

URBAN CHEMISTRY INCLUDING THE TRAJECTORY MODEL

CERC

In this document 'ADMS' refers to ADMS-Roads 5.1, ADMS-Urban 5.1 and ADMS-Airport 5.1. Where information refers to a subset of the listed models, the model name is given in full.

1. INTRODUCTION

In ADMS, both NO_x 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_x 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_x-NO₂ Correlation</i>	<i>Chemical Reaction Scheme</i>	<i>Chemical Reaction Scheme with Trajectory Model</i>
Derwent-Middleton Correlation	NO _x	✓		
Generic Reaction Set	NO _x		✓	✓
EMEP Model	Sulphate		✓	✓
Trajectory Model	NO _x 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 _x pollutants)	Temperature Solar radiation, or cloud cover, year, day and hour
Chemical Reaction Scheme with Trajectory Model (NO _x 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 (NO₂) concentrations for given concentrations of nitrogen oxides (NO_x) by employing an empirical function for the volume ratio of NO₂:NO_x 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_x concentrations are calculated using the dispersion formulae described in [2]. The NO₂ concentrations are then estimated by applying the above function.

This scheme is only valid for NO_x 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_x and NO₂ 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, NO₂, O₃ 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 NO₂ concentrations unless the initial NO concentration is sufficiently high for a long period of time. For example, at 15°C, less than 3 µg/m³ of NO₂ is produced from a NO concentration of 200 µg/m³. The effect becomes more significant at NO concentrations of about 1000 µg/m³ 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 reaction coefficients for these reactions, where R₁ corresponds to reaction (1), R₂ to reaction (2) etc., are defined as

$$\begin{aligned} R_1 &= A_{\text{ROC}} \times R_3 \times \exp\left(-4700\left(\frac{1}{T_0} - \frac{1}{316}\right)\right) & \text{s}^{-1} \\ R_2 &= \frac{358.1}{6T_0} & \text{s}^{-1}\text{ppb}^{-1} \\ R_3 &= \begin{cases} \min(R_3(K_{\text{max}}), \overline{R_3}) & K > 0 \text{ (daytime)} \\ 0 & K = 0 \text{ (nighttime)} \end{cases} & \text{s}^{-1} \\ R_4 &= 4.405 \times 10^{-2} \exp\left(\frac{-1370}{T_0}\right) & \text{s}^{-1}\text{ppb}^{-1} \\ R_5 &= \frac{1}{6} & \text{s}^{-1}\text{ppb}^{-1} \\ R_6 &= 2 \times 10^{-3} & \text{s}^{-1}\text{ppb}^{-1} \\ R_7 &= 2 \times 10^{-3} & \text{s}^{-1}\text{ppb}^{-1} \end{aligned}$$

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

where

$$R_3(K) = \begin{cases} 8 \times 10^{-4} \exp\left(\frac{-10}{K}\right) + 7.4 \times 10^{-6} K & K > 0 \\ 0 & K = 0 \end{cases}$$

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

K is solar radiation in W/m^2 , K_{\max} is the maximum value of K 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 0.05 as a result of validation work.

$\overline{R_3}$ is calculated from the background concentrations of ozone, NO and NO_2 ($C_{BGD}(O_3)$, $C_{BGD}(NO)$ and $C_{BGD}(NO_2)$ respectively). If any of these values are zero, $R_3 = R_3(K)$ is used. In case of erroneous background data, a minimum of $R_3(K_{\max})$ and $\overline{R_3}$ is taken to ensure that the reactions occur at a realistic rate.

The above formulation for R_3 in the daytime assumes that a photochemical reaction rate derived from the background concentrations is more representative than a rate calculated from solar radiation values. However, an option exists to override this assumption and simply use $R_3 = R_3(K)$. When this option is used, the background concentrations of ozone, NO and NO_2 are adjusted in order to ensure that they are in equilibrium. This is done by assuming:

- conservation of NO_x ,
- conservation of the sum of NO_2 and O_3 , and
- photo-stationary equilibrium for NO_2 , NO and O_3 .

During the night there is no photo-stationary equilibrium for NO_2 , NO and O_3 . A local night-time chemistry option is available (with either R_3 formulation), 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.

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 NO_x , NO_2 , 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} .

