



Project Summary

EPA/IFP European Workshop on the Emission of Nitrous Oxide from Fossil Fuel Combustion

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This report summarizes the proceedings of an Environmental Protection Agency (EPA/Institut Francais du Petrole (IFP) cosponsored workshop addressing direct nitrous oxide (N_2O) emission from fossil-fuel combustion. The third in a series, the workshop was held at the IFP in Rueil-Malmaison, France on June 1-2, 1988.

Increasing atmospheric N_2O concentrations have been linked to depletion of atmospheric ozone (O_3) and to global climatic warming. The combustion of fossil fuels has been identified as a potential major anthropogenic source of N_2O . This workshop had two goals: (1) to exchange information among various international research and industrial groups that are involved in N_2O chemistry, modeling, and N_2O measurement; and (2) to develop a network for coordinating future related efforts.

The five technical sessions addressed: stratospheric O_3 depletion and global climate change, mechanisms of N_2O formation and destruction during combustion, N_2O measurement techniques, full-scale field data, and practical conclusions based on general discussion.

A sampling artifact discovered during EPA research revealed that N_2O can be generated in a sample container in the presence of nitrogen oxides (NO_x), sulfur dioxide (SO_2), and water. This

artifact potentially discredits much of the N_2O emissions data collected from samples containing the above compounds when stored for some time prior to analysis. Recent sampling techniques that minimize the artifact have produced data from stationary sources that indicate that direct emission of N_2O from fossil-fuel combustion may not be a major contributor to the measured annual increase. Limited data also indicate that some specific sources (e.g., fluid bed combustors) may be high N_2O emitters. A standardized sampling protocol would help validate current data.

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 activities at a workshop on direct nitrous oxide N_2O emissions from fossil fuel combustion, held in Rueil-Malmaison, France, on June 1-2, 1988. The workshop was the third in a series on N_2O emissions and was cosponsored by the U.S. Environmental Protection Agency (EPA) and the Institut Francais du Petrole (IFP). Its primary focus was to assess and evaluate the role that combustion of fossil fuels plays in

directly emitting N_2O into the atmosphere. This subject is significant because the ambient levels of N_2O have been reported to be increasing and because N_2O has been linked to stratospheric ozone (O_3) depletion and global climatic warming. Another focus was to establish an international network for exchanging information related to N_2O emissions.

The workshop brought together a complementary group of experts involved in various aspects of N_2O research. Specifically discussed were the role of N_2O in stratospheric O_3 depletion and global climate change, the mechanisms of N_2O formation/destruction (involving both homogeneous and heterogeneous reactions), and the status of N_2O measurement techniques. Presentations were also made on emissions data collected from a variety of stationary, sub- and full-scale facilities, as well as on data from mobile sources. After these presentations/discussions, conclusions were reached regarding the current status and future direction of N_2O research.

This report documents both the formal and informal material presented at the workshop, and it covers vigorous discussion periods that followed formal presentations. It is an account of the proceedings and summarizes the workshop's content chronologically.

Atmospheric Concerns

Representatives of EPA, NASA, OECD, and Max Planck Institute presented overviews of each agency's program relating to stratospheric ozone depletion and global climate change.

EPA believes that human activities are responsible for increases in atmospheric gases that are causing global climate change through warming (a result of the greenhouse effect) and stratospheric ozone (O_3) depletion. NASA believes that in the last 100 years, the trace gas composition of the atmosphere has changed more than in the previous 4.5 billion years, owing to increased human activity. Carbon dioxide (CO_2), chlorofluorocarbons (CFCs), and methane (CH_4) are anthropogenic gases known to participate in reactions contributing to climatic warming and ozone depletion.

Nitrous oxide (N_2O) is another trace gas that contributes to both stratospheric ozone depletion and climatic warming. Ice core data show steady levels of N_2O

until the start of the industrial revolution and that currently, ambient concentrations are increasing at an annual rate of about 0.2 percent. Although natural sources are thought to comprise over 50 percent of total emissions, combustion of fossil fuels and biomass burning are considered to be major anthropogenic contributors.

N_2O contributes to the greenhouse effect through the absorption of infrared radiation. Global temperatures have already increased 0.6 °C since 1880, and the four hottest years on record have occurred in the 1980s. The modeled predictions of global temperature, using recorded data, suggest that temperatures may rise by as much as 5°C worldwide by the year 2030. About 10 percent of this warming may be due to increased N_2O concentrations. Many global features are expected to be adversely affected by drastic climatic changes. Global warming will melt polar ice caps, change important weather patterns, and tax human health and society.

Some scientists suggest that ozone, the only atmospheric gas that absorbs ultraviolet radiation, may be second only to oxygen as the earth's most important gas. A 50 percent reduction in stratospheric ozone has been observed over a ten-year period over the South Pole. This depletion probably represents the largest geophysical perturbation ever measured over so short a period.

It has been determined that N_2O plays a key role in stratospheric ozone depletion. A catalytic loss mechanism involving the oxides of nitrogen (NO_x) destroys stratospheric ozone. It is interesting to note that the main source of NO in the stratosphere originates from N_2O .

Currently, the N_2O data base is insufficient. There is a critical need to foster research directed at developing a better inventory of N_2O emissions sources and contributions, and to improve understanding of both the combustion processes related to N_2O emissions and control options. Accelerated research is vital, because critical decisions are being made to control NO_x , new combustion devices are being designed and built, and developing nations are growing and contributing to the N_2O problem, all with insufficient information.

Mechanisms of N_2O Formation and Destruction During Combustion

Basic Kinetics

Nancy Brown (Lawrence Berkeley Laboratory) described her ongoing investigation of the formation/destruction chemistry of N_2O in premixed, laminar, lean, atmospheric-pressure flames. The study involves both experiments and modeling.

For the experiments, CH_4 /air/nitrogen compound flames and H_2/O_2 /argon/nitrogen compound flames were chosen. The H_2 flames were chosen to provide results without the complexities of carbon chemistry and to allow a comparison of results to model predictions. Experimental variables were bulk flow rate (28-40 Lpm), to include the effects of heat transfer to the burner, equivalence ratio (0.75-0.9), and nitrogen additive (NH_3 , NO, N_2O , and N_2). Thermochemistry, probe, and quenching effects were also studied.

For modeling, she used Sandia codes Premix with full chemistry and transport, Chemkin with full chemistry, and Thermochemistry-1987 Chemkin release. For modeling, actual measured temperature profiles were used rather than solutions of the energy equation.

