Summary Results from the UK NO_2 Network Field Intercomparison Exercise 1998

INTRODUCTION

As part of the quality assurance and control procedures of the DETR's UK NO_2 Network, a field intercomparison exercise was organised to test the performance of NO_2 diffusion tubes supplied and analysed by the 38 analytical laboratories which provide analytical services for the UK NO_2 Network. The objectives of this field intercomparison exercise were as follows:

1. To identify estimates of bias and precision under normal field operating conditions for all laboratories performing analysis in the UK NO_2 Network.

2. To investigate the distribution of bias in diffusion tube measurements in the field.

3. To estimate the average uncertainty associated with measurements made within the UK NO_2 Survey.

4. To provide information to laboratories on the performance of their diffusion tubes under field conditions with view to improving their performance.

5. To provide information and guidance to Local Authority's on NO_2 diffusion tube performance in the field.

The exercise follows on from previous intercomparisons held between 1993, 1994 and 1995 (Stevenson et al) and is designed to complement the existing laboratory quality assurance programme for the UK NO_2 Network which is currently utilises information supplied by the WASP scheme under the management of the Health and Safety Laboratory (HSL).

Since 1996, the UK NO_2 Network has employed a laboratory performance testing programme (Bush et al) which uses artificially doped diffusion tubes to test the accuracy of laboratory analyses on a monthly basis. This scheme provides valuable information on the analytical performance of laboratories. However, owing to the use of artificially doped diffusion tubes in this scheme, uncertainties arising from the sampling phase of diffusion tube monitoring cannot be assessed. This field intercomparison exercise was implemented to complement the UK NO_2 Network's monthly laboratory performance testing programme by examining the overall uncertainty associated with both the sampling and analytical phase of NO_2 diffusion tube monitoring.

Full details of the performance of individual laboratories in the WASP scheme and the 1998 field intercomparison exercise are available direct from the laboratory.

ORGANISATION OF THE FIELD INTERCOMPARISON

Thirty eight analytical laboratories were invited to take part in the field intercomparison exercise. All laboratories provide diffusion tube analysis for UK NO_2 Network participants.

Seven nitrogen dioxide diffusion tubes (six exposure tubes and one travel blank) were supplied by each laboratory on a monthly basis over a period of three months, between August and October 1998. 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. Exposure dates and periods were as defined by the UK NO_2 Network monitoring calendar for 1998 and are listed below in Table 1.

Table 1 Exposure dates for the 1998 UK NO_2 Survey Field Intercomparison Exercise

Exposure Period	***Month***	***Start Date***	***Duration in weeks***
1	August	4 August 1998	4
2	September	1 September	4
3	October	29 September (to 3 November)	5

Upon completion of each exposure period, diffusion tubes were capped and the exposure time noted. Three exposed diffusion tubes were returned to the supplying laboratory for analysis along with the travel blank and exposure details. The remaining three diffusion tubes were analysed by a single analytical laboratory in order to standardise the analytical variability in these measurements.

Travel blanks accompanied exposure tubes to and from the test site and were kept in isolation, under refrigerated conditions throughout the duration of the exposure periods. Analysis results were forwarded to AEA Technology for collation on a monthly basis. Results reported in microgrammes per cubic metre ($\mu g/m^3$) were converted to parts per billion (ppb) using a conversion factor of 0.523.

SUMMARY OF RESULTS FROM THE FIELD TESTING EXERCISE

Summary results of the average performance of laboratories from all three exposure periods of the field intercomparison are presented in Table 2. Outlying data were not removed from the dataset prior statistical analyses in order to best represent the performance characteristics of data reported to the UK NO_2 Network; under normal operating conditions within this network, data are derived from single diffusion tubes exposures at each monitoring site. Hence, there is no opportunity for outlier identification within these data.

Table 2 presents the average bias (relative to the overall average of all diffusion tube measurements per period), and the average standard deviation associated with the three sets of triplicate diffusion tube measurements made over the exposure periods of the intercomparison exercise. Laboratories are identified by code number.

