A Review of Nitrous Oxide Behavior in the Atmosphere, and in Combustion and Industrial Systems

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ABSTRACT

Tropospheric measurements show that nitrous oxide (N_2O) concentrations are increasing over time. This demonstrates the existence of one or more significant anthropogenic sources, a fact that has generated considerable research interest for several years. The debate has principally focused on (1) the identity of the sources, and (2) the consequences of increased N_2O concentrations. Both questions remain open, to at least some degree.

The environmental concerns stem from the suggestion that diffusion of additional N_2O into the stratosphere can result in increased ozone (O_3) depletion. Within the stratosphere, N_2O undergoes photolysis and reacts with oxygen atoms to yield some nitric oxide (NO). This enters into the well known O_3 destruction cycle. N_2O is also a potent absorber of infrared radiation and can contribute to global warming through the

greenhouse effect.

In combustion, the homogeneous reactions leading to N_2O are principally NCO + NO → N_2O + CO and NH + NO → N_2O + H, with the first reaction being the more important in practical combustion systems. During high-temperature combustion, N_2O forms early in the flame if fuel nitrogen is available. The high temperatures, however, ensure that little of this escapes, and emissions from most conventional combustion systems are quite low. The exception is combustion under moderate temperature conditions, where the N_2O is formed from fuel nitrogen, but fails to be destroyed. The two principal examples are combustion in fluidized beds, and in applications of nitrogen oxide (NO_x) control by the downstream injection of nitrogen-containing agents (*e.g.,* selective non-catalytic reduction with urea). There remains considerable debate on the degree to which homogeneous vs. heterogeneous reactions contribute to N_2O formation in fluidized bed combustion. What is clear is that the N_2O yield is inversely correlated with bed temperature, and conversion of fuel nitrogen to N_2O is favored for higher-rank fuels.

Formation of N_2O during NO_x control processes has been confined primarily to selective non-catalytic reduction. Specifically, when the nitrogen-containing agents urea and cyanuric acid are injected, a significant portion (typically > 10%) of the NO that is reduced is converted into N_2O. The use of promoters to reduce the optimum injection temperature appears to increase the fraction of NO converted into N_2O. Other operations, such as air staging and reburning, do not appear to be significant N_2O producers. In selective catalytic reduction, the yield of N_2O depends on both catalyst type and operating condition, although most systems are not large emitters.

Other systems considered include mobile sources, waste incineration, and industrial sources. In waste incineration, the combustion of sewage sludge yields very high N_2O emissions. This appears to be due to the very high nitrogen content of the fuel and the low combustion temperatures. Many industrial systems are largely uncharacterized with respect to N_2O emissions. Adipic acid manufacture is known to produce large amounts of N_2O as a byproduct, and abatement procedures are under development within the industry.

INTRODUCTION

Nitrous oxide (N_2O) was long neglected as a pollutant species in comparison to the attention given to the other nitrogen oxides (NO_x). Unlike other NO_x species, N_2O is known to be extremely inert in the troposphere. This inertness suggested that little environmental consequence was associated with N_2O emissions, so it was relatively easy to consider it a non-pollutant.

In a more practical vein, the difficulty involved in obtaining N_2O measurements probably contributed to its neglect for many years. At times when NO_x were being measured routinely on many sources, N_2O was still a specialty measurement requiring return of batch samples to the laboratory, followed by a difficult gas chromatographic analysis.

Interest in N_2O emissions was largely started by atmospheric chemists, who observed that the tropospheric concentration was increasing with time at a rate of approximately 0.25%/yr. This increase suggested the existence of at least one unknown, substantial anthropogenic source. It also triggered interest in the consequences of this increased tropospheric N_2O burden.

Examination of the global N_2O budget shows that, while its source (natural and anthropogenic) is through ground level emissions into the troposphere, its primary sink occurs through diffusion to the stratosphere. Here, the N_2O is finally destroyed by either photolysis or reaction with singlet oxygen atoms. The result is that a portion of the N_2O is converted into nitric oxide (NO), which enters the ozone (O_3) destruction cycle. Thus, increased tropospheric N_2O concentrations can lead to increased O_3 removal rates. (It is critical to remember that considerable N_2O is made naturally, and this represents a major contribution to *natural* O_3 destruction in the stratosphere. The concern is that increased anthropogenic N_2O will accelerate this natural rate. This differs from the chlorofluorocarbon (CFC) problem where the natural tropospheric concentrations of CFC's are zero.)

In addition to its impact on stratospheric O_3, N_2O contributes to global warming. The N_2O molecule is a strong absorber of infrared radiation at wavelengths where carbon dioxide (CO_2) is transparent. Although the concentration of N_2O is much less than that of CO_2, it is a much stronger absorber on a molecule-by-molecule basis. This suggests that increased N_2O concentrations in the troposphere could lead to more retention of long wavelength radiation emitting from the surface of the Earth.

The search for the anthropogenic sources has concentrated on (1) industrial processes that may emit globally significant quantities of N_2O, and (2) biological processes that may produce N_2O on a widespread basis. Although there has been extensive work in both of these areas, the work has been hampered by measurement difficulties. Nonetheless, a substantially improved picture of the global N_2O budget has emerged. Based on this understanding, steps are being taken to modify the processes that generate anthropogenic N_2O.

Certain features have come to be recognized as contributing to N_2O emissions from combustion systems. First and foremost is the oxidation of fuel nitrogen under relatively low-temperature conditions. This allows N_2O to form, and to avoid subsequent destruction. Thus, any system in which nitrogen in a combined form is oxidized under relatively low temperatures can lead to N_2O emissions. Practical examples include combustion fluidized beds, and NO_x control processes that involve the downstream injection of nitrogen -containing compounds, such as urea. In most combustion systems, however, the flame temperature is sufficiently high that any N_2O formed in the flame zone is destroyed before the gases are emitted. Thus, most combustion systems do not emit much N_2O.

This paper describes atmospheric behavior and the behavior of N_2O in combustion systems including pulverized coal and fluid bed combustion systems, and thermal waste remediation. The paper concludes with a review of information on N_2O behavior during NO_x control activities, and N_2O from both mobile, and other industrial sources. Notably missing is any discussion of N_2O from biological activities. Although this is an important component of the global N_2O budget, it falls outside of the scope of the paper.

1. ATMOSPHERIC CHEMISTRY AND ENVIRONMENTAL CONSEQUENCES

Role of N_2O in Global Warming

With an effective surface temperature of approximately 6000 K, most of the sun's radiation is emitted within a spectral range of 100 to 3000 nm. These wavelengths include the visible and portions of the ultraviolet and infrared spectra. The Earth's atmosphere is transparent to most of this incident radiation and, as this radiation reaches the Earth, it is either reflected back to space or absorbed to heat the surface. To maintain constant temperatures, heat gained by the sun's incident radiation must be balanced by heat losses through re-radiation. With an average temperature of approximately 300 K, the Earth emits most of its radiation at infrared wavelengths above 3000 nm. Unlike incident solar radiation, the Earth's atmosphere is not entirely transparent to outgoing infrared radiation. Atmospheric gases such as water (H_2O), CO_2, methane (CH_4), N_2O, O_3, and more than a dozen synthetic gases such as CFC's and chlorinated solvents, absorb the Earth's radiation. These gases then re-emit this energy. A portion is radiated toward space at cooler atmospheric temperatures, and another portion is radiated back to Earth's surface where it results in additional surface heating. The net result is increased surface temperatures. This 'greenhouse' effect is necessary for the existence of life on Earth, and accounts for a temperature enhancement from 253 K (-4°F), the calculated average surface temperature without a greenhouse effect, to 288 K (59°F), the Earth's current average temperature.[1,2] Without the greenhouse effect, the Earth would be covered with ice.

While H_2O vapor absorbs radiation across the entire spectrum, other predominant greenhouse gases absorb radiation in distinct bands. These absorption bands are for CO_2 (13000 to 17000 nm), CH_4 (7000 to 8000 nm), N_2O (8000 to 8500 nm), and O_3 (9000 to 10000 nm). In the pre-industrial atmosphere, nearly 80% of the radiation emitted by the Earth was in the spectral range of 7000 to 13000 nm. This region was referred to as the 'window' because of its relative transparency to outgoing radiation.[1] However, as the natural balances of these atmospheric gases are changed (*i.e.*, increased) through human activities, and as previously unknown synthetic greenhouse species, such as CFC's, and chlorinated solvents, are introduced into the atmosphere, this balance is upset, resulting in increased absorption in the CO_2, CH_4, N_2O, and O_3 bands, and new absorption by synthetic gases which absorb strongly in the window region. This increased absorption decreases the Earth's heat loss, and increases the greenhouse effect and net global warming. Since surface temperatures also drive climate and hydrological cycles, the excess energy now available powers changes to weather and precipitation patterns. These effects cannot be easily predicted, however, because of the nonlinear interactions involved.[1]

Table 1 summarizes key greenhouse gas concentrations in the atmosphere.[1,2,3] Comparison is made between pre-industrial concentrations, determined through polar ice core analysis, and current ambient concentrations. The data indicate a trend of increasing atmospheric concentrations for these species. Ramanathan[1] suggests that atmospheric increases in CH_4 and carbon monoxide (CO), such as those seen during the past century, may have increased tropospheric O_3 concentrations by 20%. Levine[4] identifies the relative contribution of several atmospheric gases to global warming: CO_2 (49%), CH_4 (18%), CFC's (Refrigerant-11 and -12) (14%), N_2O (6%), and other trace gases (13%).

