Air Quality Consultants

The Relationship Between Diffusion Tube Bias and Distance From the Road

Document Control

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Job Number	J211

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Document Status and Review Schedule

Issue No.	Date	Status	Reviewed by
1	January 2006	Draft Report	Stephen Moorcroft
2	July 2006	Final Report	Stephen Moorcroft
3			

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1 Introduction

1.1 Nitrogen dioxide diffusion tubes are widely used for measuring ambient nitrogen dioxide concentrations. Recent work has shown that the tubes are frequently subject to significant bias, as judged by comparison with chemiluminesence analysers. Annual mean concentrations can be over- or under-estimated by more than +/- 30%. A substantial component of this bias has been identified as being dependent on the laboratory preparing and analysing the tube, as well as the on tube preparation method[1] (Laxen and Wilson, 2002, AQEG, 2004). Some laboratories supply and analyse tubes that routinely under-read, while others, using the same tube preparation method supply and analyse tubes that routinely over-read. Other sources of bias that can affect diffusion tubes include: a) the period of exposure, with bias tending to reduce for longer exposure periods[2], although the effect of this on tube uncertainty can be minimised by standardising the exposure period, with monthly exposure being the norm[3] in the UK; b) the chemistry taking place within the tube, whereby nitric oxide is oxidised by ozone to form additional nitrogen dioxide; and c) the potential for shortening of the diffusion length as a result of turbulence induced by wind blowing across the mouth of the tube. These latter two exposure-related effects are expected to lead to over-predictions of concentrations.

1.2 The uncertainty in diffusion tube results can be minimised by adjusting for the systematic biases associated with exposure and laboratory factors, using the results of collocation studies, whereby diffusion tubes are run for a year alongside an automatic monitor[4]. To this end, Defra and the Devolved Administrations have established an on-going survey of diffusion tube collocation studies being undertaken by local authorities throughout the UK. The results of the survey are published 4 times a year as a spreadsheet that can be downloaded from the Review and Assessment Helpdesk website (www.uwe.ac.uk/aqm/review). The adjustment factors cover individual laboratory / tube-type groupings and are year-specific to allow for potential changes in laboratory procedures over time, which may affect tube performance. Combined adjustment factors are provided for each 'laboratory / tube-type / year' grouping based on an averaging of the bias results[5]. Advice on the use of local and/or combined adjustment factors is provided in a FAQ on the Review and Assessment Helpdesk website.

1 There are basically four tube preparation methods: 50% tri-ethanolamine (TEA) in acetone; 50% TEA in water; 20% TEA in water; and 10% TEA in water. These are referred to as 'tube type' in this report.

2 In other words, tubes that over-read will over-read by less at higher concentrations, while those that under-read will under-read by more at high concentrations.

3 This report only considers results from tubes exposed monthly.

4 In most instances the diffusion tubes are exposed in triplicate.

5 The averaging is based on weighted orthogonal regression.

1.3 Application of a bias adjustment factor for a particular 'laboratory / tube-type / year' grouping provides a better estimate of the true annual mean concentration[6]. With such an adjustment the residual uncertainty in individual annual mean diffusion tube results should be of the order of +/-20% (AQEG, 2004). This residual uncertainty in diffusion tubes, after controlling for laboratory and tube preparation method, is probably related to some aspect of tube siting, although the nature of this influence is uncertain. Linked to this, the view has been expressed that the performance of diffusion tubes varies systematically between roadside and background locations (anecdotal evidence from tube users), and that this is to be expected due to chemical reactions between ozone and nitric oxide taking place within the tubes (e.g. Heal and Cape, 1997; Kirby *et al*., 2001). There has thus been speculation that it might be appropriate to use separate adjustment factors for roadside and background monitoring sites to improve the performance of diffusion tubes, i.e. to reduce the residual uncertainty.

1.4 This report uses the results from 252 separate long-term collocation studies (111 Roadside and 114 Background), conducted at a range of sites across the UK in 2000-2005, to test whether there is a significant relationship between distance from the road and diffusion tube bias. If systematic differences are found, then it may be possible to provide additional advice on the use of diffusion tubes, so as to further minimise uncertainty.

6 Diffusion tubes are most reliable for annual means. Individual monthly values will have a much greater uncertainty.

2 Methodology

Data Source

2.1 The analysis has been carried out using data provided by local authorities and consultancies as part of an on-going nation-wide survey of diffusion tube collocation studies. Full details of the survey are provided on the Review and Assessment Helpdesk website (www.uwe.ac.uk/aqm/review). Version 09/05 of the database has been used for the analysis. This includes data up to September 2005. The database includes 315 data entries. Each entry covers one collocation study covering a year (minimum of 9 months data required to provide a valid annual mean). The data represent 22 laboratories and four different tube preparation methods[7].

2.2 The requirement for inclusion in this study was that all data sets should have a minimum of 3 entries in a given year for a particular laboratory / tube preparation method (henceforth shortened to 'tube type'). This was considered necessary to make the analysis more robust. As a result the analysis has been carried out on 252 data entries representing 12 laboratories and four different tube preparation methods (Table 1).

