

Nitrous Oxide Emissions From Fossil Fuel Combustion

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The role of coal combustion as a significant global source of nitrous oxide (N_2O) emissions was re-examined through on-line emission measurements from six pulverized-coal-fired utility boilers and from laboratory and pilot-scale combustors. The full-scale utility boilers yielded direct N_2O emission levels of less than 5 ppm. The sub-scale combustor test data were consistent with full-scale data, and also showed N_2O emission levels not exceeding 5 ppm, although these levels increased slightly when various combustion modifications to lower NO emissions were employed. These on-line emission measurements are very different from previously published data. The discrepancy is shown to be due to a sampling artifact by which significant quantities of N_2O can be produced in sample containers which have been used in establishing the previously employed N_2O data base. Consequently, we conclude that N_2O emissions bear no direct relationship to NO emissions from these combustion sources, and that this direct source of N_2O is negligible. Other indirect routes for the conversion of NO into N_2O outside the combustor and other combustion sources not examined by this study, however, cannot be ruled out.

INTRODUCTION

The atmospheric concentration of nitrous oxide (N_2O) is reported to be increasing at a rate of between 0.18 and 0.26 percent per year [Weiss, 1981; Khalil and Rasmussen, 1983]. This is a matter of concern because N_2O has been implicated as both a "greenhouse" gas and a reactant in stratospheric ozone depletion mechanisms. Fossil fuel combustion has been proposed as being the major contributor to the measured increases in ambient N_2O concentrations, as these increases seem to track measured increases in ambient CO_2 concentrations. Furthermore, Hao *et al.* [1987] presented data of direct N_2O emissions from fossil fuel combustion, indicating stack emissions exceeding 100 ppm N_2O , and an approximate average N_2O -N: NO_x molar ratio of 0.58:1. From these data, Hao *et al.* confirmed earlier suggestions [Pierotti and Rasmussen, 1976; Weiss and Craig, 1976] that combustion of fossil fuels represents a dominant factor in the observed increase of N_2O and that, consequently, combustion related sources of N_2O increased rapidly during the twentieth century, in parallel with the volume of coal being burned. Using their $\text{N}_2\text{O}/\text{NO}_x$ emission ratio and future projections of coal usage, these authors were then able to project a 20 percent increase in atmospheric N_2O concentrations by the year 2050. This corresponds to a 367 ppb atmospheric concentration by the year 2050 from its 1987 level of

approximately 303 ppb. They also suggested that deployment of low NO_x burners may offer a means to reduce anthropogenic emissions of N_2O in the future.

The N_2O emissions from fossil fuel combustion reported by Hao *et al.* [1987] can be put into perspective through an analysis of the anthropogenic N_2O flux. Weiss [1986] estimates the total anthropogenic N_2O flux to be approximately 1.4×10^{11} g-moles/yr (approximately 32 percent of the total flux). World energy usage (global market) in 1975 was estimated to be approximately 223.5 Quads (2.235×10^{17} Btu) [Kavanaugh, 1986]. By assuming that the fraction of the world energy derived from coal combustion is the same as that for the U.S. (approximately 21 percent) [Kavanaugh, 1986], and assuming the volumetric air requirements of a medium value bituminous coal and 20 percent excess air, then the necessary concentration of N_2O in the exhaust gases of all coal combustion sources to account for the entire anthropogenic flux is approximately 175 ppm. Comparison of this figure with the 100 ppm N_2O emission levels measured by Hao *et al.* [1987], strongly suggested coal combustion to be a dominant source of the global anthropogenic N_2O flux.

The argument that coal combustion might be a significant source of global N_2O emissions was further strengthened by the fundamental work of Kramlich *et al.* [1989], who showed that fuel nitrogen release from fossil fuels in the cooler portion of a combustor could result in significant quantities of N_2O in the exhaust gas. Martin and Brown [1987] reported similar N_2O increases at the quenched edges of laminar flames. Whether the appropriate conditions actually occur in full-scale coal combustors was not determined. Fundamental

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considerations, however, did not support the suggestion that a constant N₂O/NO_x molar ratio was applicable for coal combustion sources in general. The U.S. Environmental Protection Agency (EPA) initiated a research program to stimulate collaborative national and international research programs with industry, academia, and other government agencies to better characterize and understand the anthropogenic sources of N₂O. Partial results from these programs, which have been reported in the proceedings of three workshops sponsored by EPA [Lanier and Robinson, 1986; Kramlich *et al.*, 1988; Ryan and Srivastava, 1989], suggested the need to undertake additional combustion research to substantiate the N₂O emission data base on which so many of the previous conclusions relied. Results from portions of this investigation are presented here.

The present paper is concerned solely with a re-examination of the issues relating to the direct role of combustion sources on the observed global rise of N₂O in the atmosphere. Other anthropogenic sources or natural sources [Cofer *et al.*, 1988; Anderson *et al.*, 1988; Levine *et al.*, 1988] of N₂O are not discussed. Specifically, we address the following issues: how valid is the historical N₂O data base; how valid is the use of the N₂O/NO_x emission ratio, reported above; to what extent can apparent discrepancies between different sources of data be explained through a sampling artifact; and what is the potential impact of NO_x abatement procedures on N₂O emissions from combustion sources? These questions are addressed through the application of on-line N₂O measurement techniques to extracted flue gas samples from several full-scale pulverized-coal-fired utility boilers and from laboratory combustors burning pulverized coal, fuel oils, and natural gas. Furthermore, discrepancies between the on-line N₂O measurements and those constituting the historical data base are then examined in detail, and the relationship of these discrepancies to a sampling artifact which influenced the existing data base is explored. Results allow a reassessment of

the role of direct coal combustion N₂O emissions in the global N₂O budget. However, since secondary reactions converting NO to N₂O in the sample containers were found to occur at room temperature [Muzio and Kramlich, 1988; de Soete, 1988; Muzio *et al.*, 1989; Lyon and Cole, 1989; Lyon *et al.*, 1989], an indirect relationship between NO emissions and the global N₂O increase cannot be ruled out at this time, without further research in atmospheric conversion chemistry.

