

**17th International Conference on
Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes
9-12 May 2016, Budapest, Hungary**

A VALIDATION STUDY OF THE ADMS PLUME CHEMISTRY SCHEMES

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Abstract: The paper presents validation, from two sites in Alaska, of two ADMS chemistry schemes for the prediction of in-plume NO₂ concentrations. Both the standard scheme, which assumes instantaneous mixing of ambient O₃ into the plume at source, and the dilution and entrainment scheme which takes account rate of the entrainment of O₃ into the plume, show good performance. A novel methodology comprising a scatter plot of the ratio of modelled to observed NO₂ vs. modelled to observed NO_x is used to distinguish errors in the chemistry schemes from errors in the prediction of NO_x. This shows the dilution and entrainment model has superior performance.

Key words: plume chemistry, nitrogen dioxide, ADMS, validation

INTRODUCTION

Combustion sources emit a combination of oxides of nitrogen (NO_x), but air quality standards are generally expressed in terms of one component of NO_x, nitrogen dioxide (NO₂). For example the EU imposes limit values for annual and hourly average concentrations of NO₂. As the components of NO_x are chemically reactive in the atmosphere it is necessary to model this conversion to predict concentrations of NO₂ for comparison with the standards. The simplest models assume a fixed conversion rate, empirically based formulae (e.g. Carslaw *et al.*, 2013), or use an ozone limiting method in which all available ozone is used to oxidize NO to NO₂ (Cole and Summerhays, 1979). A more advanced plume based chemical scheme, PVMRM, is available in AERMOD (Hanrahan, 1999). The Atmospheric Dispersion Modelling System ADMS 5 (Carruthers *et al.*, 1994, Carruthers *et al.*, 2003) includes two plume based schemes for predicting NO₂, a standard chemistry scheme and a newly developed scheme that takes account of the rate of entrainment of air into the plume and its dilution as it travels downstream.

This paper presents validation of both the ADMS 5 chemistry schemes and includes a new graphical method which allows the performance of a chemistry scheme to be considered in isolation from a model's performance in predicting NO_x. An ideal validation dataset for NO₂ would include observations of NO₂, NO_x (total NO and NO₂) and O₃ concentrations from several monitors around an emission source with well quantified emissions and appropriate meteorological observations. Such a dataset does not exist, but two adequate datasets were identified, in Wainwright and Prudhoe Bay, both of which are in Alaska.

ADMS CHEMISTRY SCHEMES

Both chemical reaction schemes within ADMS consider the two reactions which take place over short timescales:



where the photochemical reaction (2) may only take place during daylight. In the standard scheme, concentrations of primary NO and NO₂ within the plume are first calculated using the standard dispersion algorithms. The background concentrations of NO_x, NO₂ and O₃ are assumed to be well-mixed into this 'primary' plume at the source; to calculate in-plume concentrations of NO₂ and O₃, reactions (1) and (2) take place for a 'reaction time' calculated as the concentration-weighted average of the travel time from

the sources to a receptor. In the dilution and entrainment scheme, rather than full entrainment of the background at source, background pollutants are entrained into the plume at a rate determined by the rate of entrainment of ambient air into the instantaneous plume, as given by the concentration fluctuation module of ADMS (Davies *et al.*, 1998). It is to be anticipated that the dilution and entrainment scheme will better reflect the mixing processes in the plume and therefore more accurately predict concentrations of NO₂; the standard scheme would be expected to be conservative in NO₂ since entrainment of ozone into the plume is effectively assumed to be instantaneous.

VALIDATION CASES

The two validation sites that were used in this study are from Wainwright and Prudhoe Bay, both in Alaska. ADMS version 5.0.2.0 was used throughout.

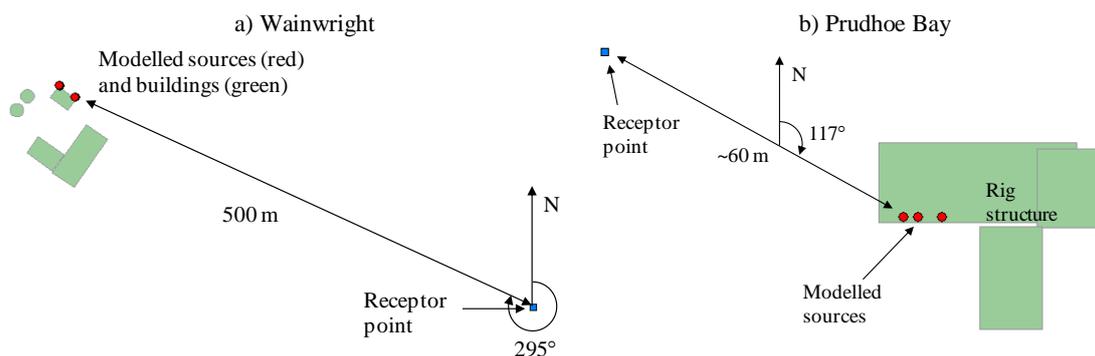


Figure 1. Diagram of the study area for a) Wainwright and b) Prudhoe Bay

At Wainwright the NO_x emissions source is a power plant on edge of the small town of Wainwright (Hendrick *et al.*, 2013). It consists of five diesel generators with exhaust stacks located on two corners of the power plant building. Concentrations of NO, NO₂ and O₃ and the meteorological parameters of wind speed, wind direction, temperature and solar radiation were measured at a single location 500 m to the east, as shown in