Table 1 Summary of data sets used in the analysis

Laboratory	Tube Type	Years
Bristol Scientific Services	20% TEA in water	2003, 2004
Casella Seal / GMSS / Casella CRE[a]	10% TEA in water	2002, 2003, 2004
Glasgow Scientific Services	20% TEA in water	2002
Gradko	20% TEA water	2002, 2003, 2004
Gradko	50% TEA water	2001, 2003, 2004
Gradko	50% TEA acetone	2001, 2002, 2003, 2004
Harwell Scientific Services	50% TEA acetone	2001, 2002, 2003, 2004
Jesmond Dene Laboratory	50% TEA acetone	2003, 2004
Kent Scientific Services	50% TEA acetone	2002, 2003
Lambeth Scientific Services	50% TEA acetone	2000, 2001, 2002, 2003, 2004
Rotherham MBC/South Yorkshire[a]	50% TEA acetone	2000, 2001, 2002, 2003, 2004
Staffordshire County Council	50% TEA water	2002
Walsall MBC	50% TEA acetone	2003, 2004
West Yorkshire Analytical Services	50% TEA acetone	2002, 2003, 2004

[a] The laboratory name changed during this period.

[7] The database only covers tubes exposed for a month at a time.

2.3 The analysis has made use of the following information:

- **Raw Unadjusted Bias (to be termed 'Raw Bias').** This represents the direct output from the collocation study, with the bias expressed as the percentage difference between diffusion tube and automatic monitor. The raw bias (B) is derived from the equation

  B = (Dm – Cm) / Cm

  where Cm is the average concentration measured by chemiluminesence analyser, and Dm is the average concentration measured by the diffusion tube.

- **Residual Bias after adjustment for Laboratory / Tube Type (to be termed 'Laboratory Bias').** This is derived as above, but using the diffusion tube result adjusted for laboratory bias using the adjustment factor for the relevant laboratory / tube-type / year, as published in version 09/05 of the collocation study spreadsheet.

- **Site Type.** Monitoring sites are generally classified according to the type of environment in which they are located. The terms used in national automatic monitoring networks (Urban Centre; Urban Background; Suburban; Roadside; Kerbside; Industrial; and Rural) as well as the terms used in the National Diffusion Tube Survey (Background; and Intermediate[8]) have been used by respondents to the questionnaire to describe their sites. For the purposes of this report the sites have been grouped into two categories;
  - Ø **Roadside**: covering Kerbside and Roadside sites[9]; and
  - Ø **Background**: covering Urban Centre; Urban Background; Suburban; Rural Background; and Intermediate sites.

- **Distance from road.** Respondents to the survey also provided details of the distance between the collocated monitors and the kerb of the nearest road. This information was available for 72% of the data entries, the majority of missing data applying to background sites. In a very small number of cases the distance was described as a range or as a distance greater than x. Exact values have been ascribed to the ranges, by using the midpoint, e.g. 5 to 10 m is represented as 7.5 m, while distances reported as greater than x have been given the value of x+10, e.g. >50 m is represented as 60 m. In practice the uncertainty introduced by this procedure will not have had a significant impact on the analysis, as the number of values for which distances had to be estimated was small.

- **Concentrations of nitrogen dioxide and nitrogen oxides.** Nitrogen dioxide concentrations are available from both diffusion tubes and automatic monitors for each of the data entries. In addition, some local authorities made available the comparable nitrogen

8 The term Intermediate is no longer used as part of the national diffusion tube survey.

9 The categories were applied by the local authorities. Sites described as roadside are likely to be within 15 m of the road.

oxides concentrations from the automatic monitors. This information was available for 33% of the data entries.

Uncertainty

2.4 No specific consideration has been given to the uncertainty of the individual collocation results. This uncertainty will vary from study to study, depending on the QA/QC applied to both the automatic analysers and the diffusion tubes, as well as the tube handling procedures applied by the local authority and the laboratory. The majority of the studies included in this analysis have used triplicate exposures of diffusion tubes. Some, however, have only used single tube exposures, which will give rise to increased uncertainty. Procedures are now available to calculate uncertainty from duplicate and triplicate exposures of diffusion tubes[10]. There will also be variable uncertainty associated with the automatic monitors. Some will have been operated to the national automatic urban and rural network (AURN) standard, while others may have been run to local procedures adopted by individual local authorities.

[10] Netcen (2005) Spreadsheet for calculating Precision, Accuracy and Bias Adjustment Factors of Diffusion Tubes, available at www.airquality.co.uk/archive/laqm/tools.php .

3 Results and Discussion

Background / Roadside Differences

3.1 The 'raw bias' and 'residual bias after adjustment for laboratory bias' are shown as box and whisker plots for background and roadside sites in Figure 1. These plots show two features:

- a much reduced bias after adjustment for laboratory bias
- a slight difference between background and roadside sites, which is significant at p=0.001 level in two-tailed Student's t test after adjustment for laboratory bias. The difference between mean bias values is about 6%, with roadside bias lower than background.