HISTORICAL DATA BASE

A summary of the N₂O data base from stationary fossil fuel combustion as presented by Hao *et al.* [1987] is presented in Figure 1. The open symbols represent data reported by that group from three studies [Castaldini *et al.*, 1982]. Shaded symbols represent preliminary on-line measurements taken by our group, using a laboratory-scale downfired coal combustor (2.3 kg/hr, 5 lb/hr) burning two western coals. Also included in Figure 1 is a line representing the proposed N₂O-N:NO_x molar ratio of 0.58:1 [Hao *et al.*, 1987]. Clearly, the significant discrepancies between these data sets cast doubt both on an N₂O emission factor that was proportional to NO_x emissions from fossil fuel combustors, and on its use to estimate the global flux of N₂O resulting from this source.

Additional data gathered by a number of research groups using various on-line and container sampling methods served only to increase the scatter. An explanation for this scatter was presented at the third N₂O workshop (June 1988) [Ryan and Srivastava, 1989], when data presented by one research group suggested the presence of an N₂O sampling artifact [Muzio and Kramlich, 1988]. They presented evidence that indicated that N₂O might be produced in sampling containers awaiting analysis. They further hypothesized a mechanism of this formation involving NO, SO₂, and water. This evidence questioned the validity of all existing data which involved container sampling.

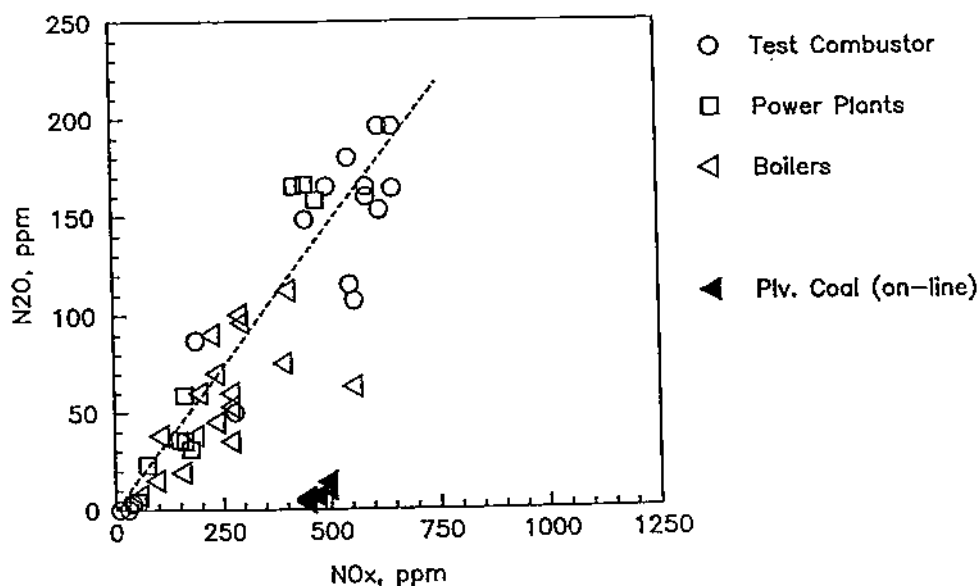


Fig. 1. Historical N₂O/NO_x data base. Open symbols represent the data presented by Hao *et al.* [1987]. Shaded symbols represent preliminary data taken by this group burning two western coals in a laboratory-scale combustor using an on-line GC/ECD sampling/analysis technique. The dashed line represents a proposed N₂O-N:NO_x molar ratio of 0.58:1 [Hao *et al.*, 1987].

As a consequence of these new developments the EPA, through its Air and Energy Engineering Research Laboratory (AEERL), renewed efforts to characterize, by on-line means, direct N₂O emissions from several laboratory and pilot-scale combustion systems burning a variety of coals, fuel oils, and natural gas. Additionally, we sought to compare the results from these sub-scale systems to direct N₂O measurements (by on-line techniques) from full-scale pulverized-coal-fired utility boilers. Furthermore, in order to reconcile the apparent discrepancies between old and new data in terms of the sampling artifact reported by Muzio and Kramlich [1988], we also characterized the time dependent evolution of N₂O, NO, and SO₂ in container samples of various moisture contents.

ON-LINE MEASUREMENTS

Laboratory and Pilot-Scale Experiments

Three EPA combustion systems that were used for the sub-scale experiments included a 29 kW (100,000 Btu/hr) refractory-lined, downfired, coal-fired tunnel combustor (Downfired Tunnel Furnace), a 733 kW (2,500,000 Btu/hr) gas/oil-fired, firetube package boiler (North American Boiler), and an 588 kW (2,000,000 Btu/hr) gas/oil-fired, watertube package boiler simulator equipped with a precombustion-chamber low NO_x burner (Low NO_x Burner/Package Boiler Simulator). Details regarding the specific designs of these systems have been presented elsewhere [Snow and Lorrain, 1987; Pershing et al., 1973; Mulholland and Srivastava, 1988].

