Understanding Uncertainty in Greenhouse Gas Emission Estimates: Technical Considerations and Statistical Calculation Methods

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ABSTRACT

The global oil and natural gas industry has been active in promoting consistency and harmonization for greenhouse gas (GHG) emission inventories. Inventories of typical oil and natural gas operations are quite complex, combining measured and estimated emission data according to regulatory requirements and available information. With the emergence of GHG emissions trading systems and new reporting schemes, data quality assurance is receiving increased attention as a prerequisite for accurate GHG emissions reporting and emission reductions.

The uncertainties inherent in the data used for emission inventories help inform and improve understanding for the data's use, and also enable identifying specific areas for enhanced data collection and targeted inventory improvements. The uncertainty of an inventory, or of quantified emission reductions, is determined largely by the uncertainties of the largest contributing sources. In turn, each of these uncertainties depends on the quality and availability of sufficient data to estimate emissions, or on the ability to measure these emissions and properly account for their variability.

This paper will present an overview of API-sponsored work to develop technical considerations and statistical calculation methods for quantifying the uncertainty in GHG emissions, which complements the API GHG methodology compendium.[1] In general, these efforts will augment existing industry guidance and provide technically valid approaches to assess uncertainty ranges beyond single point data accuracy determinations. The topics included are: clarification of the sources of uncertainty in entity emission inventories; information on measurement practices and their associated uncertainties; and explanation of statistical procedures that can be used to quantify uncertainties.

INTRODUCTION

A collaborative effort among API, it's global affiliate the International Petroleum Industry Environmental Conservation Association (IPIECA), and it's European counterpart Conservation of Clean Air and Water in Europe (CONCAWE), resulted in the publication of a technical document titled, "Addressing Uncertainty for Oil and Natural Gas Industry GHG Inventories: Technical Considerations and Calculation Methods" (Uncertainty Document).[2] This document is a companion to the API "Compendium of Greenhouse Gas Emission Methodologies for the Oil & Natural Gas Industry".[1] It provides a summary of technical considerations that are important for understanding and calculating GHG emission inventory uncertainty. The goal of these guidelines is to augment existing industry guidance and provide technically valid approaches to improve GHG emissions estimation robustness and data quality. Although the focus of the Uncertainty Document is on measurement uncertainty and statistical calculation methods that are relevant to the oil and natural gas industry, the document has broader application to GHG inventory development for any industry sector that utilizes fossil fuels.

ROLE OF UNCERTAINTY ANALYSIS

"Uncertainty analysis" has been increasingly recognized as an important tool for improving national, sectoral, and corporate inventories of GHG emissions and reductions.[3] As new mandatory reporting regulations and emission reduction compliance obligations emerge, new requirements are being promulgated for the accuracy of fuel flow measurements when such flows are used to quantify GHG emissions.

Policymakers use entity GHG inventories and reported facility-level GHG emissions to develop strategies for emission reductions and to track the progress of these policies. Both regulatory agencies and corporations rely on inventories to better understand emission sources and trends. GHG inventory data are associated with varying degrees of uncertainty, and such uncertainties have both technical and policy implications. National and regional regulatory programs are starting to define expected uncertainty boundaries for demonstrating compliance. Description of two such programs and their methods for addressing uncertainty associated with GHG regulatory reporting are provided below.

European Union Emissions Trading System (EU-ETS)

The EU-ETS specifies a tiered approach for emission calculations combined with required uncertainty ranges as provided in the Monitoring and Reporting Guidelines.[4] This program defines a matrix of uncertainty requirements for different facility sizes and measurement approaches used.

- For facilities emitting between 50,000 to 500,000 tonnes of fossil CO_2 – Uncertainty ranges specified are ±7.5%, +5%, and ±2.5% when the facilities employ Tiers 1, 2, and 3 calculation approaches, respectively;
- For facilities emitting over 500,000 tonnes of fossil CO_2 – Uncertainty ranges are expected to be as low as ±1.5% for facilities required to employ Tier 4 approaches.

It is important to note that the EU-ETS requirements are applicable to a limited set of industry installations and that facility inventories are tracked only for CO_2 emissions from fuel combustion and flaring. The requirement to quantify these sources within such tight uncertainty ranges is a reflection of the fact that they are the largest emission sources and the key contributors to most installations' GHG emissions, and these are also the sources for which accurate emission calculation methods are available.

Environmental Protection Agency (EPA) Mandatory Reporting of Greenhouse Gases

EPA published the final GHG mandatory reporting rule on October 30, 2009.[5] The rule includes provisions to ensure the accuracy of emissions data through monitoring, recordkeeping and verification requirements. Flow meters that measure liquid and gaseous fuel feed rates, feedstock flow rates, or process stream flow rates that are used in the GHG emissions calculations are required to be calibrated to an accuracy of 5 percent (fuel billing meters are exempted from the calibration requirements). Recently proposed amendments clarify that the calibration accuracy requirements only apply when specified in an applicable subpart of the regulation and do not apply where the use of company records or the use of best available information is specified to quantify fuel usage or other parameters.

EMISSION INVENTORY UNCERTAINTY

For a facility-level or company-level GHG emission inventory, the overall uncertainty is determined by the uncertainties of the largest contributing sources. Although very high levels of uncertainty may be associated with some small sources, their overall impact on the uncertainty of a facility or entity-wide emissions inventory may often be very small.

