l bulletin

ncasi

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC., 260 MADISON AVENUE, NEW YORK, N.Y. 100[illegible]

WOOD WASTE
COMBUSTION IN
BOILERS
AP-42 Section 1.6
Reference No. 24

AP42 Section 1.6
4/93
Reference 20

A STUDY OF NITROGEN OXIDES EMISSIONS FROM WOOD RESIDUE BOILERS

ATMOSPHERIC QUALITY IMPROVEMENT
TECHNICAL BULLETIN NO. 102

NOVEMBER 1979

TABLE OF CONTENTS

Page

I INTRODUCTION 1

II BACKGROUND AND LITERATURE REVIEW 1

- A. General 1
- B. NOx Formation Characteristics 2
- C. Oxides of Nitrogen Measurement Methodology 5
- D. Source NOx Emissions and Control Strategies 12
- E. Ambient Effects of Oxides of Nitrogen 20
- F. Nitrogen Oxide Ambient Air Standards 24

III DESCRIPTION OF OXIDES OF NITROGEN MONITORING SYSTEM USED IN THIS STUDY 25

- A. General 25
- B. Principle of Operation of the Model 8440E NOx Monitor 26
- C. Monitoring System Adaptation to Source NOx Measurements 26
- D. Calibration of Source NOx Monitor 29

IV DESCRIPTION OF INDIVIDUAL WOOD RESIDUE POWER BOILER SYSTEMS SURVEYED 30

V PRESENTATION AND DISCUSSION OF RESULTS FROM OXIDES OF NITROGEN FIELD MEASUREMENTS 35

- A. Measured NOx Emissions from Wood Residue-Fired Boilers 35
- B. Wet Scrubber Influence on NOx Emissions 38
- C. Wood Residue and Oil Fuel Fired Combination Boiler NOx Emissions 40

VI REVIEW OF RECENT EPA REPORT ON NOx EMISSION FACTORS FOR WOOD FIRED BOILERS 43

VII CURRENT NOx COMBUSTION SOURCE EMISSION STANDARDS AND THEIR RELATIONSHIP TO FINDINGS OF THIS STUDY 44

- A. Current Standards 44
- B. NOx Emission Rates from Burning Combinations of Wood Residue and Fossil Fuel 44

VIII SUMMARY 45

IX LITERATURE REFERENCES 48

A STUDY OF NITROGEN OXIDES EMISSIONS FROM WOOD RESIDUE BOILERS

I INTRODUCTION

The United States Environmental Agency has designated nitrogen dioxide (NO_2) as a criteria pollutant. Reliable estimates of oxides of nitrogen (NOx) emissions are also required for carrying out the modelling of combustion source emissions required for satisfying Prevention of Significant Deterioriation regulations. Since available information is limited relative to the potential for emission of oxides of nitrogen (NOx) from combustion processes associated with the manufacture of pulp and paper and power generation from boilers fired on wood residue, the establishment of a larger data base is desirable.

The NCASI is currently conducting a national program in cooperation with individual member mills designed to provide information on oxides of nitrogen emissions from kraft recovery furnaces, lime kilns, and wood residue-fired power boilers. This particular bulletin will discuss the emission rate of NOx from wood-residue fired boilers. The boiler sites sampled in the Northwestern United States included four conventional spreader-stoker fixed grate boilers, one fluidized bed boiler and one modified spreader-stoker boiler capable of burning dried wood residue, wood fines and oil. A wood residue-fired cyclone burner in the Northwest was also tested. The Southeastern test sites represented two traveling grate spreader-stoker boilers, one conventional spreader-stoker boiler and a recovery boiler that had been converted to a bark boiler.

II BACKGROUND AND LITERATURE REVIEW

A. General

The emission of oxides of nitrogen (NOx) from combustion sources is influenced by a number of factors which include combustion temperature, "instantaneous" flame temperature, fuel bound nitrogen and operational parameters such as excess oxygen and the method of fuel firing. An extensive search of recent and significant literature pertaining to NOx formation in a combustion process and the measurement and subsequent ambient effects of oxides of nitrogen was made and will be reported on in this section.

While man made NOx has accounted for only 10 percent of the total found around the world, approximately half of this amount was estimated to be attributable to the United States. Stationary combustion sources have been noted as responsible for about one-half of the United States total (43).

Aghassi et al (1) reported that world wide NOx emissions were roughly 53,000,000 tons per year. Stationary boilers in the United States accounted for 10,000,000 tons per year in 1969 and 1970. The residence time of NOx in the atmosphere was given as only a few days which defined source emissions as a regional rather than global concern. Critical parameters affecting NOx production rate were noted as furnace and boiler geometry, flame temperature, nitrogen content of the fuel and the quantity of excess air. A model to estimate the actual furnace flame temperature was presented as an aid in predicting the anticipated level of nitric oxide (NO) production. Common control techniques to reduce flame temperature were also discussed by the authors.

Percentages of NOx from mobile and stationary man-made sources in the United States based on a 1970 survey indicated norms of 51 percent and 46 percent, respectively. Motorized vehicles represented almost 80 percent of the mobile NOx sources reported. The contribution of oxides of nitrogen from sources connected with electric power generation alone could by 1990 evolve levels two to four times the 1972 estimated total for this classification of 3.95 x 10^6 tons NOx per year (46).

One author (46) stated that roughly 90 percent of the world's oxides of nitrogen was attributable to natural sources with the predominate species nitrous oxide (N_2O). This naturally occurring compound was not considered a significant pollutant such as NOx compounds since it has only been found to be present in low ambient concentrations. There is a relatively high portion of combustion generated or man-made NOx which, contrary to N_2O, does enter into photochemical reactions and acts to form several secondary pollutant products.

B. NOx Formation Characteristics

(1) General - Bartok et al (11) estimated that using the year 1968 as an example, 60 percent of the total 16 x 10^6 tons of NOx emitted in the United States were accountable by stationary sources. Of this total roughly 29 percent was attributable to industrial boilers. NOx emissions based on fossil fuel combustion were shown to have coal and gas responsible for forty percent each of the total contribution for this type of source with oil corresponding to 15 percent of the total for industrial boilers. Refuse and other minor fuels were responsible for the remaining five percent. This last designation included wood residue-fired boilers and indicated the contribution from this type of source was low.

An explanation was given (11) for the presence of nitric oxide in the emission from combustion sources. These were said to be formed from fuel nitrogen at low temperatures and fixed from atmospheric nitrogen at relatively high temperatures. A short residence time in the combustion zone was found to inhibit NO_2 production which conversely was the most thermodynamically stable NOx species at low temperatures. Only about 5 to 10 percent of NO was judged to oxidize to NO_2 within the combustion exhaust gases before exit to the atmosphere.

A general review (28) of nitric oxide control options presented the equilibrium NO concentration as about 2 percent in air under controlled conditions with a small enclosed volume at temperatures of 3800°F. If the NO produced was cooled slowly to ambient temperatures, it was suggested that most would return to N_2 and O_2. Rapid cooling of NO from 4000 to 3000°F was responsible for what was termed by the author as "nitrogen fixation."

MacKinnon (71) reported on the mechanism of formation of NO from gas mixtures of N_2 and O_2. A peak temperature of 3860°F was found to produce the maximum NO formation with a residence time of five seconds. Above five seconds no further increase of NO formation was noted. The formation of NO was found dependent on percent N_2 to the first power and percent O_2 to the one-half power. Keeping all other parameters equal, increasing the combustion process excess air (or more specifically the oxygen content of the exit gas) will enact an increase in the rate of formation of NO.

(2) <u>Nitric Oxides (NO) Kinetic Theory</u> - An interesting finding (7) related to the fate of nitric oxide in flue gas plumes indicated that with less than one minute of plume transport time the level of NO_2 in the exhaust gas was found to increase by an order of magnitude. Diffusion effects in the plume were considered to predominate with kinetic theory suggesting higher than measured NO_2 conversion rates.

Nitric oxide was presented by Hardison (51) as non-toxic before conversion to NO_2. The conversion was understood to occur easily at high concentrations. An NO level between 1 to 5 ppm suggested that the reaction proceeded very slowly and would be insignificant with the exception of photochemical effects.

Shahed *et al* (93) delved into the kinetics of nitric oxide formation and arrived at the conclusion that for high pressure hydrocarbon flames, NO was produced in the post-flame combustion zone. The investigators also discovered that temperature and the presence of inerts affect NO formation the most in the area just following the flame front.

Kinetic gas phase behavior of nitric oxide (NO) in air was studied by Morrison *et al* (80). The oxidation of nitric oxide to nitrogen dioxide under atmospheric conditions at the ppm concentration level was the primary mechanism of interest. The rate of the reaction of 2 to 75 ppm NO with 3 to 25 volume percent oxygen was determined in a constant volume batch reactor at ambient temperatures.

(3) <u>Mechanisms Involved in the Conversion of Fuel and Thermally Fixed Nitrogen</u> - NO_2 was described (99) as a pollutant based on its toxic nature and its role as a reactant for other pollutant products such as photochemical oxidants and/or smog. The mechanism through which combustion process NOx can be produced was described as thermal fixation of nitrogen and the conversion of fuel bound

nitrogen for fuels such as coal and heavy oils. Gaseous fuel combustion was said to evolve NOx through the thermal fixation pathway only.

Reduction techniques for oxides of nitrogen through combustion modification like flue gas recirculation, water injection and the lowering of utilizable oxygen by maintaining low excess air levels to the extent of staged combustion were considered practical for control of thermally fixed NOx (99). The amount of usable oxygen and the quantity of nitrogen present in the fuel were found to govern fuel nitrogen conversion. The presence of NO as the predominate nitrogen oxide combustion product was explained as a consequence of the short residence time in the combustion zone. Subsequent conversion of NO to NO_2 in the combustion gas was judged possible after introduction into the atmosphere.

Thermal fixation was stated (99) as a process which predominately occurred at high peak temperatures in conjunction with high excess air levels. The critical condition was the dependence of the reaction on excess air. If the combustion occurs under fuel rich conditions the carbon will preferentially react with available oxygen rather than nitrogen and the reactions below would not occur.

$$N_2 + O \rightleftarrows NO + N$$

$$N + O_2 \rightleftarrows NO + O$$

The production of fuel nitrogen based NOx has been shown (99) to be of equal significance but having a lower activation energy than thermal fixation from combustion air for both coal and oil combustors. The quantity of such conversion was related to flame type, configuration and percentage of nitrogen in the fuel.

Nitric oxide production from fuel nitrogen by both diffusion and premixed flames was postulated (38) for pulverized-coal combustion. The efficiency of conversion was depicted as greater for premixed as compared to diffusion flames. The premixed flames act to volatilize the fuel nitrogen before combustion and promote burning in the flame. Fuel nitrogen was also professed as the major cause of nitric oxide formation in fluidized bed combustors. In the usual low temperature fluid bed operation, high oxygen concentrations exist at the particle surface enabling combustion either before or during fuel-nitrogen-devolatilization.

Glassman (47) described premixed flames as those which consist of fuel and air which are "homogeneously distributed." When the fuel and air come into contact in a reaction area based only on molecular and turbulent diffusion, a diffusion flame situation occurs. The combustion rate is controlled in this case through the degree of mixing. This conforms to an instance where mixing is slow with respect to reaction rates.

The major contributor of NOx emissions from pulverized and fluidized bed coal combustors was discussed in an article by Vogt et al (108) as predominately from fuel bound nitrogen. The separation of coal combustion into the two regimes of volatile and char burning has resulted in the determination that 60 to 80 percent of the NOx is produced by the volatile component. The use of a chemiluminescent monitor enabled the authors to conclude that: "(a) with furnace wall temperatures of 800 to 1100°C a 10 to 25 percent fuel nitrogen conversion to NO was possible, (b) at low temperatures, or below 750°C, coal fuel nitrogen based NO levels were temperature dependent, (c) above a wall temperature of 750 to 950°C there was a large increase in the fuel nitrogen to NO conversion, (d) above a 940°C wall temperature higher conversion efficiency was dependent on an increase in excess air, (e) NO formation from coal volatiles was found to be important at temperatures as low as 750°C."

(4) Miscellaneous Formation Characteristics - A special case of low temperature NOx formation was theorized by Martin et al (74). The occurrence of an inequality between calculated and measured NOx levels for certain low temperature sources was found. Burners producing average temperatures below 2000°F were determined to have 150 ppm NOx at 3 percent excess oxygen instead of a calculated level of 25 to 50 ppm. This difference was explained through high instantaneous peak flame temperatures which were judged to form the excess nitrogen radicals preceding NO production. The peak values were located in what was termed "molecular energy levels" rather than in the flame zones. On a molecular scale, temperatures as high as 5500°F were judged to be possible. The NOx fraction produced through such instantaneous flame peaks were considered significant only for low temperature burner situations.

Krumwiede et al (64) explained the purpose of NOx testing of a 175 MW utility boiler firing gas fuel. A majority of nitric oxide was found to be produced "within six to ten feet from the burner face." The formation rate was determined as greatest within the flame zone located only two to three feet from the burner face. This conclusion was based on both fuel rich and fuel lean firing conditions with the maximum level of NO lower and closer in proximity to the burner for the fuel rich situation. The measured NO levels in the flame zone approximated 80 percent of the total exhaust gas NO concentration.

C. Oxides of Nitrogen Measurement Methodology

(1) General - An article (17) which served to summarize recent developments in instrumentation for combustion source measurement also described the basis for EPA's "Standards of Performance." For that connotation, the definition of NOx entailed "all oxides of nitrogen except nitrous oxide as determined by the phenoldisulfonic acid method." While the regulatory standards have been specified in terms of nitrogen dioxide, the limits clearly include nitric oxide as well. The author indicated that most of the NOx contained in exhaust gases from solid and liquid fossil fuel combustors was, in fact, NO with some NO_2 found in emissions from gaseous fuel-sources. This information has, reportedly, caused the EPA to

consider a new source performance standard in terms of NO for units which utilized solid or liquid fuel.

Bambeck (9) discussed field work conducted with nitric oxide continuous monitors which were found to operate with a minimum of maintenance and with an uptime or accurate data availability in excess of 99 percent of the operational interval.

A summary (81) of stack sample collection and analysis methods included mention of those appropriate for oxides of nitrogen. The phenoldisulphonic acid method was presented as appropriate in the 15 to 1,500 ppm NOx concentration range with a sensitivity of 1.5 ppm. Continuous photometric NOx and spectroscopic NO analyzers were also described. An electrochemical method capable of NOx measurement at the 5,000 ppm level was noted, as was a chemi-. uminescent detector for determination of NO concentrations to 1,000 ppm.

Measurement methodology for nitric oxide and nitrogen dioxide was summarized by Allen (3). Wet chemical methods were explained as being NO_2 specific. The NO_2 content may be determined directly, or upon sample oxidation for conversion of NO to NO2, total NOx can be obtained. Nitric oxide levels can then be found by difference. The phenoldisulphonic acid (PDSA) procedure was described as long and tedious with potential error from the "incomplete absorption and conversion of NO and NO_2 to the nitrate ion." The Griess-Saltzman reagent procedure was suggested due to the ease and speed of the analysis which was noted as having few interferences. The chemiluminescent NOx monitoring principle was praised for "high sensitivity, specificity and reliability." Electrochemical NOx devices were presented as prone to interferences with gas chromatography generally dismissed as unsatisfactory for this application.

Guidelines were enumerated (40) for the use of continuous monitoring systems (CMS) for new source compliance testing. EPA personnel structured this commentary for those individuals interested in using continuous monitoring systems for field measurement applications. Monitors appropriate for the measurement of NOx, O_2, CO_2, and SO_2 were mentioned.

The use of confidence intervals to statistically interpret the accuracy of gas monitoring instruments through the analyses of calibration procedures and the examination of typical calibration data was proposed by Feigley et al (36). Instrumentation such as that required for NO_2 measurement was one area dealt with in the paper.

Temperature profiles of a combustor were accomplished in one study (43) with a Leeds and Northrup optical pyrometer. These devices have allowed thermal measurements to be taken in the hottest portions of a combustion zone. Such measurements may be utilized in NOx formation investigations related to the thermal fixation mechanism.

(2) Instrumental Continuous Monitoring - The application of instrumental NOx measurement systems as an alternative to wet chemical techniques were analyzed by Shen (95). Human errors were considered the most important criteria to switch to what was referred to as "simple, reliable, reproducible, quick result, continuous data output and low cost" instrumental monitors. Although such monitors were not accepted technology, the author predicted their widespread use in the future after demonstrated reference method equivalence and the development of chemiluminescent and fluorescent techniques.

An evaluation of four respresentative NOx monitoring systems was conducted by Shen et al (96). Chemiluminescence, ultraviolet spectrophotometry, electrochemical transducer, and dispersive infrared spectrometry were selected and compared to the current phenoldisulfonic acid (PDSA) reference method. The PDSA method was described as suitable under laboratory conditions, but not as appropriate as a continuous monitor for field applications. The method was said to be a "nonrepresentative sampling technique" since an instantaneous NOx concentration was measured. The reported reproducibility of field tests has been poor "due to human error in handling the tedious sampling and analytical procedures." In addition, one to two days following sampling are required for complete sample analysis.

The above report (96) also presented EPA test data for the PDSA method which indicated that a statistical determined inaccuracy existed with the method as the measured NOx concentration fell below 650 ppm. Of the four continuous monitors compared to the PDSA method, the chemiluminescent method was termed the most accurate and free from interference with a small sacrifice in portability. Losses of NO in the condensate trap were shown to be insignificant based on that compound's low solubility. While NO_2 was determined to be less soluble than nitric oxide and would therefore represent a potential condensate loss, only about 3 percent or less of the total oxides of nitrogen from combustion sources has been measured as NO_2.

A treatise (107) on chemiluminescent analyses pinpointed "seven possible sources of error" in the use of the devices. These involve "(a) non-linearity, (b) inefficiency in NO_2 to NO conversion, (c) unequal flows in the NO and NOx channels, (d) interferences, positive or negative, (e) spurious (false) response to NO_2 in the NO determination, (f) holdup and reduction of NO_2 in the gas handling systems, and (g) inaccurate calibration procedures. All of these sources of error may be eliminated by following certain procedures. Monitors designed on the chemiluminescent principle applied to NOx measurement displayed no effect or interference from moisture, hydrocarbons, carbon monoxide or sulfur dioxide. Carbon dioxide can result in depletion of the ozone supply if the monitor is operated under low excess ozone conditions.