Figure 1a. Modelling using both the standard and dilution and entrainment ADMS chemistry schemes was conducted for the period September 2009 to September 2010. At Prudhoe Bay the NO_x emissions source consists of a drilling rig on an oil well; of the considerable number of sources only three were significant. Concentrations of NO, NO₂, and O₃ and meteorological parameters including wind speed, wind direction, rms vertical velocity (σ_w), temperature and solar radiation were measured at a single monitoring station approximately 60 m away from the rig, as shown in

Figure 1b. Modelling was conducted for the first 40 days of 2007 using only the standard ADMS chemistry scheme, as the dilution and entrainment scheme has not yet been implemented for multiple sources. As the drilling rig was large and close to the monitor, its effect on airflow and hence dispersion has been included in the modelling. Rather than use the ADMS meteorological pre-processor to estimate the Monin Obukhov length (L_{MO}), which is likely to be subject to significant error in the very stable conditions prevailing at Prudhoe Bay in January and February, the measured σ_w was used to estimate L_{MO} using an approximate relationship for the wind speed in stable conditions:

$$u(z) = \frac{u_*}{\kappa} \left(\ln \left(\frac{z+z_0}{z_0} \right) + \frac{5z}{L_{MO}} \right) \quad (3)$$

where $u_* \sim \frac{\sigma_w}{1.3}$, z is the height above ground, z_0 is the surface roughness and κ (≈ 0.4) is von Karman's constant. As there were no measured upstream values of pollutant concentrations in either study, it was necessary to estimate background values of NO_x, NO₂ and O₃ from the single receptor in each. NO_x and NO₂ background concentrations were estimated from time periods that were not included in the model analysis. At Wainwright these values were found to be negligible so were set to zero. At Prudhoe Bay, an

average diurnal, wind direction dependent background was used. The O₃ background was then estimated assuming conservation of oxidant (NO₂ + O₃).

RESULTS AND DISCUSSION

Tables 1 and 2 show the model validation statistics for Wainwright and Prudhoe Bay respectively.

Figure 2 shows, for Wainwright, the quantile-quantile plots for NO_x (a) and NO₂ (b), the scatter plots of modelled vs. observed ratios NO₂/NO_x for standard chemistry (c) and the dilution and entrainment chemistry (d), and the scatter plots of modelled to observed ratios of NO₂ vs. modelled to observed ratios of NO_x for standard chemistry (e) and the dilution and entrainment chemistry (f). Figure 3 shows the equivalent plots for Prudhoe Bay, without those for dilution and entrainment chemistry which was not modelled at Prudhoe Bay.

The focus of this validation is on the performance of the chemical reaction schemes, so the discussion highlights the insight that the tables and graphs provide about this. We first note for Wainwright that NO_x is underestimated although the correlation is high, and both the standard and dilution and entrainment schemes underestimate NO₂, with a greater underestimate for the dilution and entrainment chemistry; ratios of NO₂ to NO_x are overpredicted for the standard scheme but well predicted for the dilution and entrainment scheme. At Prudhoe Bay both NO_x and NO₂ are underestimated for low observed concentrations but well predicted for higher levels; there is wide scatter in the ratios of NO₂ to NO_x. However, to assess the performance of the reaction schemes it is necessary to distinguish the errors in NO_x from errors in NO to NO₂ conversion. This is achieved by the scatter plots of ratios of modelled to observed NO₂ vs. ratios of modelled to observed NO_x (Figures 2(e,f) and 3(d)). When NO_x is overpredicted then NO₂ should be overpredicted but the ratio of NO₂ to NO_x underpredicted as it must decrease with increasing NO_x, and conversely for underprediction of NO_x; when NO_x is well predicted then NO₂ should also be well predicted. This means that the points should lie between the diagonal and horizontal blue lines on the plots and the line of best fit should pass through (1,1). This is indeed, in the main, the case for the dilution and entrainment scheme for Wainwright (Figure 2(e)), which therefore has very good performance and somewhat better performance than the standard scheme. In the case of Prudhoe Bay, Figure 3 (d) shows that the standard chemistry performs well, just slightly overestimating the conversion to NO₂. Such good performance may be a consequence of the large buildings resulting in rapid mixing into the plume so that the instantaneous mixing assumption is good in this case.