Emissions inventory uncertainty depends on the quality and availability of sufficient data to estimate emissions, or on the ability to measure emissions and properly account for their variability. The uncertainty intervals associated with emission rates, activity data or emission factors are characterized by the dispersion of the respective measurement values that were used to derive them initially. Therefore assessing uncertainties for emission inventories is based on the characteristics of the variable(s) of interest as estimated from the applicable data sets or from expert judgments.

Uncertainties associated with GHG emission inventories are generally the result of three error categories:

- Spurious errors, which may be due to incomplete, unclear, or data that result from human error or machine malfunction.
- Systematic errors, which may be due to the methods (or models) used to quantify emissions for the process under consideration. Uncertainties due to models or equations are related to the proper application of estimation methodologies to the respective source categories.
- Random errors, which may be due to natural variability of the process that produces the emissions.

Some of these errors are typically eliminated as far as possible in advance, when planning the compilation of an emissions inventory and could be addressed as part of emission inventory assurance processes.[6]

Specific contributors to the uncertainty of GHG emissions characterization for oil and natural gas industry operations include its large geographic variability and the diversity of producing formations and operational practices. Operating practices vary due to the physical characteristics of the resource produced or refined, and their intended markets. Additionally, the industry segment relies heavily on self-generated fuels whose composition may vary with the nature of the producing formations, the composition of crude oil and/or gas used, and the slate of products manufactured. Although gas compositions might be constant for a given formation or for finished products, they could exhibit variability during processing due to temporal fluctuations in processing conditions.

Table 1 provides an overview of selected methods recommended by the EPA for qualitative and quantitative estimation of uncertainty associated with emissions ranges. The table also indicates the relative level of effort associated with each methodology.

Table 1. Overview of methods used to estimate emissions uncertainty.[a]

METHODOLOGY	DESCRIPTION OF METHOD	LEVEL OF EFFORT
Qualitative Discussion	– Sources of uncertainty are listed and discussed. – General direction of bias and relative magnitude of imprecision are given if known.	Low
Subjective Data Quality Ratings	– Subjective rankings based on professional judgment are assigned to each emission factor or parameter.	Low
Data Attribute Rating System (DARS)	– Numerical values representing relative uncertainty are assigned through objective methods.	Medium

Table 1. Overview of methods used to estimate emissions uncertainty.[a] , Continued

METHODOLOGY	DESCRIPTION OF METHOD	LEVEL OF EFFORT
Expert Estimation Method	– Experts estimate emission distribution parameters (i.e., mean, standard deviation, and distribution type). – Simple analytical and graphical techniques are then used to estimate confidence limits from the assumed distributional data. – In the Delphi method, expert judgment is used to estimate uncertainty directly.	Medium
Propagation of Errors Method	– Emission parameter means and standard deviations are estimated using expert judgment, measurements, or other methods. – Standard statistical techniques of error propagation typically based upon Taylor's series expansions are then used to estimate the composite uncertainty.	Medium
Direct Simulation Method	– Monte Carlo, Latin hypercube, bootstrap (resampling), and other numerical methods are used to estimate directly the central value and confidence intervals of individual emission estimates. – In the Monte Carlo method, expert judgment is used to estimate the values of the distribution parameters prior to performance of the Monte Carlo simulation. – Other methods require no such assumptions.	High
Direct or Indirect Measurement (Validation) Method	– Direct or indirect field measurements of emissions are used to compute emissions and emissions uncertainty directly. – Methods include direct measurement such as stack sampling and indirect measurement such as tracer studies. – These methods also provide data for validating emission estimates and emission models.	High

[a] Extracted from Table 4.1-1 of the Emissions Inventory Improvement Program (EIIP), Chapter IV: "Evaluating the Uncertainties of Emission Estimates," U.S. EPA, Research Triangle Park, NC, July 1996

The uncertainty associated with CO_2 emissions from combustion is primarily attributable to variation in the composition of combusted fuels and their respective consumption rates (or total volumes). A different set of parameters is important for understanding emissions associated with process vents and fugitive emissions. For many of the large process units that are found in refineries and natural gas processing plants, numerical models (equations) are available for estimating vented emissions. However, the records that installations are required to keep and report on vented or released gas might not be similar under all regimes globally.

Fugitive emission estimates exhibit the highest degree of uncertainty due to the use of average emission factors per component, device or type of operation, and due to improper conversions of existing factors that are expressed in terms of volatile organic compounds (VOCs) to CH_4. Since the CH_4 to VOC ratio varies among installations, or even within different parts of a processing plant, these average emission factors, coupled with generic conversions from VOC to CH_4 may not be the best representation of CH_4 emissions.

Emission Estimation Approaches

The four basic approaches for estimating emissions are:

1. Emission factors;
2. Continuous emissions monitoring;
3. Source testing; and
4. Material balance.

Each of these is described further.

Emission Factors

The general equation for using emission factors for calculating emissions is:
Equation (1) Emissions = Activity Rate × Emission Factor

For a given emission source, an emission estimate generally consists of an emission factor and some measure of the activity that results in the emission (referred to as the activity factor). Activity factors are generally a measured quantity, such as a count of equipment or measure of fuel consumed. Emission factors may be either based on site-specific measurements or based on published values that were derived from averaging a variety of measurements. When calculating emissions and their associated uncertainties, it is important to note that the overall uncertainty is based both on activity data (process flow, throughput, usage, or equipment count) and on the emission factors used. Each contributor to uncertainty should be assessed independently and then aggregated in the final analysis.

