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METHODOLOGY FOR UNCERTAINTY REPORTING IN AIR QUALITY STUDIES

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ABSTRACT

This report describes a metrological methodology that can be used to capture and report the traceability and uncertainty of results from Air Quality (AQ) studies together with a detailed exemplar Case Study on diffusive measurements of NO_2.

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CONTENTS

1 INTRODUCTION

This report has been prepared as part of the National Physical Laboratory (NPL) contribution to the Clean Air SPF Programme. It describes a metrological methodology that can be used to capture and report the traceability and uncertainty of results from Air Quality (AQ) studies. It is based on similar schemes developed for atmospheric reference measurements and Earth Observation (EO) systems.

The next section of the report provides some basic metrological references and definitions. Section 3 outlines a framework for producing traceability chains, a version of which can be applied in AQ applications (Section 4). The output of such an assessment is a Product Traceability and Uncertainty document, as described in Section 5. Section 6 summarises the work on exemplar Case Study and the report finishes with a short conclusions section (Section 7) together with references. Annex A provides a detailed Case Study for diffusive NO_2 measurements and Annex B is a metrological glossary.

2 METROLOGICAL REFERENCES AND DEFINITIONS

The Guide to the Expression of Uncertainty in Measurement, known as 'the GUM', provides guidance on how to determine, combine and express uncertainty [1]. It was developed by the JCGM (Joint Committee for Guides in Metrology), a joint committee of all the relevant standards organisations (e.g. ISO) and the BIPM (Bureau International des Poids et Mesures). This heritage gives the GUM authority and recognition. The JCGM continues to develop the GUM and has recently produced a number of supplements. All of these, as well as the 'VIM' (International Vocabulary of Metrology, [2]) are freely downloadable from the BIPM website.

2.1 MEASUREMENT TRACEABILITY AND THE SI

Measurement traceability is defined in the VIM as the:

> *Property of a measurement result relating the result to a stated metrological reference (free definition and not necessarily SI) through an unbroken chain of calibrations of a measuring system or comparisons, each contributing to the stated measurement uncertainty.*

Measurement traceability is an unbroken chain (i.e. it is calibrated against X, which was calibrated against Y, which was calibrated against Z, all the way back to SI, or, perhaps, a recognised authoritative reference). Additionally, effective quality assurance requires the documentary evidence that each step is done in a reliable way (ideally audited, at least thoroughly peer-reviewed). Validation of datasets requires the combination of measurement traceability, quality assurance & process traceability of the measurement systems; providing an unbroken chain between the measurement systems through a common measurand, be that the target geophysical parameter or a closely related quantity.

Measurement traceability should, ideally, be to the International System of Units, known as the SI from its French name, le Système international d'unités. The SI units provide a coherent system of units of measurement built around seven base units and coherent derived units. A coherent system of units means that a quantity's value does not depend on how it was measured. The SI is an evolving system, with the responsibility for ensuring long term consistency with the General Conference on Weights and Measures (CGPM), run through the International Bureau of Weights and Measures, the BIPM, and maintained nationally through the National Metrology Institutes (NMIs). The CIPM Mutual Recognition

Arrangement (CIPM MRA) signed in 1999 between the NMIs ensures that measurements made traceably to any NMI within the CIPM MRA are recognised by other NMIs. This is enforced by both formal international comparisons and a process of auditing and peer-reviewing statements of calibration capability. For the user, this means that traceability to the SI can be achieved through any NMI within the CIPM MRA.

2.2 THE MEASUREMENT FUNCTION/EQUATION

One approach to uncertainty analysis and metrological traceability is to start with the measurement function. The VIM 2008 formally defines a measurement function as:

> *a function of quantities, the value of which, when calculated using known quantity values for the input quantities in a measurement model, is a measured quantity value of the output quantity in the measurement model.*

where,

> *the measurement model is the mathematical relation among all quantities known to be involved in a measurement.*

Here the word “measurement” must be considered in its broadest sense and includes the concept of an indirect measurement, where an indicated quantity (e.g. a signal count) is transformed to the measurand (e.g. gas concentration), which is the quantity intended to be measured.

The measurement function is defined from the measurement model which establishes the mathematical relations between the input quantities. Input quantities are, for example, the counts and the calibration coefficients. Note that this concept is also often known as the “measurement equation”. Here we use the word “function” in the most general sense. For the sensors under consideration we can explicitly write the measurement function in terms of an analytic expression. In other cases, the measurement function is defined by e.g. the iterative solution of a measurement model through code.

We perform our uncertainty analysis by considering the different input quantities to the measurement function. Each input quantity may be influenced by one or more error effects, each of which has an associated probability distribution and our aim is to establish the probability distribution of the output quantity. In a processing (or metrological traceability) chain there will be a series of such combinations, where the output quantity of one stage becomes an input quantity of the next stage.

Note that we should also consider the extent to which the measurement function describes the true physical state of the instrument. We usually account for this by including a term zero. This explicitly represents effects expected to have zero mean that are not captured by the measurement function (i.e. there is an uncertainty associated with this quantity being zero). Therefore we write the measurement function as:

$$Y = f(X_1, X_2, \ldots, X_N) + 0. \qquad (1)$$

Uncertainty analysis is based on the relationship between the measurand (measured value) and various input quantities embodied in a measurement function. Each input quantity may be influenced by one or more error effects, each of which has an associated probability distribution.

The Guide to the Expression of Uncertainty in Measurement[1], provides guidance on how to determine, combine and express uncertainty. The GUM and its supplements describe both the Law of Propagation of Uncertainty and Monte Carlo methods as methods to propagate uncertainties from the input distributions to the measurand error distribution.

Monte Carlo methods approximate the input probability distributions by finite sets of random draws from those distributions and propagate the sets of input values through the measurement function to obtain a set of random draws from the output probability distribution. The output values are then analysed statistically, for example to obtain expectation values, standard uncertainties and error covariances. The measurement function in this case need not be linear nor written algebraically. Steps such as inverse retrievals and iterative processes can be addressed. The input probability distributions can be as complex as desired, and can include digitised distributions, where signals are digitised for on-board recording and transmission.

2.3 HIERARCHICAL UNCERTAINTY ANALYSIS AND EFFECTS

An uncertainty analysis centred on the measurement function is used to calculate a measurand from input quantities. Some of these input quantities will be directly measured, others may be determined through their own measurement function, with input quantities that are directly measured or determined through another measurement function.

At the end of each ‘branch’ of this hierarchical structure is a quantity that is directly estimated: through measurement, through modelling or through data analysis. And each such quantity will be sensitive to a number of effects, each of which has an associated uncertainty that can itself be estimated through measurement, through modelling or through data analysis. In our measurement functions we always include a term “+ 0” which represents effects relating to the assumptions underlying the form of the measurement function (e.g. that it is quadratic). Uncertainty analysis starts at the effects and propagates these through each measurement equation (perhaps several through the hierarchy). Almost all quantities in the measurement equation will have one or more associated effects, with the exception of mathematical and physical constants and a small number of other terms used either as indicators or as agreed references.

Uncertainty analysis assumes that the result of a measurement has been corrected for all recognized significant systematic effects and that every effort has been made to identify such effects. This effectively means that the measurand will be as accurate as possible given the current state of knowledge. When we perform analyses at the effects level we need to decide whether the effect could be fully, or partially corrected for, and if so we should apply the correction. The residual effect uncertainty is the uncertainty associated with the correction. The metrological thinking involved in performing uncertainty analysis therefore often has the unexpected side effect of improving the ECV product as effects are corrected for.

2.4 ERRORS, UNCERTAINTIES AND CORRECTIONS

The terms ‘**error**’ and ‘**uncertainty**’ are not synonyms, although they are often confused in scientific applications. To understand the distinction, consider the result of a measurement – the **measured value**. The value will differ from the true value for several reasons, some of which we may know about. In these cases, we may be able to identify and apply a correction. A **correction** is applied to a measured value to account for known differences, for example the measured value may be multiplied by a gain determined during the instrument’s calibration. This correction will never be perfectly known and there will also be other effects that cannot be corrected, so after correction there will always be a residual, unknown error – an unknown difference between the measured value and the (unknown) true value.

The specific error in the result of a particular measurement cannot be known, but we describe it as a draw from a probability distribution function. The uncertainty associated with the measured value is a measure of that probability distribution function; in particular, the **standard uncertainty** is the standard deviation of the probability distribution, and the equivalent of this for other distributions.

There are generally several 'sources of uncertainty' that jointly contribute to the uncertainty associated with the measured value. These will include uncertainties associated with the way the measurement is set up, the values indicated by instruments, and residual uncertainties associated with corrections applied. The final (unknown) error on the measured value is drawn from the overall probability distribution described by the uncertainty associated with the measured value. This is built up from the probability distributions associated with all the different sources of uncertainty. The use of the words 'error' and 'uncertainty' described here is consistent with paragraph 2.2.4 of the GUM, and described graphically in Figure 1.

Conversely it is worth considering what is not a measurement uncertainty:

- Mistakes made by operators are not measurement uncertainties. They should generally be avoided, and identified through quality checks on the results obtained.
- Tolerances are not uncertainties. They are acceptance limits which are chosen for a process or a product.
- Specifications are not uncertainties. A specification tells you what you can expect from a product or what a user requires from a product. It may be very wide-ranging, including 'non-technical' qualities of the item, such as its appearance. Specifications may or may not be attainable.

2.5 THE LAW OF PROPAGATION OF UNCERTAINTIES

The aim of any uncertainty analysis is to estimate the uncertainty associated with the measured value, which may be the result of a process involving several different parameters being controlled and set or measured, and a calculation. To obtain the final uncertainty, uncertainties due to each and every element in the process that affect the final result must be combined – i.e. they must be propagated through this process.

The GUM[1] gives the Law of Propagation of Uncertainty as,

$$u_c^2(y) = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} u(x_i, x_j), \tag{2}$$

which applies for a measurement model of the form

$$Y = f(X_1, X_2, X_3, \ldots, X_i, \ldots) \tag{3}$$

where an estimate x_i of quantity X_i has an associated uncertainty $u(x_i)$. The quantity $u_c^2(y)$ is the squared standard uncertainty (standard deviation of the probability distribution) associated with the measured value y which comes from a combination of the uncertainties associated with all the different effects, x_i . The square of the standard uncertainty is also known as the **variance**. The second term on the right hand side of eqn. 2 sums the

covariance terms. The covariance is a measure of the uncertainty common to the two quantities in the measurement model.

It can help to write the Law of Propagation of uncertainties in terms of **sensitivity coefficients** as

$$u_c^2(y) = \sum_{i=1}^{n} c_i^2 u^2(x_i) + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} c_i c_j u(x_i, x_j), \quad (4)$$

where the sensitivity coefficient $c_i = \delta f/\delta x_i$. The sensitivity coefficient is a 'translation' from one variable to another. It answers the question: "how sensitive is y to an uncertainty associated with x_i ?"

The law of propagation of uncertainties is written in this slightly complex notation of two parts to separate two terms:

- The first term is the sum of the squares of the standard uncertainties $u(x_i)$ (the sum of the variances) associated with each individual effect multiplied by the relevant sensitivity coefficient (the partial derivative). This first term is what is meant by the description 'combining in quadrature'.
- The second term deals with the covariance of correlated quantities. The covariance is a measure of how much the two quantities vary together. If the covariance term is zero, this term becomes zero by definition.

Note that the covariance term covers all pairs of different quantities, i.e. $(x_1,x_2),(x_1,x_3),(x_2,x_3),\ldots$ Since the covariance $u(x_1,x_2) = u(x_2,x_1)$, the summation is only over the combinations where $i < j$ (i.e. only half the cases). The 2 in front of this term in equation 4 accounts for the opposite cases.

2.6 COVERAGE FACTOR K

Having scaled the components of uncertainty consistently, to find the combined standard uncertainty, we may then want to re-scale the result. The combined standard uncertainty may be thought of as equivalent to 'one standard deviation', but we may wish to have an overall uncertainty stated at another level of confidence, e.g. 95 percent. This re-scaling can be done using a coverage factor, k. Multiplying the combined standard uncertainty, u_c , by a coverage factor gives a result which is called the expanded uncertainty, usually shown by the symbol U,

$$U = k.\, u_C \quad (5)$$

A particular value of coverage factor gives a particular confidence level for the expanded uncertainty. Most commonly, we scale the overall uncertainty by using the coverage factor k = 2, to give a level of confidence of approximately 95%. This is often reported as the **expanded uncertainty**. Note that k = 2 is correct if the combined standard uncertainty is normally distributed. This is usually a fair assumption, but the reasoning behind this is explained elsewhere, in [3]. Some other coverage factors (for a normal distribution) are:

- k = 1 for a confidence level of approximately 68 percent
- k = 2.58 for a confidence level of 99 percent
- k = 3 for a confidence level of 99.7 percent

Other, less common, shapes of distribution have different coverage factors. Conversely, wherever an expanded uncertainty is quoted with a given coverage factor, you can find the standard uncertainty by the reverse process, i.e. by dividing by the appropriate coverage factor.

2.7 CLASSIFICATIONS

2.7.1 Random and Systematic Effects

Correlation will be introduced whenever there is something in common between two measured values that will be combined (i.e. two values that will be averaged, or two quantities used in a measurement equation, or values at different wavelengths that will be combined through interpolation or integration). The simplest way to describe this is in terms of random and systematic effects.

Random effects are those that are not common to the multiple measurements being combined. A typical example is noise: two measured values may both suffer from noise, but the effect of noise will be different for each of the two measured values (for example, if noise has increased one measured value, this provides no information about whether any other measured value is increased or decreased by that noise, nor by what extent).

Systematic effects are those that are common to all measured values. If one measured value has been increased as a result of a systematic effect, then we can make a reliable prediction regarding whether any other measured value will be increased, and by how much. For example if all the instruments used to measure a particular air quality gas concentration within a study are calibrated against the same reference standard then the uncertainty on the concentration of that standard will be common to all the measurements resulting in a systematic effect across all the data. As another example, if all the data are processed using a common model then uncertainties in any assumptions within the model processing steps could result in systematic effects in the model outputs.

Some effects, such as noise, are always random; other effects can be either random or systematic depending on the measurement process. There may be additional uncertainty types, such as quasi-systematic, which will be systematic over one timescale, but effectively random over longer timescales. Taking the first example above, if the calibration gas used as the reference standard is changed every month then the calibration uncertainty will be effectively randomised over long (e.g. annual) measurement periods.

The error in the measured value due to a random effect will change from one measured value to another. In this case the uncertainty associated with the effect may be the same for each measured value (the probability distribution for the effect is the same for each measured value), but each measured value is independent of each other measured value, as influenced by this effect. The unknown random error at each measured value is an independent draw from the probability distribution, meaning that the error due to the random effect is not only different from, but also independent of, the error on any other measurement. The standard uncertainty associated with random effects is usually (but not always) determined by calculating the standard deviation of repeated measured values.

Such repeat measurement is difficult, if not impossible, in the atmospheric domain as the measured quantity is almost invariably non-static. In a few cases pseudo repeat measurements are possible, that is, if measurements can be taken sufficiently close in time and space and also close in sensitivity, so that the contribution of natural variability to the obtained standard deviation becomes negligible. But those cases are not the rule and in general any estimate of the standard deviation will include contributions from spatial, temporal and sensitivity mismatch.

Another important consideration in the atmospheric domain are influence quantities. Influence quantities do not affect the instrument measurand directly, but affects the derived geophysical measurand through departure from the assumptions of the processing model; e.g., changing temperatures may affect the gain of a sensors' response.

