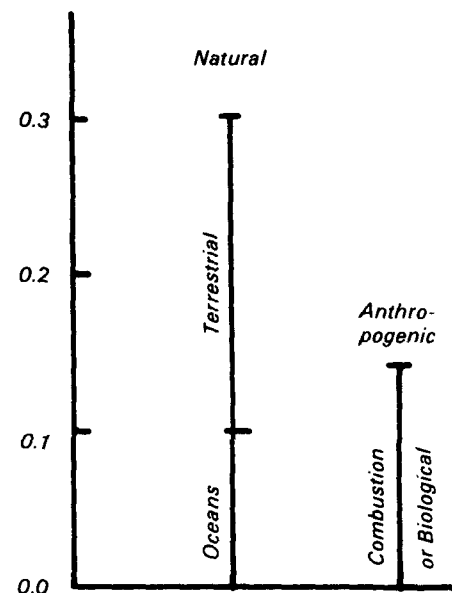


Figure 1. Estimated N₂O global fluxes (Source: R. F. Weiss, Scripps Institution of Oceanography, 1986).

jections are the cumulative effect from all such gases.

Various studies of the global atmospheric budget have been performed, including present loading levels and projections of the sources and distribution of emissions. One such analysis indicates that the U.S. is currently the largest contributor to atmospheric N₂O due primarily to emissions from coal- and heavy-oil-fired boilers. In the future the undeveloped countries are likely to be the leaders in emission rates. The results from this study are intended to focus the attention of research on areas that are identified to be the most significant emission sources. The results point primarily toward examining large, coal-fired industrial and utility boilers.

N₂O Measurement

EPA is critically concerned with the quality assurance and quality control of their funded research activities, particularly of those data impacting policy and regulatory decisions. The first technical session of the workshop dealt with potential N₂O measurement techniques in order to define the appropriate techniques for different types of experiments, as well as

to exchange information among the participants on potential sources of measurement error. Most of the N₂O concentrations data reported at the workshop were obtained by using gas chromatograph (GC) with electron capture detector (ECD). Taking into account the state of development, precision, detection limit and the cost of measurement, GC/ECD is an appropriate measuring technique for most of the EPA funded research activities, including stack gas measurement. Other measurement techniques could be appropriate for other applications, but each measurement system must be adapted to the particular experiment being performed. Table 1 shows some of the types of measurement systems which could be used for various experiments.

N₂O Formation/Destruction

The second technical session examined the combustion chemistry controlling N₂O formation and destruction. Figure 2 shows field test data on N₂O exhaust concentration from various boilers firing different fuels. These data clearly indicate a trend of decreased N₂O emission with decreased NO_x. A straight line correlation of these data indicates a constant

Table 1. Comparison of Measurement Systems for Different Applications

Measurements	Standards	Chromatography		FTIR	Diode IR	NDIR
		ECD	N ₂ O/CO ₂			
Ambient	X ^a	X	X			
Stack		X				X
Plumes		X	X	X	X	X
Flame					X	

^aStandards available only for ambient measurements. Standards are needed for all measurements.

