Estimating measurement uncertainty for particulate emissions from stationary sources

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Abstract

The estimation of measurement uncertainty with regards to hazardous air pollution emissions from stationary sources is currently the most uncertain element associated with respect to obtaining relevant, valid particulate matter (PM) emission data in South Africa. This project is aimed at developing an appropriate method to evaluate the uncertainty associated with PM measurements conducted for stationary source emissions in the South African context. A series of In-Stack measurements were taken in accordance with recognized international methodology (ISO 9096:1992 and 2003) on two different industrial processes, representing a compliant and non-compliant scenario. A comparison between the two scenarios was made in an attempt to establish what components of the sampling technique have the greatest error.

The overarching goal of this project was to establish an estimate of the cumulative uncertainty on the final emission values obtained, inclusive of both analytical, field sampling and process related variables that may result in a cumulative error associated with quantifying stationary source PM emission values.

The results of the study found that the estimated combined expanded uncertainty for both sets of data was calculated to be between 62 – 72%. Upon closer analysis of the data it was ascertained that the data obtained were inadequate and the calculation of the uncertainty of the results both with the compliant and non-compliant sampling campaigns revealed that the variability of the results was too great for both scenarios to make any statistically valid observations or conclusions about the data.

In lieu of this the author has developed an alternative tool (a sampling suitability matrix) for assessing the quality and reliability of reported emission figures. It is expected to add significant value to the interpretation of the quality and reliability of the final emission results reported. The intention of this tool is to be incorporated as supplementary information into all emission reports in future. This will enable the plant operator and regulator to assess the quality of reported data and final emission results, thus assisting in establishing whether the plant is in compliance with their Air Emission License (AEL) requirements or not.

Keywords

uncertainty, particulate emissions, stationary sources, gum

Introduction

In 2010, emission standards under the National Environmental Management - Air Quality Act of 2004 (Act 39:2004 or AQA) were promulgated and included priority pollutants identified by the Department of Environmental Affairs (DEA) as having, or may have, a significant detrimental effect on the environment, including health, social conditions, economic conditions, ecological conditions or cultural heritage. Particulate matter was identified as one of the main priority pollutants that may cause harm as particulate matter emissions are regulated in almost every category for listed activities under section 21 of the Act.

The uncertainty of these measurements is difficult to quantify due to the physical nature of particles which may affect their behavior in an off-gas stream. To compensate for the inhomogeneous nature of particulate concentration in the gas stream, the samples are extracted isokinetically from the gas stream utilizing recognized, validated methods (USEPA Methods 5 and 17 and ISO 9096:1992/2003.

Good quality data are essential in the decision-making process for plant operators and regulatory authorities alike. Decisions made on questionable data can lead to costly mistakes from upgrading plant off-gas cleaning systems unnecessarily, to not taking action where necessary as a result of questionable data. The air quality monitoring field is still in its relative infancy in South Africa. The implementation of the new air quality legislation is an ongoing process and is not without its teething problems. This project aims to coincide with the demands of the

new legislation to ensure data quality and reliability of reported results. The implementation of a standardized methodology to assess PM monitoring data quality is the ultimate goal of this project.

Main objectives of the study

The main objective of the project is to establish the validity of source emission data (particulate matter emissions) obtained in South Africa. This was achieved by employing the general approach or framework to calculate uncertainty as set out in the "Guide to the Expression of Uncertainty in Measurement" (ISO GUM1995), in which individual uncertainty sources are identified, quantified and combined to provide the measurement uncertainty. This philosophy has been adopted as the underpinning approach within the European and International Standardization bodies and will be used in standardized measurement methods in the future (Robinson 2004).

For the purposes of this study the ISO 9096:1992 and 2003 methods will be utilized for the measurement campaigns. These methods have been chosen due to the fact that the ISO 9096 method was utilized by Levego for the sampling to produce the data sets that will subsequently be utilized in this study. The abovementioned methods are deemed as equivalent methods by the international measurement community and utilizing either method should produce a similar result (environment agency technical guidance note M2:2011 version 8.1).

An attempt is made to estimate the uncertainty of the final emission results and to quantify the effects of not adhering to the requirements of the ISO 9096 methods.

Literature review and research hypothesis

Overview

In reviewing stack emission monitoring surveys conducted in the past, it has been suggested that the greatest components of error are those that are out of control of the sampling specialist. The "International Organization for Standardization ISO 9096 (1992)" method was utilized for conducting the particulate matter measurements for the study, which includes stationary source emissions – the determination of concentration and mass flow rate of particulate material in gas-carrying ducts – manual gravimetric method. According to the method, the following parameters are deemed to be out of the control of the sampling specialist: plant operating conditions, environmental conditions, and the non-compliance of the sampling location to the minimum requirements as set out in ISO 9096:1992 and 2003.

A critical element of a quality system is to ensure that the systems of calibration and measurement are traceable to national standards of measurement and that confidence can be placed in the quality of measurements carried out at all steps in the traceability chain (Clarke et al 1998). Validation is necessary to demonstrate the instrument response over the full working range of the parameter being measured. The methodology utilized in this study is an internationally validated method and therefore the traceability of the method has been determined

If all the minimum components of the standard are complied with then the final reported emission results would be guaranteed to be within + 10 % of the reported value (ISO 9096:1992 and 2003). The problem arises when the minimum requirements are not adhered to. In South Africa, most existing industrial plants have been in operation for decades and as a result have been built without due consideration for complying with the minimum current environmental standards. This poses a problem, especially with regards to obtaining a suitably compliant sampling location.

In contrast to the measurement of gaseous emissions which can be routinely undertaken with an accuracy of a few percent, the measurement of particulate emissions is far more difficult. This arises primarily from the non-uniform distribution of particle concentration within the duct or chimney coupled with the non-uniformity of the gas velocity/off gas flow (Hawksley et al 1977). The above scenarios may occur due to several factors such as bends, dampers etc. in the off-gas ducting. The basic requirement of all extractive sampling techniques is that a sample of the gas taken into the measurement system should be representative of the bulk of the gas stream in the flue. For these reasons, very precise guidelines for particle sampling are required and these are given in the various standard sampling methods utilized (ISO9096:1992/2003 and USEPA 5/17). One can conclude then from the abovementioned properties of particles that firstly the choice of sampling position is vital, and secondly that multipoint sampling should be utilized in almost all applications (Hawksley et al 1977). In practice the adherence to the minimum requirements for a sampling location is said to be the most commonly non-compliant parameter (Hawksley et al 1977).

