

# URBAN CHEMISTRY INCLUDING THE TRAJECTORY MODEL

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*In this document 'ADMS' refers to ADMS-Roads 4.1, ADMS-Urban 4.1 and ADMS-Airport 4.1. Where information refers to a subset of the listed models, the model name is given in full.*

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## 1. INTRODUCTION

In ADMS, both NO<sub>x</sub> and sulphate chemical reactions occurring in the boundary layer can be modelled. In addition, in ADMS-Urban and ADMS-Airport a simple Lagrangian Trajectory Model is included that allows the calculation of spatially varying background values over a large area.

The current standard model options are summarised in Table 1, with the scheme names listed in the first column, and the corresponding options in the ADMS interface given in the three right-hand columns. The Derwent-Middleton Correlation and the Generic Reaction Set (GRS) can be used to model NO<sub>x</sub> chemistry. The EMEP Model treats sulphate chemistry. In ADMS-Urban and ADMS-Airport, both the GRS and EMEP schemes can be used with or without the Trajectory Model.

Scheme name	Pollutant	Option in interface		
		<i>NO<sub>x</sub>-NO<sub>2</sub> Correlation</i>	<i>Chemical Reaction Scheme</i>	<i>Chemical Reaction Scheme with Trajectory Model</i>
Derwent-Middleton Correlation	NO <sub>x</sub>	✓		
Generic Reaction Set	NO <sub>x</sub>		✓	✓
EMEP Model	Sulphate		✓	✓
Trajectory Model	NO <sub>x</sub> and Sulphate			✓

**Table 1** – Summary of the schemes relating to the chemistry options chosen in the ADMS interface

This document describes each of these schemes in turn.

## 1.1 Meteorological Data requirements

The different chemistry schemes and the Trajectory Model have different meteorological data requirements. These are summarised in Table 2 below.

Chemistry scheme	Additional met data required
Derwent-Middleton Correlation	None
Chemical Reaction Scheme (NO <sub>x</sub> pollutants)	Temperature Solar radiation, or cloud cover, year, day and hour
Chemical Reaction Scheme with Trajectory Model (NO <sub>x</sub> pollutants)	Temperature Solar radiation or cloud cover Year, day and hour Hourly sequential met data
Chemical Reaction Scheme (sulphate pollutants)	Year, day and hour
Chemical Reaction Scheme with Trajectory Model (sulphate pollutants)	Year, day and hour Hourly sequential met data

**Table 2** – Summary of the meteorological data requirements for the different chemistry / pollutant combinations

## 2. THE DERWENT-MIDDLETON CORRELATION

The ADMS *Derwent-Middleton Correlation* scheme estimates nitrogen dioxide (NO<sub>2</sub>) concentrations for given concentrations of nitrogen oxides (NO<sub>x</sub>) by employing an empirical function for the volume ratio of NO<sub>2</sub>:NO<sub>x</sub> in the atmosphere [1]. This function has the form:

$$[\text{NO}_2]=2.166-[\text{NO}_x](1.236-3.348A+1.933A^2-0.326A^3)$$

where  $A=\log_{10}[\text{NO}_x]$  and both  $[\text{NO}_x]$  and  $[\text{NO}_2]$  are hourly-averaged concentrations in ppb. The way in which this function is applied in ADMS is that firstly NO<sub>x</sub> concentrations are calculated using the dispersion formulae described in [2]. The NO<sub>2</sub> concentrations are then estimated by applying the above function.

This scheme is only valid for NO<sub>x</sub> concentrations in the range 9 ppb to 1141.5 ppb and the correlation is independent of ozone concentrations. However, it can be used with statistical met data sets i.e. met data that does not include information on cloud cover, making this scheme suitable for first estimate calculations, whereas the other two ADMS chemistry schemes can only be used with hourly-sequential met data sets. Hourly sequential met data typically includes cloud cover data from which solar radiation values can be calculated.

The correlation was originally derived from analysis of London ambient monitoring data although it has been tested against data collected in other cities in the UK. The user should be aware that correlation between NO<sub>x</sub> and NO<sub>2</sub> concentrations can vary significantly with location.