From Table 2, the overall performance of individual laboratories can be assessed. Measurements from the majority of laboratories (79%) are within ±25% of the average diffusion tube measurement in each period. However, there is a substantial range in the average bias exhibited by laboratories of -39% to +58%.

The overall distribution of bias in measurements is presented in Figures 1-3. These graphs show the average bias in the triplicate measurement data for each laboratory and by exposure period. Figures 1-3 clearly show that the distribution of bias in laboratory measurements is close to normal. This distribution may explain the good agreement between the average diffusion tube measurement over the three exposure periods and average measurement from the co-located chemiluminescent NO_x analyser.

From a comparison of the diffusion tube and automatic measurement data over the three periods of exposure, it estimated that averaged data produced by these laboratories (i.e. equivalent to the national annual and monthly average NO_2 concentrations reported in the UK NO_2 Networks reports) will be within 2% of the actual NO_2 concentration defined by the automatic technique. On average, over the 3 exposure periods diffusion tube measurements had a precision of ±2.56 ppb (based on the average standard deviation from all triplicate measurements).

Table 2 Average bias and standard deviation on NO_2 diffusion tubes by laboratory

Laboratory Code	*Average Bias[1] of Measurements from Reference Value (%)*	*Average Standard Deviation[2] in Measurements (ppb)*
1	49.0	1.14
2	16.8	3.52
5	-21.7	2.02
6	9.4	3.06
7	-1.8	3.83
8	-26.2	2.44
9	-16.5	0.68
10	-0.5	1.21
11	-23.6	1.15
12	-5.9	1.94
13	40.2	4.17
15	26.7	1.46
16	11.8	0.96
17	7.6	1.81
18	16.0	1.53
19	-26.3	0.96
21	12.8	2.29
22	-23.5	2.27
23	57.9	5.21
26	10.3	2.27
27	10.4	5.15
28	-16.6	0.76
30	22.0	1.09
32	3.2	2.41
34	-11.1	0.72
35	-7.8	7.50
36	14.1	3.15
37	19.9	5.00
38		1.97
39	21.9	7.43
40	-1.7	2.36
41	-23.8	1.30
42	-39.3	1.28
43	-23.2	1.79
44	1.6	2.63
47	-14.3	2.56
48	-8.5	0.73
49	2.6	5.73
Average	1.7	2.56

Note:

1. Average bias (%) is derived from average percentage bias of each set of triplicate measurements from exposure periods 1-3 relative to the average measurement from all diffusion tube results reported per exposure period)
2. Average standard deviation is derived from the average standard deviation associated with each set of triplicate measurements from exposure periods 1-3.

Figure 1 Average Bias in Measurements for Laboratories in Period 1 of the 1998 Field Intercomparison Exercise (Bias relative to overall average of diffusion tube measurements, laboratories indicated by code)