The reason for the above assumption (non-compliance of the sampling location), is that the laboratory analysis of the samples obtained are done under controlled laboratory conditions to ensure minimal external interference with the sample. The sampling equipment utilized can be adequately controlled by the sampling specialist and all the components of the sampling train can be verified and calibrated where necessary. For these reasons, process type, variability and continually changing environmental conditions have the greatest effect on the final measurement result obtained as these factors are outside of the control of the test technician and are part of the random set of uncertainties that are difficult to quantify and account for (Environment Agency Technical guidance note M2 1993).

From the assumptions mentioned above, several scientific questions can be asked;

- Does the non-compliance of the sampling location and process operating conditions have the greatest influence on the sampling results?
- Can the uncertainty of the measured emissions be determined statistically?
- Can a suitable method of evaluating the acceptability or quality of final emissions data be developed?

In an attempt to answer these questions, two sampling campaigns have been conducted (refer to data and methodology on page 4 for details of sampling campaigns). The first sampling campaign was conducted with all the minimum requirements of the standard) being met. The second sampling campaign was conducted where the minimum requirements for the sampling location and process operations did not adhere to the minimum requirements of the standard. The subsequent comparison and analyses of the data sets obtained from a fully compliant (Source A) and non-compliant (Source B) stack emission campaign will endeavor to answer the abovementioned questions. Once these findings have been established, an attempt is made to use statistical methods to estimate the uncertainty of the measurement when faced with a non-compliant stack.

Whether the estimation of the overall uncertainty is feasible will be determined once the data are evaluated. If it is found that it is not feasible to obtain an estimate of the uncertainty pertaining to the non-compliant measurement scenario, this study will provide the impetus to inform industry of the potential dire consequences of not spending money on projects to ensure that the sampling locations and plant operations are satisfactory for obtaining good quality emissions data.

The trend by many industries at present is to save costs by doing the bare minimum to comply with the relevant standards. As South Africa, which is classified as a developing nation, tends to follow developed country trends, it is safe to say that industry will have to start taking environmental issues seriously and spend money to ensure good quality data. Best practice in developed nations is easier to obtain as they tend to have well established standards and norms, whilst in South Africa one generally has to look abroad for guidance. This situation, although cost effective, is not always appropriate as the standard methods and norms adopted in a developed country may not be entirely relevant or suitable for application in a developing country such as South Africa.

Key findings of Dutch validation study (1999)

According to the findings of the study, the results were disappointing as the reproducibility of the Dutch field study were deemed to be less than satisfactory (ISO 9096:1992 p39). During subsequent meetings with the project support committee and members of the quality committee it was established that the performance characteristics of the Netherlands Standardization Institute (NEN)-ISO 9096:1992 were related to the characteristic properties of the waste gases. This conclusion is based mainly on the discrepancies in the results of repeatability as determined at the three sources. Two of the three sources showed a repeatability of approximately 12-14% (RSD), while the third source had a significantly higher repeatability value, representing poor repeatability, the results also produced disappointing reproducibility. A great difference between the first two and the third source was attributed to the high water vapour content. Moreover, there may be differences in physical composition of the dust in the waste gases. The conclusion, based on the matrix discrepancies in the waste gases, is that evidently a distinction is to be made between 'simple' and 'difficult' sources. It would appear that 'difficult' sources place too high a demand on the measuring method (ISO9096:1992 pg. 39).

On the project support committee's recommendation and after approval thereof by the quality committee, the Nederlanse Onderneming voor Energie en Milieu (NOVEM) / (Netherlands agency for Energy and the Environment) commissioned the performance of supplementary dust measurements on an emission simulation plant as installed at the Hessische Landesanstalt für Umwelt (HLfU) in Kassel, Germany. The purpose thereof was to demonstrate the reproducibility and correctness of measurements for 'simple' sources, so that the result may serve as a basis for the problems experienced with 'difficult' sources. At this plant, not only the reproducibility of the measuring method was determined but also its trueness, as well as the ability of the participating Dutch measuring institutes. The reproducibility was determined at two concentration levels (approximately 10 and 20 mg/m^3). Based on measurements at this plant, a reproducibility of 4.5mg/m^3 (44%) was determined at the concentration level of 10mg/m^3"

A similar order of magnitude was determined at the 20 mg/m^3 concentration level. When taking these Dutch findings into consideration in the context of this study, the conclusion is that the errors and uncertainties with regards to spatial and temporal variations are too great to allow much value to be derived from an in-depth statistical analysis of the results obtained, other than to confirm that there are large uncertainties contained in trying to reproduce results utilizing this method on various plants – be they compliant or non-compliant. Therefore, the imperative to utilize a qualitative approach to complement the emission result is vital in determining the quality of the results obtained, and ultimately the decisions made.

Data and methodology

Overview

The source emission data utilized in this study were obtained from two stack sampling campaigns conducted for the determination of concentration and mass flow rate of particulate matter. The surveys were undertaken by a leading South African source monitoring organization.

The first sampling campaign involved conducting twelve (12) one (1) hour isokinetic stack samples over two days for

particulate matter from a large industrial boiler installation, typical of a coal fired power plant found in South Africa (Source A). These data are representative of the best-case scenario where the results represent a stack that complies with all the minimum requirements as set out in ISO 9096:1992 and 2003.

The second sampling campaign involved conducting three (3) one (1) hour isokinetic stack samples over an eight hour shift from a cement kiln installed on a typical cement manufacturing plant (Source B). These data are representative of the worst-case scenario where the results represent a stack that does not adhere to all the minimum requirements as set out in ISO 9096:1992 and 2003. The requirements not adhered to are the requirements specifically related to the suitability of the sampling location.

The comparison of the flow profile data sets for both surveys is included as this has been determined as the most appropriate way to assess the suitability of the sampling location, as an uneven and unstable flow profile is assumed to have the largest single effect on the uncertainty of the final reported results.

Process information

Many sampling campaigns achieve unrepresentative results as the sampling period chosen does not accurately represent the process emission. It is important to note that many sampling techniques have been developed for relatively steady stack emissions, such as power stations, but in some sources it is not unusual to have a 100 fold difference in reported emissions over relatively short time periods from 10days to relatively long time periods of up to 10 months. It is important to obtain as much information as possible about the process before commencing any sampling campaign. However, in practice, little data may be available concerning the process as a result of intellectual property and patent rights resulting in limited information being made available to third parties, such as the test house.

