

Factors affecting inter-annual variability of NO_x and NO₂ concentrations from single point sources

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1. INTRODUCTION

In the application of dispersion modelling for regulatory purposes questions frequently arise regarding the meteorological data used for the study: in particular how many years data are sufficient; is the meteorological site representative of the dispersion site? Although studies have been conducted on the impact of meteorology from different years on ground level concentrations from point sources [1,2] these studies have generally focussed on the source contribution, without consideration of background concentrations or of any chemical reactions that may take place. This approach is sufficient for releases of SO₂ from large dominant sources. However, most regulatory studies now focus on NO₂, for which background concentrations and chemical reactions are important. Investigation of the inter-annual variability of only the process contributions to NO_x may give little indication of what is actually important, that is, the inter-annual variability of the NO₂ concentration.

In this note we present some calculations of NO_x and NO₂ using ADMS 3.1 [3], in which the impacts of both background pollutant concentrations and chemical reactions are assessed. The focus is on isolated point sources without building impacts. The impact of the choice of meteorological site is not considered here.

2. MODEL INPUT DATA

2.1 Source data

Two 'standard' sources were modelled, a typical power station and a buoyant release from a height of 50m. The source details are given in Table 1. The NO_x emissions are assumed to be 10% NO₂ by volume.

Table 1 *Source data*

Source	Power station	50m source
Height (m)	199	50
Diameter (m)	13	1
Exit velocity (m/s)	22	9
Temperature (°C)	130	200
Emission rate NO _x (g/s)	1000	15

2.2 Met data

Five years of sequential met data, from 1992-96, from Birmingham (Elmdon) were used. Table 2 gives the mean wind speed at 10m for each year. This can be seen to vary by up to about 20% from year to year.

Table 2 *Mean wind speeds*

Year	Mean wind speed (m/s)
1992	3.8
1993	3.8
1994	4.2
1995	3.6
1996	3.4

2.3 Background data

Background concentrations of NO_x, NO₂ and O₃ from Lullington Heath (a rural monitoring site) from 1992-96 were used. Harwell monitoring site, which is nearer to Elmdon meteorological station was not used as there were insufficient data for the years in questions.

If data for any pollutant were missing for a particular hour, values for all 3 pollutants were replaced by the average values over all 5 years. This was necessary for 21% of hours in 1992, 26% in 1993, 38% in 1994, 7% in 1995 and 15% in 1996.

Statistics of the background data are given in Tables 3 and 4. The annual mean values show little variation from year to year. There is more variation in the high percentiles – in particular the maximum hourly concentration of NO_x and NO₂ and the 99.9th percentile of NO_x were unusually high in 1992.

Table 3 *Statistics of hourly NO_x and NO₂ background data (ppb)*

	1992		1993		1994		1995		1996	
	NO _x	NO ₂	NO _x	NO ₂	NO _x	NO ₂	NO _x	NO ₂	NO _x	NO ₂
Annual mean	9.2	7.5	10.0	8.5	9.9	8.4	8.7	7.5	10.2	8.3
98 th percentile	40	30	39	30	35	30	32	25	43	29
99.8 th percentile	162	46	92	42	81	58	71	37	80	40
Maximum	311	90	102	53	101	64	93	43	109	46

Table 4 *Statistics of hourly O₃ background data (ppb)*

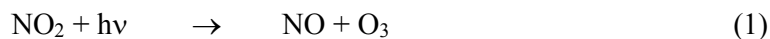
	1992	1993	1994	1995	1996
Annual mean	31	28	29	30	27
98 th percentile	68	60	62	77	59
99.9 th percentile	99	96	102	122	85
Maximum	104	117	117	134	90

3. MODELLING METHODOLOGY

Two chemistry schemes were used – the GRS (Generic Reaction Set) and the OLM (Ozone Limiting Method).

