Summary Results from the UK NO$_2$ Network Field Intercomparison Exercise 2001

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 (28 in year 2001) are responsible for preparation and analysis of the NO$_2$ diffusion tubes used by these Authorities. In order to ensure that the data obtained by this Network is of the highest possible quality, all laboratories carrying out analysis of diffusion tubes for the UK NO$_2$ Network are required to take part in its Quality Assurance/Quality Control programme[1], which comprises the following activities.

1. **The Workplace Analysis Scheme for Proficiency (WASP) programme for NO$_2$ diffusion tube analysis.** This round-robin type performance testing scheme was first introduced in 1996, and integrated into the WASP scheme in 1999. It is operated independently by the Health and Safety Laboratory (HSL). Artificial analytes (doped tubes) are used to test the quality of laboratory analyses on a monthly basis.
2. **QC Solution Testing Scheme.** This involves the monthly analysis of a nitrite solution of known concentration by all participating laboratories. Every six months approximately 150ml of a stock nitrite solution is distributed to each laboratory. The laboratories analyse a sample of this stock solution on a monthly basis and return the result to AEA Technology.
3. **The Annual Field Intercomparison Exercise.** This is an annual field exposure trial, designed to provide information on the uncertainties arising from both the sampling and analysis phases of diffusive sampling in the field. Thus, the Field Intercomparison Exercise is intended to complement the WASP and QC Solution Testing schemes.

Criteria for data acceptance within the UK NO$_2$ Network are set on the basis of the WASP Scheme and the Field Intercomparison. Laboratories unable to demonstrate satisfactory performance in these two key quality systems are identified and the measurement data supplied by these laboratories may be excluded from the UK NO$_2$ Network report.

This report describes the 2001 Field Intercomparison exercise, which follows six previous intercomparisons held between 1993 and 2000[2,3,4,5,6,7]. Full details of the performance of individual laboratories in the WASP scheme and the 2001 Field Intercomparison exercise are available direct from the individual laboratory concerned.

1.2 Scope and Objectives of 2001 Field Intercomparison

The main objective of the 2001 Field Intercomparison was to estimate bias and precision, under field operating conditions, for all laboratories performing analysis in the UK NO$_2$ Network during 2001. In recent years, the intercomparison has also been used to investigate the effect of tube preparation technique on performance of diffusion tubes.

2. ORGANISATION OF THE 2001 FIELD INTERCOMPARISON

The 28 analytical laboratories providing diffusion tube analysis for UK NO_2 Network participants were invited to take part in the 2001 Field Intercomparison exercise. All 28 laboratories completed the exercise. The 2001 intercomparison comprised two exposure periods. Diffusion tube results were compared with the results from two colocated automatic analysers.

2.1 Exposure Details

Seven nitrogen dioxide diffusion tubes (six tubes for exposure, and one travel blank) were supplied by each laboratory, for each exposure period. The two four-week exposure periods were as follows:
- Period 1 (September): 12.00 5th September - 10.00 3rd October 2001.
- Period 2 (October): 11.00 3rd October - 13.00 31st October 2001.

As in previous studies, diffusion tubes were exposed simultaneously upon purpose made exposure racks located close to the automatic chemiluminescent NO_x monitoring equipment installed at DEFRA's Automatic Urban Network (AUN) site, Walsall Alumwell. The chemiluminescent analyser provided a reference measurement, with which the diffusion tube results were compared.

Prior to the 1st exposure period, a duplicate chemiluminescent analyser was installed at Walsall Alumwell, in the same enclosure and sampling through an independent inlet. This was intended to provide a "backup" reference measurement, in the event of technical problems affecting the AUN chemiluminescent analyser, such as occurred during the 2000 intercomparison. Both analysers were calibrated fortnightly throughout the study. Both performed reliably, and achieved data capture of greater than 95%.

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 (µg m^{-3}). Prior to 2000, results were expressed in parts per billion (ppb). 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 µg 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 in 1999 and 2000 to remove outliers from the Field Intercomparison dataset. The decision to remove outliers was taken in order to provide better estimates of average 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.

Two values were removed from the Period 1 dataset by this procedure. Grubb's test did not identify any outliers in the Period 2 dataset; however, one result was discarded as droplets had been observed in the tube prior to exposure. The analysis result for this tube was also considerably lower than the other 5 from the same laboratory.

Particular problems were also encountered with split end caps. Because of this, results from 9 tubes in Period 1 and 2 tubes in Period 2 were rejected. This appears to have been due to a faulty batch of caps from one manufacturer.

3. SUMMARY OF RESULTS FROM THE FIELD TESTING EXERCISE

3.1 Comparison with chemiluminescent technique

The two chemiluminescent analysers installed at the Walsall Alumwell site were used to provide reference measurements with which the diffusion tube results could be compared.

Both chemiluminescent analysers appeared to be operating normally throughout, and gave similar results.
Period 1: Walsall Alumwell AUN analyser: mean NO_2 concentration $=40.1$ μg m^{-3} (21ppb).
Period 1: Duplicate Analyser: mean NO_2 concentration $= 38.2\mu$g m^{-3} (20 ppb)

Period 2: Walsall Alumwell AUN analyser: mean NO_2 concentration $= 36.3$ μg m^{-3} (19ppb)
Period 2: Duplicate Analyser: mean NO_2 concentration $= 40.1$ μg m^{-3} (21ppb).

The differences are within the precision of the analyser. For each period, the average of the two chemiluminescent analysers' results was taken as the reference value. Thus, the reference concentration for period 1 (September) was 39.2 μg m^{-3}, and the reference concentration for period 2 (October) was 38.2 μg m^{-3}. A summary of the data from the chemiluminescent analysers is provided at the end of this report.

