A review of biases in the measurement of ambient nitrogen dioxide (NO_2) by Palmes passive diffusion tube

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Summary

Palmes-type passive diffusion tubes (PDTs) are widely used in air quality assessment and management to measure concentrations of NO_2. It is well-known that the accuracy (or bias) of a PDT measurement may by influenced by a range of factors in all stages of the PDT method: preparation, exposure conditions, quantification of absorbed nitrite and calculation of the NO_2 concentration. The state of knowledge on these biases was reviewed around 2007-8 when Defra established a Working Group to recommend harmonisation procedures for the NO_2 PDT methodology in the UK. The purpose of the current review is to provide a comprehensive update on the understanding of sources and extent of potential biases in the NO_2 PDT method. The key conclusions are as follows.

The biases act independently of each other. Since the PDT-derived NO_2 concentration is the net summation of all (if any) individual positive and negative biases that influence all aspects of that PDT deployment, it is very difficult to disentangle the relative contributions of different sources of bias, particularly in ambient deployments.

PDT preparation and analysis

- A dearth of new evidence means it is still unclear whether method of preparation has significant influence on PDT accuracy. The corollary is that no new evidence contradicts the Defra WG recommendation that preparation via dipping grids in 50% TEA in water or pipetting 50 µL of 20% TEA in water have least bias. In principle, it should not matter how the TEA is transferred to the grids as long as sufficient TEA is permanently transferred for the TEA to be greatly in excess of the NO_2 to be captured, which should generally be the case.
- The complete absence of published evidence on effect of colour reagent conditions for the colorimetric quantification of absorbed NO_2^- means that no update can be provided. It must be assumed that where a high standard of laboratory QC/QA procedures is maintained, particularly where laboratories are subject to regular 'round robin' and other external quality assurance procedures, the extraction and quantification of the absorbed NO_2^- should not contribute a significant source of bias.

Effect of humidity on stoichiometric conversion of NO_2 to NO_2^-

- The potential for low ambient humidity during deployment to cause negative bias in TEA-based NO_2 passive samplers is not sufficiently acknowledged by users of PDTs. A recent study has argued that for relative humidity (RH) less than ~75-80% the conversion of NO_2 to NO_2^- is less than unity, and hence concentrations calculated under the assumption that all NO_2 was converted to NO_2^- are biased low. For much of the UK, average RH is around 80%, but there are locations around the UK and/or substantial periods during the year when RH during a PDT exposure is lower than 75% and hence potentially giving rise to negative bias (or 'under-read') from this cause.

Effect of wind speed, humidity and temperature on uptake rate

- Both chamber and field experiments still provide some contradictory results on the significance of wind effects on Palmes-type PDTs, but it seems clear from consideration of all the literature to date that positive bias from wind effects exists and can be very large, albeit that the extent of sensitivity of the bias to increasing wind speed is not clear. Under even moderate wind conditions, a number of chamber and field experiments suggest 50% or greater positive bias. Close inspection of data across

a number of chamber experiments suggests some consistency for an overestimation of the order of 20% compared with the theoretical uptake rate even at the lowest wind speeds that will be routinely encountered in ambient deployments– however, as noted below, this could be due to the assumed value of diffusion coefficient, rather than wind effects (or both).

- Results from chamber experiments show that lower RHs reduce quantitative performance of PDTs, which is consistent with the observation described earlier of low RH reducing stoichiometric conversion of NO_2 to NO_2^-.
- Of the three meteorological variables, the evidence suggests that sensitivity of PDT uptake rate is smallest for temperature, of the order of a few % per 10°C. Temperature influences the rate of NO_2 diffusion (this is a known, relatively small effect), the RH, and potentially also the physical phase of the TEA, although the latter is not believed to be important for ambient conditions. Due to the link between temperature and RH, it is possible that effects attributed to temperature may be through its effect on RH.
- It is difficult to pinpoint the individual effects of these factors on bias because the bias between a PDT and a reference analyser values may be the net effect of several potential factors acting together, e.g. wind, humidity, within-tube chemistry, long-term degradation of absorbed NO_2^-. This is particularly the case for field evaluations where PDT exposures can vary between a few days to 5 weeks, and which are subject to varying environmental conditions during exposure that are usually not measured, or measured a long way from the PDT deployments.
- An alternative explanation for chamber exposure data that suggest positive bias compared with the theoretical uptake rate, even at low wind speeds, is that an inappropriate value for the diffusion coefficient of NO_2 in air is being used for the theoretical uptake rate – one that is too low and consequently has the effect of giving rise to a positive bias in derived average NO_2 concentration. This has not been discussed in the literature (but is discussed separately below).
- Considerable accumulated evidence indicates that positive bias from wind effects can be offset either by use of a coarse mesh across the tube and/or with the tubes placed within a shelter. Membranes across the mouth of the tube may overcompensate for wind-induced positive bias by providing resistance to free molecular diffusion and reducing uptake below its theoretical value derived from Fick's first law of diffusion. At present local and national network NO_2 PDTs in the UK are not deployed with either meshes or protective shelters.

Within-tube chemical generation of additional NO_2

- Model simulations clearly demonstrate potential for intrinsic positive bias from additional NO_2 produced from reaction between NO and O_3 also diffusing within the tube. For locations where both NO and O_3 are relatively high compared with NO_2 (e.g. urban background) the simulations indicate this positive bias can average as high as ~25%. For roadside locations, where O_3 may be low, and for rural locations where most NO_x is already in the form of NO_2, this bias may be only a few %.
- Experimental validation of a chemical bias is again complicated by the presence of other potential biases (wind and humidity effects, long-term absorbent degradation) that simultaneously impact on PDT performance.

Exposure-duration 'loss' of absorbed NO_2^-

- Although the evidence is sparse, it is consistent that there may be a small negative bias in PDT-derived NO_2 concentrations associated with a slow chemical degradation of the absorbed NO_2^-, of a few % per week, particularly in sunnier, warmer conditions, which becomes more relevant for exposure durations of several weeks.

Uncertainty in the value of the NO_2 diffusion coefficient

- The original Palmes value for the NO_2 diffusion coefficient (temperature corrected for the UK) has been used in all subsequent PDT measurements seemingly without further question. The value was derived from semi-empirical theoretical consideration of gas behaviour because it is very hard to measure experimentally. The one experimental value (from 1937) is a factor 0.89 of the Palmes value. Although semi-empirical methods for estimation of gas diffusion coefficients are well-established, a more recent calculated value is a factor 1.20 of the Palmes value.
- The greater PDT uptake rates measured in some chamber experiments compared with uptake rates derived using the theoretical equation ($A.D/L$) could be explained if D was greater than the standard Palmes value used. However, it is difficult to control for all variables that may influence uptake experimentally, even in a chamber study. If the true value of D was larger than the Palmes value currently used then NO_2 concentrations currently calculated from PDT measurements are positively biased compared with the true NO_2 concentrations, i.e. PDT-derived values would be positively biased (and vice versa).
- There should be much greater acknowledgement that the value for D is not known with certainty, and particularly that it is not known to the precision implied by use of a value expressed to 3 significant figures. One evaluation suggests an uncertainty in D of ±35%. This does not mean random uncertainty across individual PDT exposures in the range ±35%, because D has a single true value; instead it means that collectively all PDT-derived NO_2 values may be a certain (unknown) percentage too high or a certain percentage too low. It is important to note, however, that this particular potential source of PDT bias is not an issue for PDTs that are 'bias adjusted' against a chemiluminescence analyser, since if this was the only source of PDT bias at all PDT exposure locations, including the co-location, then it would be accounted for through the bias adjustment factor.

Bias in comparison against a reference analyser determination of NO_2

- PDT bias is assessed by co-location with chemiluminescence analysers. PDT values calculated using the Defra WG recommended value for D (which assumes an average ambient temperature of 284 K) must be decreased by a factor 284/293 = 0.969 to compare against a chemiluminescence analyser that has been set up to report NO_2 concentrations referenced to the EU reporting temperature of 293 K. Failure to make this adjustment means the PDT-derived value in the comparison is ~3% too high.
- Chemiluminescence analysers using a heated molybdenum NO_x-to-NO converter (as is usually the case in the UK) are subject to positive bias in NO_2 measurement from HNO_3, HONO and PAN also present in the air. The bias is much lower (e.g. a few %) for locations close to fresh emissions of NO_x, such as roads, compared to locations with more photochemically-aged air. Bias between a 'thermal converter' chemiluminescence analyser and co-located PDT due to this issue would be offset if the other oxidised N-containing gases also gave rise to absorbed NO_2^- in the PDT, but this has not been tested.
- Analyser values may be uncertain by up to ±15%, as set out in the EU Directive for these measurements.

Contents

1. The Palmes passive diffusion tube methodology

Local Authorities in the UK continue widely to use Palmes-type passive diffusion tubes (PDTs) (Palmes et al., 1976) to provide spatial assessment of NO_2 concentrations, taking advantage of the sampler's simplicity and lack of power and infrastructure requirement, albeit that it has greater uncertainty than a chemiluminescence monitor. Since at most locations attainment of the annual average objective for NO_2 is more stringent than attainment of the hourly average objective, the inherent long averaging time for PDT measurements is not a disadvantage. Many thousands of NO_2 PDT measurements are made annually in the UK to support assessment of objective compliance and mitigation effectiveness.

A feature of the tube geometry of the PDT compared with other passive sampler designs is that the large ratio of internal length L (typically 7.1 cm) to cross-sectional area A (typically 0.91 cm^2) of the diffusion path means that uptake rates should be minimally influenced by external factors that can perturb the diffusion gradient within the tube – most notably ambient wind, which can shorten the diffusion length. Consequently the exposure-averaged ambient concentration can be obtained directly from theoretical considerations without calibration. A disadvantage of the high L/A ratio of the tube geometry is the comparatively low NO_2 uptake rate. Hence PDTs for ambient measurement are typically exposed for 1-5 weeks at a time.

The PDTs used in the UK are usually made of transparent acrylic. The triethanolamine (TEA, $N(CH_2CH_2OH)_3$) reagent used as the absorbent is coated on two stainless steel grids at the internal end. The TEA is assumed to be 100% efficient at facilitating the 1:1 stoichiometric conversion of NO_2 molecules into nitrite (NO_2^-) ions.

After exposure, the NO_2^- in the TEA absorbent is extracted into a known volume of water and quantified either directly by ion chromatography or by a colorimetric procedure. The latter involves adding solutions of sulphanilamide (at acid pH) and N-1-naphthyl ethylene diamine dihydrochloride (NEDD) to form a pink-purple-coloured azo dye whose absorbance intensity (measured at a wavelength of 540 nm) is proportional to the NO_2^- concentration in the extracted solution.

The average NO_2 in the air at the open end of the tube during the exposure is then calculated from the following equation where Q is the total amount of collected NO_2^-, t is the duration of the exposure, and D is the diffusion coefficient for NO_2 in air.

$$[\mathrm{NO_2}]_{\mathrm{av}} = \frac{QL}{ADt}$$

2. Summary of sources of potential bias in PDT methodology

It has long been recognised that a range of factors may influence the precision and accuracy (or bias) of NO_2 concentration derived by the PDT methodology, and the EU Directive on air quality permits an overall measurement uncertainty of ±25% for this method compared with the permitted measurement uncertainty of ±15% for the chemiluminescence analyser method (EC Directive, 2008).

Uncertainties in the PDT methodology may arise at every stage of the method, including the preparation of the PDT prior to exposure, the exposure, the quantification of the absorbed NO_2^- and the calculation of the exposure-average NO_2 concentration.

A summary of potential sources of bias (i.e. inaccuracy) in the PDT methodology is given in Table 1. All these biases should act independently (apart from any relationship between T and relative humidity (RH)). Therefore the overall effect on PDT accuracy should be the net linear sum of any biases from individual contributing factors.

3. Summary of the understanding of NO_2 PDT bias at the time of the 2007 UK working group on harmonisation of NO_2 PDT methods

In 2007, Defra commissioned both a review of factors potentially influencing NO_2 PDT performance, subsequently published in the peer-reviewed literature as Cape (2009), and a Working Group (WG) to make recommendations on harmonisation of NO_2 PDT methods in the UK (Defra WG, 2008). The recommendations of the WG were to be adopted from January 2009 by all UK local and national authorities reporting NO_2 concentrations derived from PDTs.

In addition to providing recommendations on PDT methods that the WG evaluated as providing greatest accuracy, a secondary aim of recommending harmonised protocols was to reduce the magnitude of inter-laboratory variation.

The following is a summary of the understanding of PDT bias at the time of the WG's harmonisation recommendations. Details are contained in Defra WG (2008) and Cape (2009).

