DET NORSKE VERITAS

Report

Atmospheric Chemistry Modelling of Components from Post-Combustion Amine-Based CO_2 Capture

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CCM Mongstad Atmospheric Chemistry Modelling	DET NORSKE VERITAS LTD, UK Palace House SE19DE London, United Kingdom Tel: +44 (0)20 7357 6080 Fax: +44 (0)20 7357 6048 http://www.dnv.com
For: GASSNOVA SF Dokkvegen 10 3920 PORSGRUNN Norway	
Account Ref.:	

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Summary:

This report describes the derivation of a reaction scheme that involves chemical reactions of amines in the atmosphere, photochemical reactions and physical equilibria processes involving condensed phase water (moisture). The simplified scheme is derived from basic research reports and implemented as a modification to the CALPUFF Modelling System dispersion tool.

Prepared by:	*Name and Position* Dr Tim Fowler Principal Consultant Graham Vernon Senior Consultant	*Signature*
Verified by:	*Name and Position* Stavros Yiannoukas Senior Consultant	*Signature*
Approved by:	*Name and Position* Frank Ketelaars Associate Director	*Signature*

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EXECUTIVE SUMMARY

Overview

The CO_2 Capture Mongstad Project (CCM Project) is organised jointly by Gassnova SF and Statoil ASA with funding from the Norwegian government.

The purpose of CCM Project is to plan and build a large scale CO_2 capture plant. The facility will be situated next to the Mongstad refinery on the Mongstad industrial site, north of Bergen on the west coast of Norway. The facility will capture CO_2 from the flue gas of a Combined Heat and Power plant (CHP), perhaps using amine-based capture technology. The design basis is the capture of approximately 1.3 million tonnes of CO_2 per year. This will then be conditioned and compressed for pipeline transport to geological storage under the Norwegian Continental Shelf.

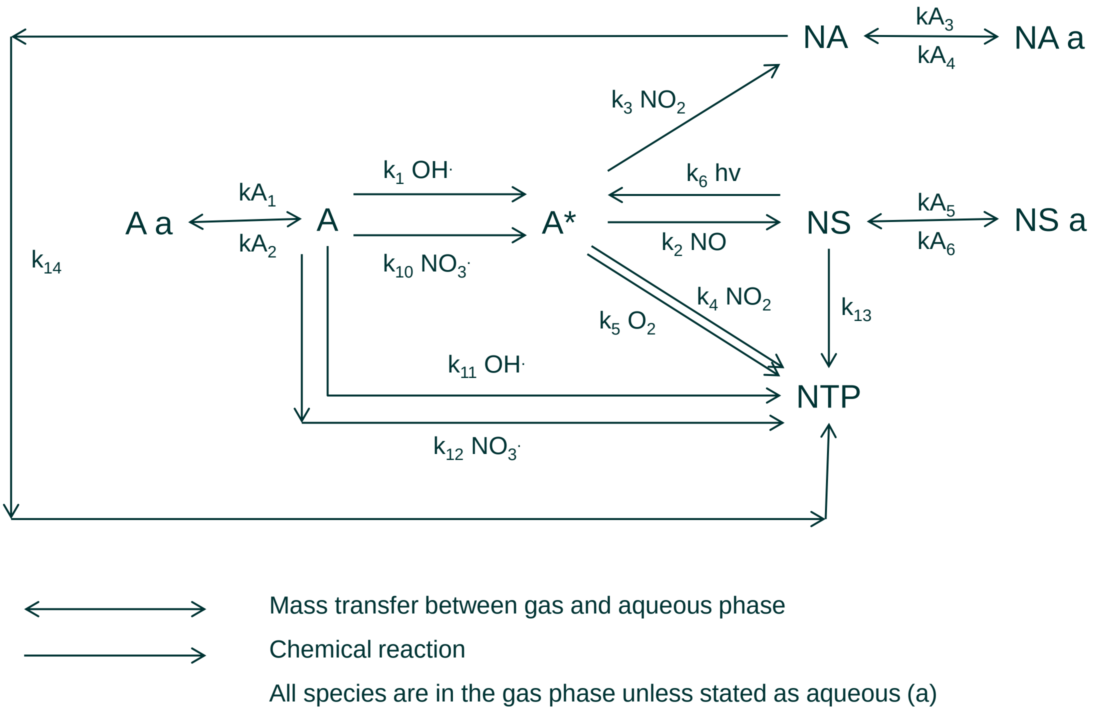
An amine-based CO_2 capture plant may cause harmful emissions to the atmosphere. Amines and their degradation products, formed either in the process unit or after release to the atmosphere, are of particular concern to CCM Project but there is limited knowledge about the behaviour of such chemicals when released from large scale industrial processes. CCM Project has therefore launched several studies to be conducted during the capture plant development in order to improve our knowledge. One of the studies is associated with the atmospheric dispersion (and the ultimate fate) of components from post-combustion amine-based CO_2 capture. The principal pollutants of concern are: NOx (NO and NO_2), NH_3, amines, nitrosamines and nitramines, amongst others. Nitrosamines and nitramines in particular are acknowledged carcinogens. Very low environmental quality criteria have been proposed for these pollutants and hence the formation, dispersion and destruction processes of these pollutants are the main interest of this report.

This report has been prepared by Det Norske Veritas Limited (DNV). It describes work done to develop and validate a computer model that can perform both complex gas dispersion calculations and complex chemical transformation reactions simultaneously. The amine chemistry model built includes photochemistry (dependencies on time of day and season of the year), gas-liquid equilibria processes and location dependent variables (NOx emitted from the process).

Results of model validation work are presented as well as the results from three case studies.

Overview of the Phase 2 Chemical Scheme Implemented

The chemical scheme implemented in this report, which includes conventional free radical gas phase reactions, photochemical (photolytic) reactions and phase equilibria processes (absorption and desorption of soluble species in liquid phase water (moisture)) is shown in the figure below.



In the figure above A, NS, NA and NTP represent amine, nitrosamine, nitramine and non-toxic products (mainly imine initially) respectively. A* is a reactive intermediate and species with an "a" are in the condensed liquid phase. Some of the steps shown are included to only provide future model flexibility and so their rate constants are set to zero in the case studies described in this report. The concentration of the counter species ($OH^{\cdot}$, $NO_3^{\cdot}$, NO, NO_2 and O_2) may depend on the time of day, the season of the year or the location depending on the species as described in the report.

Conclusions

The key conclusions from the study are as follows:

- DNV believe that the amine chemistry scheme implemented into the modified CALPUFF model is both correct and is demonstrated to be correct (validated).
- The modified CALPUFF model is flexible and capable of representing a variety of different amine chemistry schemes, provided rate constants and similar data are available from the academic reports.
- The modified CALPUFF model is suitable to help support the evaluation of different amine-based technology options under consideration by the CCM Project.

- The results from the example case studies conclude that dispersion processes, not chemical reaction processes, dominate the decrease of concentration of amine emitted into the environment (when emitted at about 1 part per million). Two of the case study results (A and 00) are about a factor of 5 lower than the air quality criterion used (that is, they are compliant). However Case B (the worst case) exceeded the air quality criterion by 60% (ratio of predicted concentration to criterion of 1.6). The case studies continue to include conservatism in a number of parameters and modelling assumptions as discussed in the main report.

Finally, if required the modified CALPUFF model can be adapted to implement different chemical schemes with significantly less effort than that used to develop this report.

Recommendations

The key recommendations from the study are as follows:

- The model validation process should be discussed with the regulator to ensure that results from the model will be acceptable in an assessment of environmental impacts.
- The model should be used to evaluate the impacts to the environment for real process emission parameters. That is, the emission parameters for the three case studies should be refined to represent, as far as possible, real process operating conditions.
- The model results could be compared with ambient measurements of pollutant concentrations (environmental monitoring results) if available.

1 INTRODUCTION

1.1 Background

The CO_2 Capture Mongstad Project (CCM Project) is organised jointly by Gassnova SF and Statoil ASA with funding from the Norwegian government. This report is prepared by Det Norske Veritas Limited (DNV). Hereafter the joint clients (Gassnova SF and Statoil ASA) will be referenced as “CCM Project”, whereas the technology development process at Mongstad will be referred to as “the CCM project”.

The purpose of CCM Project is to plan and build a large scale CO_2 capture plant. The facility will be situated next to the Mongstad refinery on the Mongstad industrial site, north of Bergen on the west coast of Norway. The facility will capture CO_2 from the flue gas of a Combined Heat and Power plant (CHP), perhaps using amine-based capture technology. The design basis is the capture of approximately 1.3 million tonnes of CO_2 per year. This will then be conditioned and compressed for pipeline transport to geological storage under the Norwegian Continental Shelf.

An amine-based CO_2 capture plant may cause harmful emissions to the atmosphere. Amines and their degradation products, formed either in the process unit or after release to the atmosphere, are of particular concern to CCM Project but there is limited knowledge about the behaviour of such chemicals when released from large scale industrial processes. CCM Project has therefore launched several studies to be conducted during the capture plant development in order to improve our knowledge. One of the studies is associated with the atmospheric dispersion (and the ultimate fate) of components from post-combustion amine-based CO_2 capture. The principal pollutants of concern are: NOx (NO and NO_2), NH_3, amines, nitrosamines and nitramines, amongst others. Nitrosamines and nitramines in particular are acknowledged carcinogens. Very low environmental quality criteria have been proposed for these pollutants and hence the formation, dispersion and destruction processes of these pollutants are the main interest of this report.

The key environmental factors that determine the selection of the CO_2 capture process are:

- How much amine, nitrosamine and nitramine is released from the CO_2 capture process.
- How quickly does amine convert to nitrosamine and/ or nitramine in the environment.
- How quickly does nitrosamine and/ or nitramine decay in the environment.
- How quickly does the released gas flow, including any released or subsequently formed nitrosamine and/ or nitramine, disperse in the environment.

The magnitude of the environmental impact due to nitrosamine and/ or nitramine will be determined by the magnitude of the environmental quality criteria set by the regulator and the inter-play between the key factors above.

The overall objective of the work described in this report is to develop and demonstrate a model that is capable of assessing the environmental impacts of amines and their degradation products. This model can then be used to help evaluate the preferred CO_2 capture process to be installed at Mongstad.

1.2 Overview of the CCM Project

The CCM project is required to address many aspects including technology selection, detailed engineering, performance specification (including demonstrating acceptable environmental impacts) and research of basic physical and chemical processes where improvements in understanding are required.

In order to improve basic knowledge of amine chemistry in the process and in the atmosphere the CCM Project has commissioned many studies involving researchers and consultants. Some of these reports are referenced by this report.

DNV has produced 2 main reports for CCM Project prior to this one. These are briefly described here.

During 2010 DNV was engaged by CCM Project to evaluate if relatively simple air quality models could be used to satisfy the requirements of the CCM project (Call-Off 01). In this study, DNV reviewed the academic reports then available that described amine chemistry (which we now define to include the chemistry of amine degradation products) and DNV used an unmodified conventional Gaussian plume air dispersion model (ADMS v4) to estimate environmental impacts of nitrosamine and nitramine using various approaches and limiting assumptions /1/.

After Call-Off 01 it became clear that simple models that do not allow the definition of amine chemical transformation processes would not provide sufficient flexibility to predict the environmental impacts of amines and their degradation products with the degree of confidence required.

In April 2011 DNV began their work under Call-Off 02 (this present contract). DNV's objective for Phase 1 of Call-Off 02 was to include simple gas-phase chemistry in an open-source dispersion model called CALPUFF Modelling System Version 6.4 (CALPUFF). CALPUFF has a number of advantages over ADMS. In particular:

- The "time" parameter is an important factor in the simulation of amine chemical reactions. ADMS is a steady-state plume model, where the parameter "time" is not explicitly considered. CALPUFF is a time-varying model, where the pollutant can be followed step by step from the source to the receptor. This capability provides a good base for a more accurate implementation of an amine chemistry model using CALPUFF.

- CALPUFF also allows for more accurate simulation of pollutant transport in complex terrain areas. Within this context, the use of 3D LAM data as meteorological input would maximise this capability.

Last but not least, CALPUFF is an open-source model written in FORTRAN. It can, therefore, be modified to represent amine chemical processes. The CALPUFF model as modified by DNV may be referenced as “the DNV model” or “the modified CALPUFF model” below.

Within Phase 1, DNV demonstrated that CALPUFF was capable of meeting CCM Project’s objectives by the implementation of a simple gas-phase amine chemistry scheme /2/.

Another DNV report that assessed wet and dry deposition effects was produced under Call-Off 02 during 2011 /3/. The objective of this report was to demonstrate a methodology to assess the impacts of amines, nitrosamines and nitramines to surface water and subsequent receptors.

This DNV report is the Phase 2 final report of Call-Off 02. It extends the complexity of the physical and chemical transformation processes implemented in the modified CALPUFF model. References to previous reports are used wherever practicable in order to keep this report as concise as possible.

1.3 Scope and Objectives of Phase 2 Report

The key objective of this report is to achieve higher precision predictions of the ambient air concentrations of amines and their degradation products (specifically nitrosamines and nitramines) emitted from the amine-based CO_2 capture process. It does this by the inclusion of more representative and more complex physical and chemical processes in the modified CALPUFF model, compared to Phase 1.

The primary goal of this report is to improve the *flexibility* of the modified CALPUFF model to represent different physical and chemical processes, and to demonstrate that the modified model gives reasonable results for different input parameters. If this can be achieved, then it is possible that the modified model may be used to support a technology selection process under a Call-Off 03 contract later in 2012.

The additional processes to be implemented during Phase 2 were initially specified as:

- Inclusion of equilibria processes that could transfer chemical species to a condensed aqueous phase (hereafter referred to as “moisture”).
- Inclusion of transformation processes within atmospheric moisture.

- Inclusion of amine activation reactions involving reactive species in addition to $OH^{\cdot}$, such as $Cl^{\cdot}$, $NO_3^{\cdot}$, etc.
- Inclusion of photochemical reactions which will be slower in winter and may be absent at night.

Consistent with the above, the following items are not within the scope of work of Phase 2:

- Consideration of non-steady state or abnormal operating conditions at the Mongstad site.
- Consideration of wet and dry deposition effects. These were considered in another report /3/.
- Consideration of what environmental receptors might be impacted, or the appropriate environmental quality criteria that should be applied.
- Identification or evaluation of physical or chemical data to be applied. These are provided to DNV by the CCM Project as input data.
- Consideration of emissions from emission sources other than the CHP absorber source.