Table 1 shows the performance of each laboratory, in terms of bias relative to the reference value, and precision, expressed as the standard deviation of the six individual tube results. Code numbers are used to identify each laboratory. (Laboratory 12 supplies diffusion tubes prepared by a choice of three different methods, and all three types were tested in this intercomparison. The three types are denoted by 12a, 12b, and 12c).

The average bias in the results provided by each laboratory are shown as bar charts in Figure 1 (for period 1), Figure 2 (for period 2) and Figure 3 (mean of both periods). Code numbers are used to identify each laboratory. The range of bias exhibited by individual laboratories in the two tests was between +57% to -58%.

Some laboratories produced similar results in terms of bias and precision in both exposure periods. However, many did not. It should be noted that intercomparison studies such as this can only provide a "snapshot" of laboratory performance at a specific time, and must be supplemented by continuous studies such as the WASP programme.

Table 1. Bias and Precision in 2001 NO₂ Network Field Intercomparison

Laboratory Code	% Bias in Period 1	Precision in Period 1	% Bias in Period 2	Precision in Period 2	Mean % Bias	Mean Precision
2	-1.4	3.12	5.0	3.72	1.8	3.42
5	16.0	2.24	44.4	2.63	30.2	2.43
6	19.3	11.95	24.8	2.92	22.0	7.44
7	-9.7	5.80	17.4	5.19	3.8	5.49
9	20.2	1.97	27.6	5.93	23.9	3.95
10	2.5	4.21	18.0	9.39	10.2	6.80
12a	-9.4	1.78	12.4	4.77	1.5	3.27
12b	-4.2	3.88	10.1	3.33	2.9	3.61
12c	-23.4	1.86	-7.5	2.19	-15.4	2.03
13	5.0	6.31	26.5	8.94	15.8	7.62
15	43.8	0.91	56.6	1.24	50.2	1.07
16	33.9	1.76	45.3	3.15	39.6	2.45
17	28.6	4.45	21.3	8.07	24.9	6.26
19	33.1	1.63	48.4	1.43	40.7	1.53
21	8.8	5.82	-28.4	4.72	-9.8	5.27
22	-7.9	0.23	22.1	4.50	7.1	2.36
26	10.7	1.82	38.0	6.69	24.3	4.26
28	18.7	6.02	44.8	1.97	31.7	3.99
30	2.0	4.51	37.2	5.76	19.6	5.13
32	46.7	2.88	51.0	2.58	48.8	2.73
34	30.5	1.60	-19.3	1.47	5.6	1.54
36	-7.7	1.60	22.6	1.47	7.4	1.54
38	14.6	3.11	23.8	5.54	19.2	4.32
40	-5.3	2.21	-1.1	2.64	-3.2	2.43
41	-58.1	3.72	-34.9	3.31	-46.5	3.52
42	-29.3	3.60	2.6	7.84	-13.3	5.72
47	11.9	4.65	28.5	1.41	20.2	3.03
48	7.6	1.66	26.9	9.84	17.2	5.75
49	25.3	2.70	30.1	3.82	27.7	3.26
50	-18.4	1.00	11.0	5.32	-3.7	3.16
Mean	6.8	3.30	20.2	4.39	13.5	3.85

Reference concentrations (chemiluminescent automatic analyser) 2001 = 39.2 μg m^{-3} in Period 1 and 38.2 μg m^{-3} in Period 2.