Shen (94) proposed the use of emerging electronic instrumentation for NOx measurement such as the chemiluminescence technique over the traditional wet chemical phenoldisulfonic (PDSA) procedure. The author specified the importance of portability, setup time, operation simplicity and maintenance minimization.

Chemiluminescent monitors were described (83) as incorporating the collection of a gas sample containing oxides of nitrogen and employing intimate contact with ozone to produce a resultant glow that could be optically and electronically measured. This type of monitor was found by Allen et al (4) to produce an "extremely stable, accurate, sensitive, linear and fast response method of measuring NO in combustion exhaust gases."

The use of an instrumental chemiluminescent technique was refined by Black and Sigsby (14). The method utilized the "photoelectric amplification of the signal produced by the chemiluminescent reaction of nitric oxide (NO) and ozone." Similar to the above reaction, NOx can be determined through the reaction of atomic oxygen, produced by the thermal decomposition of ozone with oxides of nitrogen in the form of NO and NO_2. The latter reaction is an alternative to the traditional procedure of converting the NO_2 to NO through a thermal catalytic converter allowing subsequent chemiluminescent analysis.

Wolf (110) described the chemiluminescent NOx measurement effect as utilization of the absorption of visible light energy produced by a gas reaction. A photomultiplier tube was the usual energy transducer employed in these systems. The significant reaction involved a combination of nitric oxide in the sampled gas combined with ozone produced by the monitor. The reaction of ozone and nitric oxide causes a release of measurable light energy at wavelengths of 6000 A and higher. NOx monitors that employ this principle usually include a thermal-catalytic converter to convert all oxides of nitrogen to nitric oxide. This enables the determination of total NOx while just NO is measured without the converter engaged.

Gas phase chemiluminescent methods were used by Stevens et al (102) for the measurement of ambient levels of nitrogen oxides (NOx). As a consequence of the study, NO_2 chemiluminescent monitors were shown to provide excellent zero and span stability. In addition, good agreement was found for 24 hour NO_2 data developed by several measurement methods which included chemiluminescent and the Jacobs-Hochheiser and the Salzman techniques.

The use of several NOx chemiluminescent continuous monitors adapted for a portable ambient measurement system was described by Altshuler et al (6). Difficulty with temperature stability was mentioned as a problem for one of the chemiluminescent monitors employed for this study.

The use of a chemiluminescent reactor cell at atmospheric pressure was demonstrated as capable of NO detection by several investigators (55). The device employed utilized the chemiluminescent reaction between nitric oxide and ozone. The four study areas in which work was conducted included: (a) atmospheric pressure chemiluminescent NO detector development, (b) the thermal conversion of NO_2 to NO over gold wool, (c) field measurements of NO_2 and NO in St. Louis, and (d) the chemiluminescent detection of atmospheric NH_3 by oxidation to NO. Sensitivity of the system was reported as 0.005 ppm.

(3) Wet Chemical NOx Measurement - A modification of the EPA NOx reference measurement Method 7 was the focus of a presentation by James et al (59). Flue gases were sampled with a "volumetrically calibrated glass flow through type bomb." By injection of hydrogen peroxide into the collected sample, oxides of nitrogen were converted to nitrate ions which were measured by the phenoldisulfonic acid technique.

A review of available wet chemical methodology was presented by Berger et al (13). A specific study on the phenoldisulfonic acid method concluded that statistically interpreted precisions of ±3 percent and ±19 percent were considered appropriate for 1000 and 100 ppm NOx concentrations from a coal fired boiler.

Levaggi et al (67) expressed criticism with the phenoldisulfonic acid grab sampling method for NOx determinations. The inadequate representation of flue gas NOx concentration at the 100 ppm level with the use of grab sampling techniques was documented.

Work conducted with the phenoldisulfonic acid EPA Method 7 by one set of investigators (43) determined that there was no significant operational interference apparent from the presence of reduced sulfur compounds or particulate.

Another laboratory evaluation (78) of the EPA Method 7 or phenoldisulfonic acid method for NOx determination indicated no interference effects with the procedure. The method was presented as unbiased and accurate within the limits of its precision.

An attempt to shorten the analysis time for the phenoldisulfonic acid NOx measurement procedure was discussed in an article by Margolis et al (73). The authors discovered that the use of pure oxygen could shorten the standing time of a sample containing 400 ppm NO from 24 hours to about five hours at atmospheric pressure and to roughly 10 minutes at a pressure of 10 atmospheres.

The Saltzman NOx method was studied by Halstead et al (49) and favored over the phenoldisulfonic acid method for flue gas analysis from combustion sources firing natural gas. The authors advised rapid field sampling rates with silica or silica lined probes in order to avoid the possiblity of sample NOx alteration.

A critical review of the Saltzman technique for batch analysis of flame produced NOx was undertaken by Fine (37). He indicated that if the oxygen content was greater than 20 percent in the collection vessel the Saltzman method would be more accurate than the phenoldisulfonic acid (PDSA) procedure for NOx determinations. This could occur during sample processing if pure oxygen is used as the oxidizer. The PDSA method was judged to give low results under high oxygen conditions (>20%).

An investigation into the sodium arsenite method for nitrogen dioxide determination in the ambient air was described by Margeson et al (72). The authors found the method to have greater than 80 percent collection efficiency for nitrogen dioxide with relative insensitivity to variations in sampling parameters. Positive and negative interferences were indicated with the method for nitric oxide and carbon dioxide, respectively. A bias of 9.9 ug/m^3 for ambient levels of 100 ug/m^3 was determined for the interferents.

An extremely accurate and automatic 24 hour NOx sample analyzer was described by Jacobs et al (58). Through absorption of the NO_2 in an alkali solution the content can be determined colorimetrically at ambient concentrations as low as parts per hundred million.

The incorporation of "a new time integrated sampling method and rapid analysis technique" that essentially sums or totals NOx emissions over a specified time interval and allows quick NO_2 determinations was described by Dee et al (26). Deficiencies in other manual methods such as the phenoldisulfonic acid procedure which were circumvented by the new technique were stressed. The new method utilized heated crystalline PbO_2 to absorb NOx. The resultant lead nitrate was extracted with water and measured with a nitrate liquid ion exchange electrode.

(4) Sample Conditioning Systems - A treatise (111) on continuous stack gas monitoring included guidance for the construction and maintenance of extractive sample handling and conditioning systems. The essential components to the system were listed as "sampling, cleaning, precipitation of condensate, elimination of interfering components, and transporting." The system components were presented as: "Sampling probe, dust filter, cooler, adsorption or absorption filter, flowmeter, and pump." The solubility of several gases were presented with respect to the condensor system. Nitrogen and nitric oxide solubilities were given as 0.015 and 0.047 volume absorbed per volume of water, respectively. The absorption of NOx molecules noted on PVC tubing made teflon the most highly recommended material.

A sample conditioning system utilizing "precision dilution of flue gas with clean dry air" was represented (89) as useful for continuous NOx monitoring. One month of unattended operation was accomplished with the system which operated through the reduction of the dewpoint of the sampled gas to a lower level.

Lusis (70) concluded that Teflon was the most highly recommended material for the construction of gas handling systems NOx montoring measurement sample lines. Losses in NOx were observed with polyethylene tubing but relative humidity was not found to affect the measurement.

Sample line losses and transformations of oxides of nitrogen were studied by Samuelsen et al (90,91). The reduction of nitrogen dioxide to nitric oxide was observed at temperatures exceeding 300°C when transported through 316 or 321 stainless steel tubing. Similar NO_2 reduction was noted with the use of 304 stainless steel at temperatures higher than 100°C. However, no loss in total NOx were measured with the use of probes or sample lines constructed of the above materials. Additional investigations into teflon constructed sample line losses produced mixed results. Experimental work conducted by several investigators have concluded that TFE teflon was both a passive (109) and an absorption (52,106) medium for NO_2 to some degree. The degree of NO_2 loss was judged to be dependent on the concentration of NO_2 and the sample line total pressure.

Allen (2) supported the theory that a catalytic reduction of NOx caused by metallic probes also existed with noncatalytic or silica probes. These reactions were judged to present abnormally high ratios of NO_2/NO while maintaining the appropriate total NOx level in the gas sample. These results were indicated through the use of an uncooled probe which sampled emissions from premixed methane-air flames.

In work (27) related to sampling probe NO losses, catalytic reduction effects were noticed for quartz and stainless steel probes when sampling fuel rich flames. The loss of NO was held to minimal levels through the use of cooled quartz probes. Sampling of fuel lean flames with probes of stainless steel construction was judged acceptable.

The use of a glass lined probe was suggested (43) as appropriate for oxides of nitrogen sampling based on the possible catalytic effects of stainless steel in combination with carbon monoxide in hot stack situations.

A unique sample conditioning system preceding a chemiluminescent measurement device was described by Lucero (69). A "diffusion interface module" was employed (which eliminated the need of a condensate trap) along with the use of unheated TFE or FEP one-eighth inch O.D. sample lines. Interferences from CO_2 and NH_3 were virtually nonexistent with the system. Particulate was removed in the probe assembly.

(5) Oxides of Nitrogen Measurement Calibration Procedures - A discussion (82) presented on developmental work by the National Bureau of Standards (NBS) with standard reference materials (SRM) included comments on the establishment of cylinder gas containing nitric oxide in nitrogen. The prepared cylinder gas was noted as applicable for monitor span calibrations.

Low storage stability of nitric oxide (NO) in nitrogen (N_2) SRM's when contained in steel cylinders was reported on by Robertson et al (88). A drop in NO of 3.3 percent over a six to ten month time period has been found for the steel cylinders with no testing conducted with NO in N_2 when stored in anodized aluminum cylinders.

Cylinder gas calibration standards of NO in nitrogen were reported (107) as having small NO_2 impurities. The use of a triethanolamine scrubber was suggested as helpful in removing the NO_2 in order to have an instrument response corresponding to the "true" NOx level, or in this case the NO span value.

A unique calibration technique for NOx monitors utilizing the Saltzman principle was developed by Higuchi et al (54). The method used NO_2 in nitrogen as a primary standard with concentrations verified through the phenoldisulphonic acid method. The primary standard was diluted with prepurified air to form a secondary standard for use in the field calibration system.

The calibration technique employed to estimate sampling accuracy in a health related study (97) involved the use of NO_2 permeation tubes. The constant temperature system used prefiltered dryed compressed air as a dilution medium at carefully controlled flow rates to produce a specific concentration of NO_2. The NO_2 calibration stream was then sent to a bubbler analysis system. In this way sampling accuracy could be approximated through comparison of known NO_2 concentrations with sampling results. The possibility of the NO_2 calibration gas being slightly different than an ambient level "control" was mentioned. This was reportedly due to the ambient air characteristics not conforming to the specifications of the span gas (i.e. particulate-free, constant temperature and dry).

D. Source NOx Emissions and Control Strategies

(1) General - EPA's continuing involvement in stationary source NOx emissions control regulation was the focus of a review by Ricci (87). Mention was made of new EPA data relating low concentrations of NOx with "adverse health effects, high-nitrate rains, photochemical smog and ozone depletion." Japan was noted as the leader in the field of add-on NOx emission control technology for gas and oil fired boilers. However, since the United States utility boiler growth has been directed toward coal, the Japanese experience may not be considered useful. The 1977 Clean Air Act Amendments called for EPA to examine the need for a short term ($\leq$3 hr average) primary ambient NO_2 standard and, if necessary, promulgate such a standard by August 1978. EPA had not proposed any short term NO_2 standards at the end of 1979.

A 1976 listing (87) of the 24 highest NOx emitting industrial operations depicted coal fired steam utility generators as number one with roughly 3.5 million metric tons of NOx per year (or 30.8 percent of stationary source NOx emissions). Coal-fired industrial/commercial boilers ranked sixth with about 735,000 tons (6.5 percent) as contrasted to wood residue incineration at eighteenth with about 24,000 tons per year or approximately (0.2 percent). The expected growth in NOx emissions was given as a 66 percent increase by 1985 over the 1975 levels. Inefficient NOx control technology was blamed for the tremendous estimated rise in the quantity of NOx. Current combustion control methodology was noted for gas, oil and coal firing with staged combustion suggested one of the most effective. Expected reductions in NOx of 55 percent for gas, and 40 percent each for oil and coal were indicated. The EPA NOx best available control technology (BACT) for coal fired industrial boilers was presented as 450 ppm. Goals for 1980 and 1985 were stated as 150 and 100 ppm NOx for this type of source, respectively.

Control strategies for NOx emissions were reported by Clarenburg et al (20). Various aspects of plume dispersion requirements and the impacts of stationary source and automobile produced oxides of nitrogen on ambient receptors were noted.

A review of coal firing NOx control technology with the inclusion of significant environmental and economic considerations was detailed by Giammar et al (45). The smallest practical pulverized coal boiler size was given as 100,000 pounds of steam per hour. Since this is larger than about 98 percent of the currently operating industrial boilers, there was cause to favor stoker fired units in the design of future installations with the associated NOx control strategies.

A technique was established by Woolrich (112) to approximate NOx contributions from various combustion sources. Nomographs and equations have been developed to estimate nitrogen oxides in pounds per hour for various firing conditions and rates. The results were based on the temperature or heat input of the combustion process being a function of the exhaust gas volume and the gas carbon dioxide content. Since the NOx produced has been found to be a derivation of the combustion process heat input, two sets of relationships were shown to be applicable for oxides of nitrogen determination calculations having as a basis either heat input or exhaust gas volume and exhaust gas carbon dioxide content.

(2). Oxides of Nitrogen Emission Rates and Control Strategies for Combustion Sources - Several control techniques were proposed for the control of the NOx emission rate from combustion sources by Siddiqi et al. (99). These included lowering peak flame temperatures and combustion zone residence time, lowering the oxygen level in the combustion zone and restricting fuel nitrogen content. Procedures employed to enact these control techniques have involved flue gas recirculation, staged combustion, reduced combustion excess air quantities, the lowering of air preheat temperatures, the addition of water or steam to the flame zone as cooling mediums and the use of alternate fuels.

Combustion modification techniques were described (99) as follows. Flue gas recirculation has been accomplished by directing exhaust gas to the primary combustion zone at levels of normally 15 to 20 percent and as high as 35 percent the total combustion air. Staged or off-stoichiometric combustion can be applied to existing boilers through replacement of existing burners with air ports in the fuel rich primary combustion zone, thereby introducing air for complete combustion into a secondary combustion zone and enacting a lower flame temperature. The use of lower excess air levels in combination with staged combustion was found to reduce NOx emissions. Control of excess oxygen to minimum combustion levels has been found to increase the emission rate of carbon monoxide indicating the necessity for maintaining a balanced system. Boiler efficiency losses have formed the major criteria for negating steam or water additions as peak flame temperature controls as an aid in the reduction of NOx emissions.

Several NOx combustion control techniques were studied by Blakeslee et al (16). Conclusions from this study include: (a) flue gas recirculation must be introduced to the primary combustion zone for optimum NOx reduction, (b) fuel nitrogen effects were only apparent with coal and oil firing, (c) load reductions accounted for reductions of up to 50 percent in NOx emissions for gas fired units with the nitrogen fixation mechanism the parameter most affected, (d) elimination of or a reduction of air preheating was found to lower NOx levels with significant sacrifice in boiler efficiency, (e) water injection reduced NOx emissions on one gas fired boiler accompanied by a loss of boiler efficiency, (f) tangential fired units have reduced NOx emissions through the creation of the entire furnace as a burner without air addition at each of the fuel ports and enhancing internal recirculation of the bulk gas (having local fuel rich or fuel lean conditions) which produces slower mixing of fuel and air.

The mechanisms of nitric oxide formation in several combustion systems were studied by Takagi et al (103). The effectiveness of exhaust gas recirculation, water injection and two stage combustion systems on NO reduction was evaluated through "chemical-kinetic calculations." These calculations pinpointed the success of exhaust gas recirculation at levels of about 15 percent. The total air input would reduce combustion temperature and result in a decreased reaction rate and equilibrium nitric oxide concentration. Water injection was judged to restrict nitric oxide formation by lowering flame temperatures. The utility of staged combustion for NO reduction was suggested to center on the release of a large quantity of heat in the primary fuel rich combustion zone which decreases the temperature of the secondary fuel-lean combustion zone.

A summary of NOx control practices was offered for boiler systems incorporating pre-mixed air and fuel burners (104). Effective control modifications, in their order of success, included staged combustion, water addition, flue gas recycle, pre-heat combustion air temperature reduction and lowering of excess combustion air levels. The minimal loss in boiler efficiency combined with relatively large decreases in NO production was said to favor staged combustion. The use of control procedures on boilers not featuring fuel and air pre-mixing was noted as having adverse effects on boiler efficiency and residual percent combustibles.

The relationship between NOx emission rate from stationary sources and flame temperature and quench rate was shown to be related to the type of fuel being fired (30). Representative pounds of emitted NOx were reported for each fuel type. A range of 27 to 34 pounds NOx per ton of oil fired and 14 to 16 pounds per ton of natural gas fired were indicated as an average for all boiler designs.

Reed (86) acknowledged the methodology available for NOx reduction and its impact on industrial boiler performance. The conveyance of cold flue gas to the primary combustion zone was labeled as uneconomical and plagued with problems. A guide to distinguish increases in NOx as a function of combustion air temperature was organized as follows:

Air @ 60°F = X ppm NOx

Air @ 400°F = X x 1.4 ppm NOx

Air @ 600°F = X x 2.0 ppm NOx

Air @ 800°F = X x 3.0 ppm NOx

The dependence of fuel type on potential NOx production indicated the highest NOx emissions corresponding to No. 6 oil with natural gas next, while No. 2 oil was the lowest. Data suggested the use of a large number of small burners in a boiler rather than a few large burners, since a high individual burner heat release would tend to promote higher NOx emissions from the higher localized combustion temperatures.

The author (86) traced lower NOx production to instances where rapid cooling occurred after maximum temperatures were reached. This can be seen as a consequence of lower NOx levels in a water-wall furnace as compared to just a bare-wall furnace. The water wall acts as a heat sink or guide to provide an increased cooling rate. Less NOx formation was also apparent from the flat flame versus a round flame. This was due to the slower cooling rate for the round flame with its conical flame structure.

