Compilation of Diffusion Tube Collocation Studies Carried out by Local Authorities

Air Quality Consultants

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Report Prepared by

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1 Introduction

1.1 Local Authorities throughout the UK make significant use of nitrogen dioxide diffusion tubes to support their air quality Review & Assessment work. Indeed, they are encouraged to do so in the Guidance published by Defra and the Devolved Administrations[1]. There have been a number of studies over the years looking at the performance of tubes, often producing contradictory findings and recommendations.

1.2 The performance of the tubes can be judged by running them alongside automatic monitors (chemiluminesence analysers). There have been a number of national intercomparison studies, but these have been confined to exposure over just one or two 1-month periods[2]. The results of these studies have hinted at systematic differences in the performance of the different laboratories and between the different tube preparation methods. There is also anecdotal evidence of systematic differences in the performance of diffusion tubes by type of location, e.g. roadside and background, and by season.

1.3 Local Authorities are encouraged, as part of their air quality Review & Assessment work, to locate tubes alongside automatic analysers to help determine any bias. There is thus a growing body of data on tube performance. Casella Stanger were recently commissioned by Defra to collate data from these Local Authority studies. The results of this survey have been made available to Air Quality Consultants Ltd. They have been supplemented by additional data obtained directly from Local Authorities[3]. This report examines the results from 23 Local Authority studies covering 44 site-years worth of annual comparisons. The aim is to provide Local Authorities with clearer guidance on the use of nitrogen dioxide diffusion tubes.

1 Review & Assessment: Pollutant Specific Guidance, LAQM.TG4(00), May 2000, DETR.

2 The most recent report was published by AEA Technology in February 2002 "Summary Results from the UK NO_2 Network Field Intercomparison Exercise 2001".

3 Permission has been obtained from these authorities to add the data to the database.

2 Results

2.1 The results are summarised in Tables 1-3, arranged by tube preparation method and by laboratory. Table 1 sets out the results for all tubes prepared by Gradko. This laboratory has been separated out, as 16-site years worth of results are available for tubes prepared by this laboratory. In most of these cases the tubes were also analysed by Gradko. The Gradko tubes are also separated by preparation procedure: 50% TEA in Acetone or 50% TEA in water and in one case 20% TEA in water.

2.2 Tables 2 and 3 set out the results for tubes prepared and analysed by other laboratories. Table 2 covers tubes prepared using 10% or 20% TEA in water, while Table 3 covers tubes prepared with 50% TEA in acetone. The tubes in Table 2 have been exposed over 1-week, 2-week and 1-month intervals, while all other tube results are based on 1-month exposure intervals.

2.3 Results are presented as bias relative to the automatic analysers for annual periods and for winter (October-March) and summer (April – September)[4]. They are only presented where there is 75% or greater data capture within an annual period, i.e. 9 months or more. In most cases calendar years are used, but in some, data are included where the annual period runs from one year into another.

3 Analysis

3.1 When analysing the results of diffusion tube surveys it is necessary to take account of a wide range of variables that may affect tube performance. There are four different tube preparation techniques in current use: 50% TEA[5] in water; 20% TEA in water; 10% TEA in water and 50% TEA in acetone. Tubes are most commonly exposed for monthly intervals, but in some cases for 2-week or 1-week intervals.

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4 Bias is defined as the percentage deviation of the diffusion tube (D) from the chemiluminesence (C) value. Thus bias = (D-C)/C expressed as a percentage.

There is also a large number of laboratories preparing and analysing the tubes. In some cases a different laboratory prepares the tube to that carrying out the analysis. For this study, 11 different laboratories or combinations of laboratories have been used by the 23 Local Authorities for the supply and analysis of the tubes (Tables 1-3).

3.2 As will become apparent, it is important when analysing data to identify factors that influence performance to only consider sets of results from the same laboratory[6], using the same preparation method and the same exposure interval. This limits the number of data sets that can be examined in detail.

Role of Exposure Interval

3.3 The results do not allow a direct analysis of the effect of exposure interval on tube performance, as the same laboratory and tube preparation method have not been applied over different exposure intervals. Previous studies have, however shown that tubes exposed over 1-month intervals produce lower concentrations than those exposed over 1 week. Bush et al.[7] found a small difference in their study at sites throughout the UK, with 2-weeks exposure giving 1-4% higher bias than 1-month, while Heal et al[8] found a more significant difference in their study using 10% TEA in water tubes, with an average bias of +24% for 1-week exposure, +15% for 2-weeks and +6% for 1-month. The results of the present study appear to support this general pattern of reduced bias for longer exposure intervals (Figure 1), although some care is required in the interpretation, as the tubes exposed for 1 and 2-weeks are 10% TEA in water, while the 1-month exposures are mostly based on 50% TEA in water or acetone. The laboratories are also different in each case (Tables 1-3).

5 TEA = triethanolamine, which is coated on a stainless steel mesh held within the tubes.
6 This could be the same combination of laboratories if one is used for tube supply and another for analysis.
7 Bush T, Smith S, Stevenson K and Moorcroft S (2001) Validation of Nitrogen Dioxide Diffusion Tube Methodology in the UK, Atmos. Environ., 35, 289-296.
8 Heal M R, Kirby C and Cape J N (2000) Systematic Biases in Measurement of Urban Nitrogen Dioxide using Passive Diffusion Samplers, Environmental Monitoring and Assessment, 62, 39-54.

Seasonal Pattern in Bias

3.4 The results show that the laboratories perform very differently. The annual bias values for individual site-years range from +41.4% to – 43.7%, which is greater than the ±30% normally expected. The first feature examined was the presence or absence of a seasonal pattern. The crude summer / winter analysis in Tables 1-3 shows no consistent pattern across all the laboratories and methods. A more detailed analysis is considered appropriate for the Gradko tubes, as results are available for 6 site-years using tubes prepared with 50% TEA in water and 5 site-years for tubes prepared with 50% TEA in acetone[9]. The data for Casella GMSS tubes are also examined for seasonal trends, as results are available for 2 sites for a total of 12 site-years. Finally, the results from all other laboratories using the 50% TEA in acetone method are examined together.

3.5 The results for the Gradko tubes are presented in Figure 2, separated into the two methods of tube preparation. They show two distinctly different patterns:

- the tubes prepared with 50% TEA in acetone show no evidence of a seasonal pattern, with a ratio averaging 0.74 (a negative bias of 26%)
- the tubes prepared with 50% TEA in water show a significant seasonal effect, with higher ratios in four months: August, September, October and November, averaging 0.91 (-9% bias), and lower ratios in all other months, averaging 0.68 (-32% bias) (overall ratio 0.75, i.e. –25% bias).