Figure 1. Average bias relative to chemiluminescent analyser for NO2 diffusion tube measurements in 2001 Field Intercomparison, Period 1 (September).
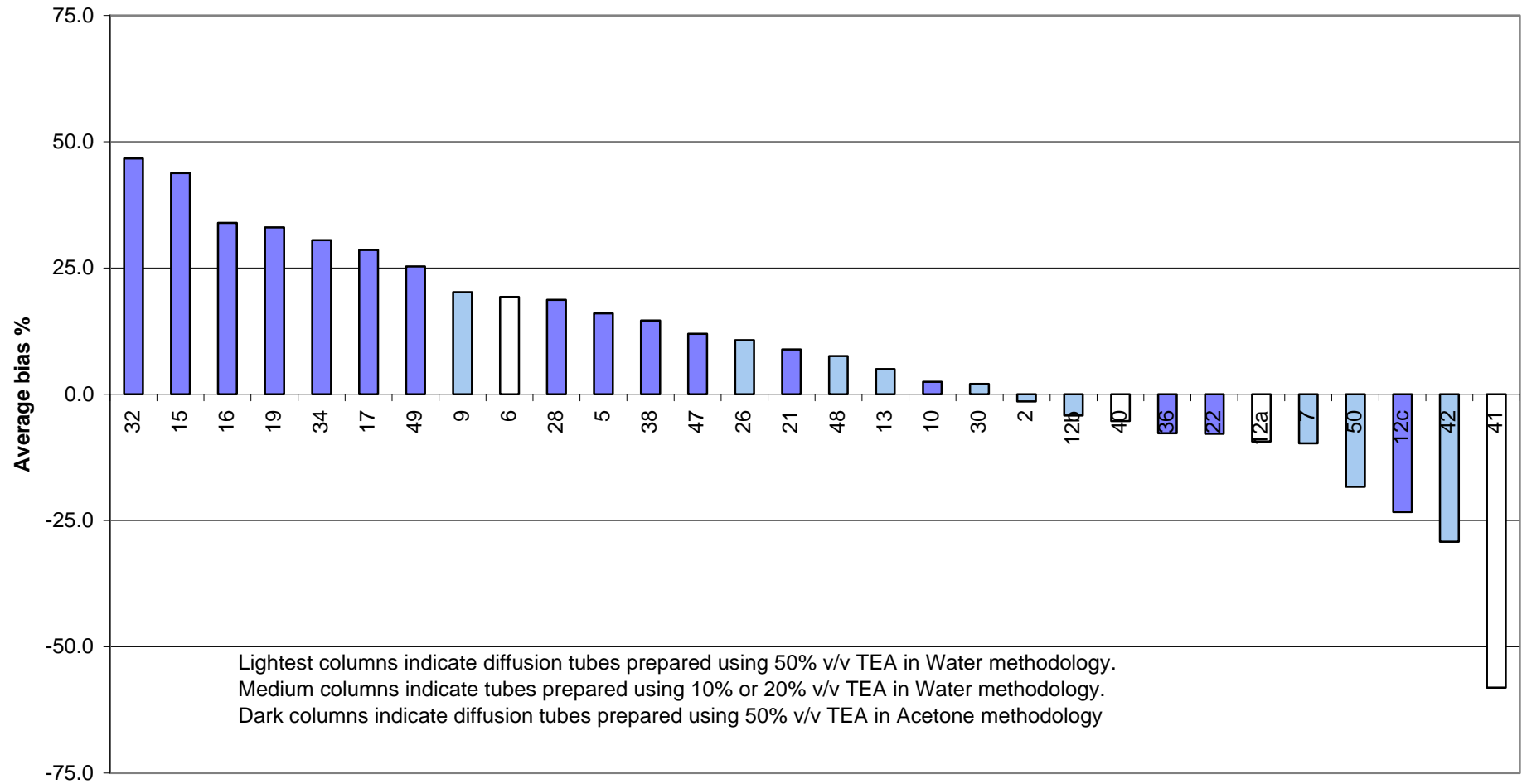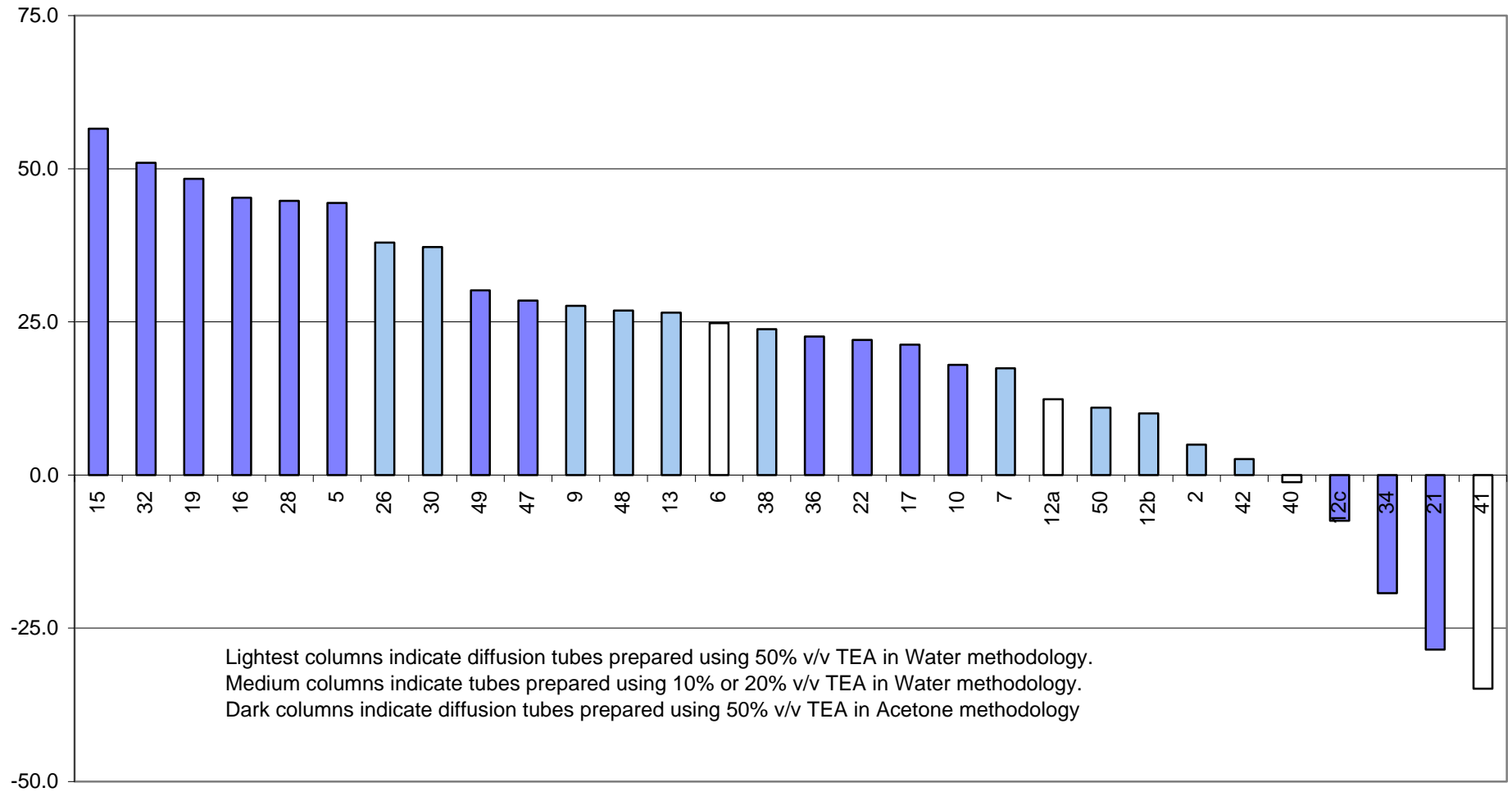
Lightest columns indicate diffusion tubes prepared using 50% v/v TEA in Water methodology.
Medium columns indicate tubes prepared using 10% or 20% v/v TEA in Water methodology.
Dark columns indicate diffusion tubes prepared using 50% v/v TEA in Acetone methodology