3.1 GRS Chemistry Scheme

The GRS chemistry scheme [4] is a semi-empirical photochemical model which reduces the complex set of reactions between NO, NO₂, O₃ and VOCs (volatile organic compounds) to just a few reactions. The two reactions involving NO, NO₂ and O₃ are:

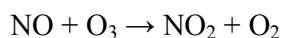


In addition there are parameterisations of reactions involving ROC, RP, SGN and SNGN which represent reactive organic compounds, radical pools, stable gaseous nitrogen products and stable non-gaseous nitrogen products respectively. *hν* represents ultra-violet radiation.

In this illustrative case we are not considering emissions or background concentrations of VOCs and thus the GRS reduces to equations (1) and (2) only. This is the NO_x chemistry scheme included in ADMS 3. The inputs to the chemistry scheme are the sum of the process contribution, the background concentration and the ultra-violet radiation which is estimated hour by hour. The chemistry model assumes that ambient air mixing into the plume as it is transported downstream is uniformly mixed across the plume. In general this assumption is likely to lead to a small overestimate of NO₂ and a corresponding underestimate of O₃ for a given NO_x concentration.

3.2 OLM Chemistry Scheme

The OLM scheme [5] estimates NO₂ concentrations by assuming NO reacts instantaneously with all available ozone via a single reaction:



For each hour, the process contribution to the NO₂ concentration is calculated using

$$[\text{NO}_2]_{\text{OUT}} = [\text{NO}_2]_{\text{IN}} + \text{Minimum} ([\text{NO}]_{\text{IN}}, [\text{O}_3]_{\text{IN}})$$

where all concentrations are in ppb, and the input concentrations [NO₂]_{IN} and [NO]_{IN} are the process contribution from the source. After this calculation has been carried out, a background NO₂ concentration suitable for the current hour is added to the concentration. This scheme has been implemented in ADMS 3 for the purposes of the current study and is also included in some US EPA dispersion models. The scheme is likely to be very conservative since the reaction is assumed instantaneous, there is no reverse photochemical reaction (the dissociation of NO₂) and, as in the standard version of ADMS, mixing is assumed uniform. The magnitude of this conservatism is considered below.

3.3 Model Calculations

ADMS 3.1 was used to calculate concentrations for each hour in the period 1992-1996 for each of the cases (1) to (6) below.

- Case (1) Without chemistry, no contribution from background (i.e. process contribution only)
- Case (2) With GRS chemistry using the appropriate year of background data
- Case (3) With GRS chemistry always using 1992 background data
- Case (4) With GRS chemistry always using 1996 background data
- Case (5) With GRS chemistry always using 1994 met data
- Case (6) With ozone limiting (OLM) chemistry using the appropriate year of background data

The hourly average concentrations were calculated on a grid of 31 by 31 points (20km square for the power station, 2km square for the 50m source) and used to derive annual average, 98th and 99.9th percentile and maximum hourly average concentrations of NO_x and NO₂.

4. MODEL RESULTS

Results shown here are the maximum ground level concentrations for each statistic calculated. Results are presented for each of the six scenarios listed above, and for the case of no process contribution i.e. assuming only background concentrations are present.

Firstly, results of NO_x and NO₂ are shown as graphs of the maximum ground level concentration against the year (Figures 1-6). The following should be noted:

- NO_x results for the ozone limiting method are not shown, as these are identical to the GRS chemistry results, since both chemistry methods conserve the total volume of NO_x.
- For the power station, the maximum ground level 98th and 99th percentile concentrations were found to be almost identical to the background concentrations, hence these graphs are omitted. The graphs of annual average and maximum hourly average concentrations are shown in Figures 1 and 2.
- For the 50m source, graphs are shown for the annual average, 98th and 99th percentile and maximum hourly average concentrations (Figures 3-6).

Secondly, the mean and standard deviation of each statistic are given, for each pollutant, for each source, in Tables 5-8. Table 9 shows the percentage of the process NO_x contribution which is NO₂ at the location of the maximum ground level concentration. This illustrates the impact of local chemistry, as modelled by the two chemistry schemes, on NO₂ concentrations.