Although several analytical techniques in addition to gas chromatography with electron capture detection (GC/ECD) are applicable to on-line N₂O analysis from combustion sources [Lanier and Robinson, 1986; Roby and Bowman, 1987; Muzio et al., 1989; Montgomery et al., 1989], most involve extractive sampling. The sampling system used at this laboratory included extractive sampling through a stainless steel sampling probe, 0.64 cm (0.25 in.) outside diameter (O.D.) heated Teflon tubing and heated filter, water removal by use of a refrigeration drying system, and then pumping by means of a Teflon diaphragm sample pump through calcium sulfate (CaSO₄) desiccant to continuous emission monitors (CEMs). CEMs included measurement of O₂, CO, CO₂, SO₂, and NO. Immediately after the sample pump, but before desiccation, a portion of the sample was directed to a 1 ml/six port GC sampling valve for on-line N₂O analysis by GC/ECD (Shimadzu Model GC-9A). SO₂ was measured from a heated sample taken downstream of the filter and upstream of the refrigeration dryer. The GC used to quantify N₂O utilized 5 percent methane in argon carrier gas at a flow rate of 20 ml/min., a 3.8 cm (1.5 in.) long by 0.64 cm (0.25 in.) O.D. P₂O₅ precolumn, a 3.66 m (12 ft) long by 0.32 cm (0.125 in.) O.D. stainless steel Poropak Super Q column (100/120 mesh) at 35°C, and a Ni⁶³ ECD maintained at 330°C.

Even though this configuration produced N₂O peaks distinctly separated from CO₂, considerable effort was made to characterize possible interferences due to co-elution. Tests were conducted with a multicomponent gas standard using the Poropak Super Q column where CO₂ elutes before N₂O and a molecular sieve 5A column where CO₂ elutes after N₂O. Comparison of the N₂O concentrations measured showed no significant differences.

To account for the non-linear properties of the ECD, multipoint calibrations were performed with N₂O standards ranging in concentration from 0.24 to 200 ppm. All calibration gases used nitrogen as the balance constituent. No column backflushing was employed and no column memory or sensitivity problems were observed during the sub-scale experiments. Laboratory conditions allowed the time to achieve very stable ECD operation, limited the number of analyses per day, and permitted sufficient column conditioning. Laboratory analyses were consistently capable of detecting ambient N₂O concentrations with minimum detection limits of 0.24 ppm (based on minimum calibration gas concentration). Method accuracy, expressed as percent deviation, was within 15 percent. Method precision, expressed as percent relative standard deviation, was within 10 percent. N₂O standards sent through the sampling system compared with those sent directly through the sampling loop, demonstrating insignificant sampling system bias.

In contrast to the laboratory measurements, column memory and sensitivity problems were observed during the field tests. Memory problems were overcome through the use of multiple instruments. While one system was being used for data collection, others were undergoing column conditioning. Due to the time constraints of field testing, and the necessity to relocate the instrumentation to a new site every several days, some instrument sensitivity was sacrificed. Sufficient time was not allowed to achieve extremely stable baseline ECD operation. However, this loss of sensitivity was deemed acceptable because the scope of these tests were to determine the relative magnitude of direct N₂O emissions from full-scale units compared to both the sub-scale experiments and historical data. Field detection limits were consistently below 5 ppm with two tests below 1 ppm. Accuracy and precision were the same as for the sub-scale tests.

Table 1 presents the combustion conditions and average on-line N₂O and CEM data for 13 EPA tests involving the three combustion units and seven fuels including four types of coal. All samples were taken from stack locations. Data in Table 1 indicate that the direct N₂O emissions from all tests never exceeded 5 ppm. The coal tests showed the highest levels (2 to 4 ppm), with several natural gas and No. 2 fuel oil data sets indicating N₂O concentrations less than 0.24 ppm. Little difference could be discerned between the two fuel oil and natural gas tests. Data from the Low NO_x Burner/Package Boiler Simulator, with and without air staging for NO_x control, showed that, while significant NO reduction was seen with air staging, no measureable effect was detected in N₂O concentrations. These N₂O data, however, are too close to the instrument detection limit for accurate comparison. The other CEM measurements are similar to those typical of full-scale units. Sulfur contents of the four coals examined ranged from 0.97 to 2.95 weight percent as received.

Independent experimental work on N₂O emissions from laboratory-scale coal combustors has also been completed at the University of Arizona (UA) under the sponsorship of the U.S. Department of Energy (DOE). The downfired laboratory combustor used in that work was very similar in size and design to that described above for the EPA tests, except that the pulverized coal flame was "premixed," and the overall configuration resembled a plug flow reactor. Sampling and analysis for N₂O was also developed and tested independently. Here the flue gas sample to be analyzed was withdrawn through

TABLE 1. Average On-Line Concentrations Taken From Laboratory and Pilot-Scale Combustion Systems