In practice, for estimating GHG emissions from oil and natural gas industry operations this means:

For CO_2:
Equation (2) Emissions = Volumetric Gas Flow × Carbon Content
– or –
Equation (3) Emissions = Fuel Energy Consumption × Carbon per Heating Value Unit

For CH_4
Equation (4) Emissions = Component or Event Count × Emission Factor

Continuous Emissions Monitoring

This technique involves continuously measuring flow and concentrations of species directly emitted into the atmosphere from a specific source, such as a stack. It is accomplished by placing an applicable monitor at the source. The error associated with these determinations varies for different compounds but is largely dependent on the representativeness of the stack locations where the measurements are performed, and the accuracy of both the flow and the concentration measurements of the target compound(s). This approach does not necessarily provide a more reliable method for measuring emissions since the measurement instruments may drift with time and exceed their performance specifications. Moreover, such methods are not available for monitoring all GHG emissions, and therefore this technique would have limited applicability to specific sectors, such as power generation units.

Source Testing

Like continuous emissions monitoring, source-testing data may be generated by either extracting a sample or placing a monitor at a source, followed by analysis to characterize the emitted species. In this application, the measurement campaign is limited to a specified number of samples or a sampling duration. Facilities then use the average emission rate calculated from source testing to estimate total annual emissions. For characterizing GHG emissions over a longer period of time (such as a year), periodic sampling and analysis can be used to determine emission variability.

This measurement approach is generally useful when appropriate test methods are used, and emission and process data are collected at a frequency that allows good characterization of emission variability. However, the resources required for increased measurement frequency should be balanced with the contribution of the tested source to the overall inventory and the incremental improvement in the range of uncertainty that is attainable by this increased testing.

Material Balance

For some emission sources, a material balance may be an appropriate means of estimating GHG emissions. Use of a material balance requires knowledge of total flows or throughput rates, and the corresponding compositions of those streams. Material balance approaches can also be used for assessment of evaporative losses or for simulation of process emissions under defined conditions.

Various material balance methods are applicable to quantifying GHG emissions. Emission estimation methods range from simple activity measurements multiplied by applicable emission factors to more sophisticated estimation algorithms. The advanced methods represent an integrated approach that relies on the use of factors and other data, including generic process simulation models, source specific models, and species profiles databases.

SOURCES OF MEASUREMENT UNCERTAINTY

Adhering to appropriate sampling, measurement, and estimation procedures – with applicable quality control and quality assurance measures – can help minimize uncertainties. Nonetheless, it is the nature of the measurement process that makes it impossible to measure a physical quantity without error. To the extent that measurement errors can be minimized, such action will have a direct influence on reducing the overall uncertainty associated with emission inventories.

The uncertainty for each measured parameter must be assessed in a way that is applicable to that measurement method and its implementation in practice. Random errors could be a major factor in the uncertainty of an individual observation; however, their contribution to the overall emission inventory diminishes as more measurements are obtained during the reporting period. In fact, determining the true value of any measured variable is not practical due to the limitations of measurement equipment and procedures, and the possibility of human error. Hence, industry measurement procedures and standards have been developed to emphasize practices that lead to collecting better quality data, especially for critical measurements.

Flow Measurement Practices

Industry has been instrumental in developing international voluntary standards establishing general principles and describing procedures for evaluating the uncertainty of measuring fluid flow rate or quantity. For example, Annex A of ISO 5168 provides a step-by-step procedure for calculating and reporting these measurement uncertainties.[7] Similarly, Chapter 14 of the API Manual of Petroleum Measurement Standards (MPMS), contains detailed procedures and practices for all aspects of natural gas (and similar gases) measurement and calculation of their associated uncertainties, at the point where oil or gas enters the marketplace ("custody transfer").[8]

The accuracy of "custody meter" measurements is historically quite high, and practices follow rigorous industry standards. Those same practices are not as rigorously applied to internal fuel accounting and process control during normal operations.

When measuring fuel flow rate, or its total volume, and using the information to calculate GHG emissions, it must be determined whether the flow meters used are properly installed and calibrated, and that they are capable of providing data that are within the uncertainty ranges required by the governing GHG program. Differences must be considered between the manufacturers' specifications of flow meters' expected measurement errors and those that are attained when using the flow meters in the field. It is common practice to test flow meters in a laboratory setting under controlled conditions, prior to field installations. However, these laboratory bench tests typically do not simulate "real world" variations in fluid flow and other possible fluctuations, and drift of the entire measurement system. For any given operating facility, there might only be a very limited number of "custody transfer" meters that are equipped for testing and calibration under real operating conditions.

Some factors to consider when evaluating the uncertainty of flow measurements used for GHG emission calculations include the following:

- Confidence range of the measurement instrument - Manufacturers' anticipated measurement errors for common flow meters could be used if on-site calibration data are not available.
- Errors associated with "context-specific" factors - Such factors may include the following considerations:
  - Are measurement instruments installed according to the manufacturer's requirements?
  - Is the measurement instrument designed for the medium (gas, liquid, solid substance) for which it is being used?
  - If manufacturer's data are not available, are the instruments operated according to the general requirements applicable to that measurement principle?
  - Are there any other factors that can have adverse consequences on the uncertainty of the measurement instrument (i.e., how the measurement instrument is used in practice)?
- Pressure and temperature corrections for gas meters - Pressure and temperature corrections are only applicable to the determination of the amount of gas and not to the measurement of liquids or solid substances. The actual amount of gas flow has to be corrected for pressure and temperature to the specified standard conditions in order to avoid major systematic errors.