5. DISCUSSION

5.1 *Process Contribution Study*

Considering first the process contribution only (Case (1)), it can be seen that the relative contribution by the process to the total concentration is greater for the 50m source than for the power station. It can also be seen that the relative contribution from the process to the total concentration is smaller for the annual average (the mean NO_x concentrations are 0.4ppb for the power station compared with the background of 9.6ppb) than for the percentiles (the maximum hourly NO_x concentrations are 57ppb for the power station compared with the 143ppb background). This is true for the both sources and both pollutants, NO_x and NO₂.

In this case process contributions of NO_x from the 50m source are greater in absolute terms than those from the power station although, of course, the power station has an impact over a much greater geographical area than the 50m source.

5.2 *Total Concentration – Process Plus Background*

Comparison of impacts of inter-annual variation of background concentrations with those of meteorology

The annual mean concentrations including background concentrations and chemistry effects are dominated by the background concentrations. The inter-annual variation in the background concentration causes more variation in the results than the inter-annual variation in the meteorology. In Figures 1 and 3, the results for the cases where the same background data are used for every year, Cases (3) and (4) show the least variation. The case where the background values used varies from year to year, Case (2), shows the greatest variation. This trend is confirmed by the tabulated values of standard deviation. The standard deviation is smaller for Cases (3) and (4) where the same background is used for all years than for Case (2). The difference is most pronounced for the power station where the background dominates the ground level

concentrations whereas for the 50m stack, where the relative contribution from the process is smaller, variations of both meteorology and background are important.

Comparison of GRS and OLM chemistry schemes

For the power station, the NO₂ annual mean results for the OLM scheme are similar to the GRS scheme due to the low process contribution from the power station in comparison with the background concentration. For the 50m source the OLM scheme predicts higher mean NO₂ concentrations than the GRS scheme as here the process contribution is higher compared with the background concentration.

Composition of process contribution at location of maximum concentration

Table 9 shows the percentage of NO_x (by volume) present as NO₂ at the point of maximum concentration for the Case (2) using GRS and Case (6) using OLM. The table shows annual averages for each year and for one case a high percentile (99.9th).

For the 50m source the GRS scheme predicts between 47% and 58% is NO₂ whereas OLM predicts between 89% and 95%. For the power station the GRS scheme predicts between 46% and 100% is NO₂ whereas OLM predicts over 98% is NO₂. The unrealistic oxidation of NO predicted by OLM, leading to over-predictions of NO₂, is most apparent for the 50m source.

This comparison shows the inadequacy of assuming that 50% of the process contribution is NO₂ at the location of maximum concentration as is often used, supposedly to give a conservative estimate of oxidation to NO₂. The percentage NO₂ depends on the averaging time, the percentile and the process contribution to total NO_x.

Comparing Case (2) (GRS chemistry), Case (6) (OLM chemistry) and Case (5) (GRS chemistry with constant meteorology), it can be seen that the differences in NO₂ results between the GRS and OLM schemes are at least as large as the variations due to meteorology.

6. CONCLUSIONS

- (i) Although it is useful to model the process contribution to NO_x, this may give little indication of either the NO_x or NO₂ climate (total concentration) if the relative contribution of the process contribution is small.
- (ii) For model calculations of NO₂ it is important to consider the background concentrations and their inter-annual variation. This has more impact on predicted concentrations than inter-annual variations in meteorology.
- (iii) In a modelling study the choice of chemistry scheme or neglect of chemical reactions is at least as significant as the inter-variation variation in meteorology.

- (iv) The Ozone Limiting Method (OLM) leads to large overestimates of NO₂ when the process contribution is significant compared with the background concentration
- (iv) Representing the process contribution to NO₂ as a fixed percentage of NO_x e.g. assuming 50% of the process NO_x is NO₂, leads to a poor estimate of the process contribution to NO₂. It may result in either over-estimates or under-estimates of total NO₂.

