United States
Environmental Protection
Agency

Air and Energy Engineering
Research Laboratory
Research Triangle Park, NC 27711

Research and Development

EPA/600/S8-88/079 July 1988

EPA

Project Summary

EPA/NOAA/NASA/USDA N_2O Workshop: Volume I. Measurement Studies and Combustion Sources September 15-16, 1987, Boulder, Colorado

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On September 15-16, 1987, the U.S. Environmental Protection Agency, the National Oceanic and Atmospheric Administration, the National Aeronautics and Space Administration, and the Department of Agriculture jointly sponsored a workshop on atmospheric nitrous oxide (N_2O) at Boulder, Colorado. This meeting follows a previous workshop which was held at Durham, North Carolina, on February 13-14, 1986. These meetings served a number of purposes. One important objective was to provide an opportunity for a more timely exchange of information among researchers than would otherwise be possible through normal technical channels. Another major purpose was to prioritize the research that is needed to determine if atmospheric N_2O is a problem, and to understand the importance of the various sources and sinks.

The technical discussion involved three areas: (1) measurement approaches, (2) combustion sources of N_2O, and (3) biogenic sources of N_2O. Within each area, the focus was on using the best current understanding to develop the research priorities needed to assess the severity of the N_2O problem. This volume focuses on the first two areas; Volume II is to focus on the third.

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

This report summarizes a workshop on the atmospheric emission of nitrous oxide (N_2O) which was held at Boulder, Colorado, on September 15-16, 1987, under the joint sponsorship of the U.S. Environmental Protection Agency (EPA), the National Oceanographic and Atmospheric Administration (NDAA), the U.S. Department of Agriculture (USDA),and the National Aeronautics and Space Administration (NASA). This was the second such workshop; the previous workshop was held in Durham, North Carolina, February 13-14, 1986. The initial Workshop was summarized in EPA report EPA-600/8-86-035 (NTIS-PB 87-113742).

These two workshops were held as part of EPA's effort to develop an appropriate research plan with respect to

N_2O. The atmospheric concentration of N_2O is increasing at a rate of approximately 0.25% per year. This is a matter of concern since N_2O is one of several trace gases which cause ozone depletion and contribute to the greenhouse effect. Depletion of the ozone layer will cause increasing amounts of solar UV radiation to reach the Earth's surface and result in increasing incidence of melanoma and other health problems. There is also concern about adverse ecological effects associated with increased UV-B radiation; e.g. = decreased plankton in the oceans. Since the lifetime of N_2O in the atmosphere is more than a century, by the time such adverse health effects became acute it would be too late for any useful action. Similarly, the greenhouse effect to which N_2O contributes has the potential for causing significant climate changes.

While there are thus substantial reasons for concern, many aspects of the N_2O problem are poorly understood. There are important scientific questions which need to be answered before any rational decision regarding action is possible. Answering these questions requires developing a coherent research plan; this workshop was a step in formulating such a plan. The approach was to bring together appropriate experts and allow them to exchange information and develop a consensus on which aspects of the N_2O problem are truly critical.

The meeting was organized into four sessions. Two general sessions addressed environmental concerns associated with N_2O, and approaches to the measurement of N_2O. Following the general sessions the attendees divided into two specialized concurrent sessions. The proceedings of the combustion sources session are summarized here. The biogenic sources session will be summarized in a separate volume.

Environmental Concerns

Representatives of EPA, NASA, and NOAA each gave overviews of their agency's programs in the area.

EPA Concerns

The EPA is charged with evaluating the potential for global climate change and the development of strategies for atmospheric stabilization. This is performed with the aid of a detailed conceptual framework which links atmospheric warming, chemistry, and emissions models. The framework indicates the extreme complexity of fully coupled atmospheric processes. For example, N_2O alone will contribute to stratospheric ozone depletion. However, if stratospheric chlorofluorocarbon (CFC) levels are high, then increased N_2O emissions may actually reduce the ozone removal rate. (This occurs by the removal of free chlorine into an inert form with NO_2.) All models suggest that N_2O contributes to global warming at the same order as CO_2, in spite of its much lower concentration.

NASA Concerns

The NASA program has focused on the characterization of the composition of the atmosphere from space. A considerable amount of work involves the Antarctic ozone "hole." A second area involves the description of stratospheric chemistry. A key point was the description of the role of natural N_2O emissions in ozone chemistry. In the natural O_3 formation and destruction cycle, natural stratospheric NO_x (from tropospheric N_2O) accounts for about 70% of the ozone sink. Thus, additional N_2O may increase the absolute rate of the sink. Since CFCs are not natural constituents of the atmosphere, their presence adds to the absolute ozone destruction rate in direct proportion to their concentration.

NOAA Concerns

The NOAA has an extensive ongoing program in N_2O tropospheric measurement. These data, as well as those of others, show that N_2O concentrations in the troposphere are increasing at the order of 0.25% per year. This strongly suggests the existence of an important anthropogenic source flux.

Measurement of N_2O

One difficulty in N_2O research has been the complexity of performing the measurement. Present methods require a relatively high skill level, and are subject to significant errors if the skills are unevenly applied. Most ambient and combustion source measurements are made by gas chromatography, with electron capture or thermal conductivity detection. Electron capture detection is normally favored for ambient work due to its high sensitivity. A discussion led by NOAA covered many of the problems involved in electron capture detection, and approaches to their solution.