A composite of NOx emissions related to boiler design specifications and function was included in a report by Barrett *et al*

(10). For only those boilers falling in the range of less than 10^7 Btu per hour (those boilers classified as residential and commercial boilers), the sum of the NOx emissions were 14 percent of the total boiler NOx emissions. The boilers firing at a rate of over 10^8 Btu per hour amounted to 54 percent of the total boiler NOx emissions. The cumulative NOx emissions for all 250 million Btu per hour rated boilers and under was determined as approximately 30,000 tons NOx per year for coal fired boilers, 220,000 tons per year for gas fired boilers, 300,000 tons per year for oil fired boilers and 600,000 tons per year total for all fuel types.

(3) Pulp and Paper Mill Sources - In sampling conducted on kraft recovery furnaces, combination fossil fuel and bark fired boilers, sulfur burners and lime kilns, very low emissions of oxides of nitrogen were found (43). Kraft recovery furnaces were deemed representative of good NOx control practices with their use of essentially off-stoichiometric operation, fairly low combustion temperatures and two-stage air input design strategies. A kraft recovery boiler sampled was rated at 256,000 lb/hr of black liquor operated at a 103 percent excess air level and a combustion temperature range of 1850 to 2250°F. The average NOx concentration measured was 32 ppm with a range of 0 to 53 ppm.

A kraft mill lime kiln sampled for NOx was rated at "250 tons per day" (assumed to be CaO product) and operated at 23 percent excess air with combustion temperatures ranging between 2300 to 2530°F. NOx testing was conducted before and after a venturi scrubber. The measurements were similar at each location and averaged 188 ppm NOx (157 to 213 ppm) and 200 ppm NOx (113 to 260 ppm) for the inlet and outlet of the scrubber, respectively (43).

To control the operation of an NSSC recovery furnace, several investigators (42) suggested that a compromise must be attained between at least eight parameters: (a) acceptable combustion efficiency, (b) chemical recovery as Na_2S and Na_2CO_3, (c) minimization of Na_2SO_4 formation, (d) low alkali dust load, (e) elimination of sulfide emissions, (f) low SO_2 emission, (g) control of CO in flue gas and (h) control of nitrogen oxides. One procedure mentioned that could represent a 50 percent decrease in NOx emissions was two-stage combustion. Normal operation of the furnace required this procedure to insure adequate inorganic chemical recovery. Lower operating temperatures (below 2100°F) were also noted as influencing the level of NOx produced in the furnace through nitrogen fixation ($N_2 + O_2 \rightleftharpoons 2NO$). Since the reaction is endothermic the nitric oxide product can be enhanced with higher temperatures. The NSSC furnace sampled was reported as having NOx emissions between 10 ppm and 50 ppm.

(4) Bark Boiler Sources - Data gathered from power boilers burning either all or a portion bark fuel indicated an average of 205 ppm NOx for a pulverized coal and bark boiler rated at 70,000 lb/hr (43). A range of 150 to 280 ppm NOx was noted with combustion temperatures varying from 2200 to 2600°F. A second power boiler

reported on was sampled when burning solely bark at a rate of 270,000 lb/hr and averaged 123 ppm NOx with a range of 101 to 145 ppm at 89 percent excess air. The measured combustion temperatures ranged from 1900 to 2080°F. EPA publication (114) earlier reported a value of 10 lb NO_2/ton wood-fired. EPA has also recently publish an updated assembly of NOx emissions from wood-fired boilers. The contents of this document are discussed in more detail later in this bulletin (119).

(5) Coal Fired Boilers - Research efforts (48) tailored to the reduction of NOx emissions from coal fired boilers have centered on tangential firing with overfire air. These specially designed units were considered capable of meeting the proposed EPA NOx limitations of 0.5 pounds NOx as NO_2 per million Btu for subbituminous coal firing and 0.6 pounds NOx as NO_2 per million Btu for bituminous coal or lignite firing. Parameters such as excess air levels and burner and overfire air port tilt were studied with respect to various aspects of coal firing.

Spreader-stoker coal fired boilers have been found to result in 30 to 60 percent lower NOx emissions than pulverized coal fired units. It was postulated that this may have been due to the tendency toward staged combustion in spreader-stoker units (45).

The effects of two stage combustion on NOx emissions from pulverized coal furnace systems was studied by McCann et al (77). Approximately 95 percent of the stoichiometric air requirement was applied to the first stage or primary combustion zone. The addition of more air to the second stage resulted in 330 ppm of NOx as measured by the phenodilsulphonic acid method with 20 percent overall excess air operation and only 260 ppm NOx at an 11 percent overall excess air level. The carbon combustion efficiency was determined to be greater than 98 percent for the 11 percent excess air mode.

A coal fired power boiler, described (43) as a 190,000 lb/hr front fired pulverized coal unit, was found to average 375 ppm NOx (310 to 445 ppm) with combustion temperatures of 2600-2700°F.

(6) Oil and Gas Fired Boiler Sources - Bagwell et al (8) remarked on data showing the success of lower peak flame temperature and off-stoichiometric combustion to limit emission of oxides of nitrogen from boilers. Custom designed burner-air port arrangements for oil and natural gas firing were found to minimize NOx emissions without increasing the smoke and carbon monoxide exhausted. Change in furnace and burner parametets were shown to be responsible for as much as 200 to 300 ppm NO. The type or grade of oil was indicated as a potential cause for a 100 to 200 ppm NO differential in total emissions.

Two gas fired power boilers rated at 100,00 lb/hr and 200,000 lb/hr were surveyed (43) and found to average 436 ppm NOx (325 to [illegible] ppm) and 190 ppm NOx (161 to 232 ppm), respectively. No combustion temperatures were noted for the first boiler which was operating at 33 percent excess air. The larger boiler was operated at 46 percent excess air with combustion temperatures of 1600 to 1800°F.

The use of combustion modifications to facilitate reductions in NOx was discussed by Siddiqi et al (99). The economic utility of in-process changes over add on control devices was detailed for fixed firebox combustion systems. Data has been obtained establishing reduction in NOx emission levels of as much as 70 percent for natural gas fired sources originally operated with high peak flame temperatures and excess air.

An enumeration of power boiler NOx control strategies indicated the effectiveness of low excess air and off-stoichiometric operation (19). Flue gas recycle was termed as a possible approach for new boilers, but uneconomical as a retrofit option on existing units. Lowering the excess air level from 4 percent to 2 percent on oil and gas boilers has been found to result in an average of 30 percent lower NOx emissions. Coal fired units were judged to require more excess air for effective combustion and thus possess less flexibility. Instrumentation requirements were noted as more extensive under low excess oxygen firing conditions. Monitoring and control of excess oxygen, air flows, distribution quantities, and exhaust gas combustibles were considered critical under these conditions. Off-stoichiometric or two-stage combustion has shown potential NOx reductions of 30 to 50 percent for oil or gas fired units. These techniques reduce peak flame temperatures through operation of the primary combustion zone under fuel rich conditions with the secondary zone having fuel lean characteristics. The end result is heat transfer between the two zones and lower overall temperatures in the firebox. Coal fired boilers were not considered to be easily adapted to this procedure. Although limited in application, the most successful flue gas recirculation strategy was described as mixing flue gas and precombustion air before routing to the primary flame zone.

Industrial/commercial boiler NOx emissions were discussed with respect to suitable control strategies (100). Conclusions indicated from the data presented included: (a) for liquid fuel firing combustors, the NOx contribution from fuel nitrogen amounted to a conversion of 40 to 50 percent. The contribution attributed to thermal NOx or nitrogen (N_2) fixation of the combustion air was dependent on the furnace design, (b) keeping excess air to a minimum was found to reduce NOx levels by 10 to 15 percent if the normal excess air averaged less than 50 percent, (c) the use of flue gas recycle does appreciably limit NOx formation from fuel nitrogen but cannot decrease that portion attributable to thermal fixation, (d) both thermal and fuel nitrogen produced NOx were controlled through the staged combustion procedures, (e) the authors suggest that flue gas recycle and two stage combustion techniques would be difficult to apply to industrial boilers, since many modifications and new design technology would be required.

Testing was conducted on a newly installed incinerator to establish NOx reduction criteria (62). The surprising results included an increased NOx emissions with an increase in steam flow directly to the system's burner. This occurred even though lower primary and secondary combustion zone temperatures were produced. The lowest NOx values were obtained through use of a minimal steam flow rate to the burner with the maintenance of the highest possible primary combustion zone temperatures. A decrease in NOx was shown with a 10 to 25 percent excess natural gas flow rate which created fuel rich conditions in conjunction with an increase in combustion temperatures and combustible fraction in the exit gas. The cause for this behavior was postulated as the "secondary recombination and formation of NOx in the presence of greater than 100 percent combustibles."

(7) <u>Oxides of Nitrogen Add-On Control Devices</u> - The impracticability of add-on control devices for NOx emissions already below 200 ppm was expressed by First <u>et al</u> (39). Absorption technique success was shown to be basically dependent on the oxidation of NO to NO_2 and elimination of unnecessary dilution.

The basics of a catalytic system which removes NOx without suffering SOx poisoning was described by several authors (75,76). The process used ammonia as a reactant with nitrogen and water as end products. A flue gas stream was treated for several months with the system with 90 percent NOx removal achieved. The initial pollutant levels were 110 to 150 ppm NOx, 660 to 750 ppm SO_2 and 40 to 90 ppm SO_3.

A dry catalytic NOx reduction system was successful using ammonia as a reducing agent (84). The mechanism utilized involved ammonia injection into the exhaust gas stream prior to passage through the dry catalyst. The operational temperature range was given as 250 to 400°C. The dry catalytic bed was described as an "intermittent moving bed reactor." The bed was found to have a working life of over 4000 hours. The NOx control was suggested as aiding in the meeting of Japan's ambient standard of 0.2 ppm NO_2 based on the daily average of hourly levels.

(8) <u>Miscellaneous</u> - Blakeslee <u>et al</u> (15) indicated that the occurrence of furnace slagging might actually increase the NOx emission levels since higher furnace gas temperatures would result as the wall surface heat transfer efficiency is decreased.

The effect of electrostatic precipitation on nitrogen oxides was studied (23) with one pulp and paper industry source chosen. Although not stated, the furnace is thought to be a DCE kraft recovery furnace. The use of two Dynascience electrochemical nitrogen oxide monitors indicated that the electroststic precipitator (ESP) had no significant effect on the NOx content of the flue gases. The reduction in NOx from roughly 130 ppm at the inlet to 40 ppm at the outlet was judged to be attributable to caustic sprays within the flue gas ducts between the ESP outlet and the NOx sample location. The possibility was also expressed by the authors of NOx catalytic decomposition in the precipitator by what was termed the "organic flyash and salt cake" contained within the gas stream. In any case, the trials conducted on the effects of electrostatic precipitation on NOx emissions indicated no significant change across the ESP.

E. Ambient Effects of Oxides of Nitrogen

1. General - Several authors (97) related that through the heat of combustion, atmospheric nitrogen can be fixed to oxygen to form nitric oxide. The oxide can then be transformed to nitrogen dioxide (NO_2) in the atmosphere. The ambient annual average level of NO_2 to be expected in rural areas is 0.01 ppm or less. Concentrations in large urban areas normally range between 0.02 to occasionally over 0.05 ppm.

The relationship between NOx concentration and ozone formation in the ambient air was indicated by Sickles et al (98). The measured level of NOx emissions in 1970 was presented as twice the amount produced in 1960. This was tied to the rise in ambient ozone concentrations in nonurban locations. The interdependence of hydrocarbons and sunlight for ozone formation was also described. Ozone background levels were described that suggested nonurban air quality was hydrocarbon rich with deficient levels of NOx. Ambient levels of ozone were found to be directly dependent on increases in NOx rather than hydrocarbons for nonurban locations.

Paskind et al (85) determined that ambient oxidant levels were not directly related to oxides of nitrogen emissions. At the location studied, oxides of nitrogen ambient levels were actually shown to increase, while average ambient oxidant concentrations declined. The data did indicate, however, that both oxides of nitrogen and hydrocarbon emissions would have to decrease to lower overall oxidant concentrations.

A discussion on the importance of oxides of nitrogen in the ozone production mechanism was offered by Jeffries et al (60). Controlled experiments undertaken with oxides of nitrogen and hydrocarbons in a specially designed outdoor chamber indicated the dependence of NO to NO_2 conversion on the hydrocarbon concentration.

The environmental impact of coal combustion in power boilers was detailed in a document explaining a study funded by the EPA (46). As reported in the document, nitrogen oxides can be expected to increase in the year 2000 by 61 percent over 1975 levels. The hazard stressed by this increase was most apparent with respect to acid precipitation which was noted as already significant in the Northeastern and North Central United States. However, a higher percent increase of NOx emissions was projected for the Western United States over any other region with the contribution increasing from 31 to 39 percent of the total for the United States.

(2) NOx Contributed Photochemical Effects - The traditional smog reaction was modeled (101) through data resulting from a closed laboratory system. Almost all of the initial NOx was traced to reaction products which included peroxyacetyl nitrate (PAN), residual nitrogen dioxide (NO_2) and nitric acid (HNO_3). Trace

amounts of alkyl nitrates were also in evidence. Nitric oxide (NO) and NO_2 were monitored by chemiluminescence and automated Saltzman techniques, while methyl, ethyl and peroxyacetyl nitrate were measured by a gas chromatograph.

A paper by Altshuller (5) presented selective eye irritation studies conducted in smog chambers filled with hydrocarbon-nitric oxide mixtures. He concluded from the experimental work that neither carbon monoxide, sulfur dioxide, ozone or nitrogen oxides cause eye irritation at the concentrations studied. The concentrations investigated were judged representative of levels present on a smoggy day in Los Angeles.

The factors affecting differences between smog chamber facilities used in studies conducted on oxides of nitrogen evolution were presented by Wright et al (113). The factors noted include: "the spectral distribution and intensity of the light source, the temperature range and the extent of chemical equilibrium among nitrous acid, nitric oxide, nitrogen dioxide and water" It was shown that two smog chambers could be designed that could duplicate experimental results if the above parameters were held constant.

Nitrate and sulfate fractions from hi-vol filters were determined by Sandberg et al (92) for the San Francisco Bay Area. The nitrate salts analyzed were primarily ammonium nitrate and judged to be the chief products of the photochemical smog reactions. The high nitrate levels measured were said to be related to excessive oxides of nitrogen and were termed a representative guide of photochemical activity.

The open burning of wood refuse and undergrowth was the focus of a laboratory investigation (12) on photochemical activity. The NOx levels were measured with a chemiluminescent monitor and found to average 70 percent NO with the rest NO_2.

(3) Oxides of Nitrogen Morphological Effect Studies - The results of a study determining the impact of nitrogen dioxide on a populated site which intersected Tennessee and Georgia was authored by Shy et al (97). The four areas chosen within the site included two controls or clean sectors, one high NO_2 exposure section near a trinitrotoluene (TNT) plant and one section with a high suspended particulate level. Inhalation response from second grade school children was found to be lower in the "high-NO_2 section" when compared to the two control sections. Adverse inhalation responses were noted only when an NO_2 threshold was exceeded. Beyond this threshold no further effects were detected.

The effects of indefinite or long-term human contact to low NOx levels of 0.12 ppm and less have been considered inconclusive (97). Higher levels of NO_2 have been found to cause irritation of mucous membranes. Nitrogen dioxide concentrations above 500 ppm have been known to cause "pulmonary edema" and even death to workers in industrial accidents. The application of NO_2 concentrations as low as 0.5 to 5.0 ppm to experimental animals has resulted in injury to the "epithelium of respiratory bronchioles" and lowered the animal's resistance to pathogens. Human airway resistance has also been shown to increase upon exposure to levels of 3 to 40 ppm NO_2.

The community health effects studied (97) in connection with NO_2 exposure indicated: (a) impaired ventilatory function in elementary school children, (b) higher predominance of acute respiratory illness, and (c) restricted host resistance during epidemic influenza. The health effects were related to nitrogen dioxide concentrations measured by 24 hour integrated samples collected by gas bubblers and analyzed by the Jacobs-Hochheisser method.

The investigators of an NOx exposure study (97) explained that a standard technique for monitoring NO_2, such as the Saltzman method, could not be employed in this type of study due to manpower and economic constraints. In addition, limitations in the data collection suggested the use of fewer but better trained technicians to perform the ventilatory function test. A personnel change was indicated as affecting the results by appreciably shifting the dose-response gradient within the high-NO_2 section.

The study indicated (97) that the average NO_2 level of 0.083 ppm measured in the study's high-NO_2 section was similar to that found previously in the Chicago area during the summer months of 1966 which was attributed to high-density automobile traffic.

Irradiation experiments (50) in specially designed chambers noted a correlation between the peak nitrogen dioxide concentrations produced and human eye discomfort. A second "discomfort interval" was found for the secondary time period when certain reaction products were formed. These products included peroxyacyl nitrate, ozone and aldehydes. The first irritation interval corresponded to the conditions in many large urban locations while the second irritation interval was judged to be a photochemical smog response. The relative merits of the preferential reduction of hydrocarbons or oxides of nitrogen were weighed against each other with the investigators leaning toward NOx as the most important overall criteria.

Chapman (18) offered commentary on several health effect related articles dealing with NOx exposure. The articles were noted on the whole to be inconclusive and contradictory. It was felt that no determination of adverse effects from current ambient NOx concentrations could be concluded.

An extensive NO_2 exposure study was the subject of a paper by Gardner _et al_ (44). The response characteristics of several animal species were investigated with respect to various NO_2 exposure concentrations and intervals. Enhanced mortality was found with increased NO_2 level. The conclusion was formulated that long-term low level exposure caused significantly different physical damage than high level short-term exposure.

The effects of oxides of nitrogen on animals was used as a gauge for possible effects of the compounds with humans (46) Positive as well as negative results have occurred with similar N doses on different animal species. The authors concluded that th data from a number of animal exposure studies did not indicate conclusively that the highest current ambient levels of NOx would adversely affect animal populations.

The harmful effects of nitrogen dioxide were related in a study to the mortality of mice to selected levels of NO_2 (65,66). A mortality of 4.6 percent was determined for ambient concentrations of 0.115 ppm over a year's time interval. This level of N was representative of that in downtown Los Angeles. Mice were considered an overly susceptible host for human comparison studi The direction of future work by the authors emphasized the need f a host similar to man such as monkeys.

Evans et al (29) studied the effects of nitrogen dioxide exposure on the lungs of elderly animals. The medium used for testing was aged rats. The results hinted that while age had no effect on the actual condition of the lungs, the lung repair was delayed for a significant time interval in older rats.