Table 1. Statistics for modelled NO_x and NO₂ concentrations for Wainwright. Includes observed and modelled means, correlation coefficient, fraction of modelled values within a factor of 2 of the observed values, fractional bias, and observed and modelled maximum values.

Run summary		Statistical summary						
Pollutant	NO _x chemistry method	Obs Mean	Mod Mean	R	Fac2	Fb	Obs Max	Mod Max
NO _x	N/A	43.2	27.4	0.780	0.423	-0.447	369	145
NO ₂	Standard chemistry	12.7	10.9	0.671	0.517	-0.148	72.5	66.7
NO ₂	Dilution and entrainment chemistry	12.7	8.68	0.682	0.520	-0.374	72.5	49.1

Table 2. Statistics for modelled NO_x and NO₂ concentrations for Prudhoe Bay. Same statistics as shown in Table 1.

Run summary		Statistical summary						
Pollutant	NO _x chemistry method	Obs Mean	Mod Mean	R	Fac2	Fb	Obs Max	Mod Max
NO _x	N/A	192	145	0.688	0.515	-0.279	845	498

NO ₂	Standard chemistry	57.9	37.8	0.683	0.627	-0.420	246	170
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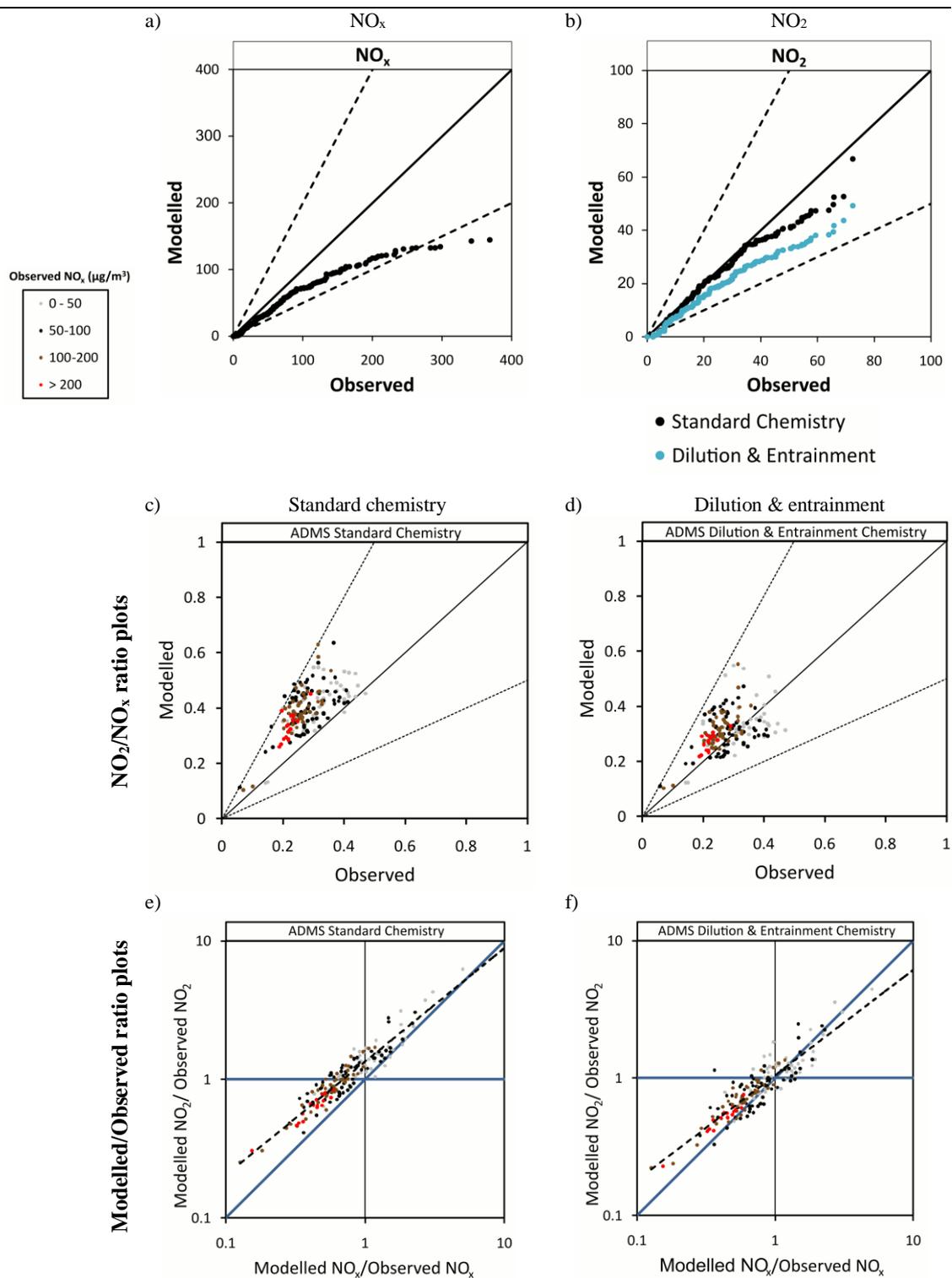