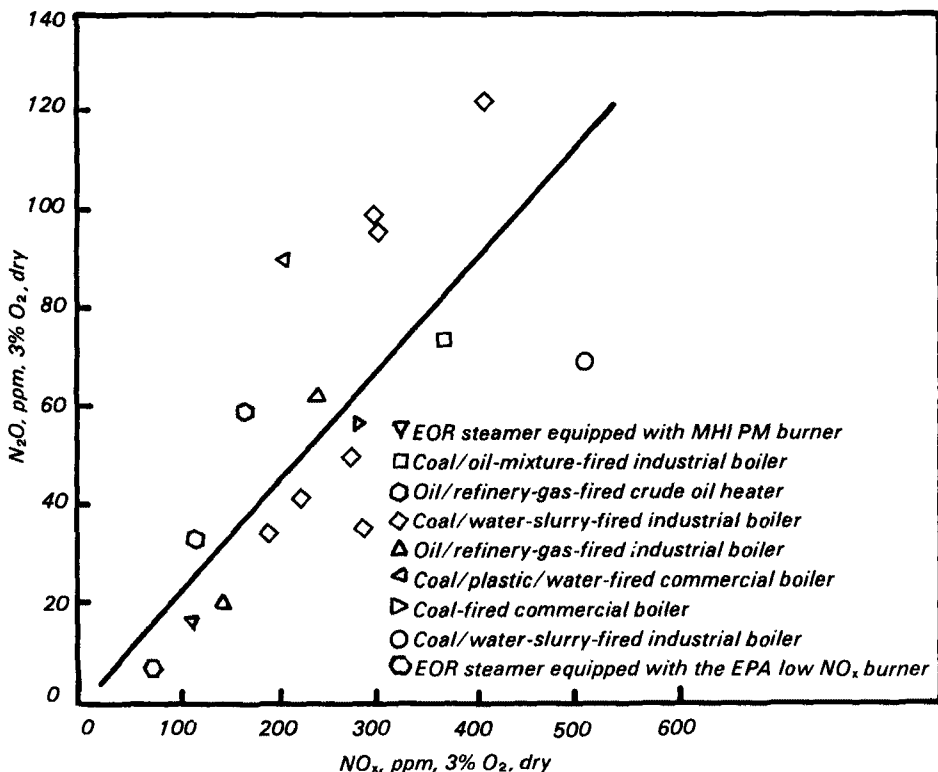


Figure 2. N₂O emissions from combustion sources as a function of NO_x emission (Source: Environmental Assessment of an Enhanced Oil Recovery Steam Generator Equipped with a Low-NO_x Burner. Volume 1. Technical Results, EPA/600/7-86/003a [NTIS PB 86-159837], February 1986).

N₂O:NO_x molar ratio of 22 percent. The control strategy implication of this data trend is that combustion modification techniques for NO_x reduction may also be effective in reducing N₂O emissions. An important workshop discussion topic was consideration of this trend. It was noted that essentially all the data were taken from different units and did not examine N₂O emissions under normal and low-NO_x conditions. In the absence of such data, a control strategy based on implementing low NO_x control is not scientifically justifiable. That is to say, additional research is required to establish a control strategy. The need for additional R&D is amplified by two sets of pilot scale data indicating conflicting N₂O emission

results. One set of data indicates that the N₂O:NO_x emission ratio remains constant as NO_x is reduced by combustion modification. The second set of data indicates that the exhaust N₂O concentration remains constant as the NO_x emission rate is reduced by a factor of 6 by applying staged combustion.

There was extensive discussion of chemical, mixing, and thermal phenomena which are important in controlling N₂O formation and destruction processes. It was generally concluded that current knowledge does not provide a sufficient understanding of N₂O control in the combustion process. Many workshop participants felt that additional fundamental research to develop a "working

hypothesis" of N₂O formation and destruction was an important first step in an EPA research program.

The second session also provided important information defining the dominant sources of N₂O emissions. Figure 3 shows results from utility boiler field tests in which the N₂O:CO₂ molar ratio in the boiler exhaust is correlated with the nitrogen to carbon molar ratio in the fuel being fired. This figure suggests a constant fractional conversion of fuel bound nitrogen to N₂O, which implies that coal- and heavy-oil-fired boilers are the most important N₂O emission sources. This trend further supports the analysis which defined large industrial and utility boilers as the largest contributors to anthropogenic N₂O emissions.

Source Prioritization

The third technical session focused on mobile versus stationary source emissions of N₂O and was included to aid EPA in determining priorities for R & D activities. The global projections referred to earlier indicate N₂O emission growth in the third world as well as in the U.S.—both in the energy and transportation sectors. It is important from both a U.S. EPA and a global perspective to define whether one sector is much more important than the other, or whether it is necessary to address both areas.

As shown in Table 2, limited data are available from mobile sources. However, available data show a large variation in emission rates: from 5 to 147 mg N₂O per mile.* Assuming an average emission rate of 100 mg/mile and estimating 1.6 x 10¹² total vehicle miles traveled per year in the U.S., the total annual U.S. N₂O emission rate from mobile sources is on the order of 1.6 x 10⁵ metric tons. It has been estimated that the total anthropogenic N₂O emission rate is 3.0 x 10⁶ metric tons per year, which implies that U.S. mobile sources account for only about 5.5 percent of the anthropogenic total.

