



NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

**METHANE (CH₄) AND
NITROUS OXIDE (N₂O) EMISSIONS
FROM BIOMASS-FIRED BOILERS
AND RECOVERY FURNACES**

**TECHNICAL BULLETIN NO. 998
SEPTEMBER 2012**

**by
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Acknowledgments

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PRESIDENT'S NOTE

The Mandatory Reporting of Greenhouse Gases Rule (40 CFR Part 98), issued by the United States Environmental Protection Agency in 2009, requires the annual reporting of greenhouse gas data and other relevant information from large emissions sources. Under this rule, reporting is required of pulp and paper mills and other facilities with stationary combustion units where facility-wide greenhouse gas emissions from applicable sources are greater than 25,000 metric tonnes of carbon dioxide (CO₂) equivalents (CO₂ eq.) per year. Wood products facilities are also required to report if the aggregate maximum rated heat input capacity of stationary fuel combustion units at the facility is 30 MMBtu/hr or greater and the facility emits 25,000 metric tonnes CO₂ eq. or more per year. While biogenic CO₂ emissions are not considered when determining if a facility's total emissions exceed the reporting threshold, emissions of methane (CH₄) and nitrous oxide (N₂O) from biogenic sources are considered. Emissions from most pulp and paper mills and a limited number of wood products facilities are expected to exceed these reporting thresholds.

As part of this reporting requirement, pulp and paper mills have to report CH₄ and N₂O emissions from all fuels, both separated by fuel type and in aggregate. This requirement applies to emissions from stationary combustion devices, chemical recovery furnaces, and lime kilns. Given the limited data availability and uncertainty surrounding currently available emission factors, NCASI has carried out a study to develop additional data for CH₄ and N₂O emissions from biomass-fired boilers and kraft recovery furnaces. CH₄ and N₂O emissions from five combination boilers, five direct contact evaporator (DCE) recovery furnaces, and three non-direct contact evaporator (NDCE) recovery furnaces were measured using Fourier transform infrared spectroscopy (FTIR). Additionally, data on CH₄ emissions from 22 biomass-fired boilers, obtained as part of the 2009 Boiler MACT/CISWI testing program, have been reviewed and summarized as part of this study.

The emission factors developed from this study are generally lower than those in current use and are likely more reflective of current emissions from sources in North America.

A handwritten signature in black ink, appearing to read "Ron Yeske", is written over a horizontal line.

Ronald A. Yeske

September 2012

NOTE DU PRÉSIDENT

Le règlement sur la déclaration obligatoire des gaz à effet de serre (*40 CFR Part 98*) qui a été publié par l'Agence de protection de l'environnement des États-Unis (EPA) en 2009 oblige les grands émetteurs à produire une déclaration annuelle sur leurs émissions de gaz à effet de serre et à fournir d'autres renseignements pertinents. En vertu de ce règlement, les usines de pâtes et papiers et tout autre établissement ayant des unités de combustion stationnaires doivent produire une déclaration si la somme des émissions de gaz à effet de serre de toutes les sources applicables de l'établissement est supérieure à 25 000 tonnes métriques en équivalents CO₂ par année. Les usines de produits du bois doivent aussi produire une déclaration si la somme de la capacité nominale maximale de chaque unité de combustion stationnaire de l'usine est égale ou supérieure à 30 MMBtu/h et si l'usine émet 25 000 tonnes métriques ou plus d'équivalents CO₂ par année. Bien que l'on ne tienne pas compte des émissions biogéniques de CO₂ pour déterminer si les émissions totales d'un établissement excèdent le seuil de déclaration, il faut cependant tenir compte des émissions de méthane (CH₄) et d'oxyde nitreux (N₂O) provenant de sources biogéniques. On prévoit que les émissions de la plupart des usines de pâtes et papiers et celles d'un petit nombre d'usines de produits du bois dépasseront les seuils de déclaration.

En vertu de ce règlement, les usines de pâtes et papiers doivent déclarer les émissions de CH₄ et de N₂O de tous les combustibles de deux façons : le total par type de combustible et le total pour l'ensemble des combustibles combinés. Cette exigence s'applique aux unités de combustion stationnaires, aux chaudières de récupération des usines de pâte kraft et aux fours à chaux. Compte tenu du peu de données existant dans la littérature et de l'incertitude entourant les facteurs d'émission actuels, NCASI a réalisé une étude pour générer des données supplémentaires sur les émissions de CH₄ et de N₂O provenant des chaudières à biomasse et des chaudières de récupération. NCASI a mesuré les émissions de CH₄ et de N₂O provenant de cinq chaudières à biomasse, cinq chaudières de récupération avec évaporateurs à contact direct (DCE) et de trois chaudières de récupération avec évaporateurs à contact indirect (NDCE) à l'aide d'un spectromètre infrarouge à transformée de Fourier (IRTF). De plus, NCASI a analysé les données sur les émissions de CH₄ de 22 chaudières à biomasse obtenues dans le cadre du programme de caractérisation *Boiler MACT/CISWI* réalisé en 2009, et a inclus un résumé de cette analyse dans la présente étude.

Les facteurs d'émission développés dans le cadre de la présente étude sont généralement inférieurs aux facteurs présentement en usage et sont probablement plus représentatifs des émissions actuelles des sources d'émission en Amérique du Nord.



Ronald A. Yeske

Septembre 2012

METHANE (CH₄) AND NITROUS OXIDE (N₂O) EMISSIONS FROM BIOMASS-FIRED BOILERS AND RECOVERY FURNACES

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ABSTRACT

NCASI conducted a study to quantify methane (CH₄) and nitrous oxide (N₂O) emissions from biomass-fired boilers and kraft recovery furnaces in order to develop emission factors for potential use in greenhouse gas (GHG) inventories. As part of this study, CH₄ and N₂O emissions from five biomass-fired boilers, five direct contact evaporator (DCE) recovery furnaces, and three non-direct contact evaporator (NDCE) recovery furnaces were measured using extractive Fourier Transform Infrared (FTIR) spectroscopy. Data on CH₄ emissions from 22 biomass-fired boilers, provided in the 2009 Boiler MACT/CISWI test reports, were also included in this study. For biomass boilers, average CH₄ and N₂O emissions were 0.0049 kg/MMBtu and 0.0019 kg/MMBtu, respectively. For DCE recovery furnaces, average CH₄ and N₂O emissions were 0.0024 kg/MMBtu and 0.00036 kg/MMBtu, respectively. In the case of NDCE recovery furnaces, average CH₄ and N₂O emissions were 0.0014 kg/MMBtu and 0.00044 kg/MMBtu, respectively. Average emissions of CH₄ and N₂O were found to be lower than the default emission factors provided by EPA in the *Federal Register* [74 FR 56260] for use in GHG reporting calculations (solid biomass fuels: 0.032 kg CH₄/MMBtu and 0.0042 kg N₂O/MMBtu in Table C-2; softwood kraft pulping liquor: 0.030 kg CH₄/MMBtu and 0.005 kg N₂O/MMBtu in Table AA-1).

KEYWORDS

biomass boilers, boilers, combination boilers, GHG emission factors, GHGRR, greenhouse gas (GHG) emissions, methane (CH₄), nitrous oxide (N₂O), recovery furnaces

RELATED NCASI PUBLICATIONS

Technical Bulletin No. 984 (April 2011). *Greenhouse gas and non-renewable energy benefits of black liquor recovery.*

Special Report No. 08-05 (September 2008). *The greenhouse gas and carbon profile of the U.S. forest products sector.*

Special Report No. 07-09 (October 2007). *The greenhouse gas and carbon profile of the Canadian forest products industry.*

Special Report No. 07-02 (February 2007). *The greenhouse gas and carbon profile of the global forest products industry.*

Special Report No. 01-05 (December 2001). *Technologies for reducing carbon dioxide emissions: a resource manual for pulp, paper, and wood products manufactures.*

Special Report No. 99-02 (June 1999). *Estimating costs for the U.S. forest products industry to meet the greenhouse gas reduction target in the Kyoto protocol.*

ÉMISSIONS DE MÉTHANE (CH₄) ET D'OXYDE NITREUX (N₂O) PROVENANT DES CHAUDIÈRES À BIOMASSE ET DES CHAUDIÈRES DE RÉCUPÉRATION

BULLETIN TECHNIQUE N° 998
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RÉSUMÉ

NCASI a réalisé une étude pour quantifier les émissions de méthane (CH₄) et d'oxyde nitreux (N₂O) provenant de chaudières à biomasse et de chaudières de récupération (procédé kraft) afin de développer des facteurs d'émission pouvant servir éventuellement à établir des inventaires de gaz à effet de serre (GES). Dans le cadre de cette étude, NCASI a mesuré les émissions de CH₄ et de N₂O provenant de cinq chaudières à biomasse, cinq chaudières de récupération avec évaporateurs à contact direct (DCE) et de trois chaudières de récupération avec évaporateurs à contact indirect (NDCE) à l'aide d'un spectromètre infrarouge à transformée de Fourier (IRTF). NCASI a également inclus les données sur les émissions de CH₄ provenant de 22 chaudières à biomasse contenues dans les rapports de caractérisation du programme *Boiler MACT/CISWI* réalisé en 2009. La valeur moyenne des émissions de CH₄ et de N₂O des chaudières à biomasse était 0,0049 kg/MMBtu et 0,0019 kg/MMBtu, respectivement. La valeur moyenne des émissions de CH₄ et de N₂O des chaudières de récupération avec évaporateurs à contact direct (DCE) était 0,0024 kg/MMBtu et 0,00036 kg/MMBtu, respectivement. La valeur moyenne des émissions de CH₄ et de N₂O des chaudières de récupération avec évaporateurs à contact indirect (NDCE) était 0,0014 kg/MMBtu et 0,00044 kg/MMBtu, respectivement. On constate que les valeurs moyennes des émissions de CH₄ et de N₂O sont inférieures aux valeurs des facteurs d'émission inscrits dans le registre fédéral [74 FR 56260] par l'EPA pour calculer les émissions de GES à déclarer (biomasse solide : 0,032 kg CH₄/MMBtu et 0,0042 kg N₂O/MMBtu dans le tableau C-2; liqueur usée de pâte kraft de résineux : 0,030 kg CH₄/MMBtu et 0,005 kg N₂O/MMBtu dans le tableau AA-1).

MOTS-CLÉS

chaudières, chaudières à biomasse, chaudières de récupération, émissions de gaz à effet de serre (GES), exigences de déclaration des GES, facteurs d'émission des GES, méthane (CH₄), oxyde nitreux (N₂O)

AUTRES PUBLICATIONS DE NCASI

Bulletin technique n° 984 (avril 2011). *Greenhouse gas and non-renewable energy benefits of black liquor recovery.*

Rapport spécial n° 08-05 (septembre 2008). *The greenhouse gas and carbon profile of the U.S. forest products sector.*

Rapport spécial n° 07-09 (octobre 2007). *The greenhouse gas and carbon profile of the Canadian forest products industry.*

Rapport spécial n° 07-02 (février 2007). *The greenhouse gas and carbon profile of the global forest products industry.*

Rapport spécial n° 01-05 (décembre 2001). *Technologies for reducing carbon dioxide emissions: a resource manual for pulp, paper, and wood products manufactures.*

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NITROUS OXIDE (N₂O) AND METHANE (CH₄) EMISSIONS FROM BIOMASS-FIRED BOILERS AND RECOVERY FURNACES

1.0 INTRODUCTION

1.1 Background

The US Environmental Protection Agency (EPA) issued the Mandatory Reporting of Greenhouse Gases Rule (40 CFR Part 98) in October 2009, requiring the annual reporting of greenhouse gas (GHG) data and other relevant information from large sources and suppliers in the United States (USEPA 2009).

Implementation of Part 98 is referred to as the Greenhouse Gas Reporting Rule (GHGRR). Under this rule, reporting is required of pulp and paper mills and other facilities with stationary combustion units where facility-wide greenhouse gas (GHG) emissions from applicable sources are greater than 25,000 metric tonnes of carbon dioxide (CO₂) equivalents (CO₂ eq.) per year. This rule is intended to facilitate the development of comprehensive, nationwide emissions data that provide a better understanding of the sources of GHGs and guide the development of policies and programs to reduce emissions. Additionally, the public availability of data is intended to allow reporters to benchmark their emissions against those from similar facilities and aid in identifying cost-effective opportunities to reduce emissions in the future.

CO₂, methane (CH₄), and nitrous oxide (N₂O) are the three major GHGs produced in pulp and paper manufacturing. Of the three major GHGs, CO₂ emissions are predominant and can be attributed to the burning of fossil fuels and solid biomass fuels (e.g., wood/wood residuals, bark, etc.) in boilers and pulping liquors in chemical recovery furnaces. The pulp and paper industry is heavily reliant on these sources for both energy and chemical recovery. Although biogenic CO₂ emissions do not apply towards the reporting threshold under GHGRR, facilities exceeding the reporting threshold are required to report biogenic CO₂ emissions under a separate category. CH₄ and N₂O emissions from these sources, both of fossil and of biogenic origin, also need to be reported, both separated by fuel type and in aggregate. CH₄ and N₂O are emitted in much lower concentrations than CO₂ from combustion sources in the pulp and paper industry. However, given the greater global warming potentials of CH₄ and N₂O (21 times and 310 times the warming potential of CO₂, respectively; IPCC 1996) it is important to develop additional data on emissions of these compounds from pulp and paper industry sources.

In the GHGRR, EPA has provided default emission factors for use in estimating CH₄ and N₂O emissions from the combustion of solid biomass fuels and kraft pulping liquors. The default CH₄ and N₂O emission factors for solid biomass fuels are 0.032 kg/MMBtu and 0.0042 kg/MMBtu¹, respectively. For North American softwood kraft pulping liquor, the emission factors are 0.030 kg CH₄/MMBtu and 0.005 kg N₂O/MMBtu (USEPA 2009). The factors for solid biomass combustion were derived by EPA from Tier 1 CH₄ and N₂O emission factors published by the Intergovernmental Panel on Climate Change (IPCC 2006). The factors for kraft pulping liquor were derived by EPA from an analysis of a summary, prepared by NCASI, of literature generated between 1985 and 2004, and published by The World Research Institute and The World Business Council for Sustainable Development (WRI/WBCSD 2005). EPA chose the highest of the values provided in the summary for use in the GHGRR.

¹ **Note on emission units:** In the GHGRR [74 FR 56260], EPA has mandated the use of specific emission factors for CH₄ and N₂O (USEPA 2009). These default emission factors are expressed in kg/MMBtu. Additionally, the rule requires the use of High Heating Values (HHV) of the fuel when using these emission factors to calculate mass emissions of GHG. The emission factors are, in essence, expressed in **kg/MMBtu HHV**. In order to be consistent with the approach used by EPA in the rulemaking and to better facilitate comparison, all emission data generated from the NCASI study are also expressed in **kg/MMBtu**, with HHV for the fuel being used as opposed to the Low Heating Value (LHV). It is assumed that there is a 5% difference between the LHV and HHV of the fuels.

An NCASI review of more recent literature indicates a dearth of accurate and direct emission measurements of CH₄ and N₂O from biomass-fired boilers and kraft recovery furnaces, especially those located in North America. As a result, the validity of existing emission factors, including those recommended by EPA, has come under scrutiny. Given the emphasis being placed on GHG inventories, the limited data availability, and uncertainty surrounding currently available emission factors, NCASI carried out a study to develop additional data for CH₄ and N₂O emissions from these sources.

As part of NCASI testing, emission measurements were conducted at 13 sources, including five biomass-fired boilers, five direct contact evaporators (DCE) recovery furnaces, and three non-direct contact evaporator (NDCE) recovery furnaces. CH₄ and N₂O concentrations in the stack gases were quantified using a portable Fourier transform infrared (FTIR) analyzer.

EPA, using its authority under Section 114 of the Clean Air Act, issued an information collection request (ICR) in June 2009 to approximately 300 industrial, commercial, and institutional boilers and commercial and industrial solid waste incineration (CISWI) sources nationwide, requiring them to conduct emissions testing for several hazardous air pollutants (HAPs) and surrogates like CH₄. The data collected from this effort have been used in the Boiler MACT rulemaking for floor determinations and setting emission standards. In addition to generating data from targeted testing, NCASI has compiled additional data on CH₄ emissions from the Boiler MACT/CISWI test reports in order to increase the sample size and develop a more robust emission factor for CH₄ from biomass-fired boilers. CH₄ emission data from 19 boilers tested as part of Boiler MACT program and three boilers tested as part of the commercial and industrial solid waste incineration (CISWI) program have been incorporated into the emission factors developed as part of this study. These boilers were predominantly burning biomass fuels during these tests (>80% of heat input from biomass fuels). CH₄ emissions at these sources were quantified using gas chromatography (GC) as required by EPA Method 18.

1.2 Study Objectives

This study was initiated in response to the need for accurate and direct emission measurements of CH₄ and N₂O from biomass boilers and recovery furnaces and the lack of availability of such data. Specific objectives of this study were to (1) obtain direct emission measurements of CH₄ and N₂O from biomass-fired boilers, DCE recovery furnaces, and NDCE recovery furnaces via FTIR analysis, (2) summarize CH₄ emissions data from EPA's recent Boiler MACT ICR, (3) develop CH₄ and N₂O emission factors for potential use in future PSD and Title V permit modifications, and (4) facilitate a comparison of these factors with the default emission factors mandated by EPA for use in GHG inventories as part of the GHGRR.

2.0 SAMPLING AND ANALYSIS METHODS

2.1 FTIR

During the NCASI testing, target analytes were quantified on site using a portable FTIR analyzer. In this instance, EPA Method 320's Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy (USEPA 1999) is the most appropriate method available. ASTM International Standard Test Method D 6348-03's Determination of Gaseous Compounds by Extractive Direct Interface FTIR Spectroscopy (ASTM 2003) is an EPA-approved alternative to Method 320. The ASTM method was employed as the primary reference method for all FTIR analyses carried out during this study.

2.1.1 Hardware Components

FTIR Spectrometer: The spectrometer used for analysis was a portable Gasmet™ DX-Series FTIR. The IR source is a ceramic element heated to 1275°C. The interferometer is a Temet Instruments CICCOR Interferometer with a resolution of 8 cm⁻¹ and an aperture of 1". The sample cell is a 0.5 L multipass cell

with gold/rhodium-coated mirrors and a fixed path length of 5 m. The detector is a thermo-electrically cooled MCT detector.

Data Acquisition System: Laptop with Temet Instruments CALCMET™ software for data acquisition and analysis of IR data. All IR spectra and supporting information were stored on the laptop.

Sample Conditioning System: A sample conditioning system was employed in this study in order to (1) prevent interferences and potential bias due to high levels of source moisture and (2) enhance bag sample stability. The conditioning system was placed in front of the heated-filter assembly and consisted of an empty impinger to condense source moisture and a silica gel impinger to remove entrained moisture and SO₂ from the gas stream. The performance of the conditioning system was evaluated both in the laboratory and in the field. The results provided in Appendix C indicate that this setup is appropriate for conditioning the gas stream.¹

Sample Probe: 3/8" stainless steel 316 tubing of sufficient length to access the sampling location on the stack.

Heated Filter Assembly: Ceramic filter, rated at 2 μm, seated inside heated-filter housing. Dilution/spike gases can be added upstream of the heated filter through a T-valve assembly.

Sampling Lines: Heated 1/4" PTFE line. Additional heated 1/4" line for dilution/spike gases.

Heated Sample Pump Assembly: The assembly contains a heated KNF pump and a ZrO₂ oxygen sensor. Assembly also includes heater controllers for the sample pump and heated lines, as well as a vacuum gauge for leak checks.

Mass Flow Control: Two Brooks® mass flow controllers capable of supplying an accurate, constant flow of dilution air or spike gas to the heated probe assembly.