Figure 2. Quantile-quantile plots of modelled against observed a) NO_x concentrations and b) NO₂ concentrations. Scatter plots of NO₂/NO_x ratio for c) standard chemistry and d) dilution & entrainment. Scatter plots of

modelled/observed ratio of NO₂ against the ratio for NO_x for e) standard chemistry and f) dilution & entrainment with a dashed line of best fit. Points in c) – f) are coloured by NO_x concentration. All at Wainwright.

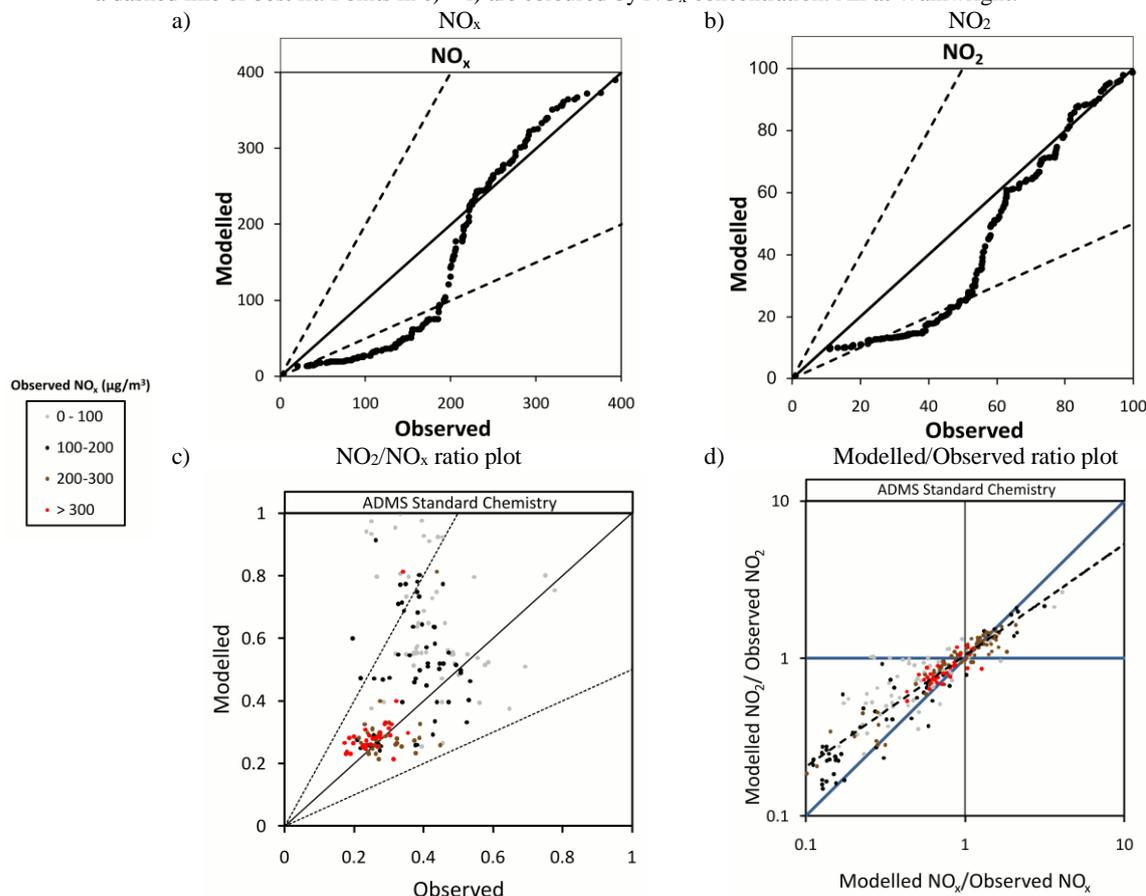


Figure 3. Quantile-quantile plots of modelled against observed a) NO_x concentrations and b) NO₂ concentrations.

Scatter plots of c) NO₂/NO_x ratio and d) modelled/observed ratio of NO₂ against the ratio for NO_x for standard chemistry with a dashed line of best fit. Points in c) and d) are coloured by NO_x concentration. All at Prudhoe Bay.

ACKNOWLEDGEMENTS

We should like to acknowledge BP International Limited for their support of this study.

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