7. REFERENCES

- [1] Davies B. M. and Thomson D. J. (1996) *Investigating the importance of pre-processing in estimating dispersion climatology*, Proc. 4th Workshop on Harmonisation Within Dispersion Modelling for Regulatory Purposes, Oostende, Belgium
- [2] Hall D. and Spanton A. (1999) *Meteorological Data and Dispersion Modelling*, Clean Air and Environmental Protection, Volume 29, No. 5
- [3] ADMS 3 Technical Specification (2002) Cambridge Environmental Research Consultants
- [4] Venkatram, A., Karamchandani, P., Pai, P. and Goldstein, R., (1994). *The development and application of a simplified ozone modelling system*. Atmospheric Environment, vol 28, pp3665-3678.
- [5] Cole, H.S., and Summerhays, J.E., (1979). *A review of techniques available for estimating short-term NO₂ concentrations*. Journal of the Air Pollution Control Association, vol 29, pp 812-817.

Figure 1 Power station, annual mean concentrations (ppb)

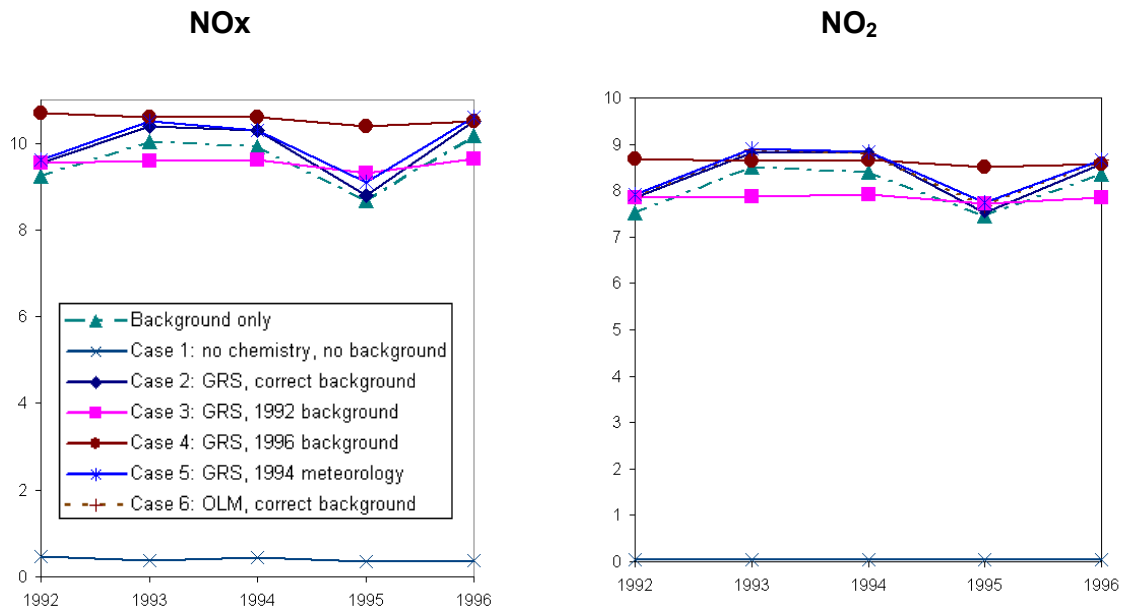


Figure 2 Power station, maximum hourly average concentrations (ppb)