3.6 Figure 3 shows the results for the GMSS tubes prepared using 10% TEA in water and exposed for 1-week at a time. The results for the Gradko tubes prepared using 50% TEA in water are also repeated from Figure 2 for ease of comparison. The GMSS tubes show evidence of a similar seasonal pattern to the Gradko water based tubes, with higher ratios in August, September and October. No explanation for the seasonal pattern of tubes prepared with TEA in water has been found. It is also not

[9] The majority of the data are for 2001 and a part of 2000, thus there could be a difference in seasonal pattern from one year to another that is not being picked up. Examination of the GMSS data sets in Figure 2 and data for other laboratories in Figure 3, which cover 6 years and 3 years respectively suggest that there is not a year to year variation in the seasonal pattern.

yet clear whether this seasonal pattern for water based tubes can be generalised across all laboratories.

3.7 Figure 4 shows the results for all other tubes prepared and/or analysed by other laboratories using 50% TEA in acetone and exposed over a 1-month interval. The results for the Gradko tubes prepared using 50% TEA in acetone are also repeated from Figure 2 for ease of comparison. These data support the view that tubes prepared with 50% TEA in acetone do not have any clear seasonal dependency to their performance.

3.8 There are important implications arising from a seasonal pattern to the performance of diffusion tubes. In many Local Authority studies diffusion tubes have been validated against automatic monitors that have only been in place for three-month periods. The results from this study suggest that, for tubes prepared with TEA in water, it would be wrong to apply a bias adjustment factor[10], derived over this three-month period, to adjust diffusion tube results collected over a whole year. Conversely, it would be wrong to apply an annual bias adjustment factor to a 3-month diffusion tube survey in the case of tubes prepared with TEA in water. The indications are that the same problems do not arise for tubes prepared with TEA in acetone.

3.9 The national intercomparison studies that have been carried out by netcen over many years are based on sampling over a one or two month period in each year, usually in the autumn. This is the period in which tubes prepared with TEA in water appear to be reading higher than the annual average. This implies extra caution should be applied to interpreting the results from these studies, especially when comparing results based on either TEA in water or TEA in acetone.

[10] The bias adjustment factor is the value C/D, where C is the chemiluminesence concentration and D the diffusion tube concentration.

Uncertainty of Short-Period Estimates of Annual Bias

3.10 On occasions local authorities find that it is only practicable to carry out a collocation study over a period of 3 months or so. It is therefore relevant to establish the uncertainty associated with an estimate of the annual ratio of diffusion tube to chemiluminesence results from a short period of monitoring. The results from sites with complete 12-months data sets have therefore been examined to establish the effect of different averaging periods, ranging from 1 month through to 11 months. These results are shown separately for tubes prepared using 50% TEA in acetone and 50% TEA in water and for tubes prepared and analysed by Gradko and by other laboratories (Figures 5 to 8). The uncertainty for different averaging periods for the different methods is summarised in Table 4, both as an average uncertainty of the annual estimate and 95% confidence limits on the uncertainty. The uncertainty in the estimate of the annual ratio of diffusion tube to chemiluminesence concentration clearly improves as the averaging period increases. The uncertainty is generally greater for the 50% TEA in water method, which undoubtedly reflects the added variability due to the seasonal pattern seen for these tubes. An estimate of annual mean ratio of diffusion tube to chemiluminesence results, based on a collocation comparison over 3 months, will have an average uncertainty in the range ± 8-14% (95% confidence range ± 18-32%). This reduces to ± 5-10% (95% confidence range ± 10-23%) when using a 6 months average and ± 3-4% (95% confidence range ± 6-12 %) for 9 months. This would suggest that a 9-month period should be the minimum for a collocation study designed to provide a reliable estimate of the annual bias, although this could probably be reduced to 6 months for Gradko 50% TEA in acetone tubes[11].

Role of the Laboratory and Tube Preparation Method

3.11 One of the main features to arise out of the survey is that the performance of the diffusion tubes depends more on the laboratory preparing and analysing them than on the preparation technique for the tubes. This is evident from an examination of

[11] This clearly does not apply in the case where a 3-month bias adjustment factor is required for a 3-month diffusion tube survey. The results do though indicate that there will be greater uncertainty associated with a 3-month bias adjustment factor.

the results for tubes exposed for 1-month periods and prepared with 50% TEA in acetone. Seven different combinations of laboratory have prepared and analysed such tubes, and the average bias for each laboratory ranges from +20.5% to –26.1% (Tables 1 and 3). The reason for this difference between laboratories is unclear. There is anecdotal evidence that the performance can change if the analyst changes, suggesting a fairly subtle change in preparation technique could be accounting for the differences. This emphasises the importance of ensuring consistency within a laboratory when preparing and analysing diffusion tubes.

3.12 The recent study by netcen into the effects of tube preparation techniques concluded that tubes made up with 50% TEA in acetone gave a positive bias, while tubes made up with 50% TEA in water gave a negative bias[12]. This is not seen in the results of the present study where one laboratory used both methods. Gradko 50% TEA in acetone tubes have a similar bias to 50% TEA in water tubes, in both cases significantly negative (Table 1). The same netcen study showed that 20% TEA in water gave an intermediate performance. Results for this method are only available for two sites. Bristol Scientific Services show a +16.5% bias, although based on 2-week exposure intervals, while the Gradko tubes for Dartford BC show a –20.8% bias. The latter is not inconsistent with the results for Gradko tubes prepared with 50% TEA in water or 50% TEA in acetone. Again, the reason for the different conclusions arising from different studies is not clear. The results do though caution against deriving generic conclusions about tube performance, as the performance seems to be so highly dependent on the laboratory preparing and analysing the tubes.

Other Factors Potentially Affecting Tube Performance

3.13 It has been suggested anecdotally that tubes perform differently at roadside and background sites. The results of the present survey nominally allow an examination of this factor, as a number of the collocation studies involved roadside sites. However, given the importance of laboratory and tube preparation method in

[12] Loader A (2001) Investigation of the Effects of Preparation Technique on Performance of Nitrogen Dioxide Diffusion Tubes, AEA Technology, April 2001.

determining tube performance, it is only valid to look for any dependency within results obtained by one laboratory, using the same tube preparation method and the same exposure interval. This narrows the examination to the Gradko tubes prepared using 50% TEA in acetone (Table 1) and the Lambeth Scientific Services tubes (Table 3). These results provide no evidence of any pattern of differences in bias between roadside and other sites. In part this is because there is only one roadside site in each data set, although the bias for these roadside sites lies in the middle of the range for each of these data sets.

