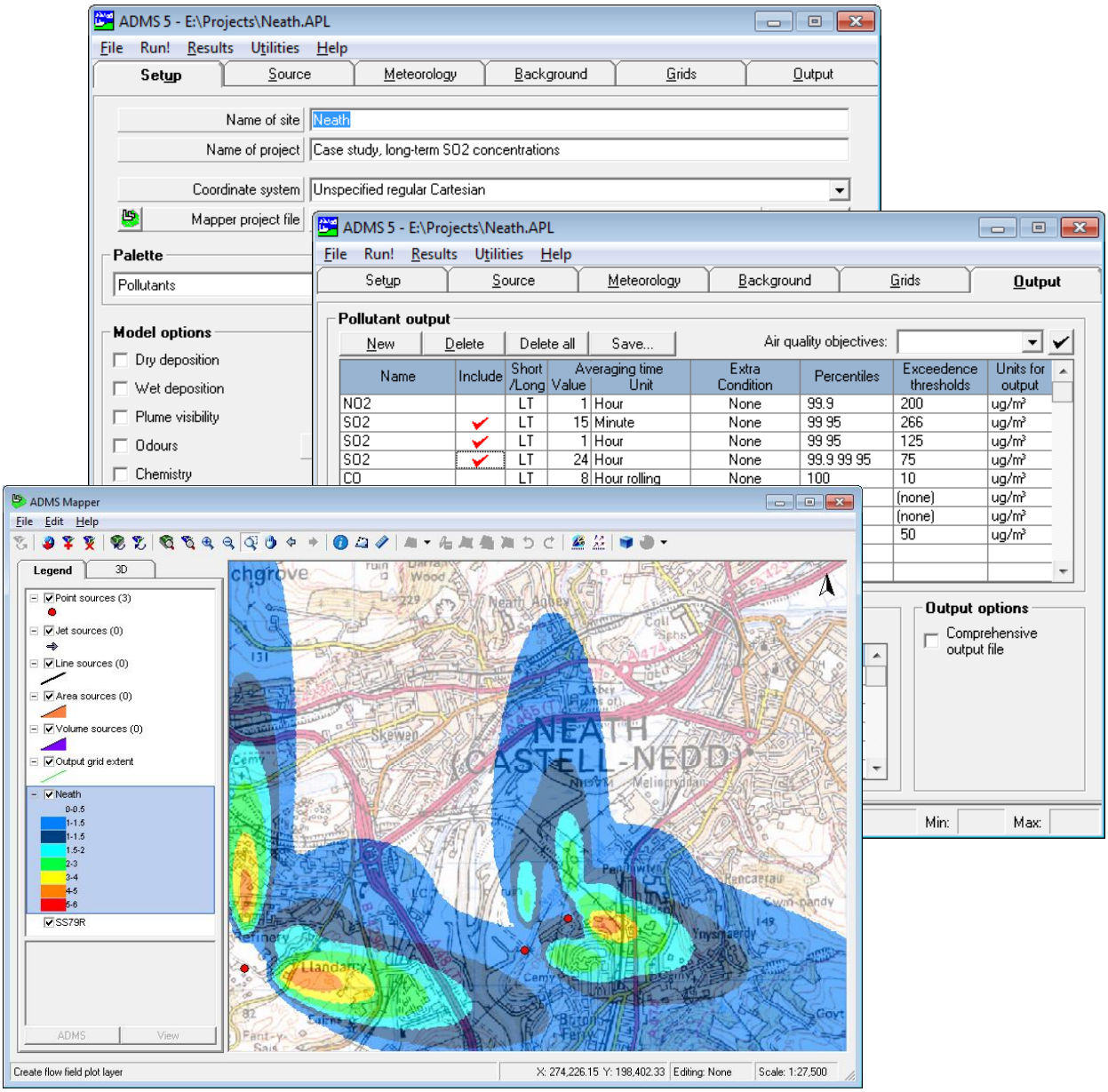
ADMS 5

Amine chemistry supplement



User Guide CERC

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ADMS 5

Amine chemistry

User Guide Supplement

Version 5.2

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SECTION 1 Introduction

ADMS 5 contains an amine chemistry scheme as an extension to the NO_x chemistry scheme. The modelling of amine chemistry can be important in assessing the impacts of emissions due to amine-based carbon capture. In these activities the amine solvent is recycled, but some of the amine can be lost via the stack. These amines can react with other species in the exhaust gas and the atmosphere to produce degradation products (nitrosamines and nitramines) that can be harmful. Recommendations from the Norwegian Institute of Public Health (NIPH) (Lag *et al.*, 2011) indicate that the annual average of the sum of nitrosamines and nitramines should not exceed 0.3 ng/m^3. The main reaction of amines in the atmosphere is with hydroxyl radicals and it is this reaction on which the amine chemistry scheme is based.

An overview of the amine chemistry scheme in ADMS 5 is given in this section together with instructions on how to install the amine chemistry module in ADMS 5. Section 2 then describes how to implement the scheme in a model run, a technical summary is given in Section 3 and Section 4 lists the references.

This document should be read in conjunction with the main ADMS 5 User Guide.

1.1 Overview of amine chemistry

ADMS 5 incorporates an amine chemistry scheme which treats the reactions initiated by the attack of an emitted gaseous amine by a hydroxyl radical ($^{\bullet}OH$), and the subsequent formation of nitrosamines and nitramines. This chemistry scheme can be applied to a variety of amines, including primary, secondary and tertiary amines and is based on the one outlined in an Atmospheric Degradation of Amines (ADA) report (Nielson *et al.*, 2011), published by the Norwegian Institute for Air Research (NILU) as part of the Climit project.

The general reaction scheme is shown below, where R represents an alkyl group and the terms in capitals are the generic names used by the model:

AMINE + $^{\bullet}OH$	→	amino RADICAL + H_2O	(1a)
	→	$RN(H)C^{\bullet}H_2$ + H_2O	(1b)
amino RADICAL + O_2	→	imine + HO_2	(2)
amino RADICAL + NO	→	NITROSAMINE	(3)
amino RADICAL + NO_2	→	NITRAMINE	(4a)
	→	imine + HONO	(4b)
NITROSAMINE	hv →	amino RADICAL	(5)

The reaction rates and kinetic parameters for the various species must be specified by the model user and each can be varied independently. The way in which these parameters are specified is described in Section 2.1

The reaction scheme also involves nitrogen oxides and ozone, so modelling will require NO_x emissions and background concentrations, and ozone background concentrations. It uses information from the ADMS meteorological pre-processor to determine photolysis rates on an hourly basis. In particular, the hydroxyl radical concentration is determined from the ambient ozone concentration and the photolysis rate constant for nitrogen dioxide.