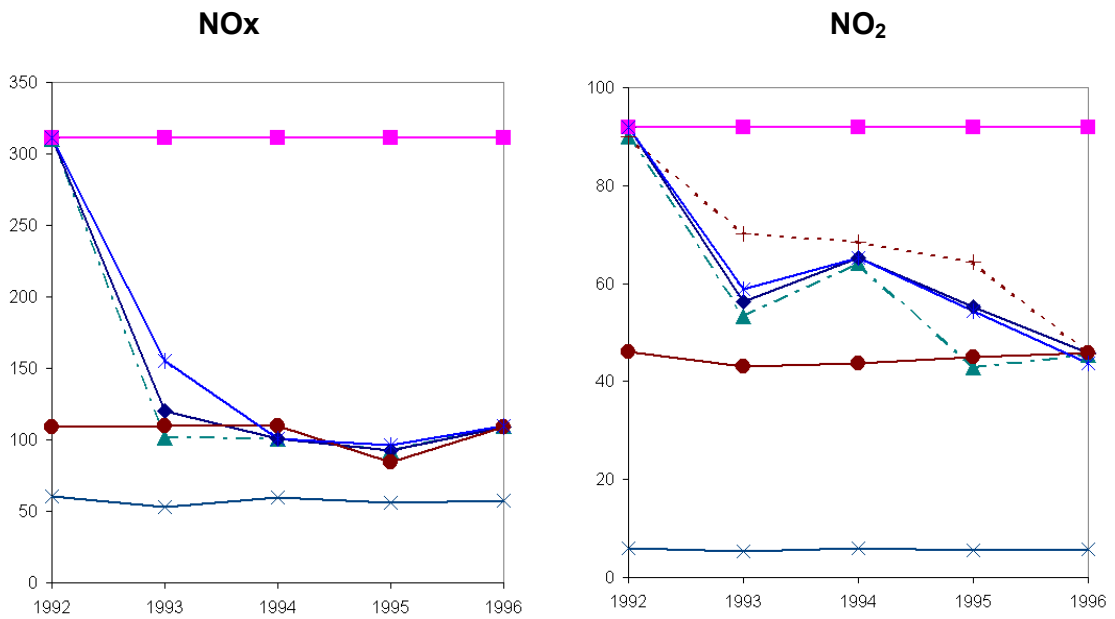


Figure 3 50m source, annual mean concentrations (ppb)

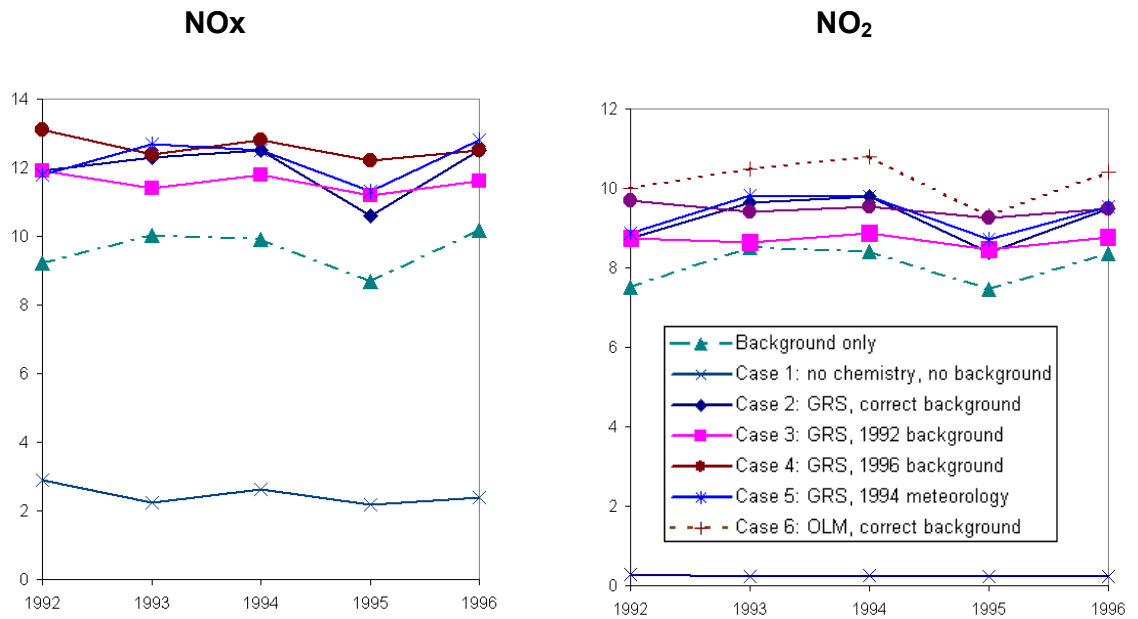


Figure 4 50m source, 98th percentile concentrations (ppb)