To avoid concentration discontinuities that might otherwise occur at dispersion time T_{crit} from a source in certain circumstances, if the dispersion time from a source to a receptor is within 10% of T_{crit} , its concentration contribution to that receptor is split into both the ‘near’ and ‘far’ source bins, with a split fraction that linearly increases from ‘100% near source bin’ to ‘100% far source bin’ as the dispersion time increases from $0.9T_{crit}$ to $1.1T_{crit}$ seconds.

There is also an option to increase the number of steps used in the chemistry scheme, and define the associated critical source-receptor travel times between these steps, which should increase accuracy but will also increase also model runtime.

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 SO₂ to SO₄. Any SO₄ produced is assumed to react immediately and irreversibly with other chemicals in the atmosphere to form ammonium sulphate, (NH₄)₂SO₄, that can be considered as small particles. Details of these reactions are given below.

The SO₂ in the atmosphere is oxidised to SO₄:



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

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

where $TDay$ is the day of the year. Note that the reaction depends only on the concentration of SO₂ 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.

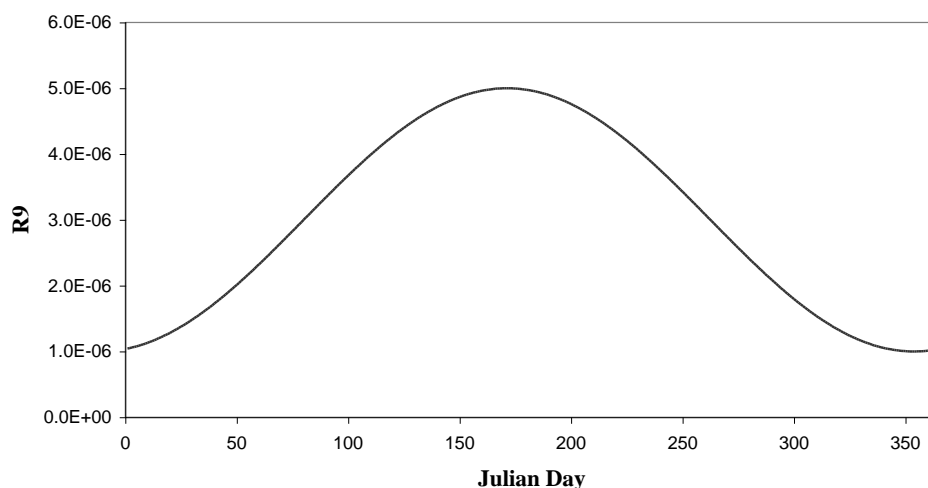
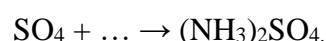


Figure 2: The reaction rate R_{S1} is sinusoidal, with the peak in the summer months

The reaction time is calculated in a similar way to that used for the GRS chemistry scheme, except that the concentrations of SO₂ are used to calculate the pollutant age, and all the sources 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 SO₂ are elevated.

The SO₄ is assumed to react immediately and irreversibly with other chemicals in the atmosphere to form ammonium sulphate:



The concentration of ammonium sulphate (in $\mu\text{g}/\text{m}^3$), $C_{(\text{NH}_3)_2\text{SO}_4}$, is calculated from the SO_4 concentration (in ppb), C_{SO_4} , using:

$$C_{(\text{NH}_3)_2\text{SO}_4} = C_{\text{SO}_4} \times \frac{m_{(\text{NH}_3)_2\text{SO}_4}}{0.25 m_{\text{SO}_4}}$$

where $m_{(\text{NH}_3)_2\text{SO}_4} = 132$ is the molar mass of ammonium sulphate, $m_{\text{SO}_4} = 96$ is the molar mass of SO_4 and 0.25 is the conversion factor of SO_4 from ppb to $\mu\text{g}/\text{m}^3$. This is then added to the particulate matter concentrations as follows:

- 100% of the ammonium sulphate is assumed to be PM_{10}
- 73% of the ammonium sulphate is assumed to be $\text{PM}_{2.5}$

With the *Chemical Reaction Scheme*, the background SO_2 value is only added on after the chemical reaction calculations to avoid depleting the background concentrations.

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.

