Summary Results from the UK NO_2 Network Field Intercomparison Exercise 2000

1. INTRODUCTION

1.1 Background

The UK NO_2 Network comprises over 1300 sites operated by 326 Local and Unitary Authorities. A number of analytical laboratories (31 in year 2000) are responsible for preparation and analysis of the NO_2 diffusion tubes used by these Authorities. It is important that the data obtained by this Network is of the highest possible quality, therefore QA/QC of laboratory analyses is very important to the Network's operation.

Since 1996, the UK NO_2 Network has employed a laboratory performance testing programme, which uses artificially doped diffusion tubes to test the accuracy of laboratory analyses on a monthly basis[1]. In May 1999 this was incorporated into the WASP scheme operated by Health and Safety Laboratory (HSL). This scheme provides valuable information on the analytical performance of laboratories. However, owing to the use of artificially doped diffusion tubes in this programme, uncertainties arising from the sampling phase of diffusion tube monitoring cannot be assessed. Field intercomparison exercises are therefore carried out annually as part of the Network's laboratory QA/QC programme, in order to define better the sampling and analytical performance of diffusion tubes under normal operating conditions.

This report describes the 2000 field intercomparison exercise which follows on from previous intercomparisons held in 1993[3], 1994[4], 1995 [2], 1998 [5] and 1999[6]. It was designed to complement the existing laboratory quality assurance programme for the UK NO_2 Network, which currently utilises information supplied by the WASP scheme under the management of the Health and Safety Laboratory.

Full details of the performance of individual laboratories in the WASP scheme and the 2000 field intercomparison exercise are available direct from the individual laboratory concerned.

1.2 Scope and Objectives of 2000 Field Intercomparison

The 2000 intercomparison was intended to build upon the experience of previous studies, and further improve performance of laboratories participating in the UK NO_2 Network. The objectives of the 2000 field intercomparison exercise were as follows:

1. To estimate bias and precision, under normal field operating conditions, for all laboratories performing analysis in the UK NO_2 Network during 2000.

2. To compare the estimated bias and precision in 2000 with the results from the field intercomparisons in 1999 and earlier years.

2. ORGANISATION OF THE 2000 FIELD INTERCOMPARISON

The 31analytical laboratories providing diffusion tube analysis for UK NO_2 Network participants were invited to take part in the 2000 field intercomparison exercise. Thirty laboratories completed the exercise.

2.1 Exposure Details

Seven nitrogen dioxide diffusion tubes (six exposure tubes and one travel blank) were supplied by each laboratory, for exposure over a period of approximately one month, October 2000. As in previous studies, diffusion tubes were exposed simultaneously upon purpose made exposure racks located immediately adjacent to the automatic chemiluminescent NO_x monitoring equipment installed at the DETR's Automatic Urban Network (AUN) site at Walsall Alumwell. The exposure time was a 28-day period from 4th October to 1st November 2000.

Upon completion of exposure the diffusion tubes were capped and the exposure time noted. The exposed samplers and travel blanks were then returned to the supplying laboratory for analysis. Travel blanks accompanied exposure tubes to and from the test site. They were isolated in sealed sample bags, and refrigerated throughout the exposure period.

The participating laboratories sent their analytical results to AEA Technology for collation. ***Results were reported in microgrammes per cubic metre ($\mu g\ m^{-3}$), and these units are used in this report. Readers should note that in previous years, results have been expressed in parts per billion (ppb). If required, microgrammes per cubic metre of NO_2 can be converted to ppb by applying a conversion factor of 0.523. To convert ppb of NO_2 to $\mu g\ m^{-3}$, multiply by 1.91.***

2.2 Statistical processing of measurement data

Prior to the interpretation of the measurement data supplied by the laboratories, outlying data within the datasets for each laboratory were removed using Grubb's Test. This statistical test was used in an iterative process, at a probability level of P=0.05. It was assumed that the sample distribution was normal. The same test was used last year to remove outliers from the 1999 field intercomparison dataset.