Role of N_2O in Stratospheric O_3 Chemistry

Approximately 85% of the Earth's atmosphere, including almost all of its H_2O vapor, is associated with the troposphere, which extends from the surface to about 15 km. The remaining 15% is associated with the stratosphere, which extends from approximately 15 to 50 km above the Earth's surface. Over 90% of the atmospheric O_3 resides in the stratosphere. Stratospheric O_3 shields the earth from biologically lethal ultraviolet (UV) radiation (wavelengths below 310 nm). Most importantly, stratospheric O_3 shields the earth from UV-B radiation with incident wavelengths from 280 to 310 nm. These wavelengths are especially harmful because they lie in a regime where the solar spectrum and DNA (biological) susceptibility overlap.[5]

In 1929, Chapman[6] identified a "classical" mechanism to describe the formation and destruction of stratospheric O_3. According to this mechanism, the chemical production of O_3 is initiated by the photodissociation of molecular oxygen by solar radiation with wavelengths of 242.3 nm or less:

$$O_2 + h\nu \rightarrow O + O \qquad l \leq 242.3\ \text{nm} \qquad (1)$$

Once dissociated, atomic oxygen may combine with molecular oxygen (O_2) and a third body, M [usually nitrogen or O_2], to form O_3:

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

O_3 destruction can also occur through photodissociation:

$$O_3 + h\nu \rightarrow O + O_2 \qquad (3)$$

or through reaction with atomic oxygen:

$$O_3 + O \rightarrow 2O_2 \qquad (4)$$

At the time, these reactions were thought to fully describe the global stratospheric O_3 balance. However, over the past 20 to 30 years three other destruction routes were discovered involving reactions with hydroxyl radical (OH):

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (5)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad (6)$$

$$HO_2 + O \rightarrow OH + O_2 \qquad (7)$$

chlorine (Cl):

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (8)$$

$$ClO + O \rightarrow Cl + O_2 \qquad (9)$$

and NO:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (10)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (11)$$

Most importantly, these three mechanisms are catalytic in nature, resulting in the destruction of O_3, without the net destruction of the OH, Cl, or NO reactant. Thus, these species are recycled and remain available for numerous O_3 destruction steps.

N_2O/NO Chemistry

The stratospheric formation of NO is the result the photolysis of N_2O and reaction with excited singlet-D oxygen, $O(^1D)$, via the reaction set:

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \qquad (12)$$

$$N_2O + O(^1D) \rightarrow 2NO \qquad (13)$$

$$N_2O + O(^1D) \rightarrow N_2 + O_2 \qquad (14)$$

Levine[2] identifies the photolysis reaction (12) as being responsible for approximately 90% of the N_2O destruction, while Reactions 13 and 14 each accounts for about 5% of its destruction. With an atmospheric lifetime of approximately 150 years, N_2O is extremely long-lived. N_2O is also very stable in the troposphere. Its destruction takes place only after its diffusion into the stratosphere.[2] Reaction 13 leads to the production of stratospheric NO and to the subsequent chemical destruction of stratospheric O_3

through the reaction set described by Reactions 10 and 11, with the net result:

$$O_3 + O \rightarrow 2O_2 \quad (4)$$

Note that NO is not destroyed during this mechanism, and is recycled for further reaction with O_3. Levine[2] identifies this catalytic NO cycle as responsible for about 70% of the global chemical destruction of stratospheric O_3. However, a large portion of this contribution is from natural sources of N_2O. With the exception of relatively minor emissions from high flying aircraft, Reaction 13 is the only known source of stratospheric NO. Other NO_x species released into the troposphere as a consequence of combustion and other industrial activities are quickly removed and do not have the atmospheric lifetimes necessary to reach the stratosphere. Table 2 summarizes the atmospheric concentrations of major gases, selected trace gases (including OH, CFC's, and NO), and trace nitrogen species compiled by Levine.[2,7] It should be noted that N_2O is the second most abundant nitrogen species in the atmosphere after molecular nitrogen.

Tropospheric Measurements of N_2O

Since the mid 1970's, systematic tropospheric measurements of N_2O have been made at locations worldwide.[8,9,10,11] These data, summarized by Khalil and Rasmussen[12] and presented in Figure 1, show the atmospheric concentration of N_2O to be currently increasing at an average rate of approximately 0.80 ± 0.02 ppbv per year or approximately 0.27 ± 0.01% per year .[12] Based on these data, current atmospheric concentrations are estimated to be 313.7 ppbv. It is also interesting to note that Weiss[8] has determined that N_2O is unequally distributed between the northern and southern hemispheres, with the northern hemisphere higher by 0.83 ± 0.15 ppbv at the time that those measurements were made (1976-1980). This may be indicative of the larger land mass or larger population centers and industrial activity in the northern hemisphere.

Data by Pearman *et al.*,[13] Khalil and Rasmussen,[12,14] Ethridge *et al.*,[15] and Zardini *et al.*[16] examining N_2O concentrations in air bubbles trapped in polar ice core samples suggest that this temporal increase is a relatively recent phenomenon. In polar regions, where yearly snow falls do not melt, air associated with the snow is trapped in tiny bubbles as subsequent accumulation and pressure convert older snow to ice. Analysis of the air within these bubbles can yield information concerning the composition of gases in the atmosphere hundreds, thousands, or tens of thousands of years ago. These data, summarized for the past 1000 years by Khalil and Rasmussen[12] and presented in Figure 2, include a composite set of measurements from 0 to 1820 A.D.,[14] 1600 to 1966 A.D.,[15] 1600 to 1900 A.D.,[16] and 1800 to 1900 A.D.[12] Understandably, these data are subject to much more uncertainty compared to the precise measurements of the past 15 years. Evident from Figure 2 is the absence of any significant trend between 0 and 1500 A.D. At that time, however, concentrations were seen to suddenly drop and then rise again. Khalil and Rasmussen[12] suggest that this phenomenon was the result of the 'little ice age' which reportedly occurred at this time and which may have resulted in reduced biological activity. For the period 1880 to 1960, the trend shows a steady increase of 0.07 ± 0.01 ppbv per year. For comparison, the most recent atmospheric data (1976-1988) (see Figure 1 and Table 1) have also been included, and show an even more expanded rate of increase (0.08 ± 0.02 ppbv). Khalil and Rasmussen[12] point out that the ice core data are often imprecise, ambiguous, and subject to potential errors. Moreover, the most recent ice core data (late 1800's - early 1900's) are subject to even greater uncertainties due to problems associated with resolving air bubble formation in ice over short time intervals. The use of ice core data to resolve historical trends of greenhouse gases is reviewed by Raynaud *et al.*[17]

Tropospheric N_2O Balance

Major uncertainties exist concerning the identification and apportionment of the global sources of N_2O. It is known, however, that these global sources must balance the global rate of atmospheric destruction plus the rate of atmospheric accumulation. Rate data suggest that Reactions 12, 13, and 14 destroy approximately 10.5 ± 3.0 teragrams of nitrogen (in the form of N_2O) per year (Tg N per year). Also, the atmospheric accumulation described above requires the production of another 3.5 ± 0.5 Tg N per year. As a result, total global production of N_2O must be approximately 14 ± 3.5 Tg N per year to balance these destruction and accumulation terms.[2]

Table 3 presents estimates of the global sources of N_2O published by several groups in recent years.[2,12,18,19,20,21,22,23] The contributions from natural and anthropogenic sources have been grouped separately for comparison. Natural sources include nitrification and denitrification of nitrogen species in soils and oceans. Denitrification involves the chemical transformation of soil nitrate (NO_3^-) to molecular nitrogen (N_2) and N_2O. Almost all of the N_2O produced by denitrification escapes into the atmosphere. Nitrification involves the oxidation of reduced soil nitrogen species [such as ammonium (NH_4^+)] to nitrite (NO_2^-) and NO_3^- with N_2O as an intermediate product. These same processes are responsible for N_2O production in oceans. However, it is uncertain whether denitrification in oxygen-deficient deep waters or nitrification in oxygen-rich surface waters is responsible.[2] Table 3 indicates general agreement among the four recent studies which have presented natural source data. The single exception is the soils source published by Khalil and Rasmussen[12] which is notably higher than the other estimates.

Table 3 suggests that the global estimates of anthropogenic sources are highly variable, with values ranging from 1.0 to 9.7 Tg N per year. In addition, the different studies often do not include the same set of sources in their anthropogenic estimates. For example, Khalil and Rasmussen[12] include a sewage source that the others do not. IPCC[20] also includes estimates from adipic and nitric acid production which are notably significant. Several data sets[12,18,23] also suggest indirect N_2O formation through atmospheric transformations from NO_x precursors, or heterogeneous mechanisms involving atmospheric nitrates, although these sources are not well quantified. Of particular interest is the potential source identified by Khalil and Rasmussen,[12] which identifies climatic feedback and accelerated biogenic activity from CO_2 increases and global warming as being responsible for approximately 0.2 Tg N per year. This estimate was taken from ice core data and N_2O trends seen during the 'little ice age'. Evident from Table 3 is that not all of the global sources of N_2O have been identified, and that those that have been identified are subject to large error as indicated by the large range of estimates presented. However, if we neglect values presented by de Soete[18] who summarized anthropogenic sources only, we see that, while the magnitude of total global sources ranges widely (5.2 to 19.2 Tg N per year), they bracket the sum of the destruction and accumulation terms determined independently (14 ± 3.5 Tg N per year).