An alternative infrared absorptic approach is under development at tl University of California -- Irvine (UC This approach uses narrow bandpa: filters to focus detection on wavelengths where N_2O absorbs heavil Selective scrubbing is used to remo the species showing the greate interferences. The goal is to develop relatively simple continuous monit suitable for stack sampling.

Aerodyne Research reported work the use of tunable diode lasers to resol N_2O absorption lines. If the pressure the sample gas is sufficiently reduce pressure-broadening of the N_2O lin can be avoided to the point where no interfering absorption measurements single lines can be obtained. This meth allows both very high sensitivity and hi selectivity. The disadvantages are hi cost and operational difficulty associat with tunable diode lasers. Thus, a maj initiative is underway to devel comparable narrow-band optic sources which are inexpensive and ea to operate.

Combustion Sources

Work reported at the previo workshop showed that pulverized co and oil-fired combustors can yie significant N_2O emissions. This findi raises at least two related questions:

- Is combustion-generated N_2O significant global source term?
- How is this N_2O formed? T answer to this will largely determi what control approaches a possible.

Work at Energy and Environmen Research (EER) supported by the E has suggested at lease one formati mechanism. The EER results show tl the introduction of HCN in the po flame region (specifically between 11 and 1500 K) will result in significant N formation and emission. The import reactions are:

$$HCN + O = NCO + H \quad (1$$
$$HCN + OH = HNCO + H \quad (2$$
$$NCO + NO = N_2O + CO \quad (3$$
$$NCO + H = NH + CO \quad (4$$
$$N_2O + H = N_2 + OH \quad (5$$

If HCN is introduced above 1500 Reaction 2 routes HCN away form NC Reaction 4 provides an alternate route NCO destruction, and Reaction 5 reduc any N_2O that is formed. Thus, all reaction pathways are directed aw from N_2O at high temperatures. Below 1150 K, the kinetics predict that Reaction 2 dominates HCN destruction, and little N_2O is produced.

One way that HCN may be introduced in this region is devolatilization or gasification of char nitrogen. A second possibility is that HCN from the primary flame is transported into the post-flame region by imperfect mixing. This portion of the mechanism remains in conjecture.

Early data suggest that NO_x and N_2O were correlated in practical combustion devices. Approximately 1 mole of N_2O was emitted for each 4 moles of NO_x. This is an important point because, if true, the extensive NO_2 data base can be used to estimate N_2O production.

An enlarged data base was presented by Fossil Energy Research Corporation (FERCo) which showed considerably more scatter than had been reported in earlier data collections. The sense of the session was that the data base was not yet adequate to permit a scientifically based extrapolation of worldwide NO_x data to worldwide N_2O emissions. On this point there was some dissent. One viewpoint was that the NO_x vs. N_2O correlation could at least be used as a rough indicator for estimating.

FERCo also presented data on the influence of natural gas reburning on N_2O from a pilot-scale cyclone simulator. The results showed approximately equivalent reductions for N_2O and NO_x. The facility was also noteworthy in that it produced the highest N_2O values reported to date from a coal-fired combustor (484 ppm).

Work on the homogeneous chemistry of N_2O in flames was presented by researchers from Stanford and Lawrence Berkeley Laboratory (LBL). The general conclusion was that most of the chemistry is sufficiently understood to not limit our understanding of the overall N_2O problem. The current state of chemical kinetics was reviewed. Some interesting results from LBL showed that the quench region near the edge of a flat-flame burner was capable of producing high N_2O. This may explain the low N_2O emissions observed from industrial gas flames. Finally, work from the Chemistry Department at Western Michigan University showed the spectrum of products that were generated by flame-mode and sub-flame oxidation of HCN. This included significant amounts of N_2O.

Conclusions

A general conclusion of the workshop members is that a significant amount of rapid progress has been made in this relatively new area. Measurement continues to be a problem due to the complexity of the various approaches. Although gas chromatographic techniques are well developed, considerable skill and experience are required to obtain reliable data. Also, the instrument does not lend itself to real-time, on-site measurements. It is hoped that development of spectroscopic techniques will continue, as these promise the eventual development of portable, user-friendly, real-time instruments.

A broad outline of the N_2O formation mechanism in coal flames has been developed. The first component of the mechanism is a means by which reduced nitrogen is transported downstream of the flame zone. If the fixed nitrogen appears as HCN within the 1150 - 1500 K temperature window, then a significant net N_2O formation can occur via homogeneous chemistry.

The following general statement of needs was developed as a conclusion to the discussions:

1. Given the critical nature of the potential problem, there is a need to establish a scientifically defensible data base related to combustion-generated N_2O.
2. The current data base on emission factors is inadequate to establish the contribution of combustion-generated N_2O to the total global budget.
3. There is a need to establish a broad-based coordinated combustion-generated N_2O program with:
   - Full-scale -- Data base
     - Emission factors
     - Mechanistic insight
   - Pilot-scale -- Guide and interpret
     - Laboratory-scale -- Guide and interpret
     - Instrumentation -- Standardize

Most attendees favored this statement. Some members took issue with the second item, and felt that the data base did allow for a crude estimation of the global contribution of combustion to N_2O. A few members disagreed with the third item, and felt that a large program is not warranted until it is better understooc if N_2O is actually a critical problem.

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The complete report, entitled "EPA/NOAA/NASA/USDA N2O Workshop: Volume I. Measurement Studies and Combustion Sources, September 15-16, 1987, Boulder, Colorado," (Order No. PB 88-214 911/AS; Cost: $14.95, subject to change) will be available only from:
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