Nitrogen Pneumatic Assembly: The assembly allows a single nitrogen source to be split for continuous optical purge and delivery of nitrogen to the heated filter assembly for background measurement.

Gas cylinders: Ultra-high purity nitrogen and EPA protocol calibration standards for analyte spiking and CTS measurements.

Figure 2.1 depicts the FTIR sampling system configuration.

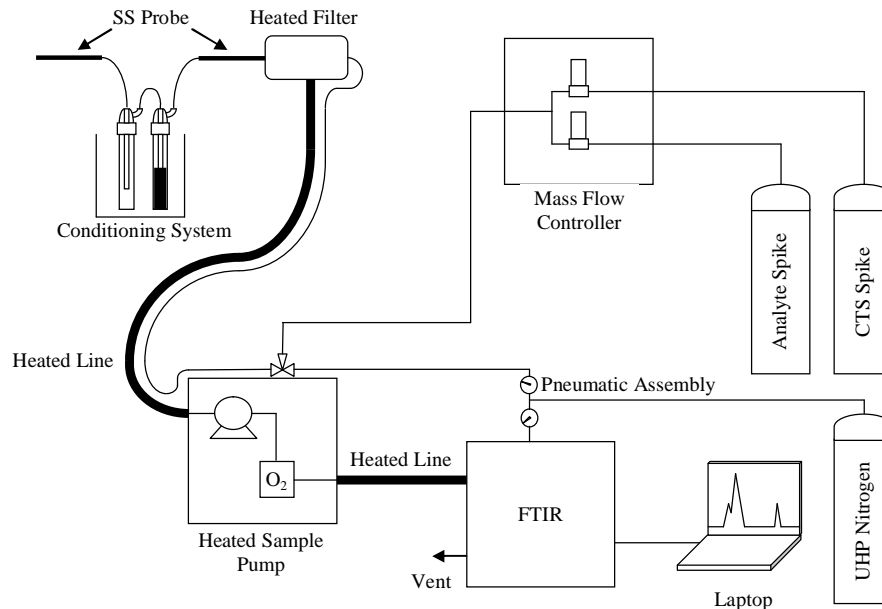


Figure 2.1 FTIR Sampling System

2.1.2 Analysis Procedure

The FTIR analysis software requires that, for each source, an appropriate analysis method be set up to deconstruct and analyze the IR spectra. The analysis method can be tailored to the source being tested and defines all elements of the analysis, including the list of compounds being analyzed (analytes), the reference spectra used for calibration, a list of compounds that could be interferences, and specific wavelengths to be evaluated for quantifying the target analytes. This approach serves to minimize interferences and maximize accuracy, given the ability to identify unique interferences for any given source. These analyses methods are provided in Appendix A. A detailed description of FTIR analyzers and the process of FTIR analysis can be found in Appendix B.

2.1.3 Sample Run

The following procedures were followed as part of a complete sample run.

Pre-Run Stack Flow Measurement ó Procedure outlined in Section 2.1.6.

Background Spectrum ó Ultra-high purity nitrogen was flushed through the system. When the sampling system was completely saturated with nitrogen, a background spectrum was obtained.

Pre-Run CTS Spike ó Calibration transfer standard (CTS) spikes were used to ensure the stability of the sampling system. Ethylene from a cylinder of known concentration was flushed through the system. A CTS spectrum was obtained and analyzed. The results from CTS spiking must be within $\pm 5\%$ of the certified cylinder value in order for the testing to proceed.

Sample Source Gas Stream ó The source gas stream was sampled from a single point for a period of 30 to 60 minutes.

Analyte Spiking – The analyte spiking procedure described in Section 2.1.5.2 was conducted for N₂O and CH₄.

Post-Run CTS Spike – The CTS spike result must be within ±5% of the certified cylinder value.

Post-Run Stack Flow Measurement – Procedure outlined in Section 2.1.6.

For each sample spectrum, the target analyte concentration and minimum detectable concentration were determined. Concentration data were combined with flow measurements and process data to determine an emission factor corresponding to each run.

To minimize the number of flow measurements taken, one set of stack flow measurements was often used for multiple runs. Run groupings can be found in Appendix A.

2.1.4 Bag Sampling

Direct source measurements using the FTIR sampling setup could not be accomplished in some cases. Where direct sampling was impossible or impractical, the source gas was collected in Tedlar® bags and subsequently analyzed onsite using the FTIR. Sample gas was drawn through the sample conditioning system described in Section 2.1.1, through a sample pump box, and into a 100 L Tedlar® bag. Sample flow was maintained around 3 L/min by employing a critical orifice. Bags were analyzed on site with the FTIR sampling setup. The sample collected in the bag was considered to be a representative composite of the source gas over the sampling period. As discussed earlier, the results from the sample conditioning evaluation provided in Appendix C indicate that the target analytes were stable in the bag for a period of up to four hours.

2.1.5 Quality Assurance/Quality Control

2.1.5.1 Minimum Detectable Concentrations

The minimum detectable concentration (MDC), or detection limit (DL), is the minimum concentration of a compound at which a change can be detected by the instrument with a given statistical probability (typically with a 95% confidence). The MDC for each analyte is a function of two parameters: instrument noise and residual noise in the analysis area. As these two noise parameters increase, the MDC will increase correspondingly. In general, instrument noise remains at a constant level throughout a sampling period. Residual noise, on the other hand, will increase or decrease based on the performance of the analysis algorithm for a particular sample. Residual noise will decrease to zero when all components of the gas stream are identified and accurately quantified. The following calculation is used to determine the MDC for each analyte.

$$MDC = \frac{REA_{rms}}{REF_{rms}} * C_{ref}$$

where

REA_{rms} = root mean square of the residual absorption peaks in the analysis area

REF_{rms} = root mean square of the reference absorption peaks in the analysis area, and

C_{ref} = concentration of the analyte reference spectra.

The number of detects obtained during each sample run at a source is also provided in Appendix A as part of the run-by-run results.

Concentrations below the DL were considered to be non-detects (ND). In the case of sample runs with a mixture of detects and NDs, the concentrations were evaluated using the Kaplan-Meier statistical method (NCASI 2009a, 2009b). The Kaplan-Meier method determines the mean, median, and standard deviation (SD) of a dataset containing both NDs and detects. The Kaplan-Meier mean was calculated and the run was subsequently characterized as a detect. In the case of data sets with all NDs, the average DL was calculated and the run was labeled as ND.

2.1.5.2 Analyte Spiking

Analyte spiking was used to determine the effectiveness of the FTIR measurement system to quantify the target analytes. From the sample runs, native analyte concentrations were quantified. Total flow was measured at the inlet of the FTIR system to calculate dilution factors (DFs). Dynamic spiking was performed while either sampling directly from the source or from a Tedlar® bag. Certified analyte gas of a known concentration was combined with sample gas upstream of the heated filter at a rate $\leq 10\%$ of the total flow. Spike flow rates were controlled using a mass flow controller. When possible, equivalent spiking concentrations were kept within $\pm 50\%$ of the native source concentration. An expected concentration was calculated based on the following calculation.

$$\text{Concentration expected} = CS + (Ua * (1 - DF))$$

where

CS = (cylinder concentration * DF)

Ua = native source gas concentration.

Percent recovery of the spiked analyte is calculated using the following formula.

$$\% \text{ Recovery} = \frac{\text{concentration observed}}{\text{concentration expected}} * 100\%$$

Concentration observed corresponds to the quantified concentration of the analyte spike sample. Spike recoveries between 70% and 130% were considered acceptable. Results on CH_4 and N_2O spike recoveries are also provided in Appendix A. Analyte spiking was used only as a quality check and the percent recoveries calculated from this procedure were not used as scaling factors to adjust the results.

2.1.5.3 Equipment Calibration and Certification

Equipment calibrations and certifications were verified ahead of each sampling trip. Recalibrations were performed, as needed, either by NCASI personnel or by the manufacturer.

2.1.5.4 Gas Cylinder Certification

Ultra-high purity nitrogen was used for background measurements and dilutions. CH_4 and N_2O cylinders used for spiking were either certified using EPA protocol or a NIST standard and the certified concentration was no more than $\pm 2\%$ of the tag concentration. The ethylene mixture used for CTS spiking was also certified at $\pm 2\%$ of the tag concentration.

2.1.5.5 Reference Spectra

Reference spectra were generated using either certified gas cylinders or from neat compounds. Dilutions were obtained by directly measuring flows using a certified bubble-tube meter. For neat compounds, only

solutions of known purity were used. Neat solutions were injected using a Cole-Parmer® syringe pump into a heated manifold, vaporized, and subsequently diluted with ultra-high-purity nitrogen to the desired concentration.

2.1.6 Stack Flow Rate and Process Data

From the list of methods provided in Appendix A of 40 CFR Part 60 (Standards of Performance for New Stationary Sources), Methods 1 through 4 (USEPA 2000, pp. 61779-61832) were used to determine flow rates and moisture content of the source. For stack flow rates, a Type S pitot tube with portable Magnehelic® pressure gauges was used. The pitot was equipped with a K-type thermocouple on the end to measure source temperature at each sample location. A Meriam Instrument digital manometer was used to measure stack and ambient pressure. Oxygen and carbon dioxide concentrations were also measured using the FTIR analyzer. Source moisture was determined using a Rockwell 175-S dry gas meter and an Ohaus® Navigator™ scale for impinger weights. Results of source flow measurements are found in Appendix A.

Data on boiler and furnace operating parameters, fuel firing rates, and fuel heat content were obtained from the facility. In the absence of recent data on fuel heating values, a representative default value provided by the mill was used. The facilities also provided data on firing rates of auxiliary fuels, if any, during sampling. A summary of the process data for each source is provided in Appendix A.

2.2 Boiler MACT/CISWI Testing

CH₄ emissions were measured in the 2009 Boiler MACT/CISWI testing program using EPA Method 18.6 Measurement of Gaseous Organic Compound Emissions by Gas Chromatography (USEPA 2000, pp. 62007-62028). It was assumed that all these tests were conducted in accordance with the appropriate equipment, procedure, and QA/QC requirements as outlined in the method. Flow rates were obtained directly from the test reports. The total heat input into the boiler during a test run was determined using F-factors and concurrent data on fuel firing rates.

3.0 SOURCE DESCRIPTIONS

3.1 NCASI Testing

3.1.1 Mill A

Mill A is a kraft mill located in the southeast United States. It produces approximately 1,200 tons per day (TPD) of bleached softwood dissolving grade/specialty pulp. One recovery furnace and one bark boiler were tested at this facility. The recovery furnace is referred to as source ARF3. The bark boiler is referred to as source ABB2.

Source ARF3 is a DCE recovery furnace with a permitted capacity of 82,350 pounds of black liquor solids per hour and a steaming capacity of 267,000 pounds per hour (PPH). Particulate is controlled via a dry bottom electrostatic precipitator (ESP). Sampling on source ARF3 was accomplished over a three-day period during which 10 runs were conducted. CH₄ and N₂O concentrations were determined using FTIR analysis. The boiler produced an average of 217,000 PPH of steam (81% capacity) during these runs. A small amount of No. 6 fuel oil was fired intermittently during the 10 runs, with an average firing rate of 1.9 gallons per minute.

Source ABB2 is a stoker bark boiler with a permitted capacity of 601 MMBtu/hr and a steaming capacity of 400,000 PPH. Particulate is controlled via a venturi scrubber. A portion of the exhaust flow leaving the boiler is diverted to a rotary bark dryer. The two gas streams are recombined before entering the venturi scrubber. Sample ports are located downstream of the scrubber. Sampling on source ABB2 was accomplished over a one-day period during which five runs were conducted. CH₄ and N₂O concentrations

were determined using GC and FTIR analyses, respectively. The boiler produced an average of 254,000 PPH of steam (66% capacity) during the runs. The boiler burned 100% bark during the sampling period.

3.1.2 Mill B

Mill B is a kraft mill located in the southeast United States. It produces approximately 2,240 TPD of unbleached softwood linerboard. One NDCE recovery furnace was tested at this facility. The recovery furnace is referred to as source BRF5.

Source BRF5 has a permitted capacity of 156,780 PPH of black liquor solids and a steaming capacity of 495,700 PPH. Particulate is controlled via a dry bottom ESP. The ESP has two chambers in parallel, with the exhaust gas venting through separate stacks. Concentration measurements were performed on a single stack. Flow data were collected from both stacks. Sampling on source BRF5 was accomplished over a four-day period during which five sample runs were conducted. CH₄ and N₂O concentrations were determined using FTIR analysis. Five additional runs were conducted as part of the method development study described in Appendix C. The source produced an average of 477,000 PPH of steam (96% capacity) during sampling.

3.1.3 Mill C

Mill C is a hardwood/softwood kraft mill located in the southeast United States. It produces a mixture of bleached tissue and unbleached kraft paper and linerboard with a total capacity of 1,447 TPD. One combination boiler was tested. The combination boiler is referred to as source CCB4.

Source CCB4 is a stoker boiler burning a combination of bark and No. 6 fuel oil. The boiler has a design capacity of 513 MMBtu/hr and 360,000 PPH of steam. Particulate is controlled via an ESP. Six runs were completed over a two-day period. CH₄ and N₂O concentrations were determined using FTIR analysis. The boiler produced 241,000 PPH of steam (67% capacity) during the sample runs. The average firing rates during the runs were 2,140 PPH of No. 6 fuel oil and 33.65 tons per hour of bark, resulting in 11% and 88% of total heat input, respectively.

3.1.4 Mill D

Mill D is a kraft mill in the southeast United States. It produces approximately 1,560 TPD of bleached softwood dissolving/specialty pulp. One NDCE recovery furnace and one bark boiler were tested at this facility. The recovery furnace is referred to as source DRF1. The bark boiler is referred to as source DBB1.

Source DRF1 is an NDCE recovery furnace with a rated capacity of 243,750 PPH of black liquor solids and a steaming capacity of 980,000 PPH. Particulate is controlled with a dry bottom ESP. Eight runs were completed over a one-day period with the boiler producing 806,000 PPH (82% capacity) during the sample runs. CH₄ and N₂O concentrations were determined using FTIR analysis.

Source DBB1 is a stoker boiler designed to burn a combination of bark and natural gas. The boiler is permitted at 642 MMBtu/hr and has a steaming capacity of 540,000 PPH. Particulate is controlled via an ESP. The ESP has two chambers in parallel, with the exhaust gas venting through a common stack. Ten runs were completed over a two-day period with the boiler producing an average of 235,000 PPH (44% capacity). The boiler burned 100% bark during sampling. CH₄ and N₂O concentrations were determined using FTIR analysis.

3.1.5 Mill E

Mill E is a kraft mill located in the southeast United States capable of producing 860 TPD of bleached softwood pulp. One NDCE recovery furnace was tested at the facility. The recovery furnace is referred to as source ERF1.

Source ERF1 is an NDCE recovery furnace with a permitted capacity of 195,800 PPH of black liquor solids and a design steaming capacity of 700,000 PPH. The gas stream is divided into two parallel ESPs and then vented out of separate stacks. Ten runs were completed over a two-day period. CH₄ and N₂O concentrations were determined using FTIR analysis. An average of 171,700 PPH of black liquor solids were fired (88% capacity) during the sample runs.

3.1.6 Mill F

Mill F is a kraft mill located in the southeast United States. It produces approximately 1,180 TPD of unbleached linerboard. Two DCE recovery furnaces and one combination boiler were tested. The two recovery furnaces are referred to as source FRF1 and source FRF3. The combination boiler is referred to as source FBB1.

Source FRF1 is a DCE recovery furnace with a steaming capacity of 110,000 PPH and a design black liquor firing capacity of 34,400 PPH. Particulate is controlled with a wet ESP. Six runs were carried out over a one-day period. CH₄ and N₂O concentrations were determined using FTIR analysis. During sampling, the boiler produced an average of 85,200 PPH of steam (78% capacity).

Source FRF3 is a DCE recovery furnace with a steaming capacity of 165,000 PPH and a black liquor capacity of 48,300 PPH. Particulate is controlled with a wet bottom ESP. Nine runs were completed over a two-day period with the boiler producing an average of 152,600 PPH of steam (92% capacity). CH₄ and N₂O concentrations were determined using FTIR analysis.

Source FBB1 is a combination of a Riley stoker boiler and a CE stoker bark boiler. The two boilers exhaust through a common stack. The Riley boiler has a steaming capacity of 225,000 PPH, while the CE bark boiler has a design steaming capacity of 150,000 PPH, for a combined total capacity of 375,000 PPH. Particulate emissions from both sources are controlled by a common venturi scrubber. Ten runs were completed over a two-day period. CH₄ and N₂O concentrations were determined using FTIR analysis. The boilers produced a total of 310,000 PPH of steam (83% total capacity). During the testing period, both boilers fired 100% wood.

3.1.7 Mill G

Mill G is a kraft mill located in the southeast United States. It produces approximately 900 TPD of bleached hardwood linerboard. Two DCE recovery furnaces and one combination boiler were tested. The two DCE recovery furnaces are referred to as source GRF1 and source GRF2. The combination boiler is referred to as source GCB3.

Source GRF1 is a DCE recovery furnace with a design capacity of 124,000 PPH of black liquor and a steaming capacity of 398,000 PPH of steam. Emissions are divided into two parallel dry bottom ESPs and then vented through separate stacks. Concentration measurements were performed on a single stack. Flow data were collected from both stacks. Six runs were conducted at the source over a one-day period. CH₄ and N₂O concentrations were determined using FTIR analysis. During sampling an average of 120,400 PPH of black liquor solids were fired (97% capacity).

Source GRF2 is a DCE recovery furnace with a design capacity of 124,000 PPH of black liquor and a steaming capacity of 398,000 PPH of steam. Emissions are divided into two parallel wet bottom ESPs and then vented through separate stacks. Concentration measurements were performed on a single stack. Flow data were collected from both stacks. Six runs were conducted over a one-day period. CH₄ and N₂O concentrations were determined using FTIR analysis. An average of 104,900 PPH of black liquor solids were fired (85% capacity) during testing.