Table 3 indicates that N_2O emissions from fossil fuel combustion sources contribute a relatively small portion of the total anthropogenic source. However, this was not always believed to be true. Only recently, fossil fuel combustion, especially coal combustion, was believed to be the major contributor to the measured increases in ambient N_2O concentrations. These increases also seemed to track measured increases in ambient CO_2 concentrations. Previous research[24] presented data indicating direct N_2O emissions from coal combustion exceeding 100 ppm, and an approximate average N_2O-N:NO_x molar ratio of 0.58:1. These data seemed to confirm earlier suggestions[25,26] that combustion of fossil fuels (and coal in particular) represented a dominant factor in the observed increase of N_2O. In addition, emissions factors generated using N_2O stack concentrations of 100 to 200 ppm were adequate to close the global anthropogenic mass balance.

Additional combustion measurements, gathered by a number of research groups, however, did not always confirm the early results. These numerous studies often used various N_2O sampling and analytical methodologies including samples measured on-line and samples extracted into containers for subsequent analysis in a laboratory environment. An explanation for the resulting growing scatter in the data was proposed by Muzio and Kramlich[27] who suggested the presence off a N_2O sampling artifact. They presented evidence that indicated that N_2O was produced in sampling containers awaiting analysis. They further hypothesized a mechanism for this formation involving NO, SO_2, and H_2O. This evidence questioned the validity of all existing data which involved container sampling. Additionally, since secondary reactions converting NO to N_2O in the sample containers were found to occur easily at room temperature,[27,28,29,30,31,32] a new indirect relationship between anthropogenic NO emissions (including combustion) and global N_2O increases was suggested (see Table 3).[12,18] Although not yet characterized or quantified, this may include NO conversion in plumes, in the troposphere, or on surfaces.[33]

Since the discovery of the sampling artifact, new research has sought to characterize N_2O emissions from fossil fuel combustion sources, and determine the effect that modifications used to control NO_x has on N_2O emissions. For conventional stationary combustion sources (including coal combustion), recent measurements indicate average N_2O emissions less than 5 ppm. These values are more than a factor of 20 times less than emissions believed to be produced several years ago. Interestingly, fluidized bed combustors, and several of the thermal DeNO_x and catalytic processes developed for NO_x

control, also seem to contribute to increased levels of N_2O. At present, these technologies are not in widespread application, and the associated increases in N_2O emissions do not add significantly to the global flux. However, as these technologies are further developed, and their use becomes more common, they have the potential of affecting global emissions. Several of these technologies will be discussed further in later sections.

3. N_2O IN GAS-FIRED COMBUSTION

Kinetic data show that N_2O can be formed as an intermediate in the combustion of fuel nitrogen. Once the fuel nitrogen is consumed, however, fast destruction reactions ensure that little escapes the flame. Higher N_2O emissions can occur only if the flame is quenched, or the fuel nitrogen is introduced downstream of the flame zone. In both cases, N_2O destruction reactions are diminished.

Although the qualitative features of the flame behavior of N_2O are understood, quantitative prediction remains uncertain. In particular, recent measurements of the rate of the critical NCO + NO reaction indicate that (1) its rate is lower at high temperatures than previously thought, and (2) potentially, only a portion of the reaction branches to N_2O. In addition, recent measurements also suggest that the destruction reaction N_2O + OH is approximately 10 times slower than the rate used in most modeling studies. Since most kinetic modeling has used both the earlier, higher NCO + NO rate with a branching ratio into N_2O of unity, and the higher rate for N_2O + NO, these findings have the potential to upset current views of N_2O formation from cyano species.

Elementary Reactions of N_2O Relevant to Gas Flames

Reactions thought to be important to the behavior of N_2O in combustion systems include:

$$N_2O + M \rightarrow N_2 + O + M \quad (15)$$

$$N_2O + O \rightarrow N_2 + O_2 \quad (16)$$

$$\rightarrow NO + NO \quad (17)$$

$$N_2O + H \rightarrow N_2 + OH \quad (18)$$

$$N_2O + OH \rightarrow N_2 + HO_2 \quad (19)$$

$$NCO + NO \rightarrow N_2O + CO \quad (20)$$

$$\rightarrow N_2 + CO_2 \quad (21)$$

$$\rightarrow N_2 + CO + O \quad (22)$$

$$NH + NO \rightarrow N_2O + H \quad (23)$$

The reactions governing NCO concentrations are also important to the problem. These include reactions forming NCO, and alternate destruction pathways that compete with Reaction 20 for available NCO. Rates for these reactions must be carefully selected with an awareness that the understanding is rapidly evolving. In contrast, the reactions and rates governing the concentration of the other precursor, NH, are more firmly established.

Reaction of Fuel Nitrogen

As noted above, the addition of fuel nitrogen to laminar flames leads to the appearance of N_2O as an intermediate. Significant emissions occur, however, only for low temperature flames (obtained either through a low adiabatic flame temperature or through high heat extraction at the burner). Also, addition of fuel nitrogen to large turbulent flames yields no more N_2O in the exhaust than if no fixed nitrogen was included with the fuel.[34,35] Modeling efforts suggested that Reaction 18 is sufficiently fast to be capable of removing all the N_2O formed in the flame zones, even if the N_2O formation rate is artificially augmented by unrealistically rapid char production rates. If N_2O is to be emitted from any fossil fuel systems, what could be the source?

One clue is provided by early data on the oxidative pyrolysis of fuel-nitrogen compounds. Researchers have recognized that, although nitrogen is bound into complex organic structures in coal, it appears in devolatilization products almost exclusively as HCN and NH_3.[36,37,38] It is now known that the HCN and NH_3 arise from secondary tar cracking reactions after primary devolatilization, although the exact mechanism remains an area of research. Early studies on the pyrolysis[39] and oxidative pyrolysis[40,41,42,43] of model fuel-nitrogen compounds showed that, under certain oxidizing, moderate-temperature regimes, compounds such as cyanogen, pyridine, and HCN could yield large amounts of N_2O.

Kramlich *et al.*[34] were able to generate large exhaust concentrations of N_2O in a tunnel furnace by the downstream injection of cyano species. The primary natural gas flame of this furnace was designed to generate 600 ppm NO. The post-flame gases were quenched by heat extraction at a rate of 350 K/s. A side-stream injector was used to introduce HCN into the furnace at various locations and temperatures. The results, shown in Figure 3, indicate that at between 1100 and 1500 K a significant fraction of the HCN was converted to N_2O. Similar results were obtained for an acetonitrile spray, with the maximum conversion temperature offset somewhat due to the time required for the evaporation of the spray. NH_3, however, generated very little N_2O under these conditions.

Application of a plug-flow reaction kinetics model (with distributed side-stream addition) to these results reproduced the major features of Figure 3: a peak in N_2O emissions as a function of injection temperature, and the lack of N_2O production from NH_3. Sensitivity analysis showed that the N_2O behavior is governed by:

$$HCN + O \rightarrow NCO + H \qquad (24)$$

$$NCO + NO \rightarrow N_2O + CO \qquad (20)$$

$$NH + NO \rightarrow N_2O + H \qquad (23)$$

$$N_2O + H \rightarrow N_2 + OH \qquad (18)$$

Above the favorable temperature window, N_2O removal via Reaction 18 was rapid, and alternate pathways for the oxidation of HCN and its intermediates were opened. At lower temperatures, HCN failed to react within the time available. In the case of NH_3 injection, competing oxidation reactions within the temperature window prevented Reaction 23 from generating significant N_2O. One feature of the model was the overprediction of the conversion of HCN to N_2O. Use of a recommended reduced branching ratio[44] of 40% was entered into the model, which resulted in much more realistic N_2O predictions. This lends global support to the fractional branching ratios recently reported.[45,46]

For such a mechanism to explain N_2O emissions in pulverized coal flames, a means of transporting volatile HCN to these cooler environments must be proposed. While late devolatilization or turbulent mixing limitations could provide some HCN within the appropriate temperature window, neither of these is likely to act as a major source in practical systems. This is consistent with the low N_2O emissions reported from oil- and coal-fired furnaces, as will be discussed shortly.

Industrial Gas Flame Data

The emission of N_2O from industrial gas flames has always been found to be quite low. Figure 4 provides a compilation of data from large-scale, turbulent gas flames.[24,25,32,34,35,47,48,49,50,51,52] The left-hand half of the plot compares NO_x and N_2O data, while data in the right-hand panel did not have accompanying NO_x data. In general, emissions are so low as to be of little environmental consequence when it is remembered that the atmosphere contains approximately 0.3 ppm N_2O. Two of these data were obtained with NH_3 doping into the fuel,[34,35] but this failed to generate significant N_2O. The highest concentrations noted in Figure 4 are associated with (1) a Swedish home heating furnace,[49] (2) early data by Hao *et al.*,[24] and (3) early data by Pierotti and Rasmussen.[25]

The home heating furnace likely involves lower overall flame temperatures and greater opportunity for quench of the flame. There is ample evidence that the quench of flames containing fuel nitrogen will produce higher levels of N_2O,[53] although it has not been shown that this is true when fixed nitrogen species are absent from the fuel.

The data of Hao *et al.*[24] were obtained by collection in 50 cm^3 syringes that had an opportunity to age before analysis. Since SO_2 was not present in these gas flames to a significant extent, it is unlikely that a large amount of N_2O was generated in the sample.[27,29,30] However, there is evidence that the formation of N_2O within sample containers can proceed to a limited extent, and at a slower rate, in the absence of one of the necessary ingredients: SO_2 or moisture.[28] Although this question cannot be conclusively settled in retrospect, the large quantity of recent data from Austria[50] and Japan[51,54] suggest that most industrial gas equipment does not produce more than 2 ppm N_2O. Reported concentrations in excess of these values must be carefully examined to determine if special combustion conditions exist which give rise to emissions above the anticipated level.