The error in the measured value due to a systematic effect will be the same from one measured value to another. The uncertainty associated with the effect is the same for each measured value and the error is the same draw from the probability distribution for all measured values. The standard uncertainty associated with systematic effects cannot be determined by repeat measurements, unless the effect is intentionally altered between repeats (e.g. by assessing a sensor response over a range of temperatures a series of different 'extreme but acceptable' temperatures can be defined to characterise the impact of external temperature within an established uncertainty.

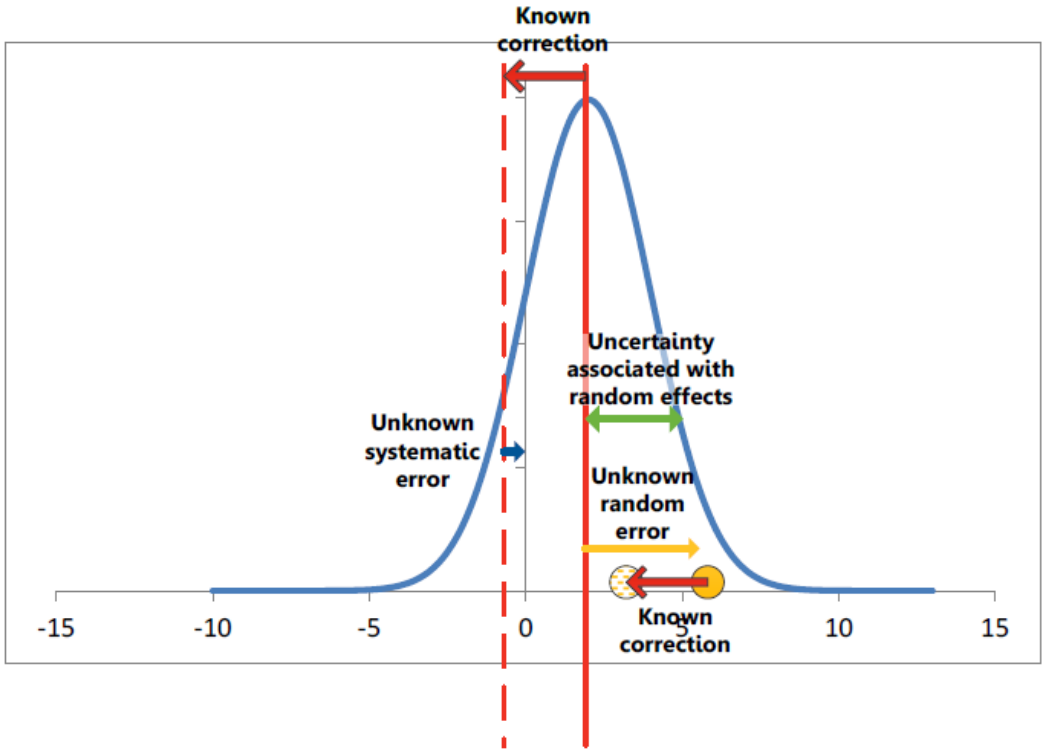


Figure 1: Representation of a measurement where there is a known correction, an unknown systematic effect and random effects

Figure 1 represents a measurement process where there is a known correction, an unknown systematic effect and random effects.

- A measurement is made (obtaining the value represented by the golden circle).
- We know of a correction – a systematic bias – and apply this correction, obtaining the value of the flecked circle.
- There is still an unknown error from the true value of zero. If we make many measurements we obtain the probability distribution function shown in blue. The spread of this, the standard deviation of the normal distribution, is the standard uncertainty associated with random effects – those effects that change from measurement to measurement. Our measured value is a draw from this probability distribution function. If we take multiple measurements we obtain different draws. The average will tend towards the value at the peak of this distribution.

When the known correction is applied, the result will be close to the true value, but differ from it by an unknown systematic error common to all the measured values. This comes from its own probability distribution function and all measured values have the same draw from that distribution (not shown in the figure, but this will take the form of a probability distribution centred at the true value with a standard deviation equal to the uncertainty associated with systematic effects).

2.7.2 Type A and Type B

The terms '**Type A**' and '**Type B**' are used with uncertainty analysis. This use comes from the GUM, which defines:

- Type A evaluation (of uncertainty) method of evaluation of uncertainty by the statistical analysis of series of observations
- Type B evaluation (of uncertainty) method of evaluation of uncertainty by means other than the statistical analysis of series of observations

Type A evaluation uses statistical methods to determine uncertainties. Commonly this means taking repeat measurements and determining the standard deviation of those measurements. This method can only treat uncertainties associated with random effects, for example the uncertainty associated with measurement noise.

Type B evaluation uses 'any other method' to determine the uncertainties. This can include estimates of systematic effects from previous experiments or the scientist's prior knowledge. It can also include random effects determined 'by any other method'. Similarly, we may say that a voltmeter with 2 digits after the decimal place has an uncertainty associated with resolution of 0.005 V because we know the rounding range.

Is it worth noting that field measurements of atmospheric properties relating to air quality will typically have a lot of Type B uncertainties and that a comprehensive uncertainty analysis would involve several quantities not quantifiable in a typical laboratory setting.

2.7.3 Absolute and relative uncertainties

The uncertainties given in the law of propagation of uncertainties by the symbol $u(x_i)$ are always standard absolute uncertainties. The term standard uncertainty means that it is a single standard deviation of the probability distribution function associated with that quantity. The term **absolute uncertainty** means that it has the same unit as the measurand. In other words, if the signal is in volts, the absolute uncertainty will also be in volts. If the distance is in metres, the absolute uncertainty will also be in metres.

It is common in many applications to describe **relative uncertainties**, with units of percent. The relative uncertainty is the absolute uncertainty divided by the quantity, i.e. $u(x_i)/x_i$.

2.8 WRITING ABOUT UNCERTAINTIES

In casual language we talk about 'averaging a set of measurements' or 'the uncertainty in the measurement is 0.5 %'. In metrology these words are defined carefully to reduce misunderstanding. We cannot 'average a set of measurements' but we can 'average the measured values' obtained from those measurements. The measurement has no uncertainty, there is an uncertainty associated with the measured value. For a non-specialist, such definitions can seem pedantic, as with jargon in all fields; but for a specialist, such careful use of words is a source of clarity. The words are defined through the VIM [2].

A **measurement** is made (instruments set up and value recorded) of a measurand (a quantity, such as concentration) to obtain a **measured value** (e.g. µg/m^3) with an associated relative standard uncertainty (e.g. 0.5 %). The VIM defines measurement as the

> *process of experimentally obtaining one or more quantity values that can reasonably be attributed to a quantity.*

The most important word here is process: it defines measurement as the act of measuring. A measurement is not a quantity nor a result. The VIM defines **measurand** as

> *the quantity intended to be measured*.

In turn, **quantity** is the

> *property of a phenomenon, body or substance, where the property has a magnitude that can be expressed by a number and a reference.*

Thus quantities are things like length, mass, instrument gain, etc. When you measure a quantity, that quantity is the measurand of the measurement. The measurement result is defined by the VIM as the set of quantity values being attributed to a measurand together with any other available relevant information. The "other available relevant information" refers to the associated uncertainty, perhaps expressed directly, perhaps as a probability density function, or perhaps implied by the number of digits provided with the result (the latter providing less reliable information). The quantity value is a

> *number and reference together expressing magnitude of a quantity.*

The reference usually means the unit. The measured quantity value (often shortened to measured value) is the quantity value that is the particular measurement result.

A fuller glossary of term is given in Annex B, see the VIM [2] for the full list of terminology.

3 FRAMEWORK FOR THE PRODUCTION OF METROLOGICAL ROBUST TRACEABILITY AND PROCESS CHAINS

Key to understanding and expressing the robust uncertainty analysis of any atmospheric data product is the ability to clearly display the processing steps taken to produce the dataset. As discussed earlier, to obtain the final uncertainty, uncertainties due to each and every element in the process that affect the final result must be combined – i.e. they must be propagated through this process. One method for achieving such a detailed understanding is developing a traceability chain. In metrology, the aim of developing a traceability chain is to demonstrate the series of calibrations which link a measurement to a reference standard. For atmospheric applications, this needs to be developed much further to allow processes to be captured in detail.

3.1 TYPES OF TRACEABILITY CHAINS

Regardless of the process being considered (instrumental or data processing), a framework of traceability models has been developed through a series of projects regarding reference atmospheric measurements and earth observation (e.g. GAIA CLIM, C3S, QA4ECV and FIDUCEO [4-7]). These are not hard and fast rules that should be blindly followed, but a method conceived to help the user think about all the contributions to the uncertainty budget. As the framework continues to be developed, it is hoped that its evolution will be guided via feedback from different user communities, including air quality. This framework involves considering the traceability in terms of three models.

1. **Physical Model** – This model considers the real-world situation, i.e. what is actually occurring in the real world and the physics driving this.
2. **Processing Model** – This model considers how the raw data collected is processed to provide the end product, through calibration to the final geophysical parameter.
3. **Metrological Model** – This model considers the calibration, or linkage, of a measurement or processed data to a reference.

Separating the types of traceability chain into these three models provides several advantages: the separation essentially provides three angles from which the problem can be approached, it allows for the persons producing the chains to have a clear set of boundaries in which to operate when considering the production of the chains as well as being able to choose the type of model with which they are the most familiar as a starting point. It is noted that there may be significant overlap between the models.

3.1.1 Physical Model

The physical model chains describe the real-world by considering the physics behind each stage of the process which contributes to the measurements taken. This includes all of the physical processes associated with the measurand detection; for example, this covers the physics of how the sampled gas enters the instrument, how the sensing element responses to the gas and how it is converted to an electrical signal which makes up the output raw signal.

The aim of the physical model is to be able to describe, reliably, the physical processes which contribute to the generation of the raw data. Therefore, obtaining a suitable physical model requires an understanding of the detector response including sources of uncertainty such as noise, the non-linearity of a detector, possible external effects and cross-interferences etc. The model would also include any processing of the signal undertaken by the instrument itself.

It is unlikely that the physical model chain would incorporate all of the possible physical processes occurring in the real-world situation due to the complexity of the real-world. The physical model would essentially represent a simplified “best guess” of the real-world. However, in producing the physical model, all contributions should be considered and those processes not included in the model, potentially as they are deemed to have a negligible effect on the data product should at least be documented.

3.1.2 Processing Model

The processing model chains are intended to describe the input data, processes and output data that contribute to the final target parameter generation from both raw data and ancillary data. This model will include all the processes and assumptions built into the calibration algorithm, as well as any external models or ancillary data used. The processing model will describe a series of calculation steps that the data undergoes to obtain the measurand of interest (i.e. equations and computational models), with inputs derived from the previous step or from pre-set parameters and coefficients, and an output that leads to the next step in the processing chain.

This chain type is conceptually the easiest to understand where a data producer would intuitively think of a traceability chain as the steps required to produce their product or undertake their process.

One of the key advantages of producing both physical and processing models is the ability to compare these models, and in so doing identify differences between the two. This would effectively give the data / product producers details of how their modelled world (represented by the processing chain) differs from the real-world (represented by the physical chain).

At a basic level the diagram would contain central boxes representing the processing steps. In addition more detailed information about that step in terms of basic documentation, provenance, assumptions employed and uncertainty analysis should also be provided.

3.1.3 Metrological Model

The metrological model chains are intended to describe the traceability of the result through a set of calibrations, or linkages, of a measurement (or of processed data) to a reference standard. The metrological model describes the origins of the input parameters for the processing model such as the origin of the calibration and characterisation coefficients; be those solely laboratory-based, or occasionally / regularly updated in the field. The aim here is to determine what the fundamental reference for the final result is. In some cases it will be possible to obtain full metrological traceability - that is, an unbroken chain of calibrations back to the International System of Units (SI). In many cases, however, such a complete chain may not be possible. It is important, however, to show what references do exist. The metrological traceability chain could also be documented as a flow diagram with additional information, containing, for example, references to calibration and characterisation results. Dotted arrows can be used where the link is not strong.

The metrological traceability chain is used to estimate the set of uncertainties (both from random and systematic effects) on the outputs. Note that to be a metrological traceability chain, there is a presumption that all processes have been included and have an estimate of an uncertainty. As part of setting up a metrological model, a review of both the physical and processing model must be made to ensure that all processes are included. As to the uncertainties, where possible, evidence for the magnitude and / or probability distribution of the uncertainties must be provided and documented either through measurements or from Monte-Carlo Analysis (MCA). If no measured uncertainty is available for a process then at least an upper limit to its magnitude should be provided with a rationale for its size.

The chain is not used to improve understanding of the processes, nor identify sources of uncertainty; these are both covered by the processing and physical model chains. Therefore, the aim of the chain is to purely demonstrate that linkage to a reference standard is achieved.

3.1.4 Approach to Producing Traceability Chains

In many cases, the processing model chain is the first type of chain that is produced when describing the traceability of an atmospheric product, as it is the most intuitive type for most users. For a number of applications, the processing model may be the only chain which can realistically be produced in a significant level of detail.

The physical model involves a more in-depth consideration of the physical processes contributing to the measurement and may be less intuitive for most users.

Ideally, the processing and physical model chains are then considered iteratively to allow any potential improvements to be made to the processing traceability chain and to ensure that the physical model traceability chain encompasses all relevant elements.

The metrological model chain should be developed from a combination of the processing and physical models. This chain may have some feedback into the processing and physical model chains; however, this is likely to be limited.

Both the processing and physical model traceability chains will be used for both describing the overall processes associated with an application, as well as being used to describe specific stages. The metrological chain, however, sits alongside the physical and processing chains, and is likely to be used when describing an overall process, rather than the details of individual stages.

The processing, physical and metrological models are then combined to provide an overall model. Alternatively, the overall model can be produced first and split to provide the other models. In either case, it is recognised that producing both the overall model and the set of three other models is not necessary; the production of one or the other is sufficient. The key aim is ensuring that all relevant data is captured in a systematic manner, whether this be as an overall model, or as three sub-models. For the technical document deliverable, a single combined chain is required. Figure 2 shows a graphical representation of the sub-model combination. It is noted that the order in which the chains are developed, and the specifics on which each focusses, may vary depending on the application being considered.

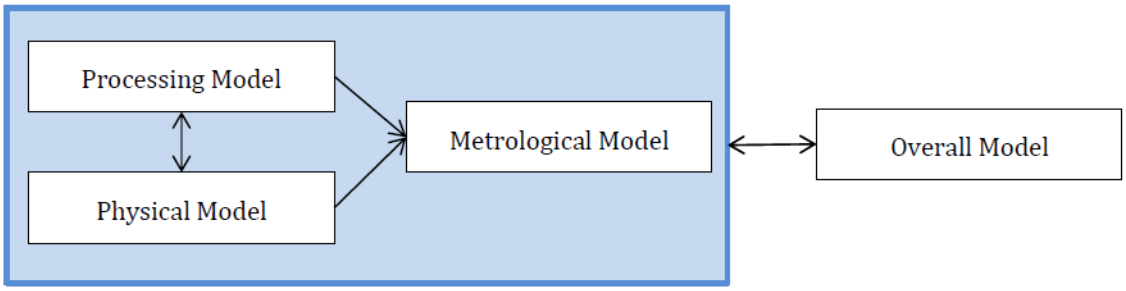


Figure 2: Traceability Chain Production Process Representation of the traceability chain

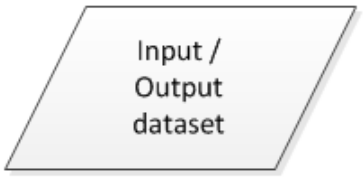
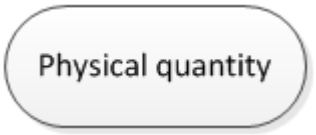
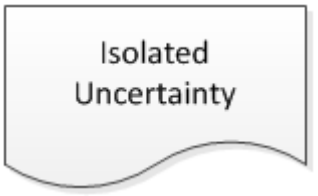
Guidance on the types of boxes to be used for each type of chain element is provided in Table 1. However, it is noted that the underlying information is the important content, so excessive effort should not be spent in formatting the diagrams. The box type convention follows that used in other application areas, but inevitably there will be some variation due to producer choice and the limitations of the software used to create the chain. To date, different producers have used MS power point, MS Visio and web-based tools, but the clear display of the information and processes should be paramount, and not limited by formatting concerns.