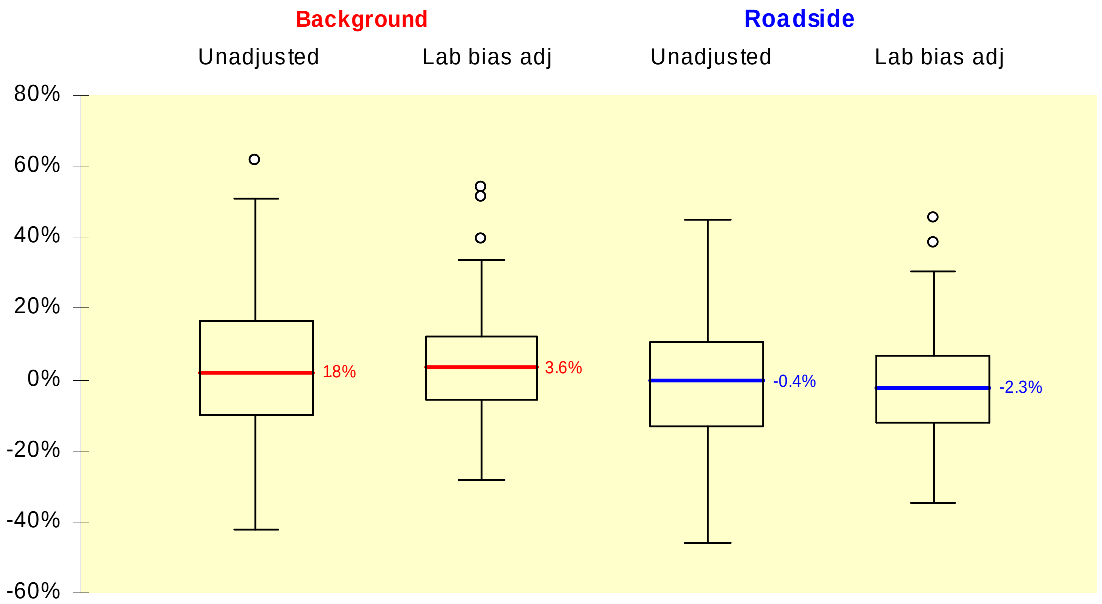

Figure 1 Box and Whisker Plots of Unadjusted Raw Bias and Residual Bias after Laboratory Bias Adjustment, for Background and Roadside sites [11].

3.2 To provide a more specific analysis of the influence of distance from the road, the data for residual bias after adjustment for laboratory bias have been plotted against the distances from the road in Figure 2. Distance is shown on a logarithmic scale, as the majority of the data points

[11] The box shows the quartile range (within the box, 25% of the data lie above and 25% below the median). The mean is shown within the box and the value given. The T bars show the range based on an additional 1.5 times the quartile range. The individual data points are those that lie outside the range defined by the T bars.

are close to the road, and their transformation provides a more normal distribution. A best fit logarithmic regression line has been added. This suggests some influence of distance from the road on the residual bias, which is consistent with the results in Figure 1. The plot of residual bias against distance is repeated in Figure 3 with distance on a linear scale. The regression line now appears as a curve, suggesting the biggest effect is close to the road. This is consistent with the higher concentrations of nitrogen oxides and nitrogen dioxide being found within about 20 m of roads. The relevance of this observation is discussed in the next section.

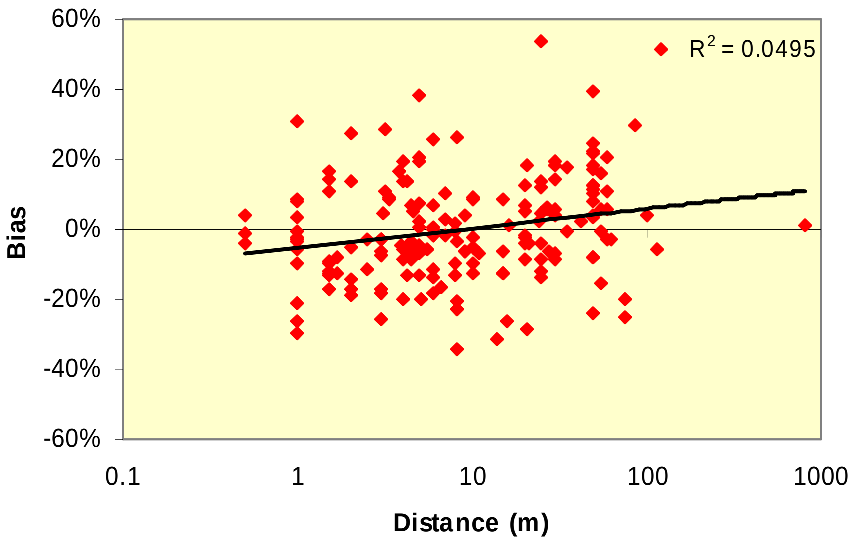

Figure 2 Residual Bias after Laboratory Bias Adjustment versus Distance from the Road. (Distance on a log scale)