4. N_2O BEHAVIOR IN OIL AND PULVERIZED COAL FLAMES

Pulverized coal flames were among the first industrial combustion sources to be characterized for N_2O emissions. The widespread use of pulverized coal, coupled with the relatively high amounts of fuel nitrogen contained in the fuel, suggested that this class of sources was worthy of attention.

The initial measurements on utility boilers were reported in 1976.[25,26] This was followed by a limited number of studies through 1986-87. It was later found that large amounts of N_2O could be formed within the flasks that were used for sample storage in many studies. Subsequent studies either modified the storage technique to avoid N_2O formation, or used on-line methods where the samples had little time to age. These later studies have shown very low emissions from pulverized-coal- or oil-fired units, generally less than 5 ppm. There have been, however, several studies of time-resolved N_2O behavior in coal flames, which indicate that much higher N_2O concentrations exist early in the flame. These studies are valuable for their mechanistic insight.

Early Coal Studies

Pierotti and Rasmussen[25] reported three measurements (32.7, 32.8, and 37.6 ppm) from a pulverized-coal-fired university power plant. They used 6 liter, electropolished stainless-steel flasks for their samples, and the subsequent analysis was by gas chromatograph/electron capture detection (GC/ECD). Nominally, these samples would have been subject to the sampling artifact, although the concentrations measured were much lower that those reported in later studies. One reason for this might have been the fact that the source and the analytical laboratory were in close proximity, and the time between sampling and analysis may have been short. Alternatively, the stainless-steel surface may have moderated the pH of the material absorbed on the walls and helped to slow the conversion of NO to N_2O.

Weiss and Craig[26] used 2 liter Pyrex sample flasks to collect stack gas from the Mohave coal-fired station in Nevada. These were preconcentrated by freezing in a liquid-nitrogen bath. The concentrated sample was then evaporated and dried. These concentrated gases (containing mainly N_2O and CO_2) were analyzed by an ultrasonic phase-shift detector.

Thus, these samples would have also been subject to in-container N_2O formation. The reported N_2O emission was 25.8 ppm, which is also low compared to subsequent studies where the sampling artifact was active.

Kramlich *et al.*[35] measured N_2O emissions from a small-scale coal-fired tunnel furnace. The goal was to identify whether the use of air staging for NO_x control would lead to enhanced N_2O emissions. These samples were obtained by an on-line preconcentration procedure similar to that of Weiss and Craig (*i.e.*, the samples withdrawn from the reactor were immediately frozen in a liquid nitrogen trap and then evaporated, dried, and analyzed on-site by thermal conductivity gas chromatography). Although the results were insensitive to the stoichiometry of the rich zone, increased reactor cooling increased N_2O emissions, and premixed coal flames yielded more N_2O than diffusion coal flames. Although the elevated N_2O emissions (20-90 ppm) could be due to sample system chemistry, it is possible that the reduced combustion temperatures in this small facility caused more of the volatile HCN to oxidize in the 1200-1500 K window where N_2O emissions can be formed.[34]

Castaldini *et al.*[55] examined a series of sources associated with NO_x abatement operations. Hao *et al.*[24] surveyed nine oil-fired and three coal-fired furnaces in the northeastern United States, as well as measurements on a pilot-scale furnace.[56] For both Castaldini and Hao a correlation was noted in which the apparent N_2O emissions (obtained using sample flasks and remote analysis) were about 25% of the NO_x emissions measured on-line at the site. This apparent proportionality was due to the conversion of NO_x within the sample flasks to N_2O at an approximate 4:1 ratio. Following the identification of this artifact, both measurement methods development and retesting of combustion sources have been priority activities.

Recent Database on Oil and Pulverized Coal Emissions

Extensive recent surveys of N_2O emissions from pulverized-coal- and oil-fired furnaces have been reported. Table 4 summarizes sources of these data.[23,32,47,50,51,54,57,58,59,60,61] It is clear from reviewing this very large database that the majority of the measurements from industrial combustion systems yield very little N_2O. Emissions in excess of 5 ppm are very rare, with the exception of combustion fluidized beds, which are discussed in the next section. One general trend is that higher emissions tend to be associated with oil-fired units, although the emission levels are still quite low. The reason for this is not known.

At these very low emission levels, the care taken in measurement becomes critical. Simple drying or SO_2 scrubbing will prevent the formation of large amounts of N_2O. However, measurement studies show that residual moisture, SO_2, and/or long sample lines will still allow a few ppm of N_2O to form. Thus, the preponderance of the data suggest very low values, and the few outliers warrant close examination to determine if unusual combustion conditions exist, or if sampling procedures were adequate.

5. COMBUSTION FLUIDIZED BEDS

Among fossil fueled combustion systems, combustion fluidized beds have consistently shown the highest N_2O emissions in field measurements. Although this unwelcome finding has become widely recognized only during the last several years, it has spawned a large research effort. The work has focused on (1) formation mechanisms, (2) emissions as a function of combustion parameters, and (3) control strategies.

Field Data

Field measurements on various full-scale fluidized bed systems have been reported. Table 5 summarizes some of the features of these measurements.[47,49,50,59,60,62,63,64,65,66,67,68] It must be borne in mind that the measurements reported at the third international workshop on N_2O emissions[49] were made before the sample container artifact was discovered, although the vast majority of these measurements were made under procedures that would minimize the in-container generation of N_2O (*i.e.*, most of the samples were dried before storage). The field tests consistently indicate emissions substantially above those found from pulverized coal flames or fuel oil flames.

Attempts to draw general conclusions from the field data are very difficult due to the wide variation in combustor configurations, operating parameters, and fuel types. In spite of this, certain trends are clear from the data. First, N_2O emissions uniformly decrease with increasing bed temperature. At the same time, NO_x emissions increase. In general, lower rank fuels deliver lower N_2O emissions. Most other operating parameters (excess air, addition of limestone) appear to have a weak influence on N_2O. Carefully obtained sub-scale data have been the means of advancing our understanding beyond that available from field data.

Summary of Major Trends

The following presents the major observations reported in the reviews by Mann *et al.*[23] and Hayhurst and Lawrence.[69] First, it cannot be overemphasized how difficult it is to extract mechanistic information from fluid bed experiments. In general, a wide variety of experimental designs and scales have been used to study N_2O formation in fluidized beds. In addition, enough information is frequently not provided to fully rationalize these data.[69] In fluidized beds many of the parameters are coupled in actual experiments (*e.g.*, excess air and bed temperature) which makes it difficult to cleanly extract the influence of a single variable. These observations show the highly empirical nature of the fluidized bed database, and suggest that much care must be taken in data analysis to develop general conclusions. In spite of these difficulties, considerable progress has been made in understanding this complex phenomenon.

The most pronounced trend is that of temperature. Reduced bed temperatures almost universally cause higher N_2O emissions, as the measurements presented on Figure 5 show.[66] Figure 5 also shows that NO increases with bed temperature, suggesting that higher operating temperature is not the best means of controlling N_2O.[70] In addition, higher operating temperatures can cause sintering of added limestone sorbents and reduce SO_2 capture.

The influence of fuel type is less significant than that of temperature. In general, lower rank fuels tend to yield lower N_2O emissions. This has been attributed to the tendency of the lower rank fuels to favor NH_3 release over HCN release.[36,37] The HCN is acknowledged to be more efficiently converted to N_2O.[34,69] Alternately, the higher surface area of lower rank fuels may promote more complete heterogeneous N_2O destruction.[70]

Other correlations have been observed, including an inverse relationship between the O/N ratio of the fuel and N_2O,[23,71]and an increase with the carbon content of the coal.[63]

Although the specific mechanisms underlying these correlations are unclear, both the O/N ratio and coal carbon content can, within limits, be indirect indicators of coal rank.

Excess air has been an unusually difficult parameter to distinguish from temperature because they are so closely coupled in fluidized bed operation. In experiments where the temperature effect was removed, higher excess air generally increases N_2O emissions. Mann *et al.*[23] examined the coupling between temperature and excess air, and found that, at higher temperatures, excess air has less of an effect on N_2O emissions, as shown in Figure 6.

Clearly, more experimental work and detailed modeling would help identify the controlling mechanisms in practical fluidized bed combustion. Many results and conclusions are contradictory, and subject to more than one interpretation. Nonetheless, fundamental data have identified two viable mechanisms for N_2O formation in fluidized beds:

- Devolatilization of fuel nitrogen as HCN and NH_3, followed by oxidation to N_2O.
- Oxidation of char nitrogen to NO, followed by the reaction of this NO with char nitrogen to yield N_2O.

On the surface, homogeneous chemistry seems to be capable of explaining many of the major trends. The release of volatile nitrogen as HCN under fluidized bed conditions yields a known N_2O precursor into an environment where N_2O formation is favored. Lower rank coals are known to yield more of their fuel nitrogen as NH_3, which does not convert to N_2O as efficiently under fluidized bed conditions. This tentatively explains the lower emissions observed with lower rank fuels. Alternately, low rank coals may experience greater heterogeneous N_2O reduction due to their different ash composition and morphology. Homogeneous chemistry is capable of reproducing the most prominent characteristic of N_2O behavior in fluidized beds, the decrease in emissions with bed temperature. It does so by showing that the key intermediate, NCO, becomes increasingly converted to NO rather than N_2O as bed temperature increases.