The decision to remove outliers was taken in order to provide better average estimates of laboratory performance and also take into account the levels of screening employed within the UK NO_2 Network whereby abnormally low or high results are investigated and deleted from the Network's dataset where appropriate.

3. SUMMARY OF RESULTS FROM THE FIELD TESTING EXERCISE

3.1 Comparison with chemiluminescent technique

As in previous intercomparisons, the intention was to use the average NO_2 concentration measured by the chemiluminescent analyser at Walsall Alumwell over the exposure period (4th October to 1st November 2000) as the reference value with which the diffusion tube results could be compared.

The chemiluminescent analyser appeared to be operating normally throughout. However, following detailed ratification of the data, and the Quality Control Audit of the Walsall Alumwell AUN site (in late February 2001), it was discovered that the automatic analyser had been affected by a technical problem. As a result, it was necessary to reject some data, in particular for the period 14th - 20th October 2000. Valid data was obtained for only 70% of the full exposure period.

A summary of the data from the chemiluminescent analyser is provided at the end of this report. NO_2 measurements from the Walsall Alumwell chemiluminescent analyser show a "spike" for the period 1700 - 1730 on 29th October 2000, with 15-minute means reaching 1283μg m^{-3} (672 ppb) for the 15-minute period 1700-1715. This coincides with a period of high wind (wind speeds upto 14 ms^{-1} were measured by Walsall Metropolitan Borough Council's meteorological monitoring station at Brickyard Road, Aldridge). It is possible that this "spike" is spurious, possibly caused by a short power interruption. However, in the absence of evidence to that effect, it has been assumed to be genuine, and retained in the ratified dataset.

The average NO_2 concentration for the exposure period 4th October - 1st November 2000, measured by the chemiluminescent NO_x analyser *and based on the ratified data only*, was 20ppb (38.2 μg m^{-3}). However, because this average is based on only 70% of the diffusion tube exposure period, it cannot be used as a reliable reference value with which to compare the diffusion tube data.

The average diffusion tube measurement for the same period was 45.0 μg m^{-3} (23.5 ppb), with a standard deviation of 4.4 μg m^{-3}. This constitutes an average bias of +18% relative to the average NO_2 concentration measured by the chemiluminescent analyser. Diffusion tubes have been shown to over-read with respect to the chemiluminescent method[7] by upto 30%. However, in previous years' intercomparisons, the exposed diffusion tubes have been found to exhibit a mixture of positive and negative bias compared to the chemiluminescent analyser. It therefore appears much more likely that the difference between the mean diffusion tube result and the automatic result is due to the latter being based on only 70% of the diffusion tube exposure period.

Table 1 presents the bias as a percentage for the averaged measurement by each laboratory relative to the average measurement from the automatic chemiluminescent analyser. Code numbers are used to identify each laboratory.