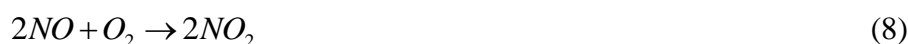
### 3. THE GENERIC REACTION SET (GRS)

The Generic Reaction Set (GRS) chemistry scheme is a semi-empirical photochemical model which reduces the complicated series of chemical reactions involving NO, NO<sub>2</sub>, O<sub>3</sub> and many hydrocarbons to just seven reactions. It was developed originally by CSIRO in Australia [3], [4]. These reactions are described by the following equations:



ROC, RP, SGN, SNGN and  $h\nu$  represent reactive organic compounds, radical pools, stable gaseous nitrogen products, stable non-gaseous nitrogen products and ultra-violet radiation respectively.

An additional reaction has been added to the GRS reactions:



This reaction will not have sufficient impact on NO and NO<sub>2</sub> concentrations unless the initial NO concentration is sufficiently high for a long period of time. For example, at 15°C, less than 3 µg/m<sup>3</sup> of NO<sub>2</sub> is produced from a NO concentration of 200 µg/m<sup>3</sup>. The effect becomes more significant at NO concentrations of about 1000 µg/m<sup>3</sup> and is likely to be more significant when the GRS chemistry scheme is used in conjunction with the Trajectory Model scheme where reactions can occur over several hours. The possibility of NO concentrations increasing to very high levels is therefore greater with the *Chemical Reaction Scheme with Trajectory Model* option than for the GRS scheme alone.

The reaction coefficients for these reactions, where R<sub>1</sub> corresponds to reaction (1), R<sub>2</sub> to reaction (2) etc., are defined as

$$\begin{aligned} R_1 &= AROC \times R_3(Q) \times \exp\left(-4700\left(\frac{1}{T_0} - \frac{1}{316}\right)\right) & \text{s}^{-1} \\ R_2 &= \frac{358.1}{6T_0} & \text{s}^{-1}\text{ppb}^{-1} \\ R_3 &= \min(R_3(Q_{\max}), \overline{R_3}) & \text{s}^{-1} \\ R_4 &= 4.405 \times 10^{-2} \exp\left(\frac{-1370}{T_0}\right) & \text{s}^{-1}\text{ppb}^{-1} \\ R_5 &= \frac{1}{6} & \text{s}^{-1}\text{ppb}^{-1} \\ R_6 &= 2 \times 10^{-3} & \text{s}^{-1}\text{ppb}^{-1} \end{aligned}$$

$$R_7 = 2 \times 10^{-3} \quad \text{s}^{-1} \text{ppb}^{-1}$$

$$R_8 = 4.61 \times 10^{-10} \exp\left(\frac{530}{T_0}\right) \quad \text{s}^{-1} \text{ppb}^{-1}$$

where

$$R_3(Q) = 8 \times 10^{-4} \exp\left(\frac{-10}{Q}\right) + 7.4 \times 10^{-6} Q,$$

$$\overline{R_3} = \frac{C_{BGD}(O_3) \times C_{BGD}(NO) \times R_4}{C_{BGD}(NO_2)},$$

Q is solar radiation in  $\text{W/m}^2$ ,  $Q_{\max}$  is the maximum value of Q possible (assuming a solar elevation angle of 90 degrees and zero cloud cover),  $T_0$  is temperature in Kelvin, and AROC represents the weighted reactivity coefficient for ROC, taken to be 0.1 as a result of validation work.  $\overline{R_3}$  is calculated from the background concentrations of ozone, NO and  $\text{NO}_2$  ( $C_{BGD}(O_3)$ ,  $C_{BGD}(NO)$  and  $C_{BGD}(NO_2)$  respectively). The above formulation assumes that a photochemical reaction rate derived from the background concentrations is more representative than a rate calculated from solar radiation values. In case of erroneous background data, a minimum of  $R_3(Q_{\max})$  and  $\overline{R_3}$  is taken to ensure that the reactions occur at a realistic rate.

Equations (3) and (4) represent exact chemical reactions, which happen very quickly, equilibrium being reached within a few minutes. The other equations are approximations.

The GRS chemistry scheme is employed in ADMS in the following manner. Firstly, dispersion of  $\text{NO}_x$ ,  $\text{NO}_2$ ,  $\text{O}_3$  and VOC pollutants is calculated using the formulae described in [2]. Background concentrations that may be hourly values (which is preferable) or constant values are then added onto these concentrations. Finally, an adaptive time stepping technique is used to model the GRS chemical reactions.