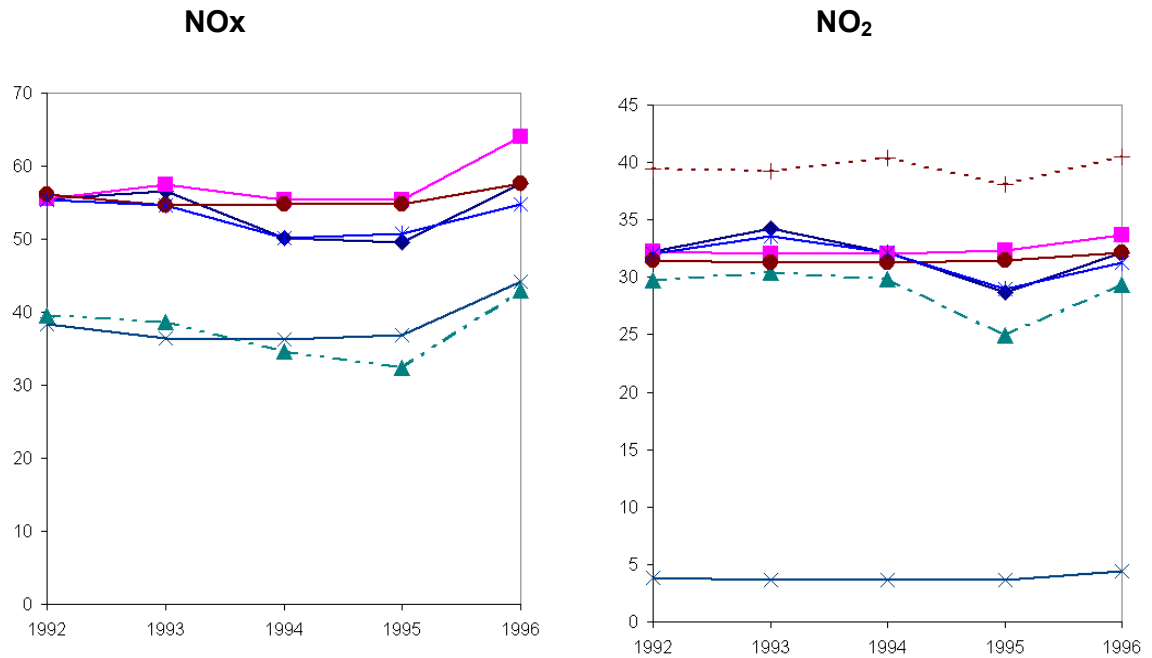


Figure 5 50m source, 99.9th percentile concentrations (ppb)