Table 3.1 NCASI Testing ó General Source Descriptions

Data Source	Mill ID	Source ID	Type	Primary Fuel	Secondary Fuel	Capacity	Capacity Units
NCASI Testing	A	ARF3	DCE Recovery	Black Liquor	No. 6 Fuel Oil	267,000	lb/hr steam
NCASI Testing	A	ABB2	Stoker	Bark		601	MMBtu/hr
NCASI Testing	B	BRF5	NDCE Recovery	Black Liquor		495,700	lb/hr steam
NCASI Testing	C	CCB4	Stoker	Bark	No. 6 Fuel Oil	513	MMBtu/hr
NCASI Testing	D	DRF1	NDCE Recovery	Black Liquor		980,000	lb/hr steam
NCASI Testing	D	DBB1	Stoker	Bark		642	MMBtu/hr
NCASI Testing	E	ERF1	NDCE Recovery	Black Liquor		700,000	lb/hr steam
NCASI Testing	F	FRF1	DCE Recovery	Black Liquor		110,000	lb/hr steam
NCASI Testing	F	FRF3	DCE Recovery	Black Liquor		165,000	lb/hr steam
NCASI Testing	F	FBF1	Combo. Stoker	Wood		375,000	lb/hr steam
NCASI Testing	G	GRF1	DCE Recovery	Black Liquor		398,000	lb/hr steam
NCASI Testing	G	GRF2	DCE Recovery	Black Liquor		398,000	lb/hr steam
NCASI Testing	G	GCB3	Stoker	Bark	No. 6 Fuel Oil	499	MMBtu/hr

Table 3.2 Boiler MACT/CISWI Testing ó General Source Descriptions

Data Source	Mill ID	Source ID	Type	Primary Fuel	Secondary Fuel	Capacity	Capacity Units
MACT	H	HCB1	Stoker	Bark	Resinated Wood, Natural Gas	470	MMBtu/hr
MACT	I	ICB1	Fluidized Bed	Bark	Municipal Solid Waste, Natural Gas	125,000	lb/hr steam
MACT	J	JCB2	Stoker	Bark	TDF, No. 6 Fuel Oil	500	MMBtu/hr
MACT	K	KCB2	Fuel Cell	Bark		100	MMBtu/hr
MACT	L	LCB1	Fuel Cell	Wood/Bark		115	MMBtu/hr
MACT	M	MCB3	Fuel Cell	Wood/Bark		29,580	lb/hr steam
MACT	N	NCB1	Stoker	Bark		435	MMBtu/hr
MACT	O	OCB4	Stoker	Bark	No. 6 fuel oil, Natural Gas	800	MMBtu/hr
MACT	P	PCB4	Fluidized Bed	Bark	WWT Sludge, TDF	877	MMBtu/hr
MACT	Q	QCB8	Stoker	WWT Sludge	Wood/Bark	236	MMBtu/hr
MACT	R	RCB1	Fuel Cell	Bark			
MACT	S	SCB1	Stoker	Bark	Cross ties, Natural Gas, WWT Sludge	454	MMBtu/hr
MACT	T	TCB1	Fuel Cell	Wood		249	MMBtu/hr
CISWI	U	UCB2	Stoker	Wood/Bark	OCC rejects, WWT Sludge, Natural Gas	940	MMBtu/hr
CISWI	V	VCB2	Stoker	Bark	WWT Sludge, Cross ties, Natural Gas	667	MMBtu/hr
CISWI	W	WCB1	Stoker	Bark	Natural Gas, WWT Sludge, OCC rejects	900	MMBtu/hr
MACT	X	XCB1	Stoker	Bark		200,000	lb/hr steam
MACT	Y	YCB1	Stoker	Bark	Natural Gas	337	MMBtu/hr
MACT	Z	ZCB1	Stoker	Bark		30	MMBtu/hr
MACT	AA	AACB1	Fuel Cell	Wood/Bark		28	MMBtu/hr
MACT	AB	ABCB1	Dutch oven	Wood/Bark		90,000	lb/hr steam
MACT	AC	ACCB1	Fluidized Bed	Bark		856	MMBtu/hr

Source GCB3 is a stoker boiler burning a combination of wood and No. 6 fuel oil. The boiler has a design capacity of 499 MMBtu/hr and 300,000 PPH of steam. Particulate is controlled with a venturi scrubber. Six runs were completed over a one-day period. CH₄ and N₂O concentrations were determined using FTIR analysis. The boiler produced an average of 183,600 PPH of steam (61% capacity). During the testing period, the source fired 244.6 MMBtu/hr of bark and 4.3 MMBtu/hr of No. 6 fuel oil, resulting in 98% and 2% of the total Btu input, respectively.

3.2 Boiler MACT/CISWI Testing

Test data from 22 biomass-fired boilers were extracted from EPA's 2009 Boiler MACT and CISWI databases (19 boilers and 3 incinerators). Boilers were selected if CH₄ testing was conducted with > 80% of the heat input on average coming from biomass fuels. With the exception of one source, OCB4, where only two tests were conducted with the boiler burning predominantly biomass, all other sources had three test runs. In all cases, CH₄ concentrations were determined using EPA Method 18. Table 3.2 provides a general description of each source selected from the database, along with information on the types of fuels being burned during testing. Appendix A contains the percentages of each fuel burned during individual runs.

4.0 RESULTS

In the final GHG reporting rule [74 FR 56260], EPA has mandated the use of specific emission factors for CH₄ and N₂O (USEPA 2009). These emission factors are expressed in units of kg/MMBtu. Additionally, the rule requires use of high heating value (HHV) of the fuel when utilizing these emission factors to calculate mass emissions of GHG (in kg). These emission factors are, in effect, expressed in **kg/MMBtu HHV**. In order to be consistent with the approach used by EPA in the rulemaking and to better facilitate comparison, all emission data in this report are also expressed in kg/MMBtu, with HHV for the fuel being used as opposed to the low heating value (LHV) in calculations. It has been assumed that there is a 5% difference between the LHV and HHV of fuels.

4.1 NCASI Testing

All reported emissions have been calculated from measured in-stack concentrations, expressed on a dry basis. Emissions are reported in kg/MMBtu to be consistent with the approach used by EPA in the GHGRR. Emissions are calculated and reported using the high-heating value (HHV) of the fuel as the basis. Detailed results for each source are listed in Appendix A.

In the case of combination boilers burning a mixture of biomass and other fuels, emissions are expressed based on the combined fuel energy input. CH₄ and N₂O emissions are expected to be dictated more by combustion conditions than fuel properties (WRI/WBCSD 2005; Bonn, Pelz, and Baumann 1995). Even though multiple fuels were being burned during some of these tests, biomass fuels were the predominant fuel and accounted for ~ 90% of heat input in all cases. Subsequently, it is reasonable to compare these emission factors against the default factors for solid biomass fuels in the GHG reporting rule.

4.1.1 Treatment of Non-detect (ND) Data

When utilizing the direct sampling and analysis methodologies with the FTIR, as outlined above in Section 2.1, each sample run involves the recording and analysis of multiple IR spectra. In effect, each reported data point (labeled as a Run in Tables 4.1 through 4.14) reflects an average of multiple measurements. For each IR spectrum analyzed, the target analyte concentration and DL were calculated. Detection limits were determined as outlined in Section 2.1.5.1. All analytical results were used to determine the minimum, maximum, mean, standard deviation (SD), and median concentrations for CH₄ and N₂O for the sample run. Non-detect (ND) data was treated as follows:

- When a sample run dataset included a mixture of detects and NDs, the concentrations were evaluated using the Kaplan-Meier statistical method (NCASI 2009a, 2009b). The Kaplan-Meier statistical mean concentration for the run was calculated and the run was characterized as a detect.
- In the case of sample runs with all NDs, the mean DL was calculated and the run was marked as ND.
- In the case of sample runs with only one detect, the ND values are reduced to $\frac{1}{2}$ the DL, the resulting mean concentration was calculated, and the run was characterized as a detect.
- ND data from multiple sample runs at a given source were also treated as described above.

Spike recoveries were calculated for each run as described in Section 2.1.5.2. In the case of data sets with a mixture of detects and NDs, spike recovery was calculated by using the Kaplan-Meier statistical mean as the native source gas concentration. For runs with all NDs, no spike recovery was calculated. Spike recoveries between 70% and 130% were considered acceptable. Runs with spike recoveries outside this range were removed.

4.1.2 *Mill A*

4.1.2.1 *Recovery Furnace (DCE) ARF3*

Ten sample runs were completed at source ARF3. One of the 10 sample runs yielded a ND for CH₄. N₂O concentrations were above the DL for all sample runs. Run 4 did not meet the QA requirements in terms of spike recovery for N₂O. Subsequently, this data point was excluded from summary calculations. The average spike recoveries for the reported CH₄ and N₂O concentrations were 91.1% and 86.8%, respectively. Table 4.1 summarizes the CH₄ and N₂O emissions for source ARF3.

Table 4.1 Recovery Furnace (DCE) ARF3, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.00015	0.00043
2	0.00068	0.00032
3	0.00010	0.00028
4	0.00014	
5	0.00019	0.00035
6	0.00016	0.00027
7	0.00012	0.00024
8	0.00008	0.00013
9	ND[0.00013]	0.00027
10	0.00027	0.00015
Range	0.00008 – 0.00068	0.00013 – 0.00043
Mean	0.00020	0.00027
St. Dev	0.00017	0.00009
Median	0.00014	0.00027

4.1.2.2 *Bark Boiler ABB2*

Five sample runs were completed at source ABB2. However, sample interferences prevented the accurate quantification of CH₄ using the FTIR. Subsequently, the bag samples were analyzed for CH₄ using a

GC/FID (equivalent to using EPA Method 18). Four of the five sample runs were analyzed. The Tedlar bag corresponding to Run 4 did not contain adequate amounts of sample gas to carry out a GC analysis. No spiking was conducted for CH₄. All sample runs were above the DL for N₂O concentrations. The average spike recovery for N₂O was 91.7%. Table 4.2 summarizes the CH₄ and N₂O emissions for source ABB2.

Table 4.2 Bark Boiler ABB2, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.00044	0.0018
2	0.00083	0.0014
3	0.0015	0.0023
4		0.0040
5	0.0016	0.0038
Range	0.00044 – 0.0016	0.0014 – 0.0040
Mean	0.0011	0.0027
St. Dev	0.0006	0.0012
Median	0.0012	0.0023

4.1.3 Mill B

4.1.3.1 Recovery Furnace (NDCE) BRF5

Five sample runs were completed at source BRF5. One of these runs yielded a ND for CH₄. Additionally, Run 2 and Run 3 CH₄ spike recovery results did not meet QA requirements. These data points were removed from summary calculations. All sample runs were above the DL for N₂O concentrations. The average spike recoveries for the reported CH₄ and N₂O concentrations were 81.2% and 113.1%, respectively. Table 4.3 summarizes the CH₄ and N₂O emissions for source BRF5.

Table 4.3 Recovery Furnace (NDCE) BRF5, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.00090	0.00062
2		0.00065
3		0.00086
4	ND[0.00039]	0.0011
5	0.0010	0.00088
Range	ND[<0.00039] – 0.0010	0.00062 – 0.0011
Mean	0.00093	0.00082
St. Dev	0.00007	0.00020
Median	0.00039	0.00086

4.1.4 *Mill C*

4.1.4.1 *Combination Boiler CCB4*

Six sample runs were completed at source CCB4. All sample runs were above the DL for CH₄ and N₂O concentrations. The average spike recovery for CH₄ and N₂O was 99.3% and 98.9%, respectively. Table 4.4 summarizes the CH₄ and N₂O emissions for source CCB4.

Table 4.4 Combination Boiler CCB4, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.00076	0.0014
2	0.00040	0.0012
3	0.0048	0.0014
4	0.0046	0.0016
5	0.0077	0.0019
6	0.00042	0.0014
Range	0.00040 – 0.0077	0.0012 – 0.0019
Mean	0.0031	0.0015
St. Dev	0.0030	0.0002
Median	0.0027	0.0014

4.1.5 *Mill D*

4.1.5.1 *Recovery Furnace (NDCE) DRF1*

Eight sample runs were completed at source DRF1. Seven of the eight runs yielded NDs for CH₄. As outlined in the approach laid out in Section 4.1.1, since seven of the eight runs were NDs, the ND values were reduced to ½ DL and characterized as detects for summary calculations. The spike recovery for the lone detect was 93.0%. Four of the eight runs were ND for N₂O. Run 1 for N₂O was ND at a detection level that was greater than the highest detected concentration for the set of runs. Since the Kaplan-Meier method states that there is no useful information in such a value, this data point was removed from the data set (NCASI 2009a). The average spike recovery for N₂O was 80.9%. Table 4.5 summarizes CH₄ and N₂O emissions for DRF1.

Table 4.5 Recovery Furnace (NDCE) DRF1, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.000042	
2	0.000047	0.00012
3	0.000041	ND[0.00018]
4	0.000046	ND[0.00016]
5	0.000034	0.00018
6	0.000047	0.00018
7	0.000037	ND[0.00014]
8	0.000038	0.00017
Range	0.000034 – 0.000047	0.00012 – 0.00018
Mean	0.000042	0.00015
St. Dev		0.00003
Median		0.00014

NOTE: Shaded values are ½ DL.

4.1.5.2 Bark Boiler DBB1

Ten runs were completed at source DBB1. All 10 runs were above the DL for CH₄ concentrations. The average spike recovery was 95.6%. Two of the 10 runs were ND for N₂O concentrations. The average spike recovery was 90.4%. Table 4.6 summarizes CH₄ and N₂O emissions for DBB1.

Table 4.6 Bark Boiler DBB1, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.00022	0.00091
2	0.00047	0.0013
3	0.00017	0.0011
4	0.00020	0.00090
5	0.00022	0.0012
6	0.00046	0.0012
7	0.00025	ND[0.00062]
8	0.00030	0.0013
9	0.00023	0.0010
10	0.00024	ND[0.00070]
Range	0.00017 – 0.00047	ND[0.00062] – 0.0013
Mean	0.00028	0.0011
St. Dev	0.00011	0.0002
Median	0.00023	0.0010

4.1.6 Mill E

4.1.6.1 Recovery Furnace (NDCE) ERF1

Ten runs were completed at source ERF1. All 10 runs were above the DL for CH₄ concentrations. The average spike recovery was 98.7%. Seven of the 10 runs were ND for N₂O concentrations. The average spike recovery was 99.9%. Table 4.7 summarizes CH₄ and N₂O emissions for ERF1.

Table 4.7 Recovery Furnace (NDCE) ERF1, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.000065	ND[0.000099]
2	0.0013	ND[0.00019]
3	0.0056	ND[0.00051]
4	0.0029	ND[0.00030]
5	0.00087	ND[0.00016]
6	0.0051	ND[0.00051]
7	0.0033	0.00065
8	0.0041	ND[0.00044]
9	0.0023	0.00065
10	0.0057	0.00027
Range	0.000065 – 0.0057	ND[0.000099] – 0.00065
Mean	0.0031	0.00034
St. Dev	0.0020	0.00015
Median	0.0031	0.00016

4.1.7 Mill F

4.1.7.1 Recovery Furnace (DCE) FRF1

Six runs were completed at source FRF1. All CH₄ and N₂O concentrations were above the DLs. The average spike recoveries for CH₄ and N₂O were 99.0% and 101.9%, respectively. Table 4.8 summarizes CH₄ and N₂O emissions for FRF1.

Table 4.8 Recovery Furnace (DCE) FRF1, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.014	0.00072
2	0.016	0.00085
3	0.0098	0.00044
4	0.0061	0.00054
5	0.0020	0.00069
6	0.015	0.00069
Range	0.0020 – 0.016	0.00044 – 0.00085
Mean	0.010	0.00065
St. Dev	0.005	0.00015
Median	0.012	0.00069

4.1.7.2 Recovery Furnace (DCE) FRF3

Nine runs were completed at source FRF1. All CH₄ and N₂O concentrations were above the DLs. The average spike recoveries for CH₄ and N₂O were 98.2% and 92.8%, respectively. Table 4.9 summarizes CH₄ and N₂O emissions for FRF3.

Table 4.9 Recovery Furnace (DCE) FRF3, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.00077	0.00045
2	0.00057	0.00044
3	0.0011	0.00049
4	0.0016	0.00049
5	0.0015	0.00042
6	0.0015	0.00060
7	0.00041	0.00039
8	0.00026	0.00034
9	0.0021	0.00076
Range	0.00026 – 0.0021	0.00034 – 0.00076
Mean	0.0011	0.00049
St. Dev	0.00063	0.00012
Median	0.0011	0.00045

4.1.7.3 Combination Boiler FBB1

Ten runs were completed at source FBB1. All CH₄ concentrations were above the DL. The average spike recovery was 100.2%. Two of the 10 runs were ND for N₂O concentrations. The average spike recovery was 101.4%. Table 4.10 summarizes CH₄ and N₂O emissions for FBB1.

Table 4.10 Combination Boiler FBB1, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.054	0.00054
2	0.078	0.00067
3	0.024	0.00028
4	0.058	ND[0.00041]
5	0.017	0.0014
6	0.017	0.0023
7	0.057	ND[0.00043]
8	0.028	0.00069
9	0.054	0.00030
10	0.027	0.00066
Range	0.017 – 0.078	0.00028 – 0.0023
Mean	0.041	0.00073
St. Dev	0.021	0.00060
Median	0.041	0.00054

4.1.8 Mill G

4.1.8.1 Recovery Furnace (DCE) GRF1

Six runs were completed at source GRF1. Five of the six runs were below the DL for CH₄. The ND values were reduced to ½ DL and marked as detect for calculations. The spike recovery for the detect run was

99.1%. All N₂O concentrations were above the DL. The average spike recovery was 98.7%. Table 4.11 summarizes CH₄ and N₂O emissions for GRF1.

Table 4.11 Recovery Furnace (DCE) GRF1, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.00011	0.00012
2	0.00010	0.00019
3	0.00011	0.00031
4	0.00015	0.00026
5	0.00011	0.00018
6	0.00010	0.00014
Range	0.00010 – 0.00015	0.00012 – 0.00031
Mean	0.00011	0.00020
St. Dev		0.00007
Median		0.00018

NOTE: Shaded values are ½ DL.

4.1.8.2 Recovery Furnace (DCE) GRF2

Six runs were completed at source GRF2. Run 2 was ND for CH₄ and the DL was greater than the highest detected concentration. The ND value was removed before statistical calculations. The average spike recovery was 94.7%. All N₂O concentrations were above the DL. The average spike recovery was 97.0%. Table 4.12 summarizes CH₄ and N₂O emissions for GRF2.

Table 4.12 Recovery Furnace (DCE) GRF2, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.00016	0.00026
2		0.00033
3	0.00013	0.000092
4	0.00010	0.00012
5	0.00011	0.00017
6	0.00013	0.00018
Range	0.00010 – 0.00016	0.000092 – 0.00033
Mean	0.00013	0.00019
St. Dev	0.00002	0.00009
Median	0.00013	0.00017

4.1.8.3 Combination Boiler GCB3

Six runs were completed at source GCB3. All CH₄ and N₂O concentrations were above the DLs. The average spike recoveries for CH₄ and N₂O were 100.9% and 103.6%, respectively. Table 4.13 summarizes CH₄ and N₂O emissions for GCB3.

Table 4.13 Combination Boiler GCB3, kg/MMBtu

Run	CH ₄	N ₂ O
1	0.00099	0.0020
2	0.00065	0.0024
3	0.00075	0.0036
4	0.00056	0.0037
5	0.00062	0.0048
6	0.00054	0.0038
Range	0.00054 – 0.00099	0.0020 – 0.0048
Mean	0.00068	0.0034
St. Dev	0.00017	0.0010
Median	0.00064	0.0036

4.2 Boiler MACT/CISWI Testing

For sources tested as part of Boiler MACT/CISWI testing, individual test results (labeled as Runs) were also subjected to the statistical treatment outlined in Section 4.1.1.

The source emissions for CH₄ reported in Table 4.14 have been calculated from the measured, in-stack concentrations expressed on a dry basis. All emissions have been calculated using the combined energy inputs from the fuel, on a high-heating value (HHV) basis. Detailed results for each source are provided in Appendix A.