In addition to the implementation of the amine chemistry reactions within the ADMS 5 model, code there is an option to improve the way that the chemistry module takes into account the effects of the dilution of pollutant species and the entrainment of background pollutants. Although this 'dilution and entrainment' effect can be switched on and off by the model user, it is recommended that it is switched on for all model runs involving amine chemistry, refer to Section 2.1 for instructions. Note that this method can only be used when there is a single point source in the run.

1.2 Installing the amine chemistry option in ADMS 5

Before the amine chemistry option can be used in ADMS 5 you must first update the Additional Input file editor so that the amine chemistry option is available. To do this, ensure you are logged onto the computer as Administrator and then navigate to the *<ADMS 5 install directory>\Support\AAI Editor\Syntax With Amine* directory and run *ToEnglish.bat*.

In addition, you must have purchased and installed a valid licence (*.lic*) file for this option. To install the licence file first make a back-up copy of any *ADMS.lic* file in your ADMS 5 install directory and then copy and paste your new licence file to the install directory.

SECTION 2 How to enable the amine chemistry scheme in ADMS 5

The specific inputs and steps needed to model amine chemistry in ADMS 5 are described in this section. All other model inputs are entered as for a standard ADMS 5 run.

The first stage is to specify the kinetic parameters for the various reaction equations. This is done via the additional input (*.aai*) file which can be easily created with the Additional Input file editor utility in ADMS 5. This is described in Section 2.1.

The second stage is to select the chemistry model option; to enter information into the palette of pollutants for each of the amine, nitrosamine, nitramine and radical species; and to enter the emissions data, background data, and output options for the model run. This is described in Section 2.2.

Additionally, some modelling tips are given in Section 2.3.

2.1 Setting up the additional input (*.aai*) file

This section describes how to specify the kinetic and other parameters for the reaction scheme via the additional input (*.aai*) file.

2.1.1 Specifying the kinetic parameters

Once the Additional Input file editor has been modified so that the amine chemistry option is enabled (see Section 1.2), it can be used to create the additional input (*.aai*) file for specifying the kinetic and other reaction parameters for the amine chemistry scheme.

To launch the Additional Input file editor, open the ADMS 5 model interface, check the box in the **Additional input file** section of the **Setup** screen and then click on **Edit**. The screen should be as shown in **Figure 1**.

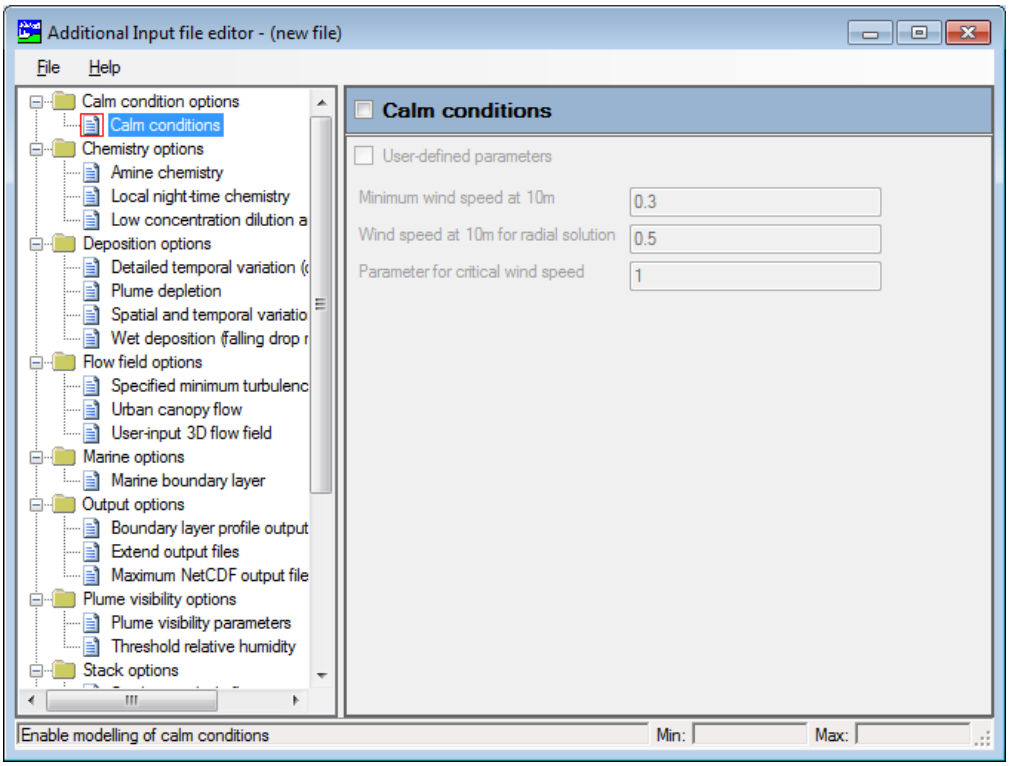


Figure 1: Additional Input file editor.

In the Additional Input file editor, select **Amine chemistry** under **Chemistry options** from the menu on the left hand side of the screen. Then check the box next to **Amine chemistry** in the main window of the Additional Input file editor. The cells for the various kinetic and other parameters are no longer greyed out, as shown in **Figure 2**.