The effects of NOx on vegetation were given (59) as secondar to other compounds involved in the photochemical complex. The vegetation injury caused by NOx compounds appeared to be through indirect mechanisms involving oxidants such as ozone and peroxyac nitrates. The actual symptoms of plant NO_2 exposure have been known to consist of metabolic changes, ultrastructural alteratio and lowered photosynthesis. These can lead to what was termed "premature senescence, chlorosis, necrosis, or abscission of leav leading to a lower growth rate and even reduced reproduction or plant death.

Concentration of NO_2 was by itself not considered sufficient to obtain a threshold limit or plant dose response (59). The concentration level in conjunction with the time of incident exposure has been the usual method of reporting the action of NO_2 on vegetation. For instance, a NO_2 level of 1.0 ppm has been suggested as causing metabolic and growth effects for an exposur period of close to one hour. The same 1.0 ppm concentration woul require about 10 hours for "Foliar Lesion." Death of vegetation might be manifested with 300 ppm of NO_2 for one hour.

Ermenc (28) discussed the importance of controlling nitric oxide (NO) from combustion sources. Aspects of NO such as its sl conversion or oxidation in the atmosphere to the brown hued nitrogen dioxide and its contribution to the formation of aldehydes, ketones and organic nitrates were mentioned. Nitrogen dioxide w described as an irritant which can injure lung tissue through nitric acid formation in the lungs. Nitric acid formation in the atmosphere was described as a potential product of nitrogen dioxide, water vapor and rain. Atmospheric nitric acid could lead to vegetation and construction material damage.

The effects and acceptable limits of NO_2 on vegetation were evaluated in a study by Thompson et al (105). The investigators determined that the lowest reported NO_2 concentrations affecting vegetation has been two to four weeks of contact at 0.15 to 0.26 ppm. The criteria followed invovled "chronic injury and associated physiological effects on sensitive plants." The synergistic effect of SO_2 with NO_2 at levels within 5 to 25 pphm was noted as potentially harmful to field grown crops and forested areas near urban sites. Crops such as tobacco, radish, soybean, oat, and pinto bean have displayed adverse effects from exposure to 0.1 ppm NO_2 plus 0.1 ppm SO_2 for a contact time of four hours.

F. Nitrogen Oxide Ambient Air Standards

The 1971 ambient air nitrogen dioxide standard was criticized by Heuss et al (53) as based on unverified data from a "questionable epidemiological study." The main faults found with the epidemiological or "Chatanooga Study" (97) were the interpretation of the medical results and the use of the Jacobs-Hochheiser NO_2 measurement method. The authors recommended that the study should not be the only basis for a nitrogen dioxide standard. In addition, the Greiss-Saltzman measurement method was suggested as the appropriate reference method until chemiluminescent NO_2 analyzers become available. The inherent interferences and lack of precision were described as reasons why the Jacobs-Hochheiser method was unacceptable.

The details of possible EPA proposed short term NOx standards was the subject of a paper by Creekmore et al (24). This standard was stated as being necessitated by the effect of short-term NO_2 excursions on moderately or highly sensitive individuals. Nitrogen dioxide was considered a secondary pollutant with its formation dependent on the presence of nitric oxide. Point sources of NO_2 for urban areas were defined as those that release over 100 tons per year, while point sources in less urbanized areas were noted as those emitting over 25 tons NO_2 per year. Source monitoring requirements similar to those currently existing for other criteria pollutants were predicted to accompany the new short-term NO_2 standard.

Jordan et al (61) expressed a concern with respect to the establishment of a short-term and revised annual standard for nitrogen dioxide (NO_2) based on mathematical models of nitric oxide (NO) data. The slow conversion of NO to NO_2 was the basis of their concern. They discovered lower conversion of NO at night versus the daytime and in the winter as compared to the summer.

Ferris (35) questioned the necessity of a 24 hour NO_2 standard on the basis of limited additional public health protection and questionable results from previous studies. He suggested that the present standard of 0.05 ppm NO_2 on an annual average of 24 hour values was adequate based on a study applying similar levels to an asthmatic population. If such a short-term standard was promulgated, a level of 0.26 ppm for one hour not to be exceeded more than two to three times a year was considered appropriate by the author. At the end of 1979 EPA had not proposed a short term NO_2 standard.

A comparison was drawn by Kiyoura (63) on nitrogen dioxide standards in Japan and the United States. Reference was made to the Japanese standard of 0.02 ppm NO_2 per 24 hours as much stricter than the United States level of 0.05 ppm per year. The author note that while population density was similar in both countries, Japan had a vehicle density only 20 to 25 percent that of the United Stat A conclusion stemming from this comparative work indicated that the Japanese standard was too low to be attained.

III DESCRIPTION OF OXIDES OF NITROGEN MONITORING SYSTEM USED IN THIS STUDY

A. General

The basic monitor used was the Monitor Labs Nitrogen Analyzer Model 8440E. The unit is a gas phase device utilizing the chemiluminescence principle for continuous detection of Nitric Oxide (NO), Nitrogen Dioxide (NO_2), and Oxides of Nitrogen (NOx) on a ppm dry basis. The operation of the monitor is based on the chemiluminescence of an activated NO_2 species (NO_2*) that is produced by a chemical reaction between ozone and NO (41).

The monitor is unique in that dual subatmospheric reaction cell resulting in minimizing measurement error (117,118) or detector systems are incorporated into the design with an independent cell for the measurement of both NO and NOx. Thus, the data produced by the monitor is spontaneous and not averaged. Optical and electronic stability is insured through temperature controls and an optical chopper. An ISOFLO pneumatic system controls each gas stream's flow rate to the respective reaction cells. These flow controllers serv to transport the gas sample through the reaction cells with the chemiluminescence emission from the reaction chambers halted and transmitted alternately to the photomultiplier tubes at the rate of 35 times per second by the optical chopper. A phase sensitive amplifi processes the photomultiplier signal which is then converted to a voltage output for recorder utilization.

The monitor is packaged as two separate modules connected electronically and physically with pneumatic flow lines. The analyzer module consists of the reaction cells and photomultiplier t (PMT) assemblies, the ISOFLO flowrate control assembly, PMT power, signal processing electronics, the front panel readout display and readout display and recorder outputs. The sample conditioner module includes the preliminary pneumatic network employing a sample filter, sample and ozone scrubber, a reaction cell vacuum regulator, and vacuum pump. A schematic diagram of the two module monitor is presented in Figure 1 (57).

B. Principle of Operation of the Model 8440E NOx Monitor

The dual channel chemiluminescence analysis system includes two detection assemblies, each of which employs a reaction cell, optical chopper, and a PMT unit. The reaction cell itself consists of three functional subsystems. These subsystems correspond to first, the concentric ozone and sample nozzles, second, the reaction chamber, and third, the exhaust ports. The operation of the monitor is dependent on the chemiluminescence of an activated molecular nitrogen dioxide species which is produced by the reaction between NO and O_3 in an evacuated reaction chamber (21). Gas containing the nitric oxide molecules enters the reaction chamber by way of a concentric nozzle while the ozone is directed to the reaction chamber via the center nozzle. A small portion of the NO molecules react with ozone to form the activated NO_2* species. A broad-band radiation, from 500 to 3000 nm with a maximum intensity at approximately 1100 nm, is emitted as activated NO_2* molecules decrease to a lower energy state (22). The manufacturer (57) indicated that the current produced by the photomultiplier tube is directly proportional to the intensity of the chemiluminescent emission.

The use of a MOLYCON (68) converter to chemically reduce the NO_2 fraction in the sample to NO was utilized in the monitor. This allows a determination of the total oxides of nitrogen through a sample and detector system which is, except for the converter, identical to that used for the NO measurement. The NO_2 content may be obtained by electronically subtracting the NO response from the total NOx response which represents the sum of the NO and NO_2 in the sampled gas.

C. Monitoring System Adaptation tb Source NOx Measurements

The apparatus used for source NOx sampling is depicted in Figure 2. Several of the components noted as "optional" in the schematic were not found to be required for accurate sampling of some of the sources. The system was designed for consistent operation for vacuum or pressure source gas conditions through the use of a high sampling flow rate and a vented "buffering chamber." This was necessitated by the sensitivity of the monitor to swings in sampling pressure. A constant two inches water pressure was maintained in the inlet line to the Sample Conditioner module of the monitor through the use of the two valves depicted. The in-line filter located after the condensor eliminated the problem of particulate which might foul either valve No. 1 or the stainless steel pump. An additional pump was located on the cyclone condensor drop-out line to insure minimal water/gas contact and to protect the monitor against possible moisture carry-over. The two

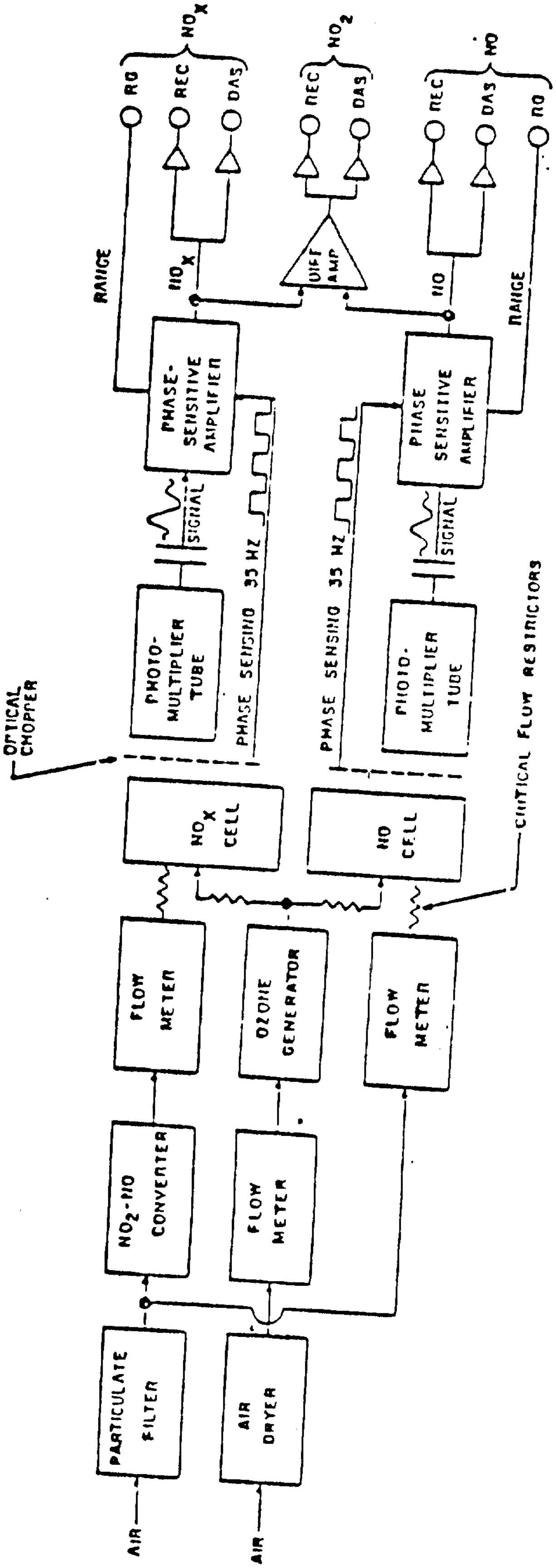

FIGURE 1

BLOCK DIAGRAM, DUAL CHANNEL NOx ANALYZER, MONITOR LABS INC. MODEL 8440E (57

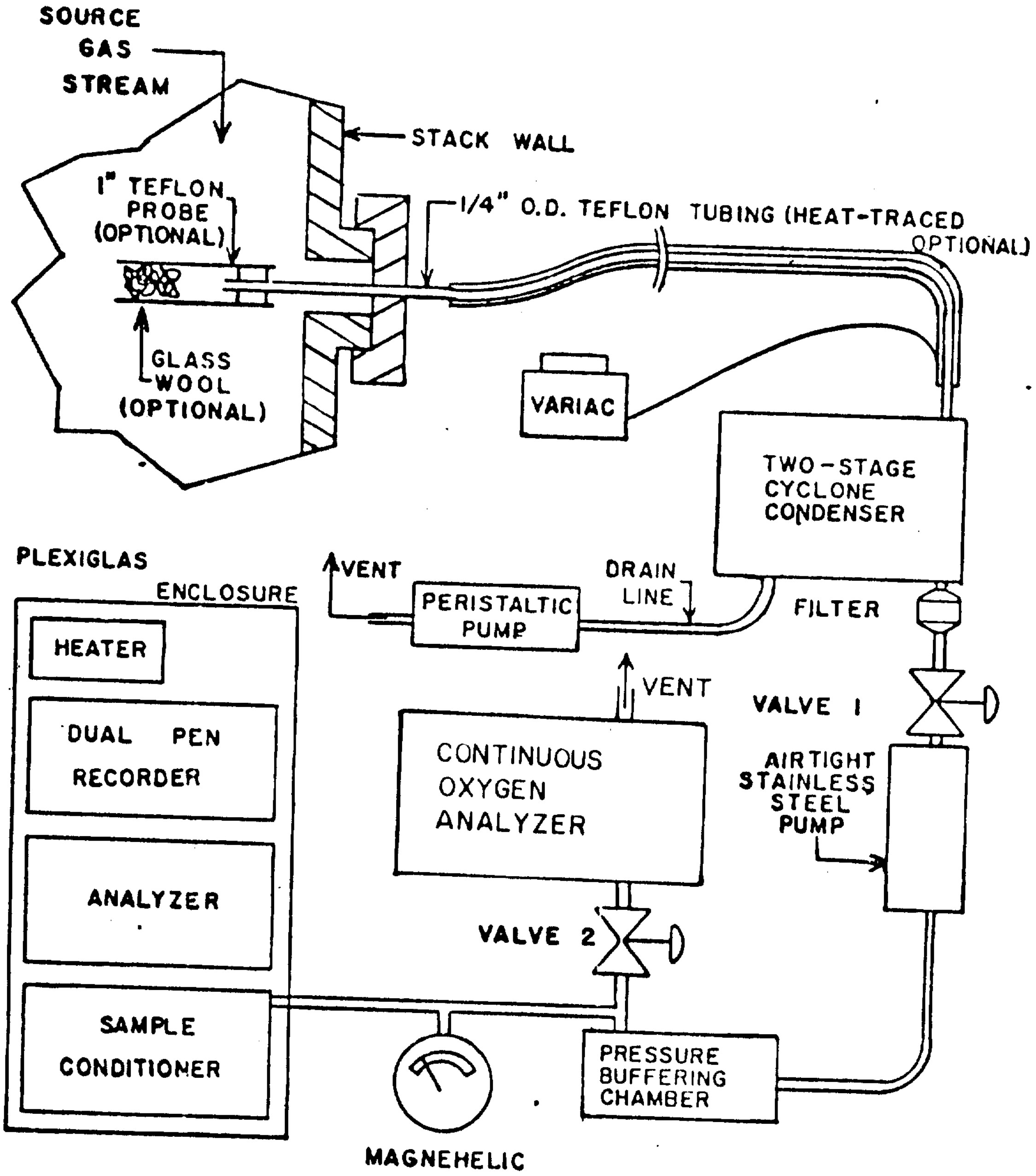

FIGURE 2

SCHEMATIC OF NOx SOURCE MEASUREMENT SYSTEM

NOx monitor modules and a two-pen recorder were housed in a heated plexiglas enclosure to minimize dirt infiltration into the circuitr and to maintain monitor operation within the manufacturer specified temperature constraints of 50 to 104°F. The two-pen heat writing recorder allowed unattended data collection for both nitric oxide (NO) and total oxides of nitrogen (NOx).

Teflon probes, fittings and sample lines were used for all sections of the transport system preceding the condensor. Since the sample gas temperature dropped below 100°C within a short distance from the stack at all sites tested, no NO_2 to NO catalytic co version was judged to occur at the stainless steel 304 condensor. The relatively high sample flow rate and limited time in the gas handling system served to minimize the potential for NO_2 absorption within the system. The stainless steel incorporated into the sample system after the condensor was limited to the No. 1 valve, air-tight pump and three fittings. The balance of the transport system was teflon instead of stainless steel for convenience in making adjustments to the sampling network.

D. Calibration of Source NOx Monitor

The span gas employed for purposes of instrument calibration was obtained from Airco Industrial Gases and contained in aluminum cylinders. Two standards were used, one at 100 and the other at 500 ppm nitric oxide (NO) packed in dry nitrogen. These gases were considered equivalent to primary standards or standard reference materials (SRM's) by the National Bureau of Standards (NBS). If desired by the purchaser, three verification tests, which included chemiluminescent detection and the phenoldisulfonic acid method, were performed by Airco to determine the exact nitric oxide concentration in each cylinder.

Full sampling system calibration spans were conducted through use of cylinder gas equipped with a two-stage regulator connected to valved flowmeter. Although the monitor operated with a one-second time constant, the total time interval required for the system to purge and respond to the full calibration gas concentration was app imately 15 minutes. For purposes of quality assurance, the sample s tem calibration was also augmented with spiking trials at some time during the testing at a majority of the sites. These trials were ca ried out by only pulling approximately half the usual combustion gas sample flow measured by the monitor with the balance of the flow sup plied by calibrated cylinder span gas. Through careful attention to sample line pressures and the chronological measurement by the NOx m itor of (a) undiluted stack gas; (b) stack gas diluted with ambient (c) stack gas diluted with calibrated standard span gas, (d) undilu calibration span gas and (e) undiluted stack gas, the spike trials d termined that the span and stack gas oxides of nitrogen mixtures we conserved at each testing site through the sample conditioning syste In all cases the difference was less than ten percent of the high value between the combined stack and span gas mixture NOx measureme and that value of NOx calculated from undiluted stack and span gas centrations by knowing the percent flow rate of each.

IV DESCRIPTION OF INDIVIDUAL WOOD RESIDUE POWER BOILER SYSTEMS SURVEYED

A total of ten wood residue fired boilers and one wood residue fired cyclone burner were investigated as part of the oxides of nitrogen survey. Six of the boilers were located in the Northwest United States with the remainder in the Southeast. One of the boilers was a fluidized bed unit while the others were either normal spreader-stoker or a modified spreader-stoker configuration. The cyclone burner site did not have a boiler section. The predominate fuel fired in all of the boilers during the study period was wood residue, although a portion of the data for some of the sources was collected while limited quantities of fossil fuel were fired with the balance of fuel wood residue. The occurrence and quantity of fossil fuel fired were noted for each site, where applicable.