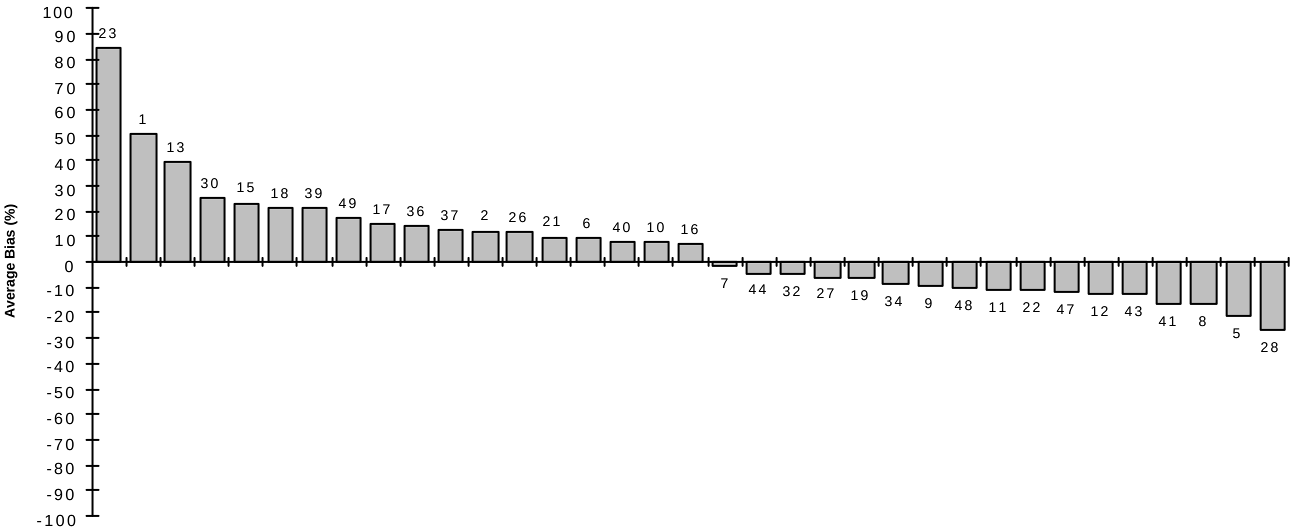


Figure 2 Average Bias in Measurements for Laboratories in Period 2 of the 1998 Field Intercomparison Exercise (Bias relative