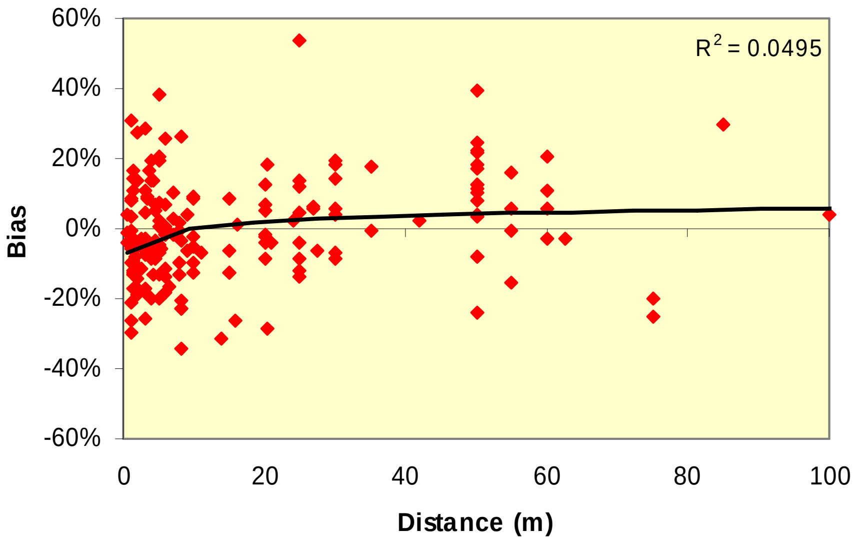

Figure 3 Residual Bias after Laboratory Bias Adjustment versus Distance from the Road. (Distance on a linear scale)

3.3 This analysis suggests that there is only a limited effect of distance from the road on the residual bias after adjustment for laboratory bias, perhaps amounting to a difference of about 10% between the kerb and background sites well away from the road. The implication is that annual mean nitrogen dioxide diffusion tube concentrations close to roads are likely to slightly under-read true values, while at background sites diffusion tubes would over-read true values.

3.4 The possibility of an effect of distance from the road on diffusion tube performance is most likely to be associated with the higher concentration of nitrogen oxides and associated lower concentrations of ozone on approaching a road, coupled with the chemistry involving nitrogen oxides and ozone taking place within the sample tube. This is explored more fully in the next section.

Role of Chemistry

3.5 A number of investigators have examined the role of nitrogen dioxide chemistry in affecting the performance of diffusion tubes (Heal and Cape, 1997; Bush *et al*,.2001; Kirby *et al*, 2001). The main features involve the reaction between nitric oxide and ozone within the diffusion tube to form additional nitrogen dioxide. As the tubes largely exclude ultraviolet light, the normal loss of nitrogen dioxide by photolysis is reduced and there is a net increase in nitrogen dioxide within the tube. The extent to which this reaction takes place depends on the availability of ozone and nitric oxide, both of which are related to the nitrogen oxides concentration. Bush *et al* (2001) have developed a model to describe the balance. This identifies a peak in nitrogen dioxide formation within the diffusion tube at nitrogen oxides concentrations around 60-70 $\mu g/m^3$. The predicted diffusion tube bias using their model is shown in Figure 4 as the upper dashed line[12]. Also shown are the diffusion tube bias values from the collocation study, after adjustment for laboratory bias, together with the linear regression line through these data. The measurements fall below the model values because they have been adjusted to match the automatic monitoring results, i.e. they have been implicitly adjusted in an overall way for exposure bias. To allow for this, the lower dashed line shows the model results shifted down to match the zero bias at around 60 $\mu g/m^3$, as predicted by the linear fit to the collocation data. This shows that the model broadly fits the data, with bias reducing at higher concentrations. The data are insufficient to confirm the slight reduction in bias predicted by the model below about 60-70 $\mu g/m^3$.

[12] This is derived by averaging the Bush et al (2001) plots for summer, winter, and equinox conditions – the latter being counted twice.

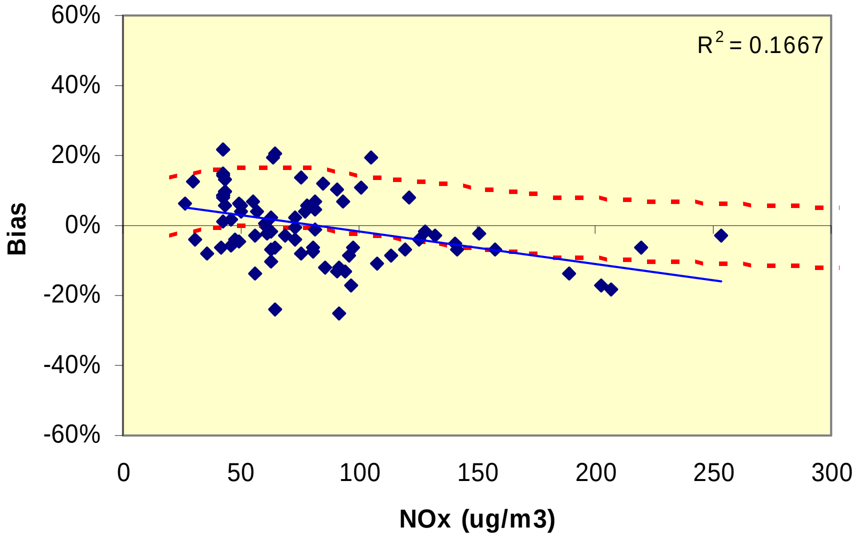

Figure 4 Residual Bias after Laboratory Bias Adjustment versus Nitrogen Oxides Concentration. Blue solid line is linear regression on the data. Red dashed line (upper) is the predicted bias behaviour from the model of Bush et al (2001). The lower red dashed line is the model shifted down – see text.