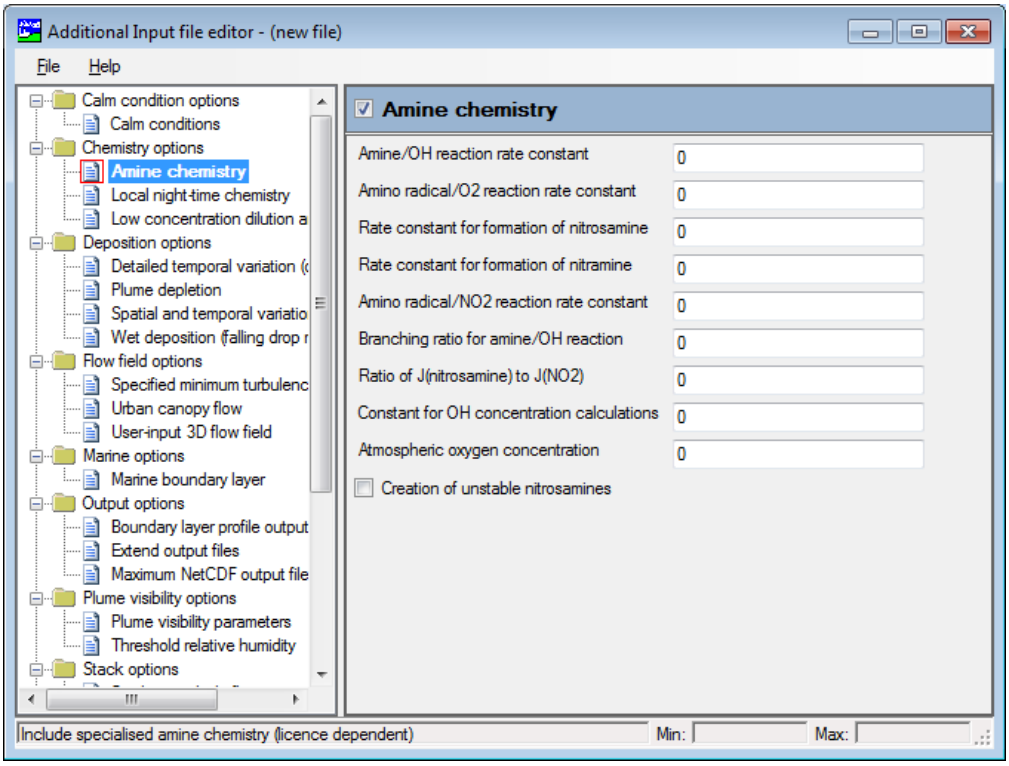


Figure 2: **Amine chemistry** section of the Additional Input file editor.

Values for each of the parameters can then be entered in each cell as appropriate. In order, the values are:

- **Amine/OH reaction rate constant**, the rate constant for the reaction of the amine with the hydroxyl radical, k_1, in units of $ppb^{-1}s^{-1}$;
- **Amino radical/O2 reaction rate constant**, the rate constant for the reaction of the amino radical with oxygen, k_2, in units of $ppb^{-1}s^{-1}$;
- **Rate constant for formation of nitrosamine**, the rate constant for the formation of nitrosamine, k_3, in units of $ppb^{-1}s^{-1}$;
- **Rate constant for formation of nitramine**, the rate constant for the formation of nitramine, k_{4a}, in units of $ppb^{-1}s^{-1}$;
- **Amino radical/NO2 reaction rate constant**, the rate constant for the reaction of the amine radical with NO_2, k_4, in units of $ppb^{-1}s^{-1}$;
- **Branching ratio for amine/OH reaction**, the branching ratio for the amine/hydroxyl radical reaction, $\frac{k_{1a}}{k_1}$, this is dimensionless;
- **Ratio of J(nitrosamine) to J(NO2)**, the ratio of the photolysis rate constants for the nitrosamine and NO_2, $\frac{j_5}{j_{NO_2}}$, this is dimensionless;
- **Constant for OH concentration calculations**, the constant, *c*, for the hydroxyl radical concentration calculations, in units of seconds. A value for c, in units of seconds, can be estimated from known typical values of $[O_3]$, $[OH]$ and j_{NO_2}, refer to Section 2.3 for further details.
- **Atmospheric oxygen concentration**, the atmospheric oxygen concentration in units of ppb. This parameter can simply be specified as 209,406,000 ppb, representing the 21% mixing ratio of oxygen.

You may find it helpful to refer to the reaction equations in Section 3 for details of the chemistry scheme.

There is also an option to specify that only unstable nitrosamines are created, **Creation of unstable nitrosamines**. If this option is selected, the nitrosamine concentrations are always set to zero. This should usually be left unchecked unless the amine being modelled produces unstable nitrosamines. This tends to be the case for primary amines, for which the nitrosamine formed rapidly isomerises to form an imine.

2.1.2 Including dilution and entrainment effects

As mentioned in Section 1, there is an option to improve the way that the chemistry module takes into account the effects of the dilution of pollutant species and the entrainment of background pollutants. This option is especially important when there are very low concentrations of chemical species. When modelling amine chemistry it

is strongly recommended that this option is selected. This option can only be used, however, when a single point source is being modelled. To include this option, click on **Low concentration dilution and entrainment** in the **Chemistry options** menu, this is found on the left hand side of the Additional Input file editor screen. Click the check box next to **Low concentration dilution and entrainment** to select this option, see **Figure 3**.

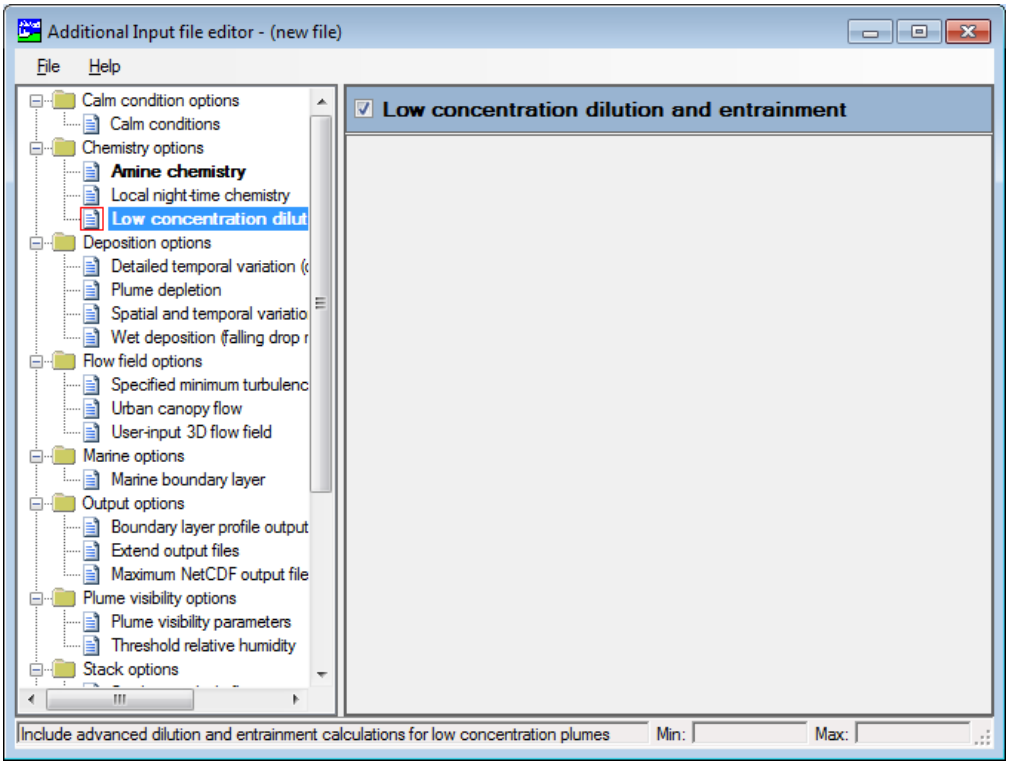


Figure 3: The **Low concentration dilution and entrainment** option.