Heterogeneous reactions are also capable of generating N_2O. The reduction of NO at a char surface to yield N_2O does not appear to occur if oxygen is not available to expose fresh char nitrogen.[72] In the presence of oxygen, the effective mechanism appears to be the reaction of NO with exposed char nitrogen to yield N_2O rather than the absorption of

NO on the surface, followed by reaction with a second NO.[73,74]

Extrapolation of these results to practical fluidized beds is more difficult. For example, the data of Tullin *et al.*[73] show that heterogeneous N_2O formation increases with NO doping, a feature used to imply that NO reduction at the char surface is the source of the N_2O. Other data for practical beds show no increase in N_2O with NO doping.[75] This implies that strong N_2O destruction reactions in the bed are active and capable of removing any additional N_2O that may be generated by the reaction of char nitrogen with NO. Since the bed does generate N_2O emissions in spite of this strong reduction reaction, the actual source flux for N_2O must be many times that represented by the emission. The key question is the identity of this source. The hypothesis is that, in a realistically loaded bed, a large amount of volatile nitrogen passes through N_2O as an intermediate. The emission is only a fraction of the total amount of N_2O formed. The yield of N_2O from char nitrogen may be masked by this active volatile chemistry in a realistically loaded bed.

An important message from these data is that both the volatile combustion and char oxidation processes involved in N_2O formation are coupled in systems operating under practical conditions. Experimental systems that seek to decouple the process by moving away from practical conditions (*e.g.*, batch processes, light loading of an otherwise inert bed, use of char instead of coal) are expected to generate sound fundamental data. These results cannot, however, be directly extrapolated to describe trends in full-scale units. To do so requires a fully coupled model that correctly integrates all of the fundamental steps.

6. BEHAVIOR OF N_2O DURING NO_x CONTROL PROCESSES

The goal of NO_x control procedures is to convert NO into N_2 by modifying the combustion environment, introducing a selective agent, or combining a selective agent with a catalyst. Since all of these processes involve nitrogenous intermediates, there is an opportunity for a portion of these intermediates to react and form N_2O. This possibility was recognized early, at least with respect to combustion modifications.[35,55]

This section will review the influence of the major NO_x control technologies on N_2O emissions, including:

- Air staging
- Reburning or fuel staging
- Selective non-catalytic reduction (SNCR), including the Thermal DeNO_x process (NH_3 injection), the urea injection process, the RapreNO_x process (cyanuric acid injection), and the use of advanced or promoted agents
- Selective catalytic reduction (SCR)

In addition, we will briefly review the steps that have been taken to specifically control N_2O from combustion fluidized beds.

Staged Combustion

Air staging generally refers to the division of the combustion air into at least two streams such that the fuel is initially processed through a region of reduced oxygen availability. Under these conditions, conversion of fuel nitrogen to N_2 is improved. The second air stream completes fuel burnout. This basic strategy is executed in a number of ways, including fuel biasing and 'burners out of service'. The low-NO_x burners that are now available from most manufacturers are based on providing staged environments within the burner. The division of the air into two or more streams has been practiced in fluidized beds to create a fuel-rich zone for improved NO_x control.

It is well established that reducing conditions leads to lower N_2O emissions from pulverized coal combustion. Thus, one might suspect that the early formation of N_2O would be reduced during staged combustion. This, however, does not always appear to be the case based on results from brown coal.[76] In spite of the overall fuel-rich conditions in the primary zone, free oxygen still persists early in the flame, and with it, early N_2O.

At the point where the secondary air is added, the fixed-nitrogen species are nominally distributed among NO, HCN, and NH_3. Thus, the oxidation of at least the HCN might be expected to form N_2O. However, the data[76] show no N_2O at the staging point. One probable reason for this is the relatively high temperature, above 1000°C. Another is the concurrent burnout of the CO from the primary zone, which will generate H atoms via

CO + OH → CO_2 + H. Thus, at the staging point, any N_2O which is formed would likely not survive. Earlier work in a smaller furnace[35] failed to find an influence of staging. The emission levels in this facility were elevated (20-90 ppm) which was attributed to the relatively cool combustion temperature. Another study examining air staging in laboratory-scale furnaces[32] found similar N_2O emissions compared to unstaged operation. This study reported N_2O emissions from the staged combustion of natural gas, No. 2 fuel oil, and No. 5 fuel oil all less than 1 ppm. Coal combustion emissions ranged from 1 to 5 ppm.

Air staging can be approached in circulating fluidized bed combustors (CFBC's) by dividing the air injection location. Mann *et al.*[23] performed a brief examination and found no influence on N_2O emissions. Likewise, Hiltunen *et al.*[68] found no direct influence of air staging beyond that attributable to temperature changes. Jahkola *et al.*[77] found a weak increase in N_2O with staging, while Shimizu *et al.*[78] and Bramer and Valk[79] all saw a concurrent decrease in NO_x and N_2O with increased staging. Hayhurst and Lawrence[69] attribute the latter results to both increasing temperature in the flue gas and the creation of a rich zone at the bottom of the bed. It is clear from the varying results that staging appears to have only a weak influence on N_2O, and its effect is difficult to separate from other parameters.

Reburning

Reburning or fuel staging involves the addition of a second fuel stream after the primary fuel burnout is completed. For example, a low-NO_x burner can be used to complete the burnout of the primary fuel. Secondary fuel is added above these burners to create a moderately fuel-rich zone. Within this zone, radicals generated by the secondary fuel decomposition attack NO to produce N_2, HCN, and NH_3. A final air stream is added to burn out the secondary fuel and convert any remaining reduced nitrogen to NO or N_2. Both coal (containing fuel nitrogen) and natural gas (nitrogen-free) have been proposed as reburning fuels. Process descriptions and development history are available in the literature.[80]

For coal reburning, the fuel is introduced under a reduced temperature compared to a normal industrial coal flame. This suggests that higher conversions of volatile nitrogen to

N_2O may occur than would be normally expected. At present, only very limited measurements have been reported in the open literature. In one subscale study, application of coal reburning to a gas-fired primary flame increased N_2O emissions from less than 1 to 11-13 ppm.[34] Although in terms of concentration this increase appears to be small, it represents a 6.5% conversion of fuel nitrogen to N_2O. This is about an order of magnitude greater than the conversion found in the coal-fired primary flame (0.7%). This is a little surprising because, according to the discussion on air staging, one would expect that the N_2O would be destroyed at the final air staging point. Whether this trend for increased N_2O formation extrapolates to large scale is yet to be seen. In contrast, reburning with natural gas over a coal-fired primary yielded a greater than 50% N_2O reduction.[34]

In their kinetic modeling study, Kilpinen *et al.*[81] studied natural gas reburning. They find no N_2O formation in the fuel-rich zone. If, however, the final air addition temperature is reduced below 1200 K then some of the HCN from the rich zone is irreversibly converted to N_2O. Such an air injection temperature is, however, too low for practical boiler operation since CO burnout times would become unacceptably long. They did not attempt to simulate coal reburning, in which such a temperature is far too low to provide adequate char burnout. They do find that the performance is strongly transport-influenced, so it is difficult to extrapolate the findings to coal. It is, however, clear that gas reburning should be a good tool against primary zone N_2O, and that coal reburning may either form or destroy N_2O, depending on the initial primary zone concentration.

An approach similar to reburning has been attempted in fluidized beds, where natural gas was injected into the cyclone of a CFBC.[67] At substantial firing rates (of the order of 10% of the heat input), N_2O reductions of the order of 50% were achieved, compared with kinetic predictions of 90%. The difference was attributed to the effects of imperfect or finite-rate mixing, possibly with a contribution due to heat loss. Alternately, the recent data of Glarborg *et al.*[82] suggest that the rate of the critical N_2O + OH destruction reaction may be much slower than that used in the model. This may account for the discrepancy.

Selective Non-Catalytic Reduction

Selective non-catalytic reduction (SNCR) had its origins in the observation that NH_3 would selectively react with NO under appropriate temperatures to yield N_2.[83] Many years of work have resulted in an excellent understanding of this process, which is summarized by Miller and Bowman.[84] The following reactions are important:

$$NH_3 + OH \rightarrow NH_2 + H_2O \tag{25}$$

$$NH_2 + NO \rightarrow N_2 + H_2O \tag{26}$$

$$NH_2 + NO \rightarrow NNH + OH \tag{27}$$

$$NNH + M \text{ fi } N_2 + H + M \tag{28}$$

$$H + O_2 \rightarrow OH + O \tag{29}$$

This reaction sequence is self-propagating under the correct conditions. That part of the NH_2 that is consumed by Reaction 27 leads to the generation of the OH radicals (via both Reactions 27 and 29) needed to facilitate Reaction 25. The only significant acknowledged means for generating N_2O is the reaction:

$$NH + NO \rightarrow N_2O + H \tag{23}$$

Both modeling and experimental studies indicate that, while some N_2O is formed, it is a very minor product.[34,85,86,87] Faster oxidation reactions effectively compete for the NH under these conditions.