Ideally, the model would treat the chemical reactions in a series of small timesteps along a trajectory to the receptor point, gradually adding in the source contributions at each timestep. However, this is not practical in terms of complexity and run time for ADMS. However, a useful compromise is to split the chemistry calculations into two steps, the first of which just considers the background and sources some way upstream of the receptor point, and the second of which additionally includes the contribution from the sources nearest to the receptor. The split between the 'near' sources and the other sources is determined using a critical source-receptor travel time  $T_{crit}$  – sources for which the source-receptor travel time is less than  $T_{crit}$  are considered the 'near' sources. Following testing and validation, a value of 150 seconds has been adopted for  $T_{crit}$ .

For each of the two steps, it is necessary to calculate the time across which the chemistry scheme is applied (the 'reaction time'). To do this, firstly a weighted age of the pollutants is calculated as

$$Age = \frac{\sum_{i=1}^N C_i A_i}{\sum_{i=1}^N C_i} \quad (9)$$

where  $N$  is the number of sources,  $C_i$  is the concentration (after dispersion calculations but before the chemistry calculations) at the output point due to source  $i$ , and  $A_i$  is the age of the pollutant at the output point due to source  $i$ . The pollutant used when calculating the age is as follows:

- i) if the concentrations of both  $NO_X$  and  $NO_2$  are non-zero, then the minimum age of  $NO_X$  and  $NO_2$  is taken as the reaction time.
- ii) if only one or other of  $NO_X$  and  $NO_2$  are non-zero, the age of that pollutant is used as the reaction time.
- iii) if both  $NO_X$  and  $NO_2$  are zero, then the minimum age of all other chemistry pollutants is used.

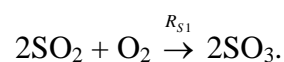
Separate values of the age are calculated for the 'near' sources ( $Age_{near}$ ) and the 'far' sources ( $Age_{far}$ ). A maximum of 1 hour is imposed on these values. The chemical reactions are firstly applied to the background and the contribution from the 'far' sources for time  $Age_{far} - Age_{near}$ . Then the contribution from the 'near' sources is added, and the chemical reactions are applied for a further time of  $Age_{near}$ .

In order to use the GRS chemistry scheme, the met data must include cloud cover data, so that the solar radiation can be calculated, and must be in an hourly-sequential format.

#### 4. THE EMEP MODEL

The sulphate reaction scheme used in ADMS has been taken from the EMEP model used by the MSC-W Norwegian Meteorology Institute, [5]. The first process modelled is the oxidation of  $SO_2$  to  $SO_3$ . Any  $SO_3$  produced reacts immediately with water in the atmosphere to form sulphuric acid. This acid reacts with other chemicals in the atmosphere (ammonia,  $NH_3$ , Potassium, K and others) to form sulphate compounds that can be considered as small particles. In ADMS, all these particulates are to be assumed ammonium sulphate,  $(NH_4)_2SO_4$ . Details of these reactions are given below.

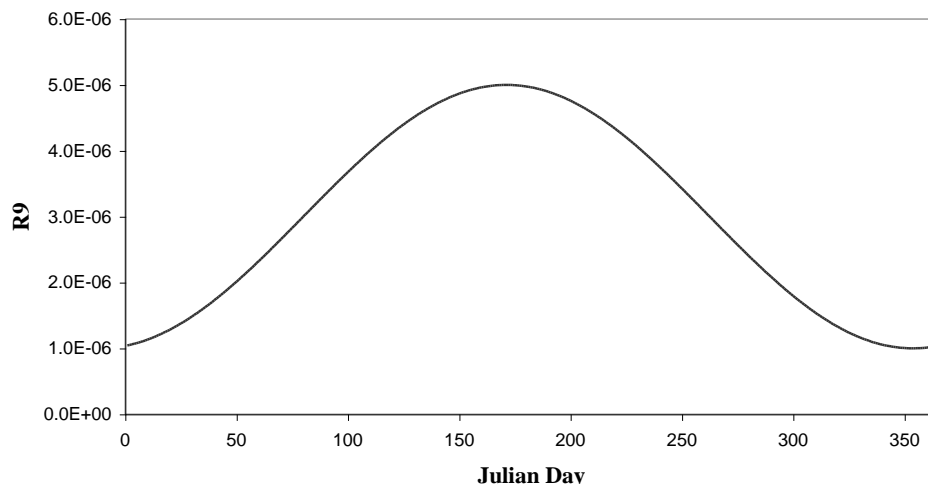
The  $SO_2$  in the atmosphere is oxidised to  $SO_3$ :



with a rate constant,  $R_{S1}$ , defined by:

$$R_{S1} = 3 \times 10^{-6} + 2 \times 10^{-6} \sin\left(2\pi \frac{(TDay - 80)}{365}\right) \quad s^{-1}$$