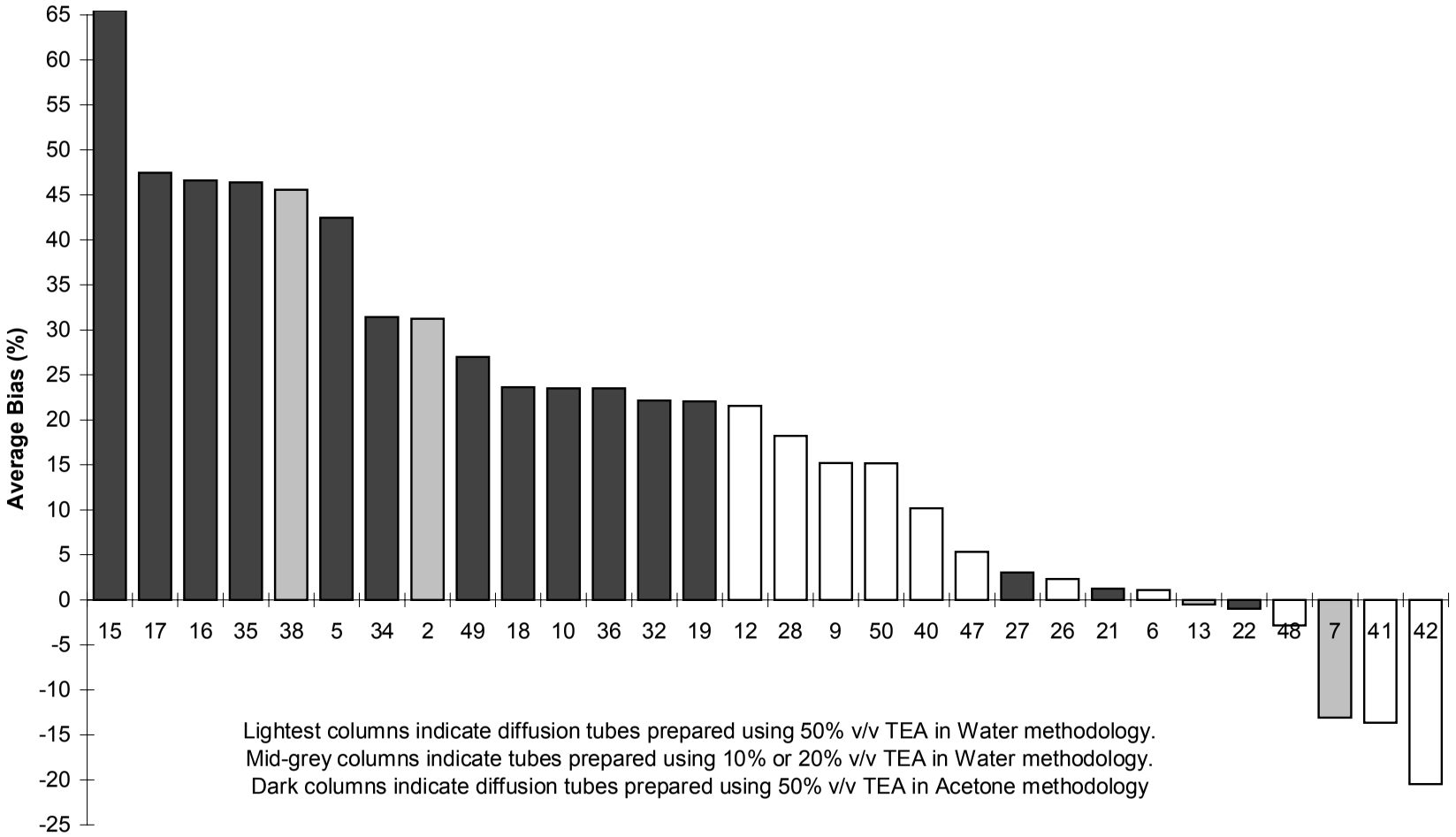
Table 1 shows that *nine* laboratories exhibited a bias relative to the automatic analyser of greater than the target of ±25%, and in the worst case the bias was over 60%. This is in contrast to the results for the 1999 intercomparison, where only three laboratories exceeded ±25%, and of those three none exceeded the target by more than 6%. In 1999 the average bias relative to the chemiluminescent analyser was -6.7%. The results of the 2000 intercomparison are illustrated in Figure 1, which also shows the preparation technique used by each laboratory.

Table 1 Average bias and standard deviation of NO_2 diffusion tube measurements, by laboratory

Laboratory code	% Bias relative to automatic analyser 2000	Standard Deviation 2000	% Bias relative to average diffusion tube conc. 2000	% Bias relative to automatic analyser. 1999
2	31.2	5.26	11	4.9
5	42.4	1.87	21	-10.6
6	1.1	1.90	-14	-4.3
7	-13.1	10.25	-26	-19.9
9	15.2	2.16	-2	-14.6
10	23.5	7.25	5	-5.9
12	21.5	1.56	3	-18.2
13	-0.5	4.56	-16	17.0
15	65.5	1.83	40	4.2
16	46.6	5.42	24	9.6
17	47.5	4.13	25	-25.2
18	23.6	5.98	5	5.2
19	22.1	7.42	3	11.1
21	1.2	4.32	-14	-30.7
22	-1.0	2.97	-16	-22.9
26	2.3	5.36	-13	-3.0
27	3.1	3.06	-13	-0.8
28	18.2	2.81	0	-28.7
32	22.2	9.52	3	14.7
34	31.4	6.52	11	-5.5
35	46.4	3.73	24	-21.7
36	23.5	5.81	5	-2.3
37	No results			-10.0
38	45.6	1.48	23	7.9
40	10.2	3.85	-7	4.2
41	-13.7	2.92	-27	-23.7
42	-20.5	7.17	-33	-15.3
47	5.3	3.66	-11	-19.9
48	-2.8	1.36	-18	-17.0
49	27.0	2.59	8	24.4
50	15.2	4.20	-2	-12.8
Average	+18.1	**4.36**	**0**	**-6.7**