Summary of the sampling method

A representative gas sample is withdrawn from the source. The degree to which this sample represents the total flow depends on the:

- Homogeneity of the gas velocity within the sampling plane (stable, uniform flow within the enclosed flue system is required). The gas flow in off-gas ducts are such that laminar flow is rarely, if at all, achieved (Hawksley et al 1977).
- A sufficient number of sampling points in the sampling plane which would depend on the size of the duct or stack (a larger sampling plane requiring more sampling points).
- The isokinetic withdrawal of the sample will also have a significant effect on the degree to which the sample is representative of the total flow in the gas stream (Hawksley et al 1977).

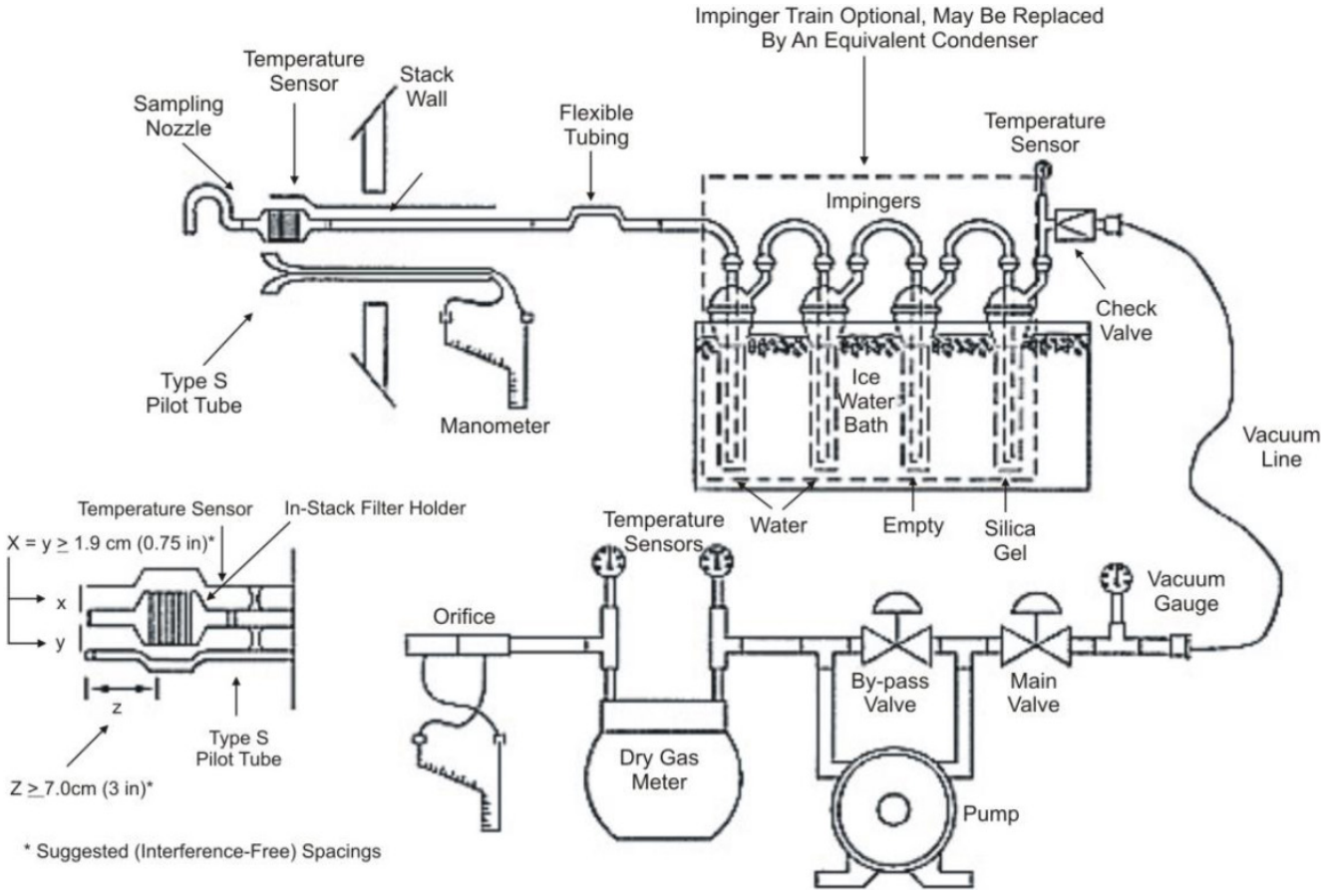

Figure 1: *Particulate Matter Sampling Train with In-Stack Filter – Source, EPA Method 17*

Normally the gas has to be sampled at multiple points within the sampling plane, depending on the sampling plane cross-sectional area. This plane is usually divided into equal areas, at the center of which the gas is withdrawn. To determine the particulate concentration in the plane, the nozzle is moved from one sampling point to the other, extracting gas isokinetically at each point. Sampling periods should be equal for each sampling point, resulting in a composite sample. If equal sampling areas cannot be chosen, the sampling period should be proportional to the sampling area.

The number of sampling points is not the only factor affecting the accuracy of a measurement emission. It also depends on the duration of sampling each increment. The reason for this is that the flow of solids at any point is never constant but fluctuates randomly above and below the average value. These random fluctuations are always present even when the plant is being operated under steady conditions (Hawksley et al 1977, p 5).

The sample is extracted through a sampling train, which principally consists of the following; a sampling probe tube with entry nozzle, a particle separator, a gas metering system, and a suction system (Figure.1). below). The particle separator and/or the gas metering system may be either located in the duct or placed outside the duct.

It is necessary to avoid condensation of the vapor (water, sulphuric acid, etc.) in the sampling train during gas sampling, as condensation will interfere with the particle separation, particulate condition and flow measurement. To this end, the probe tube, the particle separator, and the gas flow measuring device are heated to above the relevant dew-point temperature. The water vapor may intentionally be removed downstream of the particle separator to make use of a dry-gas meter for the measurement of sample gas volume if the water vapor content of the duct gas does not vary appreciably during sampling.