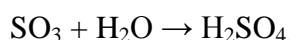
where  $TD_{day}$  is the day of the year. Note that the reaction depends only on the concentration of  $SO_2$  and the day of the year. Figure 2 shows how the reaction rate varies during the year, with reactions being up to 5 times faster in the summer months.



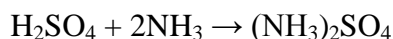
**Figure 2:** The reaction rate  $R_{S1}$  is sinusoidal, with the peak in the summer months

The reaction time is calculated in a similar way to that used for the GRS chemistry scheme, except that the concentrations of  $SO_2$  are used to calculate the pollutant age, and all the sources and background are included in a single step, rather than splitting between ‘near’ and ‘far’ sources. The two-stage process is only an advantage if the nearest sources are likely to dominate concentrations. Typically receptors are at (or close to) ground level so the nearest sources are only likely to dominate the concentration if they are at ground level, whereas most sources of  $SO_2$  are elevated.

The  $SO_3$  reacts immediately with water in the atmosphere:



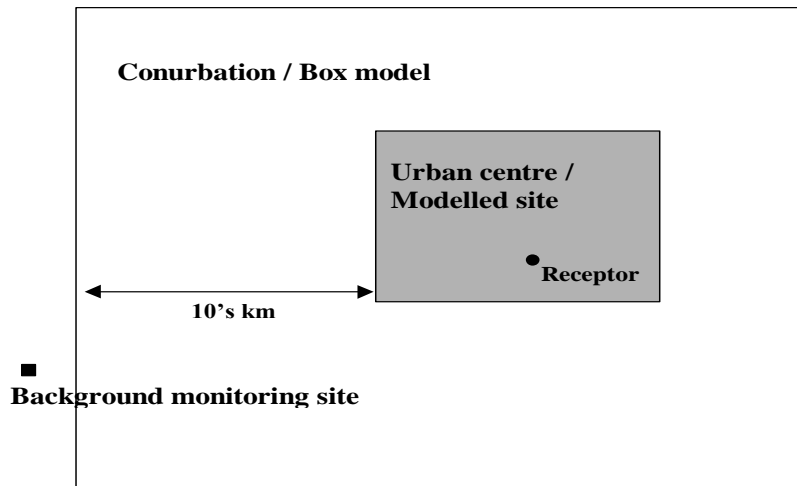
and the sulphuric acid produced reacts with ammonia to form ammonium sulphate:



This second reaction is also assumed to happen immediately.

## 5. THE TRAJECTORY MODEL SCHEME

The *Chemical Reaction Scheme with Trajectory Model* option should be used in preference to the *Chemical Reaction Scheme* when the domain over which emissions are modelled is large and/or data from a background monitoring site situated tens of km away from the modelled site are used (see Figure 1). In such circumstances, the Trajectory Model scheme is used to provide better estimates of the background concentration in the vicinity of the receptors by taking into account the travel time from the monitoring site to the modelled site and also chemical reactions which occur between these two sites.



**Figure 1:** Schematic showing a typical scenario that would be modelled using the Trajectory Model scheme

The Trajectory Model simulates a column of air, representing the atmospheric boundary layer, being advected along a trajectory from the background monitoring site to the modelled region. Emissions, deposition, entrainment of ozone and chemical conversion of pollutants along this trajectory are all incorporated in the model.

Geometrically, the Trajectory Model covers a rectangular area that overlaps the area covered by the entire modelling domain. This Trajectory Model area is divided into 5 km squares (the Trajectory Model area may be slightly larger than the modelling domain in order to accommodate an integer number of 5 km squares). Once the Trajectory Model squares are set up, each is assigned pollutant emission rates that are equal to the emissions of the grid source cells that they overlap.