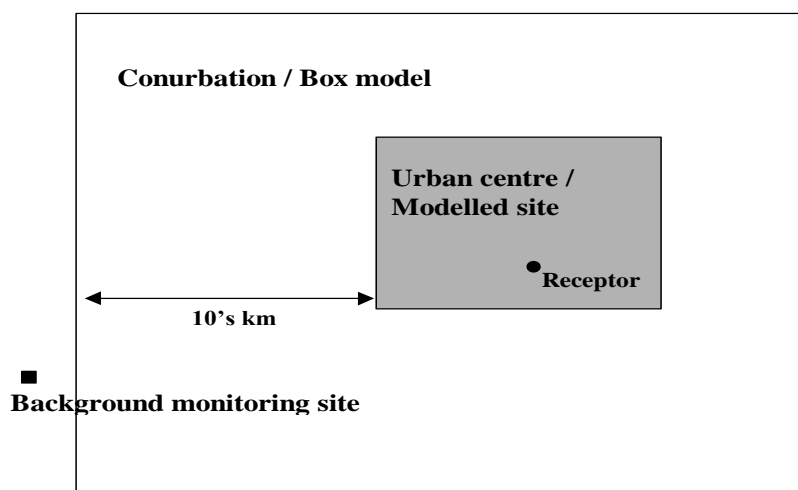


Figure 1: Schematic showing a typical scenario that would be modelled using the Trajectory Model scheme

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 Δt 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 Δt 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. Note that depletion due to deposition is only performed when dry deposition is selected as a model option, apart from for ozone, for which the depletion is always done.

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 ΔX 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 Local chemistry

After these chemistry calculations have been executed, Trajectory Model concentrations throughout the Trajectory Model region are known. For a specific receptor point R, say, the final concentrations are then calculated by applying the local chemistry scheme to concentrations taken from the Trajectory Model concentrations at an upwind point, X, which is calculated using the local wind speed and the pollutant age given by (14) below.

The ozone and radical pool concentrations that are passed to the first step of the local chemistry scheme (background plus ‘far’ sources) are taken to be a weighted average of the concentrations in the four Trajectory Model squares closest to the upstream point, X. For VOCs, the concentration passed is the same as for the standard GRS scheme (i.e. upstream background plus the pre-Trajectory Model concentration from ‘far’ sources at R). The situation for 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.

Consider:

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

For NO_x pollutants, C_{ADMS} is the concentration from ‘far’ sources only. The difference between the Trajectory Model concentration and the sum of the calculated ‘pre-Trajectory Model’ ADMS concentrations and upstream background value, ΔC , is calculated:

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

where each term above is itself the sum of two separate concentrations A and B (either NO₂ and NO, or SO₂ and SO₄). Take the concentrations passed to the first step of the local chemistry scheme (or only step for EMEP) to be $C_{ADJ}(A)$ and $C_{ADJ}(B)$. The calculation of C_{ADJ} depends on whether ΔC is greater than or less than zero.

Case 1: $\Delta C > 0$

This case is likely to occur when most of the emissions are at ground level, for example, the emissions from traffic.

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

Case 2: $\Delta C \leq 0$

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 concentrations are adjusted in proportion to the ratio of the concentration of species $A : B$ given by the Trajectory Model:

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

The first step of the local chemistry scheme (or only step for EMEP) is then applied, but using a modified 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:

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

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 second step of the local chemistry scheme is carried out after adding the contribution from the ‘near’ sources, as described in section 3 above.

This gives the final concentrations at the receptor point R.

6. REFERENCES

- [1] Derwent R.G. & Middleton D.R. (1996), An Empirical Function for the Ratio of $\text{NO}_2:\text{NO}_x$, *Clean Air*, Vol. 26, No. 3/4, pp57-60.
- [2] P10/01 & P12/01 Plume/Puff Spread and Mean Concentration Module Specifications (2025), Cambridge Environmental Research Consultants, <https://www.cerc.co.uk/TechSpecs>
- [3] 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.
- [4] Venkatram A., Karamchandani P., Pai P. & Goldstein R. (1994), The Development and Application of a Simplified Ozone Modelling System (SOMS), *Atmospheric Environment*, Vol. 28, No. 22, pp3365-3678.
- [5] Tsyro S. G. (2001) Description of the Lagrangian Acid Deposition Model, https://emep.int/publ/reports/1998/EMEP_1998_R1_p2.pdf