1.4 Report Layout

The remainder of this report is structured as follows:

- Section 2 provides an overview of the research work into the physical and chemical processes that were considered for implementation, or were actually implemented, in this work. It also summarises the chemical and physical processes and the corresponding input parameters that were used in the modified CALPUFF model.
- Section 3 summarises how the changes were implemented in CALPUFF and why DNV believe that the implementation is correct and fit for its intended purpose.
- Section 4 presents the main results calculated by the modified CALPUFF model.
- Section 5 presents the conclusions and recommendations from the study.
- Section 6 lists the references cited and the acronyms and abbreviations used.

The main report is supported by Appendix 1, which shows results of additional chemistry validation work that was performed and Appendix 2 which provides a listing of the new computer code included in the modified CALPUFF model.

2 AMINE CHEMISTRY

2.1 Overview of Research Results

CCM Project has contracted, via Tel-Tek (Norway), a number of research organisations to improve the basic understanding of amines and amine chemistry as relevant to the proposed process at Mongstad. These organisations include:

- University of Oslo, Norway.
- Leibniz-Institut für Tropospharenforschung, Germany.
- Universität Innsbruck, Austria.
- IRCELYON, France.
- Universidad de Castilla-La Mancha, Spain.
- Georgia Tech, USA.
- Norwegian University of Life Sciences, Norway.

Section 2.1 briefly summarises the work areas investigated and the key results obtained. Section 2.2 and 2.3 describe how this information has been included in the modified CALPUFF model.

2.1.1 Gas Phase Free Radical Reactions

Previous DNV reports /1, 2, 3/ have described how the amine degradation reactions are initiated in the gas phase by the abstraction of a hydrogen atom (H) by a reactive free radical ($X^{\cdot}$) (conventionally, free radicals are denoted by a “$^{\cdot}$”):

$$\text{Amine} + X^{\cdot} \rightarrow \text{Amine radical}^{\cdot} + \text{X-H}$$

Where $X^{\cdot}$ could be any one of several reactive free radicals that naturally exist in the lower atmosphere. The most important initiating free radical was thought to be $OH^{\cdot}$ and this was confirmed by the latest research work.

Other candidate species for $X^{\cdot}$ include: $Cl^{\cdot}$, $Br^{\cdot}$, $NO_3^{\cdot}$, and other non-free radical species such as NO, NO_2 and HONO. The importance of all these species was considered by the researchers with the following conclusions:

- For $Cl^{\cdot}$ and $Br^{\cdot}$, which both may have significant concentrations near the sea, it was concluded that the rate constants were larger than for $OH^{\cdot}$, but the natural concentrations of $Cl^{\cdot}$ and $Br^{\cdot}$ are so low that the overall rate of the pathway is not significant. Thus reactions involving $Cl^{\cdot}$ and $Br^{\cdot}$ are not modelled in the chemistry scheme implemented and described in this report. (DNV expect that any $Cl^{\cdot}$ and $Br^{\cdot}$ present in the atmosphere will react preferentially with the vast excess of water to form $OH^{\cdot}$.)

- The importance of $NO_3^{\cdot}$ in amine chemistry depends on the time of day. During the day, the combination of its rate constant and its concentration means that $OH^{\cdot}$ is the dominant reaction species with amine and so the presence of $NO_3^{\cdot}$ can be neglected. However $OH^{\cdot}$ is formed by the photolysis of ozone and $NO_3^{\cdot}$ is destroyed by photolysis, so during the night the concentration of $OH^{\cdot}$ reduces and the concentration of $NO_3^{\cdot}$ increases such that $NO_3^{\cdot}$ then becomes the more significant species reacting with amine. The researchers concluded that $NO_3^{\cdot}$ could be modelled by adding a correction factor to the concentration of $OH^{\cdot}$ but DNV has explicitly included reactions with $NO_3^{\cdot}$ in the chemistry scheme implemented and described in this report.
- For NO, NO_2 and HONO the researchers concluded that these species did not have a significant influence on the initiation of the amine gas phase chemistry reactions. Thus these species are not modelled in the chemistry scheme implemented and described in this report.

Thus $OH^{\cdot}$ and $NO_3^{\cdot}$ are the only species that react with amine and the subsequently formed activated amine then reacts with NO, NO_2 or O_2 to complete the gas phase chemistry modelled.

2.1.2 Gas Phase Photochemical Reactions

As discussed in Section 2.1.1 above, many atmospheric chemistry reactions are initiated by, or influenced by, sun light. Thus the chemistry at night or the chemistry during the day and in the winter at northern latitudes is likely to be significantly different compared to the chemistry near mid-day on a bright summer day. A range of different possible photochemical reactions and pathways in both the gas phase and the aqueous phase were considered by the researchers but the only three that were considered sufficiently important for implementation in the chemistry scheme were as follows:

- The influence of sun light on the concentration of $OH^{\cdot}$ should be considered. This concentration will be significantly reduced at night and during the day in the winter near the poles, see Section 2.3.
- Nitrosamine can absorb sun light and in so doing dissociates to nitric oxide and the amine radical, as follows for dimethyl nitrosamine.

  $$(CH_3)_2NNO + h\nu \rightarrow (CH_3)_2N^{\cdot} + NO$$

  This reaction has the effect of reducing the concentration of nitrosamine observed and increasing the concentration of nitramine observed. It is included in the chemistry scheme implemented and described in this report.
- The influence of sun light on the concentration of $NO_3^{\cdot}$ should be considered. This concentration is reduced during the day by photolysis of $NO_3^{\cdot}$ and hence

increases at night or in winter months due to reduced or absent photolysis, see Section 2.3.

2.1.3 Chemical Reactions in the Aqueous Phase

The researchers considered a range of possible chemical reactions that could occur in the aqueous phase, but it was concluded that no reactions that might influence the rate of formation of nitrosamine or nitramine could be identified. DNV note that in general aqueous chemistry is predominantly ionic chemistry whereas gas phase chemistry is predominantly radical chemistry. This generalisation appears to be valid for amines where researchers found that the dominant reactions in the aqueous phase are acid-base proton transfer reactions, such as:

$$CH_3NH_2 + H^+ \leftrightarrow CH_3NH_3^+$$

Thus no aqueous chemistry reactions are modelled in the chemistry scheme implemented and described in this report.

2.1.4 Gas Liquid Equilibrium Processes

The researchers were also asked to comment on the position of equilibrium (Henry's Law constant) and the speed at which equilibrium is achieved for processes such as:

$$CH_3NH_{2\,(gas)} \leftrightarrow CH_3NH_{2\,(aqueous)}$$

Only limited information resulted from the research reports in this area. DNV do not consider this to be a problem in this work because:

- In the absence of any significant chemistry in the aqueous phase, gas-aqueous equilibria processes cannot increase the maximum concentration of nitrosamine or nitramine formed, they can only reduce the maximum concentration observed.
- Even if Henry's Law constants were identified, it would be necessary to estimate the amount of moisture (liquid phase water) present in order to use this information. The approach proposed by DNV in Section 2.2.3 below based on an uncertainty analysis avoids this challenge.

2.2 Phase 2 Modelling Scheme

2.2.1 Introduction and Terminology

This section provides an overview to the relevant amine chemistry and defines some terminology that will be used throughout this report.

Figure 2.1 summarises the key gas phase amine chemistry processes relevant to the Phase 2 chemistry scheme. It also defines some short-hand nomenclature that will be used in this report.

Figure 2.1 Key Gas Phase Amine Chemistry Processes and Useful Nomenclature

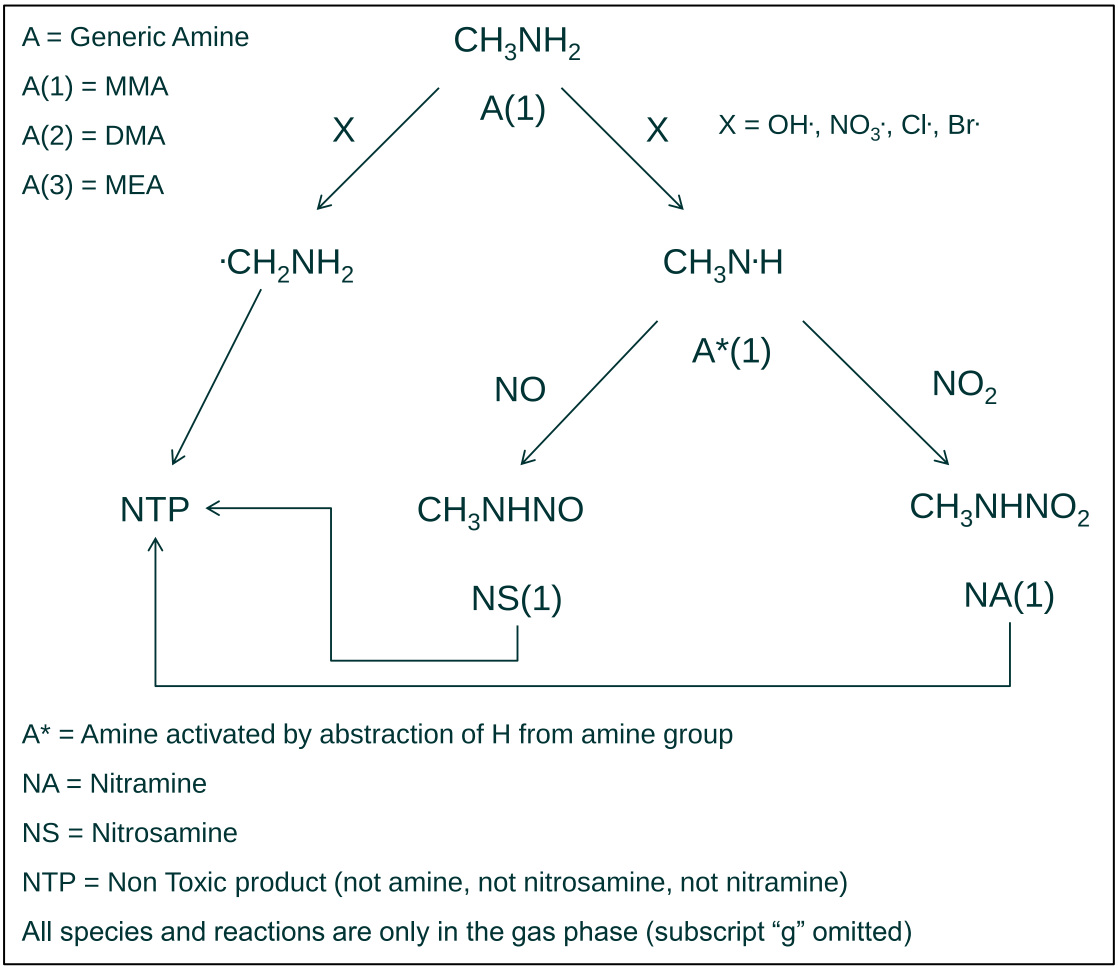


Figure 2.1 shows that gas phase amines (A_g, where subscript "g" is used to denote a species in the gas phase and subscript "a" is used to denote a species in the condensed liquid aqueous phase (moisture)) can be attacked in two main locations:

- At the amine group. This can, but does not always, lead to nitrosamine (NS) or nitramine (NA) formation.
- Not at the amine group. This always leads to the formation of Non-Toxic product (NTP) which is defined as not NS and not NA. The first product formed may be an imine.

The amine radical, A*, can then react with NO or NO_2 to form NS or NA respectively.

This report will consider 3 specific amines (mono-methyl amine (MMA or A(1)), di-methyl amine (DMA or A(2)) and monoethanolamine (MEA or A(3)) and generic amine (A). Any other amine may readily be assessed by the model provided that its chemistry can be sufficiently represented by the reactions shown in Figure 2.2 and provided the corresponding rate constants are known.

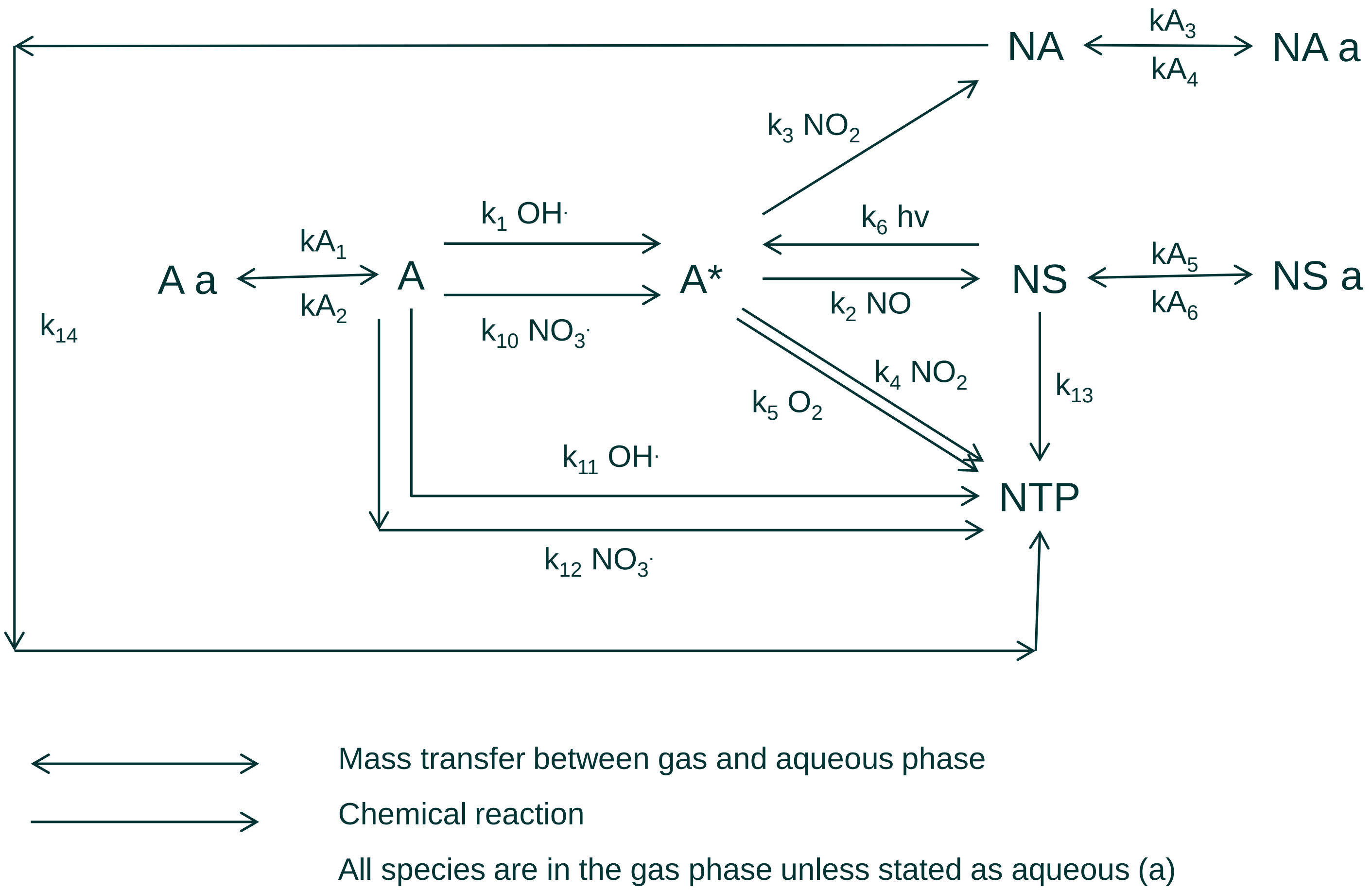
2.2.2 Phase 2 Reaction Scheme

The Phase 2 reaction scheme is show in Figure 2.2.