She concluded that agreement between the experiment and modeling was satisfactory near 1,700 K, but the chemistry at temperatures less than 1,100 K needs more clarification. Other conclusions of her research are:

- N_2O destruction results in N_2 production.
- Destruction reactions need to be determined over a wide range of temperatures and product yields.
- More information on N_2O production reactions is needed.
- Probe effects need to be eliminated because they could have a significant effect on N_2O measurements.

Gas Phase Kinetics

John Kramlich, (Energy and Environmental Research Corporation) focused on the emissions of N_2O from industrial flames. He discussed the issues of N_2O formation and emission in coal and oil flames and the effects of firing configuration and pollution control strategies on these emissions. This

study has involved both experiments and modeling.

Figure 1 summarizes the study with a mechanism overview and admits that predominant generation of N_2O occurs in the post-flame zone from conversion of HCN to N_2O . Presence of HCN in the post flame can be credited to devolatilization of char-N and to free HCN transported from the edge of volatile flame in stratified flow. Some N_2O is produced in the flame zone but is rapidly destroyed to form N_2 .

Heterogeneous Reactions

Gerard de Soete (IFP) defined a heterogeneous reaction as one between two different phases, as in gas to solid. Heterogeneous reactions implying N_2O as a reactant or as a product are numerous. Three examples are:

1. Formation of N_2O from bound N during heterogeneous char oxidation.
2. Heterogeneous reduction of N_2O on char-bound C atoms during heterogeneous char oxidation.
3. Formation of N_2O during catalytic NO reduction (coupled with catalytic N_2O reduction), which may play a larger role in N_2O emissions from mobile sources.

A heterogeneous reaction rate can be expressed by:

$$V_i = k_i e_n^m P_y$$

where k_i is the rate constant, e_n^m (a fraction) expresses the dependence of the covering degree, which is proportional to active sites in the solid involved in the reaction, and P_y is the dependence of partial pressure of one or more reactant gaseous species.

Thus the study, focusing on heterogeneous reactions that imply N_2O as a reactant or product, involved two tasks: (1) identification of the adsorption and desorption reactions composing the heterogeneous mechanisms and their reaction rates, V_i s; and (2) a time resolved study of the reactions identified in Task (1). This allowed determination of the fractions leading to determination of the rate constants, k_i s.

The formation of N_2O during NO catalytic reduction plays a major role in emissions from mobile sources using three-way catalysts.

Passing N_2O and NO over a typical metal catalyst results in:

1. Reduction of NO at a much lower temperature than N_2O , resulting in

the formation of N_2O as a function of temperature.

2. Intermediate formation of N_2O when NO is fed as a function of temperature.

The above indicates that transformation of N_2O into NO is a minor reaction. In all circumstances using graphite, N_2O will be reduced at a lower temperature than will NO, as opposed to when a metal catalyst is used with a reducing agent. Since N_2O reduces at a lower temperature than NO, little N_2O is found when NO is reduced. Reduction of NO could result in formation of N_2O ; however, this reduction of NO at the temperature where N_2O can be formed occurs so fast that the N_2O cannot be seen in the gas. For graphite, this is true in both the presence and absence of reducing gases. The situation is the same during heterogeneous reduction of N_2O and NO on char-bound carbon atoms.

Shown in Figure 2 are the experimentally determined overall reaction rates of C oxidation and, NO, N_2O , and HCN formation as a function of temperature for Eschweiler char. The subscript e in this figure implies that these reaction rates were obtained under adsorption/desorption equilibrium rates. The figure suggests a rough proportionality between V_C , V_{NO} , and V_{N_2O} .

For a Cedar Grove char, plotted in Figure 3 are fractions of nitrogen converting to NO and to N_2O as functions of fraction of carbon burnt. These results have been obtained for all fractions of carbon burnt and for temperatures up to 1,400 K. As a rough approximation, the fractions of N converted to NO and N_2O seem to be proportional to the fractions of carbon burnt. Thus it seems that a constant fraction of N is formed into NO and another constant fraction of N is converted into N_2O in a heterogeneous way. This is true for all char burnout fractions and at all temperatures up to 1,400 K.

Therefore, the main reaction path of N_2O formation from bound nitrogen, during char combustion, at temperatures below 1,400 K, is probably not a formation from HCN, occurring in the gas phase, but a heterogeneous reaction directly linked to char oxidation. This is suggested by reaction order with respect to oxygen of one for V_C (overall combustion rate), V_{NO} (overall NO formation rate), and V_{N_2O} (overall N_2O formation rate), and similar temperature dependence of their overall rate.

Thus, based on this study, the probable mechanisms involved in formation of N_2O from bound nitrogen during heterogeneous char oxidation are shown in Figure 4. The parentheses in this figure imply solid bound groups.

Overall Chemical Information from Laboratory Combustor Experiments

Jost Wendt (University of Arizona) gave results of ongoing DOE-funded research at that institution. The work focused on optimizing reburning configurations for NO_x control. A secondary focus of the work was on N_2O measurements. N_2O was measured by on-line GC/ECD following a sample conditioning system.

The experiments are being conducted on a premixed, down-fired combustor at a firing rate of 27 kW to study NO and N_2O emissions from the combustion of Beulah lignite and Utah #2 bituminous coals. NO_2 levels for both coals were found to be insignificant at less than 2 ppm for stoichiometric ratios (SR) ranging from fuel rich to fuel lean. Measurements of NO and N_2O as a function of residence time at fixed fuel lean SRs, with combustion gas temperatures in the range 850-1,290 K for Beulah coal and 1,050-1,525 K for Utah coal, showed N_2O concentrations to be less than 5 ppm and the N_2O/NO concentration ratio to be very small. Results, so far, have also indicated that there is little N_2O formation under reburn conditions using natural gas as the secondary fuel.