Unit	Fuel	SR ^a	N ₂ O, ppm	NO, ppm	SO ₂ , ppm	CO, ppm	O ₂ , %	CO ₂ , %
DF Tunnel Furnace ^b	Utah bit. coal	1.42	4.2	757	753	17	5.5	13.9
	Montana sub-bit. coal	1.43	2.2	613	380	30	5.3	14.6
	W. Kentucky bit. coal	1.46	3.7	553	1650	12	6.8	12.6
	Pittsburgh bit. coal	1.33	2.2	570	1450	^c	5.7	12.9
NA Boiler ^d	Natural gas	1.24	<0.24	62	0	0	4.4	8.9
	#2 Fuel oil	1.25	0.30	105	58	3	4.4	12.3
	#5 Fuel oil	1.25	1.3	189	236	16	4.4	14.1
	Natural gas	0.73/1.25	<0.24	50	6	11	4.6	9.2
LNB/PBS ^e	Natural gas	1.10/1.25	0.72	638	4	14	4.6	8.7
	#2 Fuel oil	0.65/1.26	<0.24	64	130	2	6.1	12.0
	#2 Fuel oil	1.13/1.26	0.27	536	130	2	6.0	12.0
	#5 Fuel oil	0.66/1.29	0.26	60	270	25	5.4	12.2
	#5 Fuel oil	1.10/1.18	0.73	682	270	25	4.1	11.0
	#5 Fuel oil	1.10/1.18	0.73	682	270	25	4.1	11.0
UA Coal Furnace ^f	Utah bit. coal	1.25	1.28	1121	-	-	4.25	14.0
	Utah bit. coal	0.65/1.08	1.99	605	-	-	3.60	14.3
	Utah bit. coal	0.86/1.08	3.80	216	-	-	3.50	14.8
	Utah bit. coal	1.10/0.90/1.06	4.45	382	-	-	3.85	13.8

Concentrations presented as measured, dry (SO₂ wet) no correction to constant percent O₂.

^a Stoichiometric ratio.

^b Downfired Tunnel Furnace.

^c Missing data.

^d North American Boiler.

^e Low NO_x Burner/Package Boiler Simulator.

^f University of Arizona Coal Furnace (corrected to 0 percent O₂ dry).

a water-cooled, water-quenched probe. The water was removed in a refrigerated knockout pot, and N₂O analysis was by GC/ECD. The latter consisted of a 1 ml sampling loop, a 3.66 m (12 ft) long by 0.32 cm (0.125 in.) O.D. Poropak Q column in stainless steel, at 35°C, and 20 ml/min. of argon/5.22 percent methane carrier gas. The column was periodically reconditioned at a temperature of 220°C. The detector temperature of 250°C led to somewhat decreased sensitivity towards N₂O but was chosen to extend the life of the ECD in the presence of oxygen in the flue gas. The detection limit for N₂O was 0.1 ppm, but the response was not linear over the entire 0 to 95 ppm range. Precision was within 2 percent of the mean. There was excellent separation between CO₂ and N₂O, and no measurable interferences by CO₂, water vapor, or oxygen. Calibrations were conducted before and after each test run. Backflushing of the column was not found to be necessary, although here the time interval between two samples was about 1.5 hours. In general, the calibration held to within 3 percent of the reference standards over five days of testing, and column memory effects were not noticed.

Figure 2a shows values of exhaust NO and N₂O emissions as a function of stoichiometric ratio for a Utah bituminous coal. N₂O levels in Figure 2a vary from 0.5 to 1.5 ppm. Residence time resolved profiles during air staging are shown on Figures 2b (primary SR=0.86) and 2c (primary SR=0.65), and demonstrate the interesting fact that staging causes an increase in N₂O near the staging point. However, N₂O levels are still exceedingly low and so the effect is not of practical significance. Air staging is a combustion modification used for NO_x control whereby a portion of the air necessary for combustion is diverted to a location downstream of the primary flame. This configuration produces an initial fuel rich zone which promotes fuel nitrogen conversion to N₂. The remaining air is then added to complete the combustion

process. Figure 2d shows residence time resolved NO and N₂O profiles along the combustor axis while using reburning as a NO_x control technique. Reburning (or fuel staging) is another combustion modification used for NO_x control whereby portions of both fuel and air are diverted to locations downstream of the primary flame. Under this configuration, three zones of different stoichiometry are established and adjusted to minimize NO_x formation. We observed an increase of N₂O at the point of air injection, similar to that observed under air staged conditions. For all configurations, however, these on-line measurements of N₂O yielded extremely low values, and indicated that direct N₂O emissions (from pulverized coal combustion) did not appear to be large, either with or without combustion modifications for NO_x control.

Field Tests

Following the laboratory and pilot-scale experiments, EPA sponsored a field study to characterize the direct emissions of N₂O from full-scale, pulverized-coal-fired utility boilers. These measurements were conducted at six boilers ranging in size from 165 to 700 MW, including Circular, Triple Cell, and Tangential designs manufactured by Babcock & Wilcox, Riley Stoker, and Combustion Engineering. These units represent a cross-section of the types of boilers currently, and historically since 1950, in use in the U.S., and burned primarily a medium sulfur Alabama bituminous coal, with a reported sulfur content between 1.5 to 2.0 percent. The sampling and analytical methods used were similar to those described above for the EPA sub-scale experiments. Table 2 presents the average on-line N₂O and CEM data for each of the six utility units. All on-line N₂O measurements were below 5 ppm. In fact, almost all of the on-line N₂O measurements were below the detection limits of the GC/ECD systems used for these field tests. These samples