Note, Figure 2.2 contains a number of reactions which are included to provide future model flexibility. Thus a number of the rate constants may be set equal to 0.0 in order to “turn off” the pathway, see Table 2.1.

In Figure 2.2 only longer lived and relevant species (that is, A, NA, NS) are allowed to equilibrate with moisture (if present). This is because reactive species are assumed to be short-lived and thus will react in the phase in which they are formed rather than equilibrate into a different phase. NTP is not allowed to equilibrate because it is the end-point of the scheme and once formed it is no longer of interest.

Figure 2.2 Phase 2 Gas Phase Chemistry and Phase Equilibria Scheme



2.2.3 Gas-Liquid Equilibria Processes

In Norway the atmosphere always contains some water (H_2O species) (the relative humidity is never zero). This water exists in 4 forms:

- Vapour (gas) phase water. Individual H_2O molecules behaving as a gas, each molecule separated from its neighbours.
- Micro-aqueous phase water or aerosol water. This is condensed phase (liquid) water formed on natural (e.g. pollen) and process (e.g. soot) particulates. This is invisible (not sufficiently large to scatter visible light) but each micro drop may consist of thousands or millions (or more) of water molecules. These will be continually evaporating and re-condensing. Micro-aqueous water behaves as a gas.
- Visible plume water. This is similar to micro-aqueous water, but the particle sizes are sufficiently large to scatter visible light. It behaves as a gas.
- Fog and precipitation (rain, snow, etc.). These conditions will tend to collect (scavenge) micro-aqueous and visible plume water and transfer it to the ground and other surfaces via wet-deposition processes. This process is modelled by the wet deposition option in CALPUFF (not within the scope of Phase 2). This form of water is sufficiently heavy to fall under gravity (no longer behaves like a gas).

The water described under bullets 2, 3 and 4 is aqueous phase water, which is also called moisture in this report. At least some moisture must be present for aqueous phase chemistry and gas-aqueous phase equilibration to occur. Unfortunately we do not have an estimate of the distribution of water between these different forms for different weather conditions, but the volume of moisture available is a parameter that is required to apply Henry's Law (because Henry's law expresses an equilibrium between a partial pressure of a gas and the concentration (moles *per litre*) in the liquid phase).

In order to avoid the need to estimate the quantity of moisture in different atmospheric conditions, DNV has developed a set of equations that represent the important processes for our model. For the gas-liquid equilibrium:

$$A_g \leftrightarrow A_a$$

The position of equilibrium is represented by the Henry's Law constant.

$$H\ (\text{atmosphere moles}^{-1}\ \text{L}) = \frac{\text{(Partial pressure of A in the gas phase)}}{\text{(Concentration of A in moisture)}}$$

The Henry's Law constant represents a position of dynamic equilibrium between absorption and desorption processes that can be represented by 2 first order rate processes as follows:

Gas phase amine to aqueous phase (absorption)	$-d[A_g]/dt = kA_1 [A_g]$
Aqueous phase amine to gas phase (desorption)	$-d[A_a]/dt = kA_2 [A_a]$

At equilibrium, these rates will be equal and there will be defined fraction of amine in the aqueous phase (moisture). We now define the equilibrium ratio R_e which varies between 0.0 and 1.0 and is related to the Henry's Law constant H, as:

R_e = Moles of amine in the aqueous phase/ (total moles amine available)
$= [A_a] /([A_g] + [A_a])$

Equilibrium will be achieved with a characteristic half-life (τ) as with any first order rate process. If the following two expressions are used for kA_1 and kA_2

$kA_1\ (s^{-1}) = R_e \ln(2)/ \tau$
$kA_2\ (s^{-1}) = (1-R_e) \ln(2)/ \tau$

Then the concentration in the aqueous phase (of A, NS or NA) will move towards the value of R_e set at a rate that corresponds to the value of τ that has been set. Note the absolute units of species in the aqueous phase are arbitrary, but have a one-to-one correspondence with the units used by the model in the gas phase (that is, if $3ng/m^3$ is transferred from the gas phase to the aqueous phase then the aqueous phase concentration increases by $3ng/m^3$).

The value of R_e is set to a larger value (0.1 assumed) if both sufficient aqueous phase water (moisture) is assumed to be available *and* the gas/ vapour is very soluble in water. Conversely R_e is set to lower values (0.0001 assumed) if either aqueous phase water is assumed to be unavailable *or* if the gas/ vapour is mostly insoluble in water.

The value of τ is set smaller (120s assumed) if equilibrium should be quickly achieved and it is set larger (1800s assumed) if equilibrium should be achieved more slowly.

2.2.4 Gas Phase Chemical Processes

Figure 2.2 defines a number of conventional second order, pseudo first order and first order chemical transformation reactions. These processes and their associated parameters are defined in detail in Section 2.3 below.

In the model developed by DNV all second order rate processes are implemented as pseudo first order rate processes. That is, when the amine species (A, A*, NS, NA) reacts with another species the concentration of the other species is assumed to be unchanged by the reaction. In the scheme in Figure 2.2, there are 5 other species as follows: $OH^{\cdot}$, $NO_3^{\cdot}$, NO, NO_2 and O_2. Collectively these are referred to as "counter species". The behaviour of each is discussed here.

The $OH^{\cdot}$ radical is formed in the atmosphere mainly by photolysis of ozone. Its concentration in the model varies with the time of day and with the time of year as described in Section 2.3 below. The depletion of $OH^{\cdot}$ by reactions such as k_1 is not represented in the model because $OH^{\cdot}$ will diffuse into the emitted plume from the bulk atmosphere where the quantity of $OH^{\cdot}$ present is very large compared to the quantity of amine emitted in the plume. This assumption is conservative with respect to the formation of NS and NA (if the assumption was not made the predicted concentration of NS and NA would be reduced).

The $NO_3^{\cdot}$ radical is destroyed in the atmosphere by photolysis. Thus its concentration is highest at night and when the light flux is low (e.g. in winter and on cloudy days). The concentration of $NO_3^{\cdot}$ in the model varies with the time of day and with the time of year as described in Section 2.3 below. Its depletion is not represented in the model and this assumption is conservative for the same reasons as given for $OH^{\cdot}$.

Both NO and NO_2 are emitted in the absorber plume at relatively high concentration but also exist in the ambient atmosphere at a lower concentration. In addition, /4/ quotes a weak variation of concentration with time of year which is not represented in the DNV model. The concentration of NO and NO_2 is assumed to be equal to the sum of the emitted concentration calculated by CALPUFF plus the background concentration. The depletion of NO or NO_2 is not represented in the model and this assumption is conservative for the same reasons as given for $OH^{\cdot}$.

Oxygen (O_2) is the second most abundant component of the atmosphere at 20.95% in dry air. In comparison with the amines emitted O_2 is in vast excess and thus the pseudo first order approximation needs no additional justification.

2.2.5 Liquid Phase Chemical Processes

The work performed by the research groups for CCM Project concluded that the rate constants for chemical transformation reactions that form nitrosamine or nitramine from amines in the aqueous phase are negligible. Hence DNV and CCM Project agreed that no reactions in the aqueous would be implemented in Phase 2.

2.3 Rate Constants and Other Parameters used in the Model

Tables 2.1 summarises the rate constants used by the Phase 2 chemistry scheme. Some of these constants vary with time of the day, time of the year and/ or location as described here.

The values of k_1 and k_{11} are not independent. The value given for k_{OH} in Table 2.1 is the maximum value provided in the academic reports. It represents the sum of rates for H abstraction from the amine group and from the non-amine group. The following relationships are used to calculate k_1 and k_{11} from k_{OH}:

$$k_{OH} = k_1 + k_{11}$$

$$OH^{\cdot} \text{ branching ratio} = k_1/(k_1 + k_{11}) = k_1/k_{OH}$$

The branching ratio represents the balance between initial attack at the amine group compared to attack not at the amine group. A low branching ratio reduces the amount of NS and NA that can be formed.

The values of k_{10} and k_{12} behave in an exactly analogous manner to k_1 and k_{11}. In the absence of firm data the $NO_3^{\cdot}$ branching ratio is assumed to be equal to the $OH^{\cdot}$ branching ratio.

The only directly represented photochemical reaction in the implemented model is the photo dissociation of the nitrosamine (k_6). In /4/ the rate constant for this process is deduced to be 3.90e-4, 8.83e-4, 4.22e-4 and 9.02e-6s^{-1} for March, June, September and December respectively (from j_{NO2} and j_{rel} = 0.32). DNV understand these values take account of cloud cover in the Mongstad area as well as the angle of the sun.

The CALPUFF model calculates the zenith angle (φ) (how many degrees from directly overhead) made by the sun at the modelled location as a function of time of day and the time of the year. Night time occurs when this angle is greater than 90^o. The maximum zenith angle observed at Mongstad (at noon in high summer) is its latitude north (63.97^o) minus the latitude north of the Tropic of Cancer (23.43^o). The zenith angle has been used as a convenient way of determining the time of day and the season of the year. Using the maximum summer value of k_6 taken from /4/, k_6 is calculated in the modified CALPUFF model by the relationship:

$$k_6 = \text{maximum}(8.83E\text{-}04 \times \cos(\varphi) / \cos(63.97\text{-}23.43), 0)\ s^{-1}$$

Thus k_6 varies between 8.83E-04s^{-1} at noon in high summer and 0 s^{-1} at night.

The value of k_{13} represents various possible transformation processes of NS to NTP. This could be by oxidation (thought to be relatively slow and not represented in the modified model) or, for primary amines, by intra-molecular re-arrangement to imine. This latter process is known to be fast. DNV estimated the maximum rate of formation of NS along the k_2 pathway and assigned a value to k_{13} that gave a rate of loss 20 times faster than this maximum rate of formation.

The remaining parameters that influence the amine chemistry are the concentrations of counter species. The concentration of $OH^{\cdot}$ is controlled by photochemical processes, thus its concentration has been linked to the zenith angle ϕ in a similar way to k_6. It was reported /4/ that $OH^{\cdot}$ concentration is 3.90E5, 2.57E6, 8.88E5 and 6.77E5 molecules per cubic centimetre in March, June, September and December at Mongstad. DNV calculate the concentration of $OH^{\cdot}$ by the equation:

$$OH^{\cdot} = \text{maximum}\ (\ 2.57E6\times\cos(\phi)/\cos(63.97-23.43),\ 1.0E4)\ \text{molecules}\cdot\text{cm}^{-3}$$

Thus $OH^{\cdot}$ varies between 8.83E-04 molecules cm^{-3} at noon at high summer and 1.0E4 molecules$\cdot cm^{-3}$ at night (this night time value is a DNV assumption). (The concentration of $OH^{\cdot}$ is also calculated by CALPUFF using a different set of equations. The advantage of the equation above is that it allows the concentration to be determined by the analyst.)

The concentration of $NO_3^{\cdot}$ is higher at night than during the day. The average night time concentration is given as 3.20E7 molecules cm^{-3} /5, 6/. DNV has assumed that its daytime concentration is a factor of 10 lower than the night time concentration. The concentration is calculated from:

$$\begin{aligned} &\text{If } \cos(\varphi) < 0.0 \text{ then } [NO_3^{\cdot}] = 3.20E7\ \text{molecules}\cdot\text{cm}^{-3} \\ &\qquad\qquad\text{else } [NO_3^{\cdot}] = 3.20E6\ \text{molecules}\cdot\text{cm}^{-3} \end{aligned}$$

Both NO and NO_2 are emitted in the CHP emission source along with the amine. The CALPUFF model calculates these concentrations as a function of location. Background values of NO and NO_2 at Mongstad are given as about the same and equal to 1.25E11 molecules cm^{-3} (about 5ppb as measured /6/). The concentration of NO and NO_2 are calculated in the modified CALPUFF model as:

$$[NO] = (\text{concentration NO calculated from the source by CALPUFF}) + 1.25E11\ \text{molecules}\cdot\text{cm}^{-3}$$

$$[NO_2] = (\text{concentration } NO_2 \text{ calculated from the source by CALPUFF}) + 1.25E11\ \text{molecules}\cdot\text{cm}^{-3}$$

Table 2.1 Gas Phase Chemical Rate Constants Used in the Phase 2 Gas Phase Chemistry