William Linak (EPA/AEERL), presented N_2O emission data from a down-fired, 60,000 Btu/h (18kW) laboratory-scale coal combustor with a variable swirl burner. The purpose of these experiments was to change NO emissions through changes in the overall turbulent diffusion flame type and thus to determine if a correlation between N_2O and NO emissions was valid. Bomb samples were drawn from a post-combustion region under stack type conditions. In an attempt to vary the NO_x concentration, burner swirl and flame shapes were altered by changing axial and radial air ratios and locations of the injector tube. A Utah bituminous coal and a Montana subbituminous coal were used in these experiments, the first having a higher organic content but lower moisture level than the other. For each coal, data were collected at three (fuel

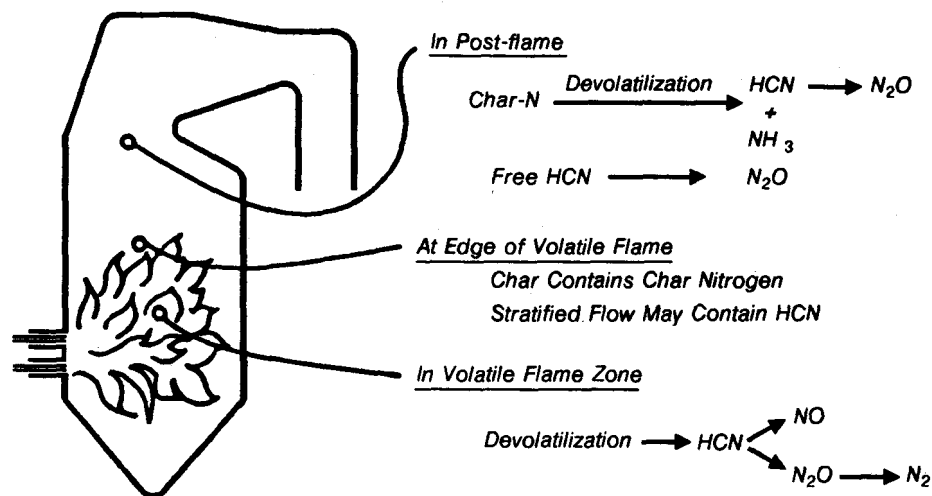


Figure 1. Mechanism overview.

lean) stoichiometric ratios and two flame shapes --- one axial and one radial. Gas samples were collected in stainless-steel containers after refrigeration drying and were analyzed for N₂O by GC/ECD. The widely scattered data show N₂O emissions of 10-250 ppm. Experiments using on-line N₂O analyses by GC/ECD, indicated N₂O emissions consistently below 10 ppm. There seems to be no correlation between N₂O emissions and NO_x emissions.

John Kramlich (EERC) described his fluid bed model as a stirred reactor for bed particles releasing volatiles such as HCN and CO, and as a plug-flow reactor for the gases moving up through the bed. Initial model results show that NO concentration initially increased because of a leaner stoichiometry, reached a maximum of about 200 ppm, and then decreased in bed region with relatively less lean stoichiometries. The final stoichiometry was taken to be 1.25. The results also show that N₂O emissions at the end of a residence time of 0.5 s, corresponding to the beginning of freeboard part, were reasonably high (about 250 ppm). The model predictions for variations in excess air, bed temperature, and fuel nitrogen speciation are shown in Figure 5. The stoichiometry in the bed was lean, so an increase in excess air did not have much effect on N₂O emissions, which are very sensitive to temperature in the range 1,000-1,200 K. NH₃ does not produce much N₂O; HCN produces reasonably high levels of

N₂O; and a combination of NH₃ and HCN produces intermediate N₂O levels. All these parametric effects, explored by the model, agree with N₂O formation/destruction chemistry understood so far. Model predictions were also made on N₂O emissions from coal and natural gas reburning. The results suggest that application of carefully picked gas reburning conditions may decrease both NO and N₂O emissions.

Alan Williams (Leeds University) summarized his own investigation. His measurements reveal that N₂O is about 10-20% of the total NO_x for fluidized bed and drop-tube combustion, with grate combustion producing higher levels than systems with sustained high temperature in the post-flame region. He suggested the mechanism of N₂O formation as outlined in Figure 6 where coal pyrolyzes to give tar+gases+char, all of which can produce N₂O. His kinetic calculations reveal that the N₂O contribution from the interaction of NH₃ + NO was only about 5 ppm. N₂O yields from both tar and char combustion were each about 10% of the NO produced. These results suggest that at each stage of combustion, either single or staged, the N₂O is about 10% (or possibly higher) of the NO (+NO₂) produced, and production of N₂O is a strong function of temperature.

John Smart (International Flame Research Foundation) presented data on his experiments on a 4 MW horizontal, swirled pulverized-coal-fired furnace.

The preliminary results indicated that HCN and NH₃ found in the flame at the 0.1m axial location were essentially gone by the 0.2 m location. N₂O values were low at the 0.1 m location, although at 0.2 m near peak values were achieved. N₂O and NO_x in furnace exhaust (at about 1,070 °C) were 43 and 720 ppm, (at 3.6 % O₂). The data suggest N₂O formation from fuel-bound N, but further work is needed to characterize this hypothesis.

N₂O Measurement Techniques

The second session began by addressing the need to develop standardized sampling and analytical techniques. Given the measured increase in atmospheric N₂O levels, it can be concluded that a significant anthropogenic source exists. The relative importance of candidate sources such as agriculture, biomass burning and fossil fuel combustion and others is unclear at this time. Therefore, a reliable, accurate method for identifying and analyzing these sources is crucial. A standardized sampling and analytical protocol is critical in verifying the reliability of N₂O data gathered worldwide. A wide variance in sampling methodology is evident. Grab samples have been collected in many types of containers, including glass, stainless-steel, and Tedlar bags. Sample moisture content also varies greatly. Furthermore, the development of an on-line real time analyzer would eliminate long analytical delays in research