Figure 2. Average bias relative to chemiluminescent analyser for NO2 diffusion tube measurements in 2001 Field Intercomparison, Period 2 (October)
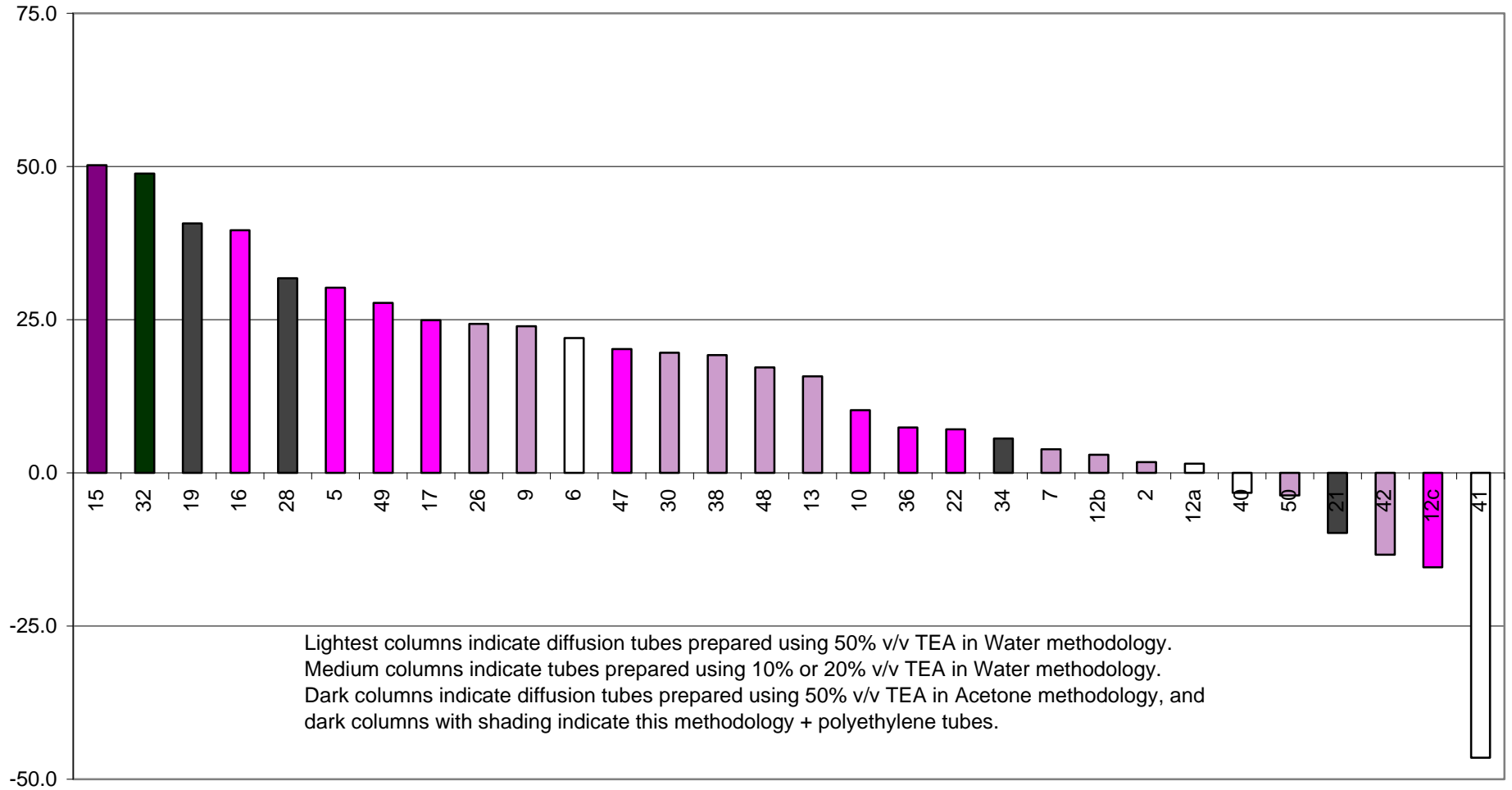

Lightest columns indicate diffusion tubes prepared using 50% v/v TEA in Water methodology.
Medium columns indicate tubes prepared using 10% or 20% v/v TEA in Water methodology.
Dark columns indicate diffusion tubes prepared using 50% v/v TEA in Acetone methodology

Figure 3. Average bias relative to chemiluminescent analyser for NO2 diffusion tube measurements in 2001 Field Intercomparison, mean of Period 1 (September) and Period 2 (October).

Lightest columns indicate diffusion tubes prepared using 50% v/v TEA in Water methodology.
Medium columns indicate tubes prepared using 10% or 20% v/v TEA in Water methodology.
Dark columns indicate diffusion tubes prepared using 50% v/v TEA in Acetone methodology, and
dark columns with shading indicate this methodology + polyethylene tubes.