Id	Chemical Equation	Rate Equation	Parameters	Comments
1	$A_g + OH^{\cdot} \rightarrow A^*_g$	$-d[A_g]/dt = k_1 [A_g] [OH^{\cdot}]$	k_{OH} generic upper limit = 9.0E-11 cm^3/molecule/s k_{OH} MMA = 3.0E-11 cm^3/molecule/s k_{OH} DMA = 6.0E-11 cm^3/molecule/s k_{OH} MEA = 3.0E-11 cm^3/molecule/s Value of k_1 (cm^3/molecule/s) depends on branching ratio	Primary activation equation. Defined to form only the amine radical (hydrogen abstraction only from amine group). The academic reports provide values for $k_{OH} = k_1 + k_{11}$. The ratio of k_1 and k_{11} represent the branching ratio for attack at the amine group of not at the amine group.
2	$A_g + NO_3^{\cdot} \rightarrow A^*_g$	$-d[A_g]/dt = k_{10} [A_g] [NO_3^{\cdot}]$	$k_{10} + k_{12}$ = 2.0E-13 cm^3/molecule/s k_{10} depends on branching ratio	Secondary activation equation. Defined to form only the amine radical (hydrogen abstraction only from amine group).
3	$A_g + OH^{\cdot} \rightarrow NTP_g$	$-d[A_g]/dt = k_{11} [A_g] [OH^{\cdot}]$	Value of k_{11} (cm^3/molecule/s) depends on branching ratio	Reaction represents hydrogen abstraction from the non-amine group. Reaction cannot form NS or NA. Rate constant depends on k_{OH} and the branching ratio, see Section 2.3.
4	$A_g + NO_3^{\cdot} \rightarrow NTP_g$	$-d[A_g]/dt = k_{12} [A_g] [NO_3^{\cdot}]$	Value of k_{12} (cm^3/molecule/s) depends on branching ratio	Reaction represents hydrogen abstraction from the non-amine group. Reaction cannot form NS or NA. Rate constant depends on k_{10} and the branching ratio, see Section 2.3.
5	$A^*_g + NO \rightarrow NS_g$	$-d[A^*_g]/dt = k_2 [A^*_g] [NO]$	k_2 = 8.53E-14 cm^3/molecule/s	Nitrosamine formation reaction /7/.
6	$A^*_g + NO_2 \rightarrow NA_g$	$-d[A^*_g]/dt = k_3 [A^*_g] [NO_2]$	k_3 = 3.18E-13 cm^3/molecule/s	Nitramine formation reaction /7/.
7	$A^*_g + NO_2 \rightarrow NTP_g$	$-d[A^*_g]/dt = k_4 [A^*_g] [NO_2]$	k_4 = 6.36E-13 cm^3/molecule/s	Formation of imine and similar non-toxic product reaction /7/.
8	$A^*_g + O_2 \rightarrow NTP_g$	$-d[A^*_g]/dt = k_5 [A^*_g] [O_2]$	k_5 =9.54E-20 cm^3/molecule/s	Formation of imine and similar non-toxic product reaction
9	$NS_g + hv \rightarrow A^*_g$	$-d[NS_g]/dt = k_6(I) [NS_g]$ I = light intensity	$k_6(I)$ = 0 /s at night $k_6(I)$ = 8.83E-4 (maximum at mid-day in summer)	Reaction represents photolytic destruction (back reaction) of nitrosamine to A^*_g and NO. The magnitude of k_6 will vary with day or night and with the intensity of light available as determined by the zenith angle (φ), see Section 2.3.
10	$NS_g \rightarrow NTP_g$	$-d[NS_g]/dt = k_{13} [NS_g]$	k_{13} =0.0 /s for secondary amines and k_{13} =1.91E-02 /s for primary amines	Reaction represents subsequent loss of nitrosamine. Rate constant depends on amine, see Section 2.3.
11	$NA_g \rightarrow NTP_g$	$-d[NA_g]/dt = k_{14} [NA_g]$	k_{14} =0.0 /s	Reaction represents subsequent loss of nitramine. Rate constant set to zero to be conservative.

3 IMPLEMENTATION OF AMINE ATMOSPHERIC CHEMISTRY

3.1 Overview of Approach to Model Development and Validation

The aim of this chapter is to present the approach used by DNV to modify the CALPUFF modelling system to account for the Phase 2 amine chemistry reactions described in Section 2.

The objective of the modified CALPUFF model is to perform both complex dispersion calculations and complex chemistry calculations simultaneously. This presents particular problems for the validation of the work performed, since the model results depend on many input variables. Whilst it may be relatively easy to develop a modified model that appears to work for specific inputs, it is not easy to demonstrate that the modified model is correct in general.

It is not usually practicable or efficient to validate a model amendment by line-by-line code verification. Instead, DNV's approach to model development and validation is to separate the dispersion processes from the chemistry processes and to validate them separately. These validated processes are then combined together and final verification checks are performed. The model development and validation process is summarised in Table 3.1.

Table 3.1 Overview of Model Development and Validation Process

Stage	Description	Comments
MathCad Box Model of chemical and equilibrium processes. Differential equations solved numerically by several different methods.	This evaluates the effect of the Phase 2 chemical scheme using mostly constant variables (no dependence on time of day, season of year, location) and no dispersion processes.	Enabled DNV to evaluate the most robust numerical method for solving the differential equations that represent the chemical scheme.
Analytical Box Model. Reduced set of differential equations solved analytically.	This evaluates a sub-set of the Phase 2 chemical scheme using mostly constant values and no dispersion processes as described for the MathCad Box Model.	Results verified against MathCad Box Model and shown to be consistent.
FORTRAN Box Model of chemical and equilibrium processes. Differential equations solved numerically using the best numerical method selected from the work with MathCad.	Numerical differential equation solver code implemented in FORTRAN. This was written to mimic the MathCad Box Model solutions exactly.	Results verified against the MathCad Box Model and the Analytical Box Model. The results agree both quantitatively and qualitatively (trends are consistent with expectations). This agreement validates the solution of the chemical scheme differential equations that represent the Phase 2 chemical scheme (Figure 2.2) in the modified CALPUFF model.
Modified CALPUFF Model combines existing dispersion calculation with the FORTRAN Box Model of the chemical processes required by the Phase 2 chemical scheme (Figure 2.2).	The FORTRAN Box Model was modified into a FORTRAN subroutine which was then called by CALPUFF. This step completes the required chemistry capability in the modified CALPUFF model.	The CALPUFF dispersion calculations are already validated. The chemistry calculations are validated by the above checking process.

As a final check of the modified CALPUFF model, DNV included a tracer species in the emission profile for each case calculation. The tracer species has identical physical properties to the emitted amine, but does not undergo chemical reactions. This enables the following comparisons to be performed:

- The effect of dispersion without chemistry is evaluated from the concentration of the tracer.
- The effect of dispersion and chemistry together is evaluated from the concentration of amine and its degradation products (NS, NA, NTP and A*).
- An *estimate* of the effect of chemistry without dispersion can be obtained by calculating the extent of dilution from the tracer species and so the concentration of other species without dispersion can be estimated. This is only an estimate because the concentration of a species reduces with dispersion and the rate of chemical reaction decreases with reduced concentration of the reactants, but only the former process is compensated by the estimate of the number of dilutions achieved. Thus it is not expected that the modified CALPUFF model results can mimic the results from the box models even with the correction for dispersion.

These final comparisons enabled DNV to demonstrate the complex qualitative trends that were expected by examination of the reaction scheme (Figure 2.2).

3.2 Theoretical Background

The reaction scheme as shown in Section 2 (Figure 2.2) is exactly equivalent to a system of ordinary differential equations (ODEs). Discovering how the concentrations of the chemical species varies with time is the same problem as solving a particular system of ODEs.

For each iteration of the chemistry scheme, the initial value of the variables (the concentration of the chemical species) is known (in this case, it is provided by CALPUFF) and the final value, after the progression of a finite period of time, is determined by the differential equations. Such problems are known as Initial Value Problems (IVPs).

In order to solve the general amine chemistry scheme as described in Section 2, eight variables are defined as shown in Table 3.2.

Table 3.2 Species defined in the amine chemistry scheme and corresponding system of DEs

Species	Short Species Name	Variable name in DE System
Amine	Amine	y_1
Activated Amine	Astar (A*)	y_2
Nitramine	NA	y_3
Nitrosamine	NS	y_4
Total Non-Toxic Products	NTP	y_5
Aqueous Amine	Amine(aq)	y_6
Aqueous Nitramine	NA(aq)	y_7
Aqueous Nitrosamine	NA(aq)	y_8

The system of differential equations that corresponds to the amine chemistry scheme as discussed in this document is shown in Figure 3.1. The independent variable *t* represents time. The initial conditions are set at *t* = 0.

Figure 3.1 The full system of differential equations corresponding to the Amine Chemistry Scheme (Figure 2.2).

$$\frac{dy_1}{dt} = -[(k_1 + k_{11})[OH] + (k_{10} + k_{12})[NO_3] + kA_1]y_1 + kA_2 y_6$$

$$\frac{dy_2}{dt} = \left[k_1[OH] + k_{10}[NO_3]\right]y_1 - [(k_3 + k_4)[NO_2] + k_2[NO] + k_5[O_2]]y_2 + k_6 y_4$$

$$\frac{dy_3}{dt} = k_3[NO_2]y_2 - (k_{14} + kA_3)y_3 + kA_4 y_7$$

$$\frac{dy_4}{dt} = k_2[NO]y_2 - (k_6 + k_{13} + kA_5)y_4 + kA_6 y_8$$

$$\frac{dy_5}{dt} = (k_{11}[OH] + k_{12}[NO_3])y_1 + (k_4[NO_2] + k_5[O_2])y_2 + k_{14}y_3 + k_{13}y_4$$

$$\frac{dy_6}{dt} = kA_1 y_1 - kA_2 y_6$$

$$\frac{dy_7}{dt} = kA_3 y_3 - kA_4 y_7$$

$$\frac{dy_8}{dt} = kA_5 y_4 - kA_6 y_8$$

We are interested in the values of the eight variables after a certain time interval has elapsed. In general, that time interval is determined by the CALPUFF modelling system and is variable.

IVPs such as this one are known to have unique solutions provided that certain conditions of continuity are met by the differential equations. These conditions are certainly met in this case, because all the functions on the right hand sides of the equations in the system above as well all their derivatives with respect to *t* are continuous over their whole domains.

Therefore we can be confident that a unique solution exists for every set of initial conditions and we can set about solving this IVP.

3.3 Solving the Differential Equation System

In order to provide the most flexible model to benefit possible future assessments that may be required by CCM Project, it was decided early in the model development process to solve the systems of DEs by numerical methods. This means that if a decision is made in the future to model a different chemical scheme, this CALPUFF+Amine Chemistry modelling system could be changed to model that revised scheme, tested and the results obtained in a very much shorter time than that from either this first model development process or than would be the case if the DEs had to be solved analytically.

DNV conducted research into the most appropriate numerical method that should be implemented to solve the DE system in the most robust and easily editable way. The method selected is described in a later section of the present document, but the process for its selection included the parallel development of the DE system in MathCad. MathCad is a symbolic mathematics engine that includes some methods for the solutions of such IVPs. This provided insight into the behaviour of the system and the suitability of different numerical solution methods for its solution.

The MathCad model became a box model for the chemistry that takes place in the absence of dispersion, and location or time of day or seasonal variation of variables. It proved to be a very useful tool for quality checking and will help in the presentation of the chemistry results. It is described in Section 3.4.

3.4 Box Modelling in MathCad

In order to establish a quality check for the chemistry module as finally implemented into CALPUFF, a box model was developed in MathCad first. This model formed an important check in the development of the model and is also useful for discussion of the nature and progression of the chemical reactions that have been modelled.

A box model is a model of the chemistry alone. That is, no dispersion is modelled and the chemistry is allowed to proceed in isolation with the assumptions of good mixing and constant reaction conditions.

In the box model, the counter species were modelled as time-independent constant concentrations. This is in contrast to the final model version as implemented in FORTRAN as part of CALPUFF in which there were multiple dependencies of those counter species on the time of day and the season, et cetera. These conditions and assumptions allow the examination of the behaviour of the amine chemistry, as described by the system of DEs shown above, to be evaluated alone and checked against expectation.

The reaction rates and the concentrations of their corresponding counter species as implemented in the box model are shown in Table 3.3, below. Note that the reaction rates do not all have the same units, because some of them are first order rates (to be multiplied by one concentration in the differential equations) and some of them are second order rates (to be multiplied by two concentrations).

Table 3.3 Constants used in Box Modelling

Constant Label	**Value used in box model**	**Counter Species and concentration** (molecules.cm^{-3})
k_1	7.2E-11 cm^3.molecules^{-1}.s^{-1}	$[OH^{\cdot}]$= 2.57E6
k_2	8.53E-14 cm^3.molecules^{-1}.s^{-1}	[NO]= 1.25E11
k_3	3.18E-13 cm^3.molecules^{-1}.s^{-1}	$[NO_2]$= 1.25E11
k_4	6.36E-13 cm^3.molecules^{-1}.s^{-1}	$[NO_2]$= 1.25E11
k_5	9.54E-20 cm^3.molecules^{-1}.s^{-1}	$[O_2]$= 5.01E18
k_6	8.83E-4 s^{-1}	n/a
k_{10}	1.6E-13 cm^3.molecules^{-1}.s^{-1}	$[NO_3^{\cdot}]$= 3.2E7
k_{11}	1.8E-11 cm^3.molecules^{-1}.s^{-1}	$[OH^{\cdot}]$= 2.57E6
k_{12}	4.0E-14 cm^3.molecules^{-1}.s^{-1}	$[NO_3^{\cdot}]$= 3.2E7
k_{13}	0 s^{-1}	n/a
k_{14}	0 s^{-1}	n/a
kA_1	2.89E-3 s^{-1}	n/a
kA_2	2.89E-3 s^{-1}	n/a
kA_3	2.89E-3 s^{-1}	n/a
kA_4	2.89E-3 s^{-1}	n/a
kA_5	2.89E-3 s^{-1}	n/a
kA_6	2.89E-3 s^{-1}	n/a

In the modified CALPUFF model the initial concentrations are provided by CALPUFF, but for the purposes of testing the implementation in the box model, the initial concentrations of all eight species are set to zero, except for amine which is set to an arbitrary initial value of 100 molecules.cm^{-3}.

For testing purposes the model calculates the values of all eight variables after 3 hours have elapsed. (In the modified CALPUFF model, this interval is provided by CALPUFF, it is variable and in general it is much shorter than 3 hours, but this relatively long period is useful for testing purposes because it allows the species to develop significantly and all the expected behaviours to be observed.)

MathCad makes available to the user various different numerical methods for the solution of systems of ordinary differential equations with initial conditions. Following experimentation with the DE system shown above, it was quickly discovered that only methods designed for so-called "stiff" systems were suitable. This corresponds with generally accepted wisdom that chemical reactions usually result in stiff systems.

The specific methods built into MathCad that are designed for stiff systems are the Bulirsch-Stoer method for stiff systems and the Rosenbrock method. The results from the MathCad box model showed no discernible variation between these methods, so only one set of results is shown.