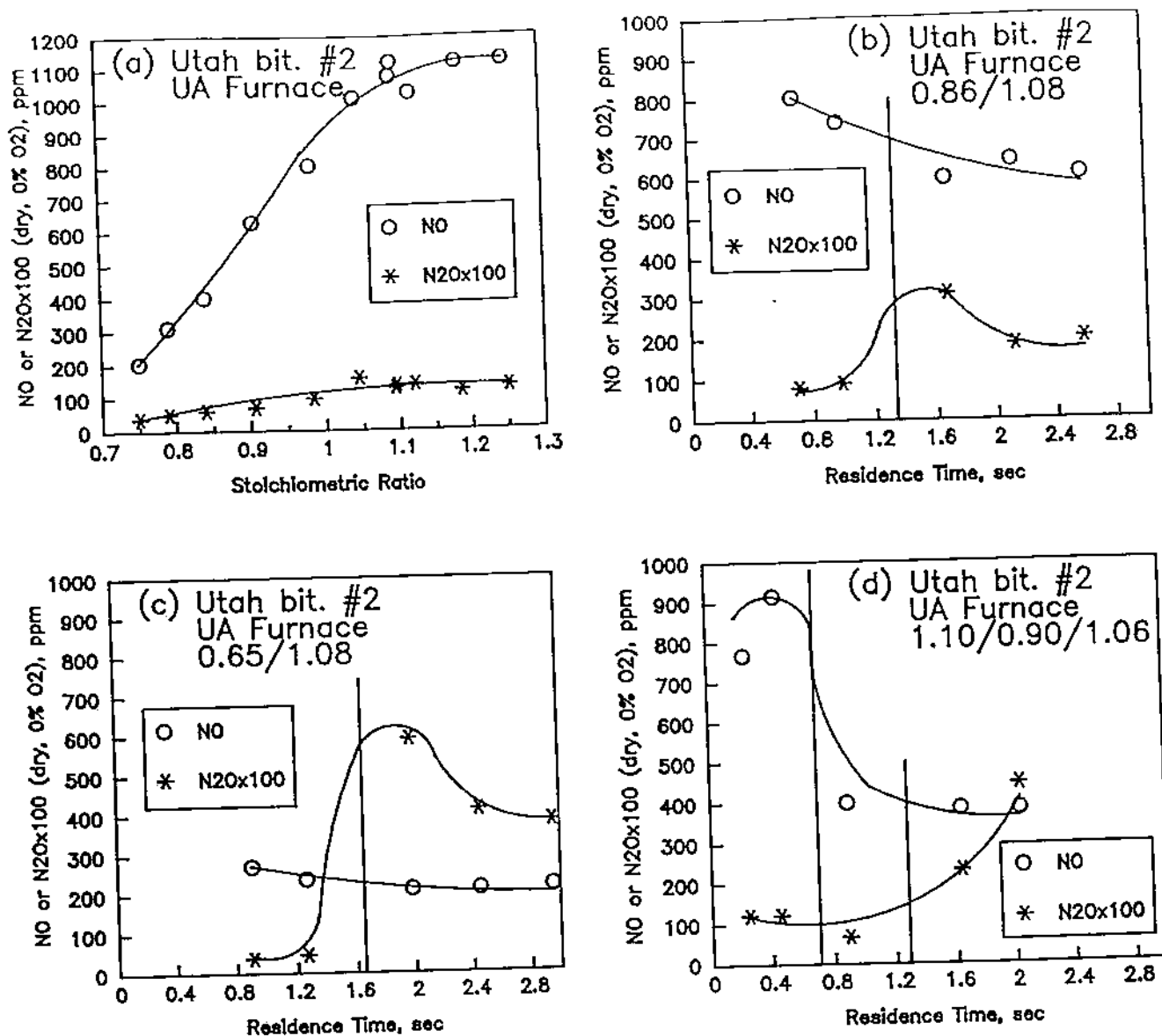


Fig. 2. NO and N_2O concentrations from a laboratory-scale coal combustor as a function of (a) stoichiometric ratio (at combustor exhaust), and residence time using air staging (b) $\text{SR}=0.86/1.08$, (c) $\text{SR}=0.65/1.08$, and natural gas reburning (d) $\text{SR}=1.10/0.90/1.06$ strategies for NO_x control.

were taken at existing sampling locations, downstream of all economizer and particulate removal equipment, either before or after the systems' induced draft fans. All six units were operated at or near full load during the tests. Limited SO_2 data were collected due to problems with the SO_2 analyzer.

A summary of the on-line data from both the sub-scale and full-scale studies is presented in Figure 3. Again, these data (indicated by the shaded symbols) are compared to the data base presented by Hao *et al.* [1987] (open symbols). These results suggest that the direct emission of N_2O from pulverized-coal-fired utility boilers is very low (less than 5 ppm), that the existing data are suspect due to a sampling artifact [Muzio *et al.*, 1989], and that no simple $\text{N}_2\text{O}/\text{NO}_x$ correlation exists. In order to build a stronger case supporting the new on-line measurements against the previous sample container derived data, it was necessary to explore, in more detail, the sampling artifact that may have distorted the historical data base shown on Figure 1.

TIME RESOLVED N_2O MEASUREMENTS FROM SAMPLE CONTAINERS

Concurrent with all on-line activities, extracted samples were collected in stainless steel sampling containers for time dependent analyses of N_2O by GC/ECD, NO by GC/thermal conductivity detector (TCD), and SO_2 by GC/flame photometric detector (FPD) techniques. These samples were collected at three degrees of dryness including wet samples (before refrigeration drier), partially dried samples (immediately after refrigeration drier), and desiccated samples (after additional drying by use of a P_2O_5 filled canister). Samples from the sub-scale experiments were analyzed after 1, 4, 24, 48, 168, and 336 hours. Samples from the full-scale tests were analyzed after 1, 4, 48, 168, and 336 hours.