When all the options in the Additional Input file editor have been selected and filled in as appropriate click on **File**, **Save** to save the additional input (*.aai*) file. Close the Additional Input file editor. Then in the **Setup** screen of the ADMS 5 interface click on **Browse...** in the **Additional input file** section to specify the file path of the *.aai* file just created, which contains the data for the amine chemistry scheme.

2.2 Setting up the ADMS interface

Additional data is required for the **Setup**, **Source**, **Background** and **Output** screens of the ADMS 5 interface when modelling amine chemistry. These are each described in turn in this section.

2.2.1 Setup screen

The first step is to select the **Chemistry** option in the **Setup** screen of the ADMS 5 interface, see **Figure 4**. To do this, click the check box next to **Chemistry**.

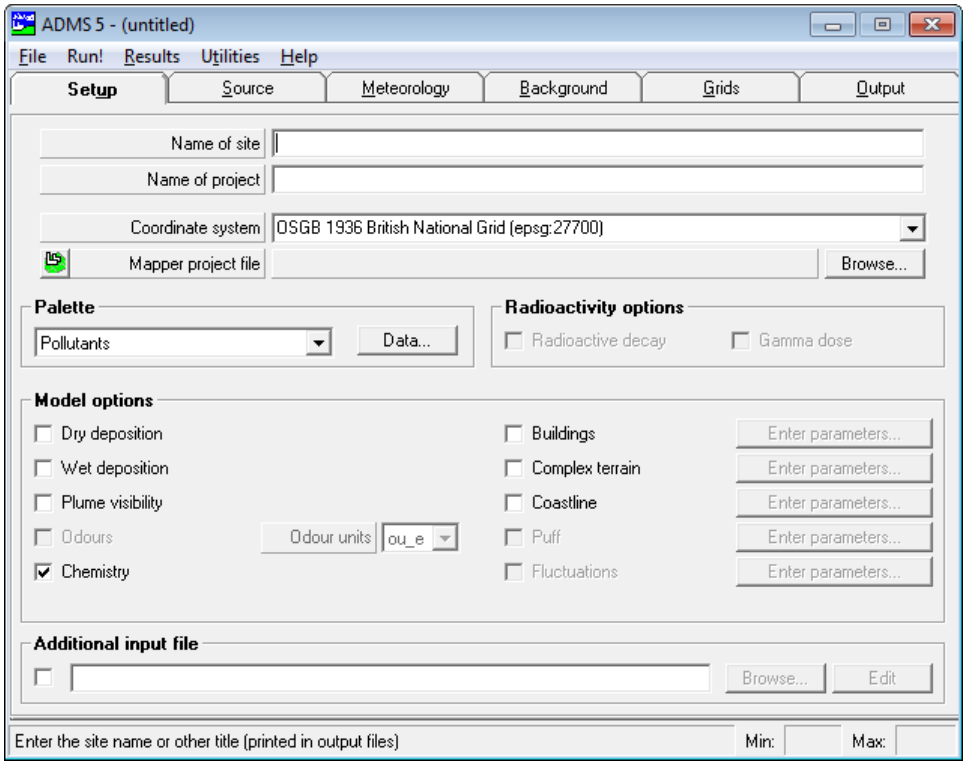


Figure 4: The **Setup** screen with the **Chemistry** option selected.

Next, the file path of the additional input (*.aai*) file that contains the data for the kinetic and other parameters must be specified. To use an additional input file, check the box in the **Additional input file** section and then enter the path to the file or click on **Browse**... to browse to find the file, see **Figure 5**.

*Neither **Dry deposition** nor **Wet deposition** should be selected if the amine chemistry scheme is being used. A method for calculating the deposition of amine and its products is given in Section 2.3.2.*

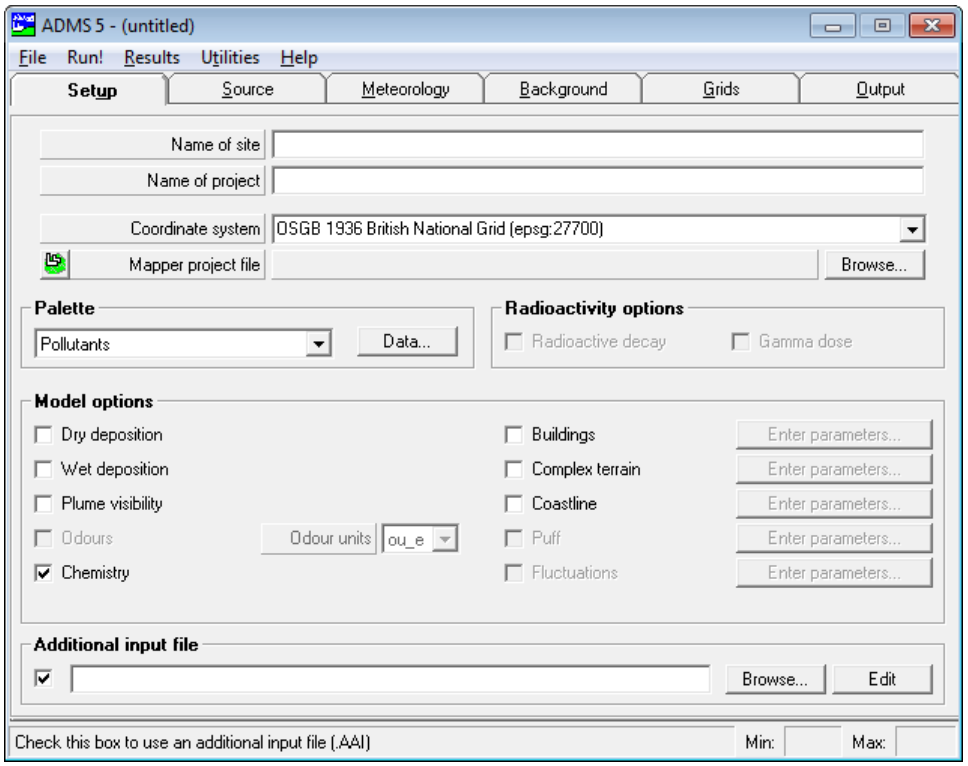


Figure 5: Selecting the **Additional input file**.

Section 2.1 describes how to create the additional input (.aai) file for the amine chemistry.

The next step is to add entries for the 'AMINE', 'NITROSAMINE', 'NITRAMINE' and 'RADICAL' species to the **Palette of Pollutants**. The model code uses generic names for the types of species involved in the amine chemistry scheme so it can be applied to a variety of amines and their products. To add these species to the pollutant palette click on the **Data...** button in the **Palette** section of the **Setup** screen. This brings up the **Palette of Pollutants** screen shown in **Figure 6**.