Limited operational and design characteristics found for the ten wood residue fired boilers are presented in Tables 1 and 2. This information includes the type of boiler at each site sampled for NOx. The mean steam production rate, temperature, and pressure was determined during the test interval. The rated source capacity or design values for these parameters are shown in parenthesis directly below each average representative of the sampling time period. The type and amount of auxiliary fuel fired is given with the percent of the total fuel on a Btu heat input basis noted. Combustion chamber volume was estimated from design drawings and presented for several of the boilers as shown. The particulate control device in service at each site is indicated with the position of the sample site with respect to the control device also specified for each of the wood residue boiler systems.

Wood residue boilers Nos. 1, 2, 3, and 6 were spreader-stoker in design. Unit No. 1 is a type "VO" bent tube boiler manufactured by Riley Union and installed by the Bumstead and Woolford Company in 1975. Pin-hole steam grates were incorporated into the system design. The moisture content of the wood residue fired in this unit ranged from 45 to 50 percent with an estimated fuel value of 9,000 Btu per pound wood fuel on an oven dry basis. The boiler identified as No. 2 was manufactured by Foster Wheeler, installed in 1975 and began operation on wood residue in 1976. The average fuel moisture level was 55 percent (±5 percent moisture) with a fuel value of roughly 8,900 Btu per pound of oven dried fuel. Boiler No. 3 was manufactured by Bumstead and Woolford and began operation on wood residue in 1970. This unit was of pin-hole grate design. The predominate fuel employed was wood residue with 50 percent moisture (±5 percent moisture) and a fuel value of 8,900 Btu per pound of oven dried fuel. The No. 6 boiler was nearly identical to No. 1 being of Riley Union manufacture and installed by Bumstead and Woolford Company in 1976. The type "VO" bent tube boiler with pin-hole steam grates fired 90 percent wood residue, while natural gas and waste sludge accounted for 10 percent of the total heat input

TABLE 1 OPERATING AND DESIGN CHARACTERISTICS FOR NOx SURVEYED WOOD RESIDUE BOILERS

Location And Boiler Type	Steam Rate Mean, pph (Rated Capacity)	Steam Temperature Mean, °F (Design)	Steam Pressure Mean, psig (Design)	Auxiliary Fuel Fired (Percent)	Combustion Chamber Volume, ft^3	Type of Control Device	Sampling Site
1: S.S.	144,800 (180,000)	585 (600)	415 (600)	None	17,940	M.C.& W.S.	W.S.I.
2: S.S.	380,900 (400,000)	950 (950)	1250 (1250)	None	25,800	M.C.	M.C.O.
3: S.S.	80,200 (150,000)	400 (400)	250 (250)	None	17,500	M.C.& D.S.	D.S.O.
4: S.S.	104,000 (110,000)	700 (755)	600 (600)	None	7,192	M.C.& V.S.	V.S.O.
5A: S.S.	263,000 (NA)	720 (750)	610 (660)	None	30,400	M.C.& V.S.	V.S.I.
6A: S.S.	132,600 (155,000)	775 (NA)	620 (625)	Nat. gas & sludge (5%&5%)	14,800	M.C.& W.S.	W.S.I.
7A: S.S.	117,000 (135,000)	720 (825)	641 (625)	None	NA	M.C.& V.S.	V.S.I.
8A: S.S.	103,000 (150,000)	720 (750)	600 (675)	None	7,150	M.C.& V.S.	V.S.I.
9A: S.S. (f)	54,200 (180,000)	780^1 (825)	840^1 (860)	$None^2$	14,400	M.C.	M.C.O.
10: F.B.	30,000 (36,000)	335 (382)	110 (200)	None	5,400	M.C.	M.C.O.

---

1. Values for both bark (62%) and oil (38%).
2. Converted to 100% bark firing through multiple regression calculations.

Spreader stoker.

F.B. Fluidized bed.
NA Not available.
M.C. Multiclones.
W.S. Wet scrubber.
D.S. [illegible]

TABLE 2 COMPARATIVE OPERATING AND DESIGN CHARACTERISTICS FOR SELECTED WOOD RESIDUE BOILERS

Location And Boiler Type	Steam Rate Mean, pph (Rated Capacity)	Steam Temperature Mean, °F (Design)	Steam Pressure Mean, psig (Design)	Auxiliary Fuel Fired (Percent)	Combustion Chamber Volume, ft^3	Type of Control Device	Sampling Site
5B: S.S.	255,000 (NA)	720 (750)	610 (660)	None	30,400	M.C.& V.S.	V.S.O.
6B: S.S.	128,300 (155,000)	775 (NA)	620 (625)	Nat. gas & Sludge (5%&5%)	14,800	M.C.& W.S.	W.S.O.
7B: S.S.	101,000 (135,000)	720 (825)	641 (625)	Oil (2%)	NA	M.C.& V.S.	V.C.I.
8B: S.S.	121,000 (170,000)	720 (750)	600 (675)	Oil (15%)	7,150	M.C.& V.S.	V.S.I.
9B: S.S.	99,700 (180,000)	784 (825)	840 (860)	Oil (35%)	14,400	M.C.	M.C.O.

---

1. Values for both bark (62%) and oil (38%).
2. Converted to 100% bark firing through multiple regression calculations.

S.S.	Spreader stoker.
S.S. (f)	Spreader stoker with fuel dryer and fines injection in the overfire air.
F.B.	Fluidized bed.
NA	Not available.
M.C.	Multiclones.
W.S.	Wet scrubber.
D.S.	Gravel bed dry scrubber.
V.S.	Venturi scrubber.

on a Btu basis. Wood residue approximated at 9,000 Btu per pound of oven dried fuel and 50 percent (±5 percent moisture) was combusted in the boiler.

Wood residue boilers Nos. 4,5,7, and 8 utilized spreader-stoker traveling grate systems. Boiler No. 5 was a converted (1977) recovery boiler that practiced flyash reinjection. Both boilers Nos. 4 and 5 were manufactured by Babcock and Wilcox in 1952 and 1954, respectively. Combustion Engineering installed the boiler designated as No. 7 in 1952 with No. 8 placed in operation in 1954.

The boiler installation labelled No. 9 was originally manufactured by Babcock and Wilcox in 1945 and was subsequently modified to burn dried wood residue in 1974. The spreader-stoker design employed an air swept spout to introduce the bark to the combination zone. The boiler had fixed pin-hole grates and water walls. Auxiliary oil fuel supplemented the wood residue on a continuous basis. A circular burner, which served to supply the oil fuel to the boiler, was located above the wood fuel chute and in the center of four Babcock and Wilcox burners formerly used for firing pulverized coal. The former coal burners were employed to convey one-eighth inch minus dried wood fines at 10 to 15 percent moisture which were blown from metering bins through a diffuser plate. The primary fuel used was dried wood residue at roughly 30 percent moisture. The estimated fuel value of this material was 9,100 Btu per pound of oven dried wood residue.

Site No. 10 was a fluidized bed combustion system that was manufactured and installed by Energy Products of Idaho and began operation on wood residue in 1978. The boiler section was manufactured by Nebraska Boiler Company. The fuel employed was wood residue which was pneumatically delivered above the combustion zone through use of a blower system which utilized ambient air. The wood residue fuel was estimated to be in excess of 60 percent moisture with one sample analyzed at 62 percent moisture. The fuel value was about 8,900 Btu per pound of oven dried wood residue fuel.

The boiler sites listed in Table 2 include Nos. 5B and 6B which corresponded to the outlet side of each boiler's wet scrubber particulate control device as contrasted to NOx sampling done at the scrubber inlet represented by Nos. 5A and 6A. The boilers designated as Nos. 7B, 8B, and 9B indicate the use of oil as auxiliary fuel while nos. 7A, 8A, and 9A in Table 1 represent operation at these sites solely on wood residues.

Boiler exhaust gas conditions which were measured during the NOx wood residue sampling interval are presented in Table 3. This information includes the number of hours sampled which averaged 45 hours for all of the sites. The boiler exit temperature represents the highest temperature preceding the air preheater which could be measured and recorded at each boiler installation. Exhaust gas

TABLE 3 BOILER EXHAUST GAS PARAMETERS MEASURED DURING SAMPLING INTERVAL

	NOx Testing Interval hours	Boiler Exit Temperature, °F	Gas Flow, SDCFM	Mean Excess Oxygen, %	Mean CO_2, %
1	98	553	64,800	9.3	9.9
2	48	738	126,000	5.2	15.1
3	45	520	40,800	8.6	11.1
4	38	NA	52,000[1]	10.0[2]	12.0[2]
5A	21	710[3]	89,500[1]	4.8	NA
5B	18	710[3]	86,700[1]	4.8	NA
6A	43	684	67,300	7.3	11.7
6B	50	668	67,300	4.2	15.5
7A	36	783[3]	72,000	12.0	NA
7B	45	783[3]	62,100	12.0	NA
8A	27	NA	61,300[1]	11.7	NA
8B	39	NA	72,000[1]	11.7	NA
9A	93	609	27,100[4]	10.5	8.1
9B	50	619	47,100	10.5	8.1
10	28	538	14,760	9.3	11.2
11*	37	NA	10,040	18.1	2.8

---

1. Calculated values from steam production, excess oxygen and combustion gas factors.
2. Estimated operating conditions for site due to equipment malfunction during the sampling interval.
3. Average for entire testing interval of A and B.
4. Calculated from steam production rate based on wood.

* Cyclone burner without boiler section.

NA Not available.

flow, percent excess oxygen and percent excess carbon dioxide are noted for the majority of the installations. In some cases the combustion exhaust gas flow was not measured which necessitated the use of estimated values. These values as shown were based on steam production, percent excess oxygen level, a boiler efficiency approximation and a standard boiler factor for bark firing taken from The Federal Register (33) of 9,640 DSCF per million Btu heat input at 0% excess oxygen.

An additional wood fired burner site was sampled to determine the influence of firing low moisture wood residues on oxides of nitrogen emissions. The location selected employed a 1974 cyclone burner with wood fuel and air entering a cylindrical combustion chamber tangentially which produced what was described as a "vortex flow pattern." The burner was installed in 1978 on a top duct feed, single zone Northwest United States veneer dryer rated at 27 million Btu per hour. Dry wood "dust" at less than four percent moisture was used as fuel with a heating value of approximately 8,500 Btu per pound of dry dust. Since wood use was monitored continuously at the site, an accurate rate of fuel heat input was determined for the testing interval.

Nitrogen oxides (NO_2) "emission factors" for wood and bark waste combustion in boilers were presented in an U.S. EPA publication (114) based on NOx Method 7 sampling. A factor of ten pounds Nox per ton of wet wood fuel (5 kg/mt) was specified for the wood waste boiler combustion sources.

V PRESENTATION AND DISCUSSION OF RESULTS FROM OXIDES OF NITROGEN FIELD MEASUREMENTS

A. Measured NOx Emissions from Wood Residue-Fired Boilers

The oxides of nitrogen emission results for the ten wood residue fired boilers sampled are presented in Table 4. As specified in the Federal Register (34) the data was compiled into first, hourly averages and then into three hour averages. The mean and range for each site are noted in the table. The NOx concentration in parts per million, unadjusted for excess oxyen, is directly above the NOx concentration mean at 0% excess oxygen or stoichiometric conditions. Both the three hour mean and range are given in Table 4 with units of pounds NOx per million Btu heat input and nanograms NOx per Joule heat input for each of the ten sites. These NOx emission values correspond to the time interval noted in Table 3. The NOx mean and upper range found for each site in units of pounds NOx per million Btu is depicted in Figure 3. All of the boiler sources represented in this figure except 6A corresponded to 100 percent wood residue fuel firing. That particular site averaged 90 percent wood residue with natural gas and waste sludge contributing only 5 percent the total Btu input each.

TABLE 4 OXIDES OF NITROGEN FIELD MEASUREMENTS FOR WOOD RESIDUE FIRED BOILERS SAMPLED

Location and Boiler Type	NOx (3) Hour Average Mean			NOx (3) Hour Average Range		
	(ppm)	(lb/10^6 Btu)	(ng/J)[1]	(ppm)	(lb/10^6 Btu)	(ng/J)[1]
1: S.S.	53.5 (96.4)*	0.111	47.6	41.0- 80.5	0.085- 0.167	36.5- 71.6
2: S.S.	93.1 (123.9)*	0.142	61.2	70.0- 104.7	0.107- 0.160	46.0- 68.6
3: S.S.	37.0 (62.8)*	0.075	32.1	25.3- 47.3	0.051- 0.095	22.0- 41.0
4: S.S.	60.4 (115.8)*	0.133	57.2	38.0- 82.0	0.084- 0.179	36.1- 77.0
5A: S.S.	133.0 (172.7)*	0.200	86.0	124.0- 136.0	0.190- 0.221	81.7- 95.0
5B: S.S.	112.0 (145.4)*	0.168	72.2	104.0- 123.0	0.152- 0.184	65.4- 79.1
6A: S.S.	95.0 (146.0)*	0.168	72.1	83.3- 106.5	0.147- 0.188	63.2- 80.8
6B: S.S.	75.7 (94.7)*	0.109	46.8	61.0- 88.7	0.087- 0.128	37.4- 54.8
7A: S.S.	67.5 (158.5)*	0.182	78.3	55.1- 73.8	0.149- 0.222	64.1- 95.5
8A: S.S.	81.4 (184.9)*	0.214	92.0	74.0- 87.0	0.190- 0.232	81.7- 99.8
9A: S.S. (f)	87.9 (176.6)*	0.218	93.9	42.1- 116.7	0.105- 0.290	45.0- 124.6
10: F.B.	109.7 (196.8)*	0.225	96.6	81.7- 134.7	0.167- 0.276	71.9- 118.5
11: C.B.	16.9 (122.4)*	0.111	47.8	9.7- 22.2	0.084- 0.140	36.2- 60.0

---

[1] 1 lb/10^6 Btu = 430 nanograms/Joule heat input.

* Adjusted to 0% excess oxygen.

S.S. Spreader stoker boiler

S.S. (f) Spreader stoker boiler with fuel dryer and fines injection in overfire air. (These results were based on bark fuel only from multiple regression analysis of NOx total (y), steam from bark (x_1), and steam produced from oil (x_2).

F.B. Fluidized bed boiler.

C.B. Cyclone burner w/o boiler section.

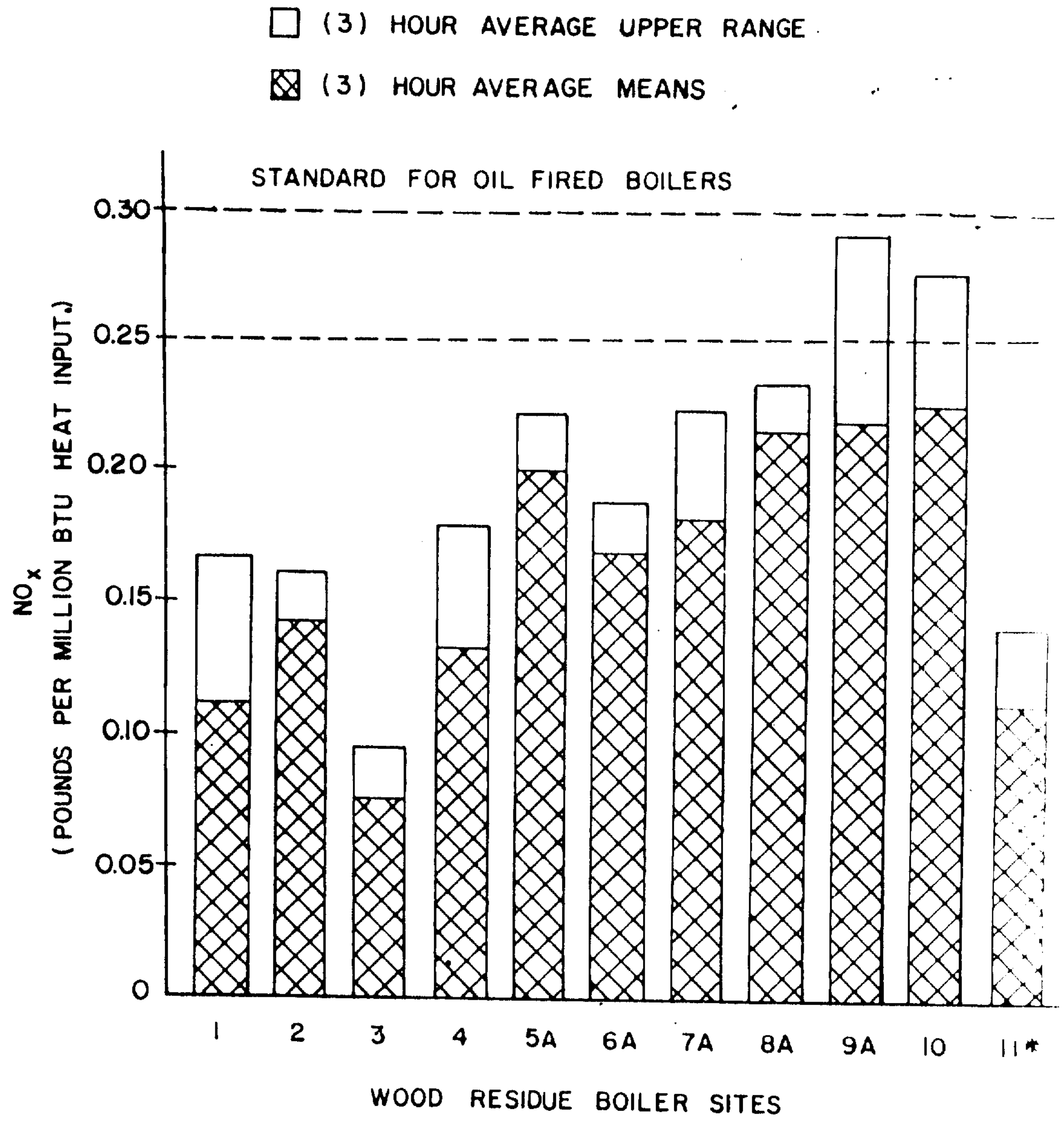

FIGURE 3 NO_x EMISSION LEVELS FOR WOOD RESIDUE BOILER SAMPLED

* CYCLONE BURNER w/o BOILER

The dashed line at 0.30 pounds NOx per million Btu in Figure 3 indicates the current standard for oil fired utility boilers. Each three hour average measured at the ten wood residue sites was found to be below this standard. The use of wood residue as fuel, then, represents lower oxides of nitrogen emissions than that which would be expected from oil firing. The partial or total conversion of oil burning facilities to wood residue firing would be expected to favorably address the overall reduction potential of NOx emissions based on alternative fuel use.

