

Appendix 1

Bias and Precision of Nitrogen Dioxide Diffusion Tubes

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Introduction

As part of the Second and Third Stage Review and Assessment of Air Quality in York a detailed discussion of the accuracy and precision of diffusion tubes was included in Technical Annex 2: Air Quality Monitoring in York. This included a detailed description of how to calculate accuracy and precision factors for diffusion tubes.

For the purpose of this Air Quality Progress Report, new accuracy and precision factors have been calculated for the nitrogen dioxide diffusion tubes. These revised factors are based on readings obtained throughout the period August 1998 to August 2004. The methodology used to calculate these factors is the same as that outlined in Technical Annex 2 of the Second and Third Stage Review and Assessment of Air Quality in York and the reader should refer to that document for further information.

Calculation of Accuracy Factors

The accuracy factors are calculated from the results obtained from diffusion tubes co-located with real time chemiluminescence analysers.

Table 1 shows all the results from diffusion tubes co-located with chemiluminescence analysers for the period July 1999 to August 2004.

To calculate the bias of the diffusion tubes scatter plots of chemiluminescence data versus diffusion tube data for roadside and background monitoring sites were plotted. These are shown in Figures 2 and 3.

For each scatter plot a $y=mx$ line of best fit was applied. In each case the gradient of the line, m was taken as the bias factor. The relevant $y=mx$ equations are shown on Figures 2 and 3.

The bias factor for the tubes located at the urban background monitoring site was found to be 0.8824, demonstrating that in general the diffusion tubes underestimated the nitrogen dioxide concentrations at the urban background site by 13.3%. For the purpose of this report bias corrected averages for intermediate sites have been calculated by increasing the annual average figure for each site by 13.3%.

The bias factor for the tubes located at the roadside monitoring sites was found to be 0.8957, demonstrating that in general the diffusion tubes underestimated the nitrogen dioxide concentrations at the roadside sites by 11.6%. For the purpose of this report bias corrected averages for roadside and kerbside sites have been calculated by increasing the annual average figure for each site by 11.6%.

Table 1 : Results from diffusion tubes co-located with chemiluminescence analysers

Chemiluminescence (ppb)	Diffusion Tube (ppb)	Chemiluminescence (ppb)	Diffusion Tube (ppb)	Chemiluminescence (ppb)	Diffusion Tube (ppb)
12.15	13	16.22	18	4.34	3
14.71	8	12.55	16	5.20	10
17.26	15	22.53	24	4.67	13
14.83	26	19.80	24	7.36	4
20.34	21	21.42	29	5.50	6
14.97	20	21.16	9	9.72	11
13.96	21	18.48	16	11.30	12
12.33	15	16.85	11	9.28	13
12.69	13	15.05	9	8.11	8
11.63	11	11.52	14	8.52	6
11.38	11	11.27	18	5.52	10
17.45	22	15.87	19	6.65	8
19.70	25	19.98	17	5.85	3
23.68	18	22.70	32	5.95	7
19.29	11	20.49	22	6.54	4
16.86	9	16.52	18	6.58	3
15.23	8	11.77	9	8.49	17
16.10	13	17.64	28	10.23	3
15.81	14	20.28	19	9.84	7
18.49	7	21.20	21	9.58	2
16.18	8	28.25	29	5.83	2
23.89	13	22.17	10	8.07	11
24.04	21	19.77	20	11.36	10
22.73	12	15.89	4	11.85	8
20.81	23	15.28	5	11.97	13
15.30	17	14.10	9	15.88	8
16.42	7	15.08	6	14.99	13
17.24	8	21.62	14	15.55	13
18.91	11	25.02	26	13.05	17
20.87	10	21.04	20	11.74	9
19.44	14	19.89	18	12.42	18
23.74	26	21.19	12	9.64	8
17.56	24	20.10	14	6.66	5
16.18	14	19.12	13	13.61	12
23.37	27	17.77	6	15.83	11
18.33	15	11.18	11	20.15	23
14.89	15	12.74	14	10.98	7
11.78	13	13.67	15	10.52	10
10.66	4	26.02	26	13.46	11
10.08	2	27.06	18	15.26	13
10.58	5	20.01	7	15.63	12
15.30	14	19.74	12	16.31	17
11.92	14	18.30	15	11.88	11
20.73	26	11.80	11	13.10	10
21.65	19	11.87	16	9.49	4
16.60	21	13.74	11	10.65	3
15.99	12	9.34	10	19.19	21
13.89	14	11.00	10	15.55	11
11.08	11	10.12	7	23.07	24
13.38	18	8.79	13	10.36	3
16.14	8	7.00	3	10.43	1
17.79	15	8.23	3	10.23	3
16.62	25	7.32	4	13.51	21
21.78	28	9.80	3	18.78	16
20.37	12	9.77	2	13.75	17
20.48	24	12.43	14	11.58	7
16.60	27	13.66	14	9.37	7
19.49	19	12.75	9	8.66	10
17.72	20	13.80	9	6.39	3
15.82	12	8.39	10	5.56	9
15.10	14	6.49	5	7.24	11
12.15	13	16.22	18	4.34	3