to overall average of diffusion tube measurements, laboratories indicated by code)

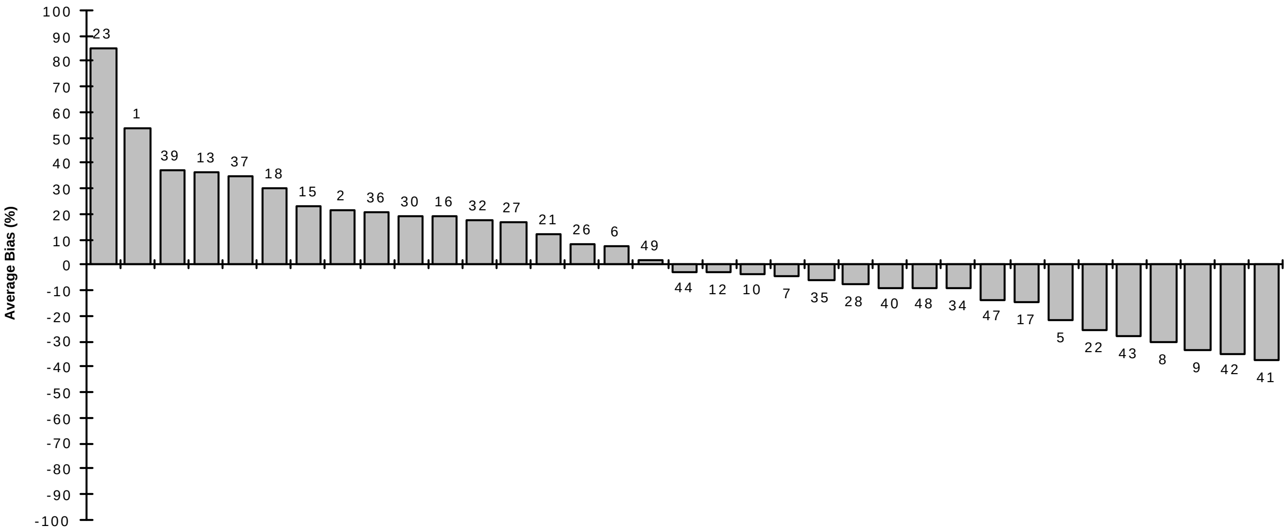
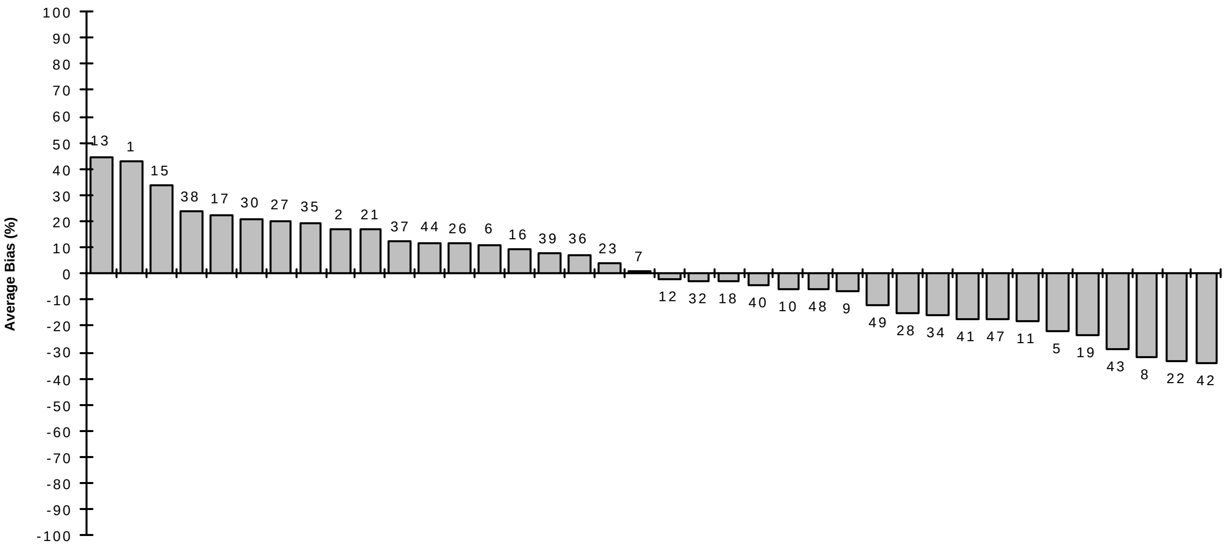