3.14 It is also possible that tube performance could relate to the absolute concentration at the monitoring site. This has been investigated by examining the bias as a function of annual mean nitrogen dioxide, as measured by the chemiluminesence analyser. The analysis has been confined to results obtained by the same laboratory, tube preparation method and exposure interval. The results are shown in Figure 9. In 8 out of the 9 data sets there is a more negative bias at higher concentrations. This would suggest that there might be some sort of relationship between tube performance and concentration. The one exception is for Gradko 50% TEA in water tubes. The pattern is quite variable and no firm conclusions can be reached at this time.

Default Bias Adjustment Factors

3.15 The results of this study indicate that the ideal position will be for each Local Authority to derive its own bias adjustment factors on an on-going basis. However, this will not always be practicable, leaving the authority uncertain as to how to treat its diffusion tube results. In these circumstances it is proposed that the authority should rely on a default adjustment factor derived from a number of studies carried out using tubes supplied by the same laboratory and with the same preparation technique. A default adjustment factor should, however, only be provided for a laboratory and tube preparation method, when results are available for a minimum of 3 different sites. On this basis, there are sufficient data from the present study to derive default adjustment factors for monthly exposure of diffusion tubes prepared and analysed by Gradko and by Lambeth Scientific Services. The default adjustment factors are shown in Figure 10, together with the range of values used to derive them[13]. The default adjustment factor for monthly exposure of Gradko tubes made up with 50% TEA in water is 1.39. For Gradko tubes made up with 50% TEA in acetone and exposed monthly the default adjustment factor would be 1.36. For Lambeth Scientific Services tubes made up in 50% TEA in acetone and exposed monthly the factor is 1.06.

3.16 The use of default adjustment factors will produce annual mean diffusion tube results that are closer to the true concentration than the unadjusted values. An independent test of the effect of applying an adjustment factor has been carried out for the three sets of data described above. For each data set an adjustment factor has been derived from all but one of the tubes in turn and then applied to that excluded tube. The results are shown in Figure 11. The majority of the adjusted annual mean diffusion tube values fall within ±15% of the chemiluminesence values. It should be remembered that some of this residual uncertainty may be due to uncertainty in the chemiluminesence values, and not just the diffusion tubes. In addition, application of the proposed default adjustment factors should produce a smaller uncertainty than shown, as the default factors are based on the average derived from one more data set than used to produce the test results shown in Figure 11.

3.17 Once a default bias adjustment factor is determined, it will clearly be important to ensure that nothing about the way in which the laboratories prepare or analyse the diffusion tubes changes, as this might affect the default bias adjustment factors. It is therefore recommended that Defra continues to collate data from collocation studies, so as to maintain up-to-date default bias adjustment factors. This work should also be aimed at providing sufficient data to propose default bias adjustment factors for other laboratories.

[13] These are the factors to multiply the annual mean diffusion tube value by.

4 Recommendations

4.1 Arising from this study, the following factors should be taken into account when using diffusion tubes:

a) Whenever a diffusion tube survey is carried out, it is essential that the laboratory bias is determined and that the survey results are adjusted for this bias, so as to provide best estimates of the true concentrations. When presenting results, information should be provided on the bias adjustment factor used and its source. The factor must be obtained for the same exposure interval as used for the survey, e.g. monthly, 2-weekly or weekly.

b) Diffusion tube bias is highly dependent on:

- the laboratory preparing the tubes;
- the laboratory analysing the tubes (if different);
- the tube preparation method that the laboratory has used;
- whether the laboratory has changed any aspect of its preparation and analysis method during the period of the survey, as this could lead to a change in performance, making earlier bias adjustment factors out of date.

It is therefore important to keep a record of all these factors, and present this information alongside the results of any survey: Particular care needs to be taken when changing the laboratory supplying and analysing the tubes.

c) Diffusion tube bias should be determined locally wherever possible. This collocation study should cover the same time period as the diffusion tube monitoring survey, especially for tubes prepared with TEA in water. This is to allow for seasonal variation in the bias factor. Such a seasonal effect does not appear to apply to tubes prepared with TEA in acetone.

d) When carrying out a collocation study to determine the annual bias adjustment factor to apply to survey data, it is recommended that this should be for a minimum of 9 months to ensure a reliable estimate of the factor to apply to annual survey results. The indications are that this could be reduced to 6 months for Gradko 50% TEA in acetone tubes.

e) Where it proves impractical to provide a local bias adjustment factor it is reasonable to apply a default bias adjustment factor. Currently, sufficient information is considered to be available to provide default bias adjustment factors for tubes exposed for 1-month intervals if they are prepared and analysed by Gradko using 50% TEA in water or 50% TEA in acetone or by Lambeth Scientific Services using 50% TEA in acetone. The factors currently recommended are 1.39, 1.36 and 1.06 respectively.

4.2 It is recommended that Defra continues to support the collection and analysis of results from Local Authority collocation studies. This should enable additional default bias adjustment factors to be derived, and a check maintained on the appropriateness of the existing default factors.

Table 1 Summary of Diffusion Tube Validation Studies. Tubes all prepared by Gradko. Results in µg/m^3.