Uncertainties of Sampling and Analysis for GHG Emissions

The emission measurement process comprises either direct measurement at the source level or sample collection followed by laboratory analysis to determine mass emissions. Emission measurement uncertainties for sampling and analytical processes depend on random errors, measurement precision, and systematic errors or bias. The importance of sampling uncertainty is a relatively new concept whose importance is slowly beginning to be recognized. Recent research has shown that sampling uncertainty is often far greater than analytical uncertainty.[2]

Gas Sampling

Proper collection and handling of natural gas samples could have a major impact on the accuracy and representativeness of the measurement results that are based on these samples. Analytical characterization of gas samples have multiple applications and are used in many process related calculations including determination of heating values, gas density and viscosity, hydrocarbon dew point, and compressibility. These analyses are essential for obtaining information about the composition, including contaminants in the gas stream. Calculations based on these analyses are key to optimization of process conditions, determination of adherence to contractual specifications, or estimation of GHG emissions when such a stream is combusted.

Some key factors impacting gas sampling and analysis uncertainty include:

- Inappropriate sampling techniques or equipment - Sampling methods require the use of a sample container for transporting the sample from the field location to the laboratory. Whenever practical, samples should be collected on a flow proportional or flow weighted basis, since spot samples, by their nature, may not fully represent a gas stream of varying composition.
- Inappropriate sample conditioning and handling - Bias could be introduced if any components of a sample are either depleted or augmented during the sampling, transport, or laboratory handling phases prior to analyses. Condensation and revaporization of hydrocarbons can cause significant distortions in the gas sample. Care should be taken to sample above the hydrocarbon dew point and/or to prevent retrograde condensation when pressure is reduced during sampling.

- Collection of samples from non-representative locations and/or under non-representative operating conditions - Sampling systems that are used in conjunction with on-line analyzers, such as chromatographs or gravitometers, are typically designed to extract, condition, and deliver a representative sample to the analyzer. Sampling lines are kept as short as possible in conjunction with proper heating and insulation to avoid condensation. The flow rate of the sampling system is adjusted to allow for close to real time data, while at the same time not increasing the flow to a level that might lead to turbulence.
- Inappropriate analytical methods - The threshold sensitivity of the analytical methods used are typically those that are well documented by industry recommended practices. Analyses are typically limited to the range of mixture concentrations and species previously identified. For complicated sample matrices, the potential for interferences is usually noted.

Carbon Content Measurement

Different types of gas chromatography (GC) systems are normally used to analyze the carbon content of gaseous streams. The GC systems might be laboratory based or set up as an online device for automated collection of samples and their analysis. The systems are typically set up to analyze the individual components in the sampled gas and provide detailed reports of properties including composition, calorific value, and density.

The results of the determination of individual – or groups – of carbon-containing species are then used to assess the total CO_2 emissions from fuel combustion. Several key considerations include:

- If the method is capable of determining CO_2 content with the rest of the carbon containing species, no further correction of the carbon content data is required in order to properly account for all CO_2 emissions;
- If the method is set up to provide information only on hydrocarbon species, the CO_2 content should be obtained by an independent measurement and added to the fuel carbon content data;
- If the method is capable of a quantitative determination of CH_4 content, these data can be used separately for calculating evaporative and processing leaks along with venting losses; and
- All carbon content measurement data should be used in conjunction with the applicable fuel flow measurements when calculating emissions.

On-line determination of fluid stream compositions is quite challenging due to possible variations in these compositions. This is especially notable for self-generated fuel gas such as refinery fuel gas or other processing plant gas. Conversely, for commercial products such as natural gas, liquid fuels, coal and coke, or for the analysis of associated gas in exploration and production operations, the challenges are more related to the ability to analyze multiple streams rapidly and ascertain that they all are within a desired property range.

INVENTORY STATISTICAL PROCEDURES

Quantifying the uncertainty for a GHG inventory involves mathematically combining individual sources of uncertainty to establish an estimate of the overall uncertainty. The general steps for quantifying uncertainty are:

- Determine the uncertainty for measured activity or emissions data;
- Evaluate the uncertainty of available emission factors data; and
- Aggregate uncertainty of individual components using standard statistical techniques.

Step by step guidance of the statistical computations and associated equations for quantifying GHG emission inventory uncertainty are included in the Chapter 4 of the Uncertainty Document.[2] The calculational sequence recommended includes the determination of:

- The arithmetic mean (mean) of the data set;
- The standard deviation of the data set (the standard error, the square root of the variance);
- The standard deviation of the mean (the standard error of the mean);
- The probability distribution of the data; and
- Covariances of the input quantity with other input quantities used in the inventory calculations.