3.1 Preparation

The WG noted variability in conclusions of studies investigating the impact on bias of the choice of solvent for TEA (acetone or water), proportion of TEA in the solvent (10, 20 or 50%) and method of application of the solution to the grids (dipping or pipetting). Interpretation of these studies is confounded by other sources of bias that may differentially contribute in different studies to the closeness of PDT values to reference concentrations (for example, duration of exposure, protection or not from wind, ambient humidity, within-tube chemistry). The WG recommended that the grids should be prepared either by dipping the grids in a solution of 50% TEA in acetone or by pipetting 50 μL of a solution of 20% TEA in water directly onto grids placed in the cap.

A shelf life of the sampling substrate of up to 2 years was noted (from Kirby et al., 2000).

3.2 Exposure

In all likely ambient PDT deployments the amount of TEA will be in large excess to the NO_2 captured, so negative bias arising from saturation of the absorbent is not considered to be an issue. For example, preparation with 50 μL of 20% TEA solution delivers ~70 μmol TEA, whilst the amount of NO_2 absorbed in a 4-week exposure with an average ambient concentration as high as 100 µg m^{-3} is only ~0.1 µmol.

Any potential impact of co-pollutants such as HONO, PAN, particulate nitrite or SO_2 (the latter causing change of acidity at the absorbent) on the PDT methodology are considered negligible given the much lower concentrations of these species relative to NO_2 in all but exceptional circumstances.

The WG noted evidence for potential positive bias due to additional within-tube production of NO_2 from reaction between co-diffusing NO_2 and O_3, and evidence for potential positive bias from wind-induced turbulence at the entrance of the tube leading to an effective shortening of diffusion path from that assumed when using the physical length of the tube. However, the WG did not recommend that PDTs should be exposed in a shelter or with any form of mesh or membrane across the open end of the tube, and NO_2 PDTs in the UK continue to be exposed without such meshes/membranes or shelters. The WG acknowledged there was evidence that shelters or meshes may improve precision and reduce bias but that further research was necessary. The WG also did not recommend a particular tube material, stating only that PDTs should be made of translucent colourless acrylic or polypropylene plastic. The WG did, however, state that a spacer block of at least 5 cm must be used between a tube and the adjacent surface and exposures should avoid locations of higher than usual turbulence such as the corner of a building.

Studies demonstrating variable effects of temperature and relative humidity during exposure on NO_2 uptake rate were noted by the WG, but they also noted that where correction algorithms had been developed the need for localised meteorological data precluded their practical application. Ambient humidity may have impact through the need for hydration of the TEA to ensure the stoichiometric conversion of NO_2 as NO_2^-, which is assumed to occur via the following reaction.

$$2NO_2 + N(CH_2CH_2OH)_3 + 2OH^- \rightarrow 2NO_2^- + {}^-O{-}^+N(CH_2CH_2OH)_3 + H_2O$$

The review by Cape (2009) concluded that a minimum of around 3 g H_2O m^{-3} is required for TEA to be effective as the NO_2 absorbent, and that this was unlikely to be a problem in UK conditions except in very cold dry weather.

3.3 Quantification of absorbed nitrite

For the colorimetric analytical approach, the WG recommended the following procedures. The sulphanilamide and NEDD solutions should be prepared and stored separately. The solution concentrations are prepared so that a 1:1 ratio of the two solutions yields a sulphanilamide:NEDD ratio of 1: 7×10^{-3}, i.e. 7×10^{-3} g of NEDD present per 1 g of sulphanilamide, which may also be expressed as 0.7% NEDD:sulphanilamide or 140:1 sulphanilamide:NEDD. Typically, the individual sulphanilamide and NEDD solutions are prepared at concentrations of 20 g L^{-1} and 140 mg L^{-1}, respectively, if analysing samples manually, or 10 g L^{-1} and 70 mg L^{-1}, respectively, if analysing samples using an automatic analyser. (Lower sulphanilamide:NEDD ratios down to 10:1 have been reported in the literature.) For manual analysis the required quantity of mixed reagent is prepared by mixing the two solutions in a 1:1 ratio immediately prior to use. For automatic analysis methods, solutions are used separately or pre-mixed depending on the nature of the instrumentation. Once mixed, the colour reagents should be used the same day, not stored.

For the extraction step in a manual analysis, typically 3.0 mL of the pre-mixed reagent solution is added to each tube. For the extraction step in an automatic analysis, typically 3.0 mL of 18 M Ω deionised water is added to the sample tube. In both instances extraction should be aided by use a vortex mixer for at least 15 s or a vibrating tray for 10-30 min, and solutions then left to stand for 10 min. The colour absorption should be measured within 2 h. In an automatic instrument the ratio of volumes of aqueous sample to reagents to be used is either 1:4 ratio of sample:pre-mixed reagents or 1:2:2 ratio of sample:sulphanilamide solution:NEDD solution. In both the manual and automatic methods the concentrations and volumes described above equate to absolute masses of 60 mg sulphanilamide and 0.42 mg NEDD relative to the absolute mass of absorbed nitrite in a given sample tube.

The WG also emphasised the need for standard analytical chemistry laboratory quality control procedures such as regular calibration of balances and pipettes. The production of the NO_2^- calibration curve should comprise four to six different NO_2^- standards including zero, and cover the full concentration range likely to be encountered in the samples.

3.4 Calculation of NO_2 concentration and comparison to chemiluminescence analyser

The value of *D* originally recommended by Palmes et al. (1976) was 0.154 $cm^2 s^{-1}$. This is the value for a temperature of 293 K. Based on the temperature-dependent expression for *D* reported by Massman (1998) (*T*-dependence of 1.81 on the ratio of temperatures in kelvin), the WG recommended that from 2009 the value for UK PDT measurements be changed to $D = 0.146 cm^2 s^{-1}$ which assumes the average ambient temperature during sampling is a more realistic 284 K. The WG also noted that since the EU reporting temperature for mass concentration values is 293 K, when PDT data are to be compared with air quality objectives or reference chemiluminescence analyser data, the PDT values need to be decreased by a factor 284/293 = 0.969.

Although the WG report does not specifically state this, the direct use of a value of $D = 0.151 cm^2 s^{-1}$ in the PDT equation has the simultaneous effect of satisfying the assumption that the average temperature during sampling is 284 K, and of correcting the derived ambient NO_2 mass concentration to 293 K.

Where UK PDT studies use the original Palmes et al. (1976) value of $D = 0.154 cm^2 s^{-1}$, the concentrations will have an intrinsic positive bias of 0.154/0.151 = 2% when compared with reference analyser data adjusted to 293 K. The positive bias will be smaller (greater) if the PDT measurements are conducted in localities where the average temperature is higher (lower) than 284 K. There will be no bias from the use of $D = 0.154 cm^2 s^{-1}$ if ambient temperature during the exposure is 293 K.

All the above assumes there is no intrinsic error in the recommended value of *D*.

The WG required that PDTs in co-location studies with chemiluminescence analysers must be located within 1 m of the analyser inlet and at the same distance from the road edge.

When comparing PDT data to chemiluminescence analyser data it must be remembered that even when analysers are operated to the EU Data Quality Objective an overall uncertainty of ±15% is permitted (EC Directive, 2008).

4. The JRC Scientific and Technical Report EUR23793: Review of the application of diffusive samplers in the European Union for the monitoring of nitrogen dioxide in ambient air

More-or-less in parallel with the UK Working Group on NO_2 measurement by passive diffusion tube (Defra WG, 2008; Cape, 2009), a European Union Working Group (that included some overlap of membership) also reviewed the performance of diffusive samplers for measurement of ambient NO_2. The report, published in 2010 (Hafkenscheid et al., 2010), indicates that the EU Working Group was primarily focused on whether the Palmes PDT methodology in its usual implementation was capable of delivering NO_2 concentrations within an 'indicative measurement' uncertainty range (±25%), which they concluded it was, rather than on a forensic analysis of sources and magnitudes of individual biases. However, consistent with the Defra WG, the EU Working Group did note evidence that (i) use of protective shelters or barrier-capped tubes could improve PDT precision and comparability against chemiluminescence analysers, and (ii) at urban sites, where unprotected open tubes were used, there was tendency for overestimation of NO_2 concentrations.

5. Updates to understanding of NO_2 PDT bias from a review of literature since 2007

A search of published literature referring to NO_2 measurement by passive sampler was undertaken in February 2018 using Web of Science, Google Scholar and Google. The primary aim was to identify relevant literature published since 2007, the date of formation of the Defra NO_2 harmonisation working group (Defra WG, 2008) and its associated literature review (Cape, 2009). However, the search also extended back to the early 1990s to check for any earlier relevant literature that may have been missed previously or that benefits from re-examination in the light of subsequent research findings.

The focus of the search was on studies relating to the Palmes-type diffusion tube, but literature reporting work with other designs of passive sampler for measurement of NO_2 was also examined for information relevant to potential bias in the PDT methodology.

This review discusses only information relating to PDT bias. Other publications report applying PDTs to measure concentrations of NO_2 in outdoor or indoor air but do not include any data or commentary on potential bias issues.

For potential sources of PDT biases not explicitly discussed in this section there is no change from the understanding at the time of the Defra Working Group described above (Section 3). This applies, for example, to understanding on the potential biases from co-pollutants, or from saturation of the absorbent by NO_2 during exposure.

5.1 PDT preparation and analysis

No literature published subsequent to the Defra WG review has reported systematic investigation of potential biases arising from the preparation and post-exposure NO_2^-

quantification of standard Palmes-type PDTs. In addition, whilst some studies with PDTs state the method of preparation, in particular the solvent and %TEA, almost no publication provides any detail on the NO_2^- extraction and the sulphanilamide and NEDD reagent conditions used. It is therefore also not possible to indirectly look for any associations between PDT performance and PDT preparation and analysis approaches.

Information from the following two studies was not openly published at the time of the WG's formation although their findings contributed to the WG's recommendations for a 50% TEA in acetone dipping preparation method and a 50 μL 20% TEA in water pipetting method.

Heal (2008) was undertaking a statistical evaluation of the effect of absorbent grid preparation method using a dataset of 680 duplicated PDT exposures spanning 146 separate exposure periods, spread over five urban exposure locations in Edinburgh and a number of years. Laxen et al. (2008) were undertaking a similar 'meta-analysis' of PDT preparation and analysis variables using data from 161 co-location studies carried out by UK Local Authorities in the years 2003-2005. The dataset incorporated a range of preparation and analysis approaches spread across 21 laboratories. The Heal (2008) evaluation concluded that both PDT precision and accuracy (as quantified by maximum concentration across a set of co-located preparation methods) were both significantly better, on average, when the PDT grids were prepared by dipping the grid in TEA solution, and that neither solvent or % TEA used for the dipping solution were important. Where PDT preparation by pipetting TEA solution onto grids was used, better performance was obtained using 20% TEA in water. The Laxen et al. (2008) evaluation similarly concluded that there was some evidence that dipping of grids in TEA solution provided better performance than pipetting of TEA solution onto grids, and that, for the former approach, there was a clear pattern that PDTs prepared with grids soaked in TEA solution for 10 min or more performed better than tubes with grids soaked in solution for less than 1 min. There was also clear pattern that allowing the grids to dry before final tube assembly was associated with better performance. They also concluded that there was a clear pattern that tubes prepared using 20% TEA in water performed better than those prepared using 50% TEA in acetone, despite the evidence that preparation by dipping (which usually uses 50% TEA) yielded better performance than preparation by pipetting. However, the authors point out that by the nature of their 'observational' study it was difficult to separate potential influence of different factors since there was incomplete data on all possible combinations of variables.

Loader et al. (2011) investigated the effects of implementation of the PDT method harmonisation by reviewing laboratory results in the quarterly WASP (Workplace Analysis Scheme for Proficiency) test of analytical proficiency in the analysis of artificially nitrite-spiked diffusion tubes and in the on-going field intercomparison at London Marylebone Road. It was concluded that there was no clear improvement overall coincident with the switch to harmonised methods, but no deterioration either, although precision had improved for the worst-performing laboratories over the time period investigated. It was acknowledged that data only until July 2010 were examined, which was only about 18 months after the January 2009 date by which laboratories supplying and analysing PDTs were required to implement the harmonisation methods.

In work published since the WG report, Tarvydaitė and Kazlauskienė (2014) investigated use of three different absorbents, but in a custom-built passive sampler for NO_2 with a geometry part-way between tube and badge, comprising a polypropylene tube 34 mm in length and 21 mm in inner diameter. Preparations of 10% TEA in water, 10% TEA in acetone, and a solution of potassium iodide (KI) with sodium hydroxide (NaOH, to enhance the capture of the acidic NO_2) were deployed in Vilnius, Lithuania. The absorbent was held on stainless steel grid for the first two solutions and glass fibre filter for the third. The authors report that only the preparations with 10% TEA in water or acetone yielded uncertainty within the 25% requirement of the EU Directive. The finding is consistent with the current recommendation to use stainless steel grids.