Samples for time resolved analyses were collected in 0.5 L stainless steel (304) containers. These containers were fitted with stainless steel needle valves at each end and one septum

TABLE 2. Average On-Line Concentrations Taken From Full-Scale Utility Boilers

Unit	Size, MW	Class/Type ^a	Manufacturer	N ₂ O, ppm	NO, ppm	SO ₂ , ppm	CO, ppm	O ₂ , %	CO ₂ , %
A	250	Pre-NSPS/Circular	Babcock & Wilcox	1.3	386	- ^b	-	4.6	14.8
B	250	Pre-NSPS/Tripole Cell	Babcock & Wilcox	<3.6	513	-	13.3	7.1	13.5
C	250	Pre-NSPS/Circular	Riley Stoker	<3.6	559	-	8.6	6.1	14.3
D	165	Pre-NSPS/Tangential	Combustion Engineering	<1.2	354	-	2.2	8.3	11.7
E	700	Pre-NSPS/Tangential	Combustion Engineering	0.7	374	-	30.7 ^c	6.0	13.1
F	165	Pre-NSPS/Tangential	Combustion Engineering	<1.2	319	930	3.1	8.1	11.9

Concentrations presented as measured, dry (SO₂ wet), no correction to constant percent O₂.

^a All units burned a medium sulfur Alabama bituminous coal.

^b Missing data.

^c CO trace showed numerous spikes.

fitting for sample extraction by gas syringe. Since we realized that much of the historical data was based on glass containers, a number of samples were collected in glass containers of similar size for comparison. While the available data for this comparison are limited, the behavior of the sample in the glass containers was similar to that in the stainless steel containers, except as noted below. The stainless steel containers were rinsed with de-ionized water and dried overnight at 107°C (225°F). After cooling, each container was fitted with a septum and then leak tested to 40 mm Hg. Following the leak check, the valves were closed and ends capped. The container interiors were not polished or treated with any coating. Combustion gas and N₂O calibration gas (10 ppm) samples of varying moisture content were passed through beds of different desiccants and analyzed to determine any effect of selective water removal on N₂O. Three desiccants were tested including phosphorus pentoxide (P₂O₅), magnesium perchlorate [Mg(ClO₄)₂], and silica gel (SiO₂). None of these desiccants was seen to affect the N₂O concentration. P₂O₅ was chosen as the desiccant of choice for these tests due to its greatest quantitative ability to remove water.

Figure 4 presents results of these time resolved analyses from sample containers containing effluent from selected laboratory and full-scale tests. Figure 4a (laboratory combustor) shows that N₂O is rapidly formed from an initial value of 4.2 ppm to a level approaching 200 ppm, when condensed water was present, to half that value when water was physically removed by a refrigerated knockout pot and to less than 30 ppm when the sample was desiccated. Data from glass containers showed similar asymptotes in N₂O, but a slower rate of increase at early analysis times. This observation is illustrated by comparing the N₂O concentrations as they evolve in the two container materials of samples taken from experiments burning a western Kentucky coal. In stainless steel, the refrigerated dried sample evolves from 3.7 ppm (on-line) to > 50 ppm within 4 hours. In glass, the evolution after 4 hours for a similar sample is only 24 ppm. In fact, concentrations approaching 50 ppm were not measured in the glass container until the analysis at 168 hours. Figure 4b shows that the rise of N₂O is accompanied by a drop in gaseous SO₂ in the sample container, indicating the importance of sulfur as well as of moisture, in this low temperature mechanism. Figure 4c presents similar N₂O evolution data for

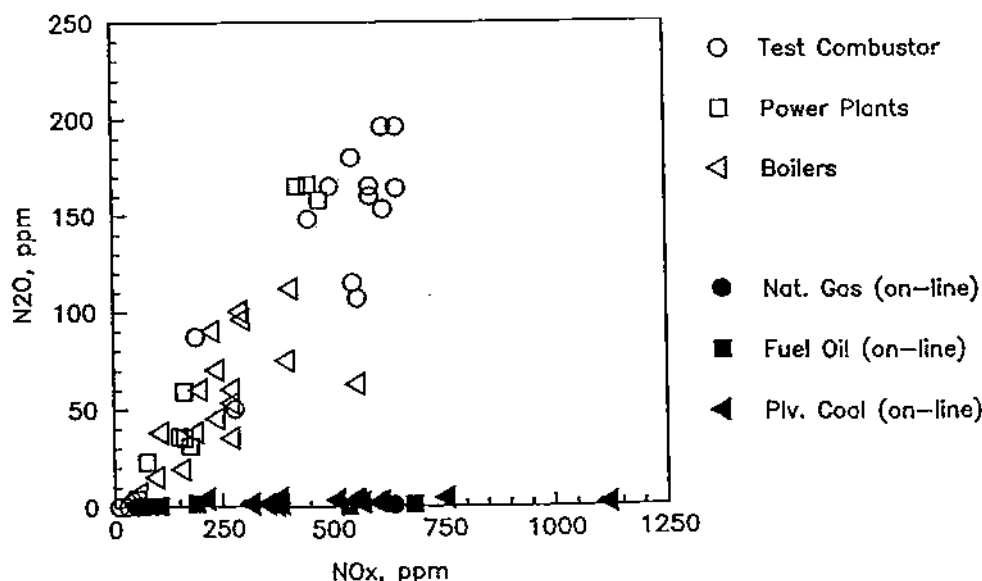


Fig. 3. Historical N₂O data base as presented in Figure 1, compared to on-line data taken by this group. Open symbols represent the data presented by Hao *et al.* [1987]. Shaded symbols represent data taken by this group from full- and sub-scale combustion systems burning several types of coals, fuel oils, and natural gas using an on-line GC/ECD sampling/analysis technique.