Reference concentration (chemiluminescent automatic analyser) = 38μg m^{-3}
Average diffusion tube measurement = 45μg m^{-3}.

Figure 1 Average bias relative to the chemiluminescent technique for NO_2 diffusion tube measurements in the 2000 Field Intercomparison Exercise (Outliers removed by Grubb's test)

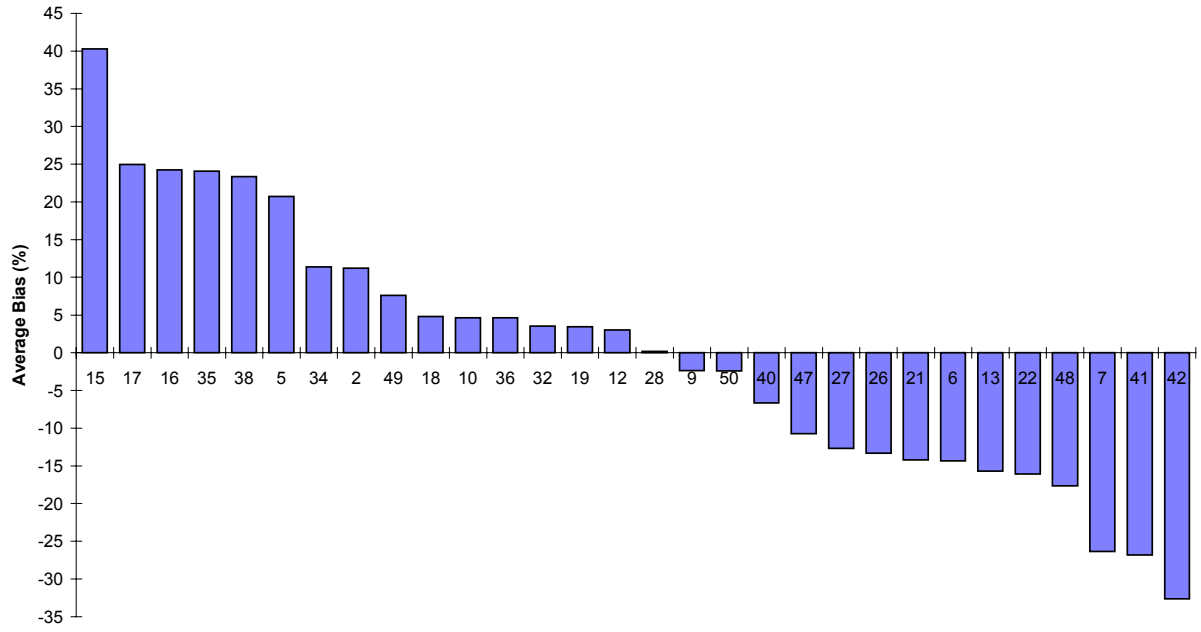


3.2 Bias relative to the average diffusion tube measurements

Table 1 also presents the average bias in measurements relative to the overall average of all diffusion tube measurements for both 1999 and 2000 field exercises. Outliers have been identified and removed from both datasets using Grubb's test. From Table 1, the overall performance of individual laboratories can be assessed. During the 2000 field intercomparison exercise, measurements from 28 of the 30 laboratories who completed the intercomparison (93%) are within ±25% of the average diffusion tube measurement. This represents a small improvement relative to the 1999 study, where 91% had an average bias within ±25%. The range in the average bias exhibited by laboratories in 2000 was slightly greater than that identified in 1999; -33% to +40%, as opposed to -31% to +24% in 1999.