As part of a general evaluation of custom-built tube-like passive samplers for NO_2, Bootdee et al. (2012) evaluated extraction and analysis of NO_2^-. Their samplers comprised either a polyethylene tube (5.4 cm long and 1.4 cm i.d.) or polypropylene tubes (5.3 cm long, 1.3 cm i.d. or 7.7 cm long, 1.6 cm i.d.), with 50 μL of 20% TEA in water applied to either glass fibre or Whatman filters. The authors investigated extraction times and colour reagent development time in the range 5-25 min and reported optimum times of at least 15 min, yielding 94 ± 3 % recovery. This finding is consistent with current understanding.

Vardoulakis et al. (2009) reported a 98% extraction efficiency of NO_2^- in their field study.

5.1.1 Conclusions – PDT preparation and analysis

A dearth of new evidence means it remains unclear whether method of preparation has significant influence on PDT accuracy. Experimentally, interpretation of influence of preparation is confounded by other potential sources of bias (for example, length of exposure, protection or not from wind, ambient humidity, within-tube chemistry, etc.) that may influence assessment of PDT accuracy via closeness of PDT values to reference concentrations. Scientific intuition, however, is that it should not matter how the TEA is transferred to the grids as long as sufficient TEA is permanently transferred for the TEA to be greatly in excess of the NO_2 to be captured, which should generally be the case. In conclusion, there is no new evidence to contradict the Defra WG recommendation that preparation via dipping grids in 50% TEA in water or pipetting 50 μL of 20% TEA in water have least bias.

The complete absence of published evidence on effect of colour reagent conditions means that no update can be provided. However, it has to be assumed that where a high standard of laboratory QC/QA procedures is followed (including, for example, regular calibration of balances and pipettes and appropriate number and range of NO_2^- standards), and particularly where laboratories are subject to regular 'round robin' and other external quality assurance procedures, the quantification of the trapped NO_2^- should not contribute a significant source of bias.

5.2 Exposure conditions – variability in ambient NO_2 concentrations

A potential source of PDT uncertainty revealed in this literature review not previously mentioned in earlier reviews concerns the impact of the breakdown of the assumption of a time-independent linear concentration profile along the tube that underpins (through Fick's first law of diffusion) the standard equation used to calculate exposure-average NO_2 concentration. Plaisance (2004) theoretically analysed the response of PDT uptake to fluctuating ambient concentrations using a mathematical methodology defined by Hearl and Manning (1980) to resolve Fick's second law of diffusion. The paper details the equations used in this theoretical approach and then applies the methodology to various patterns of concentration variations encountered in outdoor environments. The errors of the Palmes tube are computed numerically for different characteristics of the concentration variation such as the peak duration and the ratio of the peak amplitude to the background concentration.

5.2.1 Conclusions – variability in ambient NO_2 concentrations

Although fast fluctuations (of a few minutes) of high amplitude (for example, >200 $\mu g\ m^{-3}$) induce transient increases in PDT uptake compared with the standard equation that assumes a steady-state concentration profile down the tube, their contributions to the mean concentration estimated over a 14-day sampling time are negligible, less than a couple of % even under unlikely unfavourable conditions.

5.3 Exposure conditions: effect of humidity on stoichiometric conversion of NO_2 to NO_2^-

The review by Cape (2009) concluded that the availability of water was crucial to the way in which TEA reacts with NO_2. Absence of water yields N-nitroso-diethanol amine and no NO_2^-. Too much water (aqueous solution) yields NO_2^- and NO_3^- in equal amounts. Cape (2009) cited Palmes and Johnson (1987) who showed that a mole ratio of H_2O:TEA of around 3.6, which is the amount absorbed by TEA in equilibrium with ambient air at 75% RH and 26°C (18 g $H_2O\ m^{-3}$), provides 100% conversion of absorbed NO_2 to NO_2^-. Cape (2009) did not explore this further other than to conclude (using other evidence also) that a minimum of around 3 g $H_2O\ m^{-3}$ (equivalent to an RH of 35% at 5°C) is required for TEA to be effective and that this condition is normally readily met in the UK except in very cold, dry weather.

Poddubny and Yushketova (2013) have since incorporated what is known about the underlying chemistry between NO_2 and TEA into a theoretical model for calculating the expected stoichiometry of formation of NO_2^- from NO_2 reaction with TEA that is in equilibrium with ambient humidity. The key principles of their model are:
(1) NO_2 forms NO_2^- via the following accepted stoichiometric conversion reaction, only under the condition the TEA is hydrated.

$$2NO_2 + N(CH_2CH_2OH)_3 + 2OH^- \rightarrow 2NO_2^- + {}^-O{-}{}^+N(CH_2CH_2OH)_3 + H_2O$$

When the TEA is not hydrated the reaction of NO_2 does not form NO_2^- (the authors cite Aoyama and Yashiro (1983) who showed that reaction of NO_2 with non-aqueous TEA forms N-nitroso-diethanolamine $(CH_2CH_2OH)_2NNO$);
(2) conversion of NO_2 to NO_2^- is 100% with hydrated TEA;
(3) the fraction of hydrated TEA molecules depends on the humidity of the air at the time.

The authors also incorporate in their model the situation where all TEA is hydrated but there is insufficient TEA to react with all NO_2 and the excess NO_2 reacts (dissociates) with the excess water, for which the conversion of NO_2 to NO_2^- is 50%.

$$2NO_2 + H_2O \rightarrow 2H^+ + NO_2^- + NO_3^-$$

However, in all likely ambient PDT deployments the amount of TEA will be in large excess to the NO_2 captured.

The authors then evaluate the ratio of water to TEA required for full hydration of TEA and the relative humidity at which this is attained. (It is assumed it is not relevant if the TEA was initially applied in acetone since this solvent will readily evaporate and aqueous equilibrium of the TEA with ambient humidity rapidly established.) The authors cite Palmes and Johnson (1987) and Kirby et al. (2000) that the TEA in solution must be in protonated form (the proton deriving from dissociation of H_2O), which is consistent with the need for OH^- ions in the first reaction above, which must also derive from H_2O. So the minimum is one molecule of H_2O per conversion of NO_2 to NO_2^-. The authors further state that the ethanolic groups of the TEA also hydrate through hydrogen bond formation. Therefore the number of water molecules to hydrate one TEA molecule may vary between one and four, or possibly more. They cite experiments by Palmes and Johnson (1987) who report that at 26 °C and 75% RH the number is 3.6 (as cited also in the Cape (2009) review).

In their model, Poddubny and Yushketova (2013) denote the number of H_2O molecules required for hydration of one TEA molecule as β^*. Their calculation of the average concentration of NO_2 during an exposure uses the standard Fick's Law approach but with a step-wise summation over *j* time intervals τ_j (e.g. hourly intervals) with known values of RH and *T*, in each of which intervals there is an explicit inclusion of the stoichiometry of conversion of NO_2 to NO_2^-, represented by the term $k(f_j)$ in the following formula, where f_j represents the fraction RH in the interval. *m* is the mass of collected NO_2^-.

$$\bar{C} \approx \frac{m}{\frac{A}{L}\sum_{j=1}^{n} D(T_j)k(f_j)\,\tau_j}$$

The value for the conversion coefficient for NO_2 to NO_2^-, $k(f_j)$, depends as follows on whether β_j, the number of H_2O molecules present per TEA molecule in a time interval, is less than, equal to, or greater than β^*, the number of H_2O molecules required for exact full hydration of TEA.

$$k(f_j) = \begin{cases} \dfrac{\beta_j}{\beta^*}, & \text{for } \beta_j < \beta^* \\ 1, & \text{for } \beta_j \geq \beta^* \text{ and TEA well in excess of } \mathrm{NO_2} \\ \dfrac{1}{2}\left(1 + \dfrac{\beta^*}{\beta_j}\right), & \text{for } \beta_j > \beta^* \text{ and TEA not in excess of } \mathrm{NO_2} \end{cases}$$

In more detail, the three cases above correspond to the following situations.

(i) *Lack of water (partial hydration of TEA)*. A fraction of NO_2 reacts with hydrated TEA to form NO_2^- and the rest of the NO_2 reacts with non-hydrated TEA to form other products. The effective coefficient of conversion of NO_2 to NO_2^- (*k*) is proportional to the fraction of hydrated TEA:

$$k = \frac{N_{\mathrm{TEA-H2O}}}{N_{\mathrm{TEA}}} = \frac{N_{\mathrm{H2O}}}{\beta^* N_{\mathrm{TEA}}} = \frac{\beta_j}{\beta^*}$$

(ii) *Water:TEA mole ratio is equal to* β^*. In this case: $k = 1$.

(iii) *Excess water in the absorbent solution AND insufficient TEA present to react with all the* NO_2. A fraction of NO_2 reacts with hydrated TEA to form NO_2^- with 1:1 stoichiometry, and the rest of the NO_2 reacts with free water to form both NO_2^- and NO_3^- ions, i.e. a conversion to NO_2^- of 0.5. The overall coefficient for conversion of NO_2 to NO_2^- is:

$$k = 1\frac{N_{\mathrm{TEA-H2O}}}{N_{\mathrm{H2O}}} + 0.5\frac{(N_{\mathrm{H2O}} - N_{\mathrm{TEA-H2O}})}{N_{\mathrm{H2O}}} = \frac{1}{2}\left(1 + \frac{\beta^*}{\beta_j}\right)$$

In practice, the amount of TEA present should be well in excess of the amount of NO_2 being captured during an exposure, in which case $k = 1$ for all humidities for which $\beta_j > \beta^*$; i.e. at values of RH required for full hydration of TEA, and with excess TEA present, average NO_2 concentrations calculated from the passive sampling results using the standard approach and the new model are the same.

The authors use Raoult's Law to determine β_j. Assuming an ideal solution (and constant TEA amount), Raoult's Law gives

$$p_{\mathrm{H2O}} = \frac{N_{\mathrm{H2O}}}{N_{\mathrm{TEA}} + N_{\mathrm{H2O}}} p^0_{\mathrm{H2O}}$$

Re-arranging gives

$$\frac{N_{\mathrm{H2O}}}{N_{\mathrm{TEA}}} = \frac{\left({p_{\mathrm{H2O}}}/{p^0_{\mathrm{H2O}}}\right)}{1 - \left({p_{\mathrm{H2O}}}/{p^0_{\mathrm{H2O}}}\right)}$$

Therefore β_j is calculated from the RH via

$$\beta_j = \frac{N_{\mathrm{H2O}_j}}{N_{\mathrm{TEA}}} = \frac{f_j}{1 - f_j}$$

The model was evaluated using 141 2-week measurements by Palmes PDTs prepared with 20% TEA in water spread across 3 years (2007-2009) and 4 sampling locations in the Middle Urals. Of these exposures, 106 were co-located with reference analysers and the authors fitted their model to the analyser data using different empirical values of β^*. Their best fit was for β^* = 3.9, close to the previously reported value of 3.6 (Palmes and Johnson, 1987), but their fit was very similar for any β^* value in the range 3.6 to 4, so the authors suggested β^* = 3.6 was appropriate.

The value of RH required to achieve $\beta_j \geq 3.6$ can be derived from the expression given above for β_j in terms of RH. The condition is satisfied when

$$\frac{f_j}{1 - f_j} > 3.6$$

i.e. when

$$f_j > \frac{3.6}{1 + 3.6} > 0.78$$

The requirement for 75-80% RH for an equilibrium molar H_2O:TEA ratio of around 4 was also supported by data the authors cite from the Dow Chemical Company.

The authors showed that for their own PDT measurements in the Urals (details above), during which there was substantial variation in RH, PDT NO_2 concentrations calculated using the standard formula were significantly lower than the reference concentrations, but that there was no significant difference when the effect of RH per hour time step was included.

The UK generally has high, and relatively non-varying, RH at all times of the year. The following are annual average (and range in monthly averages) RHs for example UK locations obtained from climate data at www.weather-and-climate.com and www.timeanddate.com: Edinburgh, 80% (76-85%); Glasgow, 80% (73-88%); York, 79% (74-86%); Birmingham, 81% (73-88%); Bristol, 80% (73-88%); London 73% (65-82%). The lowest monthly-average RHs tend to occur in May/June and the highest in Dec/Jan. For much of the UK, therefore, average RH is around or above the threshold required for stoichiometric conversion of NO_2 to NO_2^-; however, these data are monthly averages so there will also be substantial periods during a year when RH is less than 75%, particularly in east and south-east England. PDT exposures at these times may therefore lead to negative bias in NO_2 determination due to incomplete conversion of NO_2 to NO_2^- at the TEA absorbent.

5.3.1 Conclusions – effect of humidity on stoichiometric conversion of NO_2 to NO_2^-

The role of low humidity during deployment potentially causing negative bias in TEA-based NO_2 passive samplers is not sufficiently acknowledged by users of PDTs. A recent study has argued, supported by some experimental evidence, that for RHs less than ~75-80% the conversion of NO_2 to NO_2^- is less than unity, and hence average concentrations calculated under the assumption that all NO_2 was converted to NO_2^- will be biased low. At values of RH leading to full hydration of TEA average NO_2 concentrations calculated using the standard approach are correct (assuming no other biases present). For much of the UK, average RH is around 80%, but there are locations around the UK and/or periods during the year when RH during a PDT exposure is lower than 75% and hence potentially causing negative bias.