Local Authority	Year	Data Capture	Exposure Interval	Lab Name	Tube Prep.	Tube Analysis	Prep. Technique	Site Type	Summer Tube	Summer Cont.	Winter Tube	Winter Cont.	Annual Tube	Annual Cont.	Summer Bias	Winter Bias	Annual Bias	Average by Laboratory[a] Summer Bias	Average by Laboratory[a] Winter Bias	Average by Laboratory[a] Annual Bias
Aberdeen CC	2000/01	12 mths	1 mth	Aberdeen CC	Gradko	Aberdeen CC	50% TEA in Acetone	Roadside	47	62	44	61	46	61	-24.1%	-26.7%	-25.5%			
Aberdeen CC	2001/02	12 mths	1 mth	Aberdeen CC	Gradko	Aberdeen CC	50% TEA in Acetone	Roadside	39	47	41	56	40	53	-16.2%	-27.1%	-24.8%	-20.1%	-26.9%	-25.1%
RB Kensington and Chelsea	2001	11 mths	1 mth	Gradko	Gradko	Gradko	50% TEA in Acetone	Urban Background	28	35	34	48	31	42	-19.9%	-28.6%	-25.3%			
LB Hillingdon	2001	12 mths	1 mth	Gradko	Gradko	Gradko	50% TEA in Acetone	Suburban	27	43	31	50	29	46	-37.0%	-37.9%	-37.5%			
LB Brent	2001	10 mths	1 mth	Gradko	Gradko	Gradko	50% TEA in Acetone	Urban Background	25	30	33	43	29	37	-18.8%	-23.4%	-21.5%			
LB Camden	2001	11 mths	1 mth	Gradko	Gradko	Gradko	50% TEA in Acetone	Roadside	46	65	51	67	49	66	-29.0%	-23.3%	-25.9%			
LB Camden	2001	12 mths	1 mth	Gradko	Gradko	Gradko	50% TEA in Acetone	Urban Centre	35	46	46	56	41	51	-22.6%	-17.5%	-19.8%	-25.5%	-26.1%	-26.0%
Birmingham CC	2000	12 mths	1 mth	Gradko	Gradko	Gradko	50% TEA in Water	Urban Background	30	32	28	35	29	33	-5.9%	-18.7%	-12.6%			
Birmingham CC	2001	12 mths	1 mth	Gradko	Gradko	Gradko	50% TEA in Water	Urban Background	24	30	34	43	29	36	-19.8%	-19.9%	-19.9%			
New Forest DC	2001	11 mths	1 mth	Gradko	Gradko	Gradko	50% TEA in Water	Intermediate	18	23	24	29	21	26	-22.7%	-16.6%	-19.6%			
New Forest DC	2001	11 mths	1 mth	Gradko	Gradko	Gradko	50% TEA in Water	Suburban	11	22	16	24	13	23	-51.0%	-32.4%	-42.2%			
Taunton Deane BC	2000/01	12 mths	1 mth	Gradko	Gradko	Gradko	50% TEA in Water	Urban Centre	15	25	22	32	18	29	-39.8%	-32.5%	-35.7%			
Thurrock BC	2000/01	12 mths	1 mth	Gradko	Gradko	Gradko	50% TEA in Water	Urban Background	20	32	31	38	25	35	-38.1%	-20.1%	-28.3%	-29.6%	-23.4%	-26.4%
Gateshead Council	2000	12 mths	1 mth	Jesmond Dene Laboratory	Gradko	Jesmond Dene Laboratory	50% TEA in Water	Roadside	27	29	31	33	29	31	-7.6%	-7.3%	-7.4%	-7.6%	-7.3%	-7.4%
Tonbridge and Malling BC	1998	12 mths	1 mth	Kent Scientific Services	Gradko	Kent Scientific Services	50% TEA in Water	Kerbside	32	53	29	56	31	54	-39.9%	-47.4%	-43.7%	-39.9%	-47.4%	-43.7%
Dartford BC	2001/02	9 mths	1 mth	Gradko	Gradko	Gradko	20% TEA in Water	Roadside	47	69	55	66	52	66	-32.1%	-16.8%	-20.8%	-32.1%	-16.8%	-20.8%

[a] By laboratory for same averaging period.

Table 2 Summary of Diffusion Tube Validation Studies. Tubes Prepared Using 10% or 20% TEA in Water. Results in μg/m³.

Local Authority	Year	Data Capture	Exposure Interval	Lab Name	Tube Prep.	Tube Analysis	Prep. Technique	Site Type	Summer		Winter		Annual		Summer Bias	Winter Bias	Annual Bias	Average by Laboratory[a]		
									Tube	Cont.	Tube	Cont.	Tube	Cont.				Summer Bias	Winter Bias	Annual Bias
Bristol CC	1997	12 mths	2 wks	Bristol Sci. Services	Bristol Sci. Services	Bristol Sci. Services	10% TEA in Water	Roadside	58	60	66	59	62	60	-3.2%	+12.5%	+4.2%			
Bristol CC	1998	12 mths	2 wks	Bristol Sci. Services	Bristol Sci. Services	Bristol Sci. Services	10% TEA in Water	Roadside	70	54	61	60	65	57	+28.7%	+0.4%	+13.8%			
Bristol CC	1999	10 mths	2 wks	Bristol Sci. Services	Bristol Sci. Services	Bristol Sci. Services	10% TEA in Water	Roadside	72	53	71	54	71	54	+34.3%	+31.2%	+32.2%			
Bristol CC	2000	11 mths	2 wks	Bristol Sci. Services	Bristol Sci. Services	Bristol Sci. Services	10% TEA in Water	Roadside	66	50	66	58	67	56	+31.8%	+13.9%	+19.7%	+22.9%	+14.5%	+17.5%
Bristol CC	2001	9 mths	2 wks	Bristol Sci. Services	Bristol Sci. Services	Bristol Sci. Services	20% TEA in Water	Roadside	64	48			60	53	+33.3%		+14.2%	+33.3%	+0.0%	+14.2%
Derby CC	2001	12 mths	1 mth	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Background	23	30	47	45	35	37	-22.8%	+6.0%	-5.6%	-22.8%	+6.0%	-5.6%
Manchester CC	1996	12 mths	1 wk	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Urban Centre	56	49	62	60	59	54	+15.3%	+3.7%	+9.4%			
Manchester CC	1997	11 mths	1 wk	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Urban Centre	54	33	61	51	57	42	+60.9%	+20.6%	+37.2%			
Manchester CC	1998	11 mths	1 wk	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Urban Centre	53	34	61	47	57	40	+55.5%	+31.0%	+41.4%			
Manchester CC	1999	12 mths	1 wk	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Urban Centre	53	38	60	49	56	44	+37.5%	+22.1%	+29.1%			
Manchester CC	2000	10 mths	1 wk	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Urban Centre	53	37	57	44	55	40	+42.4%	+29.1%	+35.9%			
Manchester CC	2001	11 mths	1 wk	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Urban Centre	50	39	59	48	55	44	+26.3%	+23.0%	+23.3%			
Manchester CC	1996	12 mths	1 wk	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Urban Background	56	56	65	51	61	54	-0.1%	+26.9%	+12.5%			
Manchester CC	1997	12 mths	1 wk	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Urban Background	52	47	61	57	56	52	+11.4%	+6.9%	+9.2%			
Manchester CC	1998	12 mths	1 wk	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Urban Background	52	37	63	48	57	42	+40.7%	+32.0%	+36.0%			
Manchester CC	1999	9 mths	1 wk	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Urban Background	53	39	59	45	56	42	+34.9%	+29.4%	+31.9%			
Manchester CC	2000	12 mths	1 wk	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Urban Background	49	37	53	45	51	41	+32.3%	+16.5%	+23.7%			
Manchester CC	2001	11 mths	1 wk	Casella GMSS	Casella GMSS	Casella GMSS	10% TEA in Water	Urban Background	42	40	61	53	52	47	+4.5%	+14.9%	+10.4%	+30.1%	+21.4%	+25.0%

[a] By laboratory for same averaging period.