3.4.1 MathCad Box Modelling Results

With the initial conditions arbitrarily set at amine = 100 units and all the other species set initially to zero, the results of the MathCad box modelling as described above are shown in Table 3.4. There are 15 intermediate results shown in this table, but that figure is merely a parameter of the numerical method and can be altered at will, providing it is sufficiently high to yield smooth results.

Note that, owing to a limitation in MathCad, only seven dependent variables can be modelled simultaneously, and therefore the total Non-Toxic Products (NTP) are omitted from the MathCad results. (The FORTRAN box model, described in Section 3.6, and which become the final implementation in CALPUFF reported in Section 4, does not suffer from this limitation.) Note also that the concentration units are arbitrary. The results are exactly linear with the multiplicative factor of the initial concentration of amine, so the units are immaterial. The choice of an initial value of 100 for amine means that all the results in Table 3.4 can be read as a simple yield (per cent) for each species as a function of time.

Table 3.4 Tabulated Results of MathCad Box Modelling (arbitrary units).
(All results quoted to 3 decimal places, no judgement of accuracy implied)

Time / s	**Amine**	**Astar (A*)**	**NA**	**NS**	**A(aq)**	**NA(aq)**	**NS(aq)**
0.000	100.000	0.000	0.000	0.000	0.000	0.000	0.000
720.000	44.834	0.014	0.312	0.065	45.228	0.209	0.046
1.440e3	40.557	0.013	0.497	0.088	42.238	0.407	0.077
2.160e3	37.286	0.012	0.670	0.103	38.851	0.587	0.096
2.880e3	34.289	0.011	0.829	0.111	35.728	0.752	0.107

Time / s	Amine	Astar (A*)	NA	NS	A(aq)	NA(aq)	NS(aq)
3.600e3	31.532	0.010	0.975	0.114	32.855	0.905	0.113
4.320e3	28.997	9.239e-3	1.111	0.114	30.214	1.046	0.114
5.040e3	26.666	8.506e-3	1.235	0.112	27.785	1.175	0.113
5.760e3	24.522	7.829e-3	1.349	0.108	25.551	1.294	0.109
6.480e3	22.550	7.205e-3	1.455	0.102	23.497	1.404	0.105
7.200e3	20.737	6.629e-3	1.552	0.097	21.608	1.505	0.099
7.920e3	19.070	6.099e-3	1.641	0.091	19.870	1.598	0.093
8.640e3	17.537	5.611e-3	1.723	0.085	18.273	1.683	0.087
9.360e3	16.127	5.161e-3	1.798	0.079	16.804	1.762	0.082
1.008e4	14.830	4.747e-3	1.868	0.074	15.453	1.834	0.076
1.080e4	13.638	4.366e-3	1.931	0.068	14.210	1.901	0.070

These results are presented in graphical form in Figure 3.2 to Figure 3.4 below. They are shown as three separate graphs because of the very different vertical scales. Note that more than 15 intermediate values are shown in the graphs. Note that the scales are linear in arbitrary concentration units, with 100 units of amine concentration present at t=0.

Figure 3.2 Box Model Results for Amine and Aqueous Amine

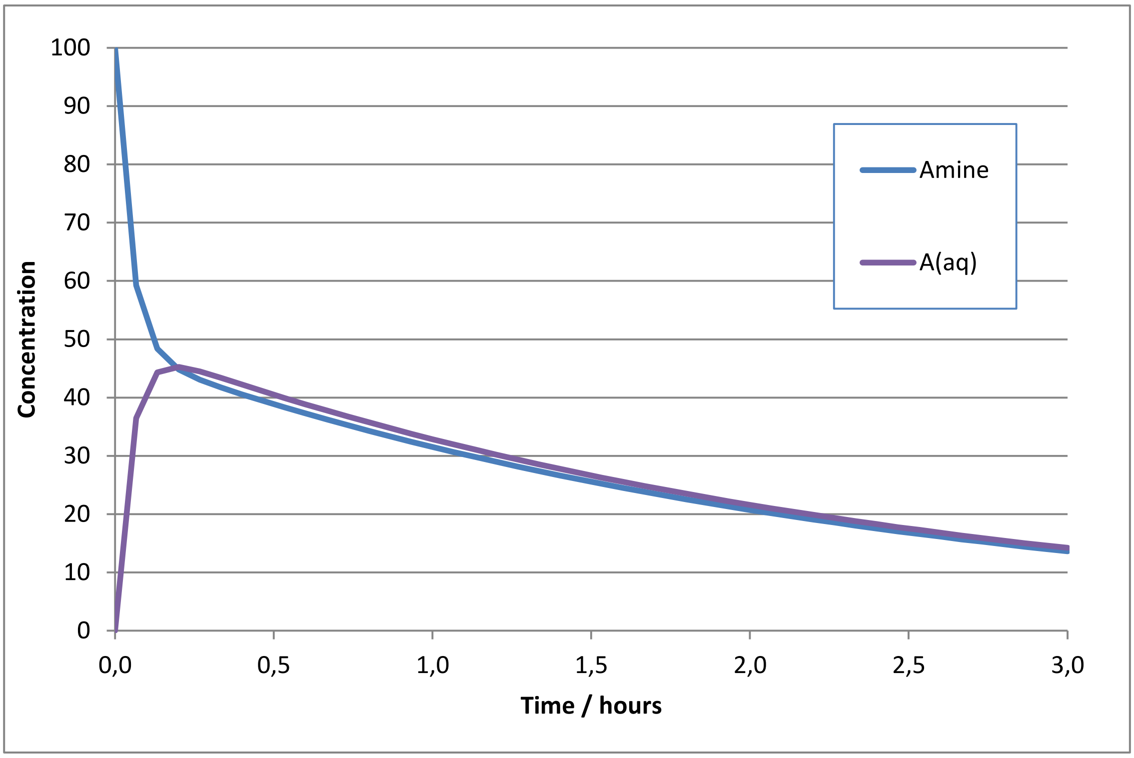


Figure 3.3 Box Model Results for NA, NA(aq), NS, NS(aq) and AStar

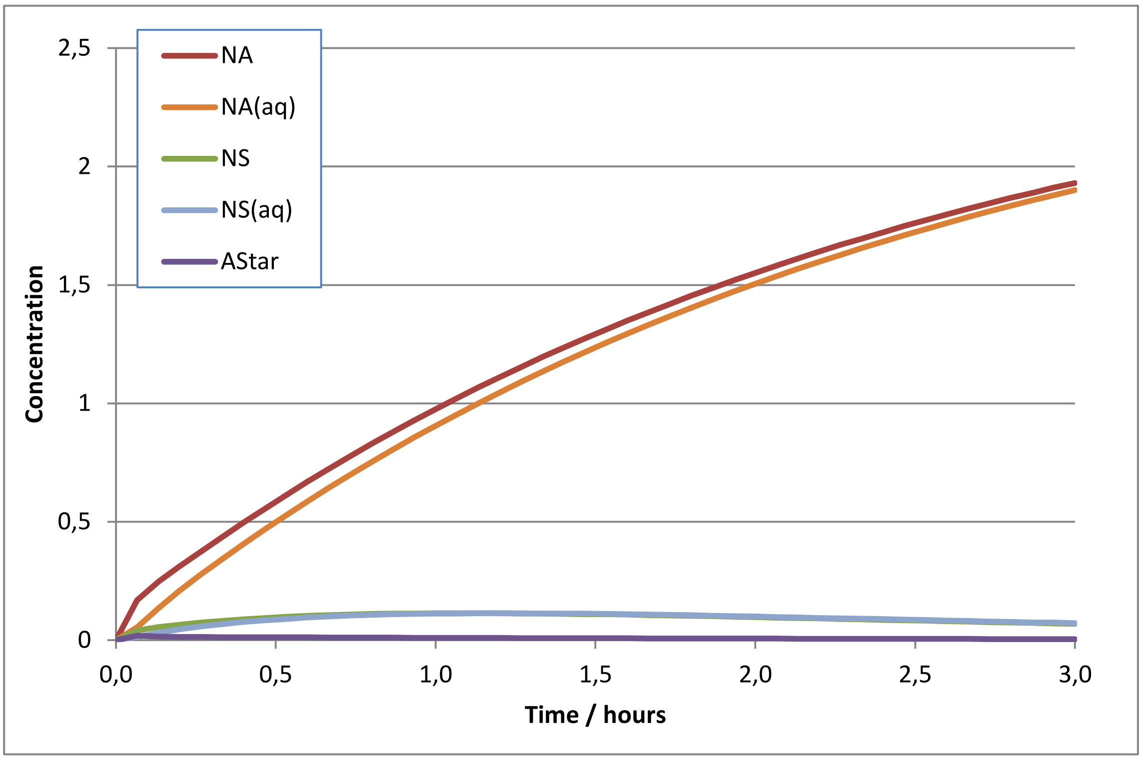
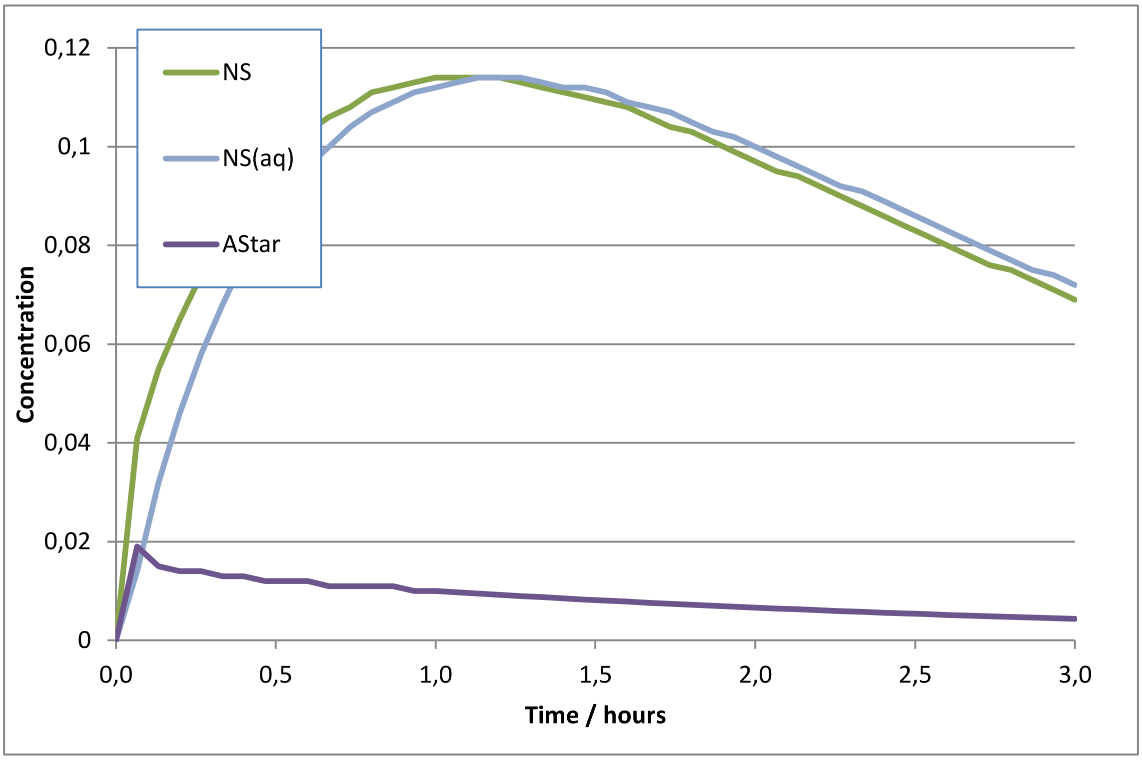


Figure 3.4 Box Model Results for NS, NS(aq) and AStar



Amine, nitramine and nitrosamine all equilibrate rapidly in 50/50 proportion with their aqueous equivalents, with the aqueous versions showing a small lag behind the gaseous species. This is as expected since the forward and backward “reaction rates” for the phase transitions are equal (see Table 3.3). Amine in the aqueous phase rises to equilibrium with gas phase amine and then falls as the gas phase amine concentration falls, as expected.

Amine reduces monotonically and exponentially, correctly reflecting the loss-only process that is dependent only on the amine species itself.

Nitramine grows monotonically but with reducing gradient, correctly reflecting the fact that there are no loss processes for nitramine in this box model (k_{14}=0 here) and the reducing stock of amine which is its precursor.

Nitrosamine behaves initially in a similar way, but grows more slowly than nitramine because $k_2 \cdot [NO]$ is smaller than $k_3 \cdot [NO_2]$. In fact the ratio is about 3.7. Interrogation of the box model for the early part of the reaction period has revealed that the ratio between these species is indeed about 3.7. In time, the concentration of nitrosamine grows sufficiently and the precursor amine reduces sufficiently that the back-reaction k_6 begins to dominate and the concentration of nitrosamine begins to reduce again, as expected.

The intermediate product AStar grows rapidly at the very beginning of the reaction period, but quickly reaches a peak and then declines slowly as the concentration of amine starts to deplete significantly (more than about 67% consumed). This provides an indication of the range of values over which the steady state concentration for reactive species approximation is valid (though this approximation is not used by DNV in the work reported here). Finally, as expected, the concentration of Astar is never high relative to all the other species. This reflects the much faster reaction rates downstream of Astar (activated amine is more reactive than amine itself).

More specific comparisons against an analytical solution of a particular special case of this scheme are presented in the following section.

3.5 Analytical Solution for a Sub-System.

To further verify the behaviour of the box model, a smaller reaction scheme was considered, namely the sub-system involving only amine and amine(aq). In this system there is net loss of mass overall and phase transfer between amine(g) and amine(aq). This sub-system is described in Figure 3.5.

Figure 3.5 DE system for amine-amine(aq) sub-system

$$\frac{dy_1}{dt} = -(K + kA_1)y_1 + kA_2 y_2$$
$$\frac{dy_2}{dt} = kA_1 y_1 - kA_2 y_2$$

where y_1 is [Amine]
y_2 is [Amine(aq)], and
$K = (k_1 + k_{11})[OH] + (k_{10} + k_{12})[NO_3]$

The initial conditions are $y_1(0)=A_0$ and $y_2(0)=0$.