5.4 Exposure conditions: effect of wind speed, humidity and temperature on uptake rate

Relationships between wind speed, humidity and temperature and PDT NO_2 uptake rate have been inferred both from controlled chamber studies and ambient deployments. The effect of wind speed has received most attention. Relative humidity and temperature have been varied in some of the chamber experiments, with their impact on NO_2 uptake rate empirically quantified but with little discussion of the underlying reasons for their influence. The separate work described in Section 5.3 has shown how RH has a role in the formation of NO_2^- in the reaction of NO_2 with TEA. Temperature influences the rate of NO_2 diffusion (but this is relatively small, discussed later), the relative humidity (RH) for a given absolute humidity, and potentially also the physical phase of the TEA. The latter is not believed to be an issue under normal sampling conditions (Cape, 2009). Because of the link between T and RH, it is possible that effects attributed to T may be through its effect on RH.

Studies investigating the impacts of these meteorological variables are described in detail below for chamber and field studies separately.

5.4.1 Chamber studies

Since the Defra WG review, two new controlled chamber studies on PDT uptake rate have been published (Plaisance, 2011; Martin et al., 2014). These studies varied only wind speed; temperature and RH were fixed.

The study by the UK National Physical Laboratory (Martin et al., 2014) exposed seven designs of Palmes-type PDT (in replicate sets of 6) for 28 days to different wind speeds in a controlled atmosphere test facility (CATFAC) containing traceable concentrations of NO_2, NO and water vapour. Temperature and RH were fixed at 20°C and 80%, respectively. Of the seven types of PDT investigated three were supplied by Gradko and four by ESG. One set from each manufacturer was exposed with an open end as normal; for the other sets either a mesh or membrane was put across the open end of the tube, as detailed in the following table and shown in the photograph (both taken from the paper). The absorbent grids in all samplers were prepared using 20% TEA in water, but whether this was by a dipping or pipetting approach is not specified.

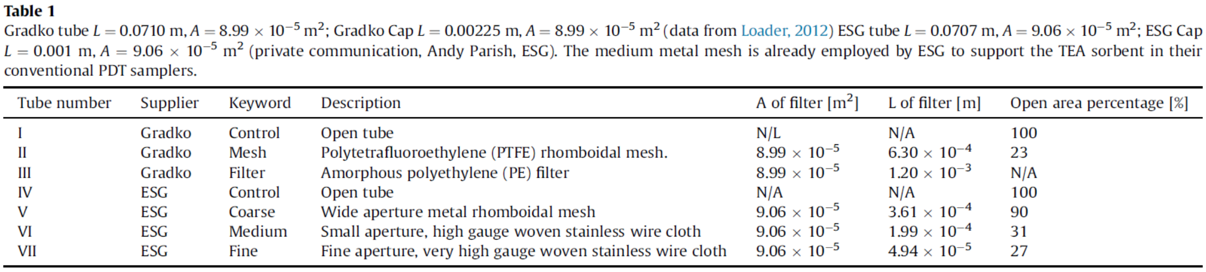
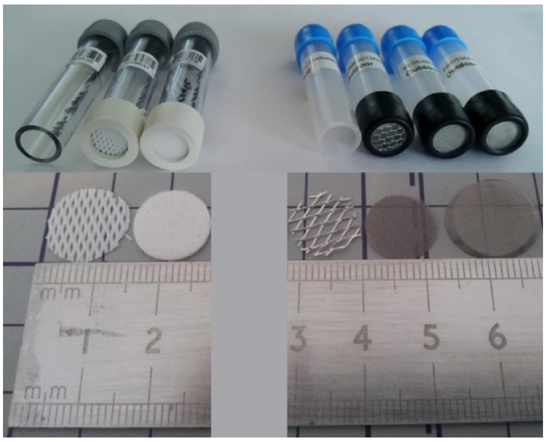


Table 1

Gradko tube $L = 0.0710$ m, $A = 8.99 \times 10^{-5}$ m^2; Gradko Cap $L = 0.00225$ m, $A = 8.99 \times 10^{-5}$ m^2 (data from Loader, 2012) ESG tube $L = 0.0707$ m, $A = 9.06 \times 10^{-5}$ m^2; ESG Cap $L = 0.001$ m, $A = 9.06 \times 10^{-5}$ m^2 (private communication, Andy Parish, ESG). The medium metal mesh is already employed by ESG to support the TEA sorbent in their conventional PDT samplers.

Tube number	Supplier	Keyword	Description	A of filter [m^2]	L of filter [m]	Open area percentage [%]
I	Gradko	Control	Open tube	N/L	N/A	100
II	Gradko	Mesh	Polytetrafluoroethylene (PTFE) rhomboidal mesh.	8.99×10^{-5}	6.30×10^{-4}	23
III	Gradko	Filter	Amorphous polyethylene (PE) filter	8.99×10^{-5}	1.20×10^{-3}	N/A
IV	ESG	Control	Open tube	N/A	N/A	100
V	ESG	Coarse	Wide aperture metal rhomboidal mesh	9.06×10^{-5}	3.61×10^{-4}	90
VI	ESG	Medium	Small aperture, high gauge woven stainless wire cloth	9.06×10^{-5}	1.99×10^{-4}	31
VII	ESG	Fine	Fine aperture, very high gauge woven stainless wire cloth	9.06×10^{-5}	4.94×10^{-5}	27



Experiments were carried out for NO_2 concentrations of 40, 60, 80 and 100 µg m^{-3} and, for the experiments with 40 µg m^{-3} NO_2, at wind speeds in the range 0.5 to 2 m s^{-1}. The chamber also contained NO at the same mixing ratio as the NO_2, but no O_3. The absence of O_3 means that there is no within-tube chemical generation of additional NO_2 from oxidation of NO.

As should be the case, no difference in uptake rate with ambient NO_2 concentration was observed. The study also did not observe significant difference in NO_2 uptake rate with wind speed, even for the open tubes, which is in contrast to a number of previous studies (both chamber and field), although the non-turbulent nature of the wind flow in this study may have led to different outcome compared with situations with variable and turbulent wind flow. Precision was better for tubes with meshes/membranes.

However, there were important differences in measured uptake rates between the tube designs and between measured and theoretically-calculated uptake rates, as presented in the following table. The measured uptake rate is the mean of the measurements across NO_2 concentrations and wind speeds of that design.

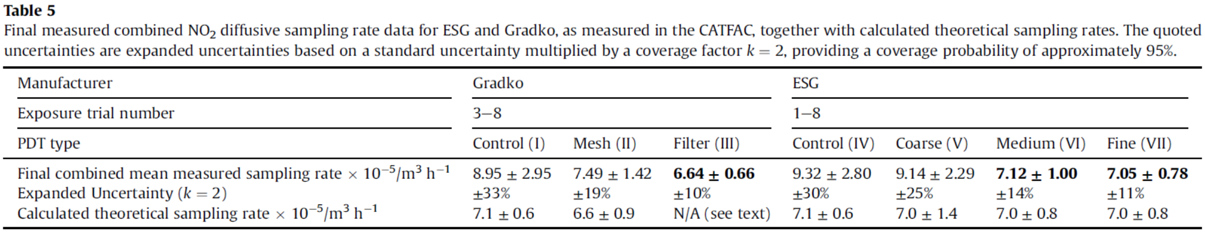


Table 5

Final measured combined NO_2 diffusive sampling rate data for ESG and Gradko, as measured in the CATFAC, together with calculated theoretical sampling rates. The quoted uncertainties are expanded uncertainties based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95%.

Manufacturer	Gradko			ESG			
Exposure trial number	3–8			1–8			
PDT type	Control (I)	Mesh (II)	Filter (III)	Control (IV)	Coarse (V)	Medium (VI)	Fine (VII)
Final combined mean measured sampling rate $\times 10^{-5}/m^3\ h^{-1}$	8.95 ± 2.95	7.49 ± 1.42	**6.64 ± 0.66**	9.32 ± 2.80	9.14 ± 2.29	**7.12 ± 1.00**	**7.05 ± 0.78**
Expanded Uncertainty ($k = 2$)	±33%	±19%	±10%	±30%	±25%	±14%	±11%
Calculated theoretical sampling rate $\times 10^{-5}/m^3\ h^{-1}$	7.1 ± 0.6	6.6 ± 0.9	N/A (see text)	7.1 ± 0.6	7.0 ± 1.4	7.0 ± 0.8	7.0 ± 0.8

The theoretical uptake rate was calculated assuming the electrical resistance analogue that the total diffusion path resistance is the sum of diffusion path resistances in series, i.e.

$$\frac{L'}{A'} = \frac{L_1}{A_1} + \frac{L_2}{A_2} + \frac{L_3}{A_3}$$

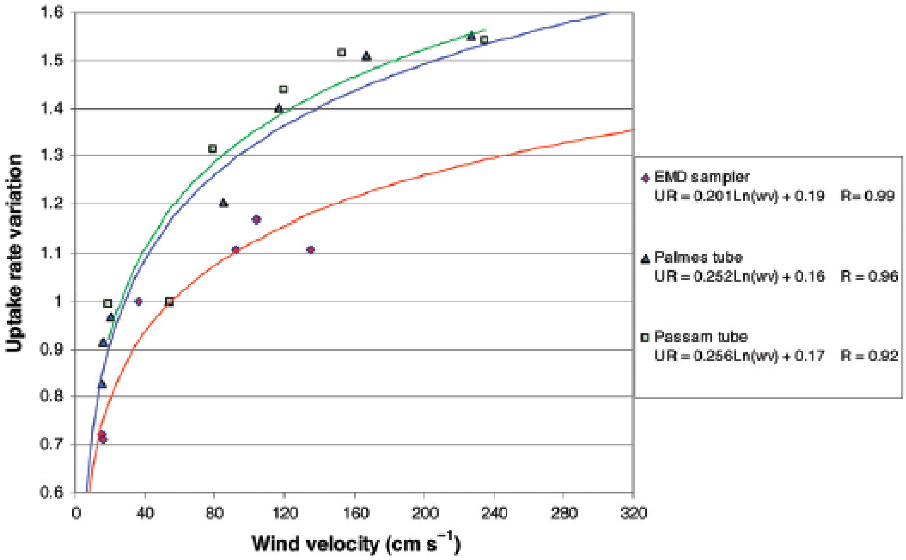
For open tubes there is only the one diffusion path to consider. For tubes fitted with meshes/membranes, two additional diffusion paths were also included: that associated with the thickness and pore area of the mesh itself, plus the small extra length by which the annular cap holding the mesh extended beyond the mesh. An uptake rate was not calculated for the Gradko tube with the polyethylene membrane since there was no robust data for the total transmission area of the pores in the membrane.

The theoretical uptake rate of 7.1×10^{-5} m^3 h^{-1} presented by Martin et al. (2014) for the open PDTs corresponds to an uptake rate of 1.18 cm^3 min^{-1} or 0.0197 cm^3 s^{-1}. Since the uptake rate corresponds to ($A.D/L$), applying L = 7.1 cm and A = 0.91 cm^2 means that NPL are using a value for D of 0.154 cm^2 s^{-1} for their chamber temperature of 20 °C. This is appropriate. The 80% RH used in these experiments is also sufficiently high that according to the work of Poddubny and Yushketova (2013) stoichiometric conversion of NO_2 to NO_2^- is anticipated.

The chamber data from this study show a measured uptake rate for the open Gradko and open ESG tubes (designs I and IV, respectively) that are 26% and 31% higher than the theoretical uptake rate, even for the lowest wind speed of 0.5 m s^{-1} investigated. (Strictly speaking, in both cases the biases are not statistically significant because the confidence intervals for the measured and theoretical uptake rates overlap.) The higher uptake rate measured in practice means that application of the standard equation leads to the equivalent positive bias on derived ambient NO_2 concentration. The authors do not discuss this important point. The use of a very coarse mesh (whose transmission area is still 90% of the tube cross-sectional area, design V) still leads to a substantially greater measured uptake rate than theoretical uptake rate, i.e. to an apparent positive bias in derived NO_2 concentration compared with using the standard equation. However, where medium or fine-weave PTFE or steel meshes are used, whose transmission areas are in the range 0.23-0.31 of the tube cross-sectional areas (designs II, VI and VII) the measured uptake rate is much closer to the theoretical uptake rate, which themselves are not much lower than the theoretical uptake rate for an open-ended tube. The use of the polyethylene membrane (design III) yields a measured uptake rate lower than the normal open-ended tube theoretical uptake rate, as expected since the membrane impedes the molecular diffusion.