Figure 2: Bias calculation for background sites

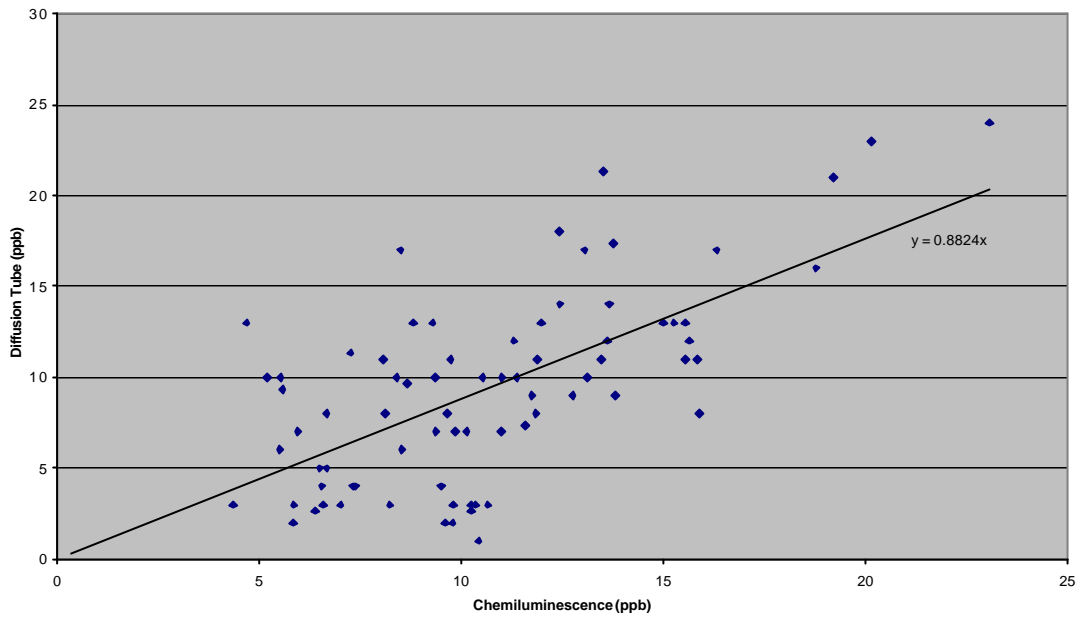
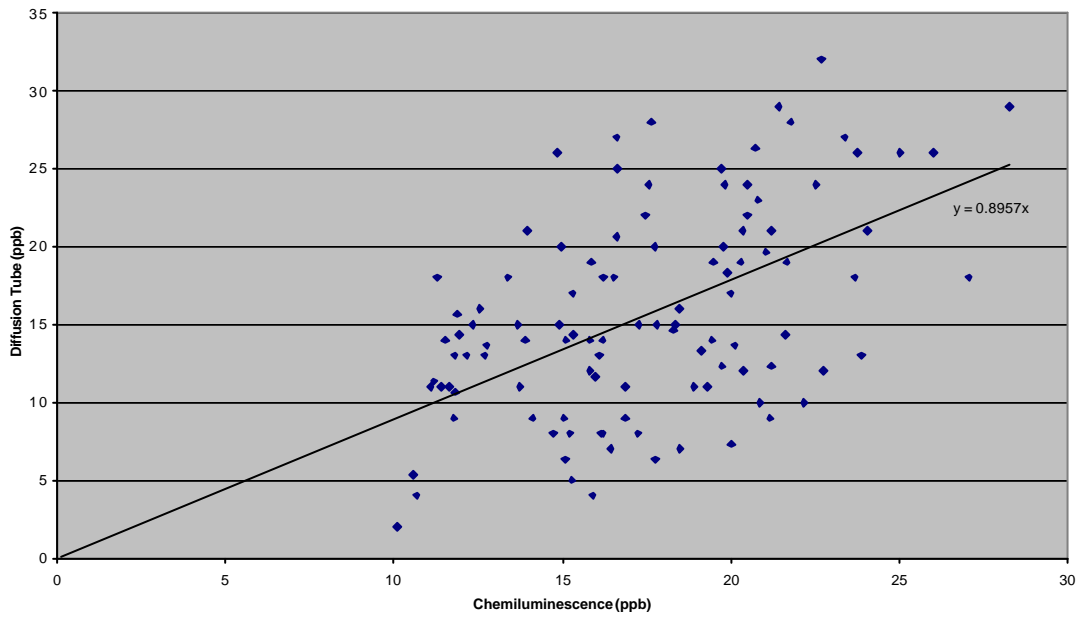


Figure 3: Bias calculation for roadside sites



Calculation of Precision Factors

The precision factors are calculated from the results obtained from diffusion tubes co-located side by side.

A measurement of the precision of the diffusion tubes has been made by calculating the Relative Standard Deviation (RSD) of the Variance of the results obtained from each of the duplicate sites¹ in York using Equations 1 and 2.

Equation 1: Variance = Sum $\{(X_a - X_{a+1}/X_m)^2\}$

Where - X_a = result 1 for month X

X_{a+1} = result 2 for month X

X_m = mean of X_a and X_{a+1}

Equation 2: RSD of Variance % = $(\text{Variance}/n)^{1/2} \times 100$

Where - n = total number of duplicate tube results

The Relative Standard Deviation of Variance for a single month at a single site was found to be 32%. This is equivalent to +/- 64% at a 95% confidence limit.

The annual mean nitrogen dioxide concentrations in most cases have been calculated by taking the mean of 12 monthly readings. It was therefore necessary to calculate the precision of the annual mean at a 95% confidence level for each site using Equation 3.

Equation 3: Precision of annual mean = $\frac{64}{(n-1)^{1/2}}$

Where n = number of readings used to calculate the annual mean at a particular site.

In most cases $n = 12$, hence the precision of the majority of the annual averages is around +/- 19.3%.

For sites where only 11 tubes were retrieved the precision of the annual averages is around +/- 20.2%.

For sites where only 10 tubes were retrieved the precision of the annual averages is around +/- 21.3%.

For sites where only 9 tubes were retrieved the precision of the annual averages is around +/- 22.6%.

¹ Where diffusion tubes were exposed in triplicate (i.e. A, B, and C), the tubes have been expressed as 3 duplicate sets for the purposes of the precision calculations (i.e. AB, AC, and BC).