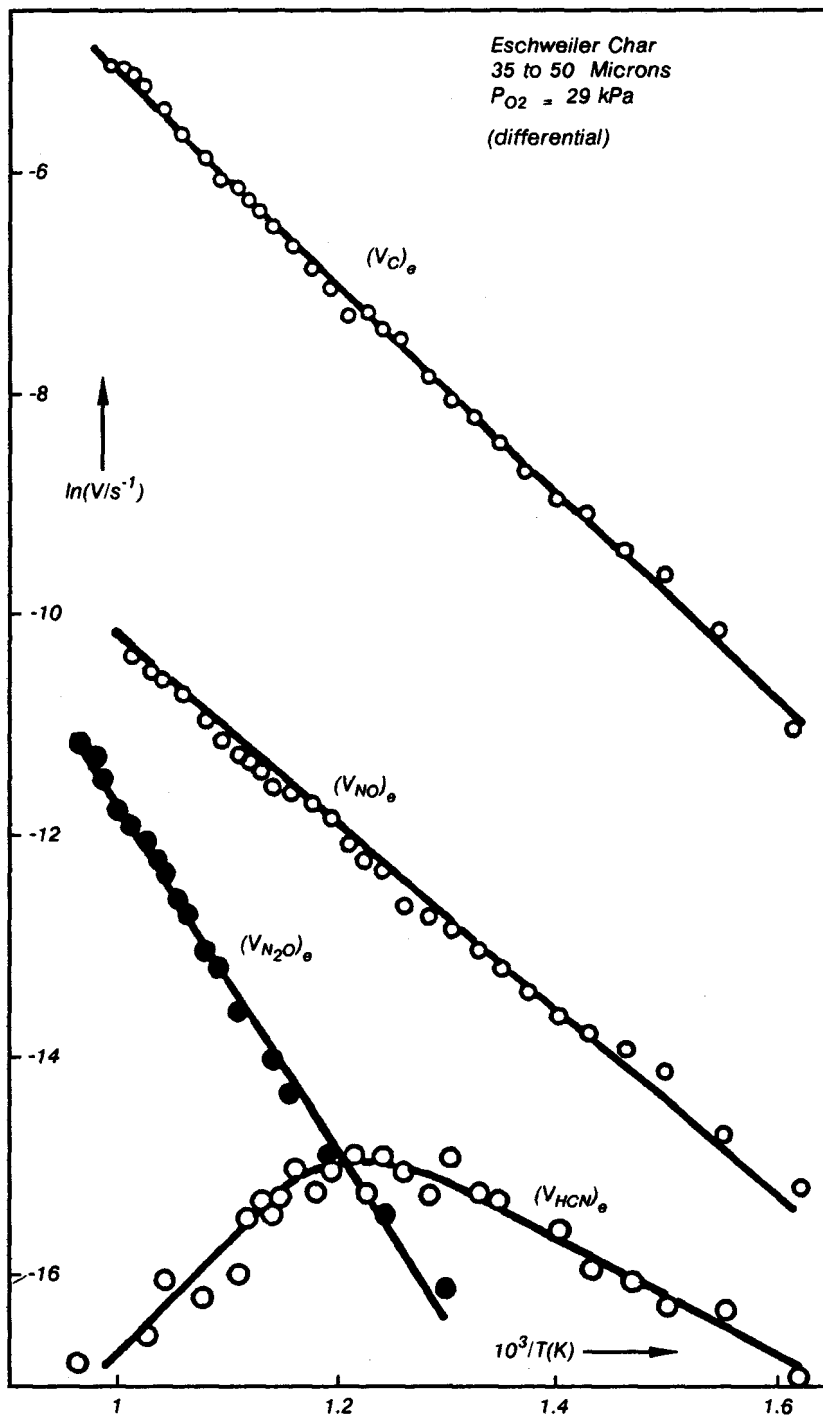


Figure 2. Reaction rates for Eschweiler char.

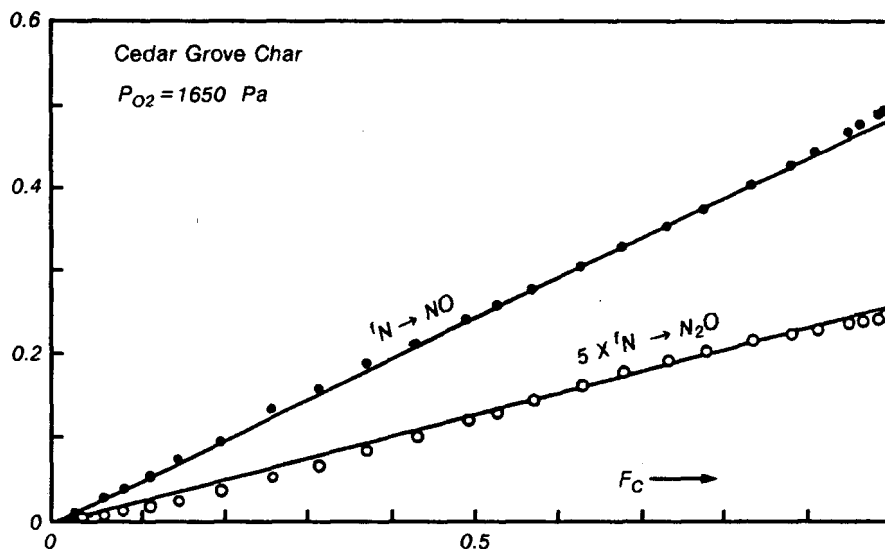


Figure 3. Cedar Grove char conversion of nitrogen.

Oxidation of (-C) and (-H)	Nitrogen Species Involving Reactions	
<p>Carbon Reactions:</p> $O_2 + 2(-C) \xrightarrow{1} 2(-CO)$ $(-CO) \xrightarrow{2} CO + \text{free site}$ $2(-CO) \xrightarrow{3} CO_2 + (-C) + \text{free site}$ $CO + (-C) \xrightarrow{4} CO_2 + (-C)$ $CO_2 + (-C) \xrightarrow{5} CO + (-CO)$ <p>Hydrogen Reactions:</p> $2(-CH) \xrightarrow{31} H_2 + 2(-C)$ $H_2 + (-CO) \xrightarrow{32} H_2O + (-C)$ $H_2O + (-C) \xrightarrow{33} H_2 + (-CO)$	<p>Formation of NO:</p> $O_2 + (-C) + (-CN) \xrightarrow{19} (-CO) + (-CNO)$ $(-CNO) \xrightarrow{20} NO + (-C)$ $(-CN) + (-CO) \xrightarrow{21} NO + 2(-C)$ <p>Formation of N₂O:</p> $2(-CNO) \xrightarrow{22} (-CO) + N_2O$ $NO + (-CN) \xrightarrow{23} N_2O + (-C)$ $(-CNO) + (-CN) \xrightarrow{24} N_2 + 2(-C)$ <p>Heterogeneous Reduction of NO and N₂O</p> $NO + 2(-C) \xrightarrow{6} (-CO) + (-CN)$ $2(-CN) \xrightarrow{8} N_2 + 2(-C)$ $NO + (-CN) \xrightarrow{9} N_2O + 2(-C)$ $N_2O + (-C) \xrightarrow{16} N_2 + (-CO)$ $N_2O + (-CO) \xrightarrow{17} N_2 + CO_2$ $N_2O + (-CO) \xrightarrow{18} 2NO + (-C)$ $NO + (-C) + (-CH) \rightarrow (-CO) + (CHN)$	<p>Formation/Destruction of HCN:</p> $(-CH) + (-CN) \xrightarrow{25} HCN + (-C)$ $H_2 + (-C) + (-CN) \xrightarrow{26} (-CH) + (-CHN)$ $(-CHN) \xrightarrow{27} HCN + \text{free site}$ $HCN + (-CN) \xrightarrow{28} N_2 + (-CH)$ <p>(HCN → NO + ...?)</p> <p>Formation/Destruction of NH₃</p> $H_2 + (-CHN) \xrightarrow{29} NH_3 + (-C)$ $NH_3 + (-CO) + (-CN) \xrightarrow{30} N_2 + H_2O + CH + (-C)$ <p>(NH₃ → HCN...?)</p> <p>(NH₃ → NO...?)</p>

Figure 4. Formation of N₂ from bound nitrogen during heterogeneous char oxidation.