Overall, the chamber data of Martin et al. (2014) indicate that even at the lowest wind speed investigated (0.5 m s^{-1}) there is a positive bias in PDT measurement compared with that expected from the standard theoretical equation, and that this can be substantially negated with meshes having a transmission area ratio of ~0.3 across the open end.

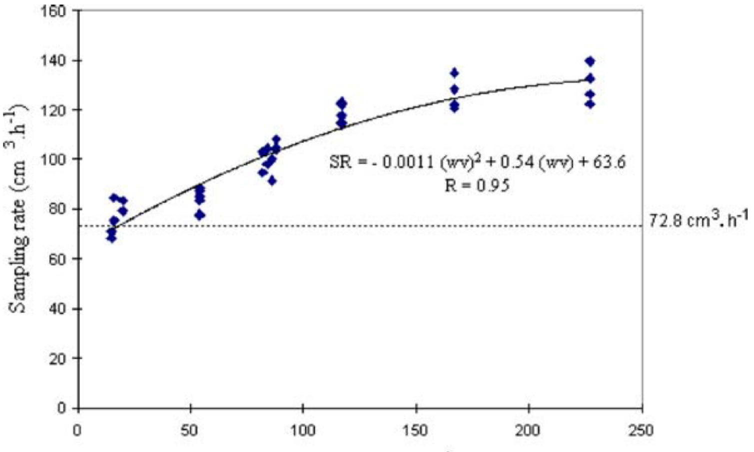
Plaisance (2011) used an exposure chamber to determine the effects of wind speed in the range 0 to 3.0 m s^{-1} on uptake by six diffusive samplers: a Palmes tube, a PASSAM tube, a badge with diffusion membrane, the EMD (Ecole des Mines, Douai, France) sampler and two radial diffusive samplers. Sensitivity to temperature and RH was not investigated. For all diffusive samplers tested, an increase in uptake rate was observed with increased air velocity usually following a logarithmic function as shown in the figure below. Uptake rates in the figure are expressed relative to that measured for a wind speed of 0.50 m s^{-1} at 40–50% RH, T = 20°C, and NO_2 concentration of 200 μg m^{-3}. The diffusion tubes were particularly affected by wind. According to the figure below the uptake rate increases by a factor of two between the lowest wind speeds of ~0.1 m s^{-1} and wind speeds of 2 m s^{-1}. Variation with wind speed for samplers equipped with a diffusion membrane was much lower (the latter data not in the figure below). This is consistent with Gerboles et al. (2005) who demonstrated that fitting membranes to diffusion tubes removed their sensitivity to wind speed in both chamber and field experiments. However, Gerboles et al. (2005) went on to develop an algorithm involving multiple environmental parameters to characterise the uptake rate of their membrane-closed Palmes tube which is not practical for normal usage.



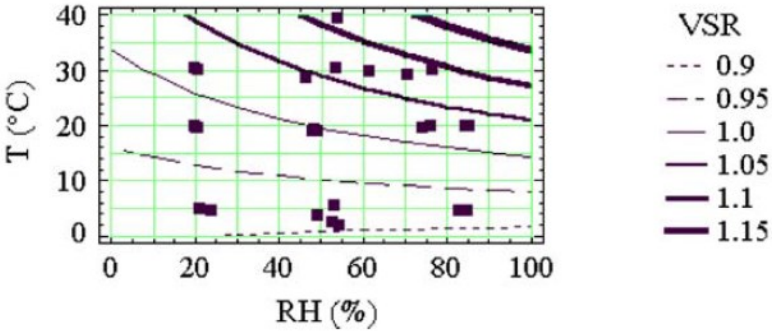
Although not discussed by Plaisance (2011), the above figure shows a very rapid increase in uptake rate for the Palmes PDT at the lowest wind speeds tested. The paper reports that the controlled chamber conditions gave an uptake rate for the standard Palmes PDT of 1.39 ± 0.07 cm^3 min^{-1} (equivalent to 8.34×10^{-5} m^3 h^{-1}) for 24 h for conditions of 40–50% RH, 20°C, wind velocity of 0.50 m s^{-1} and NO_2 concentration of 200 µg m^{-3}. This is the uptake rate against which other uptake rates are ratioed in the above figure. Applying the values given in this paper of $L = 7.116$ cm and internal diameter = 1.091 cm (i.e. $A = 0.9348$ cm^2), and a value of $D = 0.154$ cm^2 s^{-1} appropriate for 293 K, yields a theoretical uptake rate ($A.D/L$) of 1.21 cm^3 min^{-1} (or 7.28×10^{-5} m^3 h^{-1}), which is only 0.873 of the measured uptake rate. This is approximately consistent with the Palmes PDT uptake rate shown for the lowest wind speeds in the figure above. The greater-than-theoretical measured uptake rate at a wind speed of 0.5 m s^{-1} in this study means that application of the standard (theoretical) equation to the amount of captured nitrite would lead to a 15% positive bias in derived ambient NO_2 concentration under the given conditions. As with the similar study by Martin et al. (2014), Plaisance (2011) does not discuss this significant discrepancy between measured and theoretical uptake rates. It can be speculated that either there is wind effect even at the wind speed of 0.50 m s^{-1}, as is also inferred from the study of Martin et al. (2014), and/or the value of diffusion coefficient being used is too small. The positive bias between measured and theoretical uptake rates for PDTs is 26% in Martin et al. (2014) and 15% in Plaisance (2011). However, the former chamber experiments were conducted at 80% RH, but the latter only at 40-50% RH. The 80% RH is sufficiently high that, as per the work of Poddubny and Yushketova (2013), stoichiometric conversion of NO_2 to NO_2^- is anticipated. It is therefore possible that the lower positive bias in Plaisance (2011) is the net effect of positive bias from greater-than-theoretical uptake rate partially offset by negative bias from less-than-stoichiometric conversion of NO_2 to NO_2^-. (Within-tube chemical generation of additional NO_2 is not an issue in these chamber studies.)

In one further chamber study, Sekine et al. (2008) report on a different sampler design comprising a 13 mm diameter Whatman no. 1 filter prepared by dipping into 10% v/v TEA in acetone, placed immediately behind a 13 mm diameter polyethylene membrane filter. Two kinds of polyethylene filter were used: one of thickness 0.75 mm and average pore size 54 μm, and one of thickness 1.0 mm and average pore size 43 μm. This sampler is not of tube design; the relevance to PDTs is that the authors include data on effect of wind on uptake of their sampler and of a Palmes PDT. They report that their membranes gave constant mass transfer rates for external wind speeds in the range 0.5-2 m s^{-1}, and also reproduce data cited to a grouping of the same authors that the uptake rate of Palmes tubes increases from their lowest tested wind speed of 0.2 m s^{-1} to reach oversampling of the order of 50% even at low wind speeds of <1.5 m s^{-1}. However, these were measurements in a small chamber for less than 24 h. No other information or published source of these data are available.

It is worth reviewing again some of the earlier literature exposing PDTs in controlled environmental chambers in light of the more recent chamber studies discussed above. Plaisance et al. (2004) used an exposure chamber to determine the effects of wind velocity, temperature and relative humidity on the performances of Palmes-type PDTs. Tubes were prepared by pipetting 30 μL of a 10% solution of TEA in water. A total of 86 Palmes tubes were exposed to a gas stream with NO_2 concentration of 200 ± 20 μg m^{-3} at various conditions: wind velocities ranging from 0.15–2.3 m s^{-1}, temperatures from 2–40 °C and relative humidities from 20–85%. The main observation was a strong increase of sampling rate with increasing wind velocity, as shown in the figure below, conducted for NO_2 concentration 200 ± 20 μg m^{-3}, 24 h duration, $T = 20 \pm 1$ °C, and RH = 50 ± 3%. Applying the stated PDT dimensions of $L = 7.116$ cm and internal diameter = 1.091 cm (i.e. $A = 0.9348$ cm^2), and using a value of $D = 0.154$ cm^2 s^{-1} relevant for 293 K, yields a theoretical uptake rate ($A.D/L$) of 1.21 cm^3 min^{-1} (or 72.8 cm^3 h^{-1}) marked as the horizontal dotted line on the figure. The measured uptake rate matches the theoretical uptake rate for the lowest wind speeds of 0.1–0.2 m s^{-1} tested. The wind effect causes a rapid, then plateauing, increase in uptake rate, reaching a positive bias of nearly 50% for wind speed of 2 m s^{-1}. The authors attribute this positive base to the formation of eddies at the open end of tube inducing a reduction in the effective length of diffusion.



Plaisance et al. (2004) also concluded that temperature and relative humidity had smaller influences on uptake rate (than wind speed), "exceeding 10% only under unusual conditions (*T* > 30°C and RH > 80%)." The authors plotted isocurves for sampling rate variation as a function of *T* and RH as shown in the figure below. The VSR (variability of sampling rate) parameter in the figure is the ratio of the measured sampling rate at a given *T* and RH combination relative to the sampling rate at 20 °C and 50% RH, and wind speed of 0.54 m s^{-1}. (Note that according to the figure above this wind speed may itself be leading to a positive bias in uptake rate of ~10%.) It is relevant to note that the Plaisance et al. (2004) results in the figure below show the effective uptake rate decreasing with decreasing RH which is consistent with the work of Poddubny and Yushketova (2013) that lower RHs give lower conversion of NO_2 to NO_2^-. The Plaisance et al. (2004) figure suggests that at a temperature of ~15°C the uptake rate decreases by about 5% between an RH of 80% and an RH of 20%. The decrease in uptake rate with decreasing RH is more marked at higher temperatures. These decreases in uptake rate are lower than predicted by Poddubny and Yushketova (2013) but are consistent in direction. The figure also show that sampling rate increases by about 5% for each 10°C increase in temperature.



Buzica et al. (2005) exposed standard Palmes PDTs, prepared with 40 µL of 10% v/v TEA in water, for 2-week periods in a controlled laboratory chamber. Combinations of the following two levels per environmental condition were trialled: wind speed = 0.8 or 3.6 m s^{-1}; *T* = 15.5 or 30.5 °C; RH = 29.9 or 72.5%; and NO_2 concentration = 21.1 or 70.2 ppb. The experimental design was not full factorial (16 different sets of conditions were used). The authors developed the following empirical expression for the measured variation of the uptake rate as a function of *T,* RH and wind speed.

$$U\ (\text{ng ppb}^{-1}\ \text{min}^{-1}) = 7.40 \times 10^{-4} + 2.72 \times 10^{-5}\ T\ (°\text{C}) + 1.43 \times 10^{-5}\ \text{RH}\ (\%) + 5.81 \times 10^{-4}\ w\ (\text{m s}^{-1})$$

Applying the Palmes PDT physical dimensions given in the paper (L =10.94 mm, id = 10.92 mm), and using a value for D of 0.154 cm^2 s^{-1} (for T =293 K) for comparison with the chamber studies of Plaisance et al. (2004) and Plaisance (2011), the theoretical uptake rate U ($= A.D/L$) = 0.02033 cm^3 s^{-1} or 1.220 cm^3 min^{-1}. To convert this to units of ng ppb^{-1} min^{-1} used by the authors in their uptake condition requires calculating the mass concentration of 1 ppb NO_2 at the same temperature:

$$1\ \text{ppb NO}_2 = (10^{-9} \times 1.01325 \times 10^5)/(8.314 \times 293) = 4.159 \times 10^{-8}\ \text{mol m}^{-3}$$
$$= 1.913 \times 10^{-3}\ \text{ng cm}^{-3}$$

$$\therefore \text{ Theoretical Palmes PDT uptake rate, } U = 1.220\ \text{cm}^3\ \text{min}^{-1} \times 1.913 \times 10^{-3}\ \text{ng cm}^{-3}\ \text{ppb}^{-1}$$
$$= 2.33 \times 10^{-3}\ \text{ng ppb}^{-1}\ \text{min}^{-1}$$

Under the diffusion-only conditions of no effect of wind speed ($w = 0$ m s^{-1}), and $T = 293$ K and RH = 50%, the Buzica et al. (2005) empirical expression gives an uptake rate of 2.00 × 10^{-3} ng ppb^{-1} min^{-1} which is about 14% lower than the theoretical calculated uptake rate of 2.33 × 10^{-3} ng ppb^{-1} min^{-1} under these conditions. For $w = 0$ m s^{-1}, and $T = 284$ K and RH = 78%, more realistic T and RH conditions for the UK, the Buzica et al. (2005) empirical expression gives an uptake rate of 2.15 × 10^{-3} ng ppb^{-1} min^{-1}, which is only about 6% lower than the theoretical calculated uptake rate of 2.28 × 10^{-3} ng ppb^{-1} min^{-1} at this temperature.