For isokinetic sampling, the gas velocity at the sampling point in the duct must be measured and the corresponding sample gas flow calculated and adjusted. Normally, a pitot static tube is used for the measurement of duct gas velocity. The pitot static tube is utilized to measure the static and differential pressures at each equal area point in the gas stream. The stack gas temperature is also measured at each of these points. Together with an estimate of the gas density (containing carbon dioxide, oxygen and nitrogen for typical combustion process), these values are used to calculate the velocity profiles and volume flow rate of the gas stream present in the stack. If the sample gas flow measuring device is used within the duct, the relation between the measured pressure drop and the pitot static tube differential is simple, facilitating the adjustment to isokinetic conditions.

If the gas metering device is located outside the duct, the calculation of the isokinetic sample gas flow rate is more complicated. The calculation for isokineticity must also include the duct gas density under standard conditions, which may be derived from the dry gas composition and the moisture content.

The temperature and static pressure of the gas in the duct and the gas metering device must also be noted if the sample gas flow is measured after water removal.

After sampling, the collected particulate matter is completely recovered (which can necessitate cleaning of the probe and nozzle), dried and weighed. It is important to note that the filter utilized for the separation of the particulate matter from the gas stream must undergo preconditioning, where it is also dried, cooled and weighed. The difference between the post-weight and pre-weight of the filter will be the mass of the particulate matter collected from the gas stream.

Overview of statistical approach

The approaches to calculating method uncertainty utilized in the "Guide to the Expression of Uncertainty in Measurement" (ISO 1995) (generally known as GUM 1995) are the underpinning methods utilized for analysing the data sets under review. In general, the concept of measurement uncertainty as described in the GUM has been broadly accepted by the measurement community (Robinson 2004).

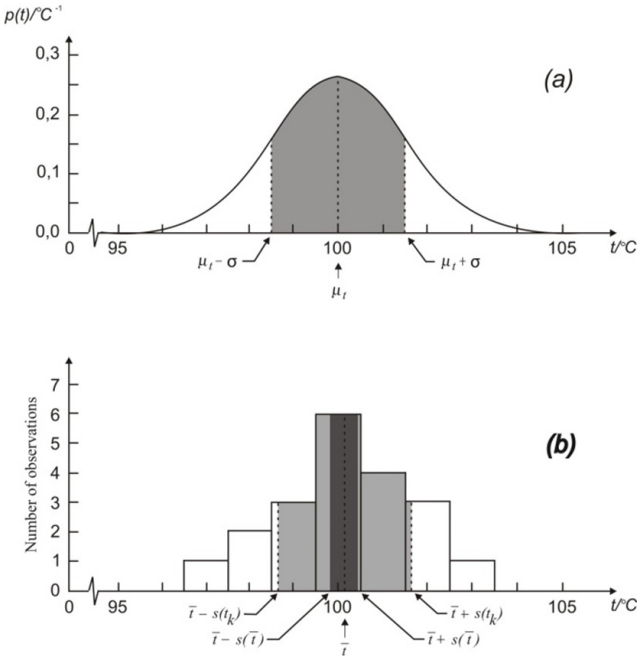

Figure 2: *Graphical illustration of evaluating the standard uncertainty of an input quantity from repeated observations (Source; GUM, 1995)*

The viewpoint of GUM is that all the components that make up the uncertainty of measurement are of the same nature and are to be treated identically (GUM 1995). As a starting point for discussions, a simplified derivation of the mathematical expression for the propagation of standard deviations is utilized, termed in the guide as "the law of propagation of uncertainty". It is important at this point to define what is meant by the term uncertainty. Two definitions are provided: "The word uncertainty means doubt, and thus in the broadest sense the 'uncertainty of measurement' means doubt about the validity of the result of a measurement." (GUM 1995 p 2)