A set colour scheme for the chain is not defined, but should be chosen by the producer to best illustrate the commonality in the specific traceability chains. For example, to indicate the raw data sources, the source of traceability, ancillary products, to group a set of boxes which contribute to a single process or, for interactive chains, that further information associated with the box is available. However, any colour coding convention that is used should be clearly described.

An example of the potential structure for a traceability chain is shown in Figure 3 which includes a convention for the traceability identifier numbering. The ‘main chain’ from raw measurand to final product forms the primary vertical axis of the diagram, with top level identifiers (i.e. 1, 2, 3 etc.). Side branch processes add sub-levels components to the top level identifier, (for example, by adding alternate letters & numbers, or 1.3.2 style nomenclature).

The key purpose of this sub-level system is that all the uncertainty from a sub-level are summed in the next level up. For instance, using Figure 3, contributors 2a1, 2a2 and 2a3 are all assessed as separate components to the overall traceability chain (have a contribution table). The contribution table for (and uncertainty associated with) 2a, should combine all the sub-level uncertainties (and any additional uncertainty intrinsic to step 2a). In turn, the contribution table for contributor 2, should include all uncertainties in its sub-levels.

Table 1. Traceability Chain Shapes and Definitions

	Parallelogram	A dataset visible to the user, be that initial input, final output product or any intermediate product that is available to the user.
	Rectangle	A process within the chain, used to describe a transformation in the dataset that may or may not have an associated uncertainty. The default box shape. The dataflow within the process is typically invisible to the user.
	Rectangle with side-bars	Essentially identical to the process rectangle. However, sometimes used to represent a sub-chain or major processing block where more granular information is available.
	Ellipse	Raw data from a measurement device central to the product value or its traceability. This can also include the data propagated from a previous Level.
	Rounded rectangle	An ancillary physical quantity dataset or product necessary in the processing chain or to give context to the product.
	Rectangle with wavy bottom	An uncertainty quantity not associated with (isolated from) an element in the traceability chain. Typically used to represent assumptions and known effects that are not directly corrected for (i.e. effects that become part of the +0 term).
	Rhombus	A decision step that may affect whether specific data appears in the output product. Such decisions may impact the probability distribution function of the uncertainty.

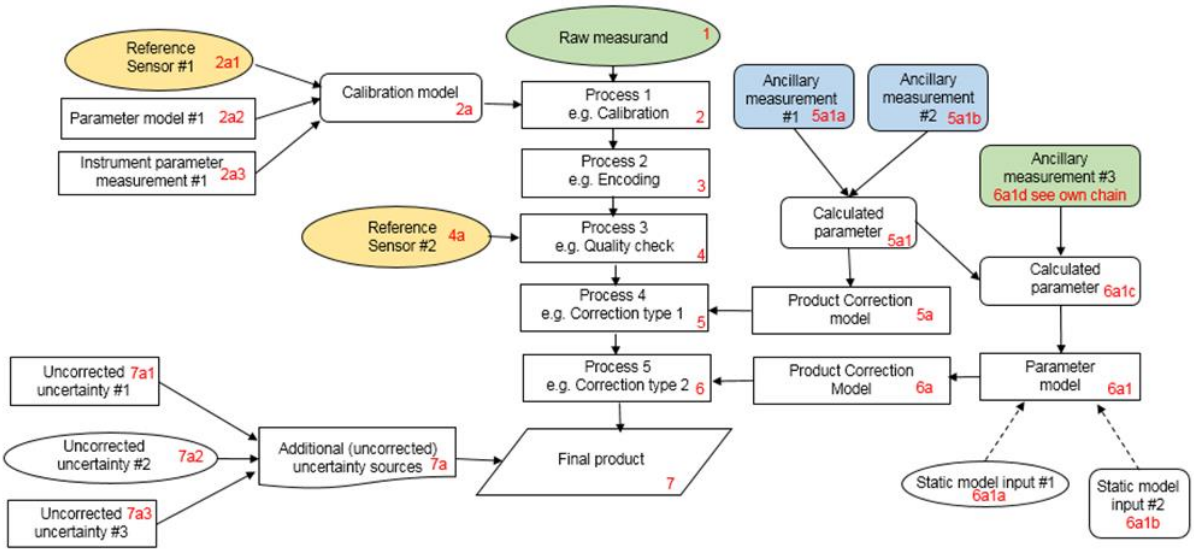


Figure 3. Example traceability chain. Green represents a key measurand or ancillary measurand recorded at the same time with the product raw measurand. Yellow represents a source of traceability. Blue represents a static ancillary measurement

Only the top level identifiers (1, 2, 3, etc.) in the summary table need be combined to produce the overall product uncertainty. The side branches can therefore be considered in isolation, for the more complex traceability chains, with the top level contribution table transferred to the main chain. For instance, see Figures 4 and 5 as an example of how the chain can be divided into a number of diagrams for clearer representation.

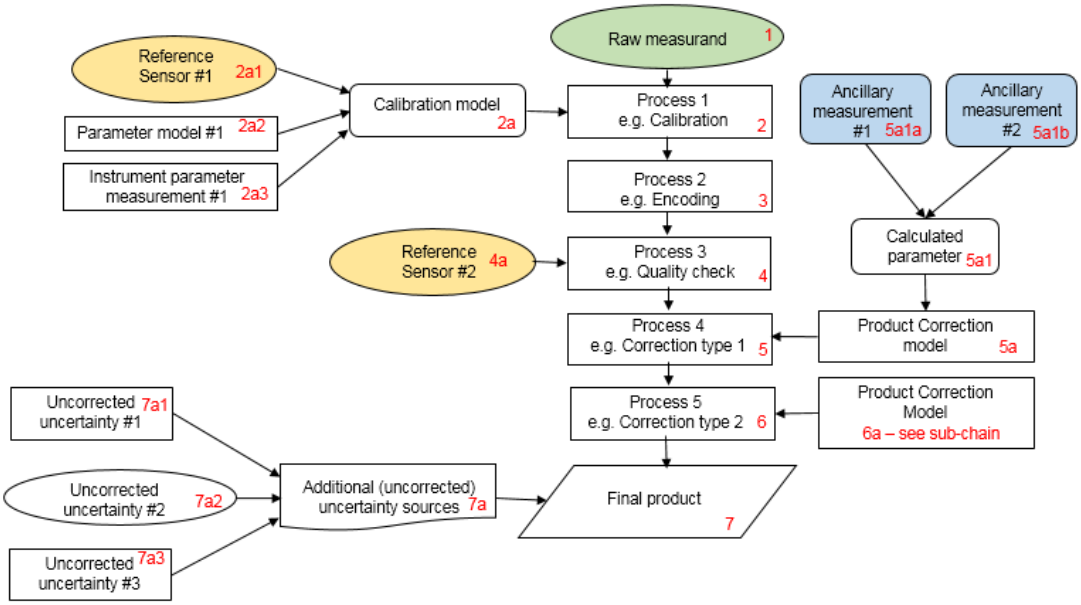


Figure 4. Example chain as sub-divided chain. Green represents a key measurand or ancillary measurand recorded at the same time with the product raw measurand. Yellow represents a source of traceability. Blue represents a static ancillary measurement.

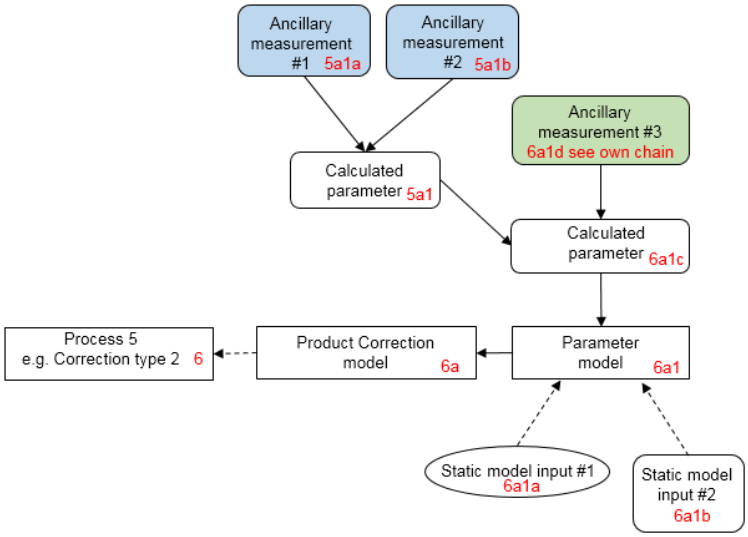


Figure 5. Example chain contribution for the 6a sub-chain

When deciding where to create an additional sub-level, the most appropriate points to combine the uncertainties of sub-contributions should be considered, with additional sub-levels used to illustrate their contributions are currently combined in the described process.

3.2 BEYOND TRACEABILITY CHAINS

The underlying vision is to move beyond simple traceability chains (which effectively capture the current understanding of the process) towards producing metrologically-rigorous traceable products and related uncertainties for the target applications and users. In this case the product is defined as the final numerical output of a study on the basis of which conclusions and/or decisions will be made. Production of such rigorous traceability assessments will not be possible for all the target air quality products, and will depend on the maturity of the particular product. However, this ultimate goal should be kept in mind. In any case, the traceability and uncertainty assessment undertaken during this process should result in a technical document describing the measurement procedure, the current understanding of the overall uncertainties and any existing gaps in the uncertainty assessment.

4 PRODUCING TRACEABILITY CHAINS FOR AIR QUALITY APPLICATIONS

The breadth of techniques, models and outputs within Air Quality research are extensive, so to try to undertake such detailed uncertainty assessments covering all possible permutations far extends the scope of the Clean Air activity in terms of available resources. However, the work being undertaken aims to describe the process as a demonstration of the value of such rigorous end-to-end treatment of product uncertainty and traceability.

4.1 PRACTICAL GUIDANCE FOR AIR QUALITY TRACEABILITY CHAINS

In characterising the uncertainty, reference to previous work/documentation should be made where relevant, but this should not detract from the independence of the product traceability document. This document needs to be stand alone, such that it can be understood if read in isolation from the referenced material.

The traceability chains produced should form the basis of this, and require limited additional effort to tailor to the specific case. One concern that should be addressed in the analysis is if data is taken from multiple sources then any differences in site-to-site or user-to-user procedure and observing practice should be considered.

The overall traceability chain should consider all contribution factors that feature in the full end-to-end process. This is likely to be sub-divided into branches representative of the major elements within the overall process. Every individual element within the chain should have a summary table of knowledge & traceability including an estimate of contribution magnitude. This assessment may be via a number of routes such as:

- a formal analytical treatment;
- a sensitivity study;
- an educated guess.

A template for capturing the relevant information on each element is provided in Table 2.

Table 2. Example of the summary table to be completed for each process contribution.

Information / data	Type / value / equation	Notes / description
Name of effect		
Contribution identifier		
Measurement equation parameter(s) subject to effect		
Contribution subject to effect (final product or sub-tree intermediate product)		
Classification		
Uncertainty PDF shape		
Single measurement Uncertainty & units (2σ)		
Sensitivity coefficient		
Correlation(s) between affected parameters		
Element/step common for all sites/users?		
Traceable to …		
Validation		

The following notes provide some explanation on the requirement for each of the entries:

- **Name of effect** – the name of the contribution, should be clear, unique and match the description in the traceability diagram.
- **Contribution identifier** - unique identifier to allow reference in the traceability chains.
- **Measurement equation parameter(s) subject to effect** – the part of the measurement function or equation influenced by this contribution. Ideally, the equation into which the element contributes.

- **Contribution subject to effect** – the top level measurement contribution affected by this contribution. This can be the main product (if on the main chain), or potentially the root of a side branch contribution. It will depend on how the chain has be sub-divided.
- **Classification** – the form and extent of any correlation this contribution has in time.
- **Uncertainty PDF shape** – the probability distribution shape of the contribution, gaussian/normal, rectangular, U-shaped, log-normal or other. If the form is not known, a written description is sufficient.
- **Single measurement Uncertainty & units** – the uncertainty value, including units and confidence interval. This can be a simple equation, but should contain typical values.
- **Sensitivity coefficient** – coefficient multiplied by the uncertainty when applied to the measurement equation.
- **Correlation(s) between affected parameters** – any correlation between the parameters affected by this specific contribution. If this element links to the main chain by multiple paths within the traceability chain, it should be described here. For instance, temperature may be used separately in a number of models and correction terms that are applied to the product at different points in the processing.
- **Element/step common for all sites/users** – is there any site-to-site/user-to-user variation in the application of this contribution?
- **Traceable to** – describe the source of the information provided in the table, ideally traceable back to a primary/community reference.
- **Validation** – describe any validation activities that have been performed for this element.

The table, explanatory notes and referenced material in the traceability chain should occupy <= 1 page for each element entry.

Once the summary tables have been completed for the full end-to-end process, the uncertainties can be combined, allowing assessment of the combined uncertainty, relative importance of the contributors and correlation scales. Depending on the level of sophistication, the key is to provide a reasonable estimate with the available information. Once the summary table has been completed for the full chain, it should become clear where further work should be focused to most effectively improve the overall level of knowledge of the process uncertainties.

4.2 PRODUCT TRACEABILITY UNCERTAINTY SUMMARY

A summary table should follow the individual element assessments, in the form given below. The product traceability uncertainty summary is a summary of the information provided above for this specific product. The purpose of this table is to summarise the assessment and demonstrate at a glance that the dominant contributions to the uncertainty chain have been robustly assessed with adequate traceability. Table 3 provides an example template for such a summary table.

Table 3. Template of product traceability uncertainty summary table

Element Identifier	Contribution name	Uncertainty contribution form	Typical value	Traceability level (L/M/H)	random, quasi-systematic or systematic?	Correlated to? (use element ID)
1						
2						
3						
…						

The table category descriptions are as follows:

Element identifier – The name and identifier should correspond to the relevant contributing lement in the product traceability uncertainty chain.
Contribution name – the name of the contribution, should be clear, unique and match the escription in the traceability diagram.
Uncertainty contribution form - the probability distribution shape of the contribution, gaussian/normal, rectangular, U-shaped, log-normal or other.
Typical value – a typical uncertainty value in the product units.
Traceability level - A description of the traceability associated with this element, following the example set out in Table 4.

Table 4. Description of different traceability levels

Traceability Level	Descriptor
High	SI traceable or globally recognised community standard
Medium	Developmental community standard or peer-reviewed uncertainty assessment
Low	Approximate estimation

Although a high level of traceability is desired, this will probably not be the case for all elements. Where that element only makes a small contribution to combined uncertainty, then a lower traceability level would be acceptable.
Random, quasi-systematic or systematic? - A descriptor of the form of the uncertainty.
Correlated to? (Use element identifier) – a descriptor as to whether the element is an independent variable, or has correlations to other elements within the product traceability uncertainty chain.