However, the Buzica et al. (2005) empirical expression shows strong sensitivity of uptake rate to changes in the three meteorological variables, particularly wind speed. Thus, for example, for $T = 11$ °C and RH = 78%, an increase in average wind speed from 0 m s^{-1} to 3 m s^{-1} increases U from 2.15 × 10^{-3} (slightly below the theoretical uptake rate) to 3.90 × 10^{-3} ng ppb^{-1} min^{-1} (71% greater than the theoretical uptake rate), an 81% increase in uptake across the entire wind speed range. On the other hand, at an RH of 78% and wind speed of 1 m s^{-1}, an increase in average T from 0 to 20 °C increases U from 2.44 × 10^{-3} to 2.98 × 10^{-3} ng ppb^{-1} min^{-1}, a 22% increase in uptake, whilst at a T of 11°C and wind speed of 1 m s^{-1}, an increase in RH from 45 to 95% increases U from 2.26 × 10^{-3} to 2.98 × 10^{-3} ng ppb^{-1} min^{-1}, a 32% increase in uptake.

Overall, therefore, the Buzica et al. (2005) empirical expression generally predicts a higher uptake value for anticipated average ambient meteorological conditions than the theoretical value even at relatively low wind speeds. Thus if average meteorological conditions were $T =$ 11 °C, RH = 78%, $w = 1$ m s^{-1}, the expression predicts $U = 2.73 \times 10^{-3}$ ng ppb^{-1} min^{-1}, ~20% higher than the zero-wind theoretical value of 2.28 × 10^{-3} ng ppb^{-1} min^{-1}.

The magnitudes of the Buzica et al. (2005) empirically-derived changes in uptake rate with temperature, RH and wind speed are broadly consistent with those reported in the separate exposure chamber study of the same parameters by Plaisance et al. (2004). At $T = 20$ °C and RH = 50%, Plaisance et al. (2004) report an increase in uptake rate of 75% for an increase in wind speed from 0.2 to 2.2 m s^{-1}. The Buzica et al. (2005) expression predicts an increase in uptake rate of 55% for these conditions (from 2.11 × 10^{-3} to 3.28 × 10^{-3} ng ppb^{-1} min^{-1}). For a change in temperature from 0 °C to 20 °C (at RH = 75%), Plaisance et al. (2004) report an increase in uptake rate of 15% (compared with the 22% increase in uptake over this temperature range predicted by the Buzica et al. (2005) expression), and for a change in RH from 45 to 95% (at $T = 11$ °C), Plaisance et al. (2004) report an increase in uptake rate of 2% (compared with the 32% increase in uptake over this RH range predicted by the Buzica et al. (2005) expression). Thus the Plaisance et al. (2004) work indicates a stronger response of wind speed on sampling rate than the Buzica et al. (2005) work, but a lower response of temperature and much lower effect of RH on sampling rate. However, the increase of uptake with wind speed of both these earlier chamber studies is in contrast to the later chamber study of Martin et al. (2014) which observed no change in uptake with wind speed (although this does not mean that wind did not have any impact, only that there was invariance across the 0.5–2 m s^{-1} of wind speed investigated in the latter study).

Overall, both Buzica et al. (2005) and Plaisance et al. (2004) show the effective uptake rate decreasing with decreasing RH which is consistent with the work of Poddubny and Yushketova (2013) that lower RHs give lower conversion of NO_2 to NO_2^-; and both the earlier chamber studies imply that uptake rate even at low wind speeds is higher than theoretical calculations, of the order of ~20% or more (at high RHs). Retrospectively it can be seen that there is consistency of these older studies with the more recent chamber study of Martin et al. (2014) that appears to show measured uptake rates of the order of 26-31% greater than theoretical uptake rate even at low wind speed (even though this later study did not also show the increase in uptake rate with increasing wind speed). One explanation for inconsistency between measured and theoretical uptake rates could be that an erroneous value of D is being used in the latter. The value of the NO_2 diffusion coefficient is discussed later.

Gerboles et al. (2006) carried out laboratory tests on different types of NO_2 diffusive sampler in an exposure chamber under extreme conditions of controlling factors according to EN 13528-2 and showed that most of the NO_2 samplers were affected by extreme exposure conditions. The majority of diffusive samplers overestimated the reference value when NO_2 concentration, temperature, humidity and wind speed were set to their highest levels of, respectively, 80 $\mu g\ m^{-3}$ NO_2, 25 °C, 75% RH and 2.5 $m\ s^{-1}$ wind speed. The reference value was underestimated by diffusive samplers when these parameters were set to their lowest levels (NO_2 concentration 40 $\mu g\ m^{-3}$, temperature 5 °C, 30% RH and 1.0 $m\ s^{-1}$ wind speed). The findings of this study are consistent with positive bias due to wind speed and negative bias at low relative humidities. The influence of temperature cannot be isolated from the influences of the other variables from the data presented. In an earlier chamber study, Gerboles et al. (2005) reported the effect of temperature on uptake was ±5% between 15°C and 30°C, which is consistent with the conclusion from the other chamber studies described above that the influence of temperature is relatively small.

De Santis et al. (2000) reported some limited basic experiments with a lab chamber to test effects of wind on both standard Palmes PDTs, and ones with a stainless-steel mesh across the open end. They report that the protective mesh substantially attenuated the effect of wind turbulence in their test range of 2–4 $m\ s^{-1}$. At maximum wind speed the NO_2 overestimation was 48 ± 3% and 7 ± 0.8% for the tubes without and with the stainless steel mesh, respectively. However, no data to support these statements are presented and many experimental details are lacking, including the nature of the mesh used, and, importantly, the humidity and temperature of the air in their chamber experiments.

5.4.2 Field studies

The different PDT designs used in the NPL controlled chamber study (Martin et al., 2014), described in detail above, were also exposed for between six and eight 4-week exposures at a central London AURN site (which is not identified but is probably Marylebone Road). There is very little discussion of the field comparison data in the paper. What discussion there is focuses on correlation coefficients and PDT precision both of which are generally better for the PDT designs with meshes. It is not possible to get a full view of the extent of the agreement between PDT measurements and reference analyser concentrations. The gradients forced through the origin are in the range 0.90 to 0.98 across the PDT designs but the measured NO_2 concentrations are high (all > 60 $\mu g\ m^{-3}$) which may lead to a distortion of the view of absolute PDT agreements. In general, however, the field data suggest the PDTs yield slightly lower NO_2 concentrations than the analyser, in contrast to their chamber tests which suggest a general positive bias in PDT performance. It can be speculated that perhaps this is associated with long-term degradation of absorbed NO_2^- in field conditions, but there is no comment at all in the paper on this discrepancy between chamber and field outcomes.

Masey et al. (2017) assessed the precision and accuracy of NO_2 concentrations measured with standard Palmes PDTs (as well as other variants of passive sampler) over 32 separate 2-day, 3-day and 7-day exposure periods at an urban background site in Glasgow. PDTs were prepared by dipping grids in 50% TEA in acetone, and analysis followed the Defra WG (2008) procedures. The authors noted that uptake rates for PDT measurements linearly increased with wind-speed. The positive bias ranged from around nothing for exposure-mean wind-speeds < ~2 m s^{-1} to about 100% for exposure-mean wind-speeds of ~8 m s^{-1}. The wind data were for Glasgow airport several km away from the PDT exposures in the centre of Glasgow. Retrospective adjustment of uptake rate using the observed relationship between uptake rate and exposure-average wind-speed during each sampling period substantially increased the accuracy of the PDTs. The authors acknowledged that individual correction for wind-speed was not practical and stated that reduction in wind-speed bias would likely be achieved by use of a mesh or membrane across the open end, although this was not tested.

The average positive bias compared with the theoretical uptake rate for a PDT in the Masey et al. (2017) study was ~25% across the 32 exposures of exposure-mean wind-speeds ranging from ~1 m s^{-1} to ~8 m s^{-1}. The magnitude of this mean bias is similar to that reported by Martin et al. (2014) from their chamber experiments, but Martin et al. (2014) did not observe variation in their bias across their tested wind-speed range of 0.5-2 m s^{-1}, whilst Masey et al. (2017) report substantial variation with wind-speed.

Sánchez Jiménez et al. (2011) deployed NO_2 PDTs adjacent to chemiluminescence analysers for twelve 1-week exposures at kerbside, urban centre and urban background locations in Glasgow as part of a study to evaluate performance of NO_x PDTs. The NO_2 PDTs were prepared (by dipping in 50% v/v TEA in acetone solution) and analysed according to the UK recommendations (Defra WG, 2008). No protective shelters were used. For the PDT exposures at the urban centre location, where hourly mean concentrations of O_3 were also available, it was possible to model the anticipated positive bias in PDT NO_2 concentration due to within-tube reaction between NO and O_3 also present in the ambient air during an individual exposure, as per Heal and Cape (1997).

There was significant positive bias between PDT and analyser NO_2 at the kerbside and urban centre locations, but duplicate PDT precision was good and correlation between PDT and analyser across the 12 exposures at all 3 sites extremely high (*R* ranging from 0.87 to 0.96), indicating that bias was systematic. Mean positive bias at the urban background site was a further ~50% greater than the mean bias of 28% simulated for within-tube $NO+O_3$ reaction. The authors attributed this to additional wind-induced positive bias at this site, supported by the observation that the co-located NO_x PDT tubes (which will not be subject to within-tube chemical bias because the reaction converts between NO and NO_2) also had a positive bias of around 50%. Allowing for the possibility also of an exposure-duration dependent negative bias over 1-week of ~8%, based on earlier work (Heal et al., 2000), the authors concluded that wind bias at this site could have been as high as 55-60%. They noted that these particular tubes were deployed in an exposed location, mounted at 3 m height without shelter on an air intake duct in the middle of a relatively open square, in one of the UK's windiest urban areas.

Although simulation of chemical overestimation bias was not possible at the kerbside location, based on unpublished simulations at other urban locations Sánchez Jiménez et al. (2011) estimated that chemical overestimation at this high NOx (thus presumably low O_3) site would likely be comparatively small, ~5-10%. The excess PDT NO_2 positive bias of ~45% at this site the authors again attributed to wind effects, noting that the kerbside location of these samplers was subject to considerable air turbulence from the high density of bus and other traffic continually passing within a metre or two of the PDTs.

Sánchez Jiménez et al. (2011) estimated that the chemical overestimation for their urban background site would likely be approximately the same magnitude as the potential exposure-dependent negative bias. The generally comparable PDT and analyser NO_2 values at this location therefore indicated a lack of any significant wind-induced bias at this site, consistent with the PDTs' position in a sheltered second-floor window recess not subject to wind or to air turbulence from passing traffic.

Vardoulakis et al. (2009) evaluated the performance of co-located NO_2, NO_x and O_3 passive diffusion tubes relative to their respective continuous analyser measurements in just over one year of monthly exposures at one urban background and two roadside sites in Birmingham, UK. (All PDT measurements in triplicate.) Wind speed and direction, ambient temperature and relative humidity were also available, but for another location. PDTs were prepared via pipetting 30 µL of 50% TEA in water. Tubes were exposed for either 4 weeks or occasionally 5 weeks, and no protective shelter was used. To convert NO_2^- to ambient NO_2 concentration the authors used an uptake rate ($A.D/L$) of 74.2×10^{-6} m^3 h^{-1} which is equivalent to 1.24 cm^3 min^{-1}. Taking the authors' stated tube dimensions of $L = 71$ mm and internal diameter 11.0 mm this uptake rate implies the authors were using a value for D of 0.154 cm^2 s^{-1}, which is about 2% greater the value recommended by the Defra WG (2008) for UK PDT data reporting to EU standard conditions and hence these authors' reported PDT values will be 2% greater than they ought to be.

Vardoulakis et al. (2009) reported no significant difference between NO_2 PDT and chemiluminescence analyser, with PDTs reading lower on an annual-average basis by 3.2-6.4% across the three sites (plus a further 2% underestimate because of the authors' use of too high a value of D). A very slightly increasing NO_2 bias with increasing exposure-average O_3 concentration was attributed to within-tube $NO+O_3$ reaction. The authors reported no significant trend of NO_2 bias with any of wind speed (which ranged from 2.7-4.7 m s^{-1}), temperature (which ranged from 4-20 °C or RH (which ranged from 65-90%) although they acknowledge that meteorological measurements were made some distance from the sampling sites, as was the case in the Masey et al. (2017) study, which could mean that wind speed in particular was different at the PDT locations.

As part of a laboratory and field validation of a combined NO_2-SO_2 Radiello radial-type diffusive sampler, Swaans et al. (2007) also exposed Gradko Palmes-type combined NO_2-SO_2 PDTs adjacent to reference analysers for three 2-week exposures in Ghent and Borgerhout. Two sets of triplicates were deployed, with one set sent to each of Gradko and VITO to analyse. PDTs were prepared with 50% TEA in water and contained a filter across the open end to prevent ingress of particles. The Gradko samplers significantly under read the analyser, with ratio of sampler:analyser ranging from 0.6 to 1 for individual exposures and averaging around 0.8 overall. The authors do not discuss any reason for the negative bias but simply note that "agreement is to within the 30% criteria for accuracy for passive samplers." (N.B. the data quality objective for accuracy for NO_2 is actually 25%.) It is not possible to draw any conclusions from these data as the number of comparisons is very limited and the PDTs included a filter (that will likely impact on uptake rate) which is not the case for standard NO_2 PDTs.