A level of 0.25 pounds NOx per million Btu was judged to be a representative value for wood residue boiler operation as signified by the lower dashed line in Figure 3. The two exceptions which exceeded this criteria as shown in the figure correspond to a boiler fed with dried fuel indicated as site 9A and site 10 which represented a fluidized bed wood residue boiler.

The data set labelled No. 9A encompassed 93 hours of monitoring and was adjusted to reflect the firing of wood residue only. During this study a total of 137 hours of data was collected while firing both wood and oil. The total NOx based upon wood residue and oil firing was related through multiple regression techniques to the steam produced from wood and the steam produced from oil. The hourly averages for each of the parameters were utilized to establish a general trend for NOx based on steam production by each of the fuels. A moderate correlation was found that enabled the oil contributed NOx to be subtracted from the total NOx measured from each of the 93 hourly averages. The resulting values for NOx emissions corresponded to that for wood residue firing only. Comparison of this calculated NOx contribution from bark firing to the total NOx measured suggested average oil based NOx levels of 0.4 pounds per million Btu. This level was judged to be reasonable based on literature values reported (19) and for the quantity of oil fired in the boiler over the study interval.

Each of the sites Nos. 9A, 10, and 11 was the only one of its type sampled for oxides of nitrogen. A greater number of fluidized bed and dried wood residue fuel boiler installations must be studied further in order to adequately determine appropriate NOx "emission factors" for these combustion source systems.

B. Wet Scrubber Influence on NOx Emissions

An attempt to address the oxides of nitrogen reduction potential of wet scrubbers in wood residue fired boiler operations was carried out at two sites. The three hour average means and upper ranges for the inlet and outlet of the wet scrubbers at the two source are depicted in Figure 4. Additional details of each boiler's operating conditions during the sampling period can be found in Tables 1, 2, 3, and 4. The NOx measurements for site No. 5 indicated a 16 percent lower mean value based on three hour averages for the venturi scrubber outlet as compared to the inlet mean. A portion of this NOx decrease can be attributed to the

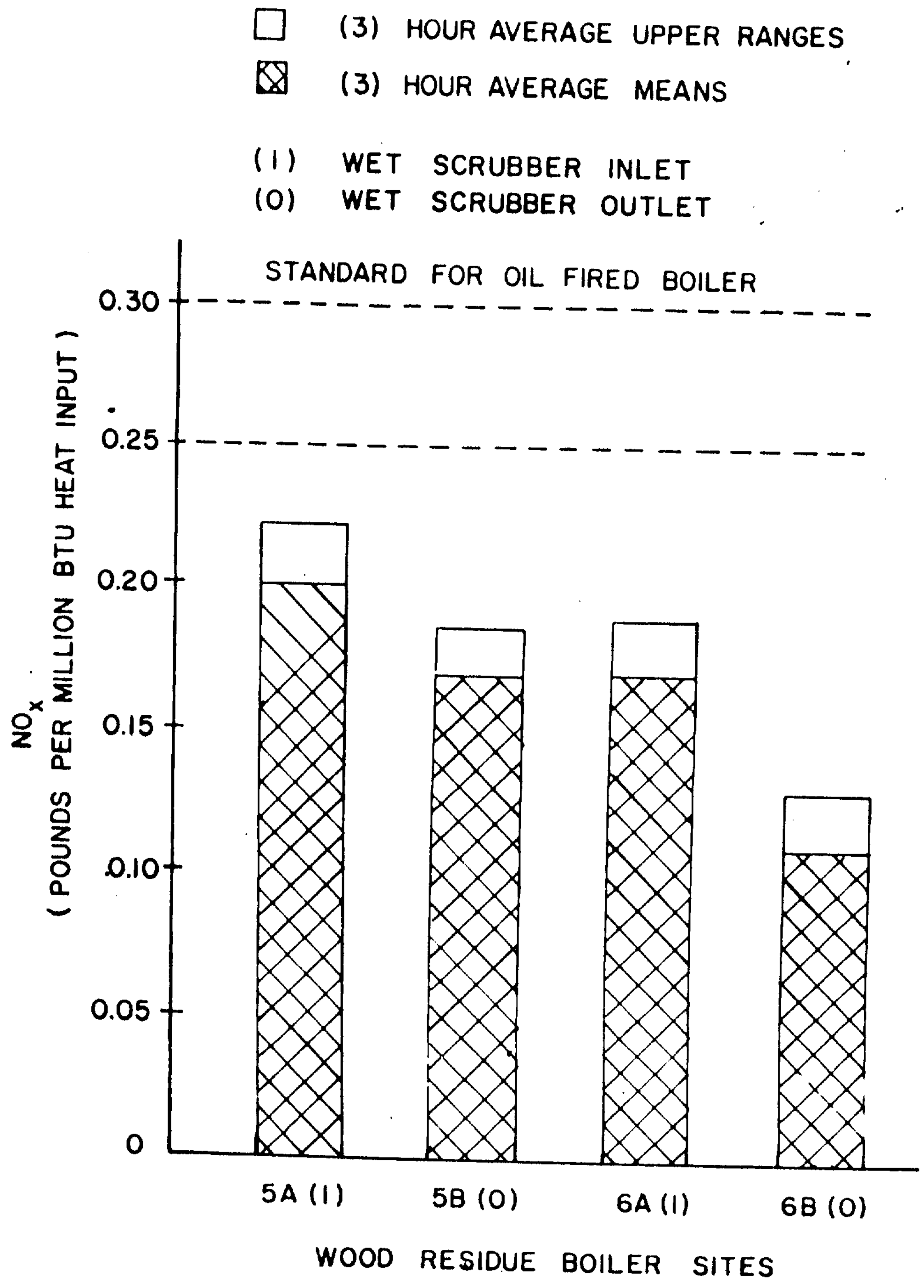

FIGURE 4 NO$_x$ MATERIAL BALANCE FOR SCRUBBER EQUIPPED BOILERS SAMPLED

lower boiler steam production as related to the wood residue firing conditions during the NOx outlet sampling interval. As shown in Tables 1 and 2, the steam production during scrubber inlet NOx testing averaged 263,000 pounds per hour while the steam load during scrubber outlet NOx measurements was 255,000 pounds per hour. A lower steam load on the boiler should reflect in lower flame temperatures with potentially lower NOx emissions.

The boiler designated as site No. 6 in Figure 4 also displayed a decrease in oxides of nitrogen emissions across the wet impingement scrubber. The 35 percent lower NOx mean emission rate at the scrubber outlet when compared to the scrubber inlet was judged to be, in part, a consequence of changes in normal boiler operating conditions between the two sampling intervals. Higher flame temperatures during sampling at the scrubber inlet was judged to be the probable cause of the higher mean NOx concentration found at that location. As indicated in Tables 1 and 2 the mean steam rate was 132,600 pounds per hour and 128,300 pounds per hour during the testing at the scrubber inlet and outlet, respectively. The mean boiler exit gas temperature immediately preceding the air preheater was 684°F for the scrubber inlet and 669°F for the scrubber outlet testing interval as noted in Table 3. The lower combustion air preheater inlet temperature for the scrubber outlet testing interval indicated a lower overall furnace combustion temperature than that representative of the scrubber inlet sampling period. In order to determine the significance of the difference in scrubber inlet and outlet NOx levels, supplementary and very short-term measurements taken at each of the sample locations were found to result in identical NOx concentration levels.

C. Wood Residue and Oil Fuel Fired Combination Boiler NOx Emissions

Several boiler sites provided the opportunity to investigate the effect of oil firing in combination with wood residue fuel on total oxides of nitrogen emissions. Three sites were studied with respect to combined wood residue and oil fired boiler NOx emission levels. As noted in Table 2, sites Nos. 7B, 8B, and 9B represented 2 percent, 15 percent, and 35 percent oil firing on a Btu basis with the balance of the fuel wood residue. The results of field NOx measurements on these sources were compiled into three hour average means and ranges as shown in Table 5 with the means and upper ranges depicted in Figure 5. The use of oil as an auxiliary fuel did not have a large effect on the mean NOx emissions for sites nos. 7B and 8B when compared to the data in Table 4 which represented 100 percent wood residue firing at these sources. While the NOx mean increased 3.8 percent for site no. 7B and 3.3 percent for site no. 8B, the values for the upper ranges increased by 25 percent and 7.8 percent, respectively. The increased level of emissions could not be directly related to the quantity of oil fired as a percentage of the total fuel heat input for these two sources. It was greater as would be anticipated however.

The oxides of nitrogen measurements for site No. 9B corresponded with a dried wood residue fuel at 30 percent moisture with

TABLE 5 OXIDES OF NITROGEN FIELD MEASUREMENTS FOR WOOD WASTE AND FOSSIL FUEL COMBINATION FIRED BOILERS SAMPLED

Location and Boiler	NOx (3) Hour Average Means			NOx (3) Hour Average Range		
Type	(ppm) Actual	(lb/10^6 Btu)	(ng/J)[1]	(ppm) Actual	(lb/10^6 Btu)	(ng/J)[1]
7A: S.S.	67.5 (158.5)*	0.182	78.3	55.1- 73.8	0.149- 0.222	64.1- 95.5
7B: S.S.	67.7 (159.0)*	0.189	81.3	55.1- 79.8	0.149- 0.278	64.1- 119.5
8A: S.S.	81.4 (184.9)*	0.214	92.0	74.0- 87.0	0.190- 0.232	81.7- 99.8
8B: S.S.	84.9 (192.9)*	0.221	95.0	74.0- 95.9	0.190- 0.250	81.7- 107.5
9A: S.S. (f)	87.9 ((176.6)*	0.218	93.9	42.1- 116.7	0.105- 0.290	45.0- 124.6
9B: S.S. (f)	112.8 (226.7)*	0.276	118.8	90.7- 144.7	0.222- 0.354	95.5- 152.4

---

1. 1 lb/10^6 Btu = 430 nanograms/Joule heat input.

* Adjusted to 0% excess oxygen.

S.S. Spreader stoker.

S.S. (f) Spreader stoker with fuel dryer and fines injection in overfire air (actual data with boiler firing an average of 65% bark and 35% oil).

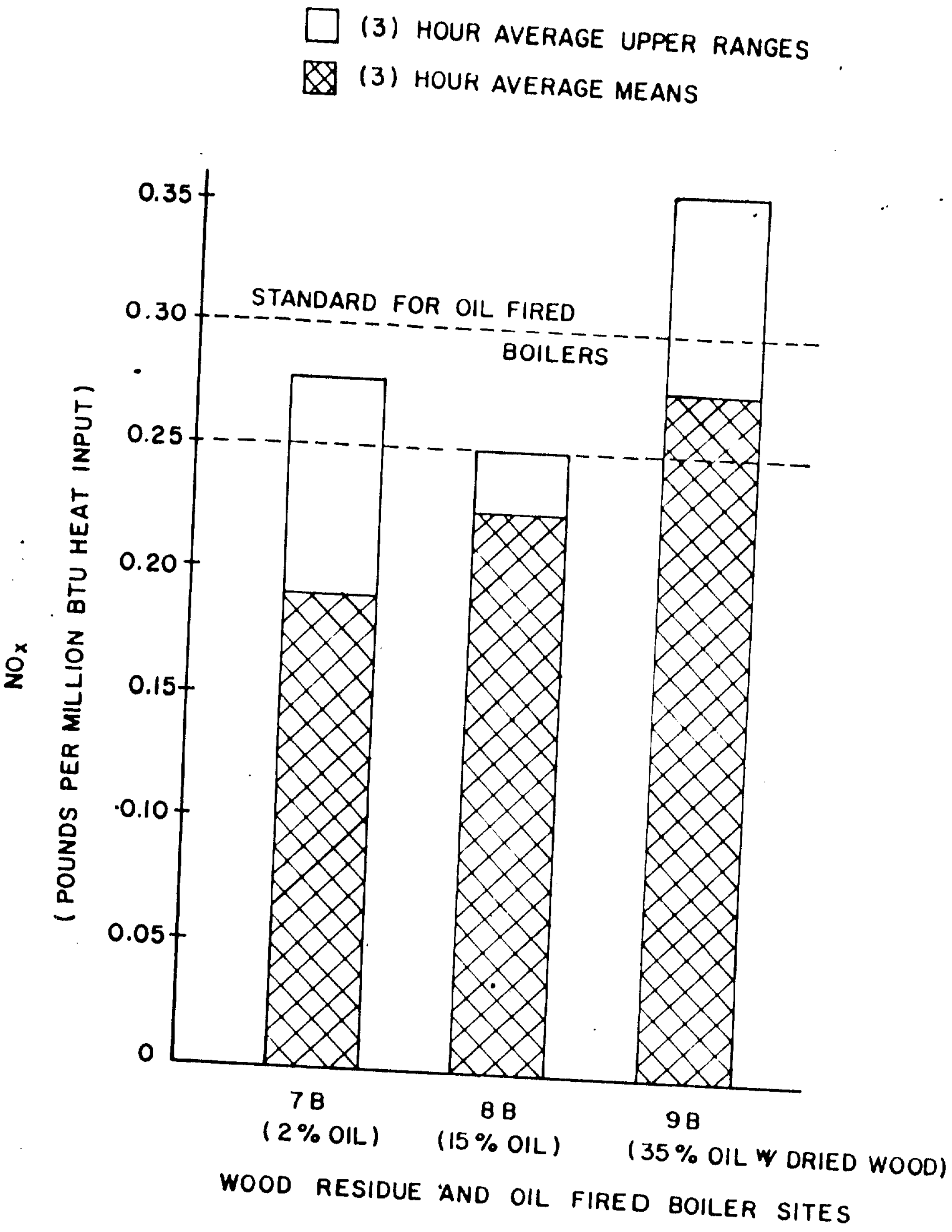

FIGURE 5 NO_x EMISSIONS FOR WOOD RESIDUE AND OIL FIRED BOILERS to 15 percent moisture fines injected into the overfire air ports in addition to the auxiliary oil fuel fired. An oil firing rate of 35 percent the total heat input produced a NOx emission mean that was roughly 27 percent higher than firing wood residue fuel alone. Inspection of Tables 4 and 5 allows a comparison of the two modes of boiler operation (i.e. w/ and w/o auxiliary oil). The upper range of NOx emissions increased by 22 percent with the quantity of auxiliary oil fired. This increase approximates that anticipated from this proportion of oil combustion.

The 50 hourly averages chosen and analyzed as the wood residue and oil data set designated as No. 9B were based on the following criteria. Only those hours of boiler operation with total steam production rates over 50 percent boiler capacity (which was equivalent to 80,000 pounds of steam per hour) and with wood residue contributed steam production rates over 50 percent the total steam rate for that hour were included in the data set. This criteria was necessitated in order to attain boiler oxides of nitrogen data during only relatively maximum normal boiler production intervals and not during very low boiler "swing" time periods. Since the oxides of nitrogen contribution based upon wood residue firing was the primary concern of this investigation, it was desirable to exclude the periods of high oil firing as an auxiliary fuel from the data base in this phase of the data analysis.

VI REVIEW OF RECENT EPA REPORT ON NOx EMISSION FACTORS FOR WOOD FIRED BOILERS

EPA recently published a report on the NOx levels arising fro the combustion of wood-residue (119). This report, issued in 1979 used information generated by Regional Office sampling teams, a contractor source sample, and EPA contractors. The population of bo ers upon which data were generated were for the most part small b ers, the largest burning wood alone when tested, being a boiler wit capacity of 50,000 lbs steam/hour. Of the boilers from which NOx emission data were available, 7 or 1/2 were less than 10,000 lbs steam/hour.

The EPA report is devoid of information on the duration of th monitoring period from which the data were drawn or the number of grab samples used in the compilation of the data. For those boile where wood alone was used as fuel, NOx emission rates were observe to be a function of boiler size. NOx emission increased with boil size, although there were exceptions to this rule. NOx was more closely related to percent excess air in the flue gas. The authors concluded that increasing amounts of excess air probably resulted in lower firebox temperatures, hence less NOx generation.

It was concluded that the NOx emissions from wood burning in smaller boilers (< than 100,000 lbs steam/hour), was considerably than fossil fuel boilers of comparable size and probably not as gr for the wood fired boilers above this size when compared to fossil fuel boilers. The NCASI study showed that NOx emissions from wood residue-fired boilers to be about the same as the standard for NOx in gas fired utility boilers (0.2 lbs/10^6 Btu) less than the standard for oil fired utility boilers (0.3 lbs/10^6 Btu) and substantially less than the standard for bituminous coal fired utility boilers, (0.6 lbs/10^6 Btu).

One of the more important observations to be made from the information presented in this report is the relationship of NOx emission factors reported and those in earlier and a frequently used reference publication. Where boilers burning wood alone were sampled, the NOx emissions ranged from < 0.1 to 2.4 lb/ton fuel or 1 to 24% of the emission factors for wood of 10 lb/ton fuel cited in AP-42 (114).

VII CURRENT NOx COMBUSTION SOURCE EMISSION STANDARDS AND THEIR RELATIONSHIP TO FINDINGS OF THIS STUDY

A. Current Standards

(1) Steam Generation - The New Source Performance Standards for steam generators firing fossil fuel at a rate of greater than 250 $(10)^6$ Btu/hour were amended to permit the use of wood in calculating allowable SO_2 emissions (120). At the time this amendment was made the NOx emission standard for boilers burning combinations of wood and fossil fuel were left the same as those for fossil fuel alone. The change in this regulation was made to encourage the substitution of wood as an alternate energy source for fossil fuels. The issue of NOx emission limits was not examined in detail since limited information indicated NOx from wood residue combustion was about the same or less than the standard for burning gas (0.2 lb/10^6 Btu) and less than the standard for oil or coal, 0.3 and 0.7 lbs/10^6 Btu respectively.

(2) Utility Boilers - The recently promulgated regulation for utility boilers firing fossil fuels at a rate over 250 $(10)^6$ Btu/hour carry NOx emission standards for the individual fossil fuels, gas, oil and bituminous coal of 0.2, 0.3 and 0.6 lbs/10^6 Btu respectively. These standards apply only to fossil fuel or fossil fuel derivatives, and are included here only for illustration and comparison of NOx emission from wood and fossil fuel (121).