Figure 3 Average Bias in Measurements for Laboratories in Period 3 of the 1998 Field Intercomparison Exercise (Bias relative to overall average of diffusion tube measurements, laboratories indicated by code)

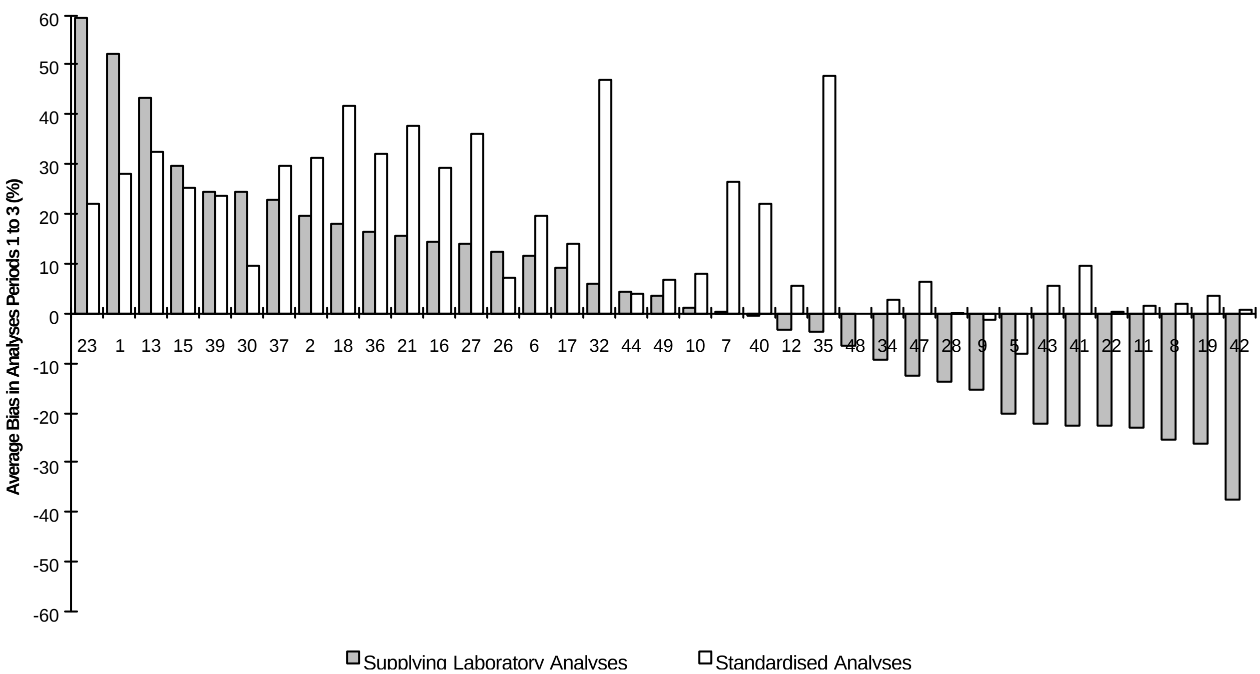


QUALITATIVE ANALYSIS OF DIFFUSION TUBE MEASUREMENT DATA PRODUCED BY STANDARDISED ANALYSIS

Three diffusion tubes from each laboratory were retained after exposure and analysed by a single laboratory. The purpose of these analyses was to standardise the analytical uncertainty in these measurements, and therefore provide a qualitative assessment of sampling uncertainty.

Figure 4 presents the average bias in diffusion tube measurement data relative to measurements from the co-located automatic chemiluminescent analyser, over the three exposure periods from co-exposed diffusion tubes analysed by the supplying laboratory and the standardised laboratory. Clearly from these data, there are substantial differences in the bias of measurements. Diffusion tubes from 29 laboratories (78%) produced higher concentrations when analysed by the standardised laboratory. However, this general increase in concentration is not uniform for all laboratories, as might be expected. Indeed for a minority of laboratories a decrease is observed.

Figure 4 Comparison of Average Bias in Measurements from Co-exposed Diffusion Tubes Analysed by the Supplying Laboratory and Standardised Laboratory (Bias relative to the chemiluminescent analyser)



Historically, diffusion tubes have been shown to over read relative to chemiluminescent measurements by up to 30% (Campbell et al). Over read in diffusion tubes may be attributed to the individual and combined effect of three interfering factors; the shortening of the diffusive path length by wind (Atkins et al), blocking of UV light resulting in reduced NO_2 photolysis in the tube (Heal et al) and the effects of PAN (Atkins et al). There are no known interference effects, other than a possible photochemical reaction between the TEA-nitrite complex with light, which reduce the amount of NO_2 absorbed on to the diffusion tube. This effect, however, has be largely minimised, by the widespread use of opaque diffusive end caps (Stevenson et al).

Given the expected over read in NO_2 diffusion tubes, it is difficult to explain the number of laboratories displaying a negative bias in their measurements relative to the chemiluminescent

technique (Figure 4). It is also noticeable that, when analysed by the standard laboratory, the large majority of samples showed more normal behaviour (i.e. they over read).
This observation may indicate that better nitrite extraction from exposed diffusion tubes was achieved during analyses by the standard laboratory and points towards extraction efficiency as a major source of analytical uncertainty in diffusion tubes.

The low extraction efficiencies observed may, in part, be explained by the mechanisms of NO_2 absorption and extraction in diffusion tubes. Under normal conditions absorbed NO_2 (as nitrite) will be approximately evenly distributed over the two grids carrying the chemical absorbent in the diffusion tube end cap; the porosity of the grids has been calculated as approximately 40%. Under extraction therefore, the technique used must be rigorous in order for the extracting solution to come into contact with both grids, assimilate the absorbed nitrite, and then make this available in the final sample for analysis. Difficulty may be experienced in this phase due to the cohesive and adhesive properties of the extracting solution and the physical barrier to mixing presented by the grids.