3.2 Differences Between the Two Exposure Periods

During period 1, the average NO_2 concentration, as measured by all diffusion tubes, was 41.9μg m^{-3} compared with the reference value of 39.2μg m^{-3} obtained using the chemiluminescent analyser. The diffusion tube measurements showed an overall average positive bias of 6.8% during this period. During period 2, the average NO_2 concentration measured by all the tubes was 46.9μg m^{-3} compared with the reference value of 38.3 μg m^{-3} - an average positive bias of 20.2%. Thus, the diffusion tubes over-read to a greater extent during the second (October) exposure period. It is not clear why this is the case, but one possibility is differences in meteorological conditions.

Meteorological data from Walsall Metropolitan Borough Council's monitoring station at Brickyard Road, Aldridge were examined for any substantial differences between the two periods. Although this site is several kilometres from the Walsall Alumwell AUN site, it is close enough to provide an indication of local meteorological conditions during the intercomparison. Table 2 summarises the meteorological data from Brickyard Road.

Table 2. Summary of Meteorological Data from Brickyard Road.

Period	Min 10-min avg. wind speed, ms^{-1}	Mean wind speed, ms^{-1}	Max 10-min avg. wind speed, ms^{-1}	Mean wind direction, degrees	Mean Temp, ^{o}C	Relative Humidity %	Mean Pressure, mb
1 *	0	2.11	6.5 (peak =13.9)	226	12.6	87.0	1013.0
2 *	0	2.04	6.4 (peak =13.6)	203	12.7	91.3	1010.3

Exposure periods 1: 12.00 5th September -10.00 3rd October, and 2: 11.00 3rd October - 13.00 31st October. Data are based on 10-minute averaging periods.

Average wind speed, wind direction, temperature, and atmospheric pressure were similar in both exposure periods. Relative humidity was slightly higher during the latter exposure period. Average wind speeds were comparable with those measured in previous years at the Brickyard Road site (2.18 in October 2000, 2.02 in October 1999, and 1.50 in September 1999).

4. DISCUSSION

4.1 Comparison with Network Data Quality Objectives

The main objective of this annual Field Intercomparison is to estimate bias and precision, under normal field operating conditions, for all participating laboratories. The results of the intercomparison are compared with the data quality objectives of the NO_2 Network.

The data quality objectives of the NO_2 Network are based upon those required under the European Union Daughter Directive for NO_2,[8] for the overall accuracy of indicative monitoring techniques (e.g. diffusive monitoring). In the case of diffusion tube monitoring of annual average NO_2, 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. Laboratories that are, on average over both exposure periods, within ±25% of the reference value, are recognised as performing satisfactorily. Conversely, laboratories with an average bias significantly greater than ±25% have performed unsatisfactorily. The reference value is that obtained using the chemiluminescent analyser.

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. As in previous years, the figure of $6\mu g$ m^{-3} has been adopted as an arbitrary guideline for acceptable precision.

Table 1 presents the average bias and precision obtained for each laboratory. Assessment with respect to the Network data quality objectives has been carried out on the basis of the mean of the two results from the two exposure periods. Eight out of the 28 laboratories exhibited an average bias greater than the target of ±25%, relative to the automatic analyser. In the worst cases the bias was over 50%, and in all but one case the bias was positive.

Four of the 28 laboratories had a mean standard deviation greater than the guideline of 6 μg m^{-3}. In all but one case this value was only marginally exceeded. 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 μg m^{-3}.

It should be noted that the calculation of uncertainty in diffusive sampler measurements is the subject of a CEN standardisation working group. The working group is preparing standard procedures for the testing of uncertainties in diffusive samplers with specific reference to the data quality objectives of the 1st Daughter Directive. The standard is currently still under preparation, although on completion it is recommended that it be adopted as the preferred method for calculation of uncertainty.

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

Under the AQS, Local Authorities have a statutory duty to review and assess 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 (40 μg m^{-3} 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 published 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 should be presented *for the period of monitoring.* Users of NO_2 diffusion tubes are referred to the Local Air Quality Management Technical Guidance Notes LAQM TG1{00}, available at www.airquality.co.uk , see under Local Air Quality Management.

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"[9]. Therefore, Local Authorities intending to use NO_2 diffusion tubes at Stage 3 or beyond will need to carry out an ongoing "intercomparison exercise" of their own, throughout the monitoring period. **Laboratories and Local Authorities should note that we do not recommend that the bias value obtained in this or previous intercomparisons is routinely used as a "correction factor" for NO_2 diffusion tubes in Review and Assessment. As explained above, short-term intercomparisons such as this can only provide a "snapshot" of laboratory performance, and factors such as bias can vary substantially from month to month.**

4.2 Causes of Over-Read and Under-Read in NO_2 Diffusion Tubes

Palmes-type NO_2 diffusion tubes, of the type used in the NO_2 Network, are affected by several mechanisms which may cause them to exhibit positive bias (over-read), or negative bias (under-read) relative to the reference technique (automatic chemiluminescent analyser).

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 turbulence at the open end of the tube caused by wind, (Atkins et al)[10].
- blocking of UV light by the tube material, resulting in reduced NO_2 photolysis in the tube (Heal et al)[11]
- the effects of PAN (Atkins et al)[10].

Factors causing under-estimation are as follows:
- Increased tube exposure period. Heal et al have found that the average of four consecutive one-week, or two consecutive two-week exposures is systematically greater than one four-week exposure[12]. This is thought to be caused by degradation of the absorbed nitrate over time.
- Insufficient extraction of nitrite from the grids. Whilst this was believed to be a widespread problem in early days of the network[2], successive intercomparisons indicate it has become much less common[6].
- In the specific case of tubes prepared using a 50% v/v solution of TEA in water, there appears to be a mechanism affecting NO_2 uptake, resulting in negative bias, sometimes substantial[13]. This is discussed in more detail in Section 4.3 below.