4.3 TEMPORAL SCALES IN UNCERTAINTY ASSESSMENT

A key challenge relates to the need to agree common method(s) to determine and report uncertainties with reference to their temporal correlation. This is particularly an issue for ambient air quality measurements where a method is required to determine measurement uncertainty correlation that is independent of atmospheric variability. Since it is not possible to use repeatability statistics from atmospheric measurements it is necessary to model the temporal behaviour of the system with individual uncertainty components. The first step is to

identify correlation behaviour of the individual components making up overall uncertainty and this is included in the uncertainty element tables. The individual elements then need to be combined and the temporal behaviour of overall uncertainty determined. This behaviour then needs to be reported in a way that is understandable and useable by the wide range of different user-groups.

There are a number of options for reporting the correlated combined uncertainties. For example, co-variance matrices can be used to represent uncertainties with random (diagonal) and correlated (off-diagonal) components. Such tools are already used for optimal estimation analysis in a number of applications. While there is extensive experience for 1-D variations, usually spatial, it is harder to implement for 2-D variation covering both spatial and temporal correlations. Another option is through uncertainty probability density functions (PDF's) and ensemble reporting. In this case, Monte Carlo sampling of individual uncertainty components can be used to generate ensemble of potential outcomes, and also giving the combined probability density function. Such methods are relatively easy to implement as long as the individual PDF's are known and can deal easily with non-normal uncertainty distributions. However, there are potential issues of data volume and, more importantly applicability and usability for end users.

Potentially the most readily usable option is to report total uncertainty for results over different timescales, aligned with different user applications, mirroring the random/systematic levels used to classify the uncertainty contribution form. For example, the uncertainty could be considered at the level of:

- Instantaneous measurement (smallest unit of reported data) – potentially dominated by random instrumental effects.
- At the calibration cycle/mid-scale temporal averaging scale (sub-annual) – where some quasi-systematic instrumental effects start to be treated as random variables.
- At the longer term (multi-annual) averaged scale for a single site/instrument typified by instrument systematic effects
- At the network level, incorporating multiple sites/instruments typified by individual site-specific data treated as random variables, but potentially linked to network-level processing.

At these different aggregation scales, different uncertainty contributors will dominate with effects on the magnitude of the overall uncertainty and its probability distribution function form. With the information available from the summary tables, this exercise should not be too onerous, and can potentially highlight considerations for user applications other than those originally planned for the product dataset.

5 PRODUCT TRACEABILITY UNCERTAINTY DOCUMENT

The output from the traceability and uncertainty assessment of a given product will be a technical document which should be stand-alone i.e. intelligible in isolation. Reference to external sources (preferably peer-reviewed) and documentation from previous studies is clearly expected and welcomed, but with sufficient explanatory content in the technical document not to necessitate the reading of all these reference documents to gain a clear understanding of the product and its associated uncertainties.

The conclusion to the document should address:

- Typical uncertainties, covering the main modes of operation.
- Typical uncertainties over a range of time periods/averaging intervals typical of the user community needs.

- Recommendations for improving the uncertainty analysis – e.g. a more detailed assessment of the larger contributors or a first assessment of terms assumed to have negligible contribution.

6 CASE STUDY

The case study presents the product traceability and uncertainty information for nitrogen dioxide (NO_2) measurements using diffusion tubes, and is provided in detail in Annex A. The numerous sources of traceability and relevant elements contributing to the uncertainty of measurement have been evaluated, mostly derived from globally recognised community standards and peer-reviewed publications. The results of the study estimated the product expanded uncertainty in good agreement with current air quality guidelines and state-of-the-art body of knowledge on the subject, considering such diffusive samplers are intended for indicative measurements. The study also addressed interpretations on the main uncertainty components, prediction of uncertainty behaviour over different timescales and recommendations for improvements.

7 CONCLUSIONS

This report sets out a methodology for establishing and reporting the traceability and uncertainty in the outputs from air quality studies. Following the definition of a number of key metrological concepts the report describes a framework for a traceability and uncertainty assessment. This framework is based around the bottom-up review of all of the elements that contributed to the evaluation of a data product and is based on concepts that have already been established in a range of applications relating to the determination of geo-physical parameters in the atmosphere and therefore of direct relevance to air quality.

A detailed exemplar Case Study has been completed for the measurement of NO_2 using diffusion tubes – one of the primary Air Quality tools used at local, regional and national scales. The results of the case study demonstrated the capability of the methodology to identify the main uncertainty components, predict uncertainty behaviour over different timescales and provide recommendations for future improvements.

8 REFERENCES

[1] JCGM, JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement, Report, 2008.
www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf

[2] JCGM, JCGM 200:2008 International vocabulary of metrology - basic and general concepts and associated terms, Report, 2008.
http://www.bipm.org/en/publications/guides/vim.html

[3] JCGM 101:2008 Evaluation of measurement data – Supplement 1 to the "Guide to the expression of uncertainty in measurement" – Propagation of distributions using a Monte Carlo method http://www.bipm.org/utils/common/documents/jcgm/JCGM_101_2008_E.pdf

[4] GAIA-CLIM project: http://www.gaia-clim.eu/

[5] Copernicus Climate Data Service: https://cds.climate.copernicus.eu/#!/home

[6] QA4ECV: Gap Analysis of QA4ECV ECV Products D2.2 http://www.qa4ecv.eu/

[7] FIDUCEO project http://www.fiduceo.eu/

9 ANNEX A - PRODUCT TRACEABILITY AND UNCERTAINTY FOR NITROGEN DIOXIDE (NO_2) MEASUREMENTS USING DIFFUSION TUBES

10 INTRODUCTION

This annex presents the product traceability and uncertainty information for ambient air nitrogen dioxide (NO_2) measurements for air quality purposes using Palmes-type diffusion tubes (PDTs), which are widely use in the UK for providing indicative measurements in the context of the Local Air Quality Management (LAQM) guidelines [1].

The principle of operation of Palmes-type diffusion tubes (PDTs) is based on the ambient NO_2 diffusion through a cylindrical tube, phenomenon that is mathematically modelled by Fick's first law. Subsequently, at the closed end of the tube, the NO_2 reaches stainless steel mesh grids coated with triethanolamine (TEA) to perform a stoichiometric chemical reaction and produce nitrite (NO_2^-) ion [2]. The mass of nitrite in each tube is quantified by either spectrophotometric or chromatographic chemical analysis and allows the calculation of the average NO_2 concentration, also considering the sampling time, sampling rate and appropriate correction factors for atmospheric temperature and pressure [3].

11 PRODUCT TRACEABILITY CHAIN

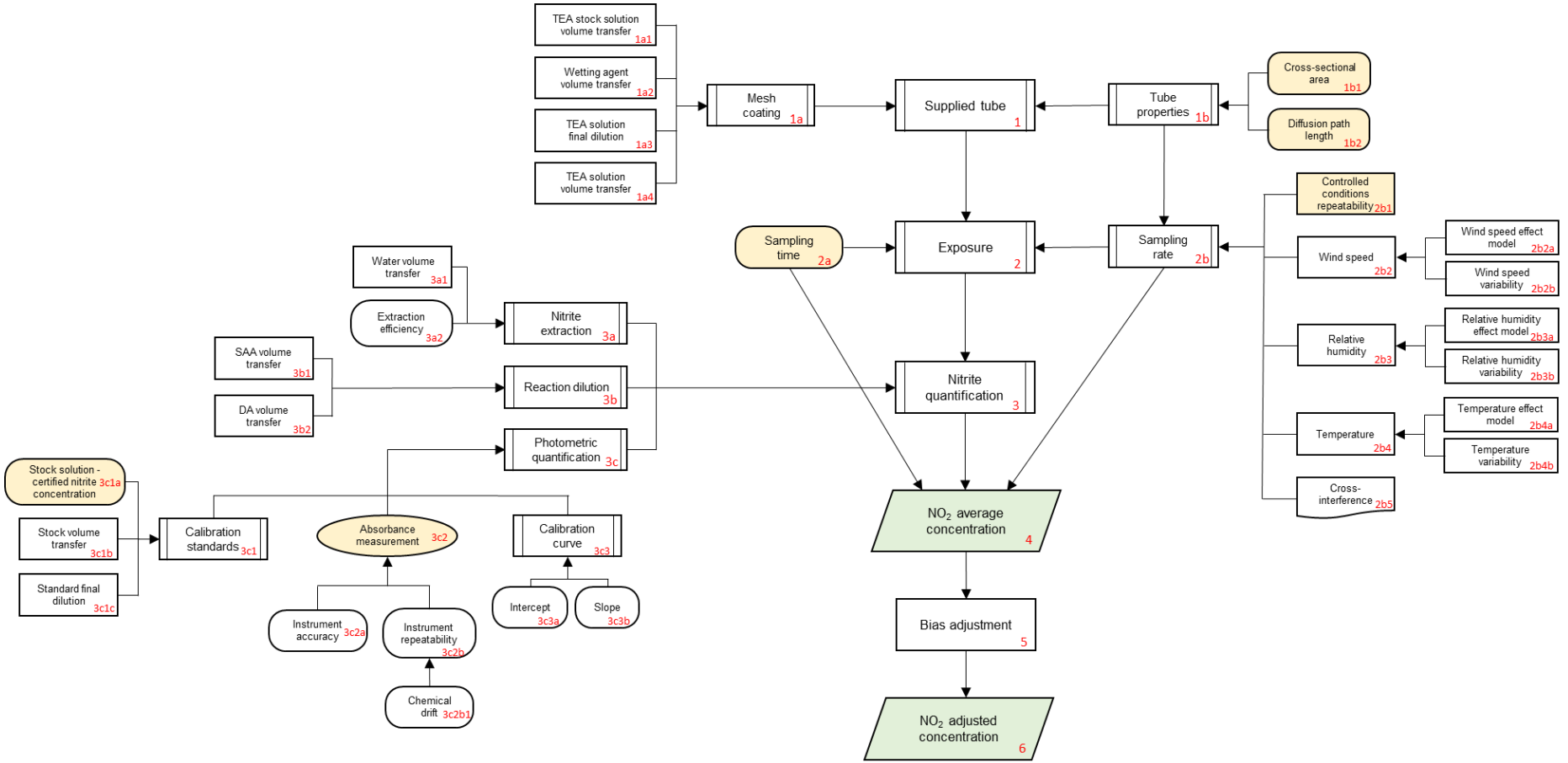


Figure A1: Product traceability chain for NO_2 measurements with diffusion tubes. Green represents a key measurand or ancillary measurand recorded at the same time with the product raw measurand. Yellow represents a source of traceability. Blue represents a static ancillary measurement

12 ELEMENT CONTRIBUTIONS

Elements are presented in order and grouped by supplied tube (1), exposure (2), nitrite quantification (3), NO_2 average concentration (4), Bias adjustment (5) and Adjusted NO_2 concentration (5).

12.1 SUPPLIED TUBE (1)

Element related to the supplied tube, which uncertainty budget is calculated by the sum in quadrature of the sub-elements Mesh coating (1a) and Tube properties (1b).

$$u_1^2 = u_{1a}^2 + u_{1b}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Supplied tube	
Contribution identifier	1	
Measurement equation parameter(s) subject to effect	$u_1^2 = u_{1a}^2 + u_{1b}^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	NO_2 average concentration	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.9% (1σ)	Combining sub-element components
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg and m	
Validation		

12.1.1 Mesh coating (1a)

Element related to the Mesh coating, which uncertainty budget is calculated by the sum in quadrature of the sub-elements TEA stock solution volume transfer (1a1), Wetting agent volume transfer (1a2), TEA solution final dilution (1a3) and TEA solution volume transfer (1a4).

$$u_{1a}^2 = u_{1a1}^2 + u_{1a2}^2 + u_{1a3}^2 + u_{1a4}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Mesh coating	
Contribution identifier	1a	
Measurement equation parameter(s) subject to effect	$u_{1a}^2 = u_{1a1}^2 + u_{1a2}^2 + u_{1a3}^2 + u_{1a4}^2$	Equation for diluting the stock solution
Contribution subject to effect (final product or sub-tree intermediate product)	Supplied tube	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.9% (1σ)	Combining sub-element components
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Considering instruments subjected to traceable calibration
Validation	Data sheet	Pipette specification provided by the manufacturer

12.1.2 TEA stock solution volume transfer (1a1)

Uncertainty budget of the volume transfer for coating the mesh with TEA solution, derived from the ±1% tolerance of an automatic pipette (100µl capacity), considering a normal distribution[4].

Information / data	Type / value / equation	Notes / description
Name of effect	TEA stock solution volume transfer	
Contribution identifier	1a1	
Measurement equation parameter(s) subject to effect	$C_{TEA} = C_{stock} . \frac{V_{transfer}}{V_{final}}$	Equation for diluting the stock solution

Contribution subject to effect (final product or sub-tree intermediate product)	Mesh coating	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.5% (1σ)	Assuming the typical tolerance limit for random error of automatic pipettes
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Considering an instrument subjected to traceable calibration
Validation	Data sheet	Pipette specification provided by the manufacturer

12.1.3 Wetting agent volume transfer (1a2)

Uncertainty budget of the wetting agent volume transfer, derived from the ±1% tolerance of an automatic pipette (100µl capacity), considering a normal distribution [4].

Information / data	Type / value / equation	Notes / description
Name of effect	Wetting agent volume transfer	
Contribution identifier	1a2	
Measurement equation parameter(s) subject to effect	$C_{TEA} = C_{stock} . \frac{V_{transfer}}{V_{final}}$	Equation for diluting the stock solution
Contribution subject to effect (final product or sub-tree intermediate product)	Mesh coating	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.5% (1σ)	Assuming the typical tolerance limit for random error of automatic pipettes

Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Considering an instrument subjected to traceable calibration
Validation	Data sheet	Pipette specification provided by the manufacturer

12.1.4 TEA solution final dilution (1a3)

Uncertainty budget of correctly filing a volumetric glass to the final volume mark, derived from the ±0.050 ml expanded uncertainty (k=2) of a 1.0 l volumetric flask [5].

Information / data	Type / value / equation	Notes / description
Name of effect	TEA solution final dilution	
Contribution identifier	1a3	
Measurement equation parameter(s) subject to effect	$C_{TEA} = C_{stock} . \frac{V_{transfer}}{V_{final}}$	
Contribution subject to effect (final product or sub-tree intermediate product)	Mesh coating	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.005%	Based on ±0.050 ml expanded uncertainty (k=2) for a 1000 ml volumetric flask
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3a, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Considering a glassware item subjected to traceable calibration

Validation	EURAMET publication	

12.1.5 TEA solution volume transfer (1a4)

Uncertainty budget of the TEA solution volume transfer to the tube's mesh, derived from the ±1% tolerance of an automatic pipette (100µl capacity), considering a normal distribution [4].