Table 3 Summary of Diffusion Tube Validation Studies. Tubes all Prepared Using 50% TEA in Acetone. Results in $\mu g/m^3$.

Local Authority	Year	Data Capture	Exposure Interval	Lab Name	Tube Prep.	Tube Analysis	Prep. Technique	Site Type	Summer		Winter		Annual		Summer	Winter	Annual	Average by Laboratory[a]		
									Tube	Cont.	Tube	Cont.	Tube	Cont.	Bias	Bias	Bias	Summer Bias	Winter Bias	Annual Bias
City of Edinburgh Council	2001	12 mths	1 mth	City of Edinburgh Council	City of Edinburgh Council	City of Edinburgh Council	50% TEA in Acetone	Roadside	43	35	43	43	43	39	+23.9%	-0.2%	+10.6%			
City of Edinburgh Council	2001	12 mths	1 mth	City of Edinburgh Council	City of Edinburgh Council	City of Edinburgh Council	50% TEA in Acetone	Roadside	42	37	46	46	44	42	+12.6%	-1.8%	+4.6%	+18.3%	-1.0%	+7.6%
Blackburn with Darwen BC	2001	9 mths	1 mth	Harwell Scientifics	Harwell Scientific	Harwell Scientific	50% TEA in Acetone	Intermediate	21	29	39	32	31	31	-27.2%	22.5%	+1.7%			
St Edmundsbury BC	2001/02	10 mths	1 mth	Harwell Scientifics	Harwell Scientific	Harwell Scientific	50% TEA in Acetone	Roadside	46	34	57	40	53	38	+34.7%	+42.0%	+39.3%	+3.8%	+32.2%	+20.5%
Eastleigh BC	2001	12 mths	1 mth	Kent Scientific Services	Harwell Scientific	Kent Scientific Services	50% TEA in Acetone	Roadside	34	29	44	41	39	35	+16.6%	+6.3%	+10.5%	+16.6%	+6.3%	+10.5%
LB of Lambeth	1999	11 mths	1 mth	Lambeth Scientific	Lambeth Scientific	Lambeth Scientific	50% TEA in Acetone	Urban Background	20	19	23	23	21	21	+7.1%	+0.9%	+4.0%			
York CC	2000/01	12 mths	1 mth	Lambeth Scientific	Lambeth Scientific	Lambeth Scientific	50% TEA in Acetone	Suburban	9	14	24	24	16	19	-37.1%	+0.9%	-13.0%			
N Hertfordshire DC	1999	12 mths	1 mth	Lambeth Scientific	Lambeth Scientific	Lambeth Scientific	50% TEA in Acetone	Roadside	31	41	46	44	39	42	-24.4%	+5.5%	-7.6%	-18.1%	+2.4%	-5.6%
LB Croydon	2000	9 mths	1 mth	SSE	SSE	SSE	50% TEA in Acetone	Roadside	31	32	38	36	35	34	-2.1%	+8.1%	+3.8%			
LB Croydon	2000	11 mths	1 mth	SSE	SSE	SSE	50% TEA in Acetone	Roadside	33	53	37	51	35	52	-38.5%	-28.6%	-34.1%	-20.3%	-10.3%	-15.1%

SSE = Stanger Science & Environment (now Casella Stanger). They no longer prepare and analyse tubes in-house.

Table 4 Uncertainty in Estimate of Annual Ratio of Diffusion Tube to Chemiluminesence Results as a Function of Averaging Period. Average and 95% Confidence Limits.

Laboratory	Method	Averaging Period			
		1 mth	3 mths	6 mths	9 mths
		Average Uncertainty			
Gradko (n=2)	50% TEA in Acetone	±15%	±8%	±5%	±3%
Gradko (n=4)	50% TEA in Water	±17%	±14%	±10%	±4%
Other Laboratories (n=5)	50% TEA in Acetone	±20%	±9%	±6%	±4%
Other Laboratories (n=2)	50% TEA in Water	±21%	±14%	±9%	±3%
		95% Confidence Limits of Uncertainty			
Gradko (n=2)	50% TEA in Acetone	±36%	±18%	±10%	±6%
Gradko (n=4)	50% TEA in Water	±41%	±34%	±23%	±10%
Other Laboratories (n=5)	50% TEA in Acetone	±56%	±28%	±16%	±12%
Other Laboratories (n=2)	50% TEA in Water	±52%	±32%	±21%	±7%

n = number of data sets in analysis

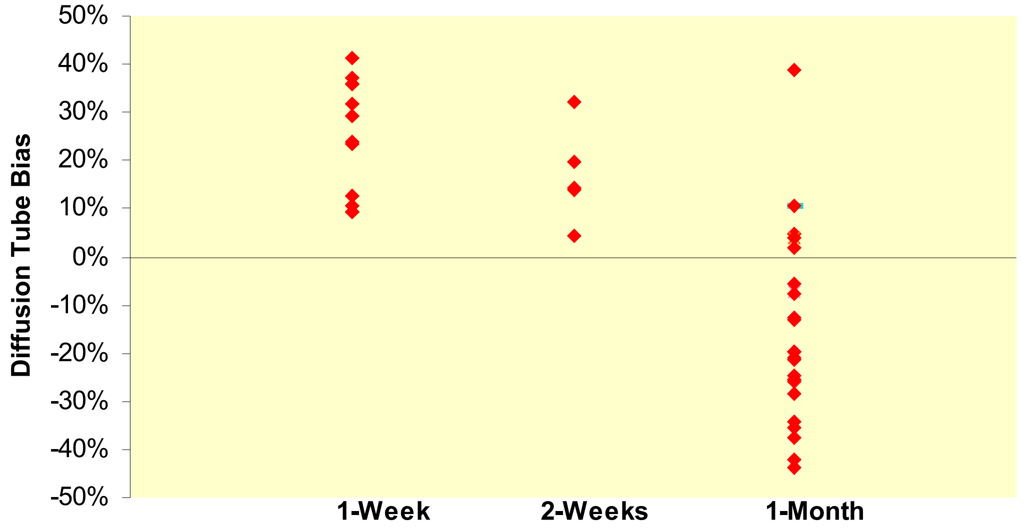

Figure 1 Diffusion tube bias for tubes exposed over different periods. Direct comparison should not be made because the data are for all studies tubes are prepared in different ways by different laboratories.