Table 4.14 Boiler MACT/CISWI Testing of CH₄ Emissions by Source, kg/MMBtu

Source	Run 1	Run 2	Run 3	Range	Mean	St. Dev.	Median
HCB1	ND[0.00012]	ND[0.00011]	ND[0.00011]	ND[0.00011] – ND[0.00012]	ND[0.00012]		
ICB1	0.0018	0.0016	0.0020	0.0016 – 0.0020	0.0018	0.0002	0.0018
JCB2	0.0087	0.0037	0.010	0.0037 – 0.010	0.0076	0.0035	0.0087
KCB2	0.00061	0.00029	0.00037	0.00029 – 0.00061	0.00043	0.00017	0.00037
LCB1	0.00092	0.00037	0.00086	0.00037 – 0.00092	0.00072	0.00030	0.00086
MCB3	0.00022	0.00025	0.00048	0.00022 – 0.00048	0.00032	0.00014	0.00025
NCB1	0.0014	0.0011	0.00050	0.00050 – 0.0014	0.0010	0.0005	0.0011
OCB4	0.00015		0.00031	0.00015 – 0.00031	0.00023	0.00011	0.00023
PCB4	0.00017	0.00016	0.00021	0.00016 – 0.00021	0.00018	0.00003	0.00017
QCB8	0.00076	0.00069	0.00064	0.00064 – 0.00076	0.00070	0.00006	0.00069
RCB1	0.0036	0.00067	0.00046	0.00046 – 0.0036	0.0016	0.0017	0.00067
SCB1	0.0012	0.0047	0.00078	0.00078 – 0.0047	0.0022	0.0022	0.0012
TCB1	0.00053	0.0017	0.0024	0.00053 – 0.0024	0.0015	0.00094	0.0017
UCB2	0.0050	0.0023	0.00075	0.00075 – 0.0050	0.0027	0.0022	0.0023
VCB2	0.00055	0.00075	0.0023	0.00055 – 0.0023	0.0012	0.00095	0.00075
WCB1	0.0013	0.0014	0.00093	0.00093 – 0.0014	0.0012	0.00023	0.0013
XCB1	0.0056	0.0038	0.0030	0.0030 – 0.0056	0.0041	0.0013	0.0038
YCB1	0.048	0.056	0.032	0.032 – 0.056	0.046	0.012	0.048
ZCB1	0.0046	0.0042	0.0034	0.0034 – 0.0046	0.0041	0.0006	0.0042
AACB1	0.0030	0.011	0.00091	0.00091 – 0.011	0.0048	0.0051	0.0030
ABCB1	0.00084	0.00063	0.00063	0.00063 – 0.00084	0.00070	0.00012	0.00063
ACCB1	0.00096	0.00014	0.00043	0.00014 – 0.00096	0.00051	0.00041	0.00043

4.3 Category Results

4.3.1 Biomass-Fired Boilers

Five biomass-fired boilers were tested using FTIR. The mean CH₄ emission from these sources was 0.0093 kg/MMBtu. Data on CH₄ emissions from 22 biomass-fired boilers were extracted from available Boiler MACT/CISWI reports. The mean CH₄ emission from these sources was 0.0039 kg/MMBtu. Combining the two data sets then results in a mean CH₄ emission of 0.0049 kg/MMBtu. The mean N₂O emission was 0.0019 kg/MMBtu. Table 4.15 summarizes the CH₄ and N₂O emissions from bark/combo boilers.

Table 4.15 Bark/Combination Boiler Category Results, kg/MMBtu

Data Source	Source ID	CH ₄	N ₂ O
NCASI Testing	ABB2	0.0011	0.0027
NCASI Testing	CCB4	0.0031	0.0015
NCASI Testing	DBB1	0.00028	0.0011
NCASI Testing	FBB1	0.041	0.00073
NCASI Testing	GCB3	0.00068	0.0034
MACT	HCB1	ND[0.00012]	
MACT	ICB1	0.0018	
MACT	JCB2	0.0076	
MACT	KCB2	0.00043	
MACT	LCB1	0.00072	
MACT	MCB3	0.00032	
MACT	NCB1	0.0010	
MACT	OCB4	0.00023	
MACT	PCB4	0.00018	
MACT	QCB8	0.00070	
MACT	RCB1	0.0016	
MACT	SCB1	0.0022	
MACT	TCB1	0.0015	
CISWI	UCB2	0.0027	
CISWI	VCB2	0.0012	
CISWI	WCB1	0.0012	
MACT	XCB1	0.0052	
MACT	YCB1	0.046	
MACT	ZCB1	0.0048	
MACT	AACB1	0.0048	
MACT	ABCB1	0.00070	
MACT	ACCB1	0.00051	
	Range	ND[0.00012] – 0.046	0.00073 – 0.0034
	Mean	0.0049	0.0019
	St. Dev	0.011	0.0011
	Median	0.0012	0.0015

4.3.2 NDCE Recovery Furnaces

Three NDCE recovery furnaces were tested. The mean CH₄ emission was 0.0014 kg/MMBtu. The mean N₂O emission was 0.00044 kg/MMBtu. Table 4.16 summarizes the CH₄ and N₂O emissions from NDCE recovery furnaces.

Table 4.16 Recovery Furnace (NDCE) Category Results, kg/MMBtu

Data Source	Source ID	CH ₄	N ₂ O
NCASI Testing	BRF5	0.00093	0.00082
NCASI Testing	DRF1	0.000042	0.00015
NCASI Testing	ERF1	0.0031	0.00034
	Range	0.000042 – 0.0031	0.00015 – 0.00082
	Mean	0.0014	0.00044
	St. Dev	0.0016	0.00035
	Median	0.00093	0.00034

4.3.3 DCE Recovery Furnaces

Five DCE recovery furnaces were tested. The mean CH₄ emission was 0.0024 kg/MMBtu. The mean N₂O emission was 0.00036 kg/MMBtu. Table 4.17 summarizes the CH₄ and N₂O emissions from DCE recovery furnaces.

Table 4.17 Recovery Furnace (DCE) Category Results, kg/MMBtu

Data Source	Source ID	CH ₄	N ₂ O
NCASI Testing	ARF3	0.00020	0.00027
NCASI Testing	FRF1	0.010	0.00065
NCASI Testing	FRF3	0.0011	0.00049
NCASI Testing	GRF1	0.00011	0.00020
NCASI Testing	GRF2	0.00013	0.00019
	Range	0.00011 – 0.010	0.00019 – 0.00065
	Mean	0.0024	0.00036
	St. Dev	0.0045	0.00020
	Median	0.00020	0.00027

5.0 DISCUSSION

5.1 Category Results

5.1.1 Biomass-Fired Boilers

Five biomass-fired boilers were tested using the FTIR as part of NCASI testing and data from 22 biomass-fired boilers were obtained from the Boiler MACT/CISWI reports. On average, CH₄ emissions from boilers were higher than those observed in DCE and NDCE recovery furnaces, and amounted to 0.0049 kg/MMBtu (with median emissions of 0.0012 kg/MMBtu). N₂O emissions from biomass boilers were higher than those observed in NDCE and DCE recovery furnaces. The mean and median N₂O emission rate from biomass-fired boilers was 0.0019 kg/MMBtu and 0.0015 kg/MMBtu, respectively.

As indicated in Table 4.15, CH₄ emissions from two out of the 27 boilers included in this study, viz., FBB1 and YCB1, were significantly higher than emissions from other boilers included in this study. Specifically, CH₄ emissions from these two sources were approximately five times greater than the next smallest value measured, and contributed to the higher mean value for CH₄ emissions as compared to the median. While typical boiler operating parameters at these two sources were within normal operating ranges, the carbon monoxide (CO) concentrations measured during these tests were significantly higher than those observed on the other sources. It is well documented that CO is a surrogate for incomplete combustion in boilers. The prevailing higher CO concentrations could therefore explain the higher CH₄ emission rates measured from these two sources. It is possible that the test runs encompassed periods of transient changes in fuel quality or boiler operation that affected the overall quality of combustion. While a more detailed examination of the correlation between CO and CH₄ emissions from the sources tested during this study is beyond the scope of this report, it is worthwhile to note this observed discrepancy in measured CO concentrations.

5.1.2 NDCE Recovery Furnaces

A total of three NDCE recovery furnaces were tested as part of this study. CH₄ emissions from this source category were low and quite variable. The mean and median CH₄ emission rate was 0.0014 kg/MMBtu and 0.00093 kg/MMBtu, respectively. Mean and median N₂O emissions were 0.00044 kg/MMBtu and 0.00034 kg/MMBtu, respectively.

Source ERF1 contained the highest and most variable CH₄ emissions, ranging from 0.000065 to 0.0057 kg/MMBtu. CH₄ results for source BRF5 were calculated using three of the five runs, as the remaining two runs provided unacceptable analyte spiking results. For this source, dynamic spiking was carried out while sampling directly from the stack. Given the observed variability in CH₄ concentrations at this source and the potential for concentrations to change between the spiking run and the sample run, it is not surprising that spike recoveries for 2 of the runs were outside the acceptable range of 70% to 130%.

5.1.3 DCE Recovery Furnaces

The mean and median CH₄ emission rate was 0.0024 kg/MMBtu and 0.00020 kg/MMBtu, respectively in the five DCE furnaces tested during this study. N₂O emissions from DCE recovery furnaces were the lowest of the three categories, with mean and median emissions rate of 0.00036 kg/MMBtu and 0.00027 kg/MMBtu, respectively.

CH₄ emissions from source FRF1 were significantly higher than emissions from the other four DCE furnaces tested during this study. One of the sample runs at source ARF3 did not meet the QA spiking requirements for N₂O and was subsequently removed from the dataset. The cause of the low spike recovery could not be determined.

5.2 Drivers of Methane (CH₄) and Nitrous Oxide (N₂O) Formation and Emissions

The variability observed in CH₄ and N₂O emissions can be attributed to a number of factors. In the case of CH₄, combustion conditions inside the boiler are expected to be the dominant contributing factor. N₂O emissions, on the other hand, can be influenced both by combustion conditions and fuel nitrogen content.

According to Flagan and Seinfeld (1988), the oxidation rate of hydrocarbons like CH₄ increases when combustion parameters are maintained at optimum levels. CH₄ oxidation rates are expected to decrease and emissions are expected to increase when combustion conditions do not allow for complete mixing of fuel and air, or when oxidation reactions are quenched early in the combustion process. In general, boiler parameters or operating conditions that result in an increase in CO concentrations are also likely to lead to increases in CH₄. As discussed earlier, both CO concentrations and CH₄ emissions at sources FBB1 and YCB1 were higher than those observed at the other sources.

The formation of N₂O within a boiler is a more complicated process. N₂O emissions depend on fuel nitrogen content and combustion parameters like temperature, excess air, boiler load, and catalytic activity of char and mineral matter. N₂O emissions, if attributed purely to fuel nitrogen content, would exhibit the following order: emissions from coal > lignite > peat > wood (Leckner 1998). The difference between wood/wood residuals/bark and kraft pulping liquor, as it relates to the potential to generate N₂O emissions, is not clear. It has been shown that most of the nitrogen in wood is transferred to the black liquor during kraft pulping. As a consequence, fuel nitrogen is not expected to be the contributing factor of the differential in N₂O emissions observed between solid biomass fuels and kraft pulping liquor in this study (Veverka et al. 1993).

While several combustion parameters can have minor effects on N₂O formation, changes in combustion temperature are expected to have the most dramatic impact. Studies have established that N₂O formation peaks around 700°C. On the other hand, combustion temperatures below 500°C and above 950°C prevent the formation of N₂O (Tsupari 2007). Although information on combustion zone temperatures was not available for the sources tested during this study, they were expected to be higher than 950°C and therefore not expected to be a factor. This parameter is potentially more important in fluidized bed boilers, where boiler temperatures can be lower than 950°C (Fortum 2001, Bonn, Pelz, and Baumann 1995).

As discussed above, several parameters can influence the formation of CH₄ and N₂O during combustion. A study that correlates CH₄ and N₂O emissions to these parameters would involve a more comprehensive testing plan that encompasses varying ranges of these parameters, in conjunction with the ability to reliably measure these variations. Such an analysis is beyond the scope of this study.

To the extent that fuel characteristics may dictate the efficiency of combustion and any related combustion parameters, the co-firing of fossil fuels along with biomass may also have an impact on both CH₄ and N₂O emissions. This study was geared towards developing emission factors for biomass firing and not intended to investigate the impact of co-firing. As discussed earlier, all the boilers included in this study were predominantly burning biomass fuels. In the case of boilers that co-fired No. 6 fuel oil, heat inputs from oil were ~ 10% and not variable enough to develop trends in emissions. The impact of co-firing can be better investigated by carrying out tests with varying levels of co-firing.

5.3 Existing Emission Factors

In the GHGRR, EPA mandates the use of specific emission factors when quantifying the emissions of CH₄ and N₂O due to the burning of solid biomass fuels and kraft pulping liquors in boilers and recovery furnaces, respectively. These factors were derived primarily from previously reported values by the IPCC and WRI/WBCSD, two of the most prominent international agencies studying GHG emissions and compiling available emission factors. Table 5.1 reproduces currently available CH₄ and N₂O emission factors published by WRI/WBCSD and Tier 1 factors from IPCC (WRI/WBCSD 2005, IPCC 2006). These factors are reported in kilogram per terajoule (kg/TJ) and utilize a low heating value (LHV).

Table 5.1 WRI/WBCSD and IPCC Emission Factors

Emission Factor Description	kg CH ₄ /TJ	kg N ₂ O/TJ	Reference
Wood waste-fired boilers			
Wood, wood waste, and other biomass and wastes	30	4	Tier 1 – IPCC 2006
Uncontrolled emissions from wood-fired stoker boilers	15	-	Tier 2 ó IPCC 1997
Average for wood residue combustion	9.5 ^a	5.9 ^a	USEPA 2001
Average for circulating fluidized bed boilers burning peat or bark	1	8.8	Fortum 2001
Average for bubbling fluidized bed boilers burning peat or bark	2 ^b	<2	Fortum 2001
Pre-1980 wood residue-fired stoker boilers sampled ahead of control devices	8.2 ^a	-	NCASI 1980
Pre-1980 wood residue-fired stoker boilers sampled after wet scrubbers	2.7 ^a	-	NCASI 1985
Wood-fired boiler	41 ^c	3.1 ^c	JPA 2001
Wood as fuel	24 ^c	3.4 ^c	AEA Tech. 2001
Wood waste	30	5	Swedish EPA 2004
WRI Median emission factors for wood waste	12	4	
	1 ó 40	1.4 ó 75	EEA 2004
Recovery furnaces			
Sulfite lyes (Black Liquor)	3	2	Tier 1 – IPCC 2006
Recovery furnace	<1	<1	Fortum 2001
Recovery furnace ó black liquor	2.5 ^d	-	JPA 2001
Black liquor	30	5	Swedish EPA 2004
WRI Median emission factors for black liquor	2.5	2	
	1 ó 17.7	1 ó 21.4	EEA 2004

^a Converted from GCV to NCV assuming a 5% difference.

^b Excludes one very high number associated with low oxygen-high carbon monoxide conditions.

^c Based on heat content of 20 GJ/t dry solids.

^d Based on liquor heat content of 13.3 GJ/t dry solids.

As discussed earlier, there is significant variability in the emission factors provided in Table 5.1. Additional factors, besides fuel and operating parameters, may have contributed to this variability in previously reported emission factors. Some of these factors have been estimated based on limited data or data derived from measurements that utilized improper sampling techniques (Fortum 2001; Muzio et al. 1989). An example of an improper sampling technique would be the collection of an unconditioned grab sample that is subsequently shipped off-site for analysis. It has been shown that N₂O can be generated within a collection vessel from compounds typically found in combination boilers and recovery furnaces. Therefore, any emission factors for N₂O that are derived from improperly conditioned grab samples are likely to overestimate actual emissions. Appendix C provides an example of this artifact formation along with a more detailed discussion of the mechanism.

IPCC has taken these considerations into account and has estimated the uncertainties in its measurements. For CH₄, it estimates an uncertainty range of 50% to 150%, while the uncertainty associated with N₂O measurement is an order of magnitude higher.

To compare the results of our study with previously published emission factors, the IPCC and WRI/WBCSD factors must first be converted to kg/MMBtu and then adjusted from a LHV to a HHV. This adjustment can be made using the assumption that there is a 5% difference in heat values for biomass fuels. The IPCC, WRI/WBCSD, and EPA factors do not distinguish between DCE and NDCE recovery furnaces. Consequently, for purposes of comparison, the existing emission factors have been assumed to apply to both recovery furnace categories. Methane and nitrous oxide emission factors are shown in Tables 5.2 and 5.3, respectively.

Table 5.2 CH₄ Emissions, kg/MMBtu

	IPCC ^{a,d}	WRI/WBCSD GHG Protocol ^{b,d}	EPA ^c	NCASI Study Mean (%RSD)	NCASI Study (range)
Biomass-fired boilers	0.032	0.012	0.032	0.0049 (232%)	ND<[0.00012] ó 0.046
Non-DCE furnaces ^e	0.0030	0.0025	0.030	0.0014 (117%)	0.000042 ó 0.0031
DCE furnaces ^e	0.0030	0.0025	0.030	0.0024 (187%)	0.00011 ó 0.010

^a IPCC (2006).

^b WRI/WBCSD (2005).

^c Emission factors mandated for use in GHG Inventories (USEPA 2009).

^d Factors are converted from LHV to HHV assuming a 5% difference.

^e DCE and NDCE furnaces have the same emission factors. EPA mandates the use of a single emission factor for kraft pulping liquor (North American Softwood).

Table 5.3 N₂O Emissions, kg/MMBtu

	IPCC ^a	WRI/WBCSD GHG Protocol ^{b,d}	EPA ^c	NCASI Study Mean (%RSD)	NCASI Study (range)
Biomass-fired boilers	0.0042	0.0042	0.0042	0.0019 (61%)	0.00073 to 0.0034
Non-DCE furnaces ^e	0.0020	0.0020	0.0050	0.00044 (79%)	0.00015 to 0.00082
DCE furnaces ^e	0.0020	0.0020	0.0050	0.00036 (57%)	0.00019 to 0.00065

^a IPCC (2006).^b WRI/WBCSD (2005).^c Emission factors mandated for use in GHG Inventories (USEPA 2009).^d Factors are converted from LHV to HHV assuming a 5% difference.^e DCE and NDCE furnaces have the same emission factors. EPA mandates the use of a single emission factor for kraft pulping liquor (North American Softwood).

As indicated in Tables 5.2 and 5.3, the emission factors for CH₄ and N₂O developed during this study are lower than those mandated by EPA for these three source categories. The CH₄ and N₂O emission factors developed during this study for biomass boilers are substantially lower than the EPA, IPCC, and WRI/WBCSD factors. In the case of kraft pulping liquors, CH₄ and N₂O emission factors developed during this study are over an order of magnitude lower than EPA mandated factors.

6.0 CONCLUSIONS

An NCASI review of more recent literature indicates a dearth of accurate and direct emission measurements of CH₄ and N₂O from biomass-fired boilers and kraft recovery furnaces. As a result, the validity of existing emission factors, including those mandated by EPA in the GHG reporting rule, has come under scrutiny. Given the emphasis being placed on GHG inventories, the limited data availability, and uncertainty surrounding currently available emission factors, NCASI carried out a study to develop additional data for CH₄ and N₂O emissions from these sources.

As part of the NCASI testing study, CH₄ and N₂O stack concentrations were measured using a portable FTIR spectrometer. When the sample stream was properly conditioned, the FTIR provided reliable analysis for the target analytes with acceptable detection limits. Quality assurance results confirmed the accuracy of the analysis. Additionally, CH₄ data from the 2009 Boiler MACT/CISWI testing were gathered and incorporated into the study.

NCASI conducted emission measurements at 13 sources, including five wood-fired combination boilers, five DCE recovery furnaces, and three NDCE recovery furnaces. From the 2009 Boiler MACT/CISWI testing program, CH₄ data from 19 boilers and three CISWI units were also incorporated into this study. For wood/biomass fired boilers, the mean and median CH₄ emission factors were 0.0049 kg/MMBtu and 0.0012 kg/MMBtu, respectively. CH₄ emissions from two of these boilers were approximately five times larger than those observed at the other sources and contributed to the higher mean emission factors as compared to the median. The higher CH₄ emissions could be explained by the higher CO concentrations observed on these sources. The mean and median N₂O emission factors for wood/biomass fired boilers were 0.0019 kg/MMBtu and 0.0015 kg/MMBtu, respectively. For DCE recovery furnaces, mean and median CH₄ emission factors were 0.0024 kg/MMBtu and 0.00020 kg/MMBtu, respectively. The mean and median N₂O emission

factors were 0.00036 kg/MMBtu and 0.00027 kg/MMBtu, respectively. For NDCE recovery furnaces, the mean and median CH₄ emission factors were 0.0014 kg/MMBtu HHV and 0.00093 kg/MMBtu, respectively. The mean and median N₂O emission factors were 0.00044 kg/MMBtu and 0.00034 kg/MMBtu, respectively.