Inventory Steps and Data Aggregation

In GHG emission inventories, emission estimates are obtained from many intermediate and independent results, each of which is calculated from a separate set of data that is characterized by a different range of uncertainties. The compilation of an entity-wide GHG emissions inventory typically follows a sequence of steps:

- Establishment of inventory boundaries - Organizational and operational boundaries for the inventory are defined and/or examined, based largely dictated by local requirements or corporate policies.
- Data collection and input - Activities data are collected and archived based on the boundaries established initially. The data are then incorporated into appropriate tools for emission calculations.
- Data validation - Various techniques are used to compare the new data with earlier versions (if available) to identify potential large errors. Such errors could include: improper changes in activity data; operations that are not accounted for; lack of supporting data for measurements or emission factors used; erroneous units or unit conversions.
- Uncertainty assessment - The confidence intervals associated with the data available for each of the emission sources are characterized independently based on documentation of data repositories, expert judgment, or on measurements conducted during the inventory year.
- Inventory completion - Quality-checked and validated data are aggregated for reporting based on company policy or local requirements. The preferable way of reporting the results is in terms of the total emissions for each of the GHG species, along with the global warming potential weighted sum of these emissions (also known as CO_2 equivalent or CO_2e emissions). Note that where a constant, such as the global warming potential, is also included in the emission estimation calculation, the absolute uncertainty should include the constant.

The overall uncertainty range for each GHG species, and CO_2e, should also be reported with the total emissions in the format of:

Equation (5) Emissions = Average Value ± % (at the 95% confidence limit)

QUANTIFYING MEASUREMENT UNCERTAINTY

Two examples are provided to demonstrate the principles and methods for quantifying uncertainty. This paper provides an overview, with additional details on the calculations available in the Uncertainty Document.[2]

Example 1 - CO_2 Emissions from Gaseous Fuel Combustion

In this example, emissions are calculated based on the product of the fuel consumption (activity) times a fuel-based emission factor in units of tonnes CO_2/fuel volume. Emission estimates are compared for three different methods of measuring the fuel consumption:

1. Measured gas consumption and a default emission factor;
2. Measured gas consumption and an emission factor derived from annual average gas composition; and
3. Aggregated measured monthly gas composition and measured gas consumption.

Each of these methods is described below. Further details and calculation parameters are provided in the Uncertainty Document.[2]

Method 1: Measured gas consumption rate and default emission factor

For this method, flow for the gaseous fuel is measured using a totalizer meter prior to being routed to a combustion device. The total annual flow rate for the fuel is 18,361 MMscf/yr. Because the meter records a cumulative flow, the uncertainty associated with this measurement is not reduced by taking daily or monthly readings of the flow. There is only a single measurement value in this application, i.e. the rate of fuel consumption. However, there may be more than one parameter that contributes to the uncertainty of the measurement.

For example, the following items need to be considered when estimating measurement uncertainty:

- Uncertainty of the measurement instrument. The random error that is expected for a properly installed and operated orifice meter is 1.5% at a 95% confidence interval when the meter is operating at 30-100% of the measurement range.[2]
- Additional uncertainty of “context specific” factors (defined previously), such as the uncertainty of measurement corrections, e.g., pressure and temperature corrections for gas meters measurements. In the absence of quantitative information about this uncertainty, this example provides a sensitivity analysis of the impact of assuming a range of context-specific uncertainty values: 10%, 25%, and 100% (on a relative uncertainty basis). These values were selected to test the sensitivity of the calculations and assess the effect over a wide range of variability.
- Measurement bias. For this example, it is assumed that it is not possible to quantify the bias. This meter was installed according to the manufacture’s requirements 17 years ago and has an expected life span of 25 years. The meter was last calibrated 7 years ago. Due to the installation and calibration of the equipment, expert judgment was used to estimate a 5% bias in the measurement.

For emission factors, uncertainties may be published in the literature associated with the initial derivation of these emission factors. If the uncertainty associated with literature value is unavailable or data are not available to calculate uncertainty, one must rely on expert judgment to estimate the uncertainty.

For this method, the emission factor is quantified as the product of the carbon content and heating value of the gas fuel. The CO_2 emissions factor for natural gas in the production sector is 0.0547 tonnes/10^6 Btu (HHV) from Table 4-2 of the 2009 API *Compendium*.[1] An uncertainty estimate for this value is not provided in the original reference, so a 10% uncertainty at the 95% confidence level is assumed based on expert judgment. Similarly, the natural gas heating value is 1,020 Btu/scf from Table 3-8 of the 2009 API *Compendium*.[1] Here again, since the uncertainty estimate for this value is not provided in the original reference a 10% uncertainty at the 95% confidence level is assumed based on expert judgment. The working assumption also includes that Bias is accounted for in the assumed uncertainties intervals. When calculating emissions as a product of the emission factors and applicable activity factors, the aggregated uncertainty is calculated as the “square root of the sum of the squares” using the relative uncertainties.

Method 2: Measured gas consumption and an emission factor derived from annual average gas composition

Where multiple measurement points are available, the corresponding uncertainty can be derived on the basis of a statistical sample. The sample standard deviation “includes contributions to the precision both from the measurement system and from the material composition variation from sample to sample.”[9] In other words, if the measured data for an emission source are derived from a statistical sample, the use of the standard deviation as a measure of the spread of the data accounts for uncertainty of the measurement instrument and the differences among the samples. For example, if one sample is taken every month and the data for the 12 samples are used to calculate a yearly mean, the uncertainty calculated from these samples accounts for both the uncertainty in the measurement instrument and the variability among observations. Thus, this uncertainty will be larger than the uncertainty due to measurement error alone. As the sample size increases, the uncertainty that combines the instrument error and context-specific factors will decrease.