4.3 Systematic Differences in Performance Due to Preparation Technique

Figure 3 also shows the preparation technique used by each laboratory to make up the diffusion tubes. In recent years, results from the intercomparisons have been used to investigate differences in diffusion tube performance thought to arise from the different preparation techniques. During 2001, there were three main preparation techniques used in the production of NO_2 diffusion tubes used in the UK NO_2 Network. These involved the following:

1. Method 1: 50% v/v TEA in acetone, grids dipped into solution and allowed to dry before insertion in tubes.
2. Method 2: 20% (or 10%) v/v TEA in deionised water, solution pipetted onto grids.
3. Method 3: 50% v/v TEA in deionised water, solution pipetted onto grids.

Prior to this intercomparison, earlier work[13, 14] observed differences in performance between these three types of tubes as follows.

- Tubes prepared using method 1 (50% v/v TEA in acetone) typically exhibit positive bias, with respect to the chemiluminescent method. This is the expected behaviour for all diffusion tubes and is attributed to several mechanisms including the effects of wind, reduced photolysis within the tube, and interference by PAN.
- Tubes prepared using method 2 (10% or 20% v/v TEA in water) typically (although not always) also exhibit the expected positive bias with respect to the chemiluminescent method. This bias has been found to be in some cases comparable with that of "method 1" tubes[13], in some cases lower[14].
- Tubes prepared using method 3 (50% v/v TEA in water) typically exhibit negative bias with respect to the chemiluminescent method. This negative bias may be quite substantial, and an independent study by researchers from Anglia University[13] has concluded such tubes are affected by a mechanism that reduces NO_2 uptake.

Thus, on the basis of the available evidence, in 2001 it was recommended that participating laboratories should use either method 1 or method 2 above, for preparation of diffusion tubes for use in the Network. This was intended to eliminate one cause of negative bias, which appears to affect 50% aqueous TEA tubes in particular. As a result, the 50% aqueous TEA method has largely been phased out within the Network.

Figure 3 shows that on average, the majority of diffusion tube measurements in the 2001 intercomparison exhibited a positive bias with respect to the chemiluminescent analyser. This was particularly the case for laboratories using tubes prepared by the acetone method; indeed the eight laboratories with the highest bias all used this technique. However, it should be noted that two laboratories obtained a negative bias despite using this technique.

Laboratories using the 20% aqueous TEA method also showed mostly (but not exclusively) positive bias. However, none of these laboratories appeared to have problems with the extreme high bias (>50% over-read) affecting some of the labs using the acetone method.

The 50% aqueous TEA method is now only used by four participating laboratories, all of which opted to continue using this technique, for reasons of data continuity or on the grounds that their results were not showing negative bias. Only one of these, laboratory 41, appeared to substantially underestimate in this test with respect to the chemiluminescent analyser. While this may be an effect relating to the preparation technique, other causes such as inefficient nitrite extraction might have been involved.

It appears from Figure 3 that tubes prepared using the acetone method may in some cases be particularly prone to large positive bias in the field. However, there is another factor besides absorbent preparation technique that may be relevant. Some suppliers who use this method have also begun to use a different material for their tubes (polyethylene, rather than the traditional acrylic), in recent years. This is shown in Figure 3 by diagonal shading. It is possible that the new polyethylene tubes may have slightly different performance characteristics during exposure. This is being investigated by

the supplier. However, until any difference is proven, we do not advise users of polyethylene tubes to change.

Finally, it is interesting to note the case of laboratory number 12. This laboratory supplies tubes made by each of the three preparation techniques described above, and one set of each type were included in the intercomparison (denoted 12a, 12b and 12c). Contrary to the typical pattern, in this case, tubes prepared by method 1 (the 50% TEA in acetone method, 12c) gave lower results than either of the other two types. However, all three types of tubes prepared by this laboratory were within the required limits of $\pm25\%$.

4.4 Comparison with Previous Field Intercomparison Exercises

Table 3 shows the main findings of intercomparisons between 1994 and 2001.

Table 3. Average Laboratory Performance in the UK NO$_2$ Network Field Intercomparison Exercises 1994-2001

	Average Performance in UK NO$_2$ Network Field Intercomparisons					
	1994	1995	1998	1999	*2000*	2001
Average Bias (%)	-11	2	1.7	-6.7	*0* (+18)*	13.1
Maximum Bias (%)	118	118	58	24	*40* (66)*	50
Minimum Bias (%)	-96	-87	-39	-31	*-33* (-21)*	-46
Standard Deviation of Bias	39	39	22	15	*18**	21
Precision μg m^{-3}	3.9	1.6	4.9	4.1	4.4	3.9

* During 2000, the chemiluminescent analyser was affected by a fault, and valid data was reduced to 70%. Therefore, laboratory performance was assessed on the basis of bias relative to the mean of all diffusion tube measurements. Bias relative to the chemiluminescent analyser is shown in brackets.

The average bias observed has changed considerably over the operation of the network, rising from -11% in 1994 to 13.1% in 2001. This probably reflects the steady elimination of problems causing substantial under-read, in particular inefficient extraction of nitrite from the grids. Such problems were widespread during the early years of the Network, but are now relatively rare.

The maximum bias observed in these intercomparisons has risen since 1999, and this is cause for concern. Reasons for the increase in large positive bias require investigation, as discussed above. Only one laboratory this year exhibited large negative bias, of -46%. Precision appears consistent with 1999 and 2000 results.