Information / data	Type / value / equation	Notes / description
Name of effect	TEA solution volume transfer	Coating volume
Contribution identifier	1a4	
Measurement equation parameter(s) subject to effect	NA	
Contribution subject to effect (final product or sub-tree intermediate product)	Mesh coating	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.5% (1σ)	Assuming the typical tolerance limit for random error of automatic pipettes
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Considering an instrument subjected to traceable calibration
Validation	Data sheet	Pipette specification provided by the manufacturer

12.1.6 Tube properties (1b)

Element related to the tube properties, which uncertainty budget is calculated by the sum in quadrature of the sub-elements Cross-sectional area (1b1) and Diffusion path length (1b2).

$$u_{1b}^2 = u_{1b1}^2 + u_{1b2}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Tube properties	

Contribution identifier	1b	
Measurement equation parameter(s) subject to effect	$u_{1b}^2 = u_{1b1}^2 + u_{1b2}^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	Supplied tube	
Classification	n/a	Combined element
Uncertainty PDF shape	n/a	Combined element
Single measurement Uncertainty & units (2σ)	±0.1% (1σ)	Combining sub-element components
Sensitivity coefficient	1	
Correlation(s) between affected parameters	2b	
Element/step common for all sites/users?	Yes	
Traceable to …	M	Considering instruments are subjected to traceable calibration
Validation	Data sheet	Specification information provided by calibration laboratory

12.1.7 Cross-sectional area (1b1)

Uncertainty budget of a dimensional measurement for defining the path cross-sectional, derived from the accuracy tolerance of a caliper and a 30 mm diameter measurement [6], considering a rectangular distribution.

Information / data	Type / value / equation	Notes / description
Name of effect	Cross-sectional area	
Contribution identifier	1b1	
Measurement equation parameter(s) subject to effect	$S = \left(\frac{d}{2}\right)^2 . \pi$	Cross-sectional area equation
Contribution subject to effect (final product or sub-tree intermediate product)	Tube properties	
Classification	Random	
Uncertainty PDF shape	Normal	

Single measurement Uncertainty & units (2σ)	±0.09% (1σ)	Accuracy tolerance of a caliper considering 30 mm diameter measurement
Sensitivity coefficient	1	
Correlation(s) between affected parameters	2b	
Element/step common for all sites/users?	Yes	
Traceable to …	m	Considering an instrument subjected to traceable calibration
Validation	Data sheet	Specification information provided by calibration laboratory

12.1.8 Diffusion path length (1b2)

Uncertainty budget of a dimensional measurement for defining the path length, derived from the accuracy tolerance of a caliper and a 70 mm diameter measurement [6], considering a rectangular distribution.

Information / data	Type / value / equation	Notes / description
Name of effect	Diffusion path length	
Contribution identifier	1b2	
Measurement equation parameter(s) subject to effect	$\nu = \frac{D \,.\, S}{L}$	Sampling rate equation
Contribution subject to effect (final product or sub-tree intermediate product)	Tube properties	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.08% (1σ)	Accuracy tolerance of a caliper considering 70 mm measurement
Sensitivity coefficient	1	
Correlation(s) between affected parameters	2b	
Element/step common for all sites/users?	Yes	

Traceable to …	m	Considering an instrument subjected to traceable calibration
Validation	Data sheet	Specification information provided by calibration laboratory

12.2 EXPOSURE (2)

Element related to the tube exposure, which uncertainty budget is calculated by the sum in quadrature of the sub-elements Sampling time (2a) and Sampling rate (2b).

$$u_2^2 = u_{2a}^2 + u_{2b}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Exposure	
Contribution identifier	2	
Measurement equation parameter(s) subject to effect	$u_2^2 = u_{2a}^2 + u_{2b}^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	NO_2 average concentration	
Classification		
Uncertainty PDF shape		
Single measurement Uncertainty & units (2σ)	±6-18% (1σ)	Combining sub-element components
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg and s	
Validation	NMI and Peer reviewed publications	

12.2.1 Sampling time (2a)

Uncertainty budget of the sampling time measurement, considering the NMI estimated standard uncertainty (1σ) of ±0.11s [7] and the sampling period of 28 days.

Information / data	Type / value / equation	Notes / description

Name of effect	Sampling time	
Contribution identifier	2a	
Measurement equation parameter(s) subject to effect	$C_{\text{STP}} = \frac{m_s - m_b}{v \cdot t} \cdot \frac{T}{293} \cdot \frac{101{,}3}{P}$	
Contribution subject to effect (final product or sub-tree intermediate product)	Exposure	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±5E-06% (1σ)	Standard uncertainty of ±0.11s considering a sampling period of 28 days
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4	
Element/step common for all sites/users?	Yes	
Traceable to …	s	Traceable to the second reference standard
Validation	NPL fact sheet	NMI publication

12.2.2 Sampling rate (2b)

Element related to the tube's sampling rate, which uncertainty budget results from combining the budgets of the sub-elements Controlled conditions repeatability (2b1), Wind speed (2b2), Relative humidity (2b3) and Temperature (2b4).

$$u_{2b}^2 = u_{2b1}^2 + u_{2b2}^2 + u_{2b3}^2 + u_{2b4}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Sampling rate	
Contribution identifier	2b	
Measurement equation parameter(s) subject to effect	$u_{2b}^2 = u_{2b1}^2 + u_{2b2}^2 + u_{2b3}^2 + u_{2b4}^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	Exposure	
Classification	Random	

Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±6-18% (1σ)	Combination of multiple elements, depending on tube design and wind speed
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	CRM for NO_2 gas mixtures
Validation	Peer reviewed publications	

12.2.3 Controlled conditions repeatability (2b1)

Uncertainty budget of the repeatability of the sampling rate, based on published laboratory study [8]. The budgets were derived from the coefficient of variation (COV) of unmodified and modified Palms tubes measurements of a traceable NO_2 concentration of 40.2 µg m^{-3} and constant wind speed of 0.5 m s^{-1} (considering a normal distribution).

Information / data	Type / value / equation	Notes / description
Name of effect	Repeatability	
Contribution identifier	2b1	
Measurement equation parameter(s) subject to effect	$v = \frac{D \,.\, S}{L}$	Sampling rate equation
Contribution subject to effect (final product or sub-tree intermediate product)	Sampling rate	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±4.8% (1σ) / ±1.7% (1σ)	Unmodified cylindrical Palmes tubes / Modified tubes with fine aperture covering meshes Demonstrated COV of the sampling rate at constant conditions: 40.2 µg NO_2 m^{-3}, 0.5 m s^{-1} wind speed, 20ºC temperature and 80% relative humidity

Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	CRM for NO_2 gas mixture
Validation	Peer reviewed publication of Laboratory validation study	

12.2.4 Wind speed (2b2)

Element related to the wind speed effect, which uncertainty budget results from combining the budgets of the sub-elements Wind speed effect model (2b2a) and Wind speed variability (2b2b).

$$u_{2b2}^2 = u_{2b2a}^2 + u_{2b2b}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Wind speed	
Contribution identifier	2b2	
Measurement equation parameter(s) subject to effect	$u_{2b2}^2 = u_{2b2a}^2 + u_{2b2b}^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	Exposure	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.7% to ~±18% (1σ)	Combination of multiple elements, depends on tube design, deployment strategy and local wind, assumed 1.5 ms^{-1}
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	m, s	
Validation	Peer reviewed publications	

12.2.5 Wind Bias (2b2a)

Uncertainty budget of the wind speed effect model [9], estimated based on a lack of fit assessment, considering the maximum residue of 4.86% at the 1.6 m s^{-1} and a normal distribution.

$$V_{SR} = 0.252Ln(wv) + 0.16$$

Uncertainty budget of the wind speed bias, estimated based on measurements in a controlled atmospheric testing facility [8] the unsheltered PDT was found to have a bias which was wind dependant and the sheltered PDT was derived from the bias at 0 wind. The modified tube uncertainty uses the mean bias found from the measurements.

Information / data	Type / value / equation	Notes / description
Name of effect	Wind speed effect model	
Contribution identifier	2b2a	
Measurement equation parameter(s) subject to effect	$V_{SR} = 0.252Ln(wv) + 0.16$	Empirical equation for sample rate variation induced by wind velocity (cm s^{-1})
Contribution subject to effect (final product or sub-tree intermediate product)	Sampling rate	
Classification	Systematic	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±(2.6+9*windspeed)% unsheltered PDT ±2.6% sheltered PDT ±0.7% Modified tubes with fine aperture covering meshes All (1σ)	
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	Effect model	
Validation	Peer reviewed publication	Laboratory validation study on the effect of wind speed

		on Palmes tubes sampling rate

12.2.6 Wind speed variability (2b2b)

Uncertainty budget of the wind speed effect on the sampling rate, derived from published mathematical model [9] and the variation amplitude on typical Palmes tubes sampling rate caused by typical amplitude for wind speed variation of 0.5 m s^{-1} to 2.5 m s^{-1}, considering a normal distribution.

$$V_{SR} = 0.252Ln(wv) + 0.16$$

Uncertainty budget on increased uncertainty due to increasing wind speed based on the CATFAC testing. Is only applied to unmodified, unsheltered PDT measurements and dependant on local wind.

Information / data	Type / value / equation	Notes / description
Name of effect	Wind speed variability	
Contribution identifier	2b2b	
Measurement equation parameter(s) subject to effect	$V_{SR} = 0.252Ln(wv) + 0.16$	Empirical equation for sample rate variation induced by wind velocity (cm s^{-1})
Contribution subject to effect (final product or sub-tree intermediate product)	Sampling rate	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±(3*windspeed)% (1σ)	
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Only unmodified unsheltered PDT	
Traceable to …	m, s	
Validation	Peer reviewed publication	Laboratory validation study on the effect of wind speed on Palmes tubes sampling rate

12.2.7 Relative humidity (2b3)

Element related to the relative humidity effect, which uncertainty budget results from combining the budgets of the sub-elements Relative humidity effect model (2b3a) and Relative humidity variability (2b3b).

$$u_{2b3}^2 = u_{2b3a}^2 + u_{2b3b}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Relative humidity	
Contribution identifier	2b3	
Measurement equation parameter(s) subject to effect	$u_{2b3}^2 = u_{2b3a}^2 + u_{2b3b}^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	Exposure	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±2.5% (1σ)	Combination of multiple elements
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	RH standards	
Validation	Peer reviewed publications	

12.2.8 Relative humidity effect model (2b3a)

Uncertainty budget of the relative humidity effect model [10], assumed to be equivalent to the wind speed effect model due to lack of representative information on peer reviewed publications.

$$V_{SR} = 2.85E-03\,.T\; -\; 1.62E-04\,.RH\; +\; 4.96E-05\,.T\,.RH\; +\; 0.9$$

Information / data	Type / value / equation	Notes / description
Name of effect	Relative humidity effect model	
Contribution identifier	2b3a	

Measurement equation parameter(s) subject to effect	$V_{SR} = 2.85E-03 \,.T\, - \,1.62E-04 \,.RH + \,4.96E-05 \,.T\,.RH + \,0.9$	Empirical isocurves model for sample rate variation induced by temperature (ºC) and relative humidity (%)
Contribution subject to effect (final product or sub-tree intermediate product)	Sampling rate	
Classification	Systematic	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±2.4% (1σ)	Assumed to be equivalent to the wind speed effect model
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	Effect model	
Validation	Peer reviewed publication	Laboratory validation study on the effect of meteorological parameters on Palmes tubes sampling rate

12.2.9 Relative humidity variability (2b3b)

Uncertainty budget of the relative humidity effect on the sampling rate, derived from published isocurves [10] and the variation amplitude on typical Palmes tubes sampling rate caused by relative humidity variation range 70% ± 20%, considering constant temperature of 11ºC and a normal distribution.

$$V_{SR} = 2.85E-03 \,.T\, - \,1.62E-04 \,.RH \, + \,4.96E-05 \,.T\,.RH \, + \,0.9$$

Information / data	Type / value / equation	Notes / description
Name of effect	Relative humidity variability	
Contribution identifier	2b3b	
Measurement equation parameter(s) subject to effect	$V_{SR} = 2.85E-03 \,.T\, - \,1.62E-04 \,.RH + \,4.96E-05 \,.T\,.RH + \,0.9$	Empirical isocurves model for sample rate variation induced by temperature (ºC) and relative humidity (%)

Contribution subject to effect (final product or sub-tree intermediate product)	Sampling rate	
Classification	Systematic	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.8% (1σ)	Sampling rate variation caused by relative humidity variation of ± 20%, considering baseline value of 70% and constant 11ºC
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	RH standards	
Validation	Peer reviewed publication	Laboratory validation study on the effect of meteorological parameters on Palmes tubes sampling rate

12.2.10 Temperature (2b4)

Element related to the temperature effect, which uncertainty budget results from combining the budgets of the sub-elements Temperature effect model (2b4a) and Temperature variability (2b4b).

$$u_{2b4}^2 = u_{2b4a}^2 + u_{2b4b}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Temperature	
Contribution identifier	2b4	
Measurement equation parameter(s) subject to effect	$u_{2b4}^2 = u_{2b4a}^2 + u_{2b4b}^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	Exposure	
Classification	Random	
Uncertainty PDF shape	Normal	

Single measurement Uncertainty & units (2σ)	±5.2% (1σ)	Combination of multiple elements
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	K	
Validation	Peer reviewed publications	

12.2.11 Temperature effect model (2b4a)

Uncertainty budget of the temperature effect model [10], assumed to be equivalent to the wind speed effect model due to lack of representative information on peer reviewed publications.

$$V_{SR} = 2.85E-03 \,.T\; -\; 1.62E-04 \,.RH \;+\; 4.96E-05 \,.T \,.RH \;+\; 0.9$$

Information / data	Type / value / equation	Notes / description
Name of effect	Temperature effect model	
Contribution identifier	2b4a	
Measurement equation parameter(s) subject to effect	$V_{SR} = 2.85E-03 \,.T\; -\; 1.62E-04 \,.RH \;+\; 4.96E-05 \,.T \,.RH \;+\; 0.9$	Empirical isocurves model for sample rate variation induced by temperature (ºC) and relative humidity (%)
Contribution subject to effect (final product or sub-tree intermediate product)	Sampling rate	
Classification	Systematic	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±2.4% (1σ)	Assumed to be equivalent to the wind speed effect model
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	Effect model	

Validation	Peer reviewed publication	Laboratory validation study on the effect of meteorological parameters on Palmes tubes sampling rate

12.2.12 Temperature variability (2b4b)

Uncertainty budget of the temperature effect on the sampling rate, derived from published isocurves [10] and the variation amplitude on typical Palmes tubes sampling rate caused by temperature variation of ±7ºC on the conventional annual average temperature of 11ºC, considering constant relative humidity of 70% and a normal distribution.

$$V_{SR} = 2.85E-03 \,.T\; -\; 1.62E-04 \,.RH\; +\; 4.96E-05 \,.T\,.RH\; +\; 0.9$$

Information / data	Type / value / equation	Notes / description
Name of effect	Temperature variability	
Contribution identifier	2b4b	
Measurement equation parameter(s) subject to effect	$V_{SR} = 2.85E-03 \,.T\; -\; 1.62E-04 \,.RH\; +\; 4.96E-05 \,.T\,.RH\; +\; 0.9$	Empirical isocurves model for sample rate variation induced by temperature (ºC) and relative humidity (%)
Contribution subject to effect (final product or sub-tree intermediate product)	Sampling rate	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±4.6% (1σ)	Sampling rate variation caused by temperature variation of ±7ºC, considering baseline value of 11ºC and constant 70% relative humidity
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	K	
Validation	Peer reviewed publication	Laboratory validation study on the effect of

		meteorological parameters on Palmes tubes sampling rate

12.2.13 Cross-interference (2b5)

Ozone induced within tube oxidation of NO to NO_2 potentially results in positive bias of up to 25% at roadside sampling sites. Urban background and rural sites are far less affected due to disadvantageous [NO] / [NO_2] and [NO] / [O_3] ratios [11]. Nevertheless, laboratory and field studies also recognize that these observations may be subjected to cofounding factors such meteorological parameters, imposing a severe challenge to isolating and estimating the cross-interference bias / uncertainty budget [12]. This effect is not quantified in the current analysis.