If the following definitions are made,

$$\gamma = \frac{K + kA_1 + kA_2}{2}$$
$$\omega = \sqrt{\gamma^2 - KkA_2}$$

it can be shown that the solution to the sub-system above is as follows:

$$Amine_g(t) = A_0 \exp(-\gamma t) \left(\cosh(\omega t) + \frac{kA_2 - \gamma}{\omega} \sinh(\omega t)\right)$$
$$Amine_{aq}(t) = A_0 \frac{kA_1}{\omega} exp(-\gamma t) \sinh(\omega t)$$

Using the constant values for the MathCad box model shown in Section 3.4, and the initial condition A_0=100, these solutions take on the numerical values:

$Amine_g$(3 hours) = 13.638
$Amine_{aq}$(3 hours) = 14.210

These numerical values confirm the results in the final row of Table 3.4. The values for intermediate values of t agree also.

This analytical solution to a subset of the full chemistry scheme gives DNV confidence that the numerical methods implemented in MathCad have provided a reliable solution to the full scheme.

3.6 Box Modelling in FORTRAN

3.6.1 Description

One of the numerical methods built into MathCad is the Rosenbrock method (appropriate for stiff systems), so it was decided to adopt this method for implementation into FORTRAN and ultimately into the modified CALPUFF model.

Standard code libraries were consulted and an implementation of the Rosenbrock method was selected and adapted. In the first instance, the method was implemented as a stand-alone box model to verify that it reproduced the results of the MathCad box model.

To allow for full computation of the chemistry scheme within CALPUFF, the scheme shown in Figure 3.1 was coded into FORTRAN and linked to the DE solver. The Rosenbrock method allows for a full specification of the precision that is required from the solutions. The algorithm is implemented with adaptive step-size so that the initial guess at an appropriate step size is never a sensitive parameter.

This implementation acts as a simple "stepper" from *time=0* to *time = endpoint*, so it provides only results at *time = endpoint* with the user-specified precision. It is possible to extract intermediate results from this implementation too, but comparison of the results at the endpoint with the corresponding results from the analytical solution and MathCad was regarded as a sufficient test of the implementation in this instance.

The code for the FORTRAN box model is provided at Appendix 2 for inspection. The implementation of the DE system is shown in the main program "TROS".

3.6.2 Comparison of the FORTRAN and MathCad Box Models.

Various different implementations of the box models were tested, as shown in Table 3.5 below. These models were run repeatedly with differing constants and time periods, including those described in Section 3.4 above.

Table 3.5 Different Implementations and Cases Tested in the Development Process

Implementation	Description
Implementations with no aqueous phases.	
Gassnova scheme 1.mcd	MathCad. Bulirsch-Stoer method for stiff systems. 5 Species (Amine, AStar, NA, NS, NTP) Fully numerical solution.
Gassnova scheme 2.mcd	MathCad. Bulirsch-Stoer method for stiff systems. 5 Species (Amine, AStar, NA, NS, NTP) Exact analytical solution for Amine(t), other species numerical.
Gassnova scheme 3.mcd	MathCad. Bulirsch-Stoer method for stiff systems. Steady-State assumption for AStar. 4 Species (Amine, NA, NS, NTP) Fully numerical solution.
Gassnova scheme 4.mcd	MathCad. Analytical solution for 3 species steady-state case. 3 Species (Amine, NA, NS)
TROS4a.f90	FORTRAN. Rosenbrock Method. 5 Species (Amine, AStar, NA, NS, NTP) Fully numerical solution.

Implementation	**Description**
Implementations including aqueous phases.	
Gassnova 5.mcd	MathCad. Bulirsch-Stoer method for stiff systems. 7 Species (Amine, AStar, NA, NS, A(aq), NA(aq), NS(aq)) Fully numerical solution. (NTP omitted owing to a limitation in MathCad)
Gassnova 6.mcd	MathCad. Analytical solution for a 2 species sub-system. 2 Species (Amine, A(aq))
TROS4b.f90	FORTRAN. Rosenbrock Method. 8 Species (Amine, AStar, NA, NS, NTP, A(aq), NA(aq), NS(aq)) Fully numerical solution.

In every case the results for all implementations agreed exactly, to within the precision that the implementation allowed, and for those species that were included in that implementation. In the case of the MathCad implementations, the results agreed for all intermediate time intervals and in the case of the FORTRAN implementations, the result at the final time-point agreed with all other implementations.

It is the final FORTRAN module shown above, TROS4b.f90, that forms the final version of the amine chemistry processor and that is incorporated into the modified CALPUFF model.

3.7 Implementation of the Chemistry Solver into CALPUFF

In its native modes, CALPUFF performs certain chemical transformations on the species that are normally considered in a CALPUFF application. DNV has expanded that list of species to accommodate amine atmospheric chemistry and expanded the FORTRAN routine that performs the chemical transformations. In particular, the FORTRAN method discussed in Section 3.6 above is added to the CALPUFF code as an additional module. The parts of the code that are required for the amine chemistry modelling are activated by a switch in the CALPUFF input file (MCHEM=8).

The FORTRAN box model is converted into a CALPUFF module by converting its main program into a subroutine that accepts inputs from the CALPUFF chemistry module and passes results back to that module. The main subroutines that participate in the amine chemistry are shown with brief descriptions in the following table.

Table 3.6 Amine Chemistry Subroutines in the DNV-modified version of CALPUFF

Subroutine Name	**Relative Level in code structure**	**Description**
<Higher Levels in CALPUFF>	1 (by definition)	Main body of CALPUFF code, handling user input, initialisation, dispersion and results reporting. DNV-modified only for "admin" purposes to allow new MCHEM=8 option.
CHEM	2	Main chemistry subroutine. Code-technical changes only. Calls CHEMI and CHEMRIV8.
CHEMI	3	Initialisation for chemistry modules. Reads user input for chemistry required. Minor changes.
CHEMRIV8	3	Preliminary work for chemistry. Gathers species information for each puff from CALPUFF as well as relevant met data. Calls CHMRIV8
CHMRIV8	4	Main chemistry subroutine, including amine chemistry. Performs all the conventional CALPUFF chemical transformations and calls Amine DE solver. Calls TROS4.
TROS4	5	The Amine DE solver. Defines the DE system and sets up the Rosenbrock method and sets time step required and stopping conditions. Reports success/failure condition back to CHMRIV8 as well as the results. Calls further subroutines.
<Rosenbrock Method subroutines>	6+	Further subroutines of the Rosenbrock method (standard library code). Includes the adaptive stepsize layer and the algorithm itself.

The parts critical to the implementation of the amine chemistry scheme into CALPUFF are in the routines CHMRIV8 and TROS4.

With the amine chemistry option (MCHEM=8) turned on, CALPUFF tracks 16 species in total, eight of which are the active amine chemistry participants. One other is the inert "tracer" compound that is assumed to be emitted at the same rate as the amine under consideration with the same molar mass. The purpose of this tracer is to allow the consideration of the effect of dispersion only by the inclusion of a compound that does not participate in any chemistry processes.

CHMRIV8 prepares the species list, selecting from the main list of species the eight that are to be submitted for processing with the Rosenbrock method using the amine chemistry scheme. CHMRIV8 then submits a call to TROS4 for each dispersion "puff". In particular, Table 3.7 shows the data that is passed between CHMRIV8 and TROS for each puff.

Table 3.7 Data passed between CHMRIV8 and TROS4.

Data	Comments
The initial concentrations of the 8 species that participate in the amine chemistry.	CHMRIV8 converts concentrations from grams / puff (the units used in higher CALPUFF levels for dispersion) to molecules.cm^{-3}.
The time-step required.	In hours, converted to seconds by TROS4. This is a variable quantity determined by the dispersion routines.
The cosine of the zenith angle of the sun at this time.	Scalar, computed by CALPUFF. Used for the calculation of the OH radical concentration and other parameters as described in the sections above.
Concentrations of NO, NO_2 and OH radicals as computed by CALPUFF.	The NO and NO_2 concentrations passed here are the concentration resulting only from the emissions at the source. Background concentrations are added by TROS4 as discussed in Section 2.3. The concentration of OH radicals is not used at present, but is included in the parameter list in case a future change is required to re-link the OH-modelling to the in-built CALPUFF methods. At present, the OH radical concentration is determined by TROS according to the methods described in Section 2.3.
Success / failure flag	Boolean. The Rosenbrock method generates a success or failure flag that is passed upwards to CHMRIV8. The processing run halts if this flag is ever set to failure.
The final concentrations of the 8 species that participate in the amine chemistry.	The concentration of the species after the passing of *time-step* as determined by the system of DEs and the Rosenbrock method is passed upwards to CHMRIV8.

Finally, the results from TROS4 are converted back to the units used by CALPUFF and go on to participate in the dispersion routines of standard CALPUFF.

4 RESULTS AND DISCUSSION

This section summarises the results obtained from the modified version of CALPUFF and the interpretation of these results.

Consistent with previous work /2/, CALPUFF outputs results in the form of airborne concentrations for each species at ground level at every point on a 140×140 grid with regular spacing of 500m. This results in too much data to tabulate exhaustively. Instead the results are displayed in two ways in this report. The following results are shown for the two main case studies (described in Section 4.1):

- Firstly, the full results are displayed as a contour plot of annual average ground level concentration.
- Secondly, the annual average ground level concentrations are shown graphically as a function of distance from the source, along a line drawn from the source to a point on the edge of the study area North-West along the main plume (see Figure 4.1). For

comparison with the contour plots, the coordinates of the point furthest from the source are (x=600km, y=6780km). The source itself is at (x=610.9km, y=6743.2km).

It should be noted that annual average meteorological conditions for 2009 are applied to all of the case calculations, consistent with previous work /2/. Thus, although the concentration plots with distance will tend to correspond with increasing time, the correspondence will not be exact.

4.1 Description of Case Studies

Table 4.1 summarises the key inputs and assumptions for the first two case studies presented in this report.

Table 4.1 Summary of Case Studies Presented for Case A and Case B

Case Name	Case A	Case B
General features	**Low impact** case	**High impact** case
Emissions	**Light primary amine** (50 g/mol) emitted at 1ppm.	**Heavy secondary amine** (100 g/mol) emitted at 1ppm.
	NO emitted at 4.62ppm	NO emitted at 4.62ppm
	NO_2 emitted at 0.502ppm	NO_2 emitted at 0.502ppm
	No nitrosamine or nitramine emitted	No nitrosamine or nitramine emitted
	Nothing emitted in the aqueous phase.	Nothing emitted in the aqueous phase.
Solubility properties	**Fast equilibration** of amine, nitramine and nitrosamine to aqueous phase during dispersion with **high transfer** (R_e = 0.1) .	**Fast equilibration** of amine, nitramine and nitrosamine to aqueous phase during dispersion with **low transfer** (R_e = 0.0001) .
Reactivity with OH radicals	$k_1 + k_{11}$ = **3.0E-11 cm^3 $molecule^{-1}$ s^{-1}**	$k_1 + k_{11}$ = **9.0E-11 cm^3 $molecule^{-1}$ s^{-1}**
	20% branching to amine radical A* for reaction with OH·	**50% branching** to amine radical A* for reaction with OH·
Reactivity with NO_3 radicals	$k_{10} + k_{12}$ = 2.0E-13 cm^3 $molecule^{-1}$ s^{-1}	$k_{10} + k_{12}$ = 2.0E-13 cm^3 $molecule^{-1}$ s^{-1}
	20% branching to amine radical A* for reaction with NO_3·	**50% branching** to amine radical A* for reaction with NO_3·
Reactions of NS	k_6 is as described in Section 2.3 k_{13} = 1.91E-02 s^{-1}	k_6 is as described in Section 2.3 k_{13} = 0.0 s^{-1}

The chief differences between these case studies are as follows.

- Case B has a faster overall reaction rate for amine ($k_1+k_{11}+k_{10}+k_{12}$).
- Case B has a higher branching ratio to the amine radical that leads to the compounds of interest.
- Case B allows far less transfer to the aqueous phase for the source amine, which will reduce the "buffering" effect of the aqueous phase (since no amine chemistry takes place in the aqueous phase).

- Case B represents a secondary amine, which will lead to a stable nitrosamine. Case A is a primary amine whose resulting nitrosamine will be subject to fast intra-molecular rearrangement (represented by the k_{13} reaction in the presently modelled scheme).
- The amine emitted in Case B has a higher molecular weight and therefore a higher mass emission rate is required to ensure that the volumetric concentration emitted is the same for Case A and Case B.

These differences lead to the anticipation of higher peak concentrations of harmful products (NA, NS) for Case B relative to Case A. This anticipated result was observed, see Table 4.3 and Table 4.4 below. DNV notes that Case B contains a number of assumptions that probably represent the "worst case".

4.2 Emissions Modelled

Table 4.2 details the emission rates as modelled by DNV for the Cases A and B described above. These emission profiles are as agreed with CCM Project.

Note that these emissions assumed that example amines of particular molecular weight would be emitted. These example amines do not correspond to particular real amines but serve as high and low impact examples only. The chemistry scheme is such that a different assumption could be made and the dispersion and chemistry of different (real) source amines could be modelled by simple alterations in the input parameters, namely the molecular weight of the species and the adjustment of the rate constants as appropriate.

Note also that the compound "tracer" is a theoretical construct, defined to be a species that is completely inert chemically and that is emitted at the same rate as the source amine and with the same molecular weight. Its inclusion helps the interpretation of the results as explained below.

Table 4.2 CHP Emission Profile for Case Studies A and B

Species Name	**Formula**	**Molecular Weight (g/mole)**	**Emission Rate (g/s)**	**Emission Concentration (ng/m^3 at 30^{o}C)**
Nitric oxide	NO	30	3.72	5570937
Nitrogen dioxide	NO_2	46	0.62	928489
Light primary amine (Case A)	n/a	50	1.343	2011228
Inert tracer (Case A)	n/a	50	1.343	2011228
Heavy secondary amine (Case B)	n/a	100	2.685	4020958
Inert tracer (Case B)	n/a	100	2.685	4020958

The concentrations in Table 4.2 assume an exit height of 65m, an exit velocity of 20m/s, an absorber stack diameter of 6.52m and an exit temperature of 30°C.

Unless otherwise stated, all input data used, such as terrain data, land use data, meteorological data, etc., is as described in the Phase 1 report /2/.

4.3 Results: Contour Plots of Annual Average Ground Level Concentration

CALPUFF produces a figure for the airborne concentration of each modelled species for every location on a user-defined grid for every hour in the time period modelled. The present results represent modelling that used the meteorological states for the entire year of 2009.