Ozden and Dogeroglu (2008) describe a field evaluation in Eskisehir, Turkey, of a tailor-made glass passive sampler for NO_2. This is not a Palmes-type PDT but is similar in concept, and the authors also deployed standard Gradko PDTs. The authors' sampler was 3.98 cm in length and 1.2 cm in diameter, and contained a fibre filter paper impregnated using 20% v/v TEA in water which is one of the preparation methods recommended by the Defra WG (2008). They trialled both transparent and dark coloured glass. Exposures were generally for 1-week duration, although the exposures including Gradko PDTs were for 2 weeks. It is important to note that the authors' own tubes were exposed with a metal mesh across the open end of the tube and within a shallow rain protection shelter which would also have afforded some protection from the wind. Another important note is that the authors' reference NO_2 data was not from a chemiluminescence analyser but from an actively-sampled Griess-Saltzman ASTM D 1607 standard test method. The authors state that the theoretical uptake rate (AD/L) for their sampler is 2.63 $cm^3\ min^{-1}$. Taking their stated tube dimensions of $L =$ 3.98 cm and diameter 1.2 cm this uptake rate implies the authors were using a value for D of 0.154 $cm^2\ s^{-1}$, which is the value of D appropriate to an assumed temperature of 293 K and may be appropriate for this study's climate. Their measured uptake rate determined from comparison against their standard method was 2.49 $cm^3\ min^{-1}$, a difference of ~6% which the authors report as good agreement with the theoretical rate. Their data show about 10% greater NO_2 from the co-located Gradko PDTs compared with their own shorter tubes. They do not discuss this but it can be speculated that it may be a consequence of the Gradko tubes not having the mesh across their open end and consequently being subject to a wind-induced positive bias. Although not having the mesh, the Gradko tubes were exposed underneath their shallow rain-protection shelter used for their own tubes.

Two further field studies involving custom-built tube-like passive samplers for NO_2 provide some information relevant to meteorology-associated biases in field deployments. The study by Bootdee et al. (2012) exposed three geometries of tube (a polyethylene tube 5.4 cm long, 1.4 cm i.d.; and two sizes of polypropylene tube, 5.3 cm long,1.3 cm i.d. and 7.7 cm long, 1.6 cm i.d.) in protective shelters in Chiang Mai, Thailand. The authors report that concentrations of NO_2 measured over short-duration exposures ($\leq$ 7 days) were not significantly different between the tube lengths, which suggests that the use of a protective shelter mitigated any potential bias from wind speed. Tarvydaitė and Kazlauskienė (2014) exposed their passive sampler comprising a polypropylene tube 34 mm in length and 21 mm in inner diameter, also in protective shelters, for 2-week periods in Vilnius, Lithuania. The authors report that NO_2 concentrations were within the permitted EU uncertainty of ±25% and that there was no significant correlations between accuracy and temperature, RH or wind-speed. However, they have a very small dataset.

5.4.3 Conclusions– effect of wind speed, humidity and temperature on uptake rate

Although both chamber and field experiments still provide some contradictory results on the significance of wind effects on Palmes-type PDTs, it seems clear from consideration of all the literature to date that positive bias from wind effects exists and can be very large, albeit that the extent of sensitivity of the bias to increasing wind speed is not clear. Under even moderate wind conditions, a number of chamber and field experiments suggest 50% or greater positive bias. Close inspection of data across a number of chamber experiments suggests some consistency for an overestimation of the order of 20% compared with the theoretical uptake rate even at the lowest wind speeds that will be routinely encountered in ambient deployments.

Results from chamber experiments also demonstrate that lower relative humidities reduce quantitative performance of PDTs, which is consistent with the observation described earlier of low RH reducing stoichiometric conversion of NO_2 to NO_2^-.

Of the three meteorological variables, evidence suggests that sensitivity of PDT uptake rate is smallest for temperature, of the order of a few % per 10°C. Temperature influences the rate of NO_2 diffusion (but this is relatively small, discussed later), the relative humidity for a given absolute humidity, and potentially also the physical phase of the TEA, although the latter is not believed to be important for ambient conditions. Because of the link between temperature and relative humidity, it is possible that effects attributed to temperature may be through its effect on relative humidity.

There is potential significant confounding in interpretation of the influence of wind (and humidity) because of low humidity causing negative bias, within-tube chemical reaction leading to additional NO_2 and hence a positive bias, and negative bias from long-term degradation of absorbed nitrite particularly for long exposures of month duration. This is particularly the case for field evaluations where PDT exposures can vary between a few days to 5 weeks, and which are subject to varying environmental conditions during exposure that are usually not being measured, or measured only at a location a long way from the PDT deployments. Chamber experiments have constant and known values of environmental variables and do not include ambient O_3 so within-tube chemistry is not an issue for the chamber experiments.

An alternative explanation for those chamber exposure data that suggests positive bias compared with the theoretical uptake rate, even at low wind speeds, is that an inappropriate value for the diffusion coefficient of NO_2 in air is being used for the theoretical uptake rate – one that is too low and consequently has the effect of giving rise to a positive bias in derived average NO_2 concentration. This has not been discussed at all in the literature, but is discussed further in this review below. Of course any error in *D* would proportionally apply universally to all NO_2 passive sampler measurements.

Considerable accumulated evidence indicates that positive bias from wind effects can be offset by either use of some form of mesh or membrane across the tube and/or with the tubes placed underneath a shelter. Membranes across the mouth of the tube may overcompensate for wind-induced positive bias by acting as a resistance to free molecular diffusion and reducing uptake below that encapsulated in Fick's first law. At present, local and national network NO_2 PDTs in the UK are not deployed with either meshes or protective shelters.

5.5 Exposure conditions – within-tube chemical generation of additional NO_2

Further quantitative evaluation of the impact of within-tube chemical reaction between co-diffusing ambient NO and O_3 has only been carried out by Heal and co-workers using the model for PDT diffusion and within-tube reactions first reported by Heal and Cape (1997). In a study primarily to investigate potential influence of preparation method on PDT performance, Hamilton and Heal (2004) reported that for 14 1-week PDT exposures at an urban centre location in Edinburgh the mean model-simulated chemical bias was +26%. In a subsequent statistical evaluation of effect of preparation method using a dataset of 680 PDT exposures, Heal (2008) again noted a systematic positive bias, on average, of the PDT NO_2 values relative to their respective analyser, consistent with the presence of positive bias due to within-tube oxidation of NO to NO_2 and/or a wind speed effect acting independently of preparation method. Heal (2008) also noted that the presence of such biases complicates the use of zero bias against an analyser as the measure of PDT accuracy.

The study of Sánchez Jiménez et al. (2011) that deployed PDTs at three sites in Glasgow, described in detail above in relation to wind effects, included model-simulated estimates of bias due to chemical overestimation for exposures at the urban centre location. The mean modelled chemical bias was +28% across 12 1-week exposures. Sánchez Jiménez et al. (2011) also refered to unpublished model simulations of chemical overestimation bias using hourly measured NO_2, NO and O_3 data from other locations at which all three species were measured. These model simulations cover a range of relative and absolute NO_2, NO and O_3 concentrations. The results indicate that positive bias from within-tube chemistry is smaller at roadside (high NOx) sites than at urban background sites because the O_3 to NO ratio is lower closer to roadside. An analysis by Laxen and Marner (2006) of bias in PDTs with distance from road utlising Local Authority PDT co-location data drew the same conclusion. They examined the results of 252 long-term co-location studies at roadside and background sites across the UK between 2000 and 2005. Results were compared with a model of in-tube chemistry developed by Bush et al. (2001) and showed broad agreement, with the model showing higher bias at intermediate concentrations of NOx and lower relative bias at higher and lower concentrations (near source and away from source, respectively).

The study by Vardoulakis et al. (2009) for a year of monthly deployments in Birmingham, also described in detail above, did not explicitly simulate chemical overestimation; however, the authors speculated that the slightly smaller underestimation they observed at their roadside sites compared with at their urban background site could be due to additional $NO+O_3$ reaction, which they supported by referring to the very slightly increasing NO_2 bias with increasing exposure-average O_3 concentration.

By comparing biases between standard acrylic PDTs and equivalent dimension quartz tubes (which transmit all NO_2 photolysis wavelengths), Kirby et al. (2001) concluded there was evidence for presence of within-tube chemical reaction bias. The magnitude of bias increased as the exposure average $NO:NO_2$ ratio increased to ~1 and the exposure average $O_3:NO_2$ ratio increased to ~2.

5.5.1 Conclusions – within-tube chemical generation of additional NO_2

Model simulations of the diffusion and chemical reaction within a PDT clearly demonstrate potential for intrinsic positive bias from additional NO_2 production along the diffusion path. For certain ratios of ambient NO, NO_2 and O_3 (where both NO and O_3 are relatively high compared with NO_2) the simulations indicate this positive bias can average as high as ~25%, or higher for individual exposures. For kerbside locations, where O_3 may be low, or for more rural locations where most NO_x is already in the form of NO_2, the PDT chemical bias may only be a few %.

Direct validation of a chemical bias in the field is again complicated by the presence of other potential biases (wind and humidity effects, long-term absorbent degradation) simultaneously impacting on PDT performance. Attempts to observe the effect of chemical bias by using UV-transmitting tubes may also be subject to confounding by differential rates of degradation of NO_2^- at the absorbent between tubes of different materials (see next section).

5.6 Exposure-duration ‘loss’ of absorbed NO_2^-

Previous evidence for an exposure-duration negative bias in PDT determination of NO_2 was derived from co-located comparisons of concentrations derived from a single long-duration exposure, e.g. of 4 weeks, or as the average of consecutive shorter 1-week or 2-week expsoures (Heal et al., 1999; Heal et al., 2000), and from differences in these comparisons between summer and winter seasons. These studies very approximately estimated a degradation rate of a few % (e.g. 5-8%) per week.

No new studies have specifically investigated the above issue. The study by Vardoulakis et al. (2009) for a year of monthly deployments in Birmingham (described in detail above) concluded from a comparison of 4 and 5-week exposures that photolysis, or other exposure-duration-dependent losses, at the absorbent was not a factor. However, the authors had only few data to make this evaluation of exposure duration and were only comparing between exposures differing in duration by a small proportion (between 4 or 5 weeks).

The study of Ozden and Dogeroglu (2008) using custom built samplers, also described in more detail above, trialled dark-coloured glass samplers alongside their transparent glass samplers. The dark-coloured glass samplers gave about 25% higher reading than their transparent samplers for exposures from spring to mid-summer. The difference was only 6% for samplers exposed during winter. The authors attributed this to possible photodegradation of NO_2–TEA complex during the summer season. However, it is not clear from the data presented whether it is the transparent or dark coloured tubes that yield the NO_2 concentrations that are consistent with their standard method measurements of NO_2, i.e. whether dark tubes had net positive bias, or transparent tubes had a net negative bias. The authors do not pick up on this point at all.

De Santis et al. (2000) investigated the stability of the NO_2^--TEA adduct as determined by the proportion of nitrite extracted after increasing lengths of storage time, including at room temperature and in a fridge, and with or without Al-foil shielding. They reported that decrease in extractable nitrite ranged from almost zero up to ~20% after a month or two of storage, with the ambient T and light conditions yielding greater loss. The authors attributed this decrease to photodegradation of the NO_2^--TEA adduct.

5.6.1 Conclusions – exposure-duration ‘loss’ of absorbed NO_2^-

Although the evidence is sparse, it is consistent that there may be a small negative bias in PDT-derived NO_2 concentrations associated with a slow chemical degradation of the absorbed NO_2^-, of a few % per week, particularly in sunnier, warmer conditions, which becomes more relevant for exposure durations of several weeks.

5.7 Value of the NO_2 diffusion coefficient

As described in Section 3.4, the Defra Working Group (Defra WG, 2008) recommended the value $D = 0.146\ cm^2\ s^{-1}$ be used, where this was derived as a temperature adjustment of the original Palmes et al. (1976) value at 293 K to a more appropriate average ambient UK temperature of 284 K. (The WG also pointed out that when PDT data are to be compared with air quality objectives or reference chemiluminescence analyser data, the PDT values need to be decreased by a factor 284/293 = 0.969, but this is a separate issue independent of considerations of the absolute value of *D*.)

The diffusion coefficient for NO_2 is very difficult to measure directly because of its dimerization to N_2O_4 at concentrations at which experiments need to be conducted. (The dimerization is not important at the very low NO_2 abundances in ambient air.)