3.6 These observations suggest that the residual bias after adjustment for laboratory bias could be further adjusted to allow for the effect of tube chemistry as revealed by the nitrogen oxides concentration. However, diffusion tubes only measure nitrogen dioxide, thus there are no nitrogen oxides values on which to base an adjustment. As nitrogen oxides and nitrogen dioxide are closely linked, the relationship with nitrogen dioxide has been explored. Figure 5 shows the residual diffusion tube bias after adjustment for laboratory bias as a function of the nitrogen dioxide concentration measured with the automatic analyser. As with nitrogen oxides in Figure 4, diffusion tube bias decreases with increasing nitrogen dioxide concentration.

3.7 The linear regression line fitted to the data in Figure 5 can be used to adjust for the bias that is believed to be related to chemistry within the diffusion tube and thus provide a better fit between diffusion tube and automatic monitor. The adjustment would be applied as follows:

$$NO_{2[NO2\ adj]} = (1-(-0.0043 \times NO_{2[Lab\ adj]} + 0.1724)) \times NO_{2[Lab\ adj]} \quad (1)$$

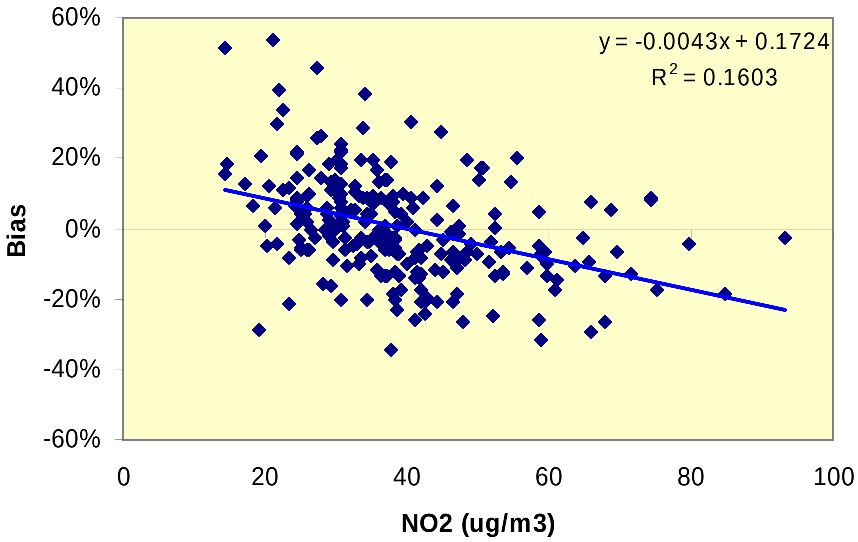

Figure 5 Residual Bias after Laboratory Bias Adjustment versus Nitrogen Dioxide Concentration Measured using Automatic Analysers. Blue solid line is linear regression on the data.

3.8 In practice, the adjustment would have to be based on the nitrogen dioxide concentration as measured by the diffusion tube, as this will be the only value available. This is recognised to be a limitation, as the adjustment is based on use of a diffusion tube result that is know to be in error (hence the need to adjust it). This effect can be minimised by adjusting the diffusion tube for laboratory bias first, so as to get the best estimate of the 'true' nitrogen dioxide concentration, before applying the tube-chemistry adjustment.

Benefits of Adjustments

3.9 The relationship between raw unadjusted annual mean nitrogen dioxide concentrations from diffusion tubes and from automatic monitors is shown in Figure 6. There is considerable scatter, and diffusion tubes tend to underestimate at high concentrations and overestimate at low concentrations.

3.10 After adjusting for laboratory bias the scatter is reduced, but there is still a dependence on concentration (Figure 7).

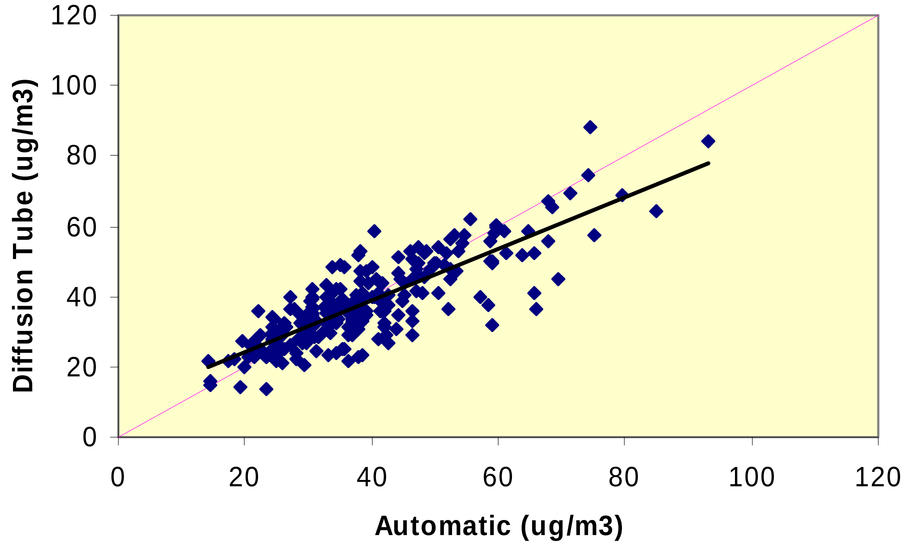

Figure 6 Annual Mean Nitrogen Dioxide Measured by Diffusion Tube and Automatic Monitor. The diffusion tube results are raw unadjusted values.