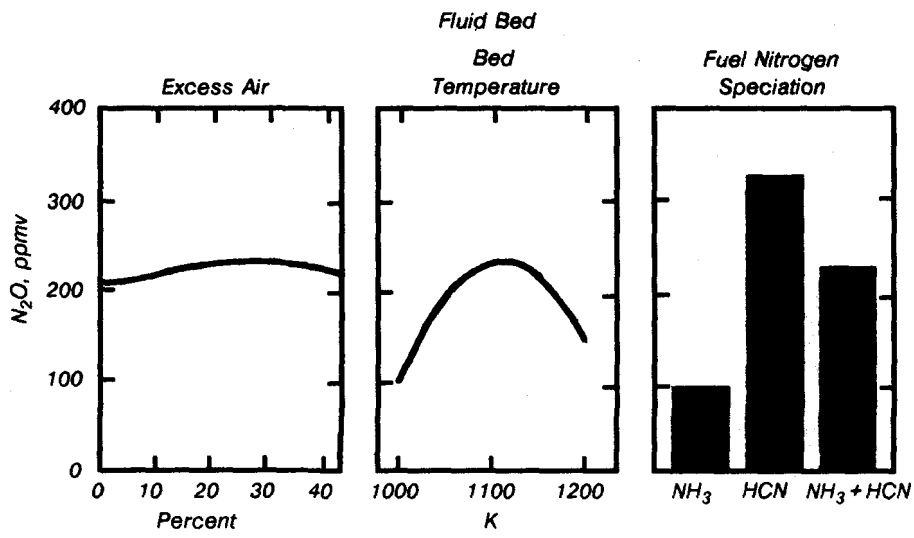


Figure 5. Predictions under varied conditions..

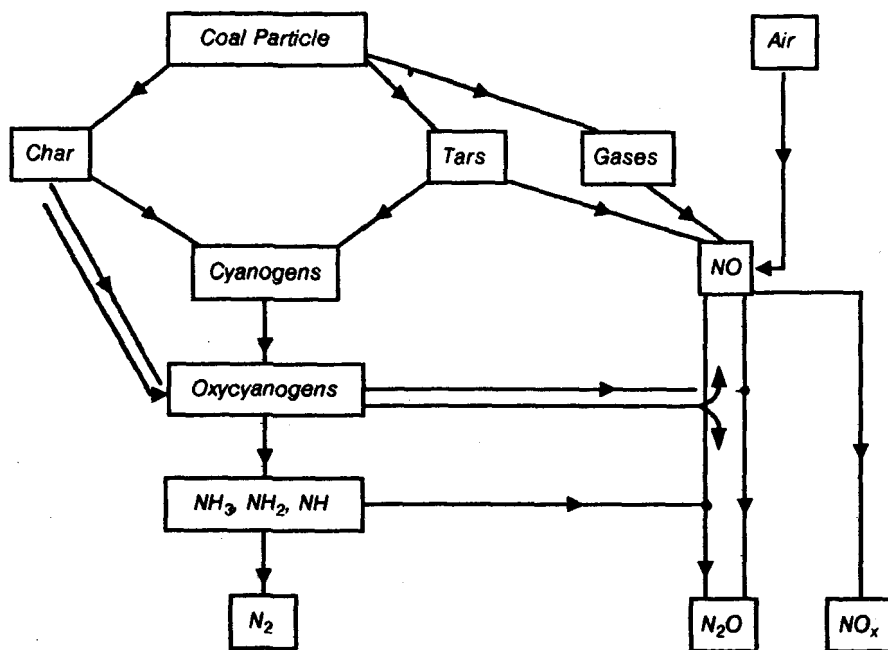


Figure 6. NO_x and N_2O formation from coal. .

programs as well as the problems associated with grab sampling

Limited methods of N₂O measurement are available. Quantitation is usually done by gas chromatography using an electron capture detector (GC/ECD). Although suitable, a disadvantage of GC analysis is that a true real time measurement is not possible and that a high skill level is required to perform the analysis.

Larry Muzio (Fossil Energy Research Corporation) reported on the status of the development of an on-line infrared N₂O analyzer. As a result of his research efforts, a prototype production model capable of measuring low ppm concentrations with high precision is currently being manufactured and will be field tested soon.

Muzio (FERCO) and Kramlich (EERC) presented startling results of a collaborative study of interferences from SO₂ with respect to N₂O, in sample containers under certain conditions. While conducting natural gas tests using FERCO's combustor, high N₂O was measured while doping with ammonia (to generate NO_x) and SO₂. N₂O samples were collected in glass flasks using an extraction system where moisture removal was not utilized prior to collection. It was discovered that, while doping with 2,500 ppm SO₂, N₂O concentrations on the order of 300 ppm were observed, while the condition without SO₂ doping measured only about 1 ppm N₂O.

Muzio and Kramlich began to suspect that a reaction in the sampling system was the source of the N₂O artifact. At this time, an attempt was made to generate N₂O in the sample container. A synthetic mixture containing N₂, O₂, CO₂ and NO was placed in the flasks, one containing deionized H₂O and no SO₂ with the other containing 1,500 ppm SO₂ and dilute sulfuric acid. Over 150 ppm N₂O was generated from the SO₂/sulfuric-acid containing mixture while virtually no N₂O was measured in the mixture lacking these components. The test was performed again without adding SO₂. This time no N₂O generation was observed, isolating the importance of SO₂ in the artifact mechanism (see Figure 7).

Tests were designed to determine if the removal of SO₂ or moisture could enable a sample of uncompromised integrity to be collected. Sodium hydroxide and sodium carbonate were found to be effective in neutralizing SO₂ while having no evident effect on known

N₂O levels. Passing the sample gas through an ice bath condenser reduced the NO/SO₂ interaction considerably, although some N₂O generation was observed.

Muzio stressed the impetus of the artifact discovery in regard to current emission data bases and to the contribution from fossil fuel combustion to the global N₂O budget.

Full Scale Field Data

The third session of the workshop included a series of presentations on data collected from both mobile and stationary sources. The presentations included data from full-scale stationary utilities in the United States and Europe. The presentations provided N₂O emission values measured from different research facilities as well as industrial equipment to provide a better representation of N₂O discharge levels and to assess the role of fossil fuel combustion on global N₂O levels. Because of the sampling artifact discussed in the previous session, each presenter was asked to include information regarding sampling and analytical techniques used, moisture and sulfur content of the sample, and any efforts taken to remove these constituents.