Note that 'RADICAL' refers to the amino radical and not the hydroxyl radical.

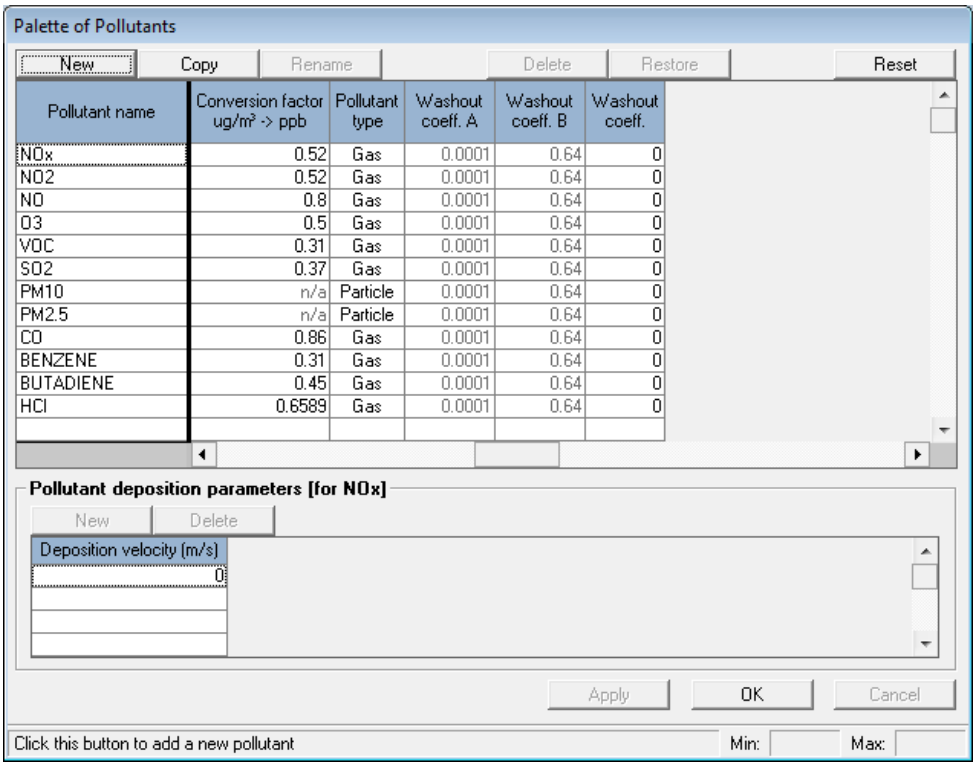


Figure 6: **Palette of pollutants**.

Clicking on the **New** button creates a new pollutant, enter the name of the pollutant and click **OK**, refer to Figure 7.

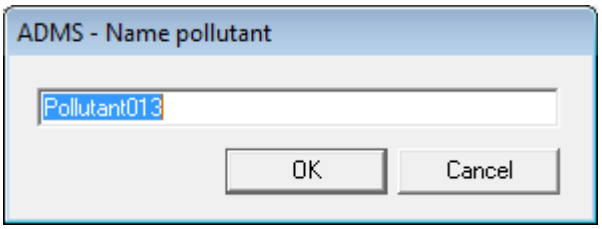


Figure 7: **Name pollutant** screen.

This step must be performed four times in total to create the additional rows for the four amine chemistry species. The data for each of the species can then be entered by clicking in each cell and typing the names or values as appropriate.

---

*Note that the species must strictly be named '**AMINE**', '**NITROSAMINE**', '**NITRAMINE**' and '**RADICAL**'.*

Values for the conversion factor from µg/m^3 to ppb are required for each of the species involved. The conversion factors are entered by clicking on the cell and typing the particular value for that species. The values are dependent on the particular amine being modelled. The pollutant type should be left as **Gas** and all the other parameters in the palette can remain as their default values.

*Even if the amine doesn't form a stable nitrosamine '**NITROSAMINE**' should still be entered into the **Palette of Pollutants**, otherwise the amine chemistry scheme will not be activated.*

Figure 8 shows an example of the pollutant palette after completion.

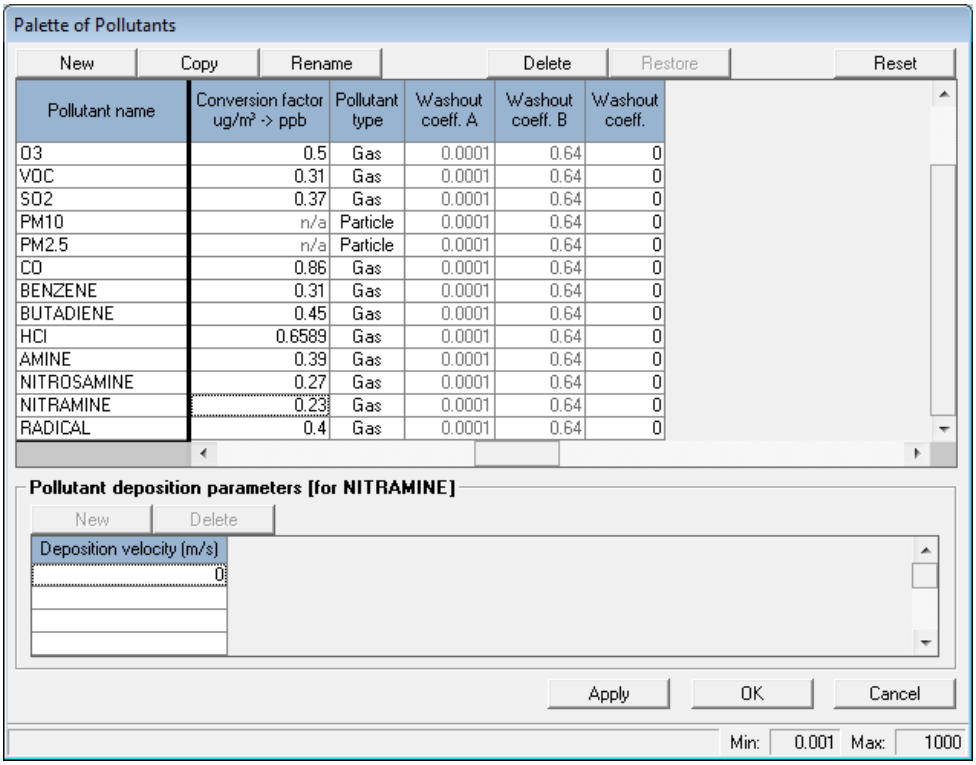


Figure 8: Completed **Palette of pollutants** with amine species added.