The overall distribution of bias in measurements, (relative to the mean of all the measurements) is presented in Figure 2. This plot shows that the distribution bias in the data for each laboratory for October 2000 was close to normal. However, the laboratories at each end of the range show evidence of extreme outlying performance.

Figure 2. Average bias in diffusion tube measurements in the 2000 Field Intercomparison Exercise relative to the average of all diffusion tube measurements (Outliers removed by Grubb's test.)



3.3 Systematic Differences in Performance Due to Preparation Technique

Currently, there are two main preparation techniques used in the production of NO_2 diffusion tubes used in the UK NO_2 Network. The diffusion tubes may be prepared using:

1. Triethanolamine (TEA) in a 50:50 v/v solution with acetone, or
2. Triethanolamine (TEA) in a 50:50 v/v solution with water and a proprietary surfactant (Brij).

A third method, triethanolamine (TEA) in a 10% or 20% v/v solution with water and a proprietary surfactant, is increasingly being used.

The tubes supplied by the participating laboratories for the 2000 field intercomparison included some tubes prepared by each of these three methods. The tube preparation method is indicated in Figure 1.

Figure 1 clearly shows that diffusion tubes prepared using TEA in a 50:50 v/v solution with acetone (shown by the dark columns), consistently gave higher results than tubes prepared using TEA in a 50:50 v/v solution with water (shown by the white columns). The diffusion tubes prepared using the "new" method, TEA in a 10% or 20% v/v solution with water (shown by the mid-grey columns) appeared to give results somewhere between the two. This pattern is evident despite the widespread positive bias in the 2000 intercomparison with respect to the chemiluminescent method.

The observed pattern is consistent with both the 1998 and 1999 field intercomparison trials[5,6], and with the additional study carried out concurrently with the 1999 intercomparison[6]. These studies clearly showed that diffusion tubes prepared using a 50% solution of TEA in water exhibited an average negative bias, while diffusion tubes prepared using a 50% solution of TEA in acetone exhibited an average positive bias.

Recent work by Kirby et al [8] investigated the properties of the TEA absorbent, and the behaviour of diffusion tubes prepared by various methods. Kirby's work included a field exposure comparison of the performance of NO_2 diffusion tubes prepared using four methods:

- 50% v/v TEA in acetone, grids dipped into solution
- 10% v/v TEA in deionised water, 30 µl aliquot of solution pipetted onto grids.
- 20% v/v TEA in deionised water, 30 µl aliquot of solution pipetted onto grids.
- 50% v/v TEA in deionised water, 50 µl aliquot of solution pipetted onto grids.

Diffusion tubes produced using the first three methods were found to give comparable results. However, those produced using the fourth (50% v/v TEA in water), produced significantly lower results than the others, and also tended to under-read compared to the chemiluminescent technique. The explanation proposed for this effect[8] involves the basicity of the 50% TEA solution reducing the uptake of NO_2. Diffusion tubes prepared using a 10% or 20% aqueous solution of TEA are believed to be unaffected by this process.

There are three mechanisms which cause diffusion tubes to over-read (the shortening of the diffusive path length by wind[9], blocking of UV light resulting in reduced NO_2 photolysis in the tube[10], and the effects of PAN[9]. Previous intercomparisons identified one mechanism, low extraction efficiency, as likely to be the largest individual source of negative bias in diffusion tube measurements. However, the recent work by Kirby has provided a second mechanism for under-read in the case of tubes prepared by the (specifically) 50% TEA in water method only.

AEA Technology have recently carried out an investigation of the performance of diffusion tubes of three types:

- TEA in a 50% solution with acetone,
- TEA in a 20% solution with water,
- TEA in a 50% solution with water.

This study comprised field exposure and laboratory based trials, and the results will be published shortly as a separate report.