This type of Trajectory Model is a particularly useful tool as it allows the large number of complicated physical processes occurring across wide-scale scenarios to be incorporated in practical models. However, modelling in this manner requires a number of approximations. In the Trajectory Model, the following approximations are made:

- emissions are assumed to be instantaneously well-mixed throughout the air column such that the model comprises a single vertical layer;
- the wind field is considered to be constant in the vertical direction (no variation with height) ; and
- meteorological conditions (e.g. wind speed, boundary layer height) are assumed to be constant across each square.

In order to run the *Chemical Reaction Scheme with Trajectory Model* chemistry option, a grid source must be included in the *.upl* file and the met data file must include cloud cover data and be hourly sequential.

The Trajectory Model calculations are executed after the dispersion calculations [2] are complete. The first step is to initialise the Trajectory Model by setting the concentrations at the edges of the Trajectory Model area equal to the background concentrations from the *.bgd* file/interface. Trajectory Model concentrations are then calculated for each Trajectory Model

square by taking into account emissions, deposition, entrainment of ozone and chemical reactions.

Changes in concentrations due to emissions and deposition are calculated using the Trajectory Model governing equation:

$$\frac{dC(t)}{dt} = \frac{F_e}{H} - \frac{V_d C(t)}{H} \quad (10)$$

where  $C(t)$  is the concentration of the chemical species at time  $t$ ,  $H$  is the depth of the atmospheric boundary layer,  $V_d$  is the deposition velocity and  $F_e$  is the emission flux of the species. Assuming steady state conditions, the solution of this equation for a time period  $\Delta t$  is given by

$$C(t_0 + \Delta t) = \begin{cases} C(t_0) \exp\left(-\frac{V_d \Delta t}{H}\right) + \frac{F_e}{V_d} \left(1 - \exp\left(-\frac{V_d \Delta t}{H}\right)\right), V_d > 0 \\ C(t_0) + \frac{F_e \Delta t}{H}, V_d = 0 \end{cases} \quad (11)$$

where  $t_0$  is the time at the current square and  $\Delta t$  represents the transit time for movement between Trajectory Model squares. This transit time is determined by the width of the squares, the wind direction and the wind speed.

As the air column traverses from one square to the next, some of the meteorological parameters (e.g. boundary layer height, wind speed) are updated. If the boundary layer height  $H$  grows during this transit, air outside the boundary layer will be entrained. This entrainment where  $H$  changes from  $H_{old}$  to  $H_{new}$  is modelled by

$$C_{NEW} = \alpha C_{OLD} + (1 - \alpha) C_{ENT} \quad (12)$$

where  $\alpha = \frac{H_{OLD}}{H_{NEW}}$ ,  $C_{OLD}$  is the concentration in the boundary layer before growth,  $C_{NEW}$  is the concentration in the boundary layer after growth, and  $C_{ENT}$  is the concentration above the boundary layer.  $C_{ENT}$  is set to the maximum of the input background value and 30 ppb for ozone and to 0 ppb for all other pollutants.

## 5.1 Chemistry within the Trajectory Model

Chemical reactions are modelled within the Trajectory Model scheme. This includes both the *GRS* chemistry scheme for  $NO_x$ , and the *EMEP* scheme for sulphate. For the chemistry calculations, a time period is required. Here the travel time between grid squares is used, calculated by

$$Time = \frac{\Delta X}{U(H/2)} \quad (13)$$



where  $\Delta X$  is distance travelled during the current step, and  $U(H/2)$  is the wind speed at half the boundary layer height. Note that this expression is not pollutant-specific.

## 5.2 Adjusting the background concentrations

After the chemistry calculations have been executed, Trajectory Model concentrations throughout the Trajectory Model region are known. For the final calculation of  $\text{NO}_x$  and sulphate concentrations, these values are then used to adjust the ‘pre-Trajectory Model’ calculated ADMS concentrations and upstream background values to obtain a more realistic concentration at the receptor point in question. This is done in one of two ways, depending on the relative magnitude of the Trajectory Model concentration to the sum of the calculated ‘pre-Trajectory Model’ ADMS concentrations and upstream background value.