European data represented about 70 different facilities ranging in firing capacities from 0.5 to 800 MW, with most facilities in the 100-600 MW range. Data from circulating and stationary fluidized bed combustors (FBCs) were included in the presentations. Data from coal combustors comprised a significant portion of the presentations, although emission data from peat, distillate oil, wood, refuse, and natural gas combustion were also discussed.

The European data, excluding those from FBCs, were considerably lower than U.S. data presented from similar facilities. Figure 8 shows data collected from full scale units using various NO_x reduction methods while firing European brown coal (RWE) that are plotted along with data presented at the Boulder, Colorado workshop. Table 1 is a compilation of data presented for easy comparison. Other data collected using on-line techniques also exhibited extremely low N₂O values, often less than 10 ppm.

Discussion To Arrive at Practical Conclusions

The remainder of the workshop was designated for open discussion of

material presented and for reaching practical conclusions on the direction of future research efforts.

Steven Lanier (EERC) offered the following conclusions to the participants for discussion:

1. A critical need exists to develop and validate sampling and analysis procedures.
2. The GC/ECD method of analysis appears adequate, but the development of a continuous emission monitor for N₂O is encouraged.
3. Following validation, repeat sampling of utility boiler and fuel classes, which have previously indicated high N₂O emissions, is urgently needed.
4. Prediction of global N₂O increases based on AP42 NO_x factors is not scientifically justifiable.
5. Mobile sources are a minor contributor to the N₂O emissions.
6. European data indicate that direct N₂O emissions from coal-fired boilers are a minor contributor of N₂O.
7. Continued evaluation of N₂O emissions from fluidized bed combustors is encouraged.
8. Other combustion sources such as catalytic crackers should be evaluated.
9. No clear consensus exists as to how NO_x combustion modifications will affect emissions

A vigorous discussion period followed Lanier's conclusions, showing general agreement with them. It was suggested that the possibility of NO's being converted to N₂O in the atmosphere be explored as well. It was also suggested that the contribution from other combustion sources should also be evaluated, biomass burning in particular. The participants agreed most strongly that a suitable and valid sampling protocol should be developed.

K. Hein (RWE) summarized the final conclusions reached from the discussion:

1. New information on N₂O formation and destruction mechanisms in stack gas samples precludes earlier coal- and oil-fired boiler data.
2. Assuming that the European data are valid, the direct emission of N₂O from coal-fired boilers is a minor contributor to observed global increases in N₂O.
3. Sampling, handling, and measurement techniques must be thoroughly studied to assess NO conversion to N₂O in sample

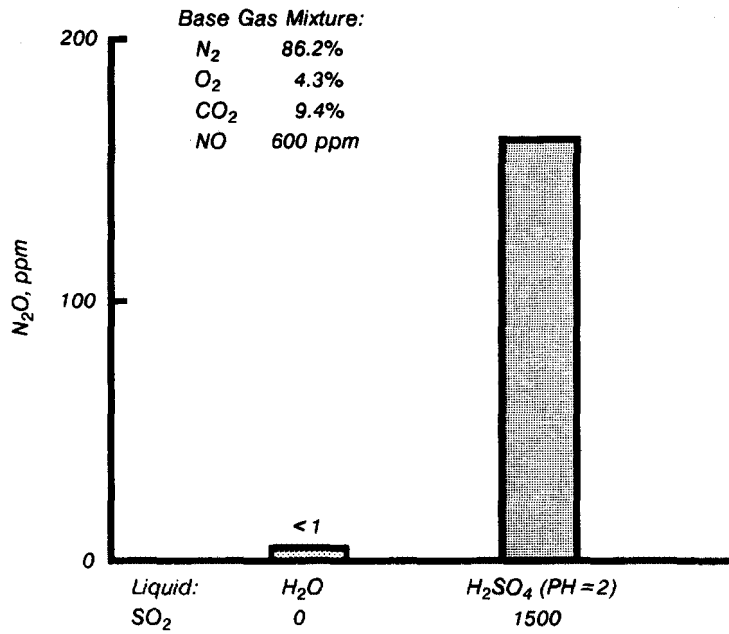


Figure 7. Synthetic gas mixtures in glass sample flask.1. Title.

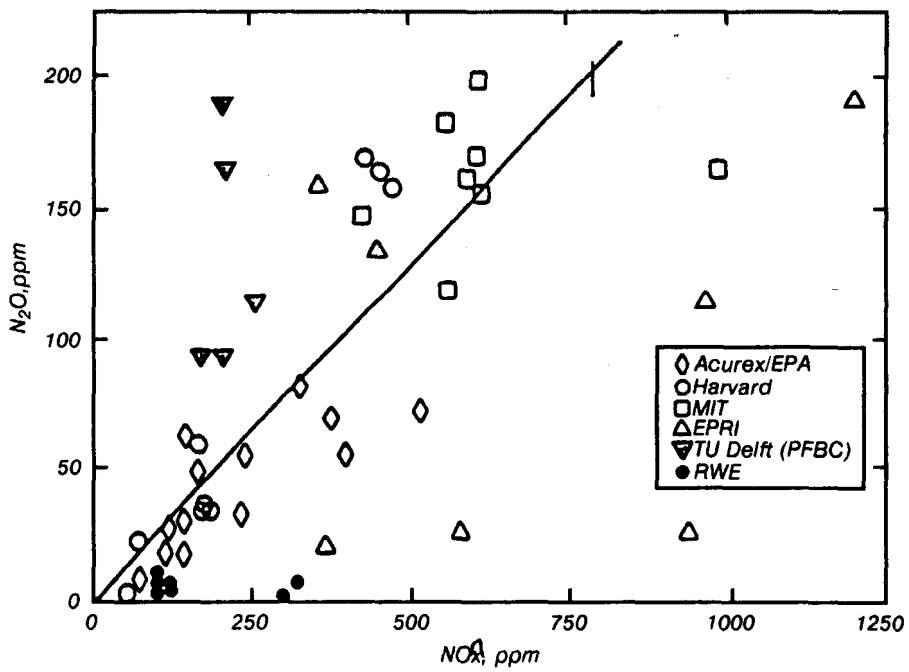


Figure 8. Comparison with previous results.

containers characterizing catalytic effects.

4. Repeat and extended measurements of NO_x and emissions from different combustion equipment types, fuel, etc., are needed, with special attention to FBC units as high emitters of N_2O .
5. All other combustion sources, including biomass burning, should be included in the evaluation of global N_2O emissions.