Method 3: Aggregated measured monthly gas composition and measured gas consumption

This method builds on the second, except in this case each monthly sample is treated as a distinct measurement. The uncertainty is examined for the measurement of each gas compound in the fuel gas. The Uncertainty Document provides reproducibility uncertainty associated with natural gas samples. These values were applied to account for the measurement error in the mole % of each gas compound. An additional 5% uncertainty is assigned by expert judgment to account for potential variability and bias in the gas composition during the month. The combined uncertainty for the summation of terms is calculated by applying the "square root of the sum of the squares" using the absolute uncertainties.

This approach also involves quantifying the uncertainty for the molecular weight of each gas sample, the weight percent carbon of each gas compound, and the weight percent carbon of each gas sample to derive the emission factor in units of tonnes CO_2/MMscf for each gas sample. The uncertainty for the gas flow rate is based on monthly measurements.

Results

Table 2 compares the emission estimate results from the three approaches.

Table 2. Summary of results for the comparison of fuel combustion measurement uncertainty.

Method	Emissions, tonnes CO_2	Uncertainty (rel) +/-%	Confidence Range, tonnes CO_2
Method 1: Emissions based on annual flow and default emission factor	66,250.86	18.09%	54,266 – 78,236
Method 2: Emissions based on annual flow and annual average carbon content	65,566.90	11.69%	57,902 – 73,232
Method 3: Emissions based on annual flow and monthly composition samples	65,550.85	3.91%	62,988 – 68,114

Example 2 – Uncertainty Comparison for FCCU Emission Estimation Methods

The following example applies uncertainty calculations to the FCCU GHG emission estimation methods presented in the API *Compendium*. The same operating parameters specified in the API *Compendium* are applied here, with the following assignment of uncertainties added.

- The catalytic cracking unit has a coke burn rate of 119,750 tonnes per year ± 15% and a blower air capacity of 2,150 m^3/min ± 15% (assigned by expert judgment). The air blower is assumed to operate continuously for the year (a ± 2% uncertainty is applied to this assumption).
- The carbon fraction of the coke is 0.93 ± 5.5% based on site-specific data determined from measured compositions.
- The flue gas concentrations are 11% for CO_2 and 9% for CO exiting the regenerator. Table D-3 of the Uncertainty Document provides reproducibility values for the precision of Reformed Gas Samples based on ASTM 1946-90.[2, 10] For molar compositions between 5 and

25 percent, a reproducibility factor of 0.5 applies. An additional 5% uncertainty is assigned by expert judgment to account for potential variability in the composition.

- It is assumed that no CH_4 is formed during the regeneration process.
- A CO boiler is used for control of the flue gas stream. Supplemental firing with natural gas is employed at a rate of $100\times10^6 \pm 5\%$ Btu/hr on a higher heating value basis.

The API *Compendium* presents three equations for estimating CO_2 emissions from FCCUs. The following demonstrates the uncertainty quantification for each of the three methods.

Method 1: Uncertainty for Regenerator CO_2 Emissions – Coke Burn Rate Approach

The first approach uses the coke burn rate expressed in mass per year. The coke burned is assumed to proceed completely to CO_2. Based on this assumption and accounting for the conversion of units, the CO_2 emission rate can be calculated from the following equation:

Equation (6)

$$E_{CO_2} = CC_{Avg} \times CF \times \frac{44 \text{ mass units } CO_2\text{/mole}}{12 \text{ mass units C/mole}}$$

where:

E_{CO_2} = emissions of CO_2 in units of mass (pounds, kg, tonnes) per year;
CC = daily average coke burn rate in units of mass per year;
CF = fraction of carbon in the coke burned (if unknown, default = 1);
44 = molecular weight of CO_2; and
12 = molecular weight of carbon (coke is assumed to be carbon).

Applying Equation 6 to the parameters defined for this example, the estimated CO_2 emissions from the regenerator would be:

$$E_{CO_2} = 119{,}750\,\frac{\text{tonnes Coke Burned}}{\text{year}} \times \frac{0.93 \text{ tonnes C}}{\text{tonnes Coke}} \times \frac{44 \text{ tonnes } CO_2}{12 \text{ tonnes C}} = \underline{408{,}348 \text{ tonnes } CO_2\text{/year}}$$

Since Equation 6 multiplies terms to quantify the emissions, the uncertainty is calculated by using the “square root of the sum of the squares” with the relative uncertainty values. This is shown in Equation 7.

Equation (7)

$$U(rel)_{CO_2} = \sqrt{U(rel)^2_{\text{Coke burned}} + U(rel)^2_{\text{C content}}}$$

$$U(rel)_{CO_2} = \sqrt{15^2 + 5.5^2} = 15.98\%$$

Method 2: Uncertainty for Regenerator CO_2 Emissions – “K_1, K_2, K_3” Approach

The second method calculates the coke burn rate using the “K_1, K_2, K_3 approach” provided in EPA Rule 40 CFR 63, Subpart UUU.[11] However, the coke burn equation can be reduced to Equation 8. The equation derivation is provided in Appendix B of the API *Compendium*.