5. CONCLUSIONS

The following conclusions may be drawn from this Field Intercomparison exercise:

1. 20 of the 28 laboratories in this Field Intercomparison exercise (71%) were within ±25%, relative to the chemiluminescent analyser.

2. 24 laboratories (86%) showed an average precision within our arbitrary guideline of 6μg m^{-3}. The average precision associated with the measurements in this study was 3.9μg m^{-3}.

3. The range in average bias of measurement data over both periods, relative to the chemiluminescent analyser, was -46% to +50%. At the lower end of the range, this is due to one laboratory exhibiting unusually large negative bias, while at the upper end of the range a number of laboratories appear to be exhibiting high positive bias.

4. The average bias in exposure period 2 (October) was higher than that observed in period 1 (September). The reason for this is not clear, as meteorological conditions were similar in both periods.

5. Recent years intercomparisons have shown an increase in large positive bias, and this requires investigation.

7. RECOMMENDATIONS FOR FURTHER IMPROVEMENT

1. It is recommended that future intercomparisons continue to comprise multiple exposure periods, where resources permit. Not only will this minimise the impact of any technical problems which might affect the chemiluminescent analyser, but also give an indication of how average bias might be expected to vary from month to month.

2. It is recommended that a longer-term field study of seasonal factors should be carried out. This should be of at least 6 months duration, and include summer and winter months. The aim would be firstly to investigate seasonal variation in the performance of diffusion tubes in the Network. Secondly, it would be useful to investigate whether tubes prepared by different techniques are affected differently by weather and other seasonal factors. Whilst it might not be possible for all the laboratories to participate in such a longer term study, some laboratories using each of the main preparation techniques should be included.

3. There remains a continuing need to investigate the differences in performance related to diffusion tube preparation method.

4. There remain **two** preferred preparation techniques for use in the NO_2 Network, which should be considered equally valid pending further investigation:

- **Method 1: 50% v/v TEA in acetone, grids dipped into solution, and**
- **Method 2: 20% v/v TEA in deionised water, solution pipetted onto grids.**

5. **This intercomparison was carried out for quality control purposes within the NO_2 Network. It is not designed to provide generally applicable "correction factors" for diffusion tube results, and we do not recommend that the results (from this or earlier intercomparisons) are used in this way.**

8. ACKNOWLEDGEMENTS

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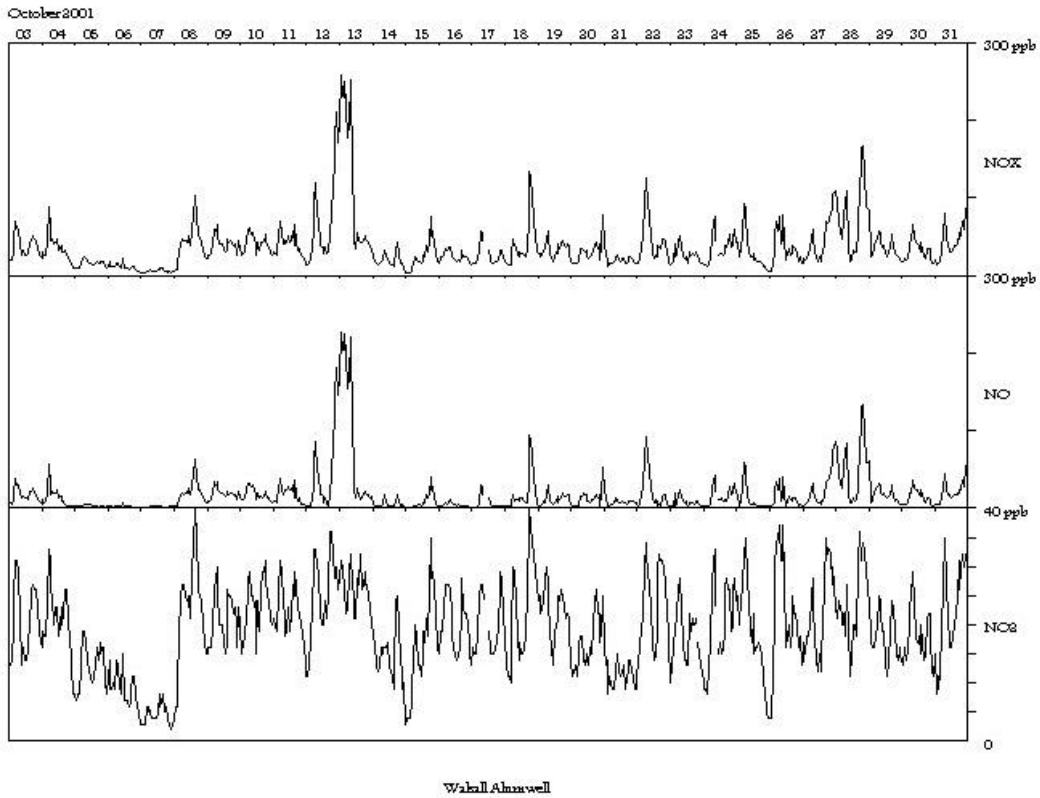
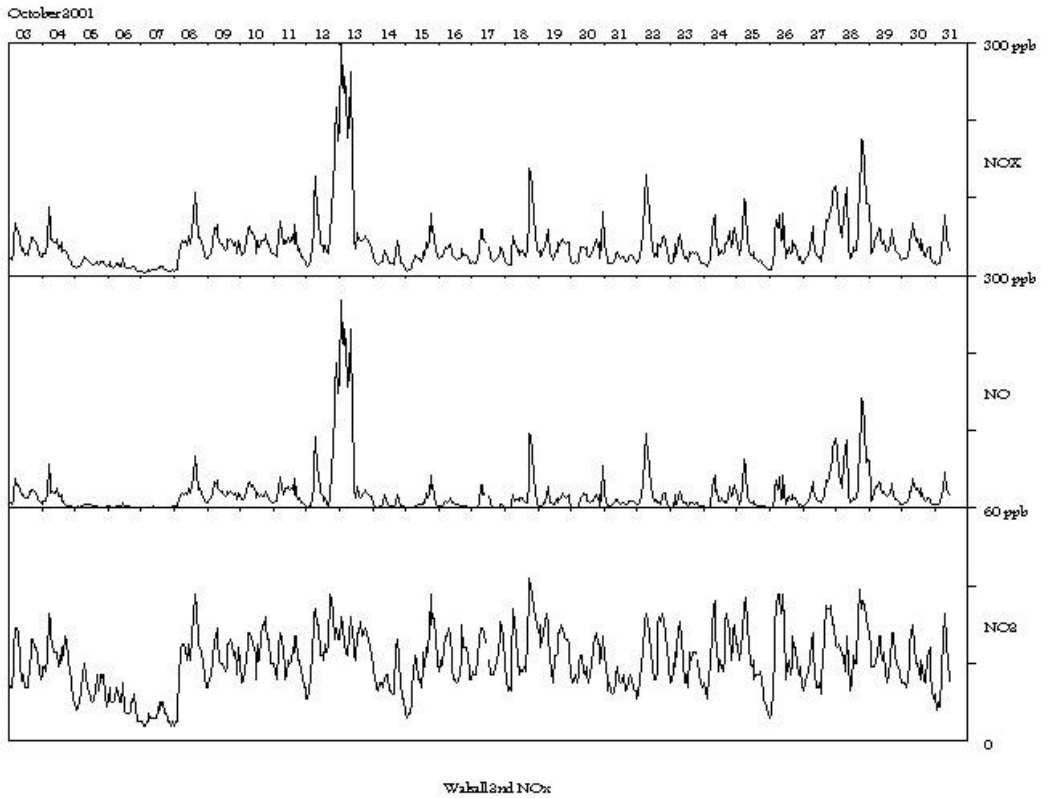**Summary of Automatic NO$_x$ Analyser Data for Walsall Alumwell, 5th September to 3rd October 2001.**