Alternate agents have been proposed to avoid the handling problems associated with NH_3 and to improve NO_x removal performance. The principal competitor for NH_3 is urea, $CO(NH_2)_2$.[88] The urea is injected as either an aqueous solution or a dry powder. Some controversy has surrounded the products of the initial thermal decomposition reaction. Arguments based on consistency between data and modeling suggest that the products are NH_3 + HNCO,[65,85] which has been confirmed by experiment.[86]

Once released into the gas phase, the HNCO reacts primarily according to the following sequence:[89,90]

$$HNCO + OH \rightarrow NCO + H_2O \tag{30}$$

$$NCO + NO \rightarrow N_2O + CO \tag{20}$$

$$HNCO + H \rightarrow NH_2 + CO \tag{31}$$

In the absence of other reactions, the chain branching associated with NH_2 and N_2O consumption must support the decomposition of the HNCO. Other reactions (*e.g.*, concurrent wet CO oxidation) can also provide the radicals needed to drive Reaction 30. The key difference between urea and NH_3 is that urea can generate HNCO, NCO, and N_2O as major products of reaction, NH_3 does not. Thus, as is well-known, urea generates substantially more N_2O emissions when used as a SNCR agent.[85,87] Typically, less than 5% of the NO reduced is converted to N_2O when NH_3 is used. This compares to conversions greater than 10% for urea.

The RapreNO$_x$ process is another SNCR process based on the use of cyanuric acid as an agent.[91,92] The cyanuric acid thermally decomposes to yield HNCO, which reacts according to Reactions 30, 20, and 31 to destroy NO, in the course of which N_2O is formed as a byproduct.[93]

Comparison of urea and cyanuric acid as agents shows that urea generates less N_2O under equivalent conditions. This is expected since only half of the nitrogen contained in the urea becomes associated with HNCO following injection. The other half forms NH_3 which does not yield significant N_2O. In the case of cyanuric acid injection, all of the nitrogen initially becomes HNCO, and thus final N_2O yields are increased.[85]

A major limitation of SNCR is the relatively narrow temperature window over which the agents are active at removing NO$_x$. Also, in large-scale facilities, the NO removal at the optimum temperature is not complete. Thus, a considerable research effort has been expended to enhance performance. One approach is the co-injection of combustible compounds (*e.g.,* CO or H_2) with the agents. This has the effect of shifting the optimum temperature window to lower temperatures. Depending on the amount of free oxygen present and the amount of combustible, the performance at the new optimum temperature can be either better or worse than the original unpromoted system. The temperature shifts because the oxidation of the combustible generates excess free radicals that are needed to initiate the reaction of the agent. Without the reaction of the combustible, the agent would not react at the lower temperature because it cannot supply sufficient radicals through chain branching.

Kinetic modeling shows that the combustible fuel acts to generate free radicals. These radicals promote agent decomposition: $HNCO + OH \rightarrow NCO + H_2O$. Next, N_2O forms via NCO + NO. At higher temperatures, the N_2O is destroyed by N_2O + H. At lower temperatures, the H-atom is still available, but the relatively high activation energy prevents the N_2O + H reaction from being effective. Thus, as the temperature window for NO removal is shifted to lower temperatures by the combustible, most of the reactions 'follow' the window due to their weak temperature sensitivity. The N_2O + H reaction is the exception due to its strong temperature dependence, and the N_2O produced from the agent reaction fails to react further.

The conclusion is that the presence of a combustible may or may not widen the SNCR window for urea injection, but that it appears to (1) reduce the temperature at which peak N_2O emissions are observed, and (2) increase these peak emissions. Note the similarity between this situation and that within a FBC. In a FBC, fuel nitrogen in the form of HCN is released by the coal. This reacts in the presence of oxidizing coal volatiles. Thus, the combustibles within the volatiles can be viewed as "promoters," which tend to reduce the optimum temperature for NO reduction and N_2O formation. With sufficient combustibles present, as would be the case in a FBC, this optimum temperature would be reduced below 700°C. Thus, as temperature is increased, N_2O emissions would be expected to be reduced, and NO emission would increase, which is the normal characteristic of FBC's.

Recent experimental work suggests that sodium additives may be one effective means of reducing N_2O formation in SNCR. Chen *et al.*[94] performed tunnel furnace experiments in which a variety of sodium compounds were co-injected with urea. Figure 7 shows NO_x reduction and N_2O emissions as a function of urea injection temperature. The figure shows that urea promoted by monosodium glutamate gave both an increase in NO_x removal performance and a substantial reduction in N_2O emissions. Other sodium compounds, such as Na_2CO_3, also reduced N_2O emissions, although SO_2 tended to reduce effectiveness. This could be due to the formation of a non-reactive sulfate coating on the sodium particles, or through suppression of sodium volatility due to sulfate formation.

Use of NH_3 for NO_x reduction in FBC's has been extensively examined. The results indicate that little N_2O is generated until NH_3 is added in high stoichiometric excess over NO.[65,77,95] Urea injection, however, is strongly correlated with increased N_2O emissions.[65] However, fixed bed studies using quartz, clay, and ash show that, even with urea injection, N_2O yields are sharply depressed.[96] This suggests that appropriate inorganic surfaces can be used to suppress N_2O formation when urea is used as a SNCR agent.

Selective Catalytic Reduction

In the present context, selective catalytic reduction (SCR) refers to the reduction of NO by added NH_3 over a catalyst. This distinguishes it from processes involving other agents, such as CO, H_2, and CH_4. The process is, at present, applied only to stationary sources of NO_x, with mobile sources being dominated by direct catalytic reduction without use of an agent like NH_3. Selective catalytic reduction is presently being applied to industrial systems in Japan and Germany, and is coming to increasing use in other parts of the world.

The formation of N_2O during SCR was noted in the early 1970's (*e.g.*, Otto *et al.*).[97] A very detailed review of the fundamentals of SCR, including the problem of N_2O production, is available.[98] In addition, a general review of the application of catalysts to environmental problems is also available, which includes SCR and other topics.[99]

Most SCR systems are based on either noble metal catalysts or vanadium in combination with other metals and various substrates. Laboratory work suggests that N_2O can be a major product of SCR over noble metal catalysts.[100] The amount of N_2O formed depends on the state of the surface, and also on the nature of the substrate.[98] The formation appears to be due to a reaction through a Langmuir-Hinshelwood mechanism between two adsorbed NO molecules.[97] The nature of the platinum surface seems to have an effect, with single crystals not yielding significant N_2O. We were unable to find published field measurements on noble metal catalysts, although unpublished information suggests that a significant portion of the reduced NO can be converted into N_2O in practical installations on gas turbine sets.[101]

In addition to the general review of Bosch and Janssen,[98] the problem of N_2O formation over vanadium has been specifically reviewed by Odenbrand *et al.*[102] In earlier work, the proposed mechanism involved the reoxidation of the vanadium surface by adsorbed NO to yield reduced N_2O.[98] Recent work suggests that N_2O arises directly from the reaction of NH_3 and NO at low temperatures, and from direct NH_3 oxidation at high temperatures. Because of this mechanism, the minimum for NO_x emissions falls at a lower temperature than the maximum in N_2O emissions.[98,103] The practical consequence is that, below about 300°C, only negligible N_2O is formed, while the formation becomes significant at higher temperatures due to NH_3 oxidation.[102] This is supported by long-term, pilot-scale testing of a wide number of vanadium catalysts.[104] Here, no significant N_2O was noted, at least to 400°C. Since catalyst sintering begins to become a problem above these temperatures,[102] this is unlikely to be a common operating condition. A survey of N_2O emissions from 22 SCR installations in Japan indicated no emissions exceeding 1 ppm.[54]

Review of the data suggests that, within the broad bounds outlined above, the actual yield of N_2O is highly variable. It depends on catalyst type, and on catalyst treatment (*e.g.*, crystal size), contamination, support, and background gas composition. It will likely depend on catalyst age. The results do suggest that vanadium catalysts do not generate significant N_2O under their normal operating conditions, but that noble metal catalysts may.

Summary

In general, NO_x control procedures have led to significantly increased N_2O if they promote the reaction of cyano species under reduced temperature conditions. Thus, coal reburning may, under some conditions, lead to enhanced N_2O due to the release of fuel nitrogen under reduced temperatures. The N_2O yields are reduced somewhat, however, by the concurrent oxidation of the volatiles, which leads to N_2O scavenging and competitive oxidation of the NCO intermediate.

The downstream injection of urea and cyanuric acid both lead to N_2O formation. Preliminary data suggest that concurrent injection of combustible promoters (*e.g.*, CO or H_2) leads to increased N_2O formation as agent injection temperatures are reduced. The application of SCR suggests that N_2O emissions are negligible from vanadium catalysts if they are operated at their nominally low temperatures. Noble metal catalysts, however, can convert significant quantities of NO into N_2O during SCR.

THERMAL WASTE REMEDIATION

To date, a limited number of field measurements have appeared describing emissions from thermal waste remediation activities. Almost all of these have dealt with municipal solid waste (MSW) or dried sewage sludge. The limited number of results available at present support only a qualitative description of the trends. Nonetheless, some significant differences between waste incineration and coal combustion are apparent.

Most of the measurements are on MSW units. The following data have been reported:

- Iwasaki *et al.*:[48] 10 units (8 stokers, 1 fluidized bed, 1 batch)
- Yasuda and Takahasi:[105] 5 units (2 stokers, 3 fluidized beds)
- Hiraki *et al.*:[106] At least one unit
- Watanabe *et al.*:[107] 12 units (5 stokers, 5 fluidized beds, 2 rotary kilns)

As illustrated in Figure 8, the most striking variation is the decrease in emissions with combustion temperature. In spite of the low combustion temperatures, however, the emissions of N_2O rarely exceed 20 ppm. This appears be due at least partly to the relatively low nitrogen content of the fuel; Iwasaki *et al.*[48] report fuel-nitrogen contents of about 0.5% and emission factors of approximately 70 g N_2O/metric ton waste. This corresponds to a fractional conversion of fuel nitrogen to N_2O of approximately 1%. Interestingly, none of the data suggest a consistent influence of combustor configuration (fluidized bed vs. stoker/grate) on emissions.