Information / data	Type / value / equation	Notes / description
Name of effect	Cross-interference	
Contribution identifier	2b5	
Measurement equation parameter(s) subject to effect	$v = \frac{D \,.\, S}{L}$	Sampling rate equation
Contribution subject to effect (final product or sub-tree intermediate product)	Sampling rate	
Classification	n/a	
Uncertainty PDF shape	n/a	
Single measurement Uncertainty & units (2σ)	n/a	Not quantified in current analysis
Sensitivity coefficient	n/a	
Correlation(s) between affected parameters	n/a	
Element/step common for all sites/users?	No	
Traceable to …	n/a	
Validation	Peer reviewed publications	

12.3 NITRITE QUANTIFICATION (3)

Element related to the nitrite mass quantification, which uncertainty is calculated by the sum in quadrature of the sub-elements Nitrite extraction (3a), Reaction dilution (3b) and Photometric quantification (3c).

$$u_3^2 = u_{3a}^2 + u_{3b}^2 + u_{3c}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Nitrite quantification	
Contribution identifier	3	
Measurement equation parameter(s) subject to effect	$u_3^2 = u_{3a}^2 + u_{3b}^2 + u_{3c}^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	NO_2 average concentration	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±2.2% (1σ)	Combining sub-element components
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	
Validation	CRM certificate, instrumentation data sheets and peer reviewed publications	

12.3.1 Nitrite extraction (3a)

Element related to the nitrite extraction from the tube's mesh, which uncertainty is calculated by the sum in quadrature of the sub-elements Water volume transfer (3a1) and Extraction efficiency (3a2), according to equation 7.

$$u_{3a}^2 = u_{3a1}^2 + u_{3a2}^2 \quad (7)$$

Information / data	Type / value / equation	Notes / description
Name of effect	Nitrite extraction	
Contribution identifier	3a	
Measurement equation parameter(s) subject to effect	$u_{3a}^2 = u_{3a1}^2 + u_{3a2}^2$	

Contribution subject to effect (final product or sub-tree intermediate product)	Nitrite quantification	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±1.7% (1σ)	Combination of multiple elements
Sensitivity coefficient	1	
Correlation(s) between affected parameters	3, 4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	
Validation	Peer reviewed publication of laboratory validation study	

12.3.2 Water volume transfer (3a1)

Uncertainty budget of water volume transfer to extract the nitrite from the tube's mesh, derived from the ±1% tolerance of an automatic pipette (100µl capacity), considering a normal distribution [4].

Information / data	Type / value / equation	Notes / description
Name of effect	Water volume transfer	
Contribution identifier	3a1	
Measurement equation parameter(s) subject to effect	$C = \frac{m}{V}$	Equation for the nitrite concentration in the extraction solution
Contribution subject to effect (final product or sub-tree intermediate product)	Nitrite extraction	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.5% (1σ)	Assuming the typical tolerance limit for random error of automatic pipettes
Sensitivity coefficient	1	

Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Considering an instrument subjected to traceable calibration
Validation	Data sheet	Pipette specification provided by the manufacturer

12.3.3 Extraction efficiency (3a2)

Uncertainty budget of the extraction efficiency, derived from validated nitrite recovery of 94 ± 3% from tubes meshes under optimum agitation regime [13], considering a normal distribution.

Information / data	Type / value / equation	Notes / description
Name of effect	Extraction efficiency	
Contribution identifier	3a2	
Measurement equation parameter(s) subject to effect	$C = \frac{m}{V}$	Equation for the nitrite concentration in the extraction solution
Contribution subject to effect (final product or sub-tree intermediate product)	Nitrite extraction	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±1.6% (1σ)	Verified nitrite extraction efficiency of 94 ± 3%, under optimum agitation regime
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	CRM used for validation purposes, traceable to NIST mass reference standards
Validation	Peer reviewed publication	

12.3.4 Reaction dilution (3b)

Element related to the dilution for promoting the nitrite chemical reaction, which uncertainty budget results from combining the budgets of the sub-elements SAA volume transfer (3b1) and DA volume transfer (3b2).

$$u_{3b}^2 = u_{3b1}^2 + u_{3b2}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Reaction dilution	
Contribution identifier	3b	
Measurement equation parameter(s) subject to effect	$u_{3b}^2 = u_{3b1}^2 + u_{3b2}^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	Nitrite quantification	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.7% (1σ)	Combination of multiple elements
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Considering an instrument subjected to traceable calibration
Validation	Data sheet	Pipette specification provided by the manufacturer

12.3.5 SAA volume transfer (3b1)

Uncertainty budget of the sulphanilamide volume transfer to allow reaction with nitrite and colour development, derived from the ±1% tolerance of an automatic pipette (100µl capacity), considering a normal distribution [4].

Information / data	Type / value / equation	Notes / description

Name of effect	SAA volume transfer	
Contribution identifier	3b1	
Measurement equation parameter(s) subject to effect	$C = \frac{m}{V}$	Equation for the nitrite concentration in the extraction solution
Contribution subject to effect (final product or sub-tree intermediate product)	Reaction dilution	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.5% (1σ)	Assuming the typical tolerance limit for random error of automatic pipettes
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Considering an instrument subjected to traceable calibration
Validation	Data sheet	Pipette specification provided by the manufacturer

12.3.6 DA volume transfer (3b2)

Uncertainty budget of the diamine volume transfer to allow reaction with nitrite and colour development, derived from the ±1% tolerance of an automatic pipette (100µl capacity), considering a normal distribution [4].

Information / data	Type / value / equation	Notes / description
Name of effect	DA volume transfer	
Contribution identifier	3b2	
Measurement equation parameter(s) subject to effect	$C = \frac{m}{V}$	Equation for the nitrite concentration in the extraction solution

Contribution subject to effect (final product or sub-tree intermediate product)	Reaction dilution	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.5% (1σ)	Assuming the typical tolerance limit for random error of automatic pipettes
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Considering an instrument subjected to traceable calibration
Validation	Data sheet	Pipette specification provided by the manufacturer

12.3.7 Photometric quantification (3c)

Element related to the photometric quantification of nitrite in the extraction solution, which uncertainty is calculated by the sum in quadrature of the sub-elements Calibration standards (3c1), Absorbance measurement (3c2) and Calibration curve (3c3).

$$u_{3c}^2 = u_{3c1}^2 + u_{3c2}^2 + u_{3c3}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Photometric quantification	
Contribution identifier	3c	
Measurement equation parameter(s) subject to effect	$u_{3c}^2 = u_{3c1}^2 + u_{3c2}^2 + u_{3c3}^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	Nitrite quantification	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±1.3% (1σ)	Combination of multiple elements

Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	
Validation	CRM certificate, instruments data sheet and peer review publications	

12.3.8 Calibration standards (3c1)

Element related to the preparing nitrite calibration standards, which uncertainty budget is calculated by the sum in quadrature of the sub-elements Stock solution – certified nitrite concentration (3c1a), Stock volume transfer (3c1b) and Standard final dilution (3c1c).

$$u_{3c1}^2 = u_{3c1a}^2 + u_{3c1b}^2 + u_{3c1c}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Calibration standards	
Contribution identifier	3c1	
Measurement equation parameter(s) subject to effect	$u_{3c1}^2 = u_{3c1a}^2 + u_{3c1b}^2 + u_{3c1c}^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	Photometric quantification	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±1.0% (1σ)	Combination of multiple elements
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	
Validation	CRM certificate, instruments data sheet and peer review publications	

12.3.9 Stock solution – certified nitrite concentration (3c1a)

Uncertainty budget derived from the certified expanded uncertainty of ± 0.0154 mg/L (k=2) for the nitrite concentration of 0.864 mg/L in the reference material solution (stock solution) [14].

Information / data	Type / value / equation	Notes / description
Name of effect	Stock solution – certified nitrite concentration	
Contribution identifier	3c1a	
Measurement equation parameter(s) subject to effect	$C_{standard} = C_{stock} . \frac{V_{transfer}}{V_{final}}$	Equation for diluting the stock solution
Contribution subject to effect (final product or sub-tree intermediate product)	Calibration standards	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	± 0.9% (1σ)	Expanded uncertainty from CRM certificate: 0.864 ± 0.0154 mg/L of nitrite (k=2)
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Traceable to NIST mass reference standards
Validation	CRM certificate	CRM prepared under ISO/IEC 17025:2005 and ISO GUIDE 34:2009

12.3.10 Stock volume transfer (3c1b)

Uncertainty budget of the volume transfer from a stock standard solution to the calibration standard, derived from the ±1% tolerance of an automatic pipette (100µl capacity), considering a normal distribution [4].

Information / data	Type / value / equation	Notes / description

Name of effect	Stock volume transfer	
Contribution identifier	3c1b	
Measurement equation parameter(s) subject to effect	$C_{TEA} = C_{stock} . \frac{V_{transfer}}{V_{final}}$	Equation for diluting the stock solution
Contribution subject to effect (final product or sub-tree intermediate product)	Calibration standards	
Classification	Systematic	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.5% (1σ)	Assuming the typical tolerance limit for random error of automatic pipettes
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Traceable to mass reference standards
Validation	Data sheet	Pipette specification provided by the manufacturer

12.3.11 Standard final dilution (3c1c)

Uncertainty budget of correctly filing a volumetric glass to the final volume mark, derived from the ±0.050 ml expanded uncertainty (k=2) of a 1.0 l volumetric flask [5].

Information / data	Type / value / equation	Notes / description
Name of effect	Standard final dilution	
Contribution identifier	3c1	
Measurement equation parameter(s) subject to effect	$C_{TEA} = C_{stock} . \frac{V_{transfer}}{V_{final}}$	Equation for diluting the stock solution
Contribution subject to effect (final product or sub-tree intermediate product)	Calibration standards	
Classification	Random	
Uncertainty PDF shape	Normal	

Single measurement Uncertainty & units (2σ)	±0.005% (1σ)	Based on ±0.050 ml expanded uncertainty (k=2) for a 1000 ml volumetric flask
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4e	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Traceable to national mass standards
Validation	EURAMET publication	

12.3.12 Absorbance measurement (3c2)

Element related to taking absorbance measurements with spectrophotometer, which uncertainty is calculated by the sum in quadrature of the sub-elements Instrument accuracy (3c2a) and Instrument repeatability (3c2b).

$$u_{3c2}^2 = u_{3c2a}^2 + u_{3c2b}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Absorbance measurement	
Contribution identifier	3c2	
Measurement equation parameter(s) subject to effect	$u_{3c2}^2 = u_{3c2a}^2 + u_{3c2b}^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	Photometric quantification	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.1% (1σ)	Combination of multiple elements
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	m	

Validation	Instrument data sheet and peer review publications	

12.3.13 Instrument accuracy (3c2a)

Uncertainty budget of the spectrophotometer accuracy, derived from specified value of ±1 nm [15], considering a measurement at 540 nm wavelength and normal distribution.

Information / data	Type / value / equation	Notes / description
Name of effect	Instrument accuracy	
Contribution identifier	3c2a	
Measurement equation parameter(s) subject to effect	$A = \varepsilon . b . C$	Beer-Lambert law equation correlating absorbance with nitrite concentration
Contribution subject to effect (final product or sub-tree intermediate product)	Absorbance	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.1% (1σ)	±1nm for 540nm measurement
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	m	Considering an instrument subjected to traceable calibration
Validation	Data sheet	Instrument specification provided by the manufacturer

12.3.14 Instrument repeatability (3c2b)

Uncertainty budget of the spectrophotometer repeatability, derived from validation study considering the value of ±0.002 AU [16] for an absorbance measurement of 1.0 AU and a normal distribution.

Information / data	Type / value / equation	Notes / description

Name of effect	Instrument repeatability	
Contribution identifier	3c2b	
Measurement equation parameter(s) subject to effect	$A = \varepsilon . b . C$	Beer-Lambert law equation correlating absorbance with nitrite concentration
Contribution subject to effect (final product or sub-tree intermediate product)	Absorbance	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.1% (1σ)	Photometric repeatability of ±0.002 AU for an absorbance measurement of 1.0 AU
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	m	Considering an instrument subjected to traceable calibration
Validation	Peer reviewed publication	Photometric measurement uncertainty estimation study

12.3.15 Calibration curve (3c3)

Element related to the calibration curve for the nitrite photometric quantification, which uncertainty is calculated by the sum in quadrature of the sub-elements Intercept (3c3a) and Slope (3c2b).

$$u_{3c3}^2 = u_{3c3a}^2 + u_{3c3b}^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	Calibration curve	
Contribution identifier	3c3	
Measurement equation parameter(s) subject to effect	$u_{3c3}^2 = u_{3c3a}^2 + u_{3c3b}^2$	

Contribution subject to effect (final product or sub-tree intermediate product)	Photometric quantification	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.4% (1σ)	Combination of multiple elements
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Traceable to mass reference standards
Validation	DEFRA Practical guidance	

12.3.16 Intercept (3c3a)

Uncertainty budget of the intercept of the calibration curve used to calculate the nitrate concentration. Derived from an intercept standard error of ±6.3E-03 of a published linear regression for nitrite quantification[2], considering a mid-range absorbance measurement of 1.05 AU and a normal distribution.

Information / data	Type / value / equation	Notes / description
Name of effect	Intercept	
Contribution identifier	3c3a	
Measurement equation parameter(s) subject to effect	$A = a \,.\, C_{nitrite} + b$	Calibration curve equation
Contribution subject to effect (final product or sub-tree intermediate product)	Calibration curve	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.3% (1σ)	Based on the ±6.3E-03 standard error, considering the mid-range absorbance of 1.05 UA
Sensitivity coefficient	1	

Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Traceable to mass reference standards
Validation	DEFRA Practical guidance	Published example of a calibration curve for nitrite spectrophotometric determination

12.3.17 Slope (3c3b)

Uncertainty budget of the slope of the calibration curve used to calculate the nitrate concentration. Derived from a slope standard error of ±9.4E-05 of a published linear regression for nitrite quantification [2], considering a slope value of 0.01778 and a normal distribution.

Information / data	Type / value / equation	Notes / description
Name of effect	Slope	
Contribution identifier	3c3b	
Measurement equation parameter(s) subject to effect	$A = a \,.\, C_{nitrite} + b$	Calibration curve equation
Contribution subject to effect (final product or sub-tree intermediate product)	Calibration curve	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±0.3% (1σ)	Based on the ±9.4E-05 standard error of a 0.01778 slope
Sensitivity coefficient	1	
Correlation(s) between affected parameters	4a	
Element/step common for all sites/users?	Yes	
Traceable to …	kg	Traceable to mass reference standards

Validation	DEFRA Practical guidance	Published example of a calibration curve for nitrite photometric determination

12.4 NO_2 AVERAGE CONCENTRATION (4)

Element related to calculating the average NO_2 average concentration for a single tube's monthly measurement. This element's uncertainty is calculated by the sum in quadrature of the sub-elements Supplied tube (1), Exposure (2) and Nitrite quantification (3).

$$u_4^2 = u_1^2 + u_2^2 + u_3^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	NO_2 average concentration	
Contribution identifier	3	
Measurement equation parameter(s) subject to effect	$u_4^2 = u_1^2 + u_2^2 + u_3^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	NO_2 average concentration	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±6.4-18.1% (1σ)	
Sensitivity coefficient	1	
Correlation(s) between affected parameters	n/a	Combined element
Element/step common for all sites/users?	Yes	
Traceable to …	n/a	Combined element
Validation	n/a	Combined element

12.4.1 Bias adjustment (5)

In the context of Review and Assessment, local authorities are required to quantify and apply a bias adjustment factor for the results of diffusion tube NO_2 measurements. The national bias adjustment factors data base is in the public domain [22]. This uncertainty element arises from the variability of the yearly adjustment factor for the same site / method / supplier / tube precision conditions. Figure A2 shows some example bias adjustments. From an urban kerbside site (Marylebone road), the COV (1σ) of the factors reported between 2011 and 2020 was 9.4%. The equivalent COV (1σ) for a rural site (West Berkshire) between 2011 and 2018 was 7.9%, whilst for the overall factor (which includes multiple studies with the

same supplier/method/tube precision conditions) between 2011 and 2020 it was 6.3%. Note that the impact of this effect should not be considered in studies focussed on the primary result of the diffusion tube measurements.