4. RECOMMENDED GUIDELINES FOR LABORATORY PERFORMANCE

4.1 Data Quality Objectives for the NO_2 Network

Under the European Union Daughter Directive for NO_2,[11] data quality objectives have been set out for the overall accuracy of indicative monitoring techniques (e.g. diffusive monitoring). In the case of diffusion tube monitoring of NO_2, in relation to the annual average, the data quality objective has been set at ±25%. Hence, it is recommended that on average, diffusion tube measurements should be within ±25% of the reference concentration.

This objective was adopted within the UK NO_2 Network in 1997, as a criterion for satisfactory data quality. It is consistent with indicators of good laboratory performance used within the WASP proficiency testing scheme for NO_2 diffusion tubes, and also the UK NO_2 Network Laboratory Performance Testing Scheme used from 1996-1999.

The intention was to apply this criterion to the 2000 field intercomparison exercise; laboratories that are, on average, within approximately ±25% of the reference value, would be recognised as performing satisfactorily. Conversely, laboratories with an average bias significantly greater than ±25% will have performed unsatisfactorily. Under normal circumstances the reference value would be that obtained using the chemiluminescent analyser.

Using these guidelines, nine of the 30 laboratories taking part in this field intercomparison exercise (30%) produced measurement data with average bias >25%, relative to the reference measurement from the chemiluminescent analyser. In all 9 cases the bias was positive, in contrast to previous years.

However, as described in section 3 above, the chemiluminescent analyser was affected by a fault which caused just over one week's worth of data from the four week exposure period to be rejected. Therefore, the average NO_2 concentration obtained using the chemiluminescent analyser cannot be used as a reliable reference value. Instead, the average of all diffusion tube measurements (rather than the chemiluminescent analyser result) has been taken as the reference value for the purpose of assessing performance. This was the approach taken in a previous intercomparison (1998), when technical problems were experienced with the chemiluminescent analyser. On this basis, **26 of the 30 laboratories which completed this field intercomparison exercise (87%) produced measurement data with average bias within ±25%, relative to the average of all diffusion tubes**.

In assessing performance, the precision of analytical measurements should also be taken into account, as it is possible to achieve an average bias of less than ±25% with very imprecise measurements (i.e. purely by chance and despite a high degree of scatter). The precision is represented here by the standard deviation of the six tube results. Last year, the figure of 3ppb was taken as an arbitrary guideline for acceptable precision. This is equivalent to 5.7 $\mu g\ m^{-3}$ (rounded up to 6 $\mu g\ m^{-3}$ for convenience).

Six of the 30 laboratories (20%) had a standard deviation greater than our arbitrary guideline of 6 $\mu g\ m^{-3}$. Of these, only one laboratory produced measurement data with an average bias >25% relative to the chemiluminescent analyser *and* an average precision standard deviation greater than our arbitrary guideline of 6 $\mu g\ m^{-3}$.

4.2 Data Quality Objectives for the Air Quality Strategy (AQS)

Under the AQS, Local Authorities are obliged to assess and review the air quality within their authority. Diffusion tube surveys may be used as screening tools within these assessments, as the annual average data derived from NO_2 diffusion tubes may be directly comparable with the AQS air quality objective for the end of 2005 (40 μg m^{-3} or 21 ppb for annual mean NO_2).

In recognition of the evidence for a potential bias in diffusion tube measurement data, and in the absence of a methodology for estimating accuracy as defined by EC Directive 1999/30/EC, information on the bias (relative to the chemiluminescent technique) and precision of diffusion tube measurement data must be presented *for the period of monitoring*. Users of NO_2 diffusion tubes are referred to the Local Air Quality Management Technical Guidance Notes produced by DETR. These are available at http://www.environment.detr.gov.uk/airq/laqm.htm on DETR's web site.