Where a result is quoted for a particular location, or in the contour plots that follow in this section, the result presented is the ground level concentration of the species under consideration, averaged over the entire year at that location. These results are appropriate for consideration against the long term environmental criteria discussed in Section 4.7 below.

Where a result is presented with no geographical location, such as in Table 4.3, it is either the peak value (i.e. the largest annual average observed over the entire geographical grid) or the average value (i.e. the average over the geographical grid of the annual averages). From the regulatory perspective, only the peak value is of importance because if the peak concentration is lower than the regulatory criterion, then the concentration is lower than that criterion at all locations. However the difference between the peak value and the average value within an area provides information on how widespread is the peak concentration and thus has some value when interpreting the results presented in tabular form.

4.3.1 Results Summarised for the Entire Study Area

Table 4.3 and Table 4.4 summarise the results for Case A and Case B.

Table 4.3 Summary of Results for Cases A and B

		A (ng/m^3)	NA (ng/m^3)	NS (ng/m^3)	A(aq) (ng/m^3)	NA(aq) (ng/m^3)	NS(aq) (ng/m^3)
Case A	Peak	50.6	0.0374	0.000749	3.54	0.00316	0.0000489
	Average	1.81	0.00716	0.0000122	0.199	0.000775	0.00000133
Case B	Peak	103	0.426	0.0606	0.00683	0.0000322	0.00000417
	Average	3.44	0.0616	0.00430	0.000341	0.00000600	0.000000418

Note the concentration of the aqueous species are in arbitrary units because the amount of available moisture is unknown

It is of particular interest where in the study area the peak concentrations are observed. In all cases, because of the dispersive effect of the atmosphere the peaks are close to the emission source, but there is some variation in distance from the source.

Table 4.4 Cases A and B. Location of peak concentrations

	Amine		**NA+NS+NA(aq)+NS(aq)**	
	Peak value (ng/m^3)	**Distance from source / km**	**Peak value (ng/m^3)**	**Distance from source / km**
Case A	50.6	0.80	0.0414	0.34
Case B	103	0.80	0.486	0.34

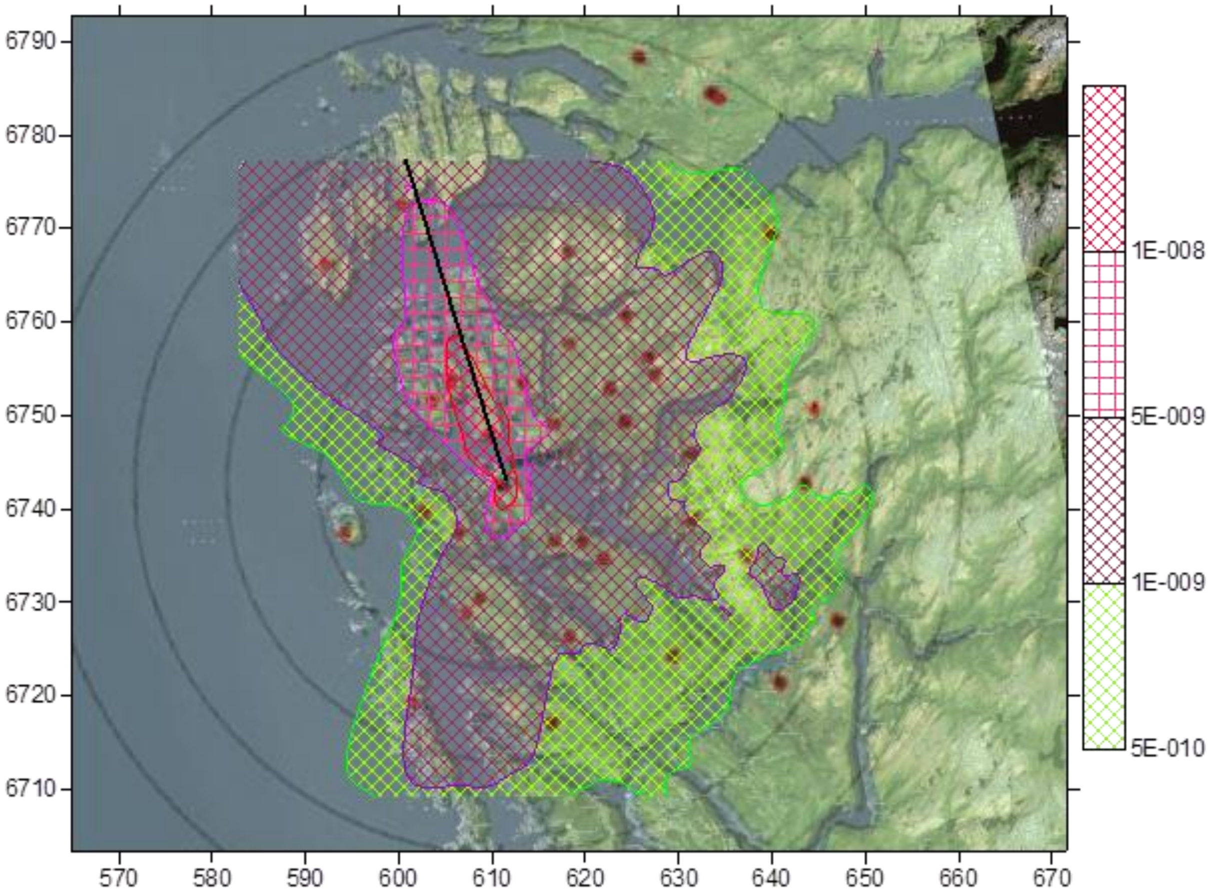
The location of the peak values can also be seen in the contour plots in the following sub-section.

4.3.2 Results Presented as Contour Plots

In the series of figures below, ground level annual average contour plots are shown for the species amine and the sum of all the harmful compounds (NA+NS+NA(aq)+NS(aq)) for Cases A and B.

Figure 4.1 includes an underlay showing the geographical location and context. The thick black line in Figure 4.1 indicates the line along which results are sampled for presentation in Section 4.4.

Figure 4.1 General Layout for Results Presentations. Illustrative example only



The contour plots that follow show real results for Case A and Case B.

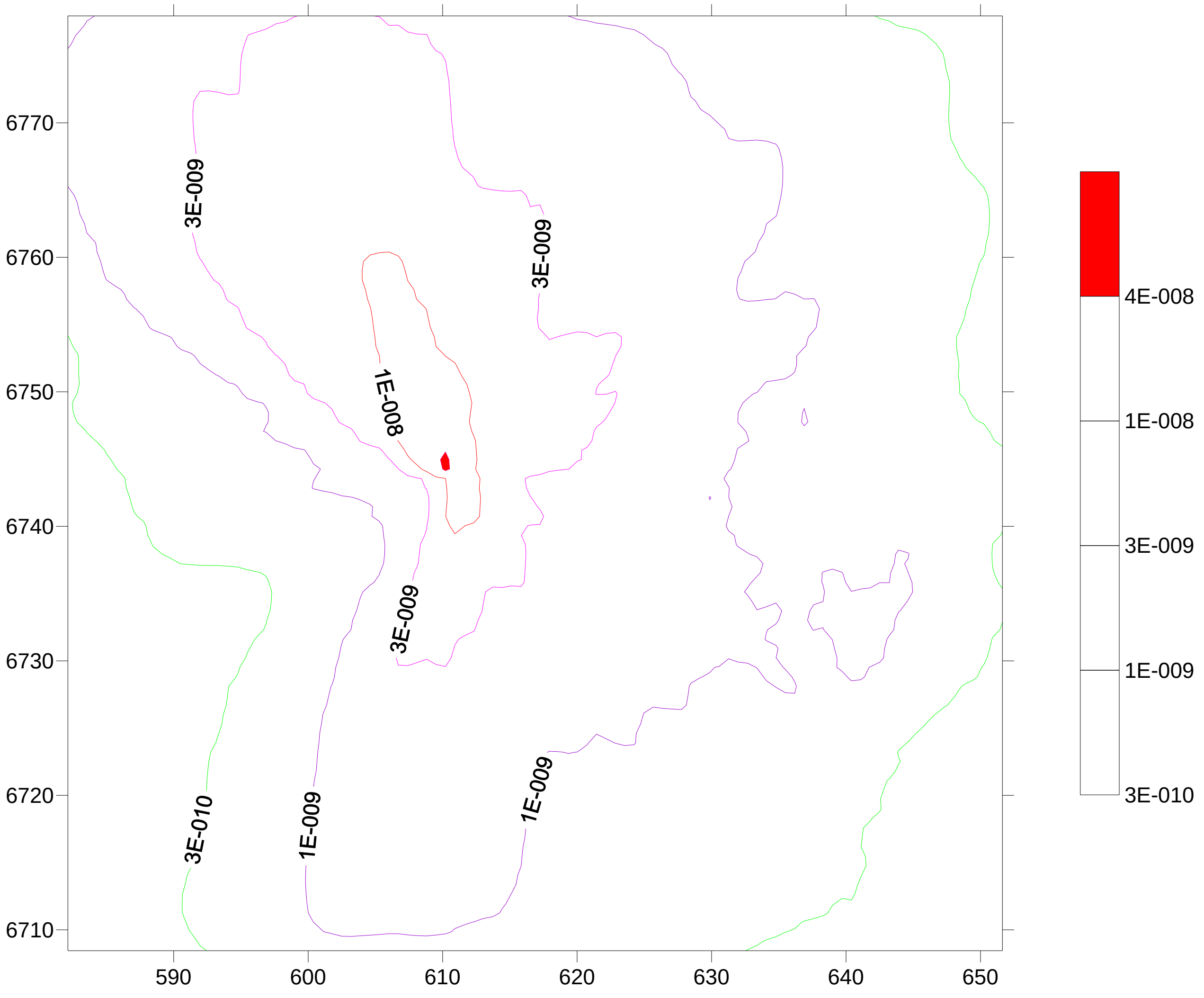
Please note that all the contour plots presented in this report have units of g/m^3 and the x and y scales are in kilometres.

4.3.3 Results: Contour Plots for Case Study A

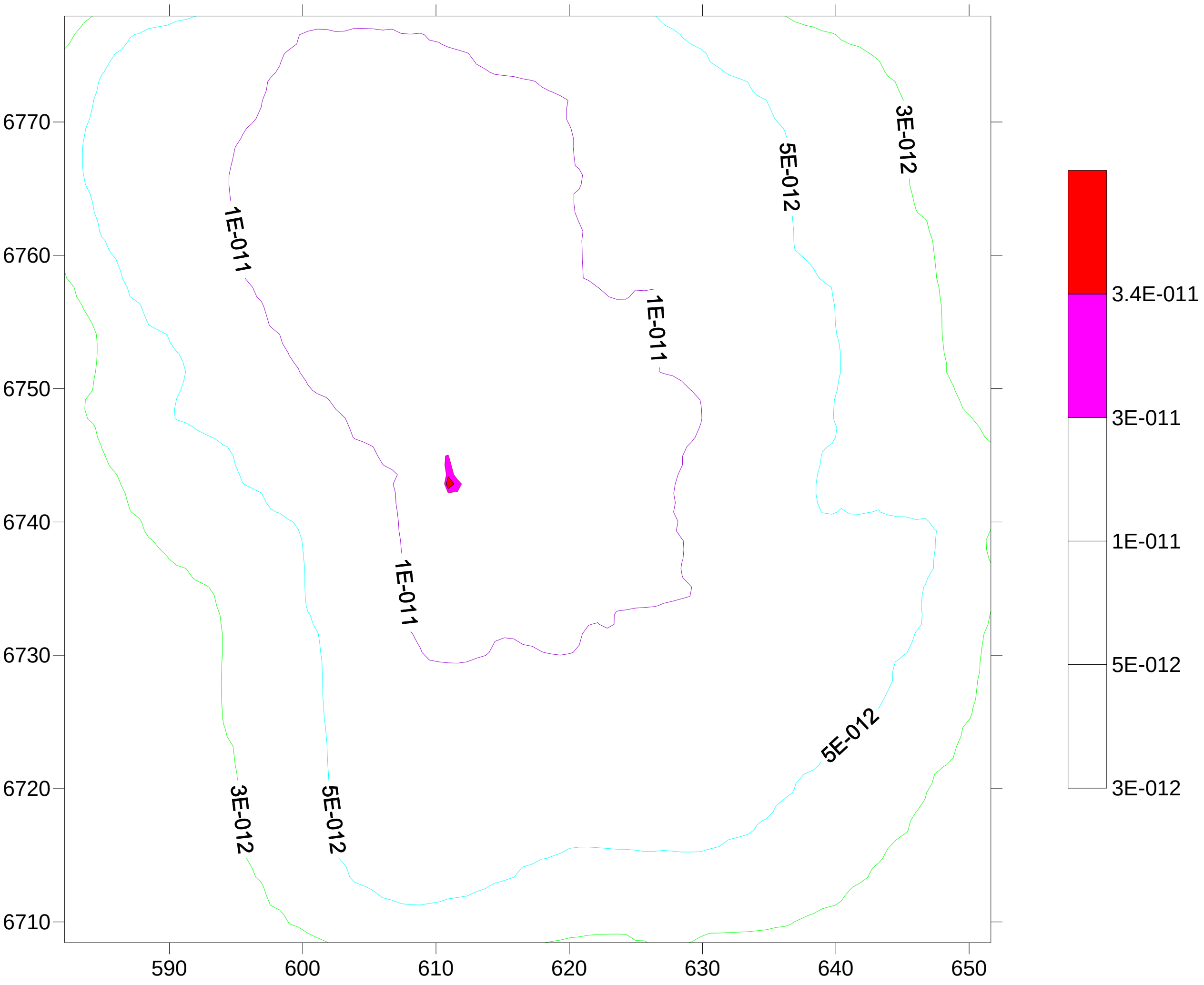
In all the plots in this section, and in all contour plots in this report, the source is located at x=610.9km, y=6743.2km.