Summary

Information presented at this workshop suggests that N_2O emissions have a significant effect on both stratospheric O_3 depletion and global climate change. Studies indicate an annual increase in N_2O in the atmosphere of 0.2-0.3 percent, and isolating the source of the increase is essential to prevent further worldwide climate change. There is still some question as to whether the combustion of fossil fuels is directly responsible for the increase. More research is needed to find reliable and accurate techniques for establishing a data base of N_2O emissions from combustion.

The mechanisms and conditions involved in N_2O combustion formation and destruction are not well characterized. N_2O formation is possible in post-flame, temperature-dependent, gas phase reactions. Material presented at the workshop suggests that volatile HCN exposed to temperatures between 1,150 and 1,500 K can be converted to N_2O . The possibility of this is supported by models and experiments. Heterogeneous N_2O formation mechanisms are also possible, but the

amount of N_2O they produce is less than observed high stack emissions. The use of catalysts for NO_x reduction methodologies has not been well characterized for N_2O formation. The production of N_2O is temperature dependent and does not seem to be significant in these reactions.

Most of the information presented at the workshop was related to N_2O measurement techniques. Muzio's presentation on N_2O generation in sample containers questions the validity and accuracy of much of the reported data. A verifiable sampling technique is essential to assess the role of fossil-fuel combustion in rising concentrations of atmospheric N_2O . Muzio pointed out that NO_x , SO_2 , and N_2O are involved in the artifact scenario. The removal of either of these components could halt the generation of N_2O . However, considerable research is still needed in this area, because these mechanisms may also occur in the atmosphere. If this is so, positive identification of the reaction mechanism is crucial, which opens an entirely new avenue of research. Although sampling questions still exist, the analytical methodologies employed in quantifying grab samples are adequate. The development of an on-line continuous N_2O monitor would be invaluable in combustion research.

Substantial data was presented on the N_2O direct-emission levels from various European stationary utilities employing several different types of combustion techniques. Fuels other than coal were included in these presentations. Considerably lower N_2O emissions were realized in relation to United States data. In the presentations, methods of sampling were also described. Much of

the European data include extensive moisture removal in sampling. A refrigeration condenser was used, and desiccants were employed. Several presentations included on-line measurements, which showed very low N_2O concentration levels on non-FBC combustors. The data presented on FBCs showed significantly higher levels of N_2O emissions, which supports predictions by computer modeling. The emission of N_2O from mobile sources appears to be very dependent on driving styles. The conversion of NO_x to N_2O is directly related to catalyst temperature, which is proportional to driving speed or revolutions per minute. Lower temperature catalysts produce higher N_2O emissions.

A general discussion period completed the 2-day workshop, put in perspective the information presented, and enabled participants to set priorities for research and goals. Standardization of a practical and accurate sampling protocol was deemed most essential. There is no way to assess N_2O emissions from fossil-fuel combustion unless an accurate measurement technique is available. Once a suitable sampling protocol has been installed, the utility boilers, catalytic crackers, and other combustion sources should be retested. The combustion of fuels other than coal and heavy distillates should be considered, particularly biomass burning, where limited sampling efforts have shown significant emissions. A general consensus was reached that direct emissions of N_2O from the combustion of fossil fuels is possibly not the major source of N_2O in the atmosphere, but more research should be conducted to support this conclusion.

Table 1. N₂O Emissions Data Summary

Country	Group	Combustor Type	Size MW	Load MW	Fuel Used	Sample Collection Method	Moisture Removal Method	Analytical Method	N ₂ O ppm	NO _x ppm	SO ₂ ppm
England	CERL	Wall Fired	450	455	Pulverized Coal	PVC Bag	Condenser	GC/ECD	32	~700	~1200
		Wall Fired	450	300	*	PVC Bag	*	GC/ECD	26	-	~1200
		Tang. Fired	500	475	*	PVC Bag(On-Line)	*	GC/ECD/(IR)	2.4	270	~1200
		Tang Fired	500	485	Pulverized Coal	PVC Bag (On-Line)	Condenserr	GC/ECD/(IR)	4.5	385	~1200
Finland	EKONO	Circ. Fl. Bed	80	85%	Coal	P.E. Lined	Silica Gel	GC/MS	96	130	-
		*	30	70%	Coal	Aluminum Bags	*	*	80	100	-
		Circ. Fl. Bed	60	100%	Milled Peat/Wood	*	*	*	7	170	-
		Stat. Fl. Bed	18	100%	Milled Peat/Oil	*	*	*	16	200	-
		*	15	75%	Milled Peat	*	*	*	43	220	-
		Stat.Fl.Bed	35	100%	Coal	*	*	*	23	130	-
		Conv. Burner	160	100%	Pulverized Peat	*	*	*	20	270	-
		*	200	85%	Pulv. Peat/Nat. Gas	*	*	*	29	240	-
		*	5.3	100%	Pulverized Peat	*	*	*	18	440	-
		*	5.3	74%	Pulverized Peat	*	*	*	21	330	-
		*	450	100%	Pulverized Coal	*	*	*	11	630	-
		*	450	60%	Pulverized Coal	*	*	*	3	500	-
		*	240	100%	Pulverized Coal	*	*	*	27	620	-
		*	3.2	95%	Heavy Oil	*	*	*	39	240	-
		*	3.2	100%	Heavy Oil	*	*	*	73	230	-
		Conv. Burner	400	86%	Natural Gas	*	*	*	1	450	-
		Grate	15	90%	Milled Peat	*	*	*	17	280	-
		*	5	80%	Pressed Peat	*	*	*	6	270	-
		*	14	60%	Wood Chips	*	*	*	1	80	-
		*	27	56%	Wood Chips	*	*	*	1	90	-
*	35	66%	Coal	*	*	*	20	150	-		
Grate	50	100%	Coal/Wood	Aluminum Bags	Silica Gel	GC/MS	34	180	-		

Table 1. (continued)

