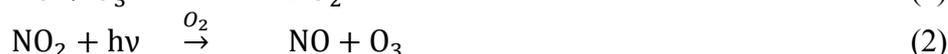# NO_X CHEMISTRY MODEL IN ADMS 5

CERC

In this document 'ADMS' refers to ADMS 5.2.

1.   Introduction

The ADMS NO_X chemistry scheme models the reactions between ozone (O_3), nitrogen monoxide (NO) and nitrogen dioxide (NO_2) given in equations (1) and (2),

$$NO + O_3 \quad \rightarrow \quad NO_2 \tag{1}$$
$$NO_2 + h\nu \quad \overset{O_2}{\rightarrow} \quad NO + O_3 \tag{2}$$

where $h\nu$ is ultra violet radiation. The reaction rates K_1 and K_2 (where K_1 is the reaction coefficient for equation (1) and K_2 is the photo-dissociation coefficient for equation (2)) are taken from the Generic Reaction Set (GRS) chemistry scheme, which is a semi-empirical photochemical model developed originally by CSIRO in Australia [1], [2]. The calculation of K_1 and K_2 is described in the next section.

2.   Calculation of Reaction Coefficients

The reaction coefficient $K_1 (s^{-1} ppb^{-1})$ depends on air temperature and is calculated using the formula

$$K_1 = 4.405 \times 10^{-2} \exp\left(\frac{-1370}{T_0}\right) \tag{3}$$

where T_0 is the air temperature in Kelvin. $K_2 (s^{-1})$ depends on the solar radiation, Q (Wm^{-2}):

$$K_2 = 8 \times 10^{-4} \exp\left(\frac{-10}{Q}\right) + 7.4 \times 10^{-6} Q \tag{4}$$

When there is significant solar radiation (spring/summer daytime) equations (1) and (2) proceed quickly and a photo-stationary equilibrium is reached within a few minutes with the following equilibrium equation:

$$[NO_2] \quad = \quad (K_1/K_2)[NO][O_3] \tag{5}$$

When the solar radiation is weaker (1) is the main reaction with generation of NO_2 until either NO and/or O_3 are reduced to low levels when further reaction proceeds only slowly.

3.   Calculation Scheme

The chemical reactions are modelled over a time period T which depends on the 'age' of the pollutants NO and NO_2. Mean ages of the emitted NO and NO_2 are calculated, and T is taken to be the minimum of these two mean ages.

The main assumption in the calculation scheme is that the background pollutants are mixed instantaneously into the plume. This may in principle lead to some conservatism in NO_2, however testing has shown that the extent of this is very small except close to the source at plume height and much less conservative than the ozone limiting method [3].

A standard adaptive time stepping scheme is used for the integration of the differential equations for (1) and (2) above.

4.   Background Concentrations

The background concentrations used by the model to initialise the chemistry scheme should not include the effect of emissions from the sources being modelled. The following guidelines for the ADMS simple chemistry scheme apply:

(i)   if modelling a source in a rural location use <u>rural</u> background values

(ii)   if modelling one or more industrial sources in an urban location, use data from an <u>urban</u> background site (but not a kerbside site that would be heavily influenced by traffic)

During the day, the background values will be adjusted in order to ensure that they are in equilibrium. This is done by assuming:

- conservation of mass for NOx,

- conservation of the total mass of NO_2 and O_3, and

- photo-stationary equilibrium for NO_2, NO and O_3.

During the night no adjustments are made to the background values. A local night-time chemistry option is available, which applies the chemistry scheme to the NO and NO_2 values before the background values of these pollutants are added on. This allows the effects of chemistry to be taken into account, without incorrectly affecting the background concentrations.

5.   Treatment of Wet and Dry Deposition

The NO_X chemistry calculations in ADMS are performed after all plume dispersion calculations have been done for all pollutants and all sources. This is because total concentrations are required in order to model chemistry correctly.

If both wet deposition and chemistry effects are modelled simultaneously, the wet deposition of NO and NO_2 is calculated *after* the chemistry calculations. Note, however, that NO is essentially insoluble, and so its wet deposition is negligible. For further details of the way in which wet deposition is modelled, refer to the ADMS Technical Specification paper P17/12.

If dry deposition and chemistry effects are modelled simultaneously, the effects of dry deposition are also calculated *after* the effects of chemistry. The concentration data input to the chemistry calculations therefore do not include the effects of plume depletion on change in plume shape due to dry deposition. As seen in ADMS Technical Specification paper P17/13, the dry deposition flux is

the product of the deposition velocity and the ground level concentration. The dry deposition fluxes of NO and NO_2 are therefore calculated by multiplying the post-chemistry ground level concentrations by the appropriate deposition velocities.

6. References

[1] Azzi M. & Johnson G. (1992) An Introduction to the Generic Reaction Set Photochemical Smog Mechanism, *Proc. 11th Clean Air Conf. 4th Regional IUAPPA Conf.*, Brisbane, Australia, July 1992.

[2] Venkatram A., Karamchandani P., Pai P. & Goldstein R. (1994) The Development and Application of a Simplified Ozone Modelling System (SOMS), *Atmospheric Environment* **28** (22), pp 3365-3678.

[3] Carruthers DJ, Dyster SJ and McHugh CA (2003) Factors affecting inter-annual variability of NOx and NO2 concentrations from single point sources *Clean Air and Environmental Protection* **33** (1), pp 15-20.