The emission factors for CH₄ and N₂O developed during this study are lower than those mandated by EPA for use in GHG inventories for these three source categories. The CH₄ and N₂O emission factors developed during this study for biomass boilers are substantially lower than the EPA, IPCC, and WRI/WBCSD factors. In the case of kraft pulping liquors, CH₄ and N₂O emission factors developed during this study for DCE and NCDE recovery furnaces are over an order of magnitude lower than EPA mandated factors.

REFERENCES

- AEA Technology. 2001. *UK greenhouse gas inventory 1990–1999: Annual report for submission under the Framework Convention on Climate Change*. Oxfordshire, England: AEA Technology National Environmental Technology Centre.
- American Society for Testing and Materials (ASTM). 2003. Standard Test Method D 6348-03 6 Determination of gaseous compounds by extractive direct interface Fourier transform infrared (FTIR) spectroscopy. West Conshohocken, PA: American Society for Testing and Materials.
- Bonn, B., Pelz, G., and Baumann, H. 1995. Formation and decomposition of N₂O in fluidized bed boilers. *Fuel* 74:165-171. [http://dx.doi.org/10.1016/0016-2361\(95\)92650-U](http://dx.doi.org/10.1016/0016-2361(95)92650-U)
- European Environment Agency (EEA). 2004. *EMEP/CORINAIR Emission inventory guidebook 3rd ed.*, September 2004 update. Copenhagen: European Environment Agency.
- Flagan, R.C., and Seinfeld, J.H. 1988. *Fundamentals of air pollution engineering*. Englewood Cliffs, NJ: Prentice Hall.
- Fortum Power and Heat Oy (Fortum). 2001. *Methane and nitrous oxide emissions in the Finnish energy production*. Fortum, Finland: Fortum Power and Heat Oy.
- Intergovernmental Panel on Climate Change (IPCC). 1996. *Climate change 1995, the science of climate change*. New York, NY: Cambridge University Press.
- _____. 1997. *Revised 1996 IPCC guidelines for national greenhouse gas inventories: Reference manual* (Vol. 3). IPCC National Greenhouse Gas Inventory Program.
- _____. 2006. *2006 IPCC Guidelines for national greenhouse gas inventories*. Hayama, Kanagawa, Japan: Intergovernmental Panel on Climate Change, Institute for Global Environmental Strategies.
- Japan Paper Association (JPA). 2002. Various personal communications between JPA and Reid Miner of NCASI. Tokyo: Japan Paper Association.
- Leckner, B. 1998. Fluidized bed combustion: Mixing and pollutant limitation. *Progress in Energy and Combustion Science* 24:31-61. [http://dx.doi.org/10.1016/S0360-1285\(97\)00021-X](http://dx.doi.org/10.1016/S0360-1285(97)00021-X)
- Muzio, L.J., Teague, M.E., Kramlich, J.C., Cole, J.A., McCarthy, J.M., and Lyon, R.K. 1989. Errors in grab sample measurements of N₂O from combustion sources. *Journal of the Air Pollution Control Association* 39:287-293.
- National Council [of the Paper Industry] for Air and Stream Improvement, Inc. (NCASI). 1980. *A study of wood-residue fired power boiler total gaseous non-methane organic emissions in the*

- Pacific Northwest*. Air Quality Technical Bulletin No. 109. New York: National Council of the Paper Industry for Air and Stream Improvement, Inc.
- ô ô ô . 1985. Volatile organic carbon emissions from wood residue fired power boilers in the Southeast. Technical Bulletin No. 455. New York: National Council of the Paper Industry for Air and Stream Improvement, Inc.
- ô ô ô . 2009a. Revised statistical data treatment procedures for pulp and paper mill 'air toxic' emissions data. In *SARA handbook* (04.F.01). Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.
- ô ô ô . 2009b. Appendix A: An overview of the steps and statistical procedures used to develop air emissions factors for the wood products industry. In *SARA handbook* (03.B.24). Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.
- Swedish Environmental Protection Agency (Swedish EPA). 2004. *Sweden's national inventory report 2004 – Submitted under the United National Convention on Climate Change*. Stockholm: Swedish Environmental Protection Agency.
- Tsupari, E., Monni, S., Tormonen, K., Pellikka, T., and Syri, S. 2007. Estimation of annual CH₄ and N₂O emissions from fluidized bed combustion: An advance measurement-based method and its application to Finland. *International Journal of Greenhouse Gas Control* 1:289-297.
[http://dx.doi.org/10.1016/S1750-5836\(07\)00019-9](http://dx.doi.org/10.1016/S1750-5836(07)00019-9)
- United States Environmental Protection Agency (USEPA). 1999. Method 320 ó Measurement of vapor phase organic and inorganic emissions by extractive Fourier Transform Infrared (FTIR) spectroscopy. Part 63, Appendix A. *Federal Register* 64(113): 31937-31951. June 14.
- ô ô ô . 2000. 40 CFR Part 60, 61, and 63 Amendments for testing and monitoring provisions; final rule. *Federal Register* 65(201): 61743-62273. October 17. <http://www.gpo.gov/fdsys/pkg/FR-2000-10-17/pdf/FR-2000-10-17.pdf>
- ô ô ô . 2001. *AP-42 emission factors for wood residue combustion in boilers – Supplement G, July 2001*. Washington, DC: United States Environmental Protection Agency.
- ô ô ô . 2009. Mandatory Reporting of Greenhouse Gases. (40 CFR Part 98). *Federal Register* 74(209): 56260-56519.
- Veverka, P.J., Nichols, K.M., Horton, R.R., and Adams, T.N. 1993. *On the form of nitrogen in wood and its fate during kraft pulping*. IPST Technical Paper Series Number 460. Atlanta, GA: Institute of Paper Science and Technology.
- The World Research Institute and The World Business Council for Sustainable Development (WRI/WBCSD). 2005. *Calculation tools for estimating greenhouse gas emissions from pulp and paper mills*. Report version 1.1. The World Resource Institute and The World Business Council for Sustainable Development Greenhouse Gas Protocol Initiative.

APPENDIX A
DETAILED SOURCE RESULTS

Table A1 Run Data for Source ARF3

Test Parameters		1/13/2009									
Date	(in. Hg)	29.68	30.06	30.03	29.96	30.17	1/14/2009	30.03	29.96	30.17	1/15/2009
Stack Pressure	(°F)	321	318	318	319	333	318	318	319	333	333
Percent O ₂	(%)	5.80	6.85	6.40	6.85	6.70	6.40	6.40	6.85	6.70	6.70
Percent CO ₂	(%)	14.25	13.65	14.05	13.65	13.95	14.05	14.05	13.65	13.95	13.95
Percent H ₂ O	(%)	33.77	33.81	34.65	33.88	34.21	34.65	34.65	33.88	34.21	34.21
Stack Velocity	(ft/sec)	67.24	60.81	60.12	60.33	66.62	60.12	60.12	60.33	66.62	66.62
Stack Flow Rate	(acfm)	184922	167220	165322	165920	183198	165322	165322	165920	183198	183198
Stack Flow Rate	(dscfm)	82065	75459	73595	74471	80869	73595	73595	74471	80869	80869
Run Number		1	2	3	4	5	6	7	8	9	10
BLS Fired	(lb/hr)	81343	81759	75040	75000	75012	74981	74958	74978	81757	71785
BLS Heat Input	(MMBtu/hr)	465.4	467.7	429.3	429.1	429.1	429.0	428.8	429.0	467.7	467.9
Oil Heat Input	(MMBtu/hr)	33.2	32.5	0	0	37.0	37.0	15.5	16.3	0	0
Total Input	(MMBtu/hr)	498.6	500.2	429.3	429.1	466.1	466.0	444.3	445.2	467.7	467.9
CH ₄ Results											
Concentration	(ppmvd)	0.79	3.65	0.50	0.68	1.04	0.90	0.63	0.43	ND[0.65]	1.36
Mass Emission	(lb/hr)	0.16	0.75	0.09	0.13	0.19	0.16	0.12	0.08	ND[0.13]	0.27
Production Based Emission	(kg/MMBtu)	0.00015	0.00068	0.00010	0.00014	0.00019	0.00016	0.00012	0.00008	ND[0.00013]	0.00027
Number of Detects		21/30	25/30	7/30	9/30	15/30	17/30	2/30	3/30	0/30	17/30
Spike Recovery	(%)		100.4		85.0		95.8		82.3		91.9
N ₂ O Results											
Concentration	(ppmvd)	0.84	0.63	0.51	0.53	0.72	0.55	0.46	0.25	0.50	0.29
Mass Emission	(lb/hr)	0.47	0.36	0.26	0.28	0.36	0.28	0.24	0.13	0.27	0.16
Production Based Emission	(kg/MMBtu)	0.00043	0.00032	0.00028	0.00029	0.00035	0.00027	0.00024	0.00013	0.00027	0.00015
Number of Detects		30/30	24/30	40/40	27/30	29/30	28/30	27/30	23/30	30/30	15/30
Spike Recovery	(%)		85.0		61.0		78.7		88.7		94.7

Table A2 Analysis Method for Source ARF3

Method: GHG Mill A Recovery						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	21	9	3200-3450	
Carbon Dioxide	%	Dry	14	7	2015-2215	
Carbon Monoxide	ppm	Dry	19	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2138-2231	2501-2647
Nitric Oxide	ppm	Dry	12	24	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	37	2800-3000	
Methane	ppm	Dry	6	14	2956-3203	
Ethylene	ppm	Dry	5	41	895-1134	2877-3180
Sulfur Dioxide	ppm	Dry	6	23	1057-1259	2439-2550
Oxygen	%		Sensor			

Table A3 Run Data for Source ABB2

Test Parameters					
Date	7/8/2008	7/8/2008	7/8/2008	7/8/2008	7/8/2008
Stack Pressure (in. Hg)	29.86	29.82	29.82	29.82	29.82
Stack Temperature (°F)	144	141	141	135	135
Percent O ₂ (%)	8.7	11.7	11.7	10.2	10.2
Percent CO ₂ (%)	11.4	7.6	7.6	9.7	9.7
Percent H ₂ O (%)	24.79	23.66	23.66	22.53	22.53
Stack Velocity (ft/sec)	50.36	50.93	50.93	51.32	51.32
Stack Flow Rate (acfm)	254419	257322	257322	259251	259251
Stack Flow Rate (dscfm)	167038	172107	172107	177544	177544
Run Number					
	1	2	3	4	5
Bark Fired (lb/hr)	53418	59728	51507	38639	41126
Bark Heat Input (MMBtu/hr)	427.3	477.8	412.1	309.1	329.0
CH ₄ Results					
Concentration (ppmv)	1.0	2.1	3.2		2.6
Mass Emission (lb/hr)	0.42	0.88	1.38		1.15
Production Based Emission (kg/MMBtu)	0.00044	0.00083	0.0015		0.0016
Number of Detects	1/1	1/1	1/1		1/1
Spike Recovery (%)					
N ₂ O Results					
Concentration (ppmv)	1.52	1.3	1.74	2.32	2.25
Mass Emission (lb/hr)	1.74	1.49	2.06	2.74	2.74
Production Based Emission (kg/MMBtu)	0.0018	0.0014	0.0023	0.0040	0.0038
Number of Detects	5/5	5/5	5/5	5/5	5/5
Spike Recovery (%)	89.9	92.7	90.5	93.7	

Table A4 Analysis Method for Source ABB2

Method: GHG Mill A Bark Boiler (Cond)						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	21	10	3200-3450	
Carbon Dioxide	%	Dry	9	7	2015-2215	
Carbon Monoxide	ppm	Dry	19	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2146-2223	2570-2647
Nitric Oxide	ppm	Dry	12	23	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	37	2800-3000	
Methane	ppm	Dry	6	14	2956-3203	
Methanol	ppm	Dry	5	37	930-1120	2688-3159
-Pinene	ppm	Dry	3	39	2625-3250	
-Pinene	ppm	Dry	4	37	2750-3105	
Limonene	ppm	Dry	3	40	895-976	2748-3072
Oxygen	%		Sensor			

Table A5 Run Data for Source BRF5

Test Parameters		5/6/2008		5/6/2008		5/7/2008		5/7/2008		5/8/2008	
Date		29.75		29.74		29.67		29.63		29.56	
Stack Pressure (in. Hg)		425		422		424		422		419	
Stack Temperature (°F)		6.9		6.5		8.8		7.0		7.0	
Percent O ₂ (%)		12.4		12.5		11.3		11.0		10.5	
Percent CO ₂ (%)		28.01		27.74		25.96		25.41		26.79	
Percent H ₂ O (%)		49.27		50.23		48.75		49.05		49.22	
Stack Velocity (ft/sec)		376131		383488		372188		374435		375746	
Stack Flow Rate (acfm)		160605		164794		163163		165557		163221	
Stack Flow Rate (dscfm)											
Run Number		1		2		3		4		5	
BLS Fired (lb/hr)		107488		112749		103360		87966		97390	
BLS Heat Input (MMBtu/hr)		432.1		453.3		415.5		353.6		391.5	
CH ₄ Results											
Concentration (ppmv)		2.14		1.75		13.95		ND[0.85]		2.13	
Mass Emission (lb/hr)		0.86		0.72		5.68		ND[0.30]		0.87	
Production Based Emission (kg/MMBtu)		0.00090		0.00072		0.0062		ND[0.00039]		0.0010	
Number of Detects		24/30		18/30		30/30		0/30		22/30	
Spike Recovery (%)		83.8		134.5		49.7				78.5	
N ₂ O Results											
Concentration (ppmv)		0.54		0.57		0.71		0.77		0.68	
Mass Emission (lb/hr)		0.59		0.65		0.79		0.87		0.76	
Production Based Emission (kg/MMBtu)		0.00062		0.00065		0.00086		0.00111		0.00088	
Number of Detects		23/30		24/30		5/30		27/30		29/30	
Spike Recovery (%)		123.7		111.4		116.7		92.2		121.6	

Table A6 Analysis Method for Source BRF5

Method: GHG Mill B Recovery Boiler (Cond)						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	21	10	3200-3450	
Carbon Dioxide	%	Dry	9	7	2015-2215	
Carbon Monoxide	ppm	Dry	19	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2146-2223	2570-2647
Nitric Oxide	ppm	Dry	12	20	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	33	1552-1625	2800-3000
Methane	ppm	Dry	6	14	2771-3203	
Hydrochloric Acid	ppm	Dry	4	28	2532-2879	
Methanol	ppm	Dry	5	30	930-1120	2688-3159
Dimethyl Sulfide	ppm	Dry	1	34	903-1142	2725-3126
Sulfur Dioxide	ppm	Dry	6	23	1057-1259	2439-2550
Oxygen	%		Sensor			

Table A8 Analysis Method for Source CCB4

Method: GHG Mill C Combination						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	22	11	3200-3450	
Carbon Dioxide	%	Dry	9	7	2015-2215	
Carbon Monoxide	ppm	Dry	19	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2146-2223	2570-2647
Nitric Oxide	ppm	Dry	12	24	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	38	2800-3000	
Methane	ppm	Dry	6	14	2956-3203	
Sulfur Dioxide	ppm	Dry	6	23	1057-1259	2439-2550
Oxygen	%		Sensor			

Table A9 Run Data for Source DRF1

Test Parameters		2/17/2009					
Date		2/17/2009					
Stack Pressure (in. Hg)		29.83					
Stack Temperature (°F)		379					
Percent O ₂ (%)		3.9					
Percent CO ₂ (%)		16.0					
Percent H ₂ O (%)		28.14					
Stack Velocity (ft/sec)		65.49					
Stack Flow Rate (acfm)		548653					
Stack Flow Rate (dscfm)		247370					
Run Number		1	2	3	4	5	6 7 8
BLS Fired	(lb/hr)	228794	228575	228768	229131	228971	228156 227299 224790
BLS Heat Input	(MMBtu/hr)	1401.4	1400.0	1401.2	1403.4	1402.4	1397.5 1390.2 1376.8
CH ₄ Results							
Concentration	(ppmvd)	0.21	0.24	0.21	0.23	0.17	0.24 0.18 0.19
Mass Emission	(lb/hr)	0.13	0.15	0.13	0.14	0.11	0.15 0.11 0.12
Production Based Emission	(kg/MMBtu)	0.000042	0.000047	0.000041	0.000046	0.000034	0.000047 0.000037 0.000038
Number of Detects		0/5	0/6	0/5	0/5	0/5	1/5 0/5 0/5
Spike Recovery	(%)						93.0
N ₂ O Results							
Concentration	(ppmvd)	ND[0.45]	0.22	ND[0.33]	ND[0.29]	0.33	0.32 ND[0.25] 0.31
Mass Emission	(lb/hr)	ND[0.77]	0.38	ND[0.55]	ND[0.49]	0.56	0.55 ND[0.43] 0.53
Production Based Emission	(kg/MMBtu)	ND[0.00023]	0.00012	ND[0.00018]	ND[0.00016]	0.00018	0.00018 ND[0.00014] 0.00017
Number of Detects		0/5	1/6	0/5	0/5	3/5	4/5 0/5 2/5
Spike Recovery	(%)		85.6			81.5	80.2 76.2

Table A10 Analysis Method for Source DRF1

Method: GHG Mill D						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	21	9	3200-3450	
Carbon Dioxide	%	Dry	14	7	2015-2215	
Carbon Monoxide	ppm	Dry	19	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2138-2231	2501-2647
Nitric Oxide	ppm	Dry	12	24	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	37	2800-3000	
Methane	ppm	Dry	6	14	2956-3203	
Ethylene	ppm	Dry	5	41	895-1134	2877-3180
Sulfur Dioxide	ppm	Dry	6	23	1057-1259	2439-2550
Oxygen	%		Sensor			

Table A11 Run Data for Source DBB1

Test Parameters										
Date	2/18/2009		2/18/2009		2/18/2009		2/19/2009		2/19/2009	
Stack Pressure (in. Hg)	29.57		29.48		29.41		30.12		30.14	
Stack Temperature (°F)	326		330		330		304		304	
Percent O ₂ (%)	11.6		12.3		11.9		12.9		13.5	
Percent CO ₂ (%)	8.4		8.2		8.6		7.2		7.0	
Percent H ₂ O (%)	15.16		14.90		14.99		12.92		11.59	
Stack Velocity (ft/sec)	66.64		74.60		73.50		59.55		60.41	
Stack Flow Rate (acfm)	263889		295393		291057		235819		239197	
Stack Flow Rate (dscfm)	148510		165580		162413		142896		147158	
Run Number	1	2	3	4	5	6	7	8	9	10
Bark Fired (lb/hr)	102643	94210	103480	103272	105986	111673	88132	66489	88325	88904
Bark Heat Input (MMBtu/hr)	461.9	423.9	465.7	464.7	476.9	502.5	396.6	299.2	397.5	400.1
CH ₄ Results										
Concentration (ppmvd)	0.61	1.18	0.42	0.49	0.58	1.27	0.61	0.55	0.56	0.57
Mass Emission (lb/hr)	0.23	0.44	0.17	0.20	0.24	0.51	0.22	0.20	0.20	0.21
Production Based Emission (kg/MMBtu)	0.00022	0.00047	0.00017	0.00020	0.00022	0.00046	0.00025	0.00030	0.00023	0.00024
Number of Detects	6/6	5/5	4/5	6/6	5/5	6/6	7/7	5/5	5/5	5/5
Spike Recovery (%)	97.3	97.7	94.5	95.5	92.9	99.7	98.2	94.3	94.0	91.7
N ₂ O Results										
Concentration (ppmvd)	0.91	1.16	1.00	0.81	1.15	1.18	ND[0.55]	0.86	0.86	ND[0.62]
Mass Emission (lb/hr)	0.93	1.18	1.13	0.92	1.28	1.32	ND[0.54]	0.84	0.86	ND[0.62]
Production Based Emission (kg/MMBtu)	0.0009	0.0013	0.0011	0.0009	0.0012	0.0012	ND[0.0006]	0.0013	0.0010	ND[0.0007]
Number of Detects	6/6	5/5	5/5	6/6	5/5	6/6	0/5	5/5	5/5	0/5
Spike Recovery (%)	87.9	96.4	91.0	90.6	87.6	92.0	87.0	87.0	91.1	91.1