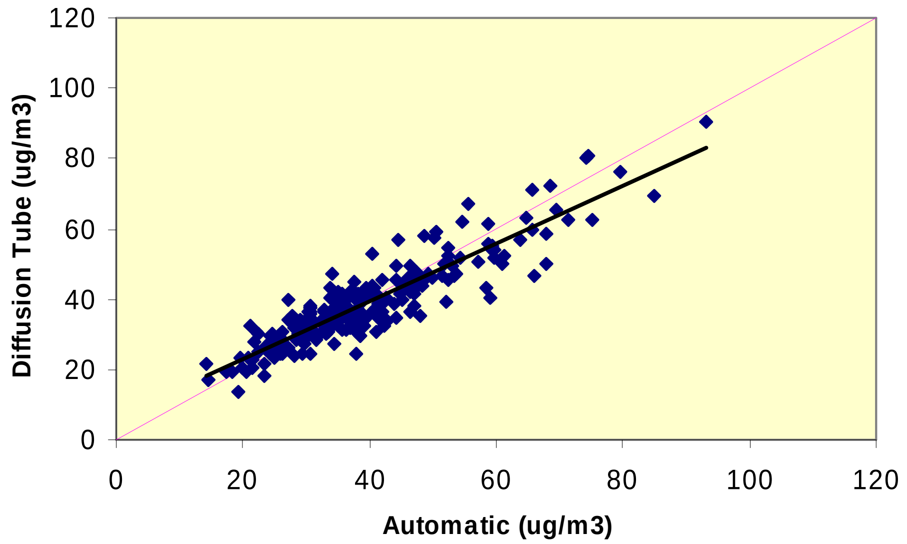

Figure 7 Annual Mean Nitrogen Dioxide Measured by Diffusion Tube and Automatic Monitor. The diffusion tube results have been adjusted for laboratory bias.

3.11 Applying the additional correction for tube chemistry, based on nitrogen dioxide concentration measured by the diffusion tube, gives a similar scatter, but removes the relationship with concentration (Figure 8).

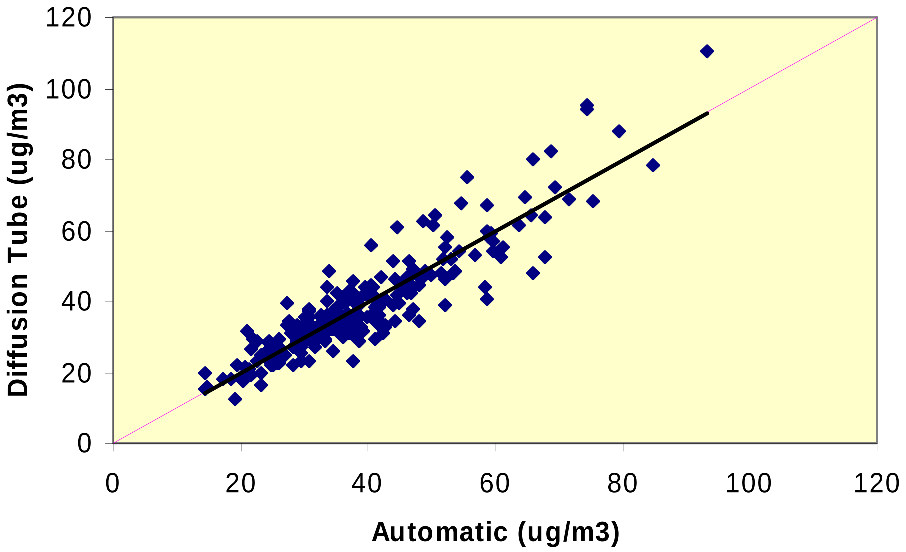

Figure 8 Annual Mean Nitrogen Dioxide Measured by Diffusion Tube and Automatic Monitor. The diffusion tube results have been adjusted for laboratory bias and tube chemistry.

3.12 The overall performance of the diffusion tubes is also summarised in the box and whisker plots in Figure 9. The mean bias for diffusion tubes is effectively zero in all cases, but the adjustment for laboratory bias clearly reduces the uncertainty. The additional recommended adjustment for tube chemistry makes little difference to the overall uncertainty, but provides a better fit over the full concentration range as previously discussed. The overall uncertainty after adjustment for laboratory bias is around +/- 30% at the 95% level (based on 2 x standard deviation), remaining the same after further adjustment for nitrogen dioxide concentration. Prior to adjustment for laboratory bias, the uncertainty for the 252 collocation results is around +/- 40%. The residual uncertainty after adjustment for laboratory bias and further adjustment for nitrogen dioxide concentration can be lower still for individual laboratories. For example tubes analysed by Harwell Laboratory have a residual uncertainty of +/- 20% (22 collocation results), while for the Rotherham / South Yorkshire Laboratory it reduces to +/- 18% (18 collocation results), the unadjusted values being +/- 28 % and +/- 26% respectively.