A smaller number of sludge incinerators were also examined, including:

- Iwasaki *et al.*:[48] 4 units (2 multi-stage and 2 fluidized beds)
- Yasuda and Takahasi:[105] 5 units (4 fluidized beds and 1 rotary grate)
- Hiraki *et al.*:[106] At least one unit

These units showed much higher emissions: in the case of Yasuda and Takahasi[105] up to 600 ppm. This appears to be primarily a response to the high nitrogen content of the sludge. Iwasaki *et al.*[48] report 5-8% fuel nitrogen, with emission factors corresponding to 400 g N_2O/metric ton sludge. This still represents only a 0.5% conversion of fuel nitrogen. Yasuda and Takahasi[105] evaluated a sufficient number of units at various temperatures to suggest that higher temperatures in fluidized beds can reduce the very high N_2O emissions associated with sludge combustion.

Interestingly, the NO_x emissions were low enough not to be influenced in a significant way by the change in temperature. For MSW incineration the NO_x levels were much higher.[48,105] Mixed MSW and sludge incineration appeared to take on the characteristics of 'diluted' sludge incineration (*i.e.*, increased N_2O emissions in proportion to the increased amount of fuel nitrogen).

Very little work has been reported on other waste treatment activities. Emissions from liquid injection incineration of high nitrogen wastes have not been reported. The high temperatures that are typical of these units are not expected to support high N_2O emissions. Fume incinerators, however, may operate at much lower temperatures. Frequently, the fume represents a relatively inert stream containing dilute fuel-nitrogen compounds. Many of these fumes have low heating values that must be supplemented by gas fuel to obtain a stable flame. For economic reasons, the gas usage is minimized, which can yield a low-temperature flame. Such an environment may favor N_2O emissions.

MOBILE SOURCES

While limited, the historical N_2O database for mobile sources appeared not to have been impacted by the sampling artifact. Although mobile source measurements using chassis dynamometers were often made by sample extraction using Tedlar sampling bags and seldom performed on-line, SO_2 concentrations in mobile source vehicle emissions are many times smaller those from stationary coal and heavy oil combustion. Thus, the sampling artifact which dominated measurements from coal-fired utility boilers did not seem to affect measurements from mobile sources. Mobile source emissions levels established in the early and mid 1980's, before the artifact issue was brought to light, compare favorably with measurements made in later years by researchers who were well aware of the potential sampling problems and took care to avoid the sampling artifact. Table 6 presents a comparison of N_2O emission rates for several classes of vehicles.[108,109,110] Of particular note is the good agreement among the values reported by the three groups, and the fact that catalytically equipped vehicles emit up to 20 times more N_2O than comparable non-catalyst equipped vehicles.

Based on the results above, a conservative estimate of 62.1 mg N_2O/km (100 mg N_2O/mile), and the 1982 estimate for the U.S. vehicle fleet size (115×10^6) and distance traveled (2.6×10^{12} km, 1.6×10^{12} miles),[108] the total U.S. production of N_2O from mobile sources is approximately 1.6×10^5 metric tons/yr (1.6×10^{11} g N_2O/yr, 1.0×10^{11} g N/yr, or 0.1 Tg N/yr). Assuming that the world fleet size and distance driven per year are three times those of the U.S., then worldwide mobile N_2O emissions are approximately 0.3 Tg N/yr. This value compares favorably with the values given in

Table 3 and constitutes approximately 8.5% of the total anthropogenic flux. However, in addition to the uncertainties regarding fleet size and distance driven used in the analysis above, many research issues remain including the applicability of different driving cycles to actual use, engine/emission control malfunction or non-optimal operation, quantification of the number of vehicles that use catalysts (including type of catalyst), and the influence of ambient conditions.

EMISSIONS FROM INDUSTRIAL SOURCES

Few industrial sources have been identified as potential emitters of significant N_2O. One receiving recent attention is the manufacture of adipic acid, used primarily in the manufacture of nylon. By one report[111] the manufacture of adipic acid accounts for about 10% of the anthropogenic flux to the troposphere, based on adipic acid production. This inventory failed to take into account existing abatement within the industry, and an improved estimate is 5-8% of the anthropogenic flux.[112]

Adipic acid is formed by the reaction of cyclohexanone and cyclohexanol under nitric acid oxidation. The reaction produces an off-gas that contains 1 mole of N_2O byproduct for each mole of adipic acid produced, along with some NO_x. This stream, which can contain 30-50 mole % N_2O, is usually passed through an absorber to recover the NO_x, and then vented to the atmosphere. Some plants incinerate the stream in process boilers to reduce the NO_x, which coincidentally destroys the N_2O. In 1990, approximately 32% of the off-gas streams were abated in this manner.[112]

Since the recognition of adipic acid as a significant atmospheric source of N_2O, the industry has launched several cooperative projects to evaluate abatement options.[112] Some of these options have the goal of simply eliminating the N_2O from the exhaust stream at the lowest cost. Others focus on converting the N_2O into NO_x, which can then be used as a nitric acid feedstock. Approaches currently under evaluation include:

- N_2O decomposition over a catalyst to yield N_2 or NO_x for byproduct recovery.
- High temperature N_2O thermal decomposition to yield NO_x as a recovered byproduct.
- Thermal destruction in boilers.

It is recognized that no one technology is likely to be applicable to all plants because of site specific technical and economic factors.

Other industrial sources that involve the oxidation of nitrogen compounds under moderate temperature conditions are candidates as N_2O emitters. One example mentioned in the literature are catalytic cracker regenerators.[30] These units are used in gasoline manufacture to regenerate the catalyst used to crack feedstock after it has become coated with a nitrogen-rich coke. The coke is burned off the catalyst in a fluidized bed. Temperatures are moderate in the bed, fuel nitrogen levels are high, and the volatile content of the coke is low. Thus, many of the factors that contribute to high N_2O emissions in fluidized bed coal combustion are present. To date, however, no emissions measurements are reported.

CONCLUDING REMARKS

This review has attempted to bring together the widely scattered literature on the relatively new problem of N_2O emissions from energy conversion and industrial equipment, and the influence of these emissions on the environment. Some of these results are summarized in Table 7.[18] This is still an evolving area, where changes in both quantitative and qualitative interpretations are likely. Far from being the last word, this paper will likely act only as a starting point for future work.

Within homogeneous chemistry, the principal issues include the products of the NCO + NO reaction, and the rates and products of the reactions consuming HCN and HNCO that give rise to NCO and other species in moderate temperature combustion. A significant amount of modeling effort has used rates for NCO + NO that are likely too high. Thus, the adequacy of homogeneous chemistry to explain N_2O yields in processes such as combustion fluidized beds and in selective non-catalytic reduction needs to be revisited.

A considerable amount of effort has gone into defining the influence of basic operating parameters on N_2O emissions from fluidized beds. While basic operating trends are now known, a clear mechanistic understanding is not yet complete. The relative roles of homogeneous vs. heterogeneous N_2O production are shrouded by the fact that char behavior is strongly dependent on the degree of devolatilization. Since fluidized beds contain chars of widely varying ages, the overall behavior represents an ensemble average. This has clearly complicated the task of identifying mechanistic information from actual fluidized bed data. Well defined mechanistic experiments are needed, and these have begun to appear. Particularly useful studies include the examination of simulated differential fluidized bed elements. Another approach is to characterize bed response to perturbations in the gas-phase environment (*e.g.*, the addition of N_2O or HCN into the feed air), or in the solid phase (*e.g.*, the spiking of a well characterized char into a combustor).

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Table 1. Summary of key greenhouse gases (adapted from Ramanathan[1], Levine[2], and Houghton *et al.*[3])[*]

	CO_2	CH_4	Refrigerant-11 CCl_3F	Refrigerant-12 CCl_2F_2	CH_3CCl_3	CCl_4	N_2O
Pre-industrial atmospheric conc. (1750-1800)	275-280 ppm	0.7-0.8 ppm	0	0	0	0	285-288 ppb
Approx. current atmospheric conc. (1985-1990)[†]	345-353 ppm	1.72 ppm	220-280 ppt	380-484 ppt	130 ppt	120 ppt	304-310 ppb
Current rate of annual atmospheric accumulation	1.8 ppm (+0.46-0.5%)	0.015 ppm (+0.9-1.1%)	9.5 ppt (+4.0-10.3%)	17 ppt (+4-10.1%)	- +15.5%	- +2.4%	0.8 ppb (+0.25-0.35%)
Projected atmospheric conc. mid 21st century[‡]	400-600 ppm	2.1-4.0 ppm	700-3000 ppt	2000-4800 ppt	-	-	350-450 ppb
Atmospheric lifetime[§]	50-200 yr	10 yr	65 yr	130 yr	-	-	150 yr

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[*] % = percent by volume, ppm = parts per million by volume, ppb = parts per billion (10^9) by volume, ppt = parts per trillion (10^{12}) by volume.

[†] 1990 concentrations are based on extrapolation of measurements reported for earlier years.

[‡] Mid 21st century concentrations are based on current annual rate of atmospheric accumulation, and do not consider activities aimed at reducing emissions.

[§] Atmospheric lifetime is the ratio of atmospheric content to the total rate of removal. CO_2 lifetime is a rough indication of the time necessary for CO_2 concentrations to adjust to changes in emissions.