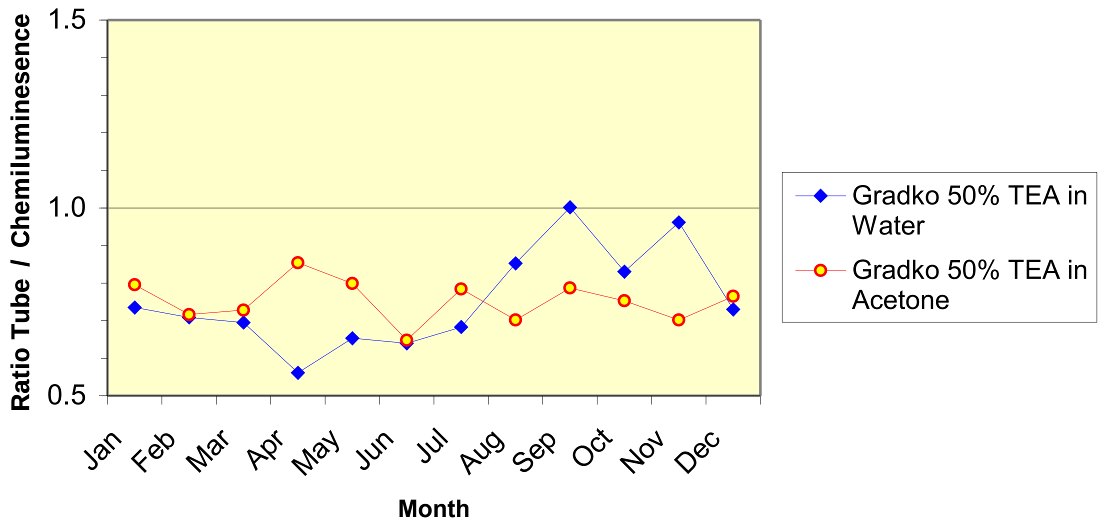

Figure 2 Ratio of tube to chemiluminesence vs time of year, for tubes prepared and analysed by Gradko using two different techniques. Results are the average of 5 site-years for 50% TEA in acetone and 6 sites for 50% TEA in water. Tubes exposed for 1-month intervals.

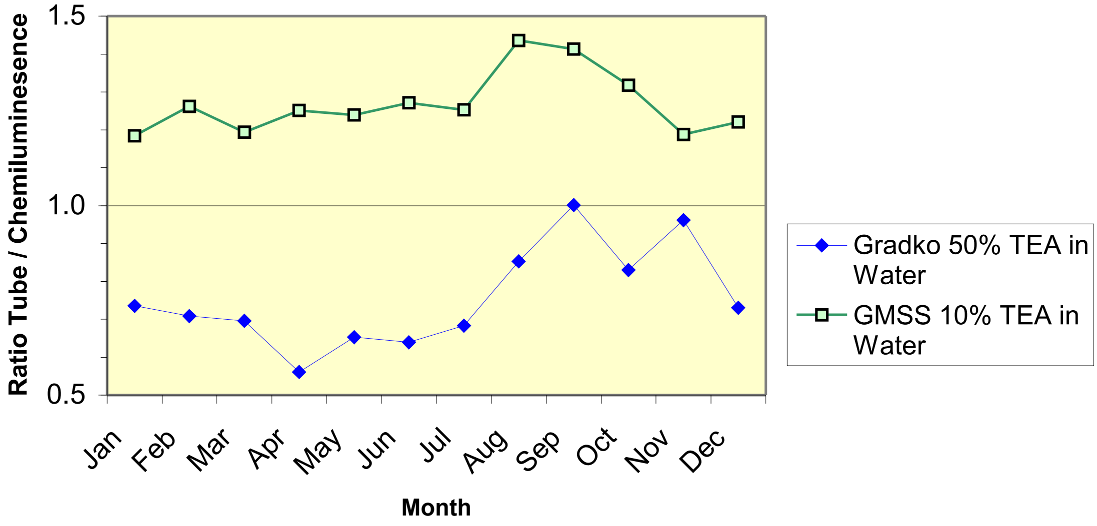

Figure 3 Ratio of tube to chemiluminesence vs time of year, for tubes prepared and analysed by Gradko and GMSS using TEA in water. GMSS results are the average for 2 sites over 6 years at each site. GMSS tubes exposed for 1-week intervals.

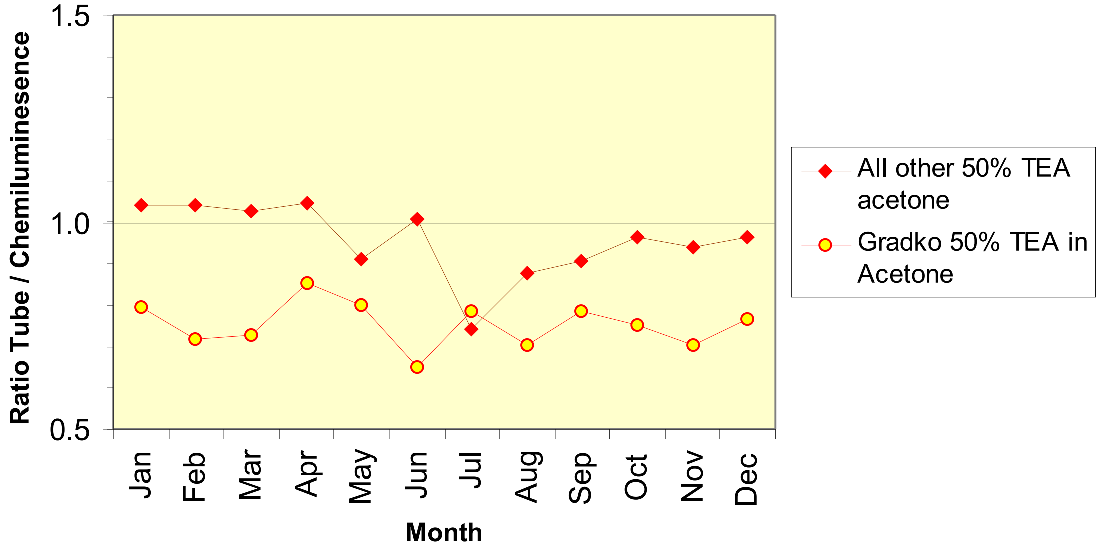

Figure 4 Ratio of tube to chemiluminesence vs time of year, for tubes prepared and analysed by other laboratories and by Gradko, using 50% TEA in acetone. Tubes exposed for 1-month intervals