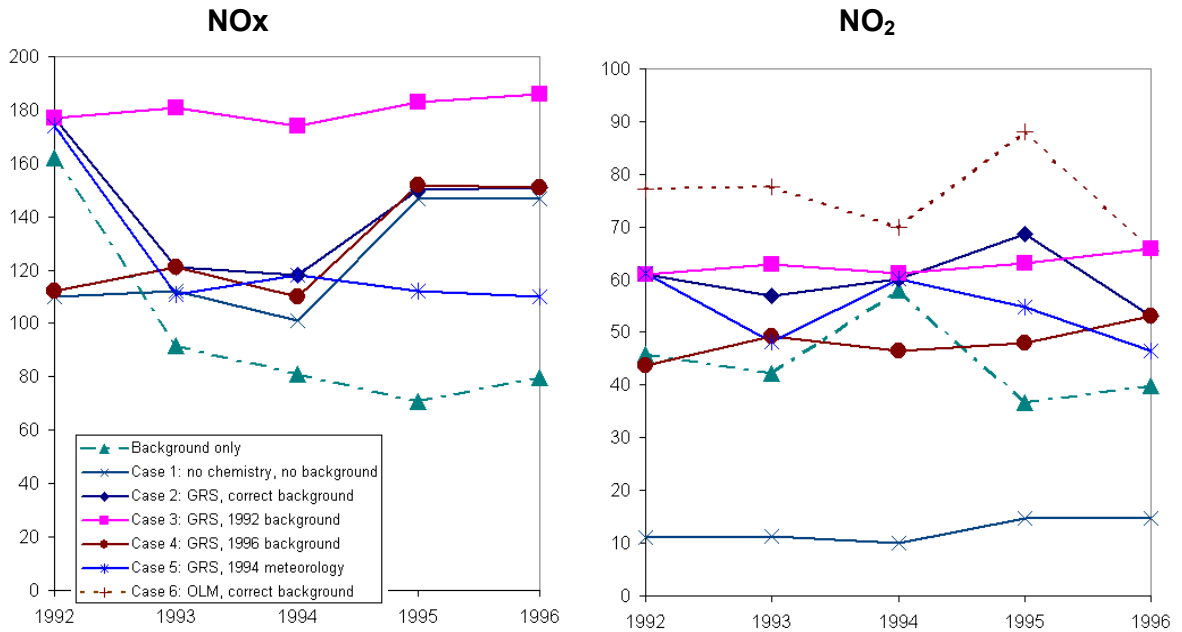


Figure 6 50m source, maximum hourly average concentrations (ppb)

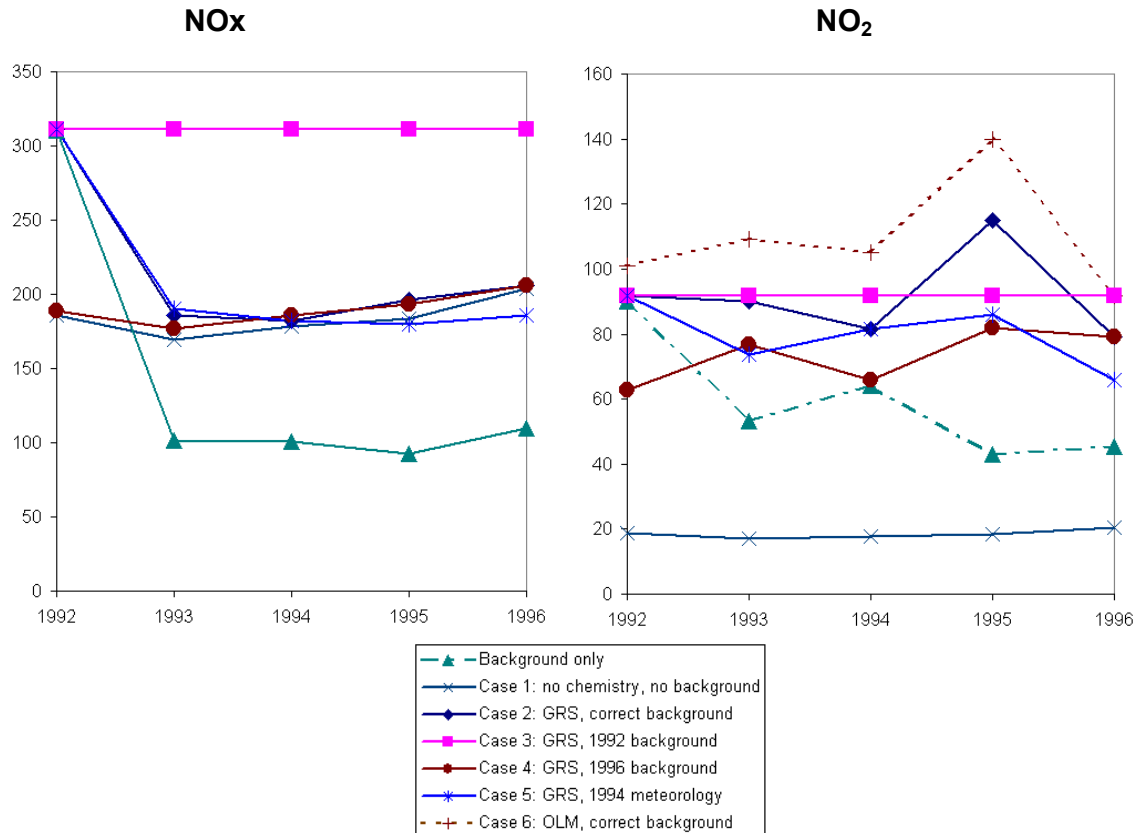


Table 5 Power station, Mean and standard deviation of hourly NO_x results (ppb)