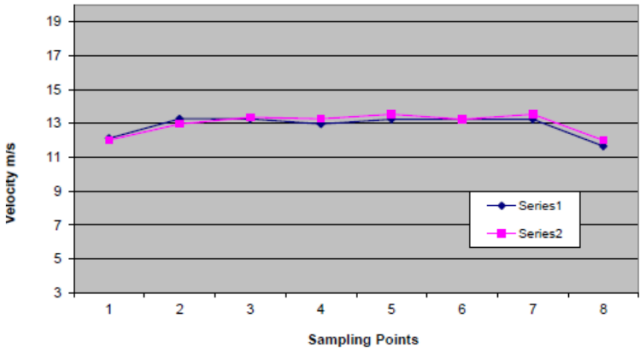

Figure 3: *Velocity profile for test 1 Source A*

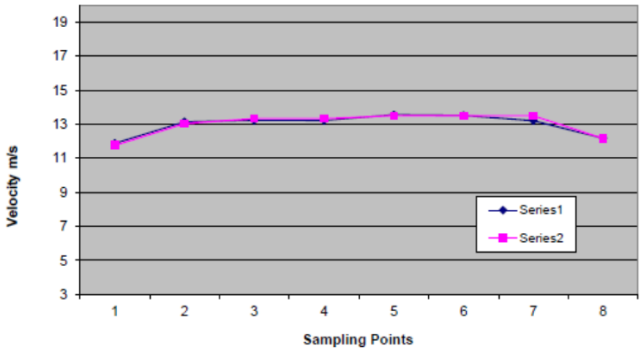

Figure 4: *Velocity profile for test 2 Source A*

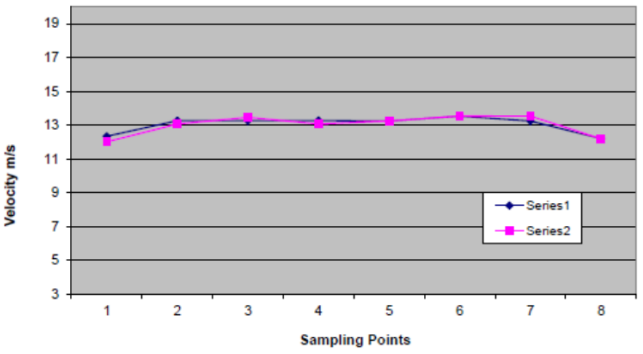

Figure 5: *Velocity profile for test 3 Source A*

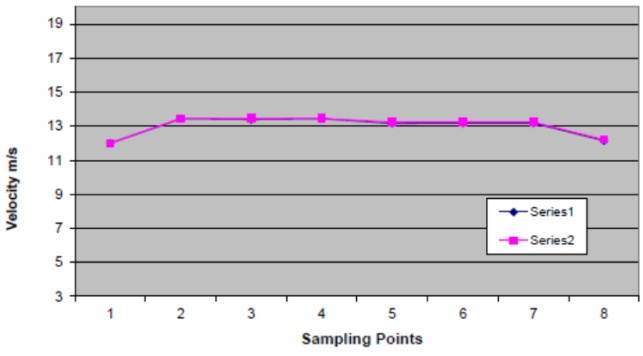

Figure 6: *Velocity profile for test 4 Source A*

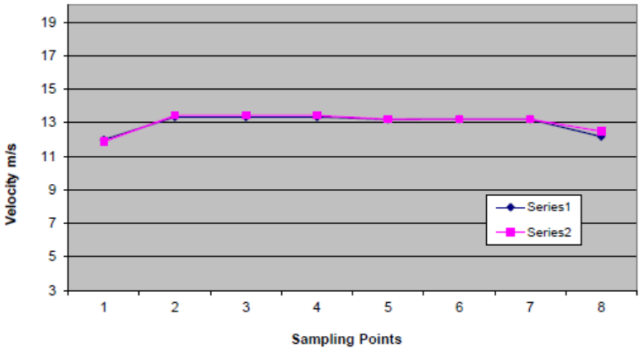

Figure 7: *Velocity profile for test 5 Source A*

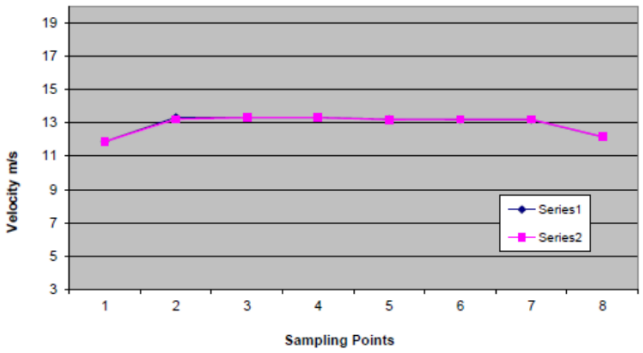

Figure 8: *Velocity profile for test 6 Source A*

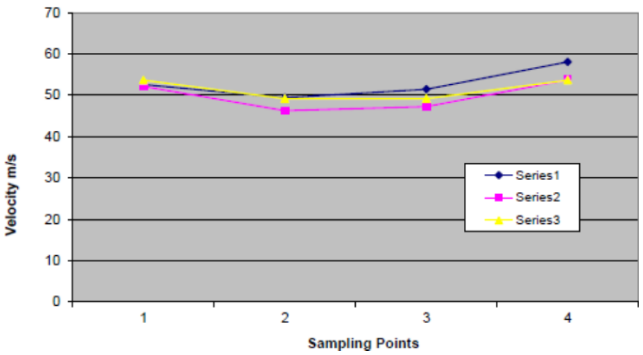

Figure 9: *Velocity profile for test 1 Source B*

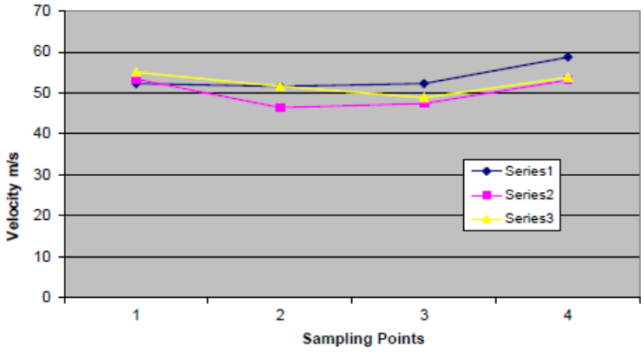

Figure 10: *Velocity profile for test 2 Source B*

"Uncertainty is the unknown (of measurement) parameter, associated with the result of a measurement, which characterizes the dispersion of the values that could reasonably be attributed to the measurand (value of a quantity)." (GUM 1995 p 2)

From these definitions, the parameter characterizing uncertainty may be a standard deviation or a multiple thereof. Uncertainty of measurement, in general, comprises of many components.

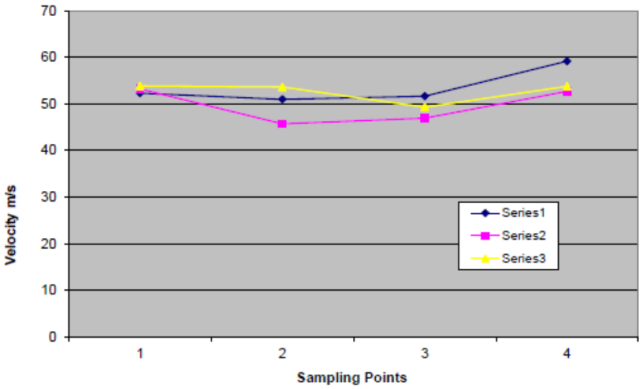

Figure 11: *Velocity profile for test 3 Source B*

Some of these components may be evaluated from the statistical distribution of the results of series of measurements and can be characterized by experimental standard deviations (Figure 2). The other components, which also can be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or relevant information; for example, one can assess the quality of data on adherence to the minimum requirements of a specific standard. If certain of the requirements are met, then one can make specific assumptions about the data. We have utilized this statistical method and applied the principles to both sets of data utilized for the study.

It is important to distinguish between repeatability and reproducibility in conducting a series of measurements and in determining the final outcome and interpretation of the results obtained.

Repeatability: measurements that are taken under the same conditions where the variables and their associated uncertainties are kept constant.

Reproducibility: The attempts to reproduce the results of the repeated observations under differing or varying conditions.

Validation of measured results

If testing was conducted at an unsuitable location, or was carried out under fluctuating plant operating conditions, the validity of the sample may be questioned and the measurement results uncertain (ISO 9096:2003). An assessment of the stability and uniformity of the flow in the flue will determine the suitability/compliance of the sampling location. For this reason the velocity flow profiles for Source A and B have been included to assess the quality and validity of emission results obtained (See Figures 3-11). Series 1, 2 and 3 in the figures are representative of the flow profiles for each sampling port utilized for repeated sampling runs. Source B is a rectangular non-compliant sampling location and it is for this reason the flow profiles will not represent a typical uniform velocity profile as there is significant uneven, non-uniform flow at this sampling location.

Combined uncertainty for measured parameters

The measured parameters for all of the individual tests conducted on Sources A and B are given in Table 1.