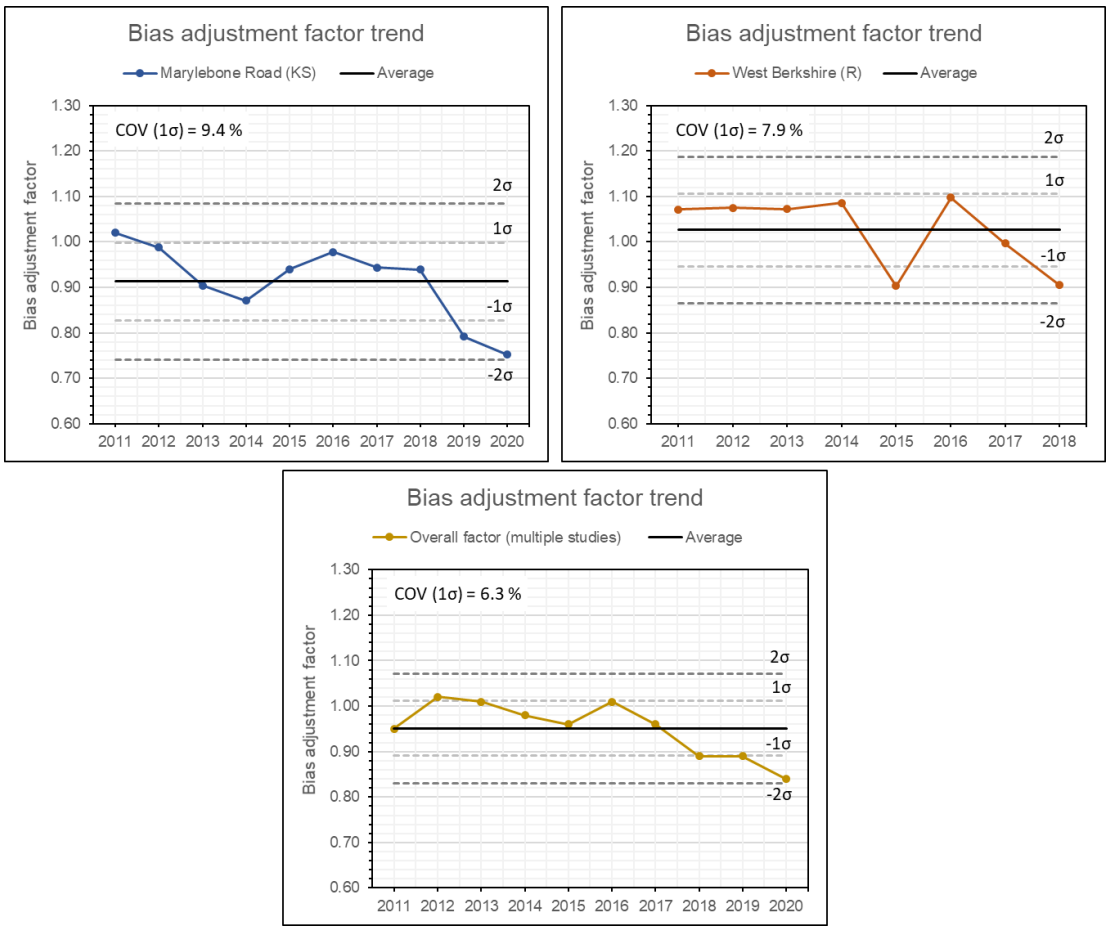


Figure 2: Variability charts of the bias adjustment factors considered in the assessment.

Information / data	Type / value / equation	Notes / description
Name of effect	Bias adjustment	
Contribution identifier	5	
Measurement equation parameter(s) subject to effect	$NO_{2\ adjust.} = NO_{2\ aver.} * f$	
Contribution subject to effect (final product or sub-tree intermediate product)	Calculation	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	9.4% (1σ)	COV (1σ) for urban kerbside site (Marylebone road) between 2011 and 2020

Sensitivity coefficient	1	
Correlation(s) between affected parameters	5	
Element/step common for all sites/users?	Yes	
Traceable to …	Certified span gases	
Validation	Co-location studies within DEFRA's bias adjustment factor programme	

12.5 NO_2 ADJUSTED CONCENTRATION (6)

Element related to the final product, the NO_2 adjusted concentration, which uncertainty is calculated by the sum in quadrature of the main elements NO_2 average concentration (4) and Bias adjustment (5).

$$u_6^2 = u_4^2 + u_5^2$$

Information / data	Type / value / equation	Notes / description
Name of effect	NO_2 average concentration	
Contribution identifier	3	
Measurement equation parameter(s) subject to effect	$u_6^2 = u_4^2 + u_5^2$	
Contribution subject to effect (final product or sub-tree intermediate product)	NO_2 average concentration	
Classification	Random	
Uncertainty PDF shape	Normal	
Single measurement Uncertainty & units (2σ)	±20.4% (1σ)	Combining elements 4 and 5 for unsheltered, unmodified PDT, not currently implemented
Sensitivity coefficient	n/a	Combined element
Correlation(s) between affected parameters	n/a	Combined element
Element/step common for all sites/users?	Yes	
Traceable to …	n/a	Combined element
Validation	n/a	Combined element

12.6 UNCERTAINTY SUMMARY

Traceability level definition is given in Table A1, whereas the summary of all elements contributions to overall product uncertainty is presented in Table A2.

Table A1 Traceability level definitions

Traceability Level	Descriptor
High	SI traceable or globally recognised community standard
Medium	Developmental community standard or peer-reviewed uncertainty assessment
Low	Approximate estimation

Table A2 Summary of the contributions of all elements to the overall product uncertainty.

Element Identifier	Contribution name	Uncertainty contribution form	Typical value (%)	Traceability level (L/M/H)	Classification	Correlated to ? (use element ID)
1	**Supplied tube**	**Normal**	**0.9**	**H**	**Random**	**2**
1a	**Mesh coating**	**Normal**	**0.9**	**H**	**Random**	**2**
1a1	TEA stock solution volume transfer	Normal	0.5	H	Random	3, 4
1a2	Wetting agent volume transfer	Normal	0.5	H	Random	3, 4
1a3	TEA solution final dilution	Normal	0.005	H	Random	3, 4
1a4	TEA solution volume transfer	Normal	0.5	H	Random	3, 4
1b	**Tube properties**	**Normal**	**0.1**	**H**	**Random**	**2**
1b1	Cross-sectional area	Normal	0.09	H	Random	2b
1b2	Diffusion path length	Normal	0.08	H	Random	2b
2	**Exposure**	**Normal**	**6-18**	**M**	**Random**	**3, 4**
2a	Sampling time	Normal	0.000006	H	Random	3, 4
2b	**Sampling rate**	**Normal**	**6-18**	**M**	**Random**	4
2b1	Controlled conditions repeatability	Normal	1.7-4.8	H	Random	3, 4
2b2	**Wind speed**	**Normal**	**0.7-18**	M	Quasi-systematic	3

2b2a	Wind Bias	Normal	0.7-16.1	M	Systematic	3, 4
2b2b	Wind speed variability	Normal	4.5	H	Random	3, 4
2b3	**Relative humidity**	**Normal**	**2.5**	M	Quasi-systematic	2b4
2b3a	Relative humidity effect model	Normal	2.4	L	Systematic	3, 4
2b3b	Relative humidity variability	Normal	0.8	H	Random	3, 4
2b4	**Temperature**	**Normal**	**5.2**	M	Quasi-systematic	2b3
2b4a	Temperature effect model	Normal	2.4	L	Systematic	3, 4
2b4b	Temperature variability	Normal	4.6	H	Random	3, 4
2b5	Cross-interference	Normal		L	Random	3, 4
3	**Nitrite quantification**	**Normal**	**2.1**	**H**	**Random**	4
3a	**Nitrite extraction**	**Normal**	**1.7**	**H**	**Random**	3
3a1	Water volume transfer	Normal	0.5	H	Random	3
3a2	Extraction efficiency	Normal	1.6	M	Random	3
3b	**Reaction dilution**	**Normal**	**0.7**	**H**	**Random**	**3**
3b1	SAA volume transfer	Normal	0.5	H	Random	3
3b2	DA volume transfer	Normal	0.5	H	Random	3
3c	**Photometric quantification**	**Normal**	**1.1**	**H**	**Random**	**3**
3c1	**Calibration standards**	**Normal**	**1.0**	**H**	**Random**	**3**
3c1a	Stock solution - certified nitrite concentration	Normal	0.9	H	Random	3
3c1b	Stock volume transfer	Normal	0.5	H	Random	3
3c1c	Standard final dilution	Normal	0.005	H	Random	3
3c2	**Absorbance measurement**	**Normal**	**0.1**	**M**	**Random**	3
3c2a	Instrument accuracy	Normal	0.1	H	Random	3
3c2b	Instrument repeatability	Normal	0.1	H	Random	3

3c3	**Calibration curve**	**Normal**	**0.4**	**H**	**Random**	3
3c3a	Intercept	Normal	0.3	H	Random	3
3c3b	Slope	Normal	0.3	H	Random	3
4	**NO_2 average concentration**	**Normal**	**6.4-18.1**	**H**	**Random**	**2, 3**
5	**Bias adjustment**	**Normal**	**9.4**	H	Random	5
6	**NO_2 adjusted concentration**	**Normal**	**20.4**	**H**	**Random**	**4**

The total relative uncertainty of the NO_2 average concentration (4), measured by typical Palmes tubes over a 4 week sampling period, is the sum in quadrature of the uncertainties from the supplied tube (1), exposure (2) and nitrite quantification (3). This is shown in the equation below.

$$u_4^2 = u_1^2 + u_2^2 + u_3^2$$

Under the reported conditions, the calculated expanded relative uncertainty of the NO_2 average concentration product is 36.2%, considering a coverage factor (k) of 2 at approximately 95% confidence level. To exemplify this outcome, the NO_2 average concentration product of 40.2 µg.m^{-3}, the same concentration level deployed in the repeatability study [8], would entail the expanded uncertainty of ± 14.5 µg.m^{-3} (k=2).
The product uncertainty is dominated by the sampling rate element, which is in turn predominantly driven by the uncertainty associated with wind speed effect, in addition to the contribution of the atmospheric temperature. These observations are aligned with the current guidelines and requirements for indicative measurements of NO_2 using diffusion tubes in the UK [2], as well as with peer reviewed publications of laboratory and field based validation studies [12].
In the UK, bias adjustment factors are determined by local authorities via co-location studies and applied to the diffusive NO_2 measurements to calculate an adjusted NO_2 concentration [22]. The present assessment indicates that applying the bias adjustment factor from an urban site to a single monthly measurement, could induce an increase of the final product expanded uncertainty to 40.8% (k=2, 95%).

12.7 TRACEABILITY UNCERTAINTY ANALYSIS

As indicated by the traceability levels and the uncertainty contributions of all considered elements, the most promising areas in which further actions are likely to improve the product uncertainty relate to the Sampling rate (2b) and the Bias adjustment factor (5). More specifically, regarding the Controlled conditions repeatability (2b1), Wind speed (2b2) and Temperature (2b4) elements of the sampling rate, which constitute the majority of the sampling rate uncertainty. Table A3 presents the details for these elements.

Table A3 Traceability uncertainty analysis for typical PDT – further action table.

Element Identifier	Contribution name	Uncertainty contribution form	Typical value (%)	Traceability level (L/M/H)	Classification	Correlated to? (element ID)
2b1	Controlled conditions repeatability	Normal	4.8	H	Random	3, 4

2b2	**Wind speed**	**Normal**	**18**	M	Quasi-systematic	3
2b4	**Temperature**	**Normal**	**5.2**	M	Quasi-systematic	2b3

Wind speed knowingly causes systematic positive bias in PDT measurements, as an effect of reducing the diffusion path by inducing turbulent transport of gases at the open end of the tubes [12]. The advent of protective covers for the PDT during the exposure period [3, 19] and especially modifying typical PDTs with a porous barrier (referred to as mesh, filter or membrane) [8, 20] have been reported as successful strategies for mitigating this effect. For instance, a recent laboratory based validation study deployed typical and modified PDTs. The modified samplers had fine aperture stainless woven cloth covering the open end of the tubes. The modified PDTs achieved significantly lower coefficient of variance (1.7%, 1σ) for NO_2 measurements at the lowest concentration and wind speed conditions, in comparison with the same typical PDTs considered in the Controlled conditions repeatability element (4.8%, 1σ) [8]. The study did not discriminate the sole contribution of wind speed to the total uncertainty. However, assuming the modification would cause an equivalent effect on this particular element, the estimated uncertainty contribution of wind speed uncertainty on modified PDTs measurements would be 0.7% (1σ), as opposed to the ~18% (1σ) of typical PDTs, previously discussed in the element 2b2 section. Table A4 presents the uncertainty contribution details of such elements considering modified PDTs.

Table A4 Traceability uncertainty analysis for modified PDT.

Element Identifier	Contribution name	Uncertainty contribution form	Typical value (%)	Traceability level (L/M/H)	Classification	Correlated to? (element ID)
2b1	Controlled conditions repeatability	Normal	1.7	H	Random	3, 4
2b2	Wind speed	Normal	0.7	M	Quasi-systematic	3

After updating these figures for elements 2b1 and 2b2, the updated expanded relative uncertainty of the NO_2 average concentration product would be 12.8% (k=2, 95%), which is comparable to the DQO requirements for continuous monitoring instruments and aligned with preceding observations [20].

Furthermore, the contribution of atmospheric temperature is also associated to a temporal aspect of deploying diffusion tubes. The temperature element (2b4) considered typical monthly average values observed in the UK. Throughout the year, monthly NO_2 measurements suffer from temperature induced biases (positive and negative) on the sampling rate. However, the intended usage of such results in the UK relates to calculating annual NO_2 average concentrations for indicative measurements. In this process, the positive and negative biases observed in monthly measurements are believed to be averaged out [2], which could potentially contribute to reducing the total expanded relative uncertainty to levels below 15% (k=2, 95%), according to field based experiments [3, 21].

Finally, the current assessment suggests that the bias adjustment of the NO_2 average concentration may significantly increase the final product uncertainty. This evaluation was based on the variability of the adjustment factors reported since 2011, considering the same supplier, method and tube precision conditions for two measurement sites (urban kerbside and rural) and for overall factors of multiple studies. By the time of writing, the lack of access to the raw data sets from the co-location studies which resulted in the reported adjustment

factors prevented further analyses. However, these data sets may be relevant to indicate the actual level of variability of the NO_2 average concentrations observed in the field and, potentially, the appropriateness of the bias adjustment factor itself based on the estimated uncertainty values.