Walsall 2nd NOx
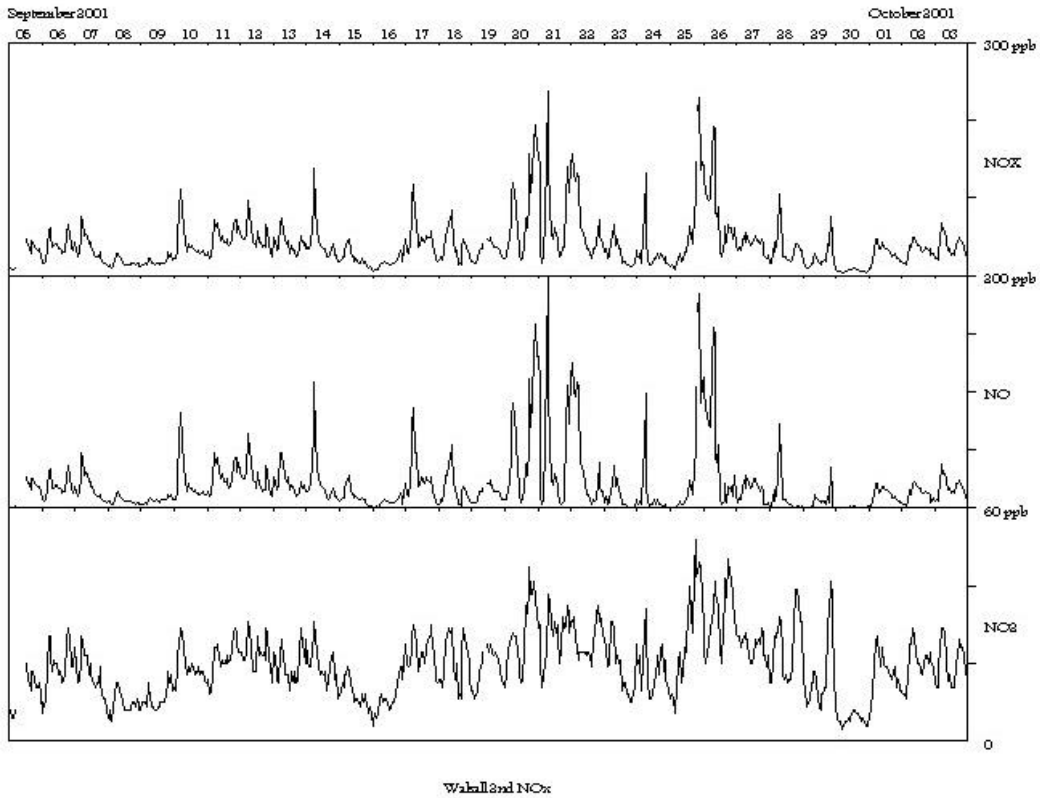
Summary of Automatic NO$_x$ Analyser Data for Walsall Duplicate Analyser, 5th September to 3rd October 2001.

October 2001

Walsall Alumwell

Summary of Automatic NO$_x$ Analyser Data for Walsall Alumwell, 3rd October to 31st October 2001.

October 2001

Walsall 2nd NOx

Summary of Automatic NO$_x$ Analyser Data for Walsall Duplicate Analyser, 3rd October to 31st October 2001.