Palmes et al. (1976) derived their value for *D* using a semi-empirical gas-theory expression incorporating molecular masses, molecular cross-sections and strength of molecular interactions. Over the several decades since, the use of the Palmes value for *D* in PDT measurements has not been questioned.

In a review of molecular diffusivities, Massman (1998) refers only to measurements made by Chambers and Sherwood (1937) for N_2O_4 in N_2, quoting an experimental value of 0.121 cm^2 s^{-1} at 273 K, and by Sviridenko et al. (1973). Massman (1998) uses these data and further gas-kinetic theoretical considerations to derive his recommendation of 0.1361 cm^2 s^{-1} for NO_2 in air at 273 K, with a *T*-dependence factor of 1.81, which yields a value for *D* at 284 K of 0.148 cm^2 s^{-1}. Massman (1998) provides a nominal estimation of uncertainty of ±10% in his recommended value, but the text also states that the "results suggest that the diffusivity of NO_2 is relatively uncertain and that experiments should be repeated."

In a more recent evaluation of diffusivities of trace gases, Tang et al. (2014) refer to the Chambers and Sherwood (1937) measurements as the only experimental data for NO_2, also quoting, as Massman (1998), an experimental value of 0.121 cm^2 s^{-1} at 273 K. They also quote an experimental value from Chambers and Sherwood (1937) of 0.129 cm^2 s^{-1} at 283 K. Although the relative magnitudes of these two experimental values are consistent with a *T*-dependence factor of 1.75 quoted by Tang et al. (2014) for the 'Fuller' semi-empirical estimation method for gas-phase diffusion coefficients (Fuller et al., 1966; Fuller et al., 1969), the absolute values are substantially smaller than the value of $D = 0.163$ cm^2 s^{-1} at 273 K that these authors derive from the Fuller estimation method. The recommendation of Tang et al. (2014) is to use the experimental value, with a ± uncertainty of 35%. These authors appear not to be aware of the earlier review by Massman.

No other independent value for *D* for NO_2 has been uncovered in the literature.

The following is a summary of all available values for *D* at 284 K, the temperature used as the average for the UK:
Palmes et al. (using Massman *T* dependence), as recommended by the WG: $D = 0.146$ cm^2 s^{-1};
Massman recommendation (using Massman *T* dependence): $D = 0.148 \pm 0.015$ cm^2 s^{-1};
Tang et al. recommendation (using 'Fuller' *T* dependence): $D = 0.130 \pm 0.045$ cm^2 s^{-1};
Tang et al. 'Fuller' estimate (using 'Fuller' *T* dependence): $D = 0.175$ cm^2 s^{-1}.
These values span a large range.

In principle, the value of *D* can be back-calculated from measurements of the amount of nitrite captured in PDT exposures in controlled chamber experiments, assuming that the conditions for Fick's law of diffusion hold perfectly. However it is difficult even in chamber experiments to exclude, or quantitatively correct for, factors that break the assumption of Fick's law (e.g. non-diffusive air movements) or that affect nitrite capture and quantification (e.g. humidity levels, uncertainties in laboratory analyses). Instances where experimental observations provide uptake rates (= *A.D*/*L*) that are higher than the theoretical uptake rate derived using the Palmes value of *D* have been discussed in earlier sections of this review.

All the values for *D* presented above are for standard atmospheric pressure. Although not relevant for the UK, when PDT measurements are made at altitudes at which atmospheric pressures are significantly lower, a larger value of *D* would need to be used.

5.7.1 Conclusions – value of the NO_2 diffusion coefficient

The original Palmes value for the NO_2 diffusion coefficient has been used in all subsequent PDT measurements seemingly without further question. The value was derived from semi-empirical theoretical consideration of gas behaviour because it is very hard to measure experimentally. The one experimental value (from 1937) is a factor 0.89 of the Palmes value, referenced to a temperature of 284 K. Although semi-empirical methods for estimation of gas diffusion coefficients are well-established, a more recent calculated value is a factor 1.20 of the Palmes value.

As discussed in earlier sections of this review, the greater PDT uptake rates measured in some chamber experiments compared with uptake rates derived using the standard equation (*A.D*/*L*) could be explained if *D* was greater than the standard Palmes value used. However, it is difficult to control for all variables that may influence uptake experimentally, even in a chamber study. If the true value of *D* was larger than the Palmes value currently used then NO_2 concentrations currently calculated from PDT measurements are overestimates of the true NO_2 concentrations (and vice versa).

There should be much greater acknowledgement that the value for *D* is not known with certainty, and definitely that its value is not known to the precision implied by use of a value for *D* expressed to 3 significant figures. One evaluation suggests an uncertainty in *D* of ±35%. This does not mean random variability across individual PDT exposures in the range ±35%, because *D* must have a single true value; instead it means that the true value of *D* is not known so that collectively all PDT-derived NO_2 values may be up to 35% too high or up to 35% too low. It is important to note, however, that this particular potential source of PDT bias is not an issue for PDTs that are 'bias adjusted' against a chemiluminescence analyser, since if this was the only source of PDT bias at all PDT exposure locations, including the co-location, then it would be accounted for through the bias adjustment factor (but it would of course lead to bias in the 'raw' PDT value against the chemiluminescence analyser).

5.8 Bias in comparison against a reference analyser determination of NO_2

Bias in PDT measurement is assessed by its comparison against a 'reference' chemiluminescence analyser determination of NO_2. Analyser values may be uncertain by up to the ±15% permitted by the EU Directive for these measurements (EC Directive, 2008). When comparing PDT and analyser NO_2 concentrations expressed gravimetrically (e.g. as $\mu g\ m^{-3}$ units) rather than as volumetric mixing ratios (e.g. ppb) it is important to ensure that both concentrations are being expressed relative to the same values of pressure and temperature. For PDT values calculated using the Defra WG recommended value for *D* (which assumes an average ambient temperature of 284 K) the PDT values then need to be decreased by a factor 284/293 = 0.969 to compare against a chemiluminescence analyser that has been set up to report NO_2 concentrations referenced to the EU reporting temperature of 293 K. Failure to make this adjustment means the PDT-derived value in the comparison is too high, although only by ~3%.

The chemiluminescence analyser does not determine NO_2 directly, but as the difference between successive measurements of NO and NO_x, where, for the latter determination, the NO_2 component of NO_x is first quantitatively converted to NO using either a heated molybdenum oxide catalyst or UV photolysis. The chemiluminescence analysers have their own biases for NO_2 determination through (i) incomplete conversion of NO_2 to NO (causing negative bias), and (ii) formation of NO in the converter from other N-containing oxidant species in the air such as HNO_3, HONO and PAN, collectively referred to as NO_z (causing positive bias). The photolytic converter is far more specific in its conversion of only NO_2 to NO. However, the vast majority of analysers in the UK utilise the thermal converter. If the PDT equivalently quantifies NO_z species as absorbed nitrite then the presence of NO_z in the air would not lead to bias between a PDT and a thermal catalytic chemiluminescence analyser.

Gerboles et al. (2003) applied the methods of the Guide to the Expression of Uncertainty in Measurement (ISO, 1995) to assess the ability of the chemiluminescence method to measure ambient NO_2, with an uncertainty within 15%, as stipulated in the EU data quality objective. They reported that the contribution of accuracy of calibration standard, linearity, converter efficiency and drift of the analyser between calibration checks to the overall uncertainty is less important than the contribution of interference, mainly humidity and, in rural areas, PAN. They assessed that the data quality objective is not met at the annual limit value of 40 $\mu g\ m^{-3}$ if NO is greater than 100 $\mu g\ m^{-3}$, but could be met by correcting the measurements for the bias due to interference.

Steinbacher et al. (2007) compared long-term co-located NO_2 measurements using analysers with molybdenum and photolytic converters at two rural sites in Switzerland. On a monthly basis, only 70-83% of the measured NO_2 was due to genuine NO_2 at their non-elevated site (and less for a higher elevations site) with greatest discrepancy in spring/summer, consistent with photochemical aging of the rural air mass creating significant amounts of NOz species such as HNO_3 and PAN relative to the NO_2.

Xu et al. (2013) similarly compared instruments with the two types of converter at four differently polluted sites in China. (The measurement period at each site was only a few weeks and not contemporaneous.) The thermal converter worked well at the urban site, which was greatly affected by fresh emissions, but, on average, overestimated NO_2 by 30%-50% at the two suburban sites and by more than 130% at the mountain-top site during afternoon hours, with a much larger positive bias seen during the highest ozone events. The degree of overestimation depended on both air-parcel age and the composition of the NO_z species. Also in East Asia, Jung et al. (2017) reported that a thermal-converter instrument overestimated NO_2 levels determined by a photolytic-converter instrument by 20.4 ± 14.7% for a monitoring period of several months at a suburban site in Daejeon, Korea, downwind of the Asian continental outflow.

In the study of Leston and Ollison (2017), comparison was made between a thermal-converter instrument and a direct NO_2-reading photometer at a ‘near-road’ site (15 m from an Interstate carriageway edge) in Hartford, USA. On average, hourly averages from the former instrument were 10% higher than for the latter. The comparison was over winter (late November to mid-March).

5.8.1 Conclusions – bias in comparison against a reference analyser determination of NO_2

PDT values calculated using the Defra WG recommended value for *D* (which assumes an average ambient temperature of 284 K) must be decreased by a factor 284/293 = 0.969 to compare against a chemiluminescence analyser that has been set up to report NO_2 concentrations referenced to the EU reporting temperature of 293 K. Failure to make this adjustment means the PDT-derived value in the comparison is ~3% too high.

It is widely acknowledged that chemiluminescence analysers using a heated molybdenum NOx-to-NO converter (as is usually the case in the UK) are subject to positive bias in NO_2 measurement from HNO_3, HONO and PAN also present in the air. The bias is much lower (e.g. a few %) for locations close to fresh emissions of NO_x, such as close to roads, compared to locations subject to more photochemically-aged air. This interference is likely part of the reason why the EU data quality objective for the chemiluminescence method is ±15%. Bias between a 'thermal converter' chemiluminescence analyser and co-located PDT due to this issue would be offset if the other oxidised N-containing gases also gave rise to absorbed NO_2^- in the PDT.

There is potential for other aspects of the chemiluminescence analyser method to contribute bias; however, at present, no evidence has been uncovered to suggest a temporal trend in any factor that could contribute to a general change in PDT bias factor against the chemiluminescence analyser across multiple co-location sites.

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Table 1: Potential factors influencing accuracy of quantification of ambient NO_2 by PDT.

Stage in the methodology	Origin of potential bias	Direction of bias
Preparation		
	Choice of TEA solvent (water/acetone)	– (presumed)[a]
	Application of TEA by pipetting or by dipping grids in solution	– (presumed)[a]
	Volume of TEA solution applied to grid	– (presumed)[a]
	Shelf-life of prepared PDT	–
Exposure		
	Effects of ambient temperature during exposure	+/–
	Effects of ambient absolute & relative humidity during exposure	+/–
	Lowered ambient concentrations of NO_2 near the tube because of dry deposition onto the tube and other nearby surfaces	–
	Still air outside of tube leading to insufficient replenishment of NO_2 at the mouth of the tube to match the rate of diffusion down the tube. i.e. boundary layer resistance	–
	Wind across open end of tube leading to turbulent rather than molecular transport of NO_2 into the first part of the tube	+
	Co-diffusing HONO and PAN gases as source of absorbed NO_2^-	+
	Co-diffusing SO_2 increasing acidity at absorbent and reducing NO_2 collection efficiency	–
	Particulate nitrite depositing internally on tube and washed into extractant solution	+
	Within-tube chemical reaction ($NO + O_3 \rightarrow NO_2 + O_2$), whose rate is in turn influenced by the absolute and relative ambient concentrations of NO and O_3 during exposure	+
	Saturation of the TEA absorbent by absorbed NO_2	–
	Non-stoichiometric conversion of NO_2 reaching the absorbent to extractable NO_2^- ion	–
	Degradative loss of the absorbed NO_2^- complex during exposure	–
Analysis		
	Failure to extract all absorbed NO_2^- into solution	–
	Ratio and absolute concentrations of the sulphanilamide and NEDD added to the solution of extracted NO_2^-	– (presumed)[a]
	Pre-mixing or sequential addition of sulphanilamide & NEDD solutions	– (presumed)[a]
	Differential degradation of dye intensity because of different length of time from addition of colour reagent to absorbance measurement between standard and sample solutions	+/–
Calculation		
	Erroneous 'standard' value of diffusion coefficient D for NO_2	+/–
Comparison of PDT with chemiluminescence analyser		
	Inaccuracy of analyser	+/–
	Failure to report PDT concentration to the same p,T reporting conditions as the analyser	+/–
	Differential interferences from ambient HONO and PAN between PDT and chemiluminescence analyser measurements	+/–

[a] These sources of potential bias are presumed negative as it is not possible for these aspects of PDT preparation and analysis to yield more nitrite than is actually present as NO_2 in the sampled air.