Table A12 Analysis Method for Source DBB1

Method: GHG Mill D						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	21	9	3200-3450	
Carbon Dioxide	%	Dry	14	7	2015-2215	
Carbon Monoxide	ppm	Dry	19	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2138-2231	2501-2647
Nitric Oxide	ppm	Dry	12	24	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	37	2800-3000	
Methane	ppm	Dry	6	14	2956-3203	
Ethylene	ppm	Dry	5	41	895-1134	2877-3180
Sulfur Dioxide	ppm	Dry	6	23	1057-1259	2439-2550
Oxygen	%		Sensor			

Table A13 Run Data for Source ERF1

Test Parameters										
Date	2/24/2009			2/24/2009			2/25/2009			
Stack Pressure (in. Hg)	30.47			30.37			30.46			
Stack Temperature (°F)	374			376			378			
Percent O ₂ (%)	4.1			3.7			3.9			
Percent CO ₂ (%)	15.1			15.4			14.9			
Percent H ₂ O (%)	24.80			24.80			24.90			
Stack Velocity (ft/sec)	87.28			87.34			89.06			
Stack Flow Rate (acfm)	497680			497993			507841			
Stack Flow Rate (dscfm)	241344			240244			244881			
Run Number	1	2	3	4	5	6	7	8	9	10
BLS Fired (lb/hr)	173298	173339	173323	173758	174545	174641	166068	166295	166472	175097
BLS Heat Input (MMBtu/hr)	947.9	948.2	948.1	950.6	954.8	955.3	908.4	909.6	910.6	957.8
CH ₄ Results										
Concentration (ppmvd)	0.23	4.38	19.42	9.98	3.07	17.87	10.83	13.39	7.61	19.82
Mass Emission (lb/hr)	0.14	2.64	11.71	6.02	1.84	10.73	6.63	8.19	4.66	12.12
Production Based Emission (kg/MMBtu)	0.00007	0.0013	0.0056	0.0029	0.0009	0.0051	0.0033	0.0041	0.0023	0.0057
Number of Detects	1/10	5/5	6/6	5/5	5/5	5/5	7/7	5/5	6/6	5/5
Spike Recovery (%)		96.8	101.3	98	97.8	98.5	97.5	97.7	98.2	102.3
N ₂ O Results										
Concentration (ppmvd)	ND[0.13]	ND[0.24]	ND[0.65]	ND[0.38]	ND[0.21]	ND[0.66]	0.77	ND[0.53]	0.78	0.34
Mass Emission (lb/hr)	ND[0.21]	ND[0.39]	ND[1.08]	ND[0.63]	ND[0.35]	ND[1.08]	1.29	ND[0.89]	1.30	0.57
Production Based Emission (kg/MMBtu)	ND[0.0001]	ND[0.00019]	ND[0.00051]	ND[0.0003]	ND[0.00016]	ND[0.00051]	0.00065	ND[0.00044]	0.00065	0.00027
Number of Detects	0/10	0/5	0/6	0/5	0/5	0/6	2/7	0/5	6/6	1/5
Spike Recovery (%)							85.3		87.9	126.6

Table A14 Analysis Method for Source ERF1

Method: GHG Mill E						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	21	9	3200-3450	
Carbon Dioxide	%	Dry	14	7	2015-2215	
Carbon Monoxide	ppm	Dry	19	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2146-2215	2501-2647
Nitric Oxide	ppm	Dry	12	24	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	37	2800-3000	
Methane	ppm	Dry	6	14	2956-3203	
Oxygen	%		Sensor			

Table A15 Run Data for Source FRF1

Test Parameters		3/28/2009					
Date		3/28/2009					
Stack Pressure	(in. Hg)	29.35					
Stack Temperature	(°F)	316					
Percent O ₂	(%)	6.9					
Percent CO ₂	(%)	12.1					
Percent H ₂ O	(%)	34.26					
Stack Velocity	(ft/sec)	40.88					
Stack Flow Rate	(acfm)	87765					
Stack Flow Rate	(dscfm)	38485					
Run Number		1	2	3	4	5	6
BLS Fired	(lb/hr)	31680	31803	31957	31737	31562	31285
BLS Heat Input	(MMBtu/hr)	186.9	187.6	188.5	187.2	186.2	184.6
CH ₄ Results							
Concentration	(ppmvd)	60.01	67.12	42.18	25.87	8.40	62.72
Mass Emission	(lb/hr)	5.77	6.45	4.05	2.52	0.82	6.12
Production Based Emission	(kg/MMBtu)	0.0140	0.0156	0.0098	0.0061	0.0020	0.0150
Number of Detects		5/5	5/5	6/6	7/7	6/6	5/5
Spike Recovery	(%)		97.8	99.4	99.3		99.5
N ₂ O Results							
Concentration	(ppmvd)	1.13	1.33	0.69	0.83	1.06	1.05
Mass Emission	(lb/hr)	0.30	0.35	0.18	0.22	0.28	0.28
Production Based Emission	(kg/MMBtu)	0.00072	0.00085	0.00044	0.00054	0.00069	0.00069
Number of Detects		5/5	5/5	6/6	7/7	6/6	5/5
Spike Recovery	(%)	112.9		97.9	91.9		105.1

Table A16 Analysis Method for Source FRF1

Method: GHG Mill F						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	21	10	3200-3450	
Carbon Dioxide	%	Dry	14	7	2015-2215	
Carbon Monoxide	ppm	Dry	20	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2138-2215	2501-2647
Nitric Oxide	ppm	Dry	12	24	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	38	2800-3000	
Methane	ppm	Dry	6	14	2956-3203	
Ethylene	ppm	Dry	5	42	895-1134	2877-3180
Sulfur Dioxide	ppm	Dry	6	23	1057-1259	2439-2550
Oxygen	%		Sensor			

Table A17 Run Data for Source FRF3

Test Parameters									
Date	3/25/2009			3/25/2009			3/26/2009		
Stack Pressure (in. Hg)	29.63			29.58			29.68		
Stack Temperature (°F)	318			318			305		
Percent O ₂ (%)	7.3			7.2			9.0		
Percent CO ₂ (%)	12.8			12.8			10.6		
Percent H ₂ O (%)	30.56			32.64			30.25		
Stack Velocity (ft/sec)	65.43			65.55			64.57		
Stack Flow Rate (acfm)	137030			137284			135242		
Stack Flow Rate (dscfm)	63957			62039			64577		
Run Number									
BLS Fired	53174	53237	53408	52703	51262	51797	46136	46470	46246
BLS Heat Input (MMBtu/hr)	313.7	314.1	315.1	311.0	302.5	305.6	272.2	274.2	272.9
CH ₄ Results									
Concentration (ppmvd)	3.34	2.48	4.95	6.84	6.51	6.69	1.52	0.98	7.84
Mass Emission (lb/hr)	0.53	0.40	0.79	1.06	1.01	1.04	0.24	0.16	1.26
Production Based Emission (kg/MMBtu)	0.00077	0.00057	0.00114	0.00155	0.00151	0.00154	0.00041	0.00026	0.00210
Number of Detects	6/6	5/5	6/6	5/5	5/5	6/6	6/6	5/5	5/5
Spike Recovery (%)	98.9	98.1	99.3	98.3	99.6		99.9	93.4	98.0
N ₂ O Results									
Concentration (ppmvd)	0.71	0.70	0.77	0.79	0.66	0.95	0.54	0.46	1.03
Mass Emission (lb/hr)	0.31	0.31	0.34	0.34	0.28	0.40	0.24	0.20	0.46
Production Based Emission (kg/MMBtu)	0.00045	0.00044	0.00049	0.00049	0.00042	0.00060	0.00039	0.00034	0.00076
Number of Detects	6/6	5/5	6/6	5/5	5/5	6/6	6/6	5/5	5/5
Spike Recovery (%)	90.0	94.3	96.2	93.2	91.9		93.6	94.5	89.0

Table A18 Analysis Method for Source FRF3

Method: GHG Mill F						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	21	10	3200-3450	
Carbon Dioxide	%	Dry	14	7	2015-2215	
Carbon Monoxide	ppm	Dry	20	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2138-2215	2501-2647
Nitric Oxide	ppm	Dry	12	24	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	38	2800-3000	
Methane	ppm	Dry	6	14	2956-3203	
Ethylene	ppm	Dry	5	42	895-1134	2877-3180
Sulfur Dioxide	ppm	Dry	6	23	1057-1259	2439-2550
Oxygen	%		Sensor			

Table A19 Run Data for Source FBB1

Test Parameters										
Date	3/23/2009			3/24/2009			3/24/2009			
Stack Pressure (in. Hg)	29.71			29.79			29.62			
Stack Temperature (°F)	147			143			145			
Percent O ₂ (%)	6.8			8.7			6.9			
Percent CO ₂ (%)	10.3			9.7			12.4			
Percent H ₂ O (%)	23.73			21.12			22.25			
Stack Velocity (ft/sec)	30.29			29.76			32.37			
Stack Flow Rate (acfm)	172724			169690			184570			
Stack Flow Rate (dscfm)	113795			116671			123963			
Run Number	1	2	3	4	5	6	7	8	9	10
Bark Fired (lb/hr)	118414	105743	114525	125992	99798	88599	126158	129422	126124	132670
Bark Heat Input (MMBtu/hr)	503.3	449.4	486.7	535.5	424.1	376.6	536.2	550.0	536.0	563.9
CH ₄ Results										
Concentration (ppmvd)	210.82	272.91	89.66	236.14	53.40	49.68	216.26	108.27	204.81	108.66
Mass Emission (lb/hr)	59.93	77.58	26.13	68.83	15.56	14.48	66.97	33.53	63.43	33.65
Production Based Emission (kg/MMBtu)	0.054	0.078	0.024	0.058	0.017	0.017	0.057	0.028	0.054	0.027
Number of Detects	5/5	5/5	5/5	6/6	6/6	6/6	6/6	5/5	5/5	6/6
Spike Recovery (%)	101.3		100.2	101.5	99.8	99.6	97.7	100.5	101.2	
N ₂ O Results										
Concentration (ppmvd)	0.76	0.85	0.37	ND[0.61]	1.58	2.37	ND[0.61]	0.98	0.42	0.96
Mass Emission (lb/hr)	0.59	0.66	0.30	ND[0.48]	1.26	1.90	ND[0.51]	0.83	0.36	0.82
Production Based Emission (kg/MMBtu)	0.00054	0.00067	0.00028	ND<[0.00041]	0.00135	0.00229	ND[0.00043]	0.00069	0.00030	0.00066
Number of Detects	2/5	5/5	1/5	0/6	6/6	6/6	0/6	5/5	1/5	6/6
Spike Recovery (%)	93.9		101.1		99.2	100.7		91.3	122.1	

Table A20 Analysis Method for Source FBB1

Method: GHG Mill F Bark Boiler						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	21	10	3200-3450	
Carbon Dioxide	%	Dry	14	7	2015-2215	
Carbon Monoxide	ppm	Dry	20	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2138-2215	2501-2647
Nitric Oxide	ppm	Dry	12	24	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	38	2800-3000	
Methane	ppm	Dry	6	14	2956-3203	
Ethane	ppm	Dry	2	39	2663-3180	
Acetylene	ppm	Dry	1	43	1219-1428	3095-3389
Ethylene	ppm	Dry	5	42	895-1134	2877-3180
Formaldehyde	ppm	Dry	5	38	2500-3211	
Benzene	ppm	Dry	3	38	949-1096	2941-3172
Oxygen	%		Sensor			

Table A21 Run Data for Source GRF1

Test Parameters						
Date	6/11/2009	6/11/2009	6/11/2009	6/11/2009	6/11/2009	6/11/2009
Stack Pressure (in. Hg)	29.82	29.77	29.75	29.77	29.75	29.75
Stack Temperature (°F)	329	330	329	330	329	329
Percent O ₂ (%)	6.6	6.9	7.0	6.9	7.0	7.0
Percent CO ₂ (%)	14.2	13.9	13.8	13.9	13.8	13.8
Percent H ₂ O (%)	32.8	33.3	32.1	33.3	32.1	32.1
Stack Velocity (ft/sec)	94.21	94.86	94.28	94.86	94.28	94.28
Stack Flow Rate (acfm)	335070	337380	335322	337380	335322	335322
Stack Flow Rate (dscfm)	150183	149616	151551	149616	151551	151551
Run Number						
BLS Fired	120100	121800	121800	121800	118600	118500
BLS Heat Input (MMBtu/hr)	672.6	682.1	682.1	682.1	664.2	663.6
CH ₄ Results						
Concentration (ppmvd)	0.44	0.40	0.45	0.59	0.42	0.39
Mass Emission (lb/hr)	0.17	0.15	0.17	0.22	0.16	0.15
Production Based Emission (kg/MMBtu)	0.00011	0.00010	0.00011	0.00015	0.00011	0.00010
Number of Detects	0/5	0/5	0/5	2/5	0/5	0/5
Spike Recovery (%)				99.1		
N ₂ O Results						
Concentration (ppmvd)	0.17	0.28	0.46	0.38	0.25	0.20
Mass Emission (lb/hr)	0.17	0.29	0.47	0.39	0.26	0.21
Production Based Emission (kg/MMBtu)	0.00012	0.00019	0.00031	0.00026	0.00018	0.00014
Number of Detects	2/5	5/5	5/5	5/5	5/5	5/5
Spike Recovery (%)	98.1	95.9		110.7	93.8	95.2

Table A22 Analysis Method for Source GRF1

Method: GHG Mill G RF1						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	21	10	3200-3450	
Carbon Dioxide	%	Dry	14	7	2015-2215	
Carbon Monoxide	ppm	Dry	20	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2153-2207	2501-2601
Nitric Oxide	ppm	Dry	12	24	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	38	2800-3000	
Methane	ppm	Dry	6	14	2956-3203	
Ethylene	ppm	Dry	5	42	895-1134	2877-3180
Sulfur Dioxide	ppm	Dry	6	23	1057-1259	2439-2550
Oxygen	%		Sensor			

Table A23 Run Data for Source GRF2

Test Parameters						
Date	6/9/2009	6/9/2009	6/9/2009	6/9/2009	6/9/2009	6/9/2009
Stack Pressure (in. Hg)	29.74	29.69	29.68	29.68	29.68	29.68
Stack Temperature (°F)	306	312	317	317	317	317
Percent O ₂ (%)	8.3	7.4	7.2	7.2	7.2	7.2
Percent CO ₂ (%)	12.8	13.6	13.8	13.8	13.8	13.8
Percent H ₂ O (%)	30.55	31.65	28.80	28.80	28.80	28.80
Stack Velocity (ft/sec)	155.06	157.73	157.8	157.8	157.8	157.8
Stack Flow Rate (acfm)	308726	314029	314177	314177	314177	314177
Stack Flow Rate (dscfm)	146816	145521	150627	150627	150627	150627
Run Number						
BLS Fired	96600	98850	105900	107100	107250	107250
BLS Heat Input (MMBtu/hr)	541.0	553.6	593.0	599.8	600.6	600.6
CH ₄ Results						
Concentration (ppmvd)	0.53	ND[0.68]	0.47	0.40	0.44	0.44
Mass Emission (lb/hr)	0.19	ND[0.25]	0.17	0.15	0.17	0.17
Production Based Emission (kg/MMBtu)	0.00016	ND[0.00020]	0.00013	0.00011	0.00013	0.00013
Number of Detects	3/30	0/30	14/30	12/31	15/30	15/30
Spike Recovery (%)				93.8	95.6	95.6
N ₂ O Results						
Concentration (ppmvd)	0.30	0.40	0.12	0.21	0.23	0.23
Mass Emission (lb/hr)	0.30	0.40	0.12	0.22	0.24	0.24
Production Based Emission (kg/MMBtu)	0.00026	0.00033	0.000092	0.00017	0.00018	0.00018
Number of Detects	29/30	30/30	11/30	27/31	25/30	25/30
Spike Recovery (%)		99.9		101.1	89.9	89.9

Table A24 Analysis Method for Source GRF2

Method: GHG Mill G RF2						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	21	10	3200-3450	
Carbon Dioxide	%	Dry	14	7	2015-2215	
Carbon Monoxide	ppm	Dry	20	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2138-2207	2501-2647
Nitric Oxide	ppm	Dry	12	24	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	38	2800-3000	
Methane	ppm	Dry	6	14	2956-3203	
Ethylene	ppm	Dry	5	42	895-1134	2877-3180
Sulfur Dioxide	ppm	Dry	6	23	1057-1259	2439-2550
Oxygen	%		Sensor			

Table A25 Run Data for Source GCB3

Test Parameters		6/10/2009					
Date		29.81					
Stack Pressure	(in. Hg)	29.81					
Stack Temperature	(°F)	147					
Percent O ₂	(%)	10.7					
Percent CO ₂	(%)	9.4					
Percent H ₂ O	(%)	26.16					
Stack Velocity	(ft/sec)	72.75					
Stack Flow Rate	(acfm)	205919					
Stack Flow Rate	(dscfm)	131835					
Run Number		1	2	3	4	5	6
Bark Fired	(lb/hr)	61600	63333	67200	64800	64000	65200
Bark Heat Input	(MMBtu/hr)	231.0	237.5	252.0	243.0	240.0	244.5
Oil Heat Input	(MMBtu/hr)	0.0	1.5	2.0	6.0	1.0	0.5
Total Heat Input	(MMBtu/hr)	231	239	254.0	249.0	241.0	245.0
CH ₄ Results							
Concentration	(ppmvd)	1.59	1.09	1.27	0.94	1.04	0.92
Mass Emission	(lb/hr)	0.50	0.34	0.42	0.31	0.33	0.29
Production Based Emission	(kg/MMBtu)	0.00099	0.00065	0.00075	0.00056	0.00062	0.00054
Number of Detects		30/30	30/30	30/30	30/30	30/30	30/30
Spike Recovery	(%)		101.3		99.0		102.3
N ₂ O Results							
Concentration	(ppmvd)	1.20	1.48	2.22	2.25	2.96	2.41
Mass Emission	(lb/hr)	1.04	1.28	2.01	2.04	2.56	2.08
Production Based Emission	(kg/MMBtu)	0.0020	0.0024	0.0036	0.0037	0.0048	0.0038
Number of Detects		28/30	30/30	30/30	30/30	30/30	30/30
Spike Recovery	(%)		101.1		109.3		100.3

Table A26 Analysis Method for Source GCB3

Method: GHG Mill G CB3						
Analyte List	Unit	Compensation	References	Interferences	Analysis Area 1	Analysis Area 2
Water Vapor	%	Wet	21	10	3200-3450	
Carbon Dioxide	%	Dry	14	7	2015-2215	
Carbon Monoxide	ppm	Dry	20	6	2005-2177	
Nitrous Oxide	ppm	Dry	6	5	2146-2200	2501-2647
Nitric Oxide	ppm	Dry	12	24	1829-2020	
Nitrogen Dioxide	ppm	Dry	5	38	2800-3000	
Methane	ppm	Dry	6	14	2956-3203	
Ethylene	ppm	Dry	5	42	895-1134	2877-3180
Sulfur Dioxide	ppm	Dry	6	23	1057-1259	2439-2550
Oxygen	%		Sensor			