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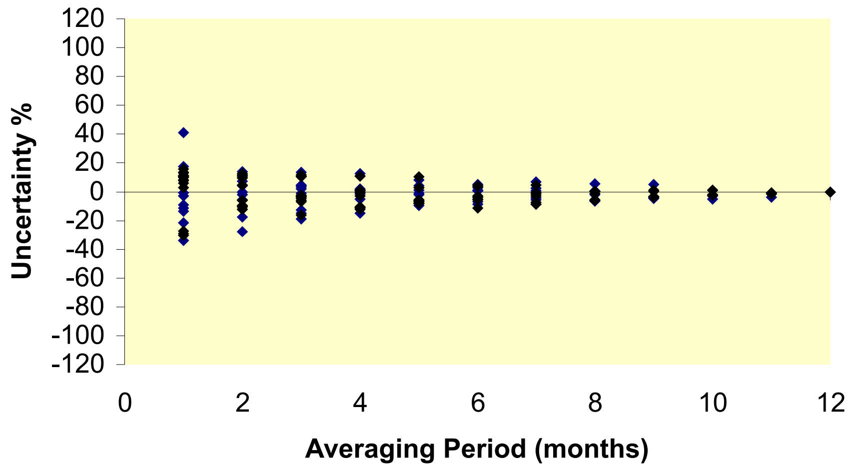

Figure 5 Uncertainty in annual ratio of diffusion tube to chemiluminesence vs. averaging period, for tubes prepared and analysed by Gradko with 50% TEA in acetone. Based on two 12-month data sets.

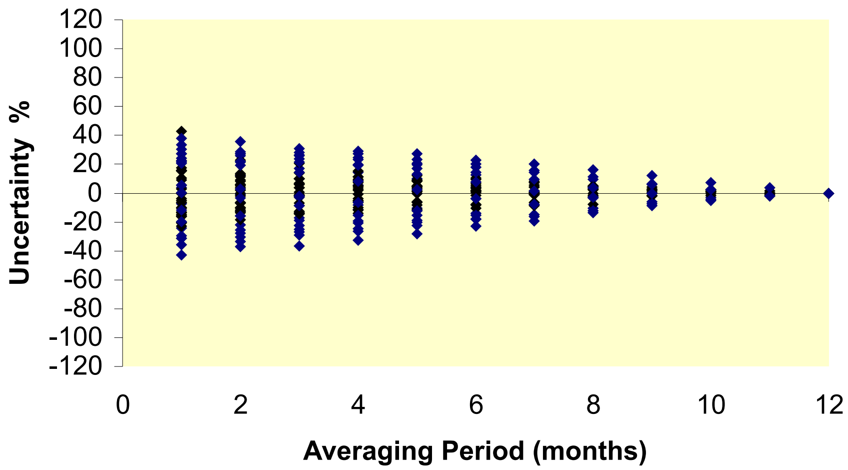

Figure 6 Uncertainty in annual ratio of diffusion tube to chemiluminesence vs. averaging period, for tubes prepared and analysed by Gradko with 50% TEA in water. Based on four 12-month data sets.

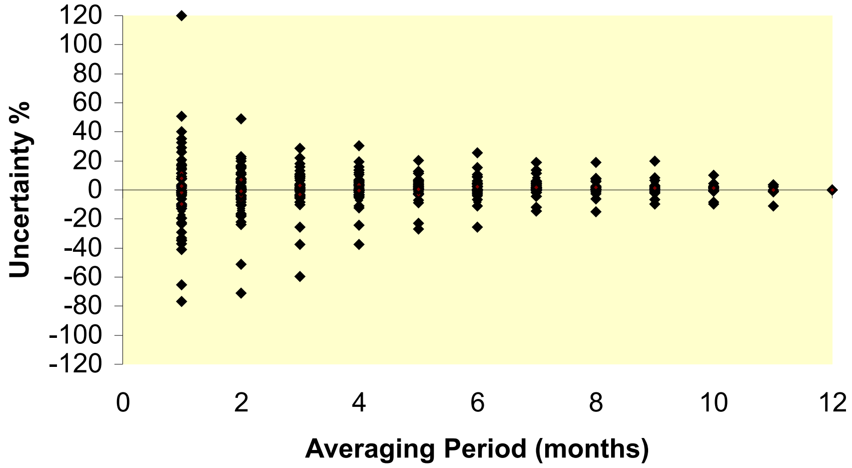

Figure 7 Uncertainty in annual ratio of diffusion tube to chemiluminesence vs. averaging period, for tubes prepared and analysed by other laboratories with 50% TEA in acetone. Based on five 12-month data sets.

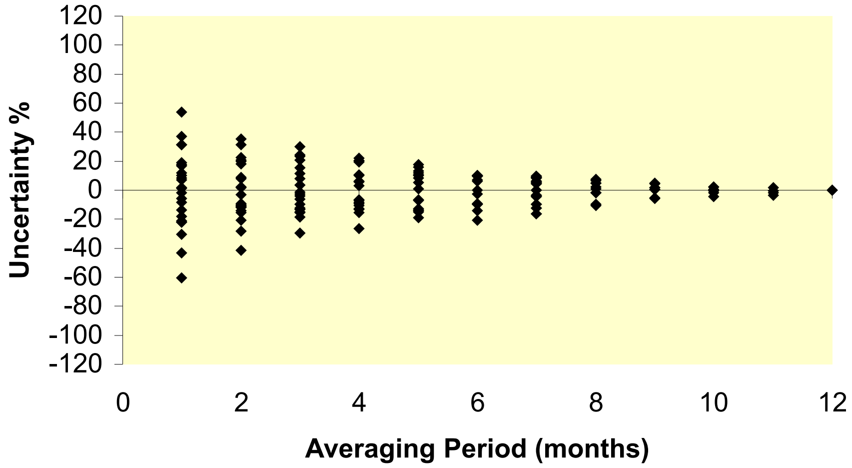

Figure 8 Uncertainty in annual ratio of diffusion tube to chemiluminesence vs. averaging period, for tubes prepared and analysed by other laboratories with 50% TEA in water. Based on two 12-month data sets.