For a specific receptor point R, say, the location of an upwind background point, X, is calculated using the local wind speed and the pollutant age given by (14). Consider:

$$\begin{aligned} C_{ADMS} &= \text{pre-Trajectory Model concentration at the receptor point R} \\ C_{BGD} &= \text{upstream background concentration} \\ C_{TRAJ} &= \text{Trajectory Model concentration at X} \end{aligned}$$

The ozone and VOC ‘background’ concentrations at R are taken to be a weighted average of the concentrations in the four Trajectory Model squares closest to the upstream point, X. The situation for  $\text{NO}_x$  and sulphate is more complicated due to the chemistry reactions involved, and the requirement that the total number of molecules of Nitrogen and Sulphur should remain constant i.e. no pollutant can be created or destroyed.

The difference between the Trajectory Model concentration and the sum of the calculated ‘pre-Trajectory Model’ ADMS concentrations and upstream background value,  $\Delta C$ , is calculated:

$$\Delta C = C_{ADMS} + C_{BGD} - C_{TRAJ} .$$

The remaining methodology depends on whether  $\Delta C$  is greater than or less than zero.

### Case 1: $\Delta C \geq 0$

This case is likely to occur when most of the emissions are at ground level, for example, the emissions from traffic. In this case, assume that the two pollutants to be adjusted are A and B (in the current version of the model, A and B are either  $\text{NO}_2$  and NO, or  $\text{SO}_2$  and  $\text{SO}_4$ ) at X. Take the final, upstream, adjusted concentrations to be  $C_{ADJ}$ .

The upstream input concentrations for the local chemistry are adjusted to account for the difference  $\Delta C$ :

$$C_{ADJ}(A) = C_{TRAJ}(A) + \frac{C_{ADMS}(A)}{C_{ADMS}(A) + C_{ADMS}(B)} \Delta C$$

$$C_{ADJ}(B) = C_{TRAJ}(B) + \frac{C_{ADMS}(B)}{C_{ADMS}(A) + C_{ADMS}(B)} \Delta C$$

Chemical reactions are then applied to the adjusted concentrations  $C_{ADJ}(A)$  and  $C_{ADJ}(B)$  (either *GRS* or *EMEP* depending on species) using the weighted pollutant age,  $T^*$ , given by:

$$T^* = \frac{\sum_{i=1}^N C_i A_i^*}{\sum_{i=1}^N C_i} \quad (14)$$

As in equation (9),  $N$  is the number of sources and  $C_i$  is the unadjusted concentration at the output point due to source  $i$ . The pollutant age in the above expression,  $A_i^*$ , is limited to be the time taken to travel across one Trajectory Model grid square, i.e:

$$A_i^* = \min\left(\frac{2X_{grid}}{\sqrt{\pi}U(H/2)}, 3600\right)$$

where  $2X_{grid}/\sqrt{\pi}$  is the diameter of a circle the same area as the grid square, and  $X_{grid} = 5000$  m. This formulation for  $A_i^*$  accounts for the fact that pollutant chemistry from distant sources has already been included in the Trajectory Model calculations (recalling that a maximum age of one hour is applied for all pollutants). For *GRS* species, the local chemistry is carried out in two steps, as described in section 3 above.

This gives the final concentrations at the receptor point R.

### Case 2: $\Delta C < 0$

This case is likely to occur when most of the emissions are high-level sources, for example, when the emissions are from industrial stacks. Here, the total pre-Trajectory Model concentration at R (i.e. ADMS contribution plus upstream background) is adjusted in proportion to the ratio of the concentration of species  $A : B$  given by the Trajectory Model:

$$C_{ADJ}(A) = \left(\frac{C_{TRAJ}(A)}{C_{TRAJ}(A) + C_{TRAJ}(B)}\right) (C_{ADMS}(A) + C_{ADMS}(B) + C_{BKG}(A) + C_{BKG}(B))$$

$$C_{ADJ}(B) = \left(\frac{C_{TRAJ}(B)}{C_{TRAJ}(A) + C_{TRAJ}(B)}\right) (C_{ADMS}(A) + C_{ADMS}(B) + C_{BKG}(A) + C_{BKG}(B))$$

This gives a final concentration; that is, chemistry does not need to be applied here, as the concentrations have already been adjusted appropriately.

## 6. REFERENCES

- [1] Derwent R.G. & Middleton D.R. (1996), An Empirical Function for the Ratio of NO<sub>2</sub>:NO<sub>x</sub>, *Clean Air*, Vol. 26, No. 3/4, pp57-60.
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- [5] Tsyro S. G. (2001) Description of the Lagrangian Acid Deposition Model, <http://www.emep.int/acid/ladm.html>