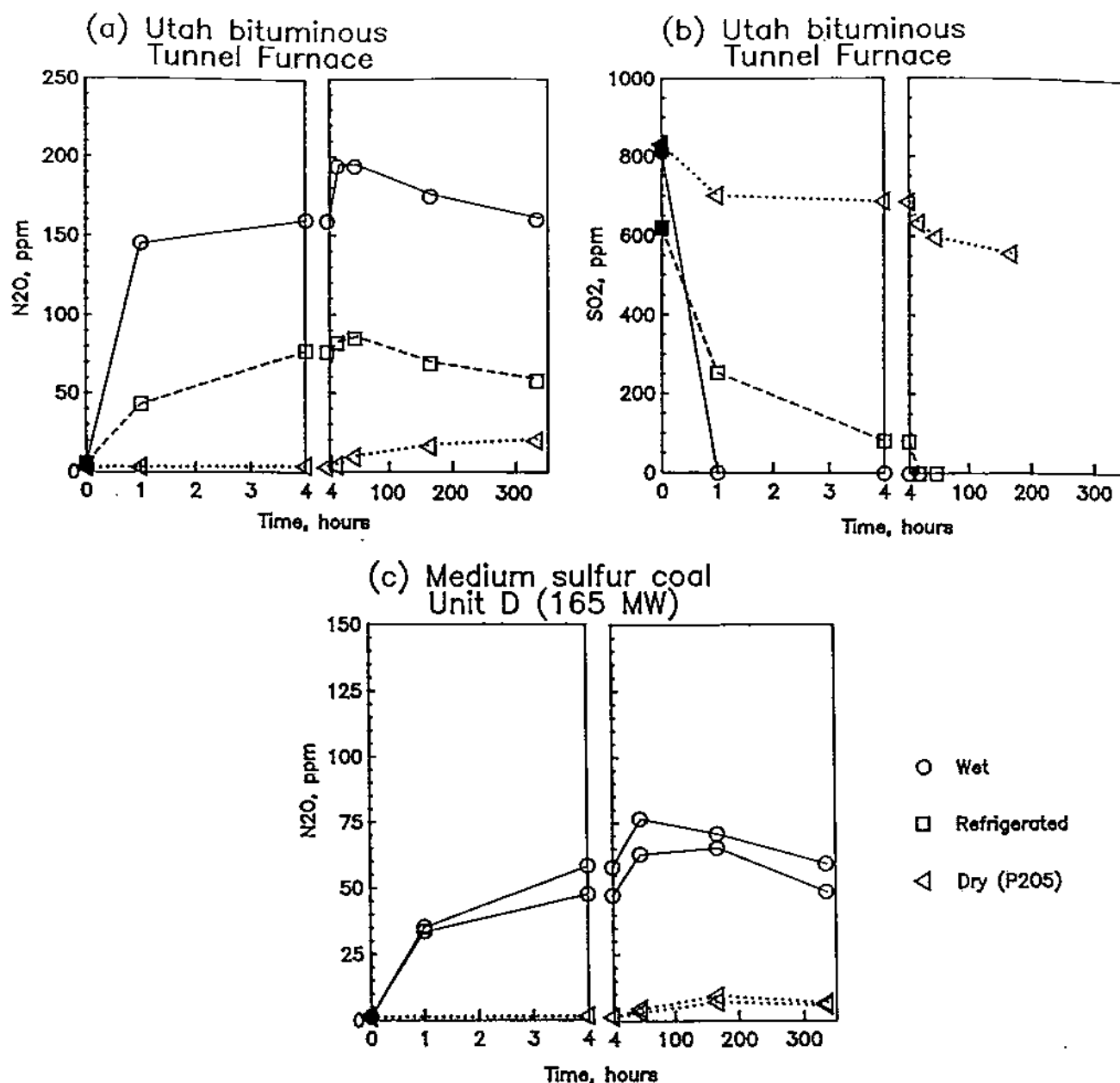


Fig. 4. Evolution of N₂O and SO₂ (vapor phase) with time from coal combustion: samples collected and stored in stainless steel sampling containers at three degrees of sample dryness. Stack emission samples were collected using the (a, b) Downfired Tunnel Furnace burning Utah bituminous coal (SR=1.42), NO(initial)=757 ppm, and (c) Unit D (full-scale utility boiler) burning medium sulfur Alabama bituminous coal, NO(initial)=354 ppm.

the full-scale coal-fired utility boiler tests from unit D. It is interesting to note that both the sub-scale and full-scale N₂O data from wet or partially dry samples show rapid increases in the first minutes and hours after sampling. The rate of production of N₂O was less in glass sample containers, although asymptotic levels, after long times, were similar. Smaller (but non-negligible) increases are seen in the dry samples. Maximum N₂O values from wet samples are seen after 24 hours. These values (200 and 75 ppm) are comparable to those presented by the historical data and the proposed N₂O-N: NO_x correlation (Figure 1). The maximum N₂O concentration is likely related to the initial NO and SO₂ concentrations. This speculation is supported by comparing the N₂O and initial NO and SO₂ data from these two tests (Tables 1 and 2). Figure 4b shows that the disappearance of

SO₂ seems to be very much dependent on the sample dryness. NO data (not presented) all show rapid removal/reaction (possibly forming NO₂) within 1 to 4 hours regardless of the moisture content of the samples. These results are consistent with the recent data of Muzio and Kramlich [1988] and de Soete [1988, 1989a, 1989b].