Table A27 Run Data for Source HCB1

Test Parameters			
Date	7/15/09	7/15/09	7/15/09
Stack Flow Rate	(dscfm)	86591	76897 73169
Run Number		1	2 3
Bark	(%)	88.8	88.8
Resin Wood	(%)	11.2	11.2
Natural Gas	(%)	0.0	0.0
Total Heat Input	(MMBtu/hr)	270.1	263.5 246.2
CH ₄ Results			
Concentration	(ppmvd)	ND[0.33]	ND[0.34]
Mass Emission	(lb/hr)	ND[0.072]	ND[0.064] ND[0.062]
Production Based Emission	(kg/MMBtu)	ND[0.00012]	ND[0.00011] ND[0.00011]

Table A28 Run Data for Source ICB 1

Test Parameters			
Date	7/14/09	7/15/09	7/15/09
Stack Flow Rate	(dscfm)	54929	55114 56963
Run Number		1	2 3
Hog Fuel	(%)	80.1	78.3
Municipal Solid Waste	(%)	19.8	20.6
Natural Gas	(%)	0.0	1.1
Total Heat Input	(MMBtu/hr)	207.6	204.5 216.5
CH ₄ Results			
Concentration	(ppmvd)	6.0	5.2
Mass Emission	(lb/hr)	0.82	0.72
Production Based Emission	(kg/MMBtu)	0.0018	0.0016 0.0020

Table A29 Run Data for Source JCB2

Test Parameters			
Date	7/1/09	7/2/09	7/2/09
Stack Flow Rate	160000	160000	160000
Run Number	1	2	3
Bark	81.5	81.5	81.5
TDF	18.0	18.0	18.0
Fuel Oil	0.6	0.6	0.6
Total Heat Input	577.3	548.4	584.5
CH ₄ Results			
Concentration	27.6	11.3	33.5
Mass Emission	11.03	4.52	13.39
Production Based Emission	0.0087	0.0037	0.0104

Table A30 Run Data for Source KCB2

Test Parameters			
Date	8/4/09	8/4/09	8/4/09
Stack Flow Rate	24393	24080	24168
Run Number	1	2	3
Bark	100.0	100.0	100.0
Total Heat Input	90.5	92.7	81.3
CH ₄ Results			
Concentration	2.0	1.0	1.1
Mass Emission	0.12	0.060	0.066
Production Based Emission	0.00061	0.00029	0.00037

Table A31 Run Data for Source LCB1

Test Parameters				
Date		8/13/09	8/13/09	8/13/09
Stack Flow Rate	(dscfm)	21242	23203	23075
Run Number		1	2	3
Wood/Bark	(%)	100.0	100.0	100.0
Total Heat Input	(MMBtu/hr)	77.7	72.2	68.5
CH ₄ Results				
Concentration	(ppmvd)	2.96	1.03	2.26
Mass Emission	(lb/hr)	0.16	0.060	0.13
Production Based Emission	(kg/MMBtu)	0.00092	0.00037	0.00086

Table A32 Run Data for Source MCB3

Test Parameters				
Date		8/6/09	8/6/09	8/7/09
Stack Flow Rate	(dscfm)	11098	11213	11090
Run Number		1	2	3
Wood Waste	(%)	100.0	100.0	100.0
Total Heat Input	(MMBtu/hr)	47.17	46.10	48.52
CH ₄ Results				
Concentration	(ppmvd)	0.82	0.92	1.87
Mass Emission	(lb/hr)	0.023	0.026	0.052
Production Based Emission	(kg/MMBtu)	0.00022	0.00025	0.00048

Table A33 Run Data for Source NCBI

Test Parameters			
Date		8/6/09	8/7/09
Stack Flow Rate	(dscfm)	80214	79123
Run Number		1	3
Bark		100.0	100.0
Total Heat Input	(%) (MMBtu/hr)	318.69	337.77
CH ₄ Results			
Concentration	(ppmvd)	4.93	4.10
Mass Emission	(lb/hr)	0.99	0.79
Production Based Emission	(kg/MMBtu)	0.0014	0.0011
			0.00050

Table A34 Run Data for Source OCB4

Test Parameters			
Date		8/11/09	8/12/09
Stack Flow Rate	(dscfm)	128000	130000
Run Number		1	3
Bark		91.4	89.3
Fuel Oil	(%)	6.1	5.9
Natural Gas	(%)	2.5	4.8
Total Heat Input	(MMBtu/hr)	431.16	427.55
CH ₄ Results			
Concentration	(ppmvd)	0.46	0.89
Mass Emission	(lb/hr)	0.15	0.29
Production Based Emission	(kg/MMBtu)	0.00015	0.00031

Table A35 Run Data for Source PCB4

Test Parameters				
Date		8/5/09	8/5/09	8/6/09
Stack Flow Rate	(dscfm)	85489	80039	82047
Run Number		1	2	3
Bark				
WWT Sludge				
TDF				
Total Heat Input	(MMBtu/hr)	337.1	351.0	338.9
CH ₄ Results				
Concentration	(ppmvd)	0.60	0.61	0.77
Mass Emission	(lb/hr)	0.13	0.12	0.16
Production Based Emission	(kg/MMBtu)	0.00017	0.00016	0.00021

Table A36 Run Data for Source QCB8

Test Parameters				
Date	7/29/2009	7/29/2009	7/29/2009	7/30/2009
Stack Flow Rate	(dscfm)	53777	54131	50798
Run Number		1	2	3
WWT Sludge	(%)	62.0	62.0	62.0
Wood/Bark	(%)	38.0	38.0	38.0
Total Heat Input	(MMBtu/hr)	164.17	163.59	153.51
CH ₄ Results				
Concentration	(ppmvd)	2.05	1.85	1.70
Mass Emission	(lb/hr)	0.28	0.25	0.22
Production Based Emission	(kg/MMBtu)	0.00076	0.00069	0.00064

Table A37 Run Data for Source RCB1

Test Parameters				
Date		9/2/2009		9/3/2009
Stack Flow Rate	(dscfm)	7226	7128	7329
Run Number		1	2	3
Bark	(%)	100.0	100.0	100.0
Total Heat Input	(MMBtu/hr)	27.92	26.47	23.29
CH ₄ Results				
Concentration	(ppmvd)	12.2	2.2	1.3
Mass Emission	(lb/hr)	0.22	0.039	0.024
Production Based Emission	(kg/MMBtu)	0.00358	0.00067	0.00046

Table A38 Run Data for Source SCB1

Test Parameters				
Date		8/14/2009		8/14/2009
Stack Flow Rate	(dscfm)	157931	159424	163355
Run Number		1	2	3
Bark	(%)	68.8	68.4	68.2
Cross ties	(%)	11.7	11.6	11.6
Natural Gas	(%)	9.4	9.3	9.3
WWT Sludge	(%)	5.9	6.2	6.2
Total Heat Input	(MMBtu/hr)	584.09	587.45	594.13
CH ₄ Results				
Concentration	(ppmvd)	4.0	15.3	2.5
Mass Emission	(lb/hr)	1.58	6.09	1.02
Production Based Emission	(kg/MMBtu)	0.00123	0.00470	0.00078

Table A39 Run Data for Source TCB1

Test Parameters			
Date	8/11/2009	8/12/2009	8/12/2009
Stack Flow Rate	53484	48369	52952
Run Number	1	2	3
Wood	100.0	100.0	100.0
Total Heat Input	182.02	139.73	159.86
CH ₄ Results			
Concentration	1.59	4.24	6.39
Mass Emission	0.21	0.51	0.85
Production Based Emission	0.00053	0.00166	0.00240

Table A40 Run Data for Source UCB2

Test Parameters			
Date	6/24/09	6/25/09	6/25/09
Stack Flow Rate	191210	190684	181706
Run Number	1	2	3
Wood/Bark	77.2	78.2	83.0
WWT Sludge	5.0	9.1	8.6
OCC Rejects	17.0	11.9	7.6
Natural Gas	0.8	0.8	0.8
Total Heat Input	725.32	765.32	590.23
CH ₄ Results			
Concentration	16.7	8.0	2.14
Mass Emission	7.98	3.81	0.97
Production Based Emission	0.00499	0.00226	0.00075

Table A41 Run Data for Source VCB2

Test Parameters			
Date	8/6/09	8/6/09	8/6/09
Stack Flow Rate	(dscfm)	132000	128000
Run Number	1	2	3
Bark	(%)	61.6	61.6
WWT Sludge	(%)	19.3	19.3
Cross Ties	(%)	16.4	16.4
Natural Gas	(%)	2.7	2.7
Total Heat Input	(MMBtu/hr)	519.57	501.89
CH ₄ Results			
Concentration	(ppmvd)	1.9	2.6
Mass Emission	(lb/hr)	0.63	0.83
Production Based Emission	(kg/MMBtu)	0.00055	0.00075

Table A42 Run Data for Source WCB1

Test Parameters			
Date	7/30/2009	7/31/2009	7/31/2009
Stack Flow Rate	(dscfm)	159000	157000
Run Number	1	2	3
Bark	(%)	73.81	89.77
OCC Rejects	(%)	6.32	4.77
Natural Gas	(%)	10.88	0.6
WWT Sludge	(%)	8.99	3.85
Total Heat Input	(MMBtu/hr)	534.70	573.22
CH ₄ Results			
Concentration	(ppmvd)	3.8	4.4
Mass Emission	(lb/hr)	1.51	1.73
Production Based Emission	(kg/MMBtu)	0.00128	0.00137
			3.1
			1.34
			0.00093

Table A43 Run Data for Source XCB1

Test Parameters			
Date	8/13/2009	8/13/2009	8/14/2009
Stack Flow Rate	(dscfm)	46530	44430
Run Number	1	2	3
Bark	(%)	100.0	100.0
Total Heat Input	(MMBtu/hr)	168.87	175.30
CH ₄ Results			
Concentration	(ppmvd)	17.9	13.1
Mass Emission	(lb/hr)	2.08	1.45
Production Based Emission	(kg/MMBtu)	0.0056	0.0038
			0.0030

Table A44 Run Data for Source YCB1

Test Parameters			
Date	8/6/2009	8/7/2009	8/7/2009
Stack Flow Rate	(dscfm)	84245	85641
Run Number	1	2	3
Bark	(%)	92.9	94.4
Natural Gas	(%)	7.1	5.6
Total Heat Input	(MMBtu/hr)	373.68	353.90
CH ₄ Results			
Concentration	(ppmvd)	189.54	205.80
Mass Emission	(lb/hr)	39.89	44.03
Production Based Emission	(kg/MMBtu)	0.048	0.056
			0.032

Table A45 Run Data for Source ZCB1

Test Parameters				
Date		10/8/2009	10/8/2009	10/8/2009
Stack Flow Rate	(dscfm)	15438	15576	14587
Run Number				
Bark	(%)	100.0	100.0	100.0
Total Heat Input	(MMBtu/hr)	15.66	16.44	15.86
CH ₄ Results				
Concentration	(ppmvd)	4.11	3.95	3.24
Mass Emission	(lb/hr)	0.16	0.15	0.12
Production Based Emission	(kg/MMBtu)	0.0046	0.0042	0.0034

Table A46 Run Data for Source AACB1

Test Parameters				
Date		7/29/2009	7/30/2009	7/30/2009
Stack Flow Rate	(dscfm)	11900	11900	9440
Run Number				
Wood/Bark	(%)	100.0	100.0	100.0
Total Heat Input	(MMBtu/hr)	17.29	13.71	17.72
CH ₄ Results				
Concentration	(ppmvd)	3.8	10.7	1.5
Mass Emission	(lb/hr)	0.11	0.32	0.035
Production Based Emission	(kg/MMBtu)	0.0030	0.0105	0.0009

Table A47 Run Data for Source ABCB1

Test Parameters				
Date		7/23/2009	7/23/2009	7/23/2009
Stack Flow Rate	(dscfm)	13100	9680	11100
Run Number				
Bark	(%)	90.0	90.0	90.0
Wood	(%)	10.0	10.0	10.0
Total Heat Input	(MMBtu/hr)	22.95	22.75	27.75
CH ₄ Results				
Concentration	(ppmvd)	1.3	1.3	1.4
Mass Emission	(lb/hr)	0.043	0.031	0.039
Production Based Emission	(kg/MMBtu)	0.00084	0.00063	0.00063

Table A48 Run Data for Source ACCB1

Test Parameters				
Date		7/29/2009	7/29/2009	7/30/2009
Stack Flow Rate	(dscfm)	140489	141268	138579
Run Number				
Bark	(%)	100.0	100.0	100.0
Total Heat Input	(MMBtu/hr)	685.26	655.20	655.82
CH ₄ Results				
Concentration	(ppmvd)	4.12	0.58	1.82
Mass Emission	(lb/hr)	1.45	0.21	0.63
Production Based Emission	(kg/MMBtu)	0.00096	0.00014	0.00043

APPENDIX B

PRINCIPLES OF FTIR ANALYSIS

Fourier transform infrared (FTIR) spectroscopy is a type of spectral analysis that pairs the fundamentals of infrared analysis with fast Fourier transform mathematics to achieve quick and reliable multi-gas analysis. The following is a basic explanation of FTIR analysis and technology (Smith 1996).

1.0 INFRARED ANALYSIS

A wavelength is the distance, usually measured in centimeters, between adjacent light wave peaks. The reciprocal of that wavelength is referred to as a wave number (cm^{-1}). Within the electromagnetic spectrum, wave numbers between 4,000 and 400 cm^{-1} are referred to as the mid-infrared range. It is within this range of wave numbers that most FTIR spectrometers operate.

Most chemical compounds absorb infrared radiation, with the exception being diatomic homogeneous molecules (N_2 , H_2 , O_2 , etc.). Chemical bonds absorb infrared energy causing the bonds to vibrate or rotate. Depending on the type of chemical bond and its placement within the molecule, specific wavelengths will be absorbed. The overall transmittance of the wavelengths intensity decreases as the wavelengths are absorbed by compounds. Plotting wave numbers versus transmittance results in a sample spectrum. Spectra also can be based on absorption, determined by the following equation.

$$A = \log (1/T)$$

where A is absorption and T is percent transmittance. The number and placement of absorption peaks across the mid-IR range is unique and constant for every compound and can be considered a physical property of that compound. This allows for qualitative analysis of samples with IR spectroscopy.

Based on Beer's law, which states that concentration and absorbance are directly proportional, IR spectroscopy may be used for quantitative analysis as well. Beer's law is summarized as

$$A = \epsilon lc$$

where A is absorption measured in peak height, ϵ is the absorptivity constant for a particular compound, l is the path length of the analyzer's sample cell, and c is the concentration of the compound. Since absorptivity is a constant for each compound, it can be seen that when the path length remains fixed, as concentrations increase so will the absorption peaks. This allows for the quantitative analysis over a wide range of concentrations.

2.0 FTIR COMPONENTS

All FTIR analyzers contain the same basic setup in terms of hardware. The five most critical components are the infrared source, interferometer, sample cell, detector, and signal/data processors (Figure B1).

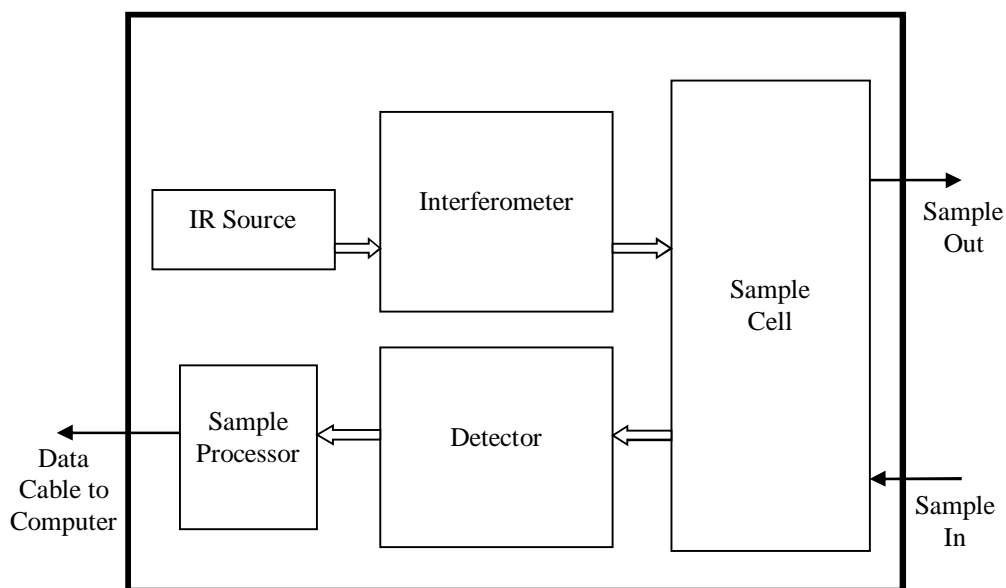


Figure B1 FTIR Components

IR Source: The purpose of the IR source is to produce light waves throughout the infrared range. Infrared radiation is sometimes referred to as heat radiation; therefore, the IR source is simply a heated element. For example, a ceramic element heated by passing electricity through it could be used as an IR source.

Interferometer: The interferometer is an important and unique part of FTIR analyzers, and it is what makes IR analysis over a wide spectral range possible. The most commonly used are Michelson interferometers which consist of a beam splitter, a fixed mirror, and a moving mirror (Figure B2).

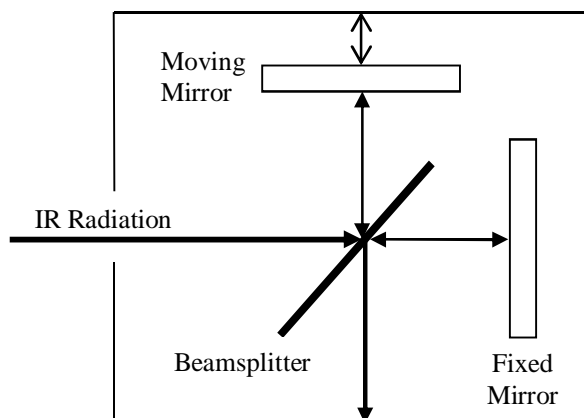


Figure B2 Interferometer

As infrared radiation from the source enters the interferometer, it encounters a beam splitter that allows half of the IR beam to continue forward while the other half is reflected. One half of the beam will go to a fixed mirror, and the other half travels to a moving mirror. The radiation is then reflected off the mirrors and recombines at the beam splitter, where it then exits the interferometer. The purpose of the interferometer is to make two beams of light travel different distances. When the moving mirror and fixed mirror are the same length from the beam splitter, the divided light waves will have traveled the same distance when they recombine. The wave amplitudes will be in phase. The waves will constructively interfere with each other, and the resulting wave leaving the interferometer will have an amplitude greater than the one that entered. As the moving mirror changes positions, the optical path length toward the moving mirror changes and wavelengths will go out of phase with each other. When they are completely out of phase, peaks and valleys cancel each other out and destructive interference occurs. The mirror continues until it reaches the maximum optical path difference and then returns to its original position, completing one scan.

Sample Cell: The sample cell is a compartment that allows for the interaction of the gaseous sample with the infrared radiation. The compounds within the gas stream will absorb the radiation at this time. For continuous analyzers, the sample gas stream flows through the cell at a constant rate. With batch analyzers, the sample is introduced into the cell, sealed off, and analyzed. The cell is evacuated before the next sample is introduced. The distance that the IR beam travels through the sample cell is the path length. Some analyzers allow for adjustment of the path length while others are fixed.

Detector: The modified IR beam travels from the interferometer, through the sample gas stream, and finally to the detector. The detector measures the infrared intensity of the incoming beam and converts it into an electrical signal. Within the interferometer, as the light waves move in and out of phase, the resulting combined light wave will increase and decrease in intensity. The output from the detector results in a plot of IR intensity, measured in voltage, versus optical path difference. This is known as an interferogram.