Table 2 shows that the N₂O emission rate from noncatalyst equipped cars was only 5-6 mg/mile, an order of magnitude less than the assumed average emission rate used in the above calculation. Since it is unlikely that other nations, such as third world countries, will require automotive catalysts, it appears that the mobile source sector will remain an insignificant contributor to atmospheric N₂O loading. Before a firm conclusion may be reached, however, it is essential that the

*1 mi = 1.61 km.

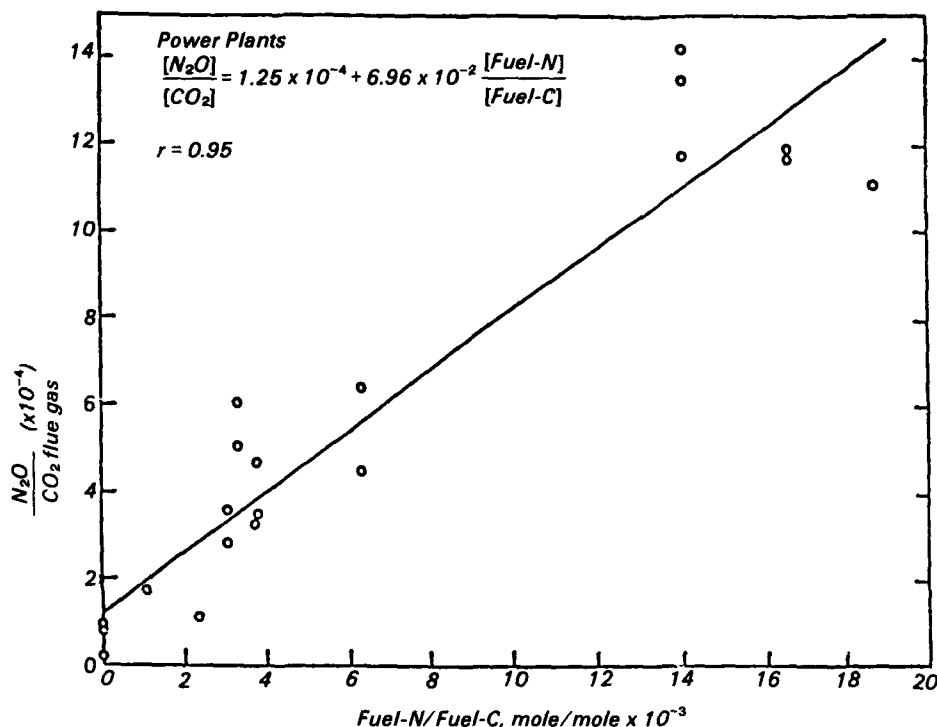


Figure 3. Relationship between N_2O emissions and fuel-nitrogen contents of natural gas, No. 6 fuel oil, and coal-fired combustion systems (Source: S. C. Wofsy et al., Harvard University, 1986).

Table 2. N_2O Emission Data for Various Vehicle Types

Vehicle Type	No. of Samples	N_2O Emission Rates, mg/mi
Noncatalyst Car	1	5-6
Catalyst Cars	22	7-137
Diesel Trucks/Buses	4	31-147
Gasoline Trucks	2	48-97

N_2O emission rate data base be significantly expanded, particularly for noncatalyst equipped vehicles. To expand that data base, it was suggested that N_2O measurements be incorporated into existing vehicle emission monitoring and certification testing. With regard to expansion of the noncatalyst equipped auto data base, it was suggested that other countries could assume responsibility through international cooperation coordinated by the United Nations.

Results from field tests of different stationary sources fired with different fuels are shown in Figure 4. These results incorporated those shown in Figure 2, showing a general correlation between N_2O and NO_x emissions. With the expanded data set there is a substantial increase in data scatter, underlining the need for additional research before reliable emission factors can be developed.