Similar data trends were obtained for No. 5 and No. 2 fuel oils burned in a standard firetube package boiler and a special research combustor designed to test NO_x abatement techniques. While the trends are similar to those seen for coal, the magnitude of the artifact is much less for the two fuel oils. These data are also consistent with the supposition that the resulting N₂O formation is dependent on the initial NO and SO₂ levels (in addition to the moisture). The N₂O increases seen in the Package Boiler Simulator samples (where NO_x control was

used) are significantly smaller than those seen in the North American Boiler samples (without NO_x control) burning the same fuels. Tests on natural gas combustion effluents indicated a measurable, albeit smaller, effect even though SO₂ values were below detectable (for our instrumentation) levels.

Figure 5 summarizes all the time resolved data and shows how the maximum yield of N₂O formed in the sample container (after approximately 48 hours) depends on the initial NO in the flue gas. We believe that the similarity with the historical data base shown in Figure 1 is not coincidental and that the previously accepted N₂O/NO_x emission ratio can be explained on the basis of this sample container artifact. The true N₂O emission levels, shown as shaded symbols, are independent of the initial NO and never exceed 5 ppm for combustion units tested.

CONCLUSIONS

The new N₂O emission data base from both field and laboratory combustion units indicated that direct N₂O emissions from conventional fossil fuel combustion units were very low, and would lead to a global N₂O flux that is lower by a factor of 50 to 100 than that inferred from previous work and that could account for less than 3 percent of the entire anthropogenic N₂O flux (less than the contribution from fertilizers [Hao *et al.*, 1987]). This has strong implications regarding the need, or lack of need, to control N₂O emissions from these combustion sources. Furthermore, in contrast to previous suggestions, our laboratory combustor data indicate that the most promising combustion modifications for NO_x control might actually lead to a small increase in N₂O emitted, although the net amount is still insignificant.

Discrepancies between these and previous data can be explained by a sampling artifact in which N₂O is produced from NO in the presence of SO₂ and water in sample containers. This artifact, which occurs at room temperatures, can easily lead to the erroneous conclusion (used in previous estimates of the global N₂O flux) that N₂O directly emitted from combustion equipment is significant and proportional to the NO emitted.

Our results do not extend to emerging coal combustion technologies, such as fluidized bed combustion, where significant emissions of N₂O (>100 ppm) have been observed by researchers who were aware of the sampling artifact [Amand and Andersson, 1989]. However, emerging technologies cannot explain the historical parallelism between the use of coal, the rise in global CO₂, and the rise in global N₂O [Weiss and Craig, 1976]. This apparent N₂O/CO₂ correlation, however, may be simply a circumstantial relationship between increased industrialization and other (non-combustion) anthropogenic sources of N₂O.

We now know that N₂O can be produced quickly in sample containers at low SO₂ levels, and at low moisture levels. Even though previous research [Martin *et al.*, 1981], examining reactions of NO_x with SO₂ in aqueous aerosols, concluded that the rate of N₂O production seemed too small to significantly change ambient concentrations, it would be most unwise to rule out coal combustion as an indirect source of global N₂O. Additional research should be completed to eliminate any connection between the emission of acid rain precursors (NO and SO₂) and global N₂O production in the atmosphere or local N₂O production in a power plant exhaust plume. Only then can the impact of fossil fuel combustion on global N₂O levels be unambiguously delineated.

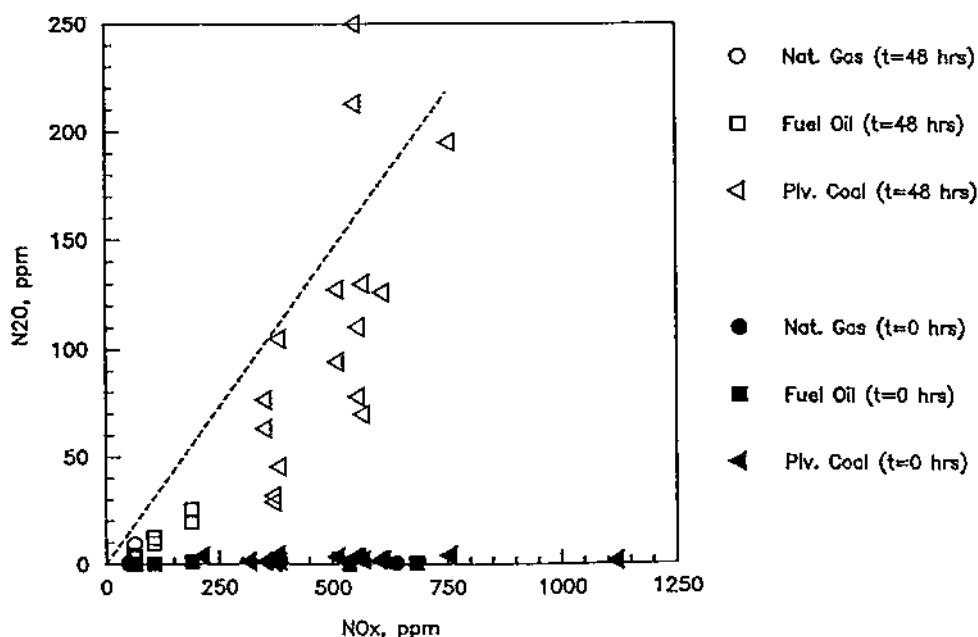


Fig. 5. Comparison of on-line NO emissions to N₂O concentrations from on-line (t=0 hours) and aged (t=48 hours) samples. Shaded symbols represent on-line data as presented in Figure 3. Open symbols represent corresponding wet samples that have been allowed to evolve in stainless steel sampling containers for 48 hours. The dashed line represents a proposed N₂O-N:NO_x molar ratio of 0.58:1 [Hao *et al.*, 1987].

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