12.7.1 Temporal behaviour of uncertainties

One of the key aspects of the traceability and uncertainty assessment is the consideration of how the uncertainties varying with results combined over different timescales. Such an evaluation is based on how the classification of different uncertainty contributions vary with time. Table 5 shows this for the uncertainty contributions in this case. It should be noted that the decisions over the classifications is often based on expert judgement.

Table 5 Uncertainty contribution classification over different reporting periods

Contribution	ref	Single Month	Multi-Month	Annual	Long term
TEA stock solution volume transfer	1a1	Random	Random	Random	Random
Wetting agent volume transfer	1a2	Random	Random	Random	Random
TEA solution final dilution	1a3	Random	Random	Random	Random
TEA solution volume transfer	1a4	Random	Random	Random	Random
Cross sectional area	1b2	Random	Random	Random	Random
Diffusion path length	1b3	Random	Random	Random	Random
Sampling time	2a	Random	Random	Random	Random
Repeatability	2b1	Systematic	Systematic	Systematic	Systematic
Wind Speed Bias	2b2a	Systematic	Systematic	Systematic	Systematic
Wind speed Variability	2b2b	Systematic	Random	Random	Random
Relative humidity effect model	2b3a	Systematic	Systematic	Systematic	Quasi-systematic
Relative humidity variability	2b3b	Systematic	Random	Random	Random
Temperature effect model	2b4a	Systematic	Systematic	Systematic	Quasi-systematic
Temperature variability	2b4b	Systematic	Random	Random	Random
Water volume transfer	3a1	Random	Random	Random	Random

Extraction efficiency	3a2	Random	Random	Random	Random
SAA volume transfer	3b1	Random	Random	Random	Random
DA volume transfer	3b2	Random	Random	Random	Random
Stock solution – certified nitrite concentration	3c1a	Systematic	Systematic	Quasi-systematic	Random
Stock volume transfer	3c1b	Random	Random	Random	Random
Standard final dilution	3c1c	Random	Random	Random	Random
Instrument accuracy	3c2a	Systematic	Systematic	Systematic	Systematic
Instrument repeatability	3c2b	Random	Random	Random	Random
Intercept	3c3a	Systematic	Systematic	Systematic	Quasi-systematic
Slope	3c3b	Systematic	Systematic	Systematic	Quasi-systematic

The results from this assessment were used to evaluate the behaviour of the NO_2 uncertainty over different reporting timescales. Figure A3 shows a breakdown of uncertainty for means containing different numbers of months for standard PDT tubes while Figure 4 shows the same breakdown for tubes which have a modification intended to reduce the effect of wind on measurements. For the standard tube the contribution to uncertainty from wind bias dominates and does not reduce and as other random effects are reduced it dominates even more, limiting the how much multiple measurements can reduce the uncertainty of the mean. The modified tubes however have a much lower wind bias uncertainty so there is much more reduction in the total uncertainty for means of several months. Because the uncertainty contributions are considered as relative uncertainties then high measurements in the later months included to cause the total uncertainty to increase slightly, although this effect is less apparent for the modified tubes.

When PDT were deployed alongside modified tubes at sites with reference instruments, allowing the uncertainty of the annual mean to be calculated using statistical methods, the annual mean uncertainty was found to be higher than that from the method described above [23]. This was particularly the case for modified tubes and sheltered PDT. These calculated uncertainties are shown in Table A6. This is possibly because of overestimating the reduction in the wind effect in these circumstances. It could also be because of underestimating another uncertainty element or overlooking a source of uncertainty.

Table A6 The annual mean and annual mean uncertainties calculated using the model and statistical method for all tube types deployed alongside reference instruments at 4 UK sites [23]

Tube type - Mounting	**Tube mean / µg m^{-3}**	***U*(model) *k* = 1 / µg m^{-3}**	***U*(stat) *k* = 1 / µg m^{-3}**
PDT-Unsheltered	30.12	5.66	6.50
PDT-Sheltered	20.05	1.31	3.42

Modified PDT-Unsheltered	25.16	0.99	3.03
Modified PDT- Sheltered	18.39	0.73	2.59

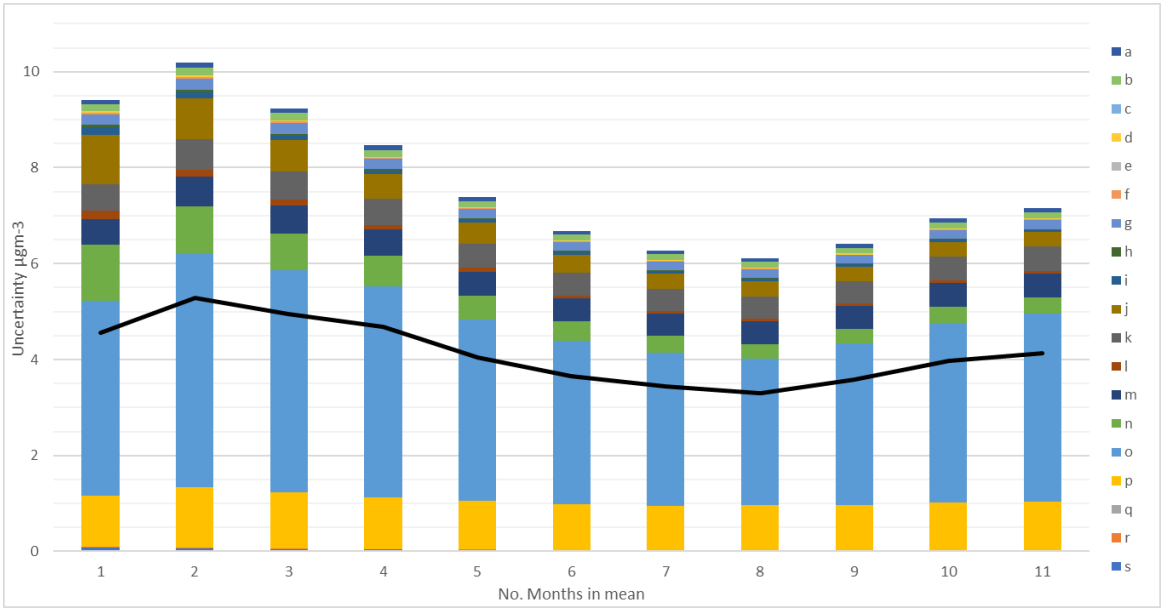


Figure A3 The value of individual uncertainty elements for 1 month mean to 11 month mean for unsheltered PDT tubes at a monitoring site in Honor Oak Park, London. As calculated using the uncertainty model. Where the different uncertainty contributions are from a) the calibration curve, b) possible chemical drift in the tube, c) repeatability of the spectrophotometer used to measure absorbed nitrates, d) accuracy of the spectrophotometer, e) final dilution of calibration standards, f) transfer of stock calibration solution, g) the stock solution certified concentration, h) diamine and nitrate reaction, i) the process of extracting nitrate from the tube, j) temperature variability over tube deployment, k) modelled temperature over tube deployment, l) relative humidity variability over tube deployment, m) modelled relative humidity over tube deployment, n) wind variability over tube deployment, o) wind bias over tube deployment, p) repeatability of tube measurement in stable conditions, q) variation in length of sampling time, r) tube dimensions, s) the solution used to coat the mesh in the tube. The black line represents the total combine uncertainty.

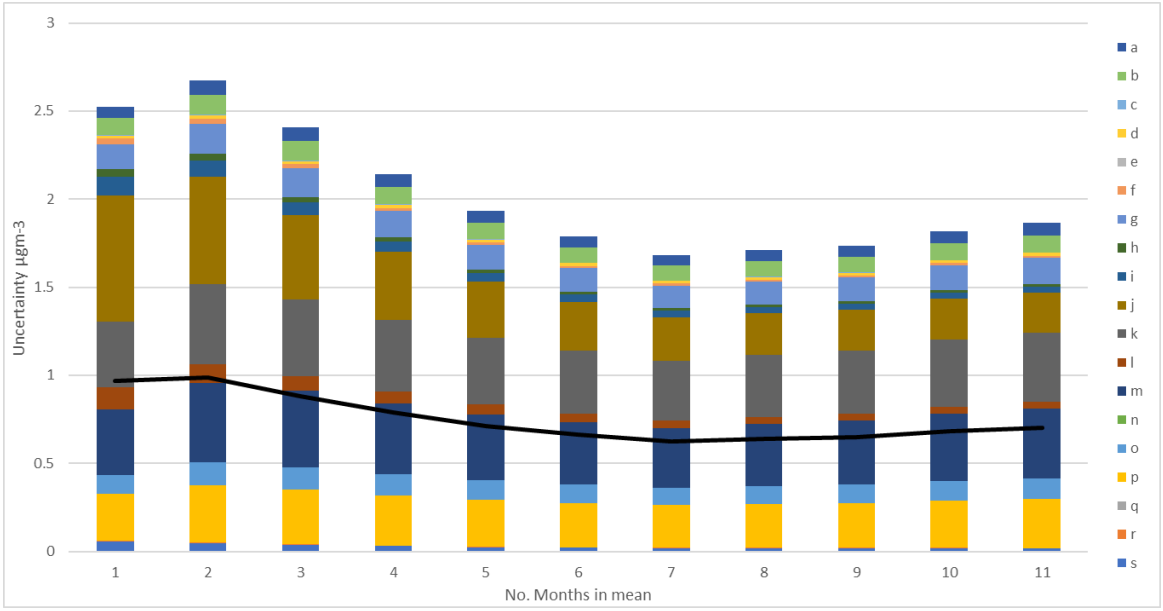


Figure 4 The value of individual uncertainty elements for 1 month mean to 11 month mean for unsheltered tubes which have been modified to reduce the wind effect at the Honor Oak Park

site as calculated using the uncertainty model. Where the individual uncertainty elements are the same as in Figure A3 and the black line represents total combined uncertainty.

12.8 CASE STUDY CONCLUSIONS

This case study presented the product traceability and uncertainty information for nitrogen dioxide (NO_2) measurements using diffusion tubes, in accordance with appropriate methodology recently developed under the Clean Air project premisses. Sources of traceability and relevant elements contributing to the uncertainty of measurement have been evaluated, mostly derived from globally recognised community standards and peer-reviewed publications. The results of the study estimated the product expanded uncertainty in good agreement with current air quality guidelines and state-of-the-art body of knowledge on the subject, considering such diffusive samplers are intended for indicative measurements. The study also addressed interpretations on the main uncertainty components, prediction of uncertainty behaviour over different timescales and recommendations for improvements. However, when comparing uncertainties of annual means calculated using this and alternative methods the uncertainty was much smaller for tubes modified to reduce wind bias effects than expected. Further work is recommended on examining the source of this discrepancy and also on evaluating the uncertainty arising from the bias adjustment factors in the UK.

12.9 CASE STUDY REFERENCES

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13 ANNEX B – TERMINOLOGY GLOSSARY

In the 'glossary' below, a few important words are explained. Precise or rigorous definitions are not given here. They can be found elsewhere, for example in the International Vocabulary of Basic and General Terms in Metrology[2]. A useful and correct set of definitions can also be found in UKAS publication M 3003 The Expression of Uncertainty and Confidence in Measurement.

accuracy - closeness of the agreement between a measurement result and true value of that measurand. (Accuracy is a qualitative concept only and is not given a numerical quantity value. It is often misused as uncertainty or precision.)

bias (of a measurement) – estimate of a systematic measurement error

bias (of a measuring instrument) – systematic error of the indication of a measuring instrument

calibration – operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication. In other words, the comparison of an instrument against a reference or standard, to find any errors in the values indicated by the instrument. In some cases, calibration assigns a relationship between the input and output of an instrument; for example, calibration of a resistance thermometer could relate its output (in ohms) to an input temperature (in degrees Celsius, or in kelvins).

confidence level – number (e.g. 95 %) expressing the degree of confidence in a result

correction (calibration correction) – compensation for an estimated systematic effect. A number added to an instrument reading to correct for an error, offset, or bias. (Similarly, a reading may be multiplied or divided by a correction factor to correct the value.)

correlation – interdependence, or relationship, between data or measured quantities

coverage factor – number larger than one by which a combined standard measurement uncertainty is multiplied to obtain an expanded measurement uncertainty, for a particular level of confidence

error – measured quantity value minus a reference quantity value. The offset or deviation (either positive or negative) from the correct ('true') value

estimated standard deviation – estimate of the standard deviation of the 'population' based on a limited sample

expanded uncertainty – product of a combined standard measurement uncertainty and a factor larger than the number one. Standard uncertainty (or combined standard uncertainty) multiplied by a coverage factor k, to give a particular level of confidence

Gaussian distribution – (See normal distribution)

influence quantity – quantity that, in a direct measurement, does not affect the quantity that is actually measured, but affects the relation between the indication and the measurement result.

interval (confidence interval) – interval containing the set of true quantity values of a measurand with a stated probability, based on the information available. The margin within which the ‘true value’ being measured can be said to lie, with a given level of confidence

level of confidence – number (e.g. 95 %) expressing the degree of confidence in the result

mean – arithmetic mean of a set of numbers

measurand – quantity intended to be measured. The particular quantity subject to measurement

normal distribution – distribution of values in a characteristic pattern of spread (Gaussian curve) with values more likely to fall near the mean than away from it

operator error – a mistake

precision – closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions. A term meaning ‘fineness of discrimination’ but often misused to mean ‘accuracy’ or ‘uncertainty’. Its use should be avoided if possible.

random error – component of measurement error that in replicate measurements varies in an unpredictable manner. An error whose effects are observed to vary randomly.

range – absolute value of the difference between the extreme quantity values of a nominal indication. The interval difference between the highest and the lowest of a set of values

reading – value observed and recorded at the time of measurement

rectangular distribution – distribution of values with equal likelihood of falling anywhere within a range

repeatability (of an instrument or of measurement results) – condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time. The closeness of the agreement between repeated measurements of the same property under the same conditions.

reproducibility (of an instrument or of measurement results) – condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects. The closeness of the agreement between measurements of the same property carried out under changed conditions of measurement (e.g. by a different operator or a different method, or at a different time)

resolution – smallest change in a quantity being measured that causes a perceptible change in the corresponding indication. (e.g. a change of one (1) in the last place of a digital display)

result (of a measurement) – set of quantity values being attributed to a measurand together with any other available relevant information. The value obtained from a measurement, either before or after correction or averaging

sensitivity – quotient of the change in an indication of a measuring system and the corresponding change in a value of a quantity being measured. The change in response (of an instrument) divided by the corresponding change in the stimulus

standard deviation – a measure of the spread of a set of results, describing how values typically differ from the average of the set. Where it is not possible to obtain an infinite set of results (in practice it never is) we instead use the estimated standard deviation.

standard uncertainty – measurement uncertainty expressed as a standard deviation.

systematic error – component of measurement error that in replicate measurements remains constant or varies in a predictable manner. A bias or offset (either positive or negative) from the correct value

true value – quantity value consistent with the definition of a quantity, i.e. the value that would be obtained by a perfect measurement

Type A evaluation of uncertainty – evaluation of a component of measurement uncertainty by a statistical analysis of measured quantity values obtained under defined measurement conditions.

Type B evaluation of uncertainty – evaluation of a component of measurement uncertainty determined by means other than a Type A evaluation of measurement uncertainty

uncertainty budget – statement of a measurement uncertainty, of the components of that measurement uncertainty, and of their calculation and combination

uncertainty of measurement – non-negative parameter describing the dispersion of the quantity values being attributed to a measurand. Alternatively described as a quantity representing the doubt in result of a measurement.

uniform distribution – distribution of values with equal likelihood of falling anywhere within a range

validation – the process of assessing, by independent means, the quality of the data products derived from the system outputs