*If the same set of amine species are to be used in multiple runs it may be convenient to **Export** the **Palette of pollutants** to a* .ptt *file which can then be imported into future runs.*

2.2.2 Source screen

Once the data for each of the amine species has been entered into the model the emissions data for each of the sources can be specified. The source information can be entered as usual, refer to Section 3.2 of the ADMS 5 User Guide for information about this. In the **Source** screen of the ADMS 5 interface (shown in **Figure 9**) click on the **Emissions** button to bring up the emissions screen shown in **Figure 10**.

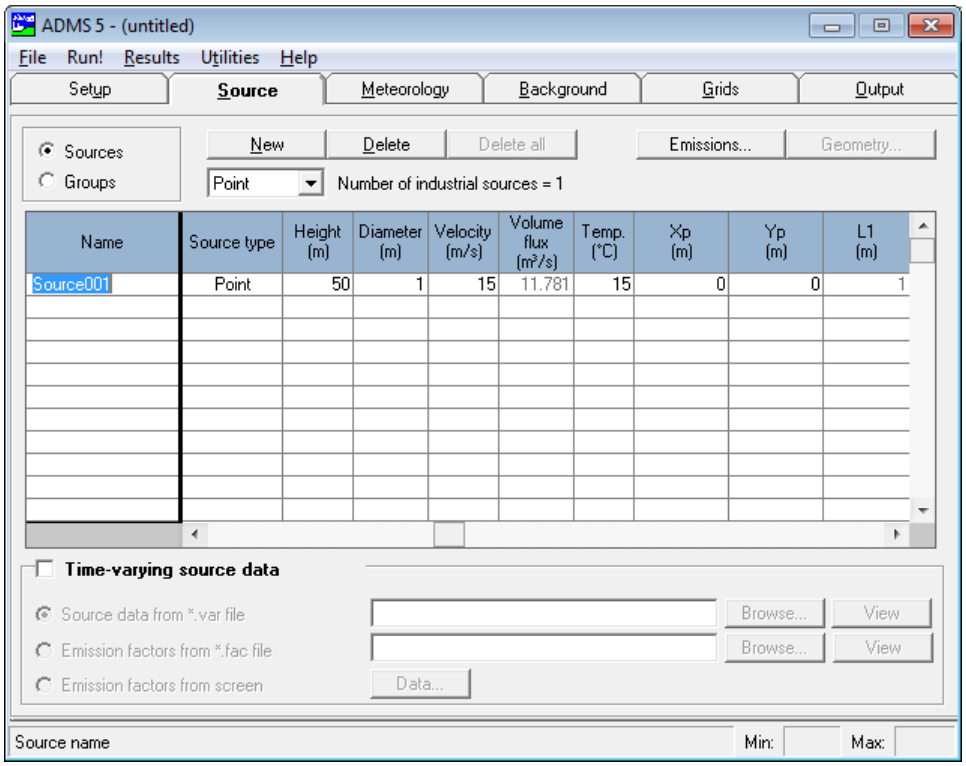


Figure 9: The **Source** screen in ADMS 5.

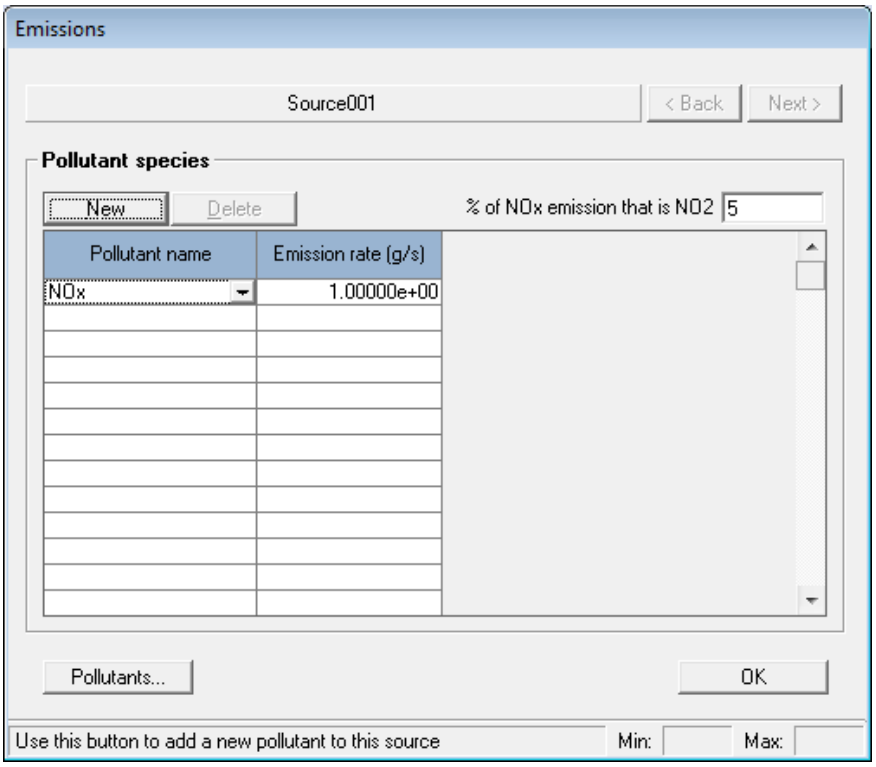


Figure 10: The **Emissions** screen.

Click on **New** to add a new pollutant and then use the drop down arrow to select **AMINE** from the list. An emission rate for the amine can be entered in g/s by clicking on the emission rate cell and typing the value.

Likewise, emissions can also be specified for **NITROSAMINE** and/or **NITRAMINE**, if directly-emitted nitrosamines and nitramines are to be modelled. To add emission rates for these or other additional species first click on **New** in the emissions screen and then select the pollutant species and enter the emission rate as usual.

*Note that **AMINE** and **NOx** must be present in the **Pollutant species** table on the **Emissions** screen for the amine chemistry scheme to be activated; if a source does not emit any amine and/or NOx, the emission rate can be set to zero.*

An example emissions screen is shown in **Figure 11**.