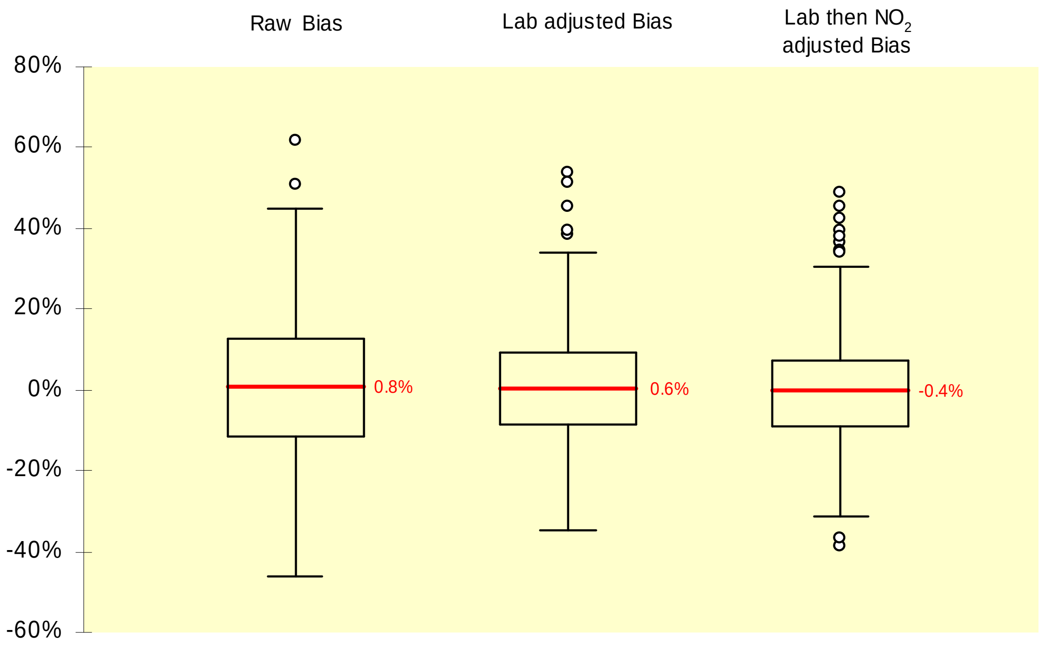

Figure 9 Box and Whisker Plots of Unadjusted Raw Bias, Residual Bias after Laboratory Bias Adjustment, and Residual Bias after Laboratory Bias Adjustment then Adjustment for Tube Chemistry using Nitrogen Dioxide Concentration.

3.13 Having adjusted the data for nitrogen dioxide concentration, it is appropriate to see if there is still any evidence of a relationship with distance from the road. The original Figure 2 has therefore been reproduced, but this time plotting the residual bias after adjustment for both laboratory bias and tube chemistry (Figure 10). This shows no significant relationship of the residual bias with distance from the road, which supports the view that the apparent relationship of diffusion tube bias with distance from the road is merely reflecting the different concentrations of nitrogen oxides at different distances from the road, as represented by the nitrogen dioxide concentration.

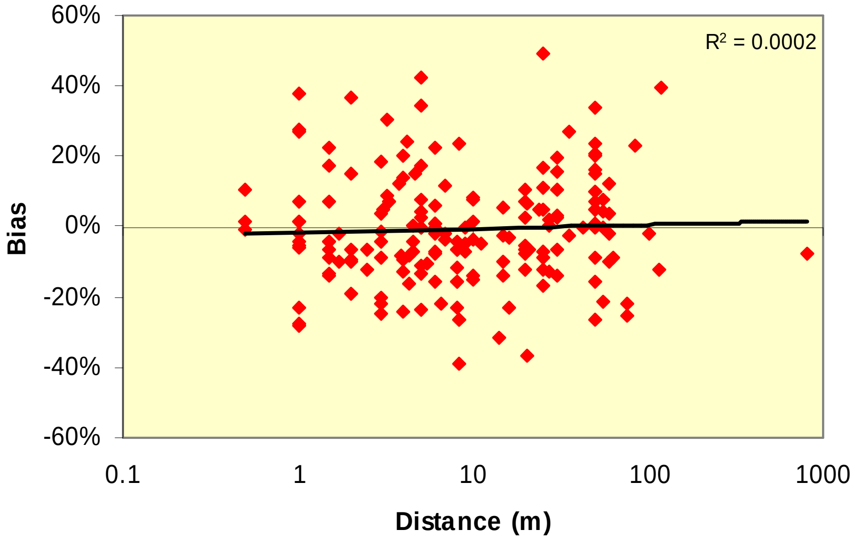

Figure 10 Residual Bias after Laboratory Bias Adjustment then Adjustment for Tube Chemistry using Nitrogen Dioxide Concentration versus Distance from the Road. (Distance on a log scale).

4 Summary and Conclusions

4.1 The results of a nation-wide survey of nitrogen dioxide diffusion tube collocation studies have been used to improve understanding of diffusion tube bias, with a view to identifying appropriate adjustments to minimise bias and uncertainty. The results for 252 separate collocation studies have been analysed to show whether there is any influence of location on the residual bias after adjustment for laboratory bias. Both a broad classification into roadside or background and a detailed examination in relation to distance from the road suggest a small influence of proximity to a road on the residual bias (Figures 1 and 2). Tubes close to a road are more likely to underestimate concentrations, once they have been adjusted for laboratory bias.