Laboratories with samples which display a negative bias or only a very small positive bias in Figure 4 may have suffered from the combined effect of low extraction efficiency and low sampling efficiency resulting from insufficient TEA on the absorbent gauze.

In order to improve the overall variability in laboratory performance, and therefore the comparability of data in the UK NO_2 Network, it is recommended that all laboratories optimise their extraction techniques, and ensure that a sufficient excess of absorbent is available throughout exposure. Hence, sampling and extraction uncertainties will be minimised. It should be noted, however, that with increased sampling and extraction efficiencies the diffusion tubes supplied by laboratories should behave in a regular way, that is show a consistent positive bias relative to chemiluminescent measurements. However, the overall variability in bias would be expected to decrease and therefore the comparability of data will be improved.

RECOMMENDED GUIDELINES FOR LABORATORY PERFORMANCE

Under the proposed European Union Daughter Directive for NO_2, data quality objectives have been set out for the overall accuracy of indicative monitoring techniques (i.e. diffusive monitoring). In the case of diffusion tube monitoring, annual average NO_2 concentration data must comply with these data quality objectives to enable comparison of measurement data with the Daughter Directive for NO_2. For indicative monitoring the data quality objective has been set at ±25%. Hence, it is recommended that on average, diffusion tube measurements be within ±25% of the reference concentration.

This objective has been used within the UK NO_2 Network 1997 as the data quality objective for the screening of diffusion tube data with unsatisfactory quality, and is broadly consistent with indicators of good laboratory performance used within the UK NO_2 Network Laboratory Performance Testing Scheme 1996-1999 and the new WASP proficiency testing scheme for NO_2 diffusion tubes. Applying this criteria to the 1998 field intercomparison exercise, laboratories that are, on average, within approximately ±25% of the reference value, may be recognised as performing satisfactorily, and conversely, laboratories with an average bias that is significantly greater than ±25% will have performed unsatisfactorily.

It must be noted however, that the precision of analytical measurements should also be taken into account. It is possible to achieve an average bias of less than ±25%, with very imprecise measurements (i.e. purely by chance). Therefore, it is recommended that the precision of diffusion tube measurements should approximate to the average figure achieved by all laboratories taking part in this field intercomparison (i.e. approximately 2.56 ppb). This guideline is broadly consistent with the precision of the chemiluminescent technique used for measuring NO_2 within the DETR automatic networks.

Using these guidelines seven of the 38 laboratories taking part in this field intercomparison exercise (18%), produced measurement data of unsatisfactory quality in terms of bias relative to the reference concentration (the average measurement from all exposed diffusion tubes per period). One laboratory did not supply sufficient samplers to calculate a robust average bias statistic. Twelve laboratories (32%) showed an average precision greater than 2.56 ppb. Two laboratories produced measurement data with an average bias >25% and an estimate of precision >2.56 ppb.

Data quality objectives for the National Air Quality Strategy (NAQS)

Under the NAQS, 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 NAQS air quality objective for the end of 2005 (21 ppb for NO_2).

Government guidance notes have been issued (LAQM.TG1(98)), which recommend data quality objectives for the accuracy of diffusive monitoring data to be used in NAQS Review and Assessment. For a Stage 2 review and assessment, an overall uncertainty of <30% is recommended. For Stage 3, an overall uncertainty of <20% is recommended. The data presented in Table 2, therefore, may be used to identify laboratory analyses that on average comply with data quality objectives recommended for Stage 2 and 3 review and assessment.

In addition to the data presented in this report, performance testing data from the UK NO_2 Network Laboratory Performance Testing Scheme 1996-1999 and the new WASP proficiency scheme are available from laboratories and may be used to provide a further information on the general performance of laboratories.

COMPARISON WITH OTHER FIELD INTERCOMPARISONS EXERCISE

A comparison of the average performance data produced from the 1998 field intercomparison exercise with data from exercises performed in 1994 and 1995 indicates that the performance characteristics of the laboratories have improved. Table 3 presents the average performance statistics from intercomparisons between 1994 and 1998.