Equation (8) $$E_{CO_2} = \left[K_1 \times Q_r \times \left(P_{CO_2} + P_{CO} \right) \right] \times \frac{44 \text{ mass units } CO_2\text{/mole}}{12 \text{ mass units C/mole}} \times H$$

where:

E_{CO_2} = emissions of CO_2 (lb/year or kg/year);

K_1 = carbon conversion factor burn term (0.0186 lb-min/hr-dscf-% or 0.2982 kg-min/hr-dscm-, given in Table B-2%);

Q_r = volumetric flow rate of exhaust gas before entering the emission control system, calculated using Equation B-2 (dscf/min or dscm/min);

P_{CO_2} and P_{CO} = percent CO_2 and CO concentrations, respectively, in regenerator exhaust, percent by volume (dry basis); and

H = annual operating time (hrs/yr); 8760 hrs/yr if operating continuously throughout the year.

Applying the parameters for this example to Equation 8, the CO_2 emission estimate is:

$$E_{CO_2} = \left[\frac{0.2982 \text{ kg - min}}{\text{hr - dscm \%}} \times \frac{2{,}150 \text{ dscm}}{\text{min}} \times \left(11\% + 9\% \right) \right] \times \frac{44}{12} \times \frac{\text{tonne}}{1{,}000 \text{ kg}} \times \frac{8760 \text{ hr}}{\text{yr}} = \underline{411{,}862 \text{ tonnes } CO_2\text{/yr}}$$

For this calculation, the uncertainty associated with the sum of the CO_2 and CO is determined first. This uncertainty is calculated using the absolute uncertainties, as shown in Equation 9.

Equation (9) $$U(abs)_{\text{concentrations}} = \sqrt{U(abs)^2_{\text{Reproducibility}} + U(abs)^2_{\text{Variability}}}$$

$$U(abs)_{CO_2} = \sqrt{0.5^2 + (0.05 \times 11)^2} = 0.743 \qquad U(rel)_{CO_2} = 100\% \times \frac{0.743}{11} = 6.76\%$$

$$U(abs)_{CO} = \sqrt{0.5^2 + (0.05 \times 9)^2} = 0.673 \qquad U(rel)_{CO_2} = 100\% \times \frac{0.673}{9} = 7.47\%$$

Equation 10, using the absolute uncertainties, is also applied to combine these compositions.

Equation (10) $$U(abs)_{\text{concentrations}} = \sqrt{U(abs)^2_{CO_2} + U(abs)^2_{CO}}$$

$$U(abs)_{\text{concentrations}} = \sqrt{0.743^2 + 0.673^2} = 1.002$$

$$U(rel)_{\text{concentrations}} = 100\% \times \frac{1.002}{11+9} = 5.01\%$$

The CO_2 uncertainty is then calculated for the product of the terms in Equation 8 using the relative uncertainty values. This is shown in Equation 11.

Equation (11) $$U(rel)_{CO_2} = \sqrt{U(rel)^2_{\text{Air rate}} + U(rel)^2_{\text{CO and CO2}} + U(rel)^2_{\text{Annual hours}}}$$

$$U(rel)_{CO_2} = \sqrt{15^2 + 5.01^2 + 2^2} = 15.94\%$$

Method 3: Uncertainty for Regenerator CO_2 Emissions – Air Blower Rate Approach

Another process calculation approach is based on the air blower capacity and flue gas concentration:

Equation (12)
$$E_{CO_2} = (AR + SOR) \times (FCO_2 + FCO) \times \frac{44}{\text{molar volume conversion}} \times H$$

where:

E_{CO_2} = emissions of CO_2 in units of mass (pounds, kg, tonnes) per year;
AR = air rate in standard cubic feet or cubic meters per minute, on a dry basis;
SOR = supplemental oxygen rate (if used) in standard cubic feet or cubic meters per minute, on a dry basis;
FCO_2 = fraction CO_2 in the flue gas, on a dry basis (enter “0.12” for 12%, not 12);
FCO = fraction CO in the flue gas, on a dry basis (enter “0.08” for 8%, not 8);
Molar volume conversion = conversion from molar volume to mass (379.3 scf/lbmole or 23.685 m^3/kgmole); and
H = annual operating time (min/yr); 525,600 min/yr if operating continuously throughout the year.

This equation is based on fundamental principles for calculating the mass of a component from the total stream flow and concentration of the subject component. The concentration term includes both CO and CO_2, because a partial oxidation regenerator flue gas contains both species, and each mole of CO will become a mole of CO_2 when emitted from the CO boiler.

Using the air rate in Equation 12 yields:

$$E_{CO_2} = \frac{2150\ m^3}{min} \times \left(\frac{0.11\ m^3\ CO_2}{m^3\ gas} + \frac{0.09\ m^3\ CO}{m^3\ gas} \times \frac{m^3\ CO_2}{m^3\ CO} \right) \times \frac{44\ kg\ CO_2/kgmole\ CO_2}{23.685\ m^3\ CO_2/kgmole\ CO_2}$$
$$\times \frac{525{,}600\ min}{year} \times \frac{tonnes}{1000\ kg}$$

$$\underline{E_{CO_2} = 419{,}859\ tonnes\ CO_2/year}$$

From an uncertainty perspective, this calculation is the same as shown for the “K_1, K_2, K_3” approach. Both equations apply the summed composition of CO_2 and CO, the air rate, and an annual operational time. The uncertainty of 15.94%, calculated above, would apply for this approach as well.