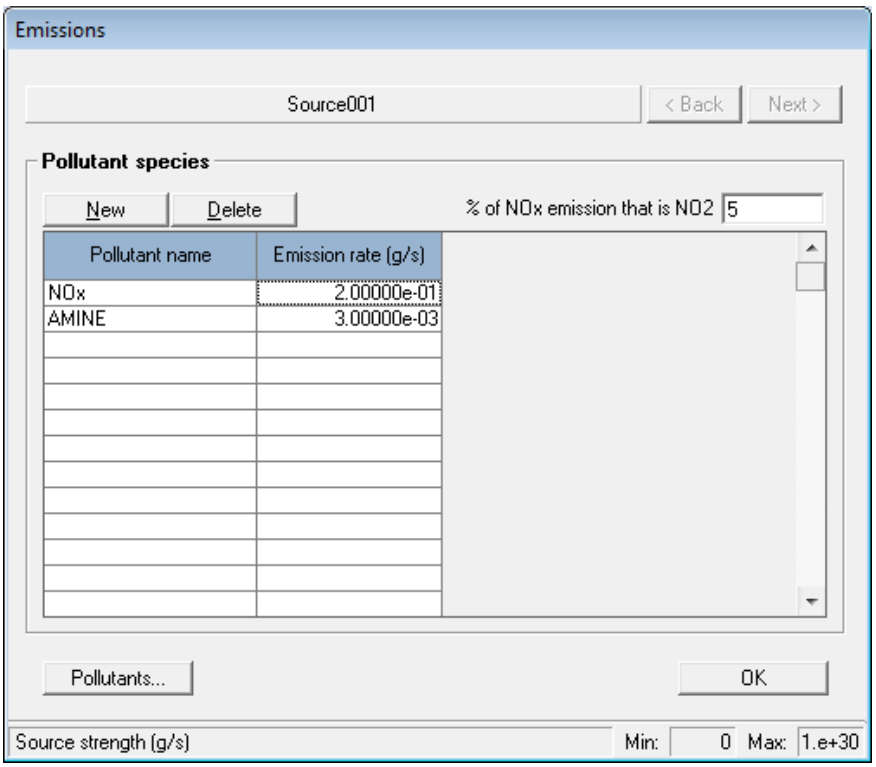


Figure 11: Example **Emissions** screen.

2.2.3 Background screen

When chemistry is being modelled in ADMS 5, ambient background concentration values for the species involved must be entered via the **Background** screen in the interface, see **Figure 12**.

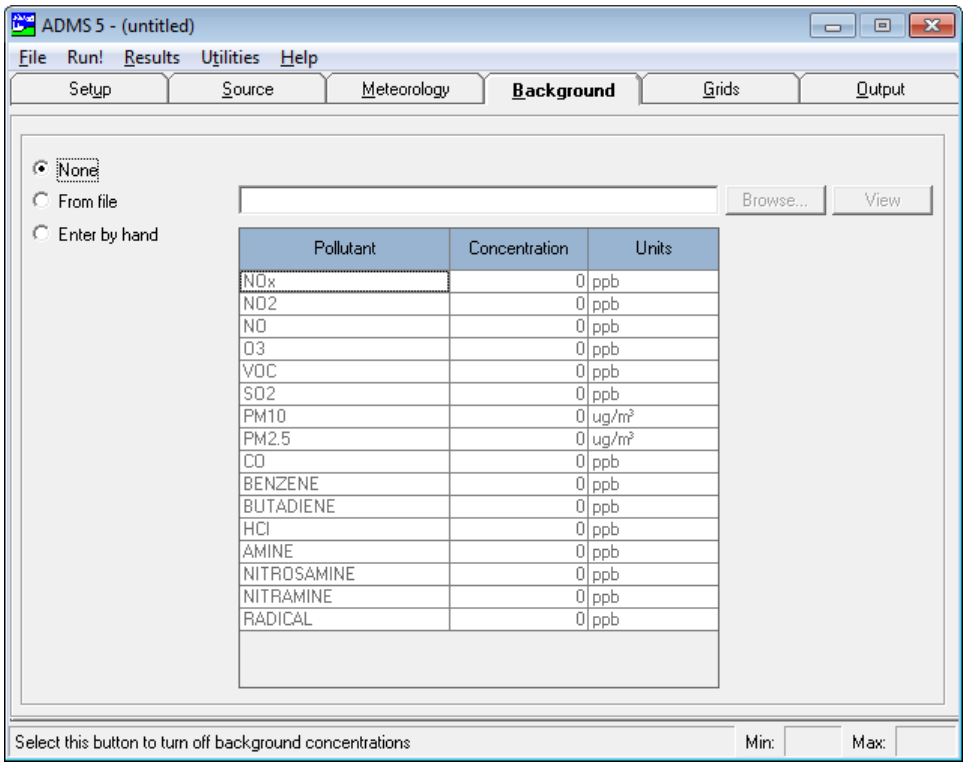


Figure 12: The **Background** screen in ADMS 5.

Ambient values must be entered for the NO_x species (i.e. NO_x, NO_2) and ozone (O_3). The values for the amine chemistry species (AMINE, NITROSAMINE, NITRAMINE and RADICAL) should be set to zero. Please refer to Section 3.4 of the ADMS 5 User Guide for further details about how to enter background data in ADMS 5.

It is strongly recommended to use hourly varying background values from a .bgd file.

2.2.4 Output screen

The output for the amine chemistry species must be specified in the Output screen of the ADMS 5 interface. To add a pollutant to the output table first click on **New** and then select the required pollutant from the list under **Name**. Options for short/long-term output; averaging details; percentiles and exceedences; and units for output are all specified in the same way as other pollutants modelled in ADMS 5, as described in Section 3.6 of the ADMS 5 User Guide. **Figure 13** shows an example output screen for a run including amine chemistry.

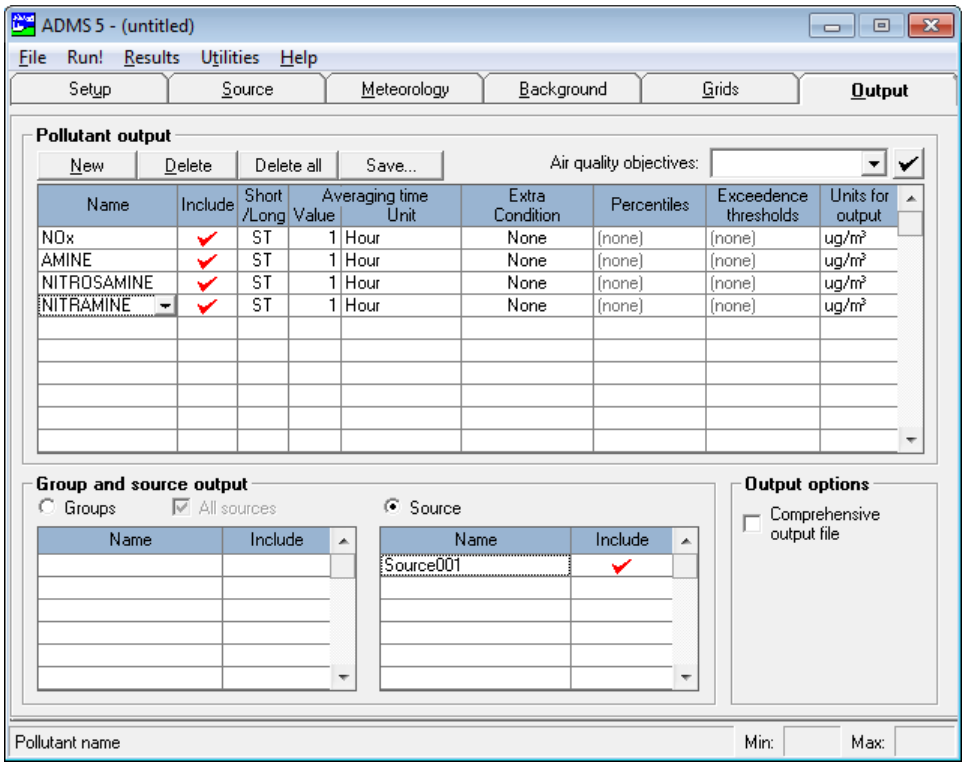


Figure 13: Example output for an amine chemistry run.