B. NOx Emission Rates from Burning Combinations of Wood Residue and Fossil Fuel

This study was not designed to determine the NOx emission rates from burning combinations of fossil fuel and wood residues since boilers designed for minimal NOx emissions from fossil fuel were not available where wood was also burned. Such installations are now being built and this issue can be studied in more detail later.

The issue of how to estimate NOx emissions from the combusti of various combinations of wood residue and fossil fuel is not resolved. The findings of this study where NOx emissions were measu ed when wood residues were burned in conjunction with modest amoun of oil (about 35% of the total being the maximum), showed that bur ing this combination does not result in any exaggeration of NOx emi sions from wood residue when compared to when it is burned alone.

While the validity of calculating NOx emission rates from bu ing combinations of wood and fossil fuel by proportioning that fro wood and fossil fuel to the ratio of fuel burned was not demonstr it appears to be a viable means for estimating NOx emissions if th proper NOx emission rate from wood combustion is used. As illust earlier, the mean of 3 hour average NOx emission rates found in th study varied but for boilers with the highest NOx emission rate it about 0.2 to 0.25 lbs NOx/10^6 Btu when burning wood alone.

VIII SUMMARY

(1) The information contained in this bulletin includes oxides of nitrogen emission data generated at 11 wood residue fired combusti sites in the Northwest and Southwest United States. A comprehensi literature search was carried out which covered recent publication associated with NOx, (a) formation kinetic theory, (b) measurement techniques, (c) field sampling methodology, (d) source control stra tegies; (e) previously reported field results, and (f) the effects of these gases on the ambient.

(2) The chemiluminescence oxides of nitrogen measurement principl were discussed and presented in the literature as accurate and easi adapted to continuous sampling of combustion sources. This was in contrast to the widely accepted phenoldisulphonic acid grab sampli method. The details of a gas handling system for use with existin but slightly modified, chemiluminescent ambient NO/NOx monitors we also presented. The 100 percent (±10 percent) recovery of nitric oxide gas spiked into sampled combustion exhaust gas during the fi trials was found to reaffirm that NOx sample line losses can be ins nificant in properly designed systems.

(3) Summarization of the data compiled in this study is presented in a tabular format in Table 6 which is a synopsis of NOx "emission factors" for the sites sampled. The mean and range found for the various combustion sources are indicated in this table based on a three contiguous hour average criteria. Some pertinent observatio can be made. NOx emissions from wood combustion when compared to emission standards for NOx in utility boilers were (a) in the rang those for gas, 0.2 lbs/10^6 Btu, less than oil, 0.30 lbs/10^6 Btu, a (c) substantially less than those for bituminous coal, 0.06 lbs/10 Btu. The use of wood as a substitute for fossil fuel is therefore a favorable tradeoff for not only SO_2 emissions but for NOx emissi as well.

TABLE 6 NOx EMISSION RATE SUMMARY FOR WOOD RESIDUE BOILERS

Sampling Site and Boiler Type	NOx (3) Hour Average Mean (lb/10^6 Btu)	(ng/J)[1]	(lb/TWWF)[2]	(3) Hour Average Range (lb/10^6 Btu)	(ng/J)[1]	(lb/TWWF)[2]
1: S.S.	0.11	48	1.10	0.09-0.17	37-72	0.84-1.65
2: S.S.	0.14	61	1.14	0.11-0.16	46-69	0.86-1.28
3: S.S.	0.08	32	0.67	0.05-0.10	22-41	0.45-0.85
4: S.S.	0.13	57	1.18	0.08-0.18	36-77	0.75-1.60
5: S.S.	0.20	86	1.78	0.19-0.22	82-95	1.69-1.97
5B: S.S.	0.17	72	1.50	0.15-0.18	65-79	1.35-1.64
6A: S.S.	0.17	72	1.51	0.15-0.19	63-81	1.32-1.69
6B: S.S.	0.11	47	0.98	0.09-0.12	38-55	0.78-1.15
7A: S.S.	0.18	78	1.62	0.15-0.22	64-96	1.33-1.98
8A: S.S.	0.21	92	1.91	0.19-0.23	82-100	1.69-2.06
9A: S.S.(f)	0.22	94	1.43	0.11-0.29	45-125	0.69-1.91
10: F.B.	0.23	97	1.52	0.17-0.28	72-119	1.13-1.87
11: C.B.	0.11	48	1.82	0.08-0.14	36-60	1.37-2.28

1. 1 lb/10^6 Btu = 430 nanograms/Joule heat input.
2. Pounds NOx per ton wet wood fuel.
S.S. Spreader stoker boiler.
S.S. (f) Spreader stoker boiler with fuel dryer and fines injection in overfire air (these results were based on bark fuel only from multiple regression of NOx total (y), steam from bark (x_1) and steam produced from oil (x_2).
F.B. Fluidized bed boiler.
C.B. Cyclone burner w/o boiler section.

(4) Sites Nos. 5B and 6B represented NOx sampling conducted at locations following wet scrubber particulate control systems. Althou not taken simultaneously Nos. 5A and 6A correspond to wet scrubber let measurements for the respective sources. The reductions in NOx emissions across the wet scrubbers noted from the inlet and outlet data were judged to be, in part, a consequence of boiler operatin conditions during the sampling interval at each location. Lower o all furnace combustion temperatures were noted for the wet scrubbe outlet sampling interval when compared to the inlet sampling inter at each site. The benefits of wet scrubbing were found to be nomin if present at all insofar as NOx reduction was concerned.

(5) The opportunity was present to study the effect of firing oil an auxiliary fuel to wood residue in the production of NOx emissio at three sites. The locations labelled as Nos. 7A, 8A, and 9A repr sent 100 percent wood residue fuel. Values given in Table 6 for th sites can be used as baseline numbers to be compared with increase NOx emissions resulting from oil addition rates. Sources designate previously as Nos. 7B, 8B and 9B represented 2 percent, 15 percent, and 35 percent oil firing on a Btu basis. Data generated during th study indicated that oil additions of up to 15 percent did not hav significant effect on NOx emission levels. The firing of oil at a rate of 35 percent the total heat input with the balance dried wood residue having a moisture content of roughly 30 percent produced calculated increased NOx emissions of over 20 percent over those fr burning wood alone at one site studied.

(6) Based on measurements while firing 100 percent wood residue at proximately 50 percent moisture, the NOx emissions on a three conti ous hour average basis ranged from 0.05 to 0.23 pounds NOx per mill Btu's heat input. This corresponded to 0.45 to 2.06 pounds NOx pe ton of wet wood. This range represents the absolute minimum and ma imum values found from the sampling at eight sites. These NOx emis rates are about 5 to 20% of those in the EPA AP-42, a widely used s of emission estimates (114). The values for NOx generation from bu ing wood residues in combustion devices was similar but generally h er than those reported in more recent EPA reports for smaller boil (119).

(7) Source No. 9 represented in Table 6 utilized dried wood residu as fuel that was considerably lower in moisture content than the ot sources. Higher NOx emissions were found for this location as a p sible consequence of this mode of operation. A level of 0.29 pound of NOx per million Btu heat input or 1.9 pounds NOx per tone of we wood fuel was the highest three hour average determined for this si An additional combustion source was tested in order to address the wood fuel/NOx emission relationship. The results from this testing are denoted as site No. 11 in Table 6. Oxides of nitrogen ranged a high as 2.3 pounds per ton of wet wood fuel or 0.14 pounds per mill Btu heat input at this burner source. The effect of fuel drying pr tices on NOx emission production cannot be completely defined at th time, but may represent a potential for modest but not significant emissions.

(8) A fluidized bed wood boiler designated as No. 10 was sampled when firing wood residue with over 60 percent moisture content. The boiler generated 1.5 pounds NOx per ton of wet wood or 0.23 pounds per million Btu heat input which did not differ significantly from other sources sampled.

(9) Many boilers burn wood residues in combination with various ratios of fossil fuel. These ratios may be reasonably well fixed or may vary widely.

This study did not address in detail the NOx emissions from combinations of wood and fossil fuel. Measurements made while burning wood residues in conjunction with oil during this study and those reported by EPA when burning wood with coal or gas suggest that NOx from wood combustion is not increased when wood is combusted in conjunction with fossil fuel. There is question, however, whether the changes made in emission standards for steam generating units (   ) burning more than 250 $(10)^6$ Btu/hour fossil fuel in conjunction with wood residue incorporated an appropriate NOx emission standard for gas and wood combbinations. If an NOx emission factor based on fuel proportions fired and using the emission factor of 0.2 lbs NOx/10^6 gas fired called for in the existing calculation procedure, the standard is somewhat low based on NOx emission factors for wood combustion observed in this study. The opportunity to remedy this situation now exists during formulation of new source performance standards for industrial boilers and represents no real deterrent to the substitution of wood as an energy source for fossil fuels.

IX LITERATURE REFERENCES

(1) Aghassi, W.J., Cheremisinoff, P.N., "NOx Control In Central Station Boilers," Power Engineering 79 (6) 46-48 (June 1975).

(2) Allen, J.D., "Probe Sampling of Oxides of Nitrogen from Flames," Combustion and Flame 24 (1) 133-136 (February 1975).

(3) Allen, J.D., "A Review of Methods for Oxides of Nitrogen," Journal of Inst. Fuel 46 (382) 123-133 (January 1973).

(4) Allen, J.D., Billingsley, J., Shaw, J.T., "Evaluation of the Measurement of Oxides of Nitrogen in Combustion Products by the Chemiluminescence Method," J. Inst. Fuel 275-280 (December 1974).

(5) Altshuller, A.P., "Assessment of the Contribution of Chemical Species to the Eye Irritation Potential of Photochemical Smog," Journal of the Air Pollution Control Assoc. 28 (6) 594-598 (June 1978).

(6) Altshuler, S.L., "Design and Use of a Van Equipped to Measure Ambient Air Quality For Sulfur And Oxides Of Nitrogen Compounds," 68th Annual Meeting of the APCA, Paper No. 75-10.4 (June 1975).

(7) Angle, R.P., Sandhu, H.S., Schnitzler, W.J., "A Preliminary Field Study of Nitrogen Oxides in the Exhaust Plume from a Compressor Installation," 71st Annual Meeting of the Air Pollution Control Assoc., Paper No. 78-28.6 (June 25-30, 1978).

(8) Bagwell, F.A., Rosenthal, K.E., Teixeira, D.P., Breen, B.P., Bayard deVolo, N., Kerho, S., "Utility Boiler Operating Modes for Reduced Nitric Oxide Emissions," *Journal of the Air Pollution Control Assoc.* *21* (11) 702-708 (1971).

(9) Bambeck, R.J., Huettemeyer, H.F., "Operating Experience with In-Situ Power Plant Stack Monitors," 67th Annual Meeting of the Air Pollution Control Assoc., Paper No. 74-109 (June 9-13, 1974).

(10) Barrett, R.E., Putnam, A.A., "Boiler Emissions--An Inventory of Emissions by Boiler Size and Use," 69th Annual Meeting of the APCA, Paper No. 76-04.6 (June 27-July 1, 1976).

(11) Bartok, W., Crawford, A.R., Skopp, A., "Control of Nitrogen Oxide Emissions from Stationary Combustion Sources," *Combustion* *42* (4) 37-40 (October 1970).

(12) Benner, W.H., Urone, P., McMahon, C.K., Ryan, P., "Photochemical Potential of Forest Fire Smoke," 70th Annual Meeting of the Air Pollution Control Assoc., Paper No. 77-05.3 (June 20-24, 1977).

(13) Berger, A.W., Driscoll, J.N., Morgenstein, P., "Review and Statistical Analysis of Stack Sampling Procedures for the Sulfur and Nitrogen Oxides in Fossil Fuel Combustion," *Amer. Ind. Hyg. Assoc. J.* *33* (6) 397 (June 1972).

(14) Black, F.M., Sigsby, J.E., "Chemiluminescent Method for NO and NOx (NO + NO_2) Analysis," *Environmental Science & Technology* *8* (2) 149-152 (February 1974).

(15) Blakeslee, C.E., Burbach, H.E., "Controlling NOx Emissions from Steam Generators," *Journal of the Air Pollution Control Assoc.* *23* (1) 37-42 (January 1973).

(16) Blakeslee, C.E., Burbach, H.E., "Controlling NOx Emissions from Steam Generators," 65th Annual Meeting of the Air Pollution Control Assoc., Paper No. 72-75 (June 18-22, 1972).

(17) Chapman, R.L., "Continuous Stack Monitoring," *Environmental Science & Technology* *8* (6) 520-525 (June 1974).

(18) Chapman, R.S., M.D., "Health Effects Discussion," Journal of the Air Pollution Control Assoc. 28 (9) 887-889 (September 1978).

(19) Cheremisinoff, P., Eaton, W.B., "Combustion Control Methods to Limit NOx Emissions," Power Engineering 80 (9) 56-58 (September 1976).

(20) Clarenburg, L.A., Goumans, H.H.J.M., Pearse, J.D., Seaman, M.A., "On the Development of a Regional NOx Abatement Strategy," 71st Annual Meeting of the Air Pollution Control Assoc., Paper No. 78-5.5 (June 25-30, 1978).

(21) Clough, P.N., Thrush, B.A., Trans. Faraday Soc. 63 915 (1976).

(22) Clyne, M.A.A., Thrush, B.A., Wayne, R.P., Trans. Faraday Soc. 60 359 (1964).

(23) Coe, E.L., Ma, J.L., "Electrostatic Precipitation and Nitrogen Oxides in Flue Gases," 65th Annual Meeting of the Air Pollution Control Assoc., Paper No. 72-106 (June 18-22, 1972).

(24) Creekmore, A.T., Sableski, J.J., "EPA's Tentative Regulations to Implement the Short-Term Standard for Nitrogen Dioxide," 71st Annual Meeting of the Air Pollution Control Assoc., Paper No. 78-5.4 (June 25-30, 1978).

(25) Danielson, J.A., "Air Pollution Engineering Manual, Air Pollution Control District County of Los Angeles, EPA Publication No. AP-40 535-577 (May 1973).

(26) Dee, L.A., Martens, H.H., Merrill, C.I., Nakamura, J.T., Jaye, F.C., "New Manual Method for Nitrogen Oxides Emission Measurement," Analytical Chemistry 45 (8) 1477-1481 (July 1973).

(27) England, C., Houseman, J., Teixeira, D.P., Combustion and Flame 20 (3) 439-442 (June 1973).

(28) Ermenc, E.D., "Controlling Nitric Oxide Emission," Chemical Engineering 77 (12) 193-196 (June 1, 1970).

(29) Evans, M.J., Cabral-Anderson, L.J., Freeman, G., "Cell Proliferation in the Lungs of Aging Rats Exposed to NO_2," 69th Annual Meeting of the APCA, Paper No. 76-32.4 (June 27-July 1, 1976).

(30) Faith, W.L., "Oxides of Nitrogen," Chemical Engineering Progress 52 (8) 342-344 (August 1956).

(31) 41 Federal Register 51397 (November 22, 1976).

(32) 42 *Federal Register* 5936 (January 31, 1977).

(33) 42 *Federal Register* 41122 (August 15, 1977).

(34) 43 *Federal Register* 9278 (March 7, 1978).

(35) Ferris, B.G. Jr. M.D., "Health Effects of Exposure to Low Levels of Regulated Air Pollutants: A Critical Review," *Journal of the Air Pollution Control Assoc.* *28* (5) 482-497 (May 1978).

(36) Fiegley, C.E., "Some Statistical Aspects of Air Monitoring Instrument Calibration," 67th Annual Meeting of the Air Pollution Control Assoc., Paper No. 74-14 (June 9-13, 1974).

(37) Fine, D.H., "Critical Evaluation of Stalzman Technique for NOx-Analysis in the 0-100 ppm Range," *Environmental Science & Technology* *6* (4) 348-350 (April 1972).

(38) Fine, D.H., Slater, S.M., Sarofim, A.F., Williams, G.C., "Nitrogen in Coal as a Source of Nitrogen Oxide Emission From Furnaces," EPA Contract No. 22-69-44.

(39) First, M.W., Viles, F.J., "Cleaning of Stack Gases Containing High Concentrations of Nitrogen Oxides," *Journal of the Air Pollution Control Assoc.* *21* (3) 122-127 (March 1971).

(40) Floyd, J.R., "The Implementation of the NSPS Continuous Emission Monitoring Regulations in EPA, Region VIII," 71st Annual Meeting of the Air Pollution Control Assoc., Paper No. 78-35.1 (June 25-30, 1978).

(41) Fontijn, A., Sabadell, A.J., Ronco, R.J., "Homogeneous Chemiluminescent Measurement of Nitric Oxide with Ozone," *Analytical Chemistry* *42* (6) 575-579 (May 1970).

(42) Galeano, S.F., Kahn, D.C., Mack, R.A., "Air Pollution: Controlled Operation of a NSSC Recovery Furnace," *TAPPI* *54* (5) 741-744 (May 1971).

(43) Galeano, S.F., Leopold, K.M., "A Summary of Emissions of Nitrogen Oxides in the Pulp Mill," *TAPPI* *56* (3) 74-76 (March 1973).

(44) Gardner, D.E., Miller, F.J., Blommer, E.J., Coffin, D.L., "Experimental Studies on the Concentration-Time Relationship of NO_2 Exposure," 69th Annual Meeting of the APCA, Paper No. 76-32.5 (June 27-July 1, 1976).

(45) Giammar, R.D., Engdahl, R.B., "Technical, Economic, and Environmental Aspects of Industrial Stoker-Fired Boilers," 71st Annual Meeting of the Air Pollution Control Assoc., Paper No. 78-28.2 (June 25-30, 1978).

(46) Glass, N.R., "Environmental Effects of Increased Coal Utilization: Ecological Effects of Gaseous Emissions from Coal Combustion," EPA-600/7-78-108, U.S. EPA (June 1978).

(47) Glassman, I., Combustion Academic Press Inc., New York, New York (1977).

(48) Habelt, W.W., Selker, A.P., "The Role of Tangential Firing and Fuel Properties in Attaining Low NOx Operation for Coal-Fired Steam Generation," 71st Annual Meeting of the Air Pollution Control Assoc., Paper No. 78-64.1 (June 25-30, 1978).

(49) Halstead, C.J., Nation, G.H., Turner, L., Analyst 97 (1150) 55-63 (January 1972).

(50) Hamming, W.J., Dickinson, J.E., "Control of Photochemical Smog by Alteration of Initial Reactant Ratios," Journal of the Air Pollution Control Assoc. 16 (6) 317-323 (1966).