Uncertainty for Supplemental Natural Gas Firing of FCCU Regenerators

The emissions from the supplemental firing are in addition to the CO_2 emissions from the FCCU regenerator calculated for each of the methods above. Emissions from the supplemental firing of natural gas are estimated using the combustion emission approaches presented in API *Compendium* Section 4.

For CO_2, the emission factor is taken from API *Compendium* Table 4-3 for natural gas.

$$E_{CO_2} = \frac{100 \times 10^6 \text{ Btu}}{\text{hr}} \times \frac{0.0531 \text{ tonne } CO_2}{10^6 \text{Btu}} \times \frac{8760 \text{ hr}}{\text{yr}}$$

$$\underline{E_{CO_2} = 46{,}516 \text{ tonnes } CO_2 / \text{yr}}$$

The CO_2 uncertainty is calculated by applying Equation 13 and using relative uncertainty values. API *Compendium* Table 4-3 does not provide an indication of the uncertainty associated with this emission factor, so a value of 5% is assigned by expert judgment.

Equation (13)

$$U(rel)_{CO_2} = \sqrt{U(rel)^2_{\text{Heat rate}} + U(rel)^2_{\text{Emission Factor}}}$$

$$U(rel)_{CO_2} = \sqrt{5^2 + 5^2} = 7.07\%$$

Table 3 summarizes the emission and uncertainty estimates for the different FCCU methodologies.

Table 3. Uncertainty Comparison for FCCU Estimation Methods.

Approach	Contribution	CO_2 Emissions, tonnes/yr
Method 1: Coke burn rate approach	Coke Burn	408,348 ± 16.0%
	CO Boiler	46,516 ± 7.07%
	Total	**454,864 ± 14.4%**
Method 2: K_1, K_2, K_3" approach	Coke Burn	411,862 ± 15.9%
	CO Boiler	46,516 ± 7.07%
	Total	**458,378± 14.3%**
Method 3: Air blower rate approach	Coke Burn	419,859 ± 15.9%
	CO Boiler	46,516 ± 7.07%
	Total	**466,375± 14.4%**

Based on the assumptions applied for the FCCU methodologies, the uncertainty associated with each of the methods provided in the API *Compendium* is comparable. In all three equations, the aggregated uncertainty is influenced primarily by the ± 15% uncertainty values assigned to the coke burn rate (used in the first and third methods) and the blower air capacity (used in the second method).

NEXT STEPS

At the time of developing the Uncertainty Document, it became clear that some of the industry recommended procedures and standards, in particular those used for flow measurements, have not been developed for the purpose of quantifying GHG emissions. Rather they were set in place to assist companies with custody transfer and financial accounting of transactions that emanate from these transfers. As a consequence the calibration and accuracy requirements far exceed what would be achievable in the context of measuring and calculating GHG emissions.

To address this gap API's Committee on Petroleum Measurement (COPM) is undertaking the development of two new standards:

1. **Fuel Gas Measurement Systems for Greenhouse Gas (GHG) Reporting**
   The purpose of this document is to allow differentiation between the design and calibration practices required to achieve custody transfer level performance and the 5% GHG measurement uncertainty required by the GHG reporting regulations;
2. **Standard Method for Calculating Carbon Content of Petroleum Products**
   The objective of this document is to provide a methodology for calculating the carbon content of hydrocarbon-based petroleum and petrochemical products using various physical property analyses, by using industry accepted mixture property data and test methods.

The technical report on fuel gas measurements is expected to be completed by early November 2010. It will form the basis for the standard for fuel gas measurements for GHG reporting. The technical report on calculating carbon content will be undertaken following the completion of the first one.

As the methodology for GHG emission reporting matures and gaps are noted during implementation, API aims to incorporate all this new information into an updated Uncertainty Document. The original 'pilot draft' that was published in September 2009 was designed to allow member companies and other stakeholders to road-test the document and provide comments on issues encountered in practice. It is expected that an update of the Uncertainty Document will be undertaken in the 2011-2012 time frame and will address issues raised by stakeholders and new industry studies and technical reports.

SUMMARY

Uncertainty analysis is a potential tool to not only assess the accuracy ranges of emissions inventories, but more importantly, to target specific activities for enhanced data collection through ranking the importance of different emission sources in terms of their overall contribution to the emissions inventory and the overall uncertainty range. The Uncertainty Document provides an overview of approaches to minimize uncertainty from measurements along with detailed discussion on the statistical methods used to calculate emissions uncertainties and aggregate them. It includes several examples on the potential application of such calculations for typical data collected by the oil and natural gas industry when assembling an emission inventory.

The Uncertainty Document is part of a decade-long initiative by the oil and gas industry to provide credible and consistent GHG emission calculation methods, and promote a systematic approach to GHG emissions inventory development. This is a vital first step to understanding the nature of the emission sources and to crafting effective methods for their mitigation or control. The oil and natural gas industry sector plans to continue its outreach and disseminate these guidelines broadly, as well as continue to develop additional guidance for selected industry sub-sectors. The industry is participating in collaborative research to obtain new and improved emission factors data for targeted operations. It will also continue to participate in public forums with governmental and intergovernmental organizations to address emerging reporting issues and provide pertinent technical information for such discussions.

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KEY WORDS

Greenhouse Gas Emissions
Greenhouse Gas Inventory
Uncertainty
Statistics
Oil and Natural Gas