If one compares the calculated overall uncertainties for Table 1, one would notice that the non-compliant data set returns a similar overall uncertainty (62.69% RSD) when compared to the compliant stack (62.52-72.98% RSD). The overall uncertainty is also much higher than anticipated; this once again is mainly attributed to the small data sets utilized and the number of external variables that cannot be accounted for (i.e. certain process operating conditions, changes in environmental conditions, etc.)

Due to a lack of sufficient data, normal distribution was assumed for all parameters but could not be statistically verified. All the measured off-gas parameters have been incorporated into table 1 together with the calculated result. For each set of data the following results were calculated in order to derive the final combined expanded uncertainty for each parameter:

Step 1: Tabulate all the raw data results

Step 2: Calculate the sum of all the results

Step 3: Calculate the average for the data set from the sum of the results

Step 4: Calculate the median for the data set

Step 5: Calculate the variance

$(s^2) = \Sigma [(x_i - \bar{x})^2]/(n - 1)$

Where:

s^2 = Variance

Σ = Summation, which means the sum of every term in the equation after the summation sign.

x_i = Sample observation. This represents every term in the set.

$\bar{x}$ = The mean. This represents the average of all the numbers in the set.

n = The sample size. This can be thought of as the number of terms in the set.

Step 6: Calculate the standard deviation

$$s = \sqrt{\frac{\sum(x - \overline{x})^2}{N - 1}}$$

Where:

- S = standard deviation
- x = each value in the sample
- $\bar{x}$ = The mean of the values
- N = the number of values (the sample size)

Step 7: Calculate uncertainty at 95% confidence interval

- Utilise the Student t-distribution table to determine the coverage K factor from the degrees of freedom for the data set for the equivalent 95% confidence interval.

Step 8: Calculate combined standard uncertainty. Each individual uncertainty is calculated as a standard deviation for each individual component. Each standard deviation is then squared and added together. The square root of the sum of the individual uncertainties are then expressed as the combined standard uncertainty as per the equation below.

$$CU = \sqrt{u_1^2 + u_2^2 + \cdots + u_n^2}$$

or

$$CU = (u_1^2 + u_2^2 + \cdots + u_n^2)^{\frac{1}{2}}$$

Where:

- CU = combined uncertainty
- U = uncertainty of individual component

Table 1: *Measured parameters and their estimated uncertainty for Sources A and B.*

ISOKINETIC TEST RESULTS | PLANT COMPLIANT SAMPLING POSITION | DATE 01-Aug-05								
DATA NO.	**Dust [conc] mg/Nm³**	**CO_2**	**O_2**	**Static Pressure**	**Moisture**	**Gas Temp**	**Gas Velocity**	**Gas Density**
1	287.65	11.10	8.20	-1.10	2.33	125.45	12.99	0.75
2	293.30	11.10	8.20	-1.11	3.80	125.65	13.03	0.75
3	315.89	11.10	8.20	-1.05	3.77	127.66	13.13	0.74
4	318.30	11.50	8.10	-1.05	2.30	123.96	13.08	0.75
5	396.23	11.50	8.10	-1.05	2.42	124.69	13.28	0.75
6	428.34	11.50	8.10	-0.98	2.19	126.03	13.22	0.75
PARAMETER								
sum	2039.71	67.80	48.90	-6.34	16.81	753.44	78.73	4.49
average	339.95	11.30	8.15	-1.06	2.80	125.57	13.12	0.75
median	317.10	11.30	8.15	-1.05	2.38	125.55	13.11	0.75
variance	2823.22	0.04	0.0025	0.0018	0.49	1.33	0.01	0.000014
SD	53.13	0.20	0.05	0.04	0.70	1.15	0.10	0.0037
confidence (95%)*	130.18	0.49	0.12	0.10	1.71	2.82	0.25	0.01
% Uncert	15.63	1.77	0.61	4.00	24.94	0.92	0.78	0.50
% Uncert (95% CI)*	38.29	4.34	1.50	9.81	61.09	2.25	1.90	1.22
Combined Standard Uncertainty		53.15						
Combined Expanded Uncertainty		130.221						
Combined Standard Uncertainty % Relative		29.79						
Combined Expanded Uncertainty % Relative		72.98						
*where CI = 95%, K = 2.45, degrees of freedom = 6								
ISOKINETIC TEST RESULTS | PLANT COMPLIANT SAMPLING POSITION | DATE 04-Aug-05								
DATA NO.	**Dust [conc] mg/Nm³**	**CO_2**	**O_2**	**Static Pressure**	**Moisture**	**Gas Temp**	**Gas Velocity**	**Gas Density**
1	159.60	11.50	8.10	-1.20	4.00	123.51	13.19	0.75
2	188.86	11.50	8.10	-1.20	2.73	125.63	13.14	0.75
3	192.32	11.50	8.10	-1.20	4.11	125.45	13.11	0.75
4	218.84	11.40	8.20	-1.07	5.26	122.91	13.12	0.75
5	236.85	11.40	8.20	-1.07	5.08	123.69	13.17	0.75
6	254.29	11.40	8.20	-1.05	4.63	124.00	13.12	0.74
PARAMETER								
sum	1250.76	68.70	48.90	-6.79	25.81	745.19	78.85	4.49
average	208.46	11.45	8.15	-1.13	4.30	124.20	13.14	0.75
median	205.58	11.45	8.15	-1.14	4.37	123.85	13.13	0.75
variance	1007.68	0.0025	0.0025	0.0047	0.70	1.01	0.0008	0.000014
SD	31.74	0.05	0.05	0.07	0.84	1.00	0.03	0.0037
confidence (95%)*	77.77	0.12	0.12	0.17	2.06	2.46	0.07	0.01
% Uncert	15.23	0.44	0.61	6.07	19.52	0.81	0.22	0.50
% Uncert (95% CI)*	37.31	1.07	1.50	14.86	47.82	1.98	0.54	1.22
Combined Standard Uncertainty		31.77						
Combined Expanded Uncertainty		77.8393						
Combined Standard Uncertainty % Relative		25.52						
Combined Expanded Uncertainty % Relative		62.52						
*where CI = 95%, K = 2.45, degrees of freedom = 6								
ISOKINETIC TEST RESULTS | PLANT NON-COMPLIANT SAMPLING POSITION | DATE 10-Nov-05								
DATA NO.	**Dust [conc] mg/Nm³**	**CO_2**	**O_2**	**Static Pressure**	**Moisture**	**Gas Temp**	**Gas Velocity**	**Gas Density**
1	1694.52	23.00	11.00	-1.00	9.68	93.17	52.44	0.83
2	1813.39	22.00	11.00	-1.00	12.89	95.00	53.50	0.82
3	2051.77	22.00	12.00	-1.08	12.72	95.75	53.39	0.82
PARAMETER								
sum	5559.68	67.00	34.00	-3.08	35.29	283.92	159.33	2.47
average	1853.23	22.33	11.33	-1.03	11.76	94.64	53.11	0.82
median	1813.39	22.00	11.00	-1.00	12.72	95.00	53.39	0.82
variance	22064.74	0.22	0.2222	0.0014	2.17	1.17	0.23	0.000022
SD	181.93	0.58	0.58	0.05	1.81	1.33	0.58	0.01
confidence (95%)*	578.53	1.84	1.84	0.15	5.74	4.22	1.85	0.02
% Uncert	9.82	2.59	5.09	4.50	15.35	1.40	1.10	0.70
% Uncert (95% CI)*	31.22	8.22	16.20	14.31	48.83	4.46	3.49	2.23
Combined Standard Uncertainty		181.94						
Combined Expanded Uncertainty		578.5778						
Combined Standard Uncertainty % Relative		19.71						
Combined Expanded Uncertainty % Relative		62.69						
*where CI = 95%, K = 3.18, degrees of freedom = 3								