Table 3 Average Laboratory Performance in the UK NO_2 Survey Field Intercomparison Exercises 1994-1998

	Average Performance in UK NO_2 Survey Field Intercomparisons		
	1994	***1995***	***1998***
Average Bias (%)	***-11***	***2***	***1.7***
Maximum Bias (%)	***118***	***118***	***58***
Minimum Bias (%)	***-96***	***-87***	***-39***
Standard Deviation of Bias	***39***	***39***	***22***
Precision (ppb)	***2.04***	***0.83***	***2.56***

From the data presented in Table 3, it can be seen that the variance in laboratory bias has reduced since 1995. This is illustrated by the standard deviation in laboratory bias, which shows that measurements in 1998 were approximately 40% less variable than in previous years and also by the reduction in the magnitude of the maximum and minimum percentage bias. Clearly from these data, a reduction in the size of the average bias and the number of laboratories exhibiting large bias has been achieved.

RECOMMENDATIONS FOR FURTHER IMPROVEMENT

Laboratories displaying a negative bias are strongly encouraged to review their procedures for preparing diffusion tubes and extracting nitrite after exposure. These diffusion tubes are performing contrary to the expectations for normal diffusion tube behaviour (i.e. under reading rather than over reading). The most likely cause of the observed under read is incomplete extraction of absorbed NO_2 in to the analysed sample and/or insufficient loading of the TEA absorbent on to the diffusion tube.

The extraction efficiency of a laboratory may be effectively tested and monitored on a monthly basis using the WASP programme for NO_2 diffusion tubes. As low extraction efficiency is likely to be the largest individual source of negative bias in diffusion tube measurements, it is strongly recommended that checks are made to ensure that laboratory performance in the WASP scheme are within ±25% of the target concentration.

It should be noted that if recommendations to improve extraction efficiencies are followed, it may be expected that the average bias in diffusion tube measurements will tend to the positive, relative to the EU prescribed chemiluminescence method, (i.e. diffusion tubes will on average over estimate).

CONCLUSIONS

The main conclusions that may be drawn from this field intercomparison exercise are as follows:

1. Thirty laboratories (79%) performed to the data quality objectives set out in the proposed EU Daughter Directive for NO_2.

2. Twenty six laboratories (68%) displayed an average measurement precision of ≤2.56 ppb.

3. The range in bias of measurement data was -39% to +58%.

4. The average bias associate with the national monthly and annual average measurement data reported by the UK NO_2 Network is estimated at 2% relative to the chemiluminescent technique.

5. The average precision associate with the measurement data reported by the UK NO_2 Survey is estimated at 2.56 ppb.

6. Local authorities are recommended to ensure that the performance for their analytical laboratory is within approximately ±25% (for bias) and 2.6 ppb (for precision). It is also recommended that additional information on performance testing and validation exercises be utilised in assessing laboratory performance where this is available. Full details on the performance of individual

laboratories are available direct from the laboratory.

7. Poor extraction efficiency during analysis was identified as the most likely contributory factor resulting in under estimation of diffusion tubes relative to the chemiluminescent technique and variability in laboratory performance.

8. Laboratories showing a negative bias (under estimating) should investigate their procedures for tube preparation and nitrite extraction from the tube, to ensure excess TEA is loaded on the absorbent grid of the diffusion tubes and also that all absorbed nitrite is made available for analysis during the extraction phase.

9. Laboratories with significant positive bias should check their tube preparation and analytical procedures to eliminate factors which may result in a systematic positive bias.

10. Recommendations to improve extraction and sampling efficiency may result in average bias in diffusion tube measurements relative to the EU prescribed chemiluminescence method tending to the positive. A reduction in the overall variability in analyses may also be expected as a result and therefore an improvement in the comparability of measurements in the UK NO_2 Network.

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