Table 2. Selected trace gases, and trace nitrogen species in the atmosphere (adapted from Levine[2,7]).

Major gases	Concentration[*]
Nitrogen (N_2)	78.08 %
Oxygen (O_2)	20.95%
Argon (Ar)	0.93%
Selected trace gases	**Concentration**
Water (H_2O)	0 to 2%
Carbon dioxide (CO_2)	353 ppm
Ozone (O_3)	
Tropospheric	0.02 to 0.1 ppm
Stratospheric	0.1 to 10 ppm
Methane (CH_4)	1.72 ppm
Refrigerant-12 (CCl_2F_2)	0.48 ppb
Refrigerant-11 (CCl_3F)	0.28 ppb
Hydroxyl (OH)	
Tropospheric	0.15 ppt
Stratospheric	0.02 to 0.3 ppt
Trace nitrogen species	**Concentration**
Nitrous oxide (N_2O)	310 ppb
Ammonia (NH_3)	0.1 to 1.0 ppb
Nitric oxide (NO)[†]	
Tropospheric	0 to 1 ppb
Stratospheric	up to 0.02 ppm
Nitric acid (HNO_3)	50 to 1000 ppt
Hydrogen cyanide (HCN)	200 ppt
Nitrogen dioxide (NO_2)	10 to 300 ppt
Nitrogen trioxide (NO_3)[‡]	100 ppt
Peroxyacetyl nitrate ($CH_3CO_3NO_2$)	50 ppt
Dinitrogen pentoxide (N_2O_5)[‡]	1 ppt
Pernitric acid (HO_2NO_2)[†]	0.5 ppt
Nitrous acid (HNO_2)	0.1 ppt
Nitrogen aerosols	
Ammonium nitrate (NH_4NO_3)	10 ppt
Ammonium chloride (NH_4Cl)	0.1 ppt

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[*] % = percent by volume, ppm = parts per million by volume, ppb = parts per billion (10^9) by volume, ppt = parts per trillion (10^{12}) by volume.

[†] Exhibits strong diurnal variation with maximum concentration during the day.

[‡] Exhibits strong diurnal variation with maximum concentration during the night.

Table 3. Estimates of global sources of N_2O (Tg N per year).[*]

	de Soete[18†]	Levine[2]	IPCC[19,20]	Elkins[22] and Mann *et al.*[23‡]	Khalil and Rasmussen[12]
		NATURAL SOURCES			
Soils					7.6
Tropical soils		3.7		3.7	
wet forests			2.2-3.7		
dry savannas			0.5-2.0		
Temperate soils		0.01-1.5		< 0.5	
forests			0.05-2.0		
grasslands			NK[§]		
Oceans		1.4-2.6	1.4-2.6	1.4-2.6	1.9
Total natural sources		5.1-7.8	4.2-10.3	5.6-6.8	9.5
		ANTHROPOGENIC SOURCES			
Biomass burning	0.5 (0.4-0.6)	0.1-1.0	0.2-1.0	0.02-0.29	1.0 (0.1-1.9)
Sewage					1.0 (0.2-2.0)
Agriculture					
Cattle operations					0.3 (0.2-0.6)
Irrigation (ground water release)				0.5-1.1	0.5 (0.5-1.3)
Use of nitrogen fertilizers	1.0 (0.7-1.3)		0.01-2.2	0.015-1.4	0.6 (0.3-1.9)
on agricultural fields		0.01-1.1			
leaching into groundwater		0.5-1.1			
Land use changes (deforestation)		0.8-1.3		0.8-1.3	0.4
Fossil fuel combustion		0.1-0.3		< 0.5	
Stationary sources	0.2 (0.1-0.3)		0.1-0.3		0.0 (0.0-0.1)
Mobile sources	0.4 (0.2-0.6)		0.2-0.6		0.5 (0.1-1.3)
Industrial activities					
Adipic acid (nylon)			0.4-0.6		NK
Nitric acid			0.1-0.3		
Global warming					0.2 (0.0-0.6)
Atmospheric formation (indirect)	NK				NK
Dry and wet deposition				0.13-5.0	
Total anthropogenic sources	2.1 (1.4-2.8)	1.5-4.8	1.0-5.0	2.0-9.6	4.5 (1.8-9.7)
Total	2.1 (1.4-2.8)	6.6-12.6	5.2-15.3	7.6-16.4	14.0 (11.3-19.2)

[*] 1 Tg = 1 x 10^6 tonnes = 1 x 10^{12} g.

[†] Anthropogenic sources only.

[‡] Data presented in the review by Mann *et al.*[23] was taken from Elkins.[21]

[§] NK - not known.

Table 4. Survey of recent N_2O data from combustion systems.*

Andersson *et al.*†	Several European plants
Dahlberg *et al.*†	17 combustion plants
Electric Power Research Institute†	14 utilities
Laird and Sloan[58]	3 corner-fired, 2 opposed-fired (1 low-NO_x) 3 wall-fired coal, 3 wall-fired oil (2 low-NO_x)
Linak *et al.*[32]	6 coal-fired
Muzio *et al.*[47]	2 oil-fired 7 coal-fired
Persson[59]	1 coal-fired
Sage[60]	2 stokers
Sloan and Laird[57]	4 wall-fired, 3 corner-fired, both normal burners and low-NO_x burners
Soelberg[61]	11 plants
Vitovec and Hackl[50]	9 coal-fired plants, including pulverized coal, lignite, stoker-firing, and briquettes 11 oil-fired plants 4 petroleum-coke plants
Yokoyama *et al.*[51,54]	7 coal-fired 21 oil-fired

*Pulverized-coal fired unless otherwise indicated.

†As reported in Mann *et al.*[23]

Table 5. Summary of field data for combustion fluidized beds.

Åmand and Leckner[63] Åmand *et al.*[62,64]	One 8 and one 12 MW CFB. Detailed parametric variations of excess air, lime addition, and char loading.
Braun *et al.*[65]	One 4 MW_T AFBC used for plant heating. Examined influence of bed temperature, fuel-type, and NO_x control strategies.
Brown and Muzio[66]	One AFBC and one CFBC were examined in detail. Variations included bed temperature, excess air, and sorbent feed. Also more limited parametric variations at three cogeneration CFBC sites.
Gustavsson and Leckner[67]	Examined gas injection for N_2O control at a 12 MW_T CFBC. Emissions range from 80 to 250 ppm as a function of temperature. Examined a number of parameters.
Hiltunen *et al.*[68]	Measurements from 8 CFBCs. Results correlated in terms of mean furnace temperature and fuel type. Emissions range from 10 to 140 ppm.
Muzio *et al.*[47]	Three CFBCs with N_2O ranging from 26 to 84 ppm at 3% O_2. One unit at 3 loads: 55, 75, 100% of full load, yielding 126, 93, 84 ppm N_2O, respectively.
Persson[59]	One 15 MW PFBC and one 40 MW CFB. Varied bed temperature in the larger unit and looked at NO_x control agents.
Ryan and Srivastava[49]	Summary of Third International N_2O Workshop; data presented on 4 Swedish units and 6 Finnish units.
Sage[60*]	Two AFBC's: 30, 22-77 ppm; one CFBC: 91 ppm.
Vitovec and Hackl[50*]	Austrian measurements. Four CFBC's, three AFBC's. CFBC results showed strong dependence on fuel type: bituminous coal = 24, lignite = 7.5, bark/sewage sludge/bituminous coal = 3.3, bark/sewage sludge = 0.8 ppm.

[*] Converted from mg/m^3 to ppm.

Table 6. Mobile source N_2O emission rates. (mg N_2O/km).

	Sigsby[108†]	Prigent and de Soete[109]	Dasch[110]
Non-catalyst auto	3.1-3.7 (5-6)*	2.9 (4.8)	1.5-3.0 (2.4-4.8)
Catalyst auto	4.3-85.1 (7-137)	9.3-62.1 (15-100) oxidation or 3-way cat.	1.9-41.0 (3-66) oxidation cat. 16.2-59.0 (26-95) dual bed cat. 8.1-62.8 (13-101) 3-way cat.
Diesel trucks/buses	19.3-91.3 (31-147)		
Gasoline trucks	29.8-60.3 (48-97)		55.3 (89) light duty, 3-way cat.

[*] Numbers in parentheses have units of mg N_2O/mi.

[†] Compilation of test data from several sources.

Table 7. N_2O emission from fossil fuel combustion (adapted from de Soete[18]).

Uncontrolled combustion	N_2O emissions
Conventional stationary combustion (coal, oil, gas)	1-5 ppm
Fluidized bed combustion (depends on temperature, oxygen conc., physical/chemical properties of fuel)	20-150 ppm
Diesel engines (value given for small passenger cars; heavy duty engine emissions may be higher)	0.03 g N per km
Gasoline engines	0.01-0.03 g N per km

NO_x control technology	Effect on N_2O emissions
Fuel staging for conventional stationary combustion	Up to 10 ppmv increase over uncontrolled combustion
Thermal $DeNO_x$ controls (SNCR)	
NH_3 injection	3-5% of NO_x reduction converted to N_2O
Urea or cyanuric acid injection	10-15% of NO_x reduction converted to N_2O
Catalytic processes	
Selective catalytic reduction (SCR)	Limited laboratory studies indicate increased emissions from some catalysts. No field data available.
3-way catalysts (gasoline engines)	
New catalysts	3-5 times the uncontrolled emissions
Medium aged catalysts	10-16 times the uncontrolled emissions