Control Approaches

The purpose of the final technical session was to identify combustion control approaches or strategies which could be used to reduce N_2O emissions. Since many potential control methods had been considered during the previous workshop sessions, this session was mainly a summary discussion. The concept of reburning was introduced as a possible NO_x control strategy which could also be applicable to N_2O emission control. However, it was emphasized that not all NO_x controls would automatically be effective in reducing N_2O emissions, and that careful study must be made to determine each method's effectiveness. "Piggybacking" of N_2O measurements onto current test programs was suggested as a cost-effective method to augment the N_2O emission data base.

Workshop Summary

The various workshop sessions identified many important data trends which may be used to form working hypotheses, but also underlined the fact that the existing data base was insufficient to reach scientifically defensible conclusions. By way of summary, it would appear that N_2O emissions from combustion of nitrogen bearing fuels is far greater than from "clean" fuels. Mobile sources appear to be negligible N_2O emitters relative to stationary sources, but the data base for mobile sources is extremely limited (particularly for vehicles without catalysts). The available stationary source field data show a direct correlation between NO_x and N_2O emissions. This indicates that installing low- NO_x burners or other NO_x control technologies may also be effective for N_2O control. It should be emphasized however, that some pilot-scale results are in direct conflict with that indication. In fact, one of the main workshop conclusions is a call for additional fundamental and bench-scale research to clarify this discrepancy.

Depletion of the ozone layer and the greenhouse effect are clearly important environmental concerns, but immediate regulatory response appears unlikely. On that basis, prudent programmatic action could include:

- Addition of N_2O measurement to existing field evaluation programs to help build the data base.
- Initiation of fundamental combustion research to identify how N_2O emissions are impacted by NO_x control combustion modifications.
- Formation of a working group to coordinate research activities at EPA, NASA, DOE, and NOAA.

These actions could be accomplished with minimal resources and would place the EPA in a better position if control technology or regulatory actions were required in the future.

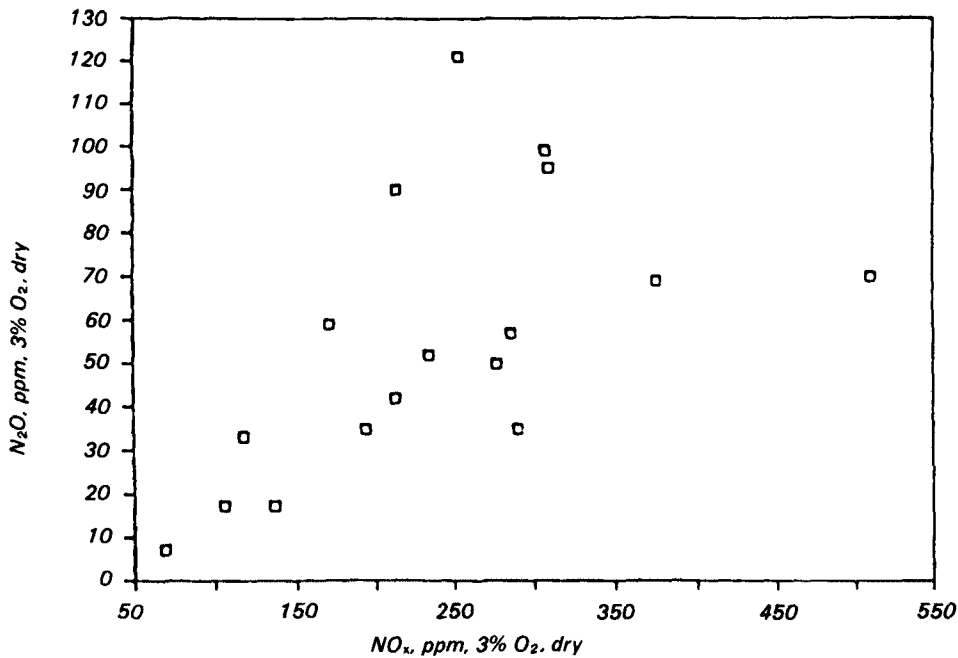


Figure 4. N₂O and NO_x emissions from various sources (Source: C. Castaldini, Acurex, 1986).

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The complete report, entitled "EPA Workshop on N₂O Emission from Combustion (Durham, NC, February 13-14, 1986)," (Order No. PB 87-113 742/AS; Cost: \$18.95, subject to change) will be available only from:

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