These Technical Guidance Notes advise that where diffusion tubes are used for NO_2 monitoring at Stage 3, "simultaneous co-exposure of triplicate diffusion tubes alongside an automatic chemiluminescent monitor is essential in order to define bias and precision associated with diffusion tube measurements throughout the period of monitoring. In the event of significant bias in diffusion tube measurement data being identified, appropriate scaling factors may be defined from the co-exposure data and applied to the diffusion tube measurement data to correct for any systematic bias"[12]. Therefore, Local Authorities intending to use NO_2 diffusion tubes at Stage 3 will need to carry out an ongoing "intercomparison exercise" of their own, throughout the monitoring period.

Performance testing data from the UK NO_2 Network Laboratory Performance Testing Scheme used from 1996 to 1999, and the WASP proficiency scheme from 1999 onwards are available from the participating laboratories and may be used to provide a further information on the general performance of these laboratories.

5. COMPARISON WITH OTHER FIELD INTERCOMPARISON EXERCISES

Due to the unexpected problems encountered during the exposure period of the 2000 field intercomparison exercise, the results cannot be compared directly with previous years. However, Table 2 shows the steady improvement in laboratory performance between 1994 and 1999.

Table 2. Average Laboratory Performance in the UK NO_2 Network Field Intercomparison Exercises 1994-2000

	Average Performance in UK NO_2 Network Field Intercomparisons				
	1994	**1995**	**1998**	**1999**	***2000***
Average Bias (%)	-11	2	1.7	-6.7	*0**
Maximum Bias (%)	118	118	58	24	*40**
Minimum Bias (%)	-96	-87	-39	-31	*-33**
Standard Deviation of Bias	39	39	22	15	*18**
Precision μg m^{-3}	3.9	1.6	4.9	4.1	*4.4** $\mu g\ m^{-3}$

⋆ All 2000 bias figures are calculated relative to the mean of all diffusion tube measurements, not the mean obtained using the chemiluminescent analyser.

The range of bias in the 2000 intercomparison was larger than in 1999, indicating a greater variability between laboratories.

6. CONCLUSIONS

The following conclusions may be drawn from this field intercomparison exercise:

1. The chemiluminescent analyser was affected by a technical fault during the 2000 Field Intercomparison Exercise, which caused the rejection of 30% of the dataset for the exposure period. As a result, the average NO_2 concentration obtained using the chemiluminescent analyser could not be considered a reliable reference value. Instead, the mean of all diffusion tubes was taken as the reference value.

2. On this basis, 26 of the 30 laboratories in this field intercomparison exercise (87%) were within ±25%, *relative to the mean of all diffusion tubes*.

3. 24 laboratories (70%) showed an average precision within our arbitrary guideline of $6\mu g\ m^{-3}$.

4. The range in bias of measurement data, relative to the average of all the diffusion tube measurements in the study, was -33% to +40%. While the lower end of the range is similar to that measured in 1999, the upper end of the range is considerably higher, due to one laboratory exhibiting unusually high positive bias.

5. The average precision associated with the measurements in this study was $4.4\mu g\ m^{-3}$. This is slightly higher than, although still comparable to, the standard deviation of $4.1\mu g\ m^{-3}$ achieved in the 1999 intercomparison.

6. Further evidence of the effect of diffusion tube preparation technique upon the performance of diffusion tubes was identified. Despite the overall prevalence of positive bias in the 2000 intercomparison, tubes prepared using a 50% solution of TEA in acetone method typically exhibited a higher or more positive bias that tubes prepared using a 50% solution of TEA in water. Tubes prepared using a 10%, or 20% solution of TEA in water appeared to produce results between the other two; this is broadly consistent with the findings of Kirby et al.

7. RECOMMENDATIONS FOR FURTHER IMPROVEMENT

1. **It is recommended that future Intercomparisons comprise multiple exposure periods, and/or exposure at more than one site, to minimise the impact of technical problems affecting the chemiluminescent analyser, such as occurred during the 2000 Intercomparison.**

2. It is recommended that the preparation method used in the Network should be standardised. Field and laboratory based investigations of the effects of preparation technique on diffusion tube performance have been carried out by AEA Technology, and these will be published shortly in a separate report.

8. ACKNOWLEDGEMENTS

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Summary of Automatic NO_x Analyser Data for Walsall Alumwell, 4th October to 1st November 2000.