(51) Hardison, L.C., "Techniques for Controlling the Oxides of Nitrogen," Journal of the Air Pollution Control Assoc. 20 (6) 377-382 (June 1970).

(52) Healy, T.E., Urone, P., "Gas Chromatography of Oxidants Using a Flowing Liquid Colorimetric Detector," Anal. Chem. 41:1777 (1969).

(53) Heuss, J.M., Nebel, G.J., Colucci, J.M., "National Air Quality Standards for Automotive Pollutants-A Critical Review," Journal of the Air Pollution Control Assoc. 21 (9) 535-544 (September 1971).

(54) Higuchi, J.E., Hsu, A., MacPhee, R.D., "A Straightforward Dynamic Calibration Procedure for Use with NOx Instruments," 67th Annual Meeting of the Air Pollution Control Assoc., Paper No. 74-13 (June 9-13, 1974).

(55) Hodgeson, J.A., Rehme, K.A., Martin, B.E., Stevens, R.K., "Measurements for Atmospheric Oxides of Nitrogen and Ammonia by Chemiluminescence," 65th Annual Meeting of the Air Pollution Control Assoc., Paper No. 72-12 (June 18-22, 1972).

(56) Hunter, S.C., Carter, W.A., Buening, H.J., Cherry, S.S., "Application of Combustion Modifications To Industrial Combustion Equipment," Second Symposium on Stationary Source Combustion, Paper No. 182 (August 29-September 1, 1977).

(57) Instruction Manual: Nitrogen Oxides Model 8440E Analyzer, Monitor Labs, Inc., (August 9, 1977).

(58) Jacobs, M.E., Hochheisser, S., "Continuous Sampling and Ultramicrodetermination of Nitrogen Dioxide in Air," Analytical Chemistry 30 (3) 426-428 (March 1958).

(59) James, R.E., Cunningham, J.E., "Comparison of Stack Sampling Methods for Nitrogen Oxides," 71st Annual Meeting of the Air Pollution Control Assoc., Paper No. 78-35.6 (June 25-30, 1978).

(60) Jeffries, H., Fox, D.L., Kamens, R., "Photochemical Conversion of NO to NO_2 by Hydrocarbons in an Outdoor Chamber," 68th Annual Meeting of the APCA, Paper No. 75-16.2 (June 1975).

(61) Jordan, B.C., Broderick, A.J., "Emissions of Oxides of Nitrogen from Aircraft," Journal of the Air Pollution Control Assoc. 29 (2) 119-124 (February 1979).

(62) Kaye, N.A., Newberger, M.R., "No NOx...But How? - An Industrial Case History," 67th Annual Meeting of the Air Pollution Control Assoc., Paper No. 74-260 (June 9-13, 1974).

(63) Kijoura, R., "International Comparison and Critical Analysis of Nitrogen Dioxide Air Quality Standards," 69th Annual Meeting of the APCA, Paper No. 76-17.03 (June 27-July 1, 1976).

(64) Krumwiede, K.R., Norton, D.M., Johnston, G.W., Thompson, R.E., Breen, B.P., Quan, V., "A Probing Study of NO Formation in the Flame Zone of a 175 Mw Gas Fired Utility Boiler," 68th Annual Meeting of the APCA, Paper No. 75-23.4 (June 1975).

(65) Larsen, R.I., Gardner, D.E., Coffin, D.L., "An Air Quality Data Analysis System for Interrelating Effects, Standards and Needed Source Reductions: Part 5. Nitrogen Dioxide Mortality in Mice," 70th Annual Meeting of the Air Pollution Control Assoc., Paper No. 77-44.3 (June 20-24, 1977).

(66) Larsen, R.I., Gardner, D.E., Coffin, D.L., "An Air Quality Data Analysis System for Interrelating Effects, Standards, and Needed Source Reductions: Part 5. NO_2 Mortality in Mice," Journal of the Air Pollution Control Assoc. 29 (2) 133-137 (February 1979).

(67) Levaggi, D.A., Zerrudo, R., Karels, G., Oyung, W., Feldstein, M., "An Integrated Manual Impinger Method for the Simultaneous Determination of NOx and SOx in Source Effluents," 67th Annual Meeting of the Air Pollution Control Assoc., Paper No. 74-192 (June 9-13, 1974).

(68) Lucero, D.P., ASTM STP 598, 301 (1976).

(69) Lucero, D.P., "Continuous NOx Source Analysis by a Chemiluminescent/Diffusion Technique," ISA Transactions 16 (2) 71-80 (1977).

(70) Lusis, M.A., "The Effects of Sample Humidity on the Response Characteristics of SO_2 and NOx Analyzer Systems: Aircraft Plume Dispersion Studies," Journal of the Air Pollution Control Assoc. 28 (1) 26-29 (January 1978).

(71) MacKinnon, D.J., "Nitric Oxide Formation at High Temperatures," Journal of the Air Pollution Control Assoc. 24 (3) 237-239 (March 1974).

(72) Margeson, J.H., Beard, M.E., Suggs, J.C., "Evaluation of the Sodium Arsenite Method for Measurement of NO_2 in Ambient Air," Journal of the Air Pollution Control Assoc. 27 553-556 (June 1977).

(73) Margolis, G., Driscoll, J.N., "Critical Evaluation of Rate-Controlling Processes in Manual Determination of Nitrogen Oxides in Flue Gases," Environmental Science & Technology 6 (8) 727-731 (August 1972).

(74) Martin, R.R., Reed, R.D., "Pollution Control Practices: How NOx is Generated," Chemical Engineering Progress 74 (12) 59-61 (December 1978).

(75) Matsuda, S., Takenchi, M., Hishinuma, T., Nakajima, F., "Selective Reduction of Nitrogen Oxides in Combustion Flue Gases," 69th Annual Meeting of the APCA, Paper No. 76-04.3 (June 27-July 1, 1976).

(76) Matsuda, S., Takeuchi, M., Hishinuma, T., Nakajima, F., Narita, T., Watanabe, Y., Imanari, M., "Selective Reduction of Nitrogen Oxides in Combustion Flue Gases," Journal of the Air Pollution Control Assoc. 28 (4) 350-353 (April 1978).

(77) McCann, C.R., Demeter, J.J., Dzubay, J., Bienstock, D., "NOx Emissions from Two-Stage Combustion of Pulverized Coal," 65th Annual Meeting of the Air Pollution Control Association, Paper No. 72-73 (June 18-22, 1972).

(78) Midgett, M.R., "How EPA Validates NSPS Methodology," Environmental Science and Technology 11 (7) 655 (July 1977).

(79) Monsanto Research Corp., "Source Assessment Overview Matrix," EPA Contract No. 68-02-1874 (September 21, 1976).

(80) Morrison, M.E., Rinker, R.G., Corcoran, W.H., "Rate and Mechanism of Gas-Phase Oxidation of parts-per-million Concentrations of Nitric Oxide, Ind. & Eng. Chem. Fundamentals 5 (2) 175 (May 1966).

(82) "NBS Steps Up Environmental Activities," Chemical & Engineering News 52 (10) 26 (March 11, 1974).

(83) "New Tests Shine for Pollutants," Chemical Week 111 (12) 61 (September 20, 1972).

(84) Ootsuka, K., et al., "Development of New Type Catalytic NOx Removal Reactor," Paper No. 77-09.6 (June 20-24, 1977).

(85) Paskind, J., Kinosian, J.R., "Hydrocarbon, Oxides of Nitrogen and Oxidant Pollutant Relationships in the Atmosphere over California Cities," 67th Annual Meeting of the Air Pollution Control Assoc., Paper No. 74-31 (June 9-13, 1974).

(86) Reed. R.D., "Nitrogen Oxides Problems in Industry," Chemical Engineering/Deskbook Issue 84 (22) 153-157 (October 17, 1977).

(87) Ricci, L.J., "EPA Sets its Sights on Nixing CPI's NOx Emissions, Chemical Engineering 84 (4) 33-36 (February 14, 1977).

(88) Robertson, D.J., Groth, R.H., Gardner, D.G. and Glastris, A.G., "Stability and Analyses of Nitric Oxide in Nitrogen," Journal of the Air Pollution Control Assoc. 27 (8) 779-780 (August 1977).

(89) Romano, A.J., Huszagh, D.W., Klein, J., Doering, R., Newman, L., "The Use of a Self-Cleaning, Low-Cost Dilution System in the Conditioning of Flue Gases for Unattended SO_2 or NOx Monitoring," Combustion 45 (11) 36-39 (May 1974).

(90) Samuelson, G.S., Harman, J.N., "Chemical Transformations of Nitrogen Oxides While Sampling Combustion Products," Journal of the Air Pollution Control Assoc. 27 (7) 648-655 (July 1977).

(91) Samuelson, G.S., Harman, J.N. III, "Transformation of Oxides of Nitrogen Composition While Sampling Combustion Products," Paper presented at First Chemical Congress of the North American Continental American Chemical Socieety, Mexico City, pp 1-36 (December 1975).

(92) Sandberg, J.S., Levaggi, D.A., DeMandel, R.E., Sin, W., "Sulfate And Nitrate Particulates As Related To SO_2 And NOx Gases And Emissions," 68th Annual Meeting of the APCA, Paper No. 75-62.5 (June 1975).

(93) Shahed, S.M., Newhall, H.F., "Kinetics of Nitric Oxide Formation in Propane-Air and Hydrogen-Air Diluent Flames," Combustion and Flame 17 (2) 131-137 (October 1971).

(94) Shen, T.T., "Online Instruments Expedite Emission Tests," Chemical Engineering 82 (11) 109-112 (May 26, 1975).

(95) Shen, T.T., "Selection of Instrument Methods for SO_2 and NOx Source Testing," 67th Annual Meeting of the Air Pollution Control Assoc., Paper No. 74-188 (June 9-13, 1974).

(96) Shen, T.T., Stasiuk, W.N., "Performance Characteristics of Stack Monitoring Instruments for Oxides of Nitrogen," Journal of the Air Pollution Control Assoc. 25 (1) 44-47 (January 1975).

(97) Shy, C.M., et al., "The Chattanooga School Children Study: Effects of Community Exposure to Nitrogen Dioxide. 1. Methods, Description of Pollutant Exposure, and Results of Ventilatory Function Testing," Journal of the Air Pollution Control Assoc. 20 (8) 539-545 (August 1970).

(98) Sickles, J.E. II, Ripperton, L.A., "Ozone-Precursor Relationship of Nitrogen Dioxide, Isopentane and Sunlight under Selected Conditions," 70th Annual Meeting of the Air Pollution Control Assoc., Paper No. 77-05.2 (June 20-24, 1977).

(99) Siddiqi, A.A., Tenini, J.W., Killion, L.D., "Control NOx Emissions From Fixed Fireboxes," Hydrocarbon Processing 55 (10) 94-97 (October 1976).

(100) Siegmund, C.W., Turner, D.W., "NOx Emissions from Industrial Boilers: Potential Control Methods," Journal of Engineering for Power: Transactions of the ASME 96 (1) 1-6 (January 1974).

(101) Spicer, C.W., Miller, D.F., "Nitrogen Balance in Smog Chamber Studies," 67th Annual Meeting of the Air Pollution Control Assoc., Paper No. 74-247 (June 9-13, 1974).

(102) Stevens, R.K., Clark, T.A., Decker, C.E., Ballard, L.F., "Field Performance Characteristics of Advanced Monitors for Oxides of Nitrogen, Ozone, Sulfur Dioxide, Carbon Monoxide, Methane, and Nonmethane Hydrocarbons," 65th Annual Meeting of the Air Pollution Control Assoc., Paper No. 72-13 (June 18-22, 1972).

(103) Takagi, T., Fujii, K., Ogasawara, M., "Evaluation of Various Factors Affecting Nitric Oxide Formation and Effectiveness of Some Emission-Control Systems," Fuel 53 (2) 114-119 (April 1974).

(104) Tarbell, J.M., Petty, C.A., "Combustion Modifications for the Control Of NOx Emissions," Chemical Engineering Science 32 (10) 1177-1188 (1977).

(105) Thompson, C.R., Tingey, D.T., Reinert, R.A., "Acceptable Limits for Air Pollution Dosages and Vegetation Effects: Nitrogen Dioxide," 67th Annual Meeting of the Air Pollution Control Assoc., Paper No. 74-227 (June 9-13, 1974).

(106) Trowell, J.M., "Gas Chromatographic Separation of Oxides of Nitrogen," Anal. Chem. 37:1152 (1965).

(107) Turner, G., "Some Considerations in Quantitative Determination of NO, NO_2, and NOx by Chemiluminesence Analyzer," 67th Annual Meeting of the Air Pollution Control Assoc., Paper No. 74-32 (June 9-13, 1974).

(108) Vogt, R.A., Laurendeau, N.M., "Preliminary Measurements of Fuel Nitric Oxide Formation in a Pulverized Coal Transport Reactor," Journal of the Air Pollution Control Assoc. 28 (1) 60-63 (January 1978).

(109) White, A., Beddowa, L.M., "The Choice of Sampling Tube Material in the Determination of Nitrogen Oxide Concentrations in Products of Combustion," J. Appl. Chem. Biotechnol. 23:759 (1973).

(110) Wolf, P.C., "Systems for Continuous Stack-Gas Monitoring," Mechanical Engineering 96 (4) 22-28 (April 1974).

(111) Wolf, P.C., "Systems for Continuous Stack-Gas Monitoring, Part 2: Gas Handling Components and Accessories," Mechanical Engineering 96 (5) 43-48 (May 1974).

(112) Woolrich, P.F., "Methods for Estimating Oxides of Nitrogen Emissions from Combustion Processes," Industrial Hygiene Journal 481-484 (December 1961).

(113) Wright, R.S., Sickles, J.E. II, Eaton, W.C., Kamens, R.M., Jeffries, H.E., "Comparison Between Two Outdoor Smog Chamber Facilities: Matched Experiments," 70th Annual Meeting of the Air Pollution Control Assoc., Paper No. 77-05.1 (June 20-24, 1977).

(114) "Compilation of Air Pollutant Emission Factors," 3rd Ed., U.S. EPA, Publication No. AP-42, RTP, N.C., pp. 1.6-2 (August 1977).

(115) 43 Federal Register 42154 (September 19, 1978).

(116) 43 Federal Register 42183 (September 19, 1978).

(117) Folsom, B.A., Courtney, C.W., "Accuracy of Chemiluminescent Analyzers Measuring Nitric Oxide in Stack Gases," Journal of the Air Pollution Control Assoc. 29 (11) 1166-1169 (November 1979).

(118) Folsom, B.A., Courtney, C.W., "Chemiluminescent Measurement of Nitric Oxide in Combustion Products," In: Proceedings of the Third Stationary Source Combustion Symposium Vol. II, Advanced Processes and Special Topics, EPA-600/7-79-050B pp. 283-314 (February 1979).

(119) NOx Emission Factors for Wood-Fired Boilers, EPA-300/7-79-219, September 1979.

(120) "Information On The Sulfur Content Of Bark And Its Contribution To SO_2 Emissions As A Fuel," Atmospheric Quality Improvement Technical Bulletin No. 96, August 1978, National Council of the Paper Industry for Air and Stream Improvement, Inc.

(121) 44 Federal Register 33612 (June 11, 1979).

SOURCE CATEGORY: Wood Waste
EXCLUSION CRITERIA CHECKLIST

REFERENCE #24 "a Study of Nitrogen Oxides Emissions from Wood Residue Boilers" (1979) NCASI

CRITERIA	YES	NO
1. Test series averages are reported in units that can be converted to the selected reporting units?	✓	
2. Test series respresent compatible test methods?	✓	
3. In tests in which emission control devices were used, the control devices are fully specified?	✓	
4. Is the source process clearly identified and described?	✓	
5. Is it clear whether or not the emissions were controlled (or not controlled)?	✓	

Form filled out by Megan Day

Date 3/27/92

INDICATE WHETHER ANSWER IS YES OR NO WITH AN "X" IN APPROPRIATE BOX.

IF ALL ANSWERS ARE "YES" PROCEED TO METHODOLOGY/DETAIL CRITERIA CHECKLIST.

[illegible]

SOURCE CATEGORY: Wood Waste

METHODOLOGY/DETAIL CRITERIA CHECKLIST

REFERENCE #24 A Study of Nitrogen Oxide emission

CRITERIA	YES	NO	COMMENTS
1. Is the manner in which the source was operated well documented in the report?	X		
Was the source operating within typical parameters during the test?	X		
2. Did sampling procedures deviate from standard methods?		X	
If so, were the deviations well documented?			
Were the deviations appropriate?			
Comment on how any alterations in sampling procedure may have influenced the results.			
3. Were there wide variations in the results?	/		[illegible]
If yes, can the variations be adequately explained by information in the report?		/	
If the variations are not well explained, should the data be considered of poor quality?		/	The purpose of the test was to measure NOx. CO_2 data was not collected at this [illegible]
4. Do the test reports contain original raw data sheets?		/	
Are the nomenclature and equations used equivalent to those specified by the EPA?	/		
Comment on the consistency amd completeness of the results.			The O_2 data is [illegible] from best available methodology.

Form filled out by

Date 3/21/92

INDICATE WHETHER ANSWER IS YES OR NO WITH AN "X" IN APPROPRIATE BOX. FILL IN COMMENTS.

IF ,BASED ON ABOVE ANSWERS, IT IS DETERMINED THAT SOURCE REPORTS PROVIDE ADEQUATE DETAIL AND DEMONSTRATE A SOUND METHODOLOGY, PROCEED TO RATING THE DATA IN THE RATING CRITERIA CHECKLIST.

SOURCE CATEGORY: Wood Waste
RATING CRITERIA CHECKLIST

REFERENCE

RATING	CRITERIA	YES	NO
A	Tests performed by a sound methodology and reported in enough detail for adequate validation?		X
B	Tests were performed by a generally sound methodology, but not enough detail for adequate validation?	X	
C	Were tests based on untested or new methodology that lacks significant amount of background data?		X
D	Were tests based on generally unacceptable methods, but may provide order-of-magnitude values for the source?		X

COMMENTS

Form filled out by L Megamlay

Date 3-24-92

BASED ON ANSWERS TO ABOVE, AND COMMENTS, ASSIGN A RANK TO THIS LITERATURE SOURCE:

C	**RANK ASSIGNED TO EMISSION SOURCE DATA**

for 2