4.2 The most likely explanation of this behaviour is chemical reactions within the diffusion tube involving nitrogen oxides, ozone and sunlight. This has been demonstrated in a theoretical model of diffusion tube bias (Bush *et al*, 2001), which shows that the effect of chemistry would be dependent on the nitrogen oxides concentration, with a broad decrease at higher concentrations. The results from a number of collocation studies included nitrogen oxides results, and the residual bias data show the expected relationship with the nitrogen oxides concentration (Figure 4).

4.3 Nitrogen oxides concentrations are not available from diffusion tubes, thus there is no basis for adjusting using nitrogen oxides values. However there is a reasonably consistent relationship between nitrogen dioxide and nitrogen oxides, thus the residual bias values have been examined in relation to the measured nitrogen dioxide (automatic monitor). There is a clear relationship with decreasing bias at higher concentrations (Figure 5). This is represented by the equation:

$$\text{Bias} = -0.0043 \times NO_2 + 0.1724 \qquad (2)$$

With Bias being the residual bias after adjustment for laboratory bias and NO_2 being the annual mean nitrogen dioxide in $\mu g/m^3$.

4.4 This relationship can be used to adjust the annual mean diffusion tube results utilising the measured concentration after adjustment for laboratory bias, as set out in equation (1).

$$NO_{2[NO2\ adj]} = (1-(-0.0043 \times NO_{2[Lab\ adj]} + 0.1724)) \times NO_{2[Lab\ adj]} \qquad (1)$$

Applying this adjustment produces a much improved fit between diffusion tube and automatic monitor concentrations (Figure 8). The effect of this tube-chemistry adjustment depends on the measured concentration: thus a laboratory bias adjusted result of 20 μg/m^3 would become 18.1 μg/m^3, after adjustment for bias due to tube chemistry, a value of 40 μg/m^3 would remain at 40 μg/m^3, and 60 μg/m^3 would become 65.1 μg/m^3. The effect of this adjustment is minimal at concentrations close to the objective of 40 μg/m^3, thus it will not have a material effect on exceedences of the objective identified using diffusion tubes.

4.5 After adjustment of the data for tube chemistry there is no longer any evidence of a relationship between residual bias and distance from the road. This confirms that the apparent relationship between residual bias (after adjustment for laboratory bias) and distance from the road is merely reflecting the different nitrogen oxides concentrations at different distances from the road and the influences they have on tube chemistry.

4.6 There are limitations inherent in the proposed adjustment for tube chemistry:

- in certain situations the method of laboratory bias adjustment will itself adjust in part for the tube chemistry effect. This will happen if the collocation results are mainly for sites with either low or high nitrogen dioxide concentrations, rather than distributed over the full concentration range;
- the adjustment would not be appropriate for a survey using a locally determined collocation factor, unless the factor was derived from more than one site covering a wide range of concentrations.
- the adjustment for tube chemistry using nitrogen dioxide concentrations measured with the diffusion tubes themselves is based on a result that is known to be in error (hence the need to adjust it). This effect is minimised by adjusting the diffusion tube for laboratory bias first, so as to get the best estimate of the 'true' nitrogen dioxide concentration, before applying the tube-chemistry adjustment. The error is considered to be small when compared with the benefit of applying a tube chemistry adjustment in the first place.

4.7 Three broad conclusions arise from this work:

- **Adjusting for tube chemistry reduces the uncertainty of diffusion tube results. It is <u>not</u> recommended, however, that this adjustment is applied routinely.** This is because the adjustment as suggested cannot be applied in every situation. It is only really applicable in those situations where at least 3 collocation studies are available that extend broadly over the range 30 to 50 μg/m^3. Where collocation studies are all at similar concentrations, for instance all at background sites with low concentrations, then the adjustment for laboratory / exposure bias will effectively incorporate the adjustment for tube-chemistry bias. In addition, the proposed adjustment has little effect at concentrations around 40 μg/m^3. Thus this adjustment will not affect decisions in relation to exceedences of the objective. **There may**

though be occasions when it is appropriate to apply the tube-chemistry bias adjustment. For example, it would improve the reliability of the diffusion tube data for use in model verification at both roadside and background sites.

- **The value of a local collocation study (and the subsequent bias adjustment) will be improved if the concentrations being measured are similar to those in the wider survey.** Broadly, this equates to carrying out a collocation study at roadside locations in order to derive a bias adjustment factor to be applied to a survey of roadside concentrations.
- **Care should be taken to avoid applying a bias adjustment factor derived from a local collocation study carried out for concentrations that are very different to those being measured in the wider survey.** In other words, collocation results from a low concentration site (typically a background site) should not be used to derive a bias adjustment factor for survey results from high concentration sites (typically roadside sites) and vice versa. There may be circumstances where this is not possible, and this will increase the uncertainty of the results.

4.8 In all cases, a clear statement should be provided when reporting diffusion tubes results as to exactly what adjustments have been applied.

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Acknowledgements

Thanks are due to all the local authorities who supplied the results of their collocation studies.

Thanks are also due to Jaume Targa and Alison Loader of netcen, for helpful comments on a draft of this report.