Sample Processor: Before the interferogram is quantified, adjustments to the spectrum are performed to maximize analysis. The spectrum is converted from analog to digital, corrected for symmetry, and peak intensities are adjusted.

3.0 SPECTRAL ANALYSIS

The final interferogram is sent to the analyzer software, where it is transformed. A complex algorithm known as a fast Fourier transform is applied to the interferogram and converts it from intensity vs. optical path difference to absorption vs. wave number.

The first step in analysis is to obtain a background spectrum, which is the detector's response with no sample in the sample cell. This can be accomplished by continuously passing nitrogen through the cell. IR absorption at all wavelengths goes to zero.

3.1 Single Component Analysis

A sample gas stream enters the cell as IR radiation is passed through it. The radiation is absorbed at certain wavelengths depending on the compound present. The detector's response to the sample is ratioed against the background response and the result is a spectrum of absorption peaks that are attributed to the sample.

Reference spectra for the compound of interest are required for analysis. These are obtained by passing the single compound through the sample cell at a known concentration and storing the spectral results. A range of reference spectra should be produced to include all concentrations that the sample may fall within. Absorptivity is calculated from these reference spectra. The absorptivity,

absorption peak height, and path length are now known. Referring back to Beer's law, the software can now quantify the concentration of the unknown sample.

3.2 Multiple Component Analysis

The calculations are more involved for analysis of two or more components. The calculation to determine the single component concentration is still used; however, a separate calculation must be performed for every additional compound present in the gas stream. The situation is complicated even more by the fact that two compounds can have absorption peaks in or around the same wave number. The absorption due to each compound must be determined within this wave number. Using matrix algebra allows for the fast computation of multiple compound concentrations over a wide wave number range. One requirement when using this method is that all compounds within the sample stream must be accounted for in the analysis. Absorption peaks from any compound not present in the analysis will interfere with the accurate quantification of the other compounds. These peaks that are unaccounted for after analysis are referred to as residual peaks. Interfering residuals can be removed by including the compound responsible for these peaks in the analysis. It is important to have a large reference library with all compounds that may be present when testing unknown sample streams.

Another cause of interference can arise from large concentrations of compounds absorbing near the target analytes. Large absorption peaks can dominate a wave number and, in extreme cases, can cause complete saturation of the wave number in which the maximum amount of radiation at that wavelength is being absorbed. If this occurs at or around the analysis area of the target analytes, it can make analysis difficult or even impossible in that area. Proper selection of the analysis area is important for this reason.

REFERENCE

Smith, B.C. 1996. *Fundamentals of Fourier transform infrared spectroscopy*. Boca Raton, FL: CRC Press.

APPENDIX C

METHOD DEVELOPMENT

1.0 INTRODUCTION

The two main methods for extractive FTIR analysis are EPA Method 320 and ASTM Method D 6348-03. Both methods require a sampling setup that includes a filter, sample lines, sample pump, and analyzer, with all components heated to avoid condensation. An equipment setup similar to the one illustrated in Figure C1 is recommended.

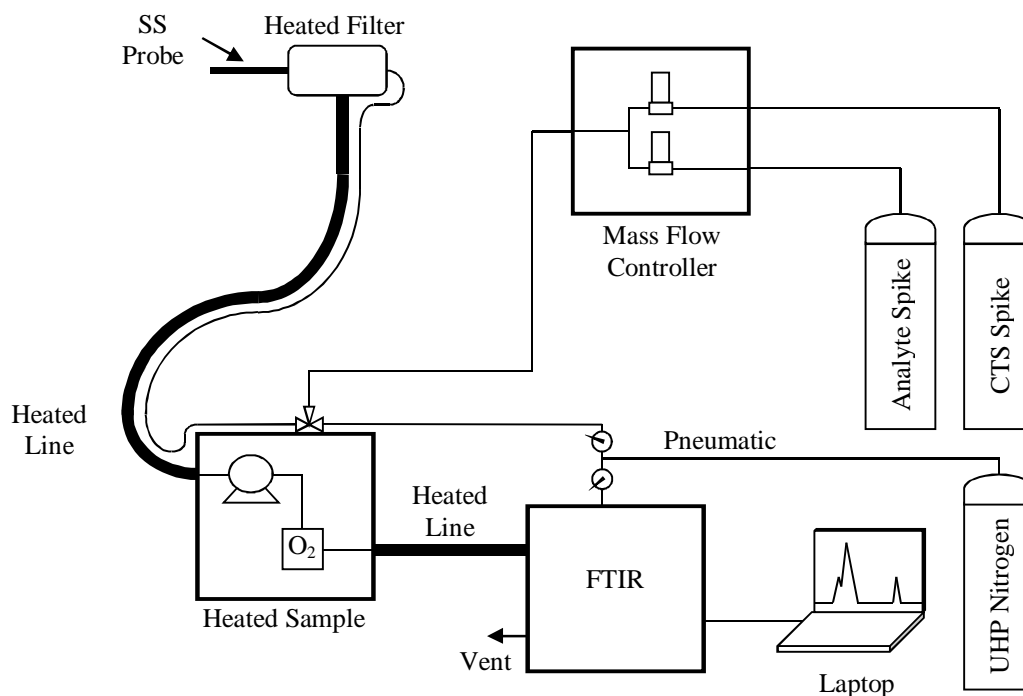


Figure C1 FTIR Sampling System

Due to the nature of FTIR spectroscopy, poorly quantified peaks absorbing in the same analysis area as the target analytes are known as interferences. These interferences can compromise the accurate quantification of the target analytes. Initial testing of biomass boilers revealed large concentrations of water and carbon dioxide, with relatively low concentrations of CH₄ and N₂O. The testing showed that water peaks were interfering with CH₄ analysis and increasing detection limit levels. Carbon dioxide was found to interfere with N₂O analysis; however, it was found that careful selection of N₂O analysis areas could avoid this problem.

The EPA and ASTM methods allow for a sample conditioning system to be placed in-line to reduce interfering compound concentrations to an acceptable level. A condenser was proposed to reduce the moisture content of the gas stream before it enters the sample system. The condenser consisted of a chilled, empty Rotavis® impinger in front of the particulate filter. The modified setup was tested at a

recovery furnace. Modified and standard setups were alternated for a total of five runs each. The results were used to evaluate the ability of the modified system to improve CH₄ analysis.

The results seen in Table C1 show a dramatic reduction in sample moisture content. The CH₄ detection limits were lowered by 1.5 ppm as a result. The recovery furnace tested contained low concentrations of CH₄, and this reduction in detection limit dramatically improved analysis.

Table C1 Standard and Modified Setup

Setup	Moisture Content (%)	Methane DL (ppm)
Standard	26.22	2.45
Modified	0.82	0.93

The reduction in moisture could allow collection of source samples in Tedlar® bags for later analysis. This would be beneficial when direct sampling at a source is not practical.

A laboratory study was performed to fully evaluate the sample conditioning system before it was incorporated into the equipment setup. The study was divided into three phases. The first phase determined which conditioning techniques were most efficient at removing moisture from the gas stream, while not affecting the N₂O and CH₄ concentrations. Phase 2 examined sample stability over time. Phase 3 of the study insured that analyte spiking could be accomplished from the Tedlar® bag. A gas manifold was constructed to create a synthetic boiler gas stream. N₂, N₂O, CH₄, NO, SO₂, and O₂ from gas cylinders were combined with steam from a steam generator to produce the synthetic gas matrix.

2.0 METHOD

2.1 Phase 1

Phase 1 evaluated methods for removal of water while preserving N₂O and CH₄ concentrations. The three conditioning systems evaluated were

1. a chilled, empty Rotavis® impinger with a shorted stem to prevent bubbling of the sample gas through the collected water;
2. a chilled impinger followed by a Nafion® dryer; and
3. a chilled impinger followed by an impinger filled with silica gel.

A dry mixture of gases was sent directly to the analyzer to determine CH₄ and N₂O concentrations. The gas stream was then sent through each of the three conditioning systems before going to the analyzer to determine if there was an effect on CH₄ and N₂O concentrations. Water vapor was added to the gas stream to bring the moisture content up to 30%. The wet gas stream was then sent through each of the three conditioning systems before going to the analyzer.

2.2 Phase 2

In Phase 2, gas samples were collected in Tedlar® bags after they passed through the most appropriate conditioning system determined in Phase 1. Samples were analyzed immediately after collection and then every hour for four hours to evaluate short-term stability. The bags were analyzed again after 48 and 72 hours to evaluate long-term stability.

2.3 Phase 3

Phase 3 was designed to ensure that dynamic spiking could be accomplished from the Tedlar® bags for quality assurance, as required by the FTIR methods. Two bags were filled with dry mixtures of gases that would result in CH₄ and N₂O concentrations of 6 ppm in the first bag and 2 ppm in the second. Bags were analyzed to determine the CH₄ and N₂O concentrations. Analyte spiking for both compounds was performed as it would be in the field, and the percent spike recovery was determined.

3.0 RESULTS

3.1 Phase 1

There was no analyte reactivity through the condenser impinger alone; however, there was a slight negative bias for CH₄ and N₂O when the Nafion® dryer or silica gel was added. The bias for N₂O was the same for both Nafion® dryer and silica gel, while the Nafion® dryer exhibited higher reactivity for CH₄ than the silica gel. The percent differences in all cases was considered minor and within an acceptable range. Table C2 summarizes the results of the dry gas tests.

Table C2 Phase 1 Results (dry gas stream)

Component	Concentration (ppmvd)			
	FTIR Direct Analysis	Impingers Only	Impingers + Nafion® Dryer	Impingers + Silica Gel
H ₂ O	0	0	0	0
N ₂ O	6.6	6.6	6.5	6.5
NO	59	59	59	51
CH ₄	7.8	7.8	7.6	7.7
SO ₂	268	268	268	-1.4
O ₂	13.9	13.9	13.8	13.4
N ₂ O Bias		0%	-1.5%	-1.5%
CH ₄ Bias		0%	-2.6%	-1.3%

All three setups were efficient at reducing the moisture content from 30% to an acceptable level. The impinger plus silica gel configuration was the most effective as it was able to remove all moisture from the gas stream. Reactivity of the target analytes was again measured with the wet gas stream. The impinger and impinger/Nafion® dryer setups showed no bias for N₂O, while the impinger/silica gel showed a slight positive bias. All three configurations showed a negative bias for CH₄ with the impinger/Nafion® dryer being the most pronounced. Table C3 summarizes the results of the moist gas tests.

Table C3 Phase 1 Results (moist gas stream)

Component	Concentration (ppmvd)			
	Dry Gas FTIR Direct	Impingers Only	Impingers + Nafion® Dryer	Impingers + Silica Gel
H ₂ O	0	0.7	0.4	0
N ₂ O	6.6	6.6	6.6	6.8
NO	59	59	58	47.3
CH ₄	7.6	7.3	7.0	7.1
SO ₂	270	245	247	0
O ₂	13.7	13.7	13.8	13.4
N ₂ O Bias		0%	0%	3.0%
CH ₄ Bias		-4.0%	-8.0%	-6.6%

3.2 Phase 2

A literature review was performed to investigate storage and stability of CH₄ and N₂O from combustion sources. An article written by Muzio et al. (1989) revealed that storing combustion gases containing SO₂, NO, and H₂O, even over a short period of time, can lead to the formation of N₂O within the vessel. A study by Preto et al. (2004) investigated the mechanism for this formation and concluded that SO₂, NO, H₂O, and O₂ can all play a role, with SO₂ being a major factor. This effect was seen in the lab study when bag samples were collected and stored with only the condenser impinger used. Water was reduced but not eliminated, and NO, SO₂, and O₂ concentrations were unaffected. There were slight increases in N₂O and CH₄ over a four-hour period. Over a two-day period, there was no significant change in CH₄ while N₂O increased by 58%. Table C4 summarizes the results. Figure C2 illustrates the changes of N₂O and CH₄ over the 48-hour time period.

It was discovered during this test that the Tedlar® bags are porous with respect to water vapor. The percent moisture, while starting out low, increased over time approaching ambient moisture content.

Table C4 Sample Stability (no dryer)

Time (hours)	0	2	4	48
Component	Concentration (ppmvd)			
H ₂ O	0.8	1.1	1.4	1.7
N ₂ O	7.1	7.1	7.2	11.2
NO	48.8	20.5	13.0	6.1
NO ₂	9.8	53.6	36.7	23.4
CH ₄	7.3	8.1	8.2	7.2
SO ₂	247.0	247.1	245.5	198.0
O ₂	13.7	13.7	13.7	13.1

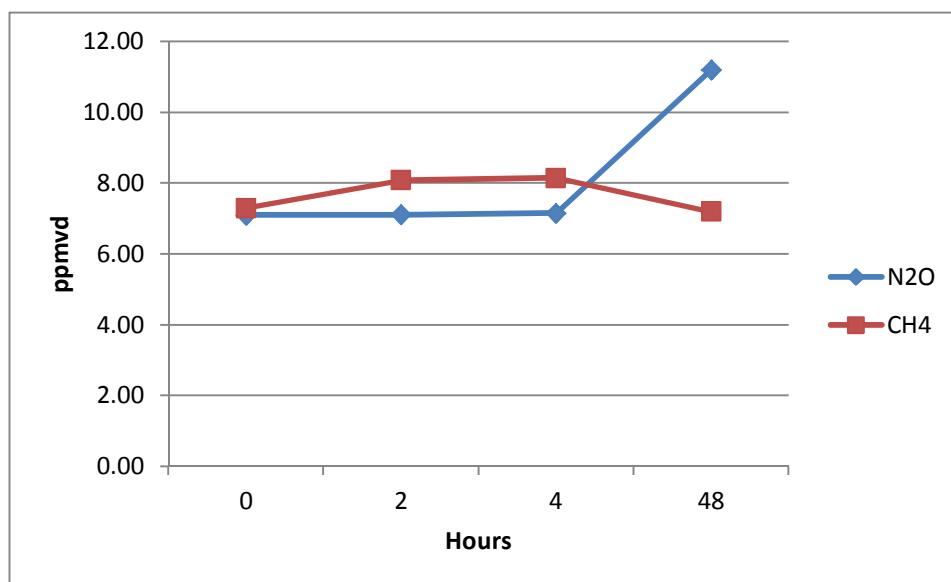


Figure C2 Stability over Time (no dryer)

During the first phase of the study, it was noted that the impinger/silica gel combination not only eliminated all water vapor, but it also had the ability to scrub out SO₂ from the gas stream. The removal of H₂O and SO₂ would greatly enhance the stability of N₂O concentrations in the Tedlar® bags. Therefore, it was determined that a chilled impinger followed by a silica gel impinger was the most appropriate sample conditioning setup.

While the silica gel is efficient at scrubbing SO₂ from the gas stream, during long runs the silica gel can become saturated and SO₂ will break through. This explains the presence of SO₂ in the stability study bag, even though the impinger/silica gel combination was used. Over a four-hour period, CH₄ and N₂O concentrations remained stable, with only slight fluctuations from sample to sample. Over a 48- and 72-hour period, CH₄ concentrations decreased slightly and N₂O concentrations increased. The increase in N₂O can be explained by the small presence of SO₂ in the samples. Table C5 summarizes the stability study results. Figure C3 illustrates the change in N₂O and CH₄ concentrations over time.

Table C5 Sample Stability (silica gel dryer)

Time (hrs)	0	0.5	1	2	3	4	48	72
Component	Concentration (ppmvd)							
H ₂ O	0	0.3	0.3	0.5	0.7	0.8	0.7	0.8
N ₂ O	7.5	7.6	7.5	7.5	7.6	7.6	7.9	8.1
NO	53	30.1	25.5	19.0	13.9	12.5	1.1	0.5
NO ₂	0	23.9	31.5	42.0	47.9	50.8	44.1	38.6
CH ₄	8.1	7.9	7.9	8.1	8.0	7.9	7.8	7.7
SO ₂	69	72.6	71.9	73.1	72.1	72.6	62.6	61.2
O ₂	13.8	14.3	13.3	13.9	14.7	13.9	12.6	12.3

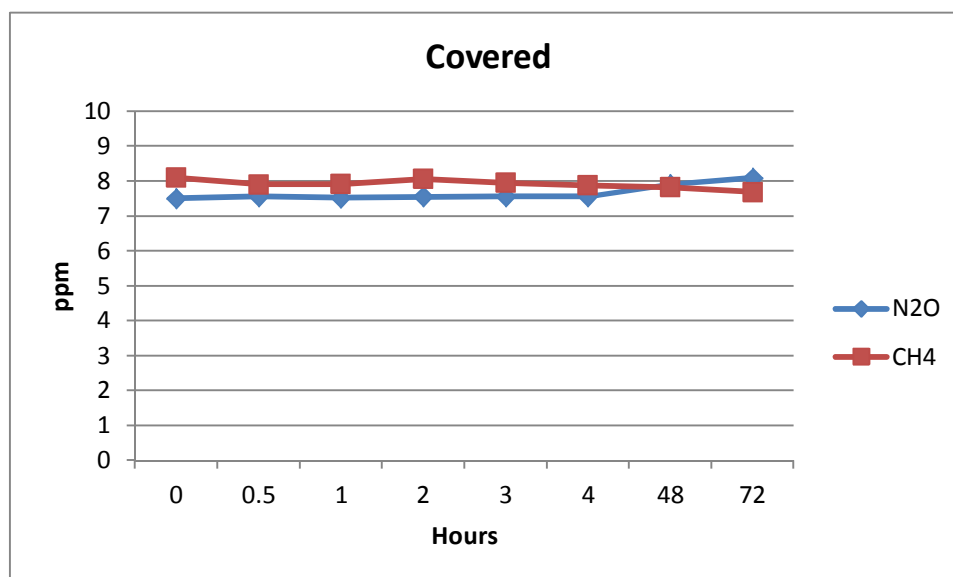


Figure C3 Stability over Time (silica gel dryer)

3.3 Phase 3

For both CH₄ and N₂O, the spike recovery from bag one was 101%. The percent spike recoveries from bag two were 97% for CH₄ and 96% for N₂O. All spike recoveries were well within acceptable ranges. Table C6 summarizes the spike recovery data.

Table C6 Phase 3 Results

Component	Concentration (ppmvd)				Percent Recovery
	Unspiked	Desired Spike Level	Expected Concentration	Spiked Concentration	
Bag One					
N ₂ O	6.4	6.0	12.0	12.1	101
CH ₄	6.7	5.5	11.5	11.6	101
Bag Two					
N ₂ O	2.2	2.0	4.2	4.0	96
CH ₄	2.7	3.0	5.5	5.4	97

4.0 CONCLUSION

The results from the lab study show that a chilled impinger followed by a silica gel impinger is an appropriate conditioning system for reducing water vapor and SO₂ concentrations within a gas stream. The system was also shown to have little to no effect on CH₄ and N₂O concentrations. The experiment demonstrated the stability of a bag sample up to four hours and possibly longer if conditioned properly. Sample run times should be limited to avoid SO₂ breakthrough. The ability to carry out accurate spiking while sampling from the Tedlar® bags was proven.

REFERENCES

- Muzio, L.J., Teague, M.E., Kramlich, J.C., Cole, J.A., McCarthy, J.M., and Lyon, R.K. 1989. Errors in grab sample measurements of N₂O from combustion sources. *Journal of the Air Pollution Control Association* 39:287-293.
- Preto, F., Wang, J., Jia, L., and Anthony, E.J. 2004. A study on mechanisms of nitrous oxide formation in post-combustion flue Gases. *Atmospheric Environment* 38:1123-1131.
<http://dx.doi.org/10.1016/j.atmosenv.2003.11.021>