To run the model save the ADMS 5 *.apl* file and click on **Run!** in the menu options at the top of the interface.

2.3 Modelling tips

2.3.1 Calculating a value of c

The user needs to specify, c, the parameter used in calculating the hourly varying hydroxyl radical concentrations. One way of determining a value for this parameter is based on annual average values for j_{NO_2}, ozone and hydroxyl radical concentrations.

To calculate an annual average value of j_{NO_2}, follow this procedure:

- Create a Meteorological output (*.mop*) file by running a simple (non-amine) run in ADMS 5 using your meteorological data;
- Locate the column labelled 'K' – this contains the values for the incoming solar radiation (in W/m^2);
- For each hour of the year, calculate the corresponding value of j_{NO_2} using the following relationship, which is used by ADMS 5 (as described in document P18/02 of the ADMS 5 Technical Specification):

$$j_{NO_2} = 8 \times 10^{-4} \exp\left(-\frac{10}{K}\right) + 7.4 \times 10^{-6} K$$

Then a typical value for c can be calculated using the value of j_{NO_2} obtained by this method, together with annual average values for the hydroxyl radical and ozone concentrations, using the relation:

$$c = \frac{[OH]}{[O_3] j_{NO_2}}.$$

2.3.2 Calculating deposition of amines and their products

If dry and/or wet deposition output is required for the amines and their products, the following method can be applied:

Carry out three model runs:

- Run (1): With amine chemistry switched on, as required
- Run (2): Run with the same model setup as Run (1), but with the amine chemistry switched off and the deposition output switched on. New pollutants can be created in the **Pollutant Palette** to represent the depositing pollutants (e.g. called 'DEP_NITROSAMINE and DEP_NITRAMINE'). Suitable deposition parameters can be assigned to each of these pollutants.
- Run (3): The same run as in (1) and (2), but with both amine chemistry and deposition output switched off

From a combination of the output from Runs (2) and (3), values for the ratio of the concentration to deposition flux can be calculated at each location.

The concentrations output from Run (1) can then be post-processed using these ratios to give values of deposition fluxes at each location.

The deposition fluxes can be determined from:

$$D = C_1 . \left(\frac{D_2}{C_3} \right)$$

Where:

- D is the deposition flux required (for the nitrosamines and/or nitramines);
- C_1 is the output concentration from Run (1);
- D_2 is the output deposition flux from Run (2);
- C_3 is the output concentration from Run (3).

2.3.3 Other parameters of importance for amine chemistry

The concentrations of nitrosamines and nitramines are highly dependent on the latitude, due to changes in solar radiation and thus the rate of photolysis of the nitrosamines and NO_2. This is in addition to the general effects on dispersion. It is important, therefore, to set this parameter to an appropriate value in the ADMS meteorology screen. Please refer to Section 3.3 of the ADMS 5 User Guide for further details.

SECTION 3 Technical summary

3.1 Reaction equations

The rate expressions used in the model for the amine chemistry scheme described in Section 1.1 are taken from the Atmospheric Degradation of Amines (ADA) report published by the Norwegian Institute for Air Research (NILU) as part of the Climit project (Nielson *et al*., 2011).

1. Loss of the AMINE

$$\frac{d[AMINE]}{dt} = -k_1[AMINE][OH]$$

2. Production of the amino RADICAL

$$\frac{d[RADICAL]}{dt} = k_{1a}[AMINE][OH] + j_5[NITROSAMINE] - k_2[RADICAL][O_2] - k_3[RADICAL][NO] - k_4[RADICAL][NO_2]$$

3. Production of NITRAMINE

$$\frac{d[NITRAMINE]}{dt} = k_{4a}[NO_2][RADICAL]$$

4. Production of NITROSAMINE

$$\frac{d[NITROSAMINE]}{dt} = k_3[RADICAL][NO] - j_5[NITROSAMINE]$$

Here k_i are the reaction rate constants where the subscript i relates to the number of the relevant chemical equation (1a) – (4) given in Section 1.1, and j_5 is the rate constant for the nitrosamine photolysis. A quantity in square brackets [X] represents the concentration of that species.

The hydroxyl radical concentration [$^{\bullet}$OH] is modelled by the equation

$$[OH] = c[O_3]j_{NO_2}$$

where c is a constant and j_{NO_2} is the rate constant for the nitrogen dioxide photolysis.

3.2 General description of the ADMS 5 amine chemistry scheme

The reaction scheme for the amine chemistry calculates concentrations at output locations using the following procedure:

1. The concentrations and age of the primary pollutants are calculated at each receptor point using the standard ADMS dispersion algorithms;
2. If the dilution and entrainment scheme is used then the primary concentrations are adjusted to remove dilution effects using the ratio of the plume spread at $t = 0$ to $t = t_{age}$, i.e. $\frac{(\sigma_y \sigma_z)_{t=0}}{(\sigma_y \sigma_z)_{t=t_{age}}}$;
3. The chemical reaction equations are applied over a time δt to all pollutants;
4. If the dilution and entrainment scheme is used then the concentrations of all pollutants are diluted as ambient air, containing the background pollutants, is entrained into the plume. The rate of dilution is given by the ratio of the plume spread at the beginning and end of this time step;
5. Steps 3 and 4 are repeated for each time step, δt, until $t = t_{age}$.

SECTION 4 References

This is the reference list for this User Guide.

Låg M, Lindeman B, Instanes C, Brunborg G, Schwarze P. Health effects of amines and their derivatives associated with CO2 capture. The Norwegian Institute of Public Health, 2011 ISBN 978-82-8082-462-2

Nielson et al, "Atmospheric Degradation of Amines (ADA). Summary Report: Photo-oxidation of Methylamine, Dimethylamine and Trimethylamine". Climit project no. 201604. Norwegian Institute for Air Research. January, 2011

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