	Background only		Case 1 No chemistry, no background		Cases 2 & 6 GRS or OLM, correct background		Case 3 GRS, 1992 background		Case 4 GRS, 1996 background		Case 5 GRS, 1994 meteorology	
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
Annual mean	9.6	0.57	0.4	0.05	9.9	0.65	9.5	0.12	10.6	0.10	10.0	0.58
98 th percentile	38	3.75	10	1.65	38	3.60	40	1.06	43	0.37	39	3.26
99.9th percentile	97	33.2	29	2.36	95	30.7	153	1.20	79	1.06	97	27.7
Maximum	143	83.9	57	2.81	147	82.6	311	0.00	104	10.2	155	80.9

Table 6 Power station, Mean and standard deviation of hourly NO₂ results (ppb)

	Background only		Case 1 No chemistry no background		Case 2 GRS, correct background		Case 3 GRS, 1992 background		Case 4 GRS, 1996 background		Case 5 GRS, 1994 meteorology		Case 6 OLM, correct background	
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
Annual mean	8.1	0.46	0.04	0.01	8.3	0.53	7.8	0.07	8.6	0.06	8.4	0.49	8.4	0.5
98th percentile	28.8	2.00	1.0	0.17	45.0	2.15	30.2	0.47	29.5	0.07	29.5	2.01	45.5	7.12
99.9th percentile	44.5	7.43	2.9	0.24	57.5	7.18	46.3	0.73	40.0	0.04	45.3	6.85	60.1	14.1
Maximum	59.2	17.1	5.7	0.28	62.9	15.7	91.9	0.00	44.7	1.16	62.8	16.2	67.7	14.1

Table 7 50m source, Mean and standard deviation of hourly NO_x results (ppb)

	Background only		Case 1 No chemistry, no background		Cases 2 & 6 GRS or OLM, correct background		Case 3 GRS, 1992 background		Case 4 GRS, 1996 background		Case 5 GRS, 1994 meteorology	
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
Annual mean	9.6	0.57	2.5	0.26	12.0	0.71	11.6	0.26	12.6	0.32	12.2	0.58
98th percentile	38	3.73	123	19.3	143	21.8	180	4.26	129	18.6	125	24.7
99.9th percentile	97	33.2	168	12.2	201	47.4	295	1.20	176	9.35	195	51.1
Maximum	143	83.9	184	11.2	216	48.1	311	0.00	190	9.50	210	50.7

Table 8 *50m source, Mean and standard deviation of hourly NO₂ results (ppb)*

	Background only		Case 1 No chemistry no background		Case 2 GRS, correct background		Case 3 GRS, 1992 background		Case 4 GRS, 1996 background		Case 5 GRS, 1994 meteorology		Case 6 OLM, correct background	
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
Annual mean	8.1	0.46	0.25	0.03	9.2	0.55	8.7	0.13	9.5	0.14	9.4	0.47	10.2	0.52
98th percentile	28.8	2.00	12.3	1.93	60.0	5.16	62.8	1.75	48.1	3.07	54.2	6.02	75.7	7.74
99.9th percentile	44.5	7.43	16.8	1.22	84.1	15.2	87.5	1.78	64.1	5.69	71.3	8.89	107	17.2
Maximum	59.2	17.1	18.4	1.12	91.6	12.6	91.9	0.00	71.8	7.80	79.8	9.21	114	15.4

Table 9 *NO₂ process contribution expressed as percentage of NO_x process contribution. Figures are annual average except those bracketed which are 99.9th percentile.*

Year	% process NO _x that is NO ₂			
	Case (2) GRS		Case (6) OLM	
	Power station	50m source	Power station	50m source
1992	100	48	100	93
1993	82	55	100	92
1994	100	58	98	92
1995	46 (< 1)	47 (66)	100 (< 1)	95 (100)
1996	73	54	100	89