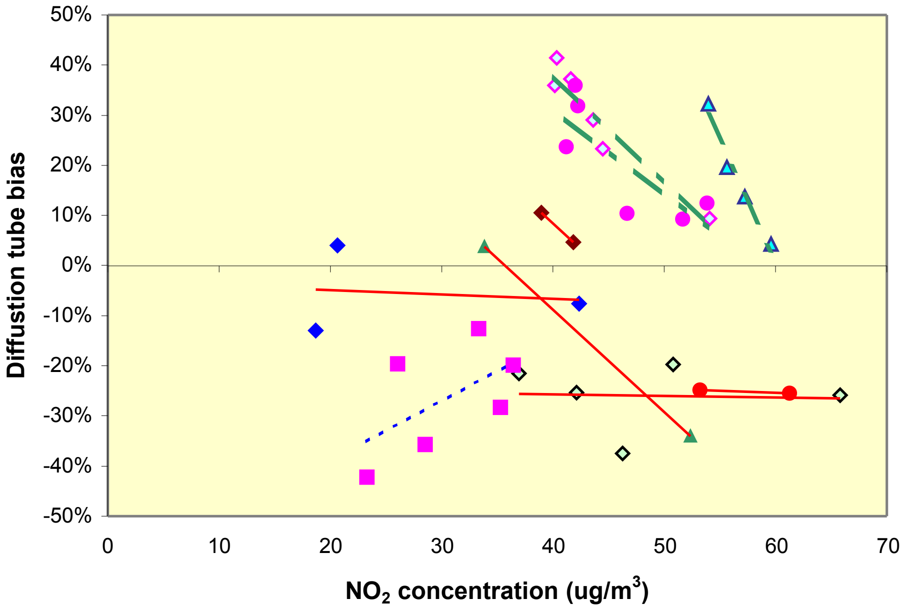

Figure 9 Diffusion tube bias vs annual mean concentration (automatic monitor). Data grouped by laboratory and tube preparation method. Lines are linear best-fit relationships: solid lines for 50% TEA in acetone, monthly exposure; small dashed line for 50% TEA in water, monthly exposure; and small/large dashed lines for 10% TEA in water, 1-week and 2-week exposure.

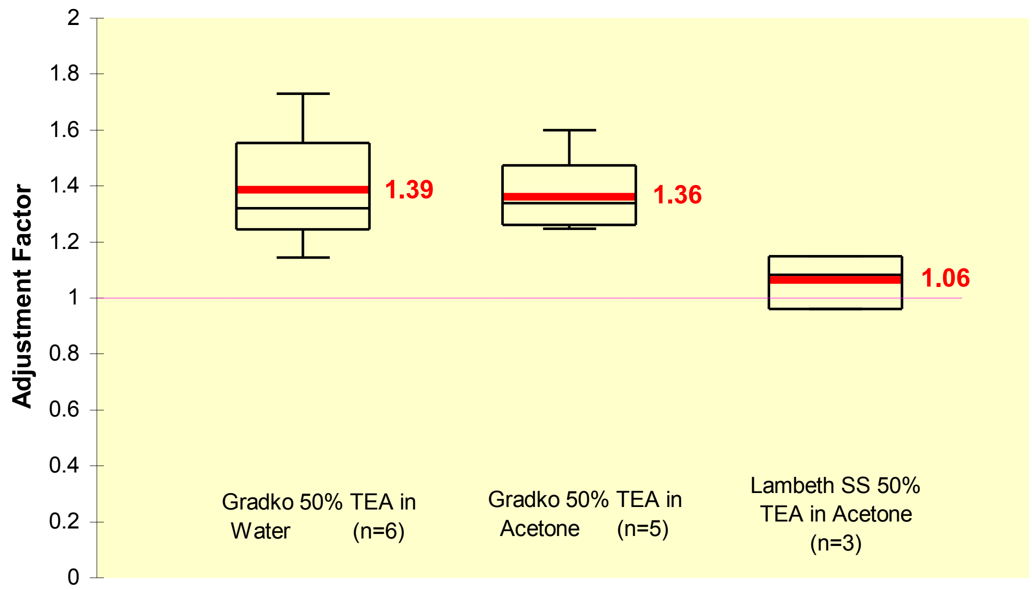

Figure 10 Proposed default bias adjustment factors to apply to annual mean results for tubes exposed monthly. Box and whisker plots summarise the full data sets.

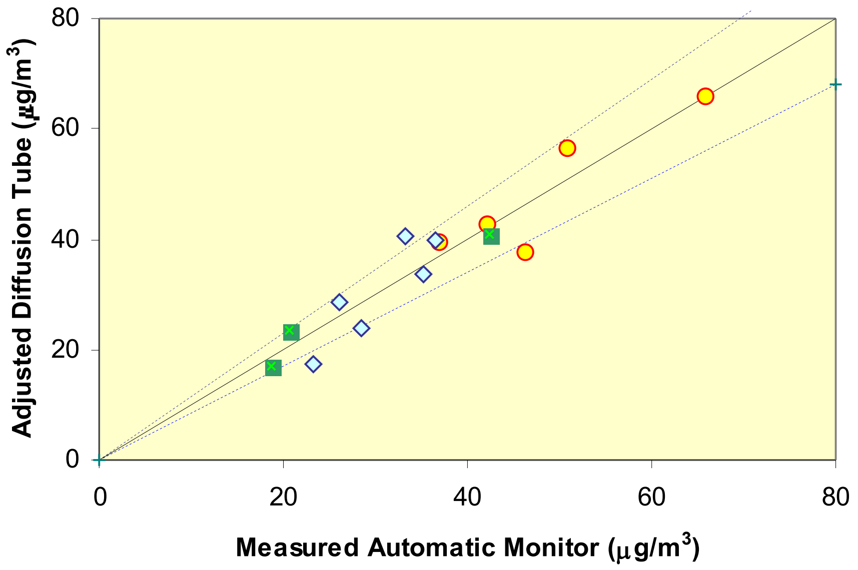

Figure 11 Diffusion tube results adjusted using independent default bias adjustment factors vs. collocated automatic monitor (see text for basis of test). Results for tubes prepared and analysed by Gradko using 50% TEA in acetone (circles) or 50% TEA in water (diamonds) and Lambeth Scientific Services using 50% TEA in acetone (squares). The dashed lines represent ± 15% about the 1:1 line.