This small study has confirmed the findings of a comparable but larger project which came to similar conclusions (discussed in section 3.2). The Dutch study mentioned in ISO 9096:2003 collected much larger data sets than the one used in this study, yet had very high levels of uncertainty when trying to calculate an overall uncertainty for the entire data set. Prior to the Dutch field-based study being undertaken (ISO 9096:2003 p38), a sensitivity analysis was conducted of the uncertainty of the entire document. "This led to the conclusion that the determination of the waste gas velocity (i.e. mispositioning of the pitot tube) had contributed most to the total measuring uncertainty" (ISO9096:2003 p38). In turn, a non-complying sampling location can also have a significant effect on the velocity profile (See figures 3 – 11) and ultimately affect the total measurement uncertainty in the same way as a mispositioned pitot tube.

Discussion

The statistical analysis of the data reveals that no conclusive opinions can be made about the data sets utilized. An estimate of the overall uncertainty was attempted but the results were not conclusive as not enough data were obtained to enable any valid statistical inferences to be made.

After applying the statistical methodology to the data sets, it was concluded that the data sets were far too small. Ideally 50 – 100 or more samples need to be included in each of the data sets (ISO GUM 1995). Unfortunately, obtaining a large enough data set has not been possible due to budget constraints and the cost and logistics of conducting the sampling. The standard deviation for the test results is relatively high over the range of results and this is mostly attributed to the small data sets obtained.

Due to the nature of field sampling, not all variables can be controlled. The samples are all taken at different times and reasonable care is taken to ensure that the sampling is conducted under similar plant operating conditions, however natural fluctuations and process variations under normal operations inevitably occur and thus cannot be adequately controlled. Although this is the case for each individual source sampled, significant variation in the results still occurs as a result of a large number of input variables involved i.e. sampling procedure, process operation, plant and prevailing environmental conditions all of which have an influence on the repeatability and reproducibility of the results.

The influence of turbulent flow is said to also have a large negative effect on the overall result. Attempts to calculate Reynolds numbers for the various flow profiles to ascertain whether the flow was laminar were conducted. The compliant as well as the non-compliant sampling positions both showed Reynolds numbers in the turbulent range. ISO 9096:1992 and 2003 does not require laminar flow but states that the flow in the duct must be as stable and uniform as possible. To achieve laminar flow, one needs to have very low flow rates. As the flow rates of a typical enclosed flue gas stream are high, (ranging between 5 – 30 m/s; for this study the velocity range was between 11.5 – 50m/s) obtaining true laminar flow is almost impossible. It is for this reason that the application of the Reynolds number did not confirm compliance or non-compliance of the sampling positions.

An alternative method/tool to utilizing statistical techniques is to use qualitative estimates of uncertainty based on experience, reasonable estimates of errors and uncertainties and adherence to the minimum requirements of the ISO 9096:1992 and 2003. The result of this approach has been the development of a sampling suitability matrix. This matrix consists of a table with all the minimum requirements, as set out in ISO 9096:2003 pg.31 (see also table 2). From the table, the accuracy and minimum requirements for all the apparatus and sampling conditions are given.

Utilizing this method, once the sampling survey has been completed the sampling specialist will check each of the components for compliance. A rating scale has been devised by the author for the influence each component is estimated to have on the final results. These values have largely been derived from experience in the field and the ability for the sampling specialist to control certain variables (systematic errors).

Sampling suitability matrix

All the measurement variables have been tabulated and categorized (see Table 2). The measurement variables have been placed into three categories namely: sampling location, equipment used for dust collection, and equipment for flue gas characteristics (ISO 9096:2003, pg. 31). Each variable has been given a rating out of ten, the higher the number out of ten, the greater the influence of the variable on the uncertainty of the final sampling results. The rating is subjective; the principle behind the rating of each variable is the ability of the test technician to control that specific variable. The less control the test technician has over the variable, the higher the score or rating that is assigned to the applicable variable

From Table 2, the accuracy for each component of the measurement variables is given. Once the sampling survey has been conducted, the sampling specialist will check each of the components for compliance to the minimum requirements (ISO 9096:2003). The ratings are based on a sliding scale with a score of ten having been estimated to have the most impact on the final measurement uncertainty and a rating of one having the lowest impact on the final measurement result. A zero value indicates that the plant is not in compliance for that parameter and therefore the overall points scored will be lowered. Once all the components or variables have been checked for compliance, the sampling specialist will calculate each specific component rating. The sampling specialist will input all the results and ratings into the sampling suitability table that will estimate the quality of the final measurement result as excellent, fair or poor see the last column of table 2.