Country	Group	Combustor Type	Size MW	Load MW	Fuel Used	Sample Collection Method	Moisture Removal Method	Analytical Method	N ₂ O ppm	NO _x	SO ₂ ppm
Italy	ENEL	Opposite Firing	320	310	#6 Fuel Oil (3%S)	On-Line	Condenserr	GC/ECD	ND	355	--
		Once Through	*	280	*	*	*	*	ND	295	-
		*	*	200	*	*	*	*	ND	235	-
		*	*	310	*	*	*	*	1	480	-
		Opposite Firing	*	250	*	*	*	*	1	335	-
		Once Through	320	160	#6 Fuel Oil(3%S)	*	*	*	ND	220	-
		Corner Fired	171	130	Bitum. Coal(.6%S)	*	*	*	5.1	-	-
		Drum Boiler	*	165	*		Condenser	*	3.3	386	-
		Corner Fired	*	165	*			*	2.1	386	-
		Drum Boiler	171	165-	Bitum. Coal .6%S)	TEF-Lined SS Bomb	Condenser	GC/ECD	2.5	-	-
		-	100	115		*	*	*	~1	215	-
		-	100	100	Nat. Gas	*	*	*	~1	190	-
		-	100	100	*	*	*	*	~1	215	-
		-	100	70	Nat. Gas	*	*	*	10	-	-
		-	120	120	Coal	*	*	*	20-25	-	-
		-	120	108	*	*	*	*	3	-	-
		-	180	144	*	*	*	*	10	-	-
		-	180	180	*	*	*	*	10-15	-	-
		-	180	400	*	*	*	*	>1	350	-
		-	400	600	*	*	*	*	>1	550	-
		-	600	600	*	*	*	*	5-8	400	-
		SCR	600	120	Coal	TEF-Lined SS Bomb	Condenser	GC/ECD	3-6	-	-
Netherlands	KEMA		120								

Table 1. (continued)

Country	Group	Combustor Type	Size MW	Load MW	Fuel Used	Sample Collection Method	Moisture Removal Method	Analytical Method	N ₂ O ppm	NO _x ppm	SO ₂ ppm
Sweden	SERI	Top Fired	12	-	Oil	P.E. Lined	Silica Gel	GC/ECD	17,28	-	-
		Top Fired Rotary	50	100%	*	Aluminum Bags	*	*	40	-	-
		Top Fired Rotary	50	70%	*	*	*	*	3	-	-
		Top Fired Rotary	50	60%	*	*	*	*	4	-	-
		Tang Fired	70	-	Oil	*	*	*	23,38	-	-
		Tang Fired	125	-	Pulv. Coal	*	*	*	3,7	-	-
		Wall Fired	90	-	Pulv. Coal	*	*	*	3-60	-	-
		Bubbling FPC	16	-	Coal	*	*	*	137	-	-
		Circ. FBC	50	60%	*	*	*	*	128	-	-
		*	*	70%	*	*	*	*	88	-	-
	*	*	80%	*	*	*	*	106	-	-	
	*	*	90%	*	*	*	*	79	-	-	
	Circ. FBC	50	-	Coal	*	*	*	165	-	-	
	Stat. Grate	5.8	70%	Wood Chips	*	*	*	5	-	-	
	Stat. Grate	*	80%	*	*	*	*	4	-	-	
	Stat. Grate	5.8	85%	*	*	*	*	3	-	-	
	Pre-Oven	30	75%	*	*	*	*	5,8	-	-	
	Pre-Oven	30	80%	Wood Chips	*	*	*	5	-	-	
	Moving Grate	5.5	-	Peat	*	*	*	9-18	-	-	
	Circ. FBC	42	-	Peat	*	*	*	52	-	-	
	Wall Fired	150	50%	Nat. Gas	*	*	*	2	-	-	
	Wall Fired	150	75%	Nat. Gas	*	*	*	2	-	-	
	GES	Recovery Furn.	*	-	Black Liquor	P.E. Lined	Silica Gel	GC/ECD	~1-2	-	-
Circ. FBC		20	18	Residual Dist Fuel	Aluminum Bags	Silica Gel	GC/ECD	10,12	-	-	
*		20	18	Peat	PP.E. Lined	Silica Gel	GC/ECD	6,10	-	-	
*		40	26	Peat	Aluminum	*	*	76	-	-	
*		33	33	Coal	*	*	*	49,56	-	-	
*		34	34	Coal/Peat	P.E. Lined	*	*	62,69	-	-	
Circ. FBC		50	51	Wood Waste	Aluminum Bags	Silica Gel	GC/ECD	14,19	-	-	
S.E.	Circ. FBC	40	27	Coal (.4% S)	Tedlar Bags	Silica Gel	GC/ECD	123-209	61-87	79-146	
	Circ. FBC	40	30	Coal (.6% S)	Tedlar Bags	Silica Gel	GC/ECD	233-444	36-64	153-166	

Table 1. (continued)

Country	Group	Combustor Type	Size MW	Load MW	Fuel Used	Sample Collection Method	Moisture Removal Method	Analytical Method	N ₂ O ppm	No _x ppm	SO ₂ ppm	
W. Germany	RWE	Press FBC	-	0.34	Coal	SS and Glass Bombs	Condenser	GC/TC	115	255	-	
			-	0.56						193	203	-
			-	0.59						168	211	-
			-	0.71						95	203	-
			-	0.75						95	173	-
			300	-	Brown Coal (~.9%)					~5-11	102-120	-
			300	-						2	102	-
			300	-						5-8	322	-
			-	510	Bitum. Coal	SS and Glass Bombs	Condenser	GC/TC	GC/TC	27	863	-
			-	465	Bitum. Coal	SS and Glass Bombs	Condenser	GC/TC	GC/TC	25	196	-
USA	L&CS	Dry Bottom	-	84	Bitum. Coal				4	307	-	
			-	42(vh)	Municipal Refuse				5	101	-	
			-	0.05	Coal Dust	SS and Glass Bombs	Condenser	GC/TC	GC/TC	30	2000	-
			-	0.1	Pulv. Coal	On-Line		IR	IR	100	-	-
			-	-	Pulv. Coal	On-Line		GC/ECD	GC/ECD	100-	300-500	-
			800	800	Pulv. Coal	SS and Glass Bombs		GC/ECD	GC/ECD	400	-	-
			800	800	Pulv. Coal	Gass Bomb		GC/ECD	GC/ECD	130	-	-
			0.029	0.017	Pulv. Bit. Coal	SS Bomb	Condenser	GC/ECD	GC/ECD	3	150-900	-
			0.029	0.017	Pulv. Bit. Coal	On-Line	Condenser	GC/ECD	GC/ECD	10-220	600	-
			0.029	0.027	Pulv. Coal	Glass Bomb	Condenser#	GC/ECD	GC/ECD	>10	400-900	-

Note: Both moisture and SO₂ were removed prior to sampling collection
 #A water quench probe was used at point of sampling

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The complete report, entitled "EPA/IFP European Workshop on the Emissions of Nitrous Oxide From Fossil Fuel Combustion (Order No. PB90-126038 \$23.00 subject to change) will be available only from:

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