Table 2: *Sampling suitability matrix*

Summary of requirements - Apparatus and sampling conditions					
SAMPLING LOCATION	**Approx. Value**	**Measured Value**	**Compliance y/n**	**Rating**	
Flow angle	<15°			10	P
Pressure difference (pitot tube)	> 5 Pa			10	P
Ratio of max gas velocity to min gas velocity	3:1			10	P
Negative flow	None			10	P
Straight length before the sampling plane	> 5 hydraulic diameters			9	P
Straight length after the sampling plane	> 2 hydraulic diameters			9	P
Straight length before emission point	> 5 hydraulic diameters			9	P
Number of sampling points	dependant on duct size			9	P
EQUIPMENT FOR DUST COLLECTION					
Alignment of the nozzle	10%			8	FS
Isokinetic Criteria	+15% and -5 %			8	FS
Leak test	< 2%			8	FS
Condenser, drying tower: residual gas moisture	< 10 g/m³			7	FS
Gas meter volume measurement uncertainty	2%			7	FS
Absolute pressure measurement uncertainty	1%			7	FS
Absolute temperature measurement uncertainty	1%			7	FS
Filter efficiency (test aerosol 0,3um)	> 99.5 %			6	EQ
Filter material (adsorption of components)	No reaction or adsorption			6	EQ
Nozzle straight length before the first bend	> 30 mm			5	EQ / P
Nozzle tip: distance to obstacles	> 50 mm			5	EQ / P
Nozzle: Length with constant internal diameter	> 10 mm			4	EQ
Nozzle: variation in diameter angle	< 30°			4	EQ
Nozzle Internal diameter	> 4mm			4	EQ
Nozzle area: measurement uncertainty	10%			4	EQ
Elbow: Radius of the bend	> 1,5 d			4	EQ
Balance resolution (mg)	0.01mg to 0.1mg			3	L
Weighing uncertainties	< 5% of the LV for process			3	L
Thermal stability (filter)	> 8h			3	L
Overall Blank Value	< 10% LV or 2 mg/m³			3	L
Sampling time measurement uncertainty	5 secs			2	FS
Linear measurement uncertainty	1% duct .2mm / 5% Nozzle			2	FS
EQUIPMENT FOR FLUE GAS CHARACTERISTICS					
Absolute temperature	1%			1	C
Flue gas density	0,05 kg/m³			1	C
Total possible Score				188	
Validity of Results obtained					%
Excellent (Fully compliant)				188	1.00
Fair (mostly compliant)				150	0.80
Poor				60	0.32
Key:					
P: Plant Restrictions					
FS: Field Sampling Restrictions					
EQ: Equipment Restrictions					
L: Laboratory Restrictions					
C: Calculated / Measured in the Field					

Discussion

From the sampling suitability matrix table, one can deduce that the restrictions of the plant as well as field sampling restrictions, time constraints, plant availability, extreme operating conditions, sampling location restrictions and access to the sampling position have the biggest impact on the final data quality, and therefore have the highest rating (the more requirements in terms of the sampling location and plant restrictions that do not comply, the greater the impact on the results). Equipment restrictions such as limits of detection, calibration and verification of sampling train components, and resolution of sampling train components utilized, may have a significant impact on the results; these variables thus received a moderate rating in terms of impacting the final data quality. The laboratory analyses and calculated values have the least impact on the final results as these are the variables that can be best controlled by the sampling specialist and laboratory personnel.

The application of the sampling suitability matrix to each data set seems to correlate well when applied to both surveys (Source A and Source B) utilized in this project. The sampling suitability matrix confirmed that the compliant plant (Source A) should generate good reliable data while the results for the

non-compliant plant (Source B) agree with the results of the sampling suitability matrix in that the results may not be as reliable as the fully compliant plant that was surveyed.

The potential importance of applying the sampling suitability matrix table to post survey results cannot be underestimated. The table's inclusion in the final emissions report will go a long way to highlighting specific problem areas with regards the measurements. The requirement of completing this suitability table will provide a tool for the sampling experts to identify areas of improvement that need to be made to sampling conditions or equipment. It will also go a long way to highlighting the need for identifying suitable sampling locations, stable operating conditions etc. to be provided for by the plant personnel.

Summary and conclusions

When conducting sampling surveys to obtain source emissions data, it has been suggested that the greatest components of error are those that are out of control of the sampling specialist (Random Error); plant operating conditions, environmental conditions, and the non-compliance of the sampling location to the minimum requirements as set out in ISO 9096:1992 and 2003, etc.

The subsequent comparison and analyses of the data between the compliant and non-compliant sampling scenarios has confirmed these suspicions. Once these findings had been established, it was endeavored to find ways through statistical treatment of the data to estimate the uncertainty of the measurements when faced with a non-compliant sampling position.
Determining the measurement uncertainty quantitatively from the analysis of the data in this project was not feasible. The reason for this was that the data sets used in the statistical analysis were too small to derive any conclusions from the results. Due to the labour-intensive, time consuming nature and budgetary constraints involved in trying to obtain sufficient quality data, an alternative qualitative approach was deemed more suitable for the purposes of this study, in order to estimate the uncertainty or overall quality of the final emission data reported. The results of this approach include the development of the sampling suitability matrix which was developed through careful analyses of the minimum requirements as set out in ISO 9096:1992 and 2003 and vast sampling experience. Values have been assigned to all the components and variables that have a significant impact on the quality of the data as set out in ISO9096:1992 and 2003.

The end result is a sampling suitability matrix table that allows the sampling specialist to analyse each component of the sampling process and assess whether adherence to the minimum requirements have been met. In instances where the minimum requirements for a specific component have not been met, a specific rating has been given to that component which corresponds to the specific impact of its non-compliance on the final emission data reported.

It should be noted that the ratings used are subjective. The matrix can however give a good indication of the quality of the data reported, in the absence of statistically validated data. This is done through careful consideration of the significance and impact that each non-compliance has on the final result.

In conclusion, the sampling suitability matrix would prove to be a valuable tool in assessing final emissions figures that are reported for sampling campaigns in the future. Even though the original goal of the project was not achieved in terms of quantifying the uncertainty of emissions data, the sampling suitability matrix will be able to give more insight to the client as well as sampling experts in the field on the interpretation and reliability of the emissions figures reported. This information will go a long way in helping the decision-making process with regards to ensuring environmental compliance. It will give insight into whether enough good quality data have been provided, or whether the results are questionable, resulting in the need for addressing changes to the prevailing sampling conditions, sampling techniques utilized or whether an alternative sampling approach is needed to obtain good quality data. Further study into the quantification and estimation of source emission uncertainty will need to be done with larger data sets to enable better interpretation of the results and to allow for a meaningful statistical analysis to be performed.

As mentioned in the introduction, the current trend by industry is to save costs by doing only what is required to comply with the relevant environmental standards. This study has shown this behavior to be short sighted and it may result in much larger costs in the long run and non-compliant permit conditions prevailing as a result of poor data quality.

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