Species: **Amine**

Average: 1.81 ng/m^3 Maximum: 50.6 ng/m^3



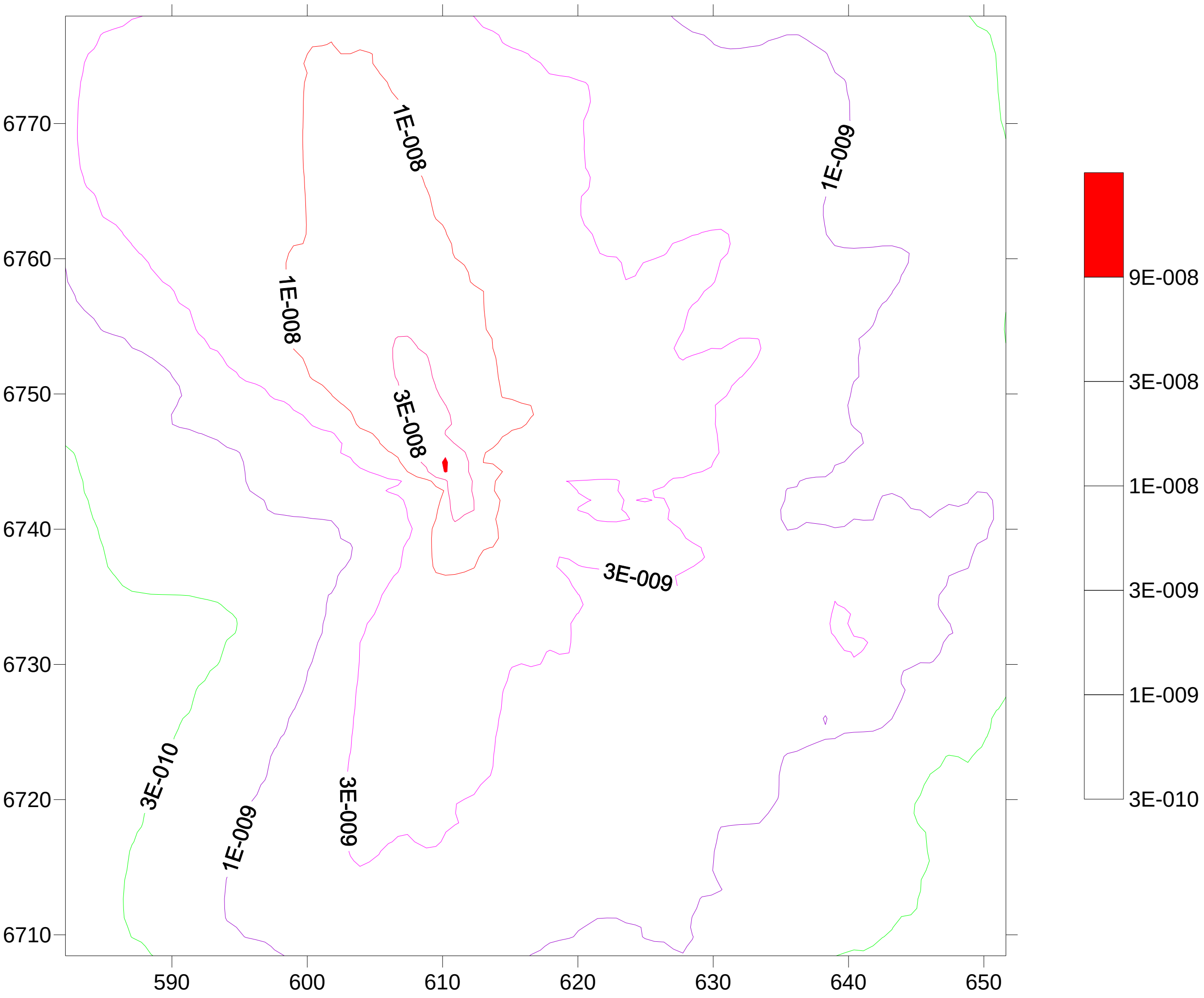
Species: **Nitramine(g)+Nitrosamine(g)**
Average: 0.00717 ng/m^3 Maximum: 0.0381 ng/m^3



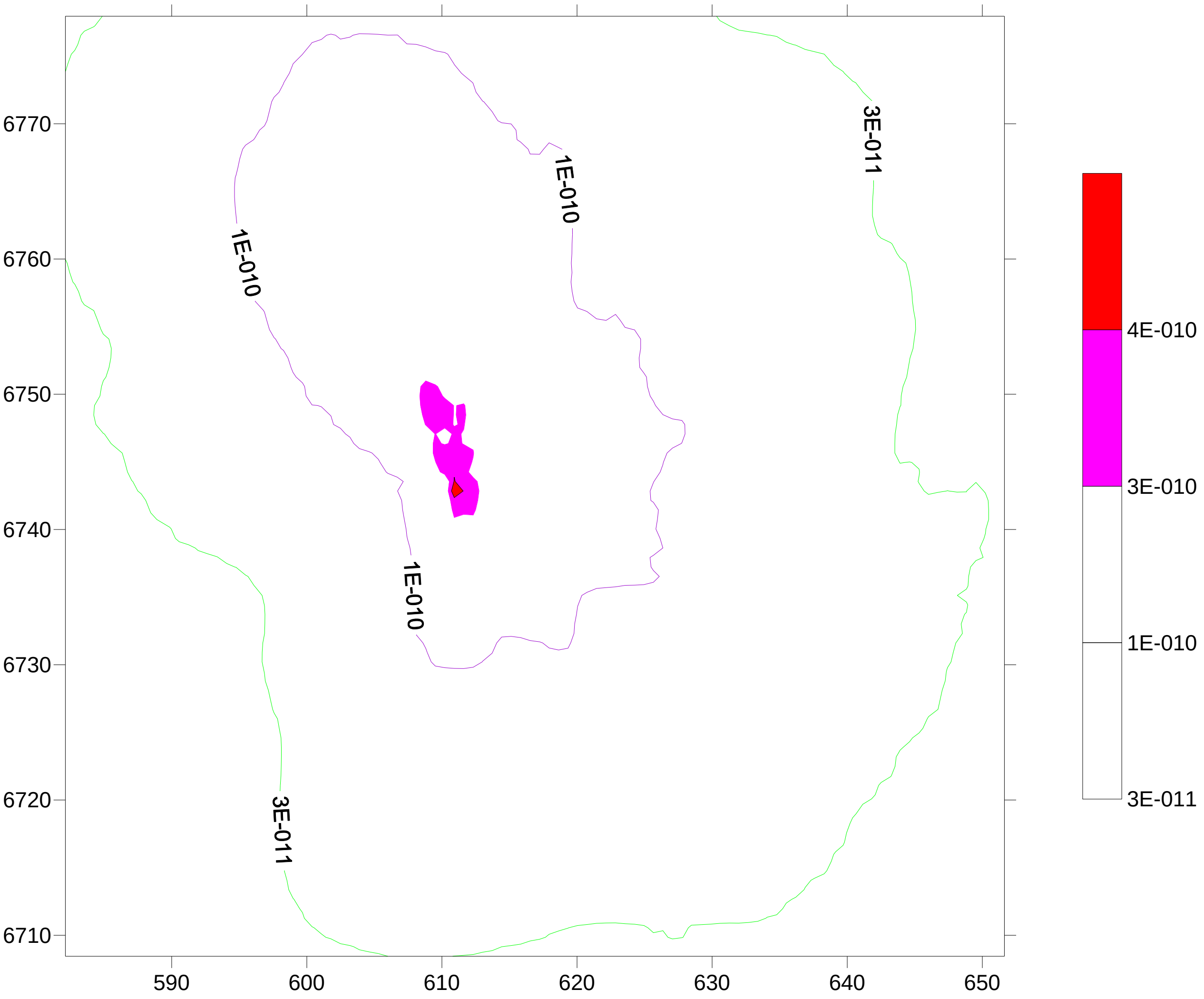
4.3.4 Results: Contour Plots for Case Study B

Species: **Amine**

Average: 3.44 ng/m^3 Maximum: 103 ng/m^3



Species: **Nitramine+Nitrosamine (g)**
Average: 0.0659 ng/m^3 Maximum: 0.486 ng/m^3



4.4 Results: As Function of Distance from Source

In order to more easily compare the results from the modified CALPUFF model with the results from the box models (concentration with time), the full gridded results were sampled along a line drawn from the source to a point at the boundary of the study area approximately along the line of the main plume over the annual average weather conditions (see Figure 4.1). These results are shown in the sequence of figures below. Note that the concentrations of the inert "tracer" compound are shown in each case, showing the effect of dispersion alone.

For each case study, two groups of figures are shown:

- Unmodified concentration.
- Concentration divided by the dilution factor. The dilution factor, shown in Table 4.5, is the extent to which the tracer compound has been diluted by dispersion alone compared to

the first location on the plume centreline. These results *estimate* the effect of the chemistry in isolation.

Table 4.5 Observed dilution factor as a function of distance from the source

Distance / km **(at ground level unless otherwise stated)**	**Concentration of the tracer compound (g/m^3) (for Case A)**	**Dilution factor (relative to 0km mark)**	**Dilution factor (relative to emission)**
At stack mouth, 65m above ground level	2.01E-03	n/a	1.00E+00
0, at ground level	2.98E-08	1.00E+00	1.48E-05
1	5.08E-08	1.70E+00	2.53E-05
2	4.09E-08	1.37E+00	2.04E-05
3	2.92E-08	9.77E-01	1.45E-05
4	2.47E-08	8.29E-01	1.23E-05
5	2.90E-08	9.70E-01	1.44E-05
10	1.93E-08	6.47E-01	9.60E-06
15	1.37E-08	4.59E-01	6.82E-06
20	1.06E-08	3.57E-01	5.29E-06
25	8.56E-09	2.87E-01	4.26E-06
30	6.98E-09	2.34E-01	3.47E-06
35	5.20E-09	1.74E-01	2.59E-06

Table 4.5 shows that the assumed 65m stack achieves dilutions in excess of about 40,000 for all locations sampled along the plume centreline compared to the concentration at the stack exit.

4.4.1 Results: By Distance for Case Study A

In each of the following figures, the horizontal axis is the distance from the source in kilometres and the vertical axis is the species annual average ground level concentration in g/m^3. Note that in some figures the concentration of some species is obscured by others.

Case Study A. Concentration Results

Figure 4.2 Case Study A: Concentration, Tracer and Amine

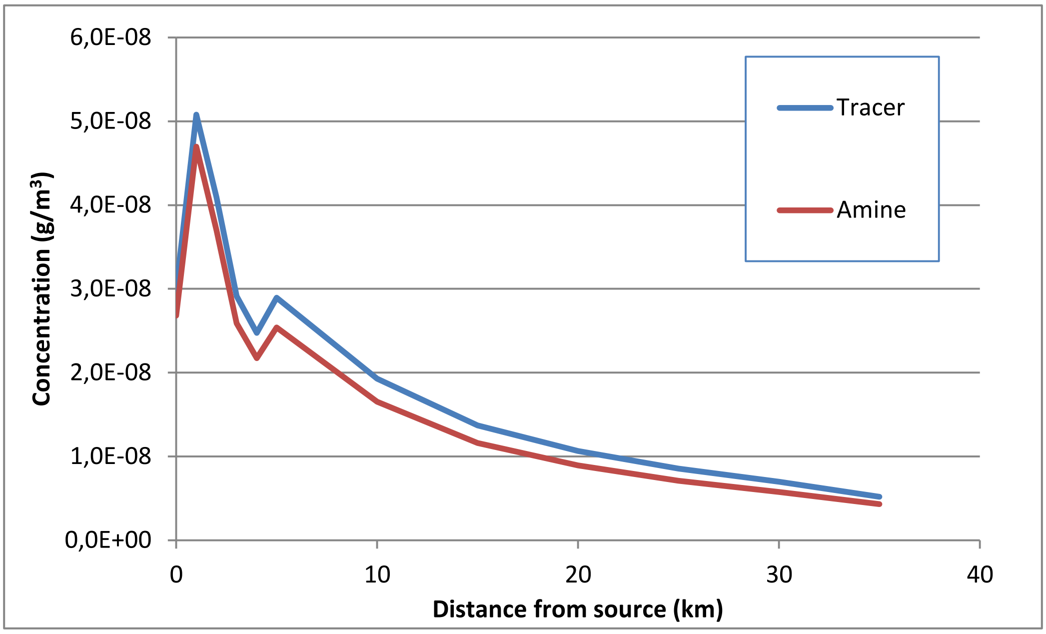


Figure 4.3 Case Study A: Concentration, NTP and Amine(aq)

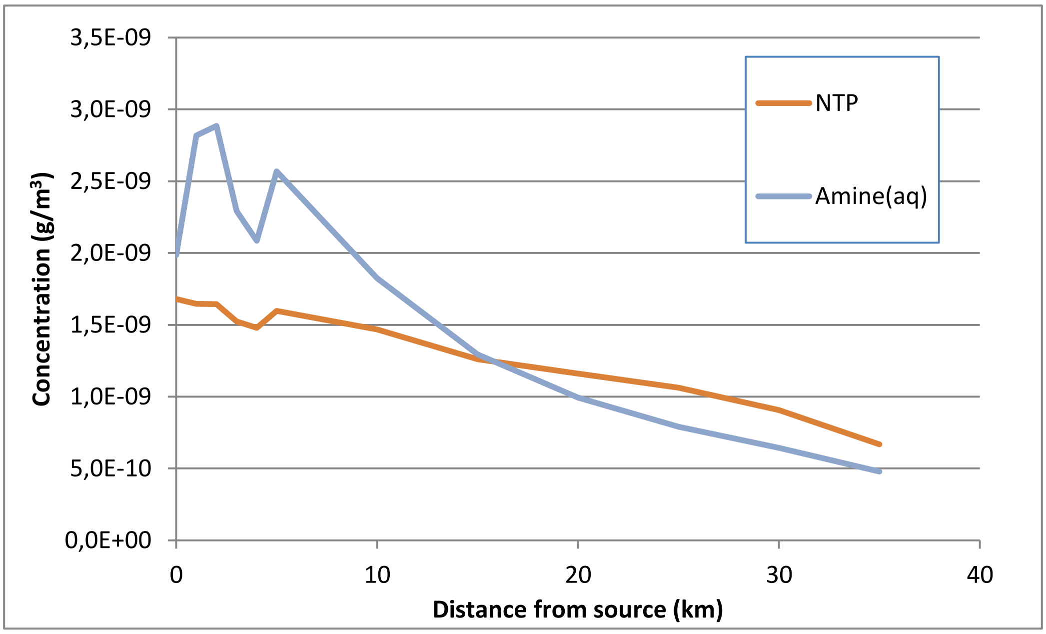


Figure 4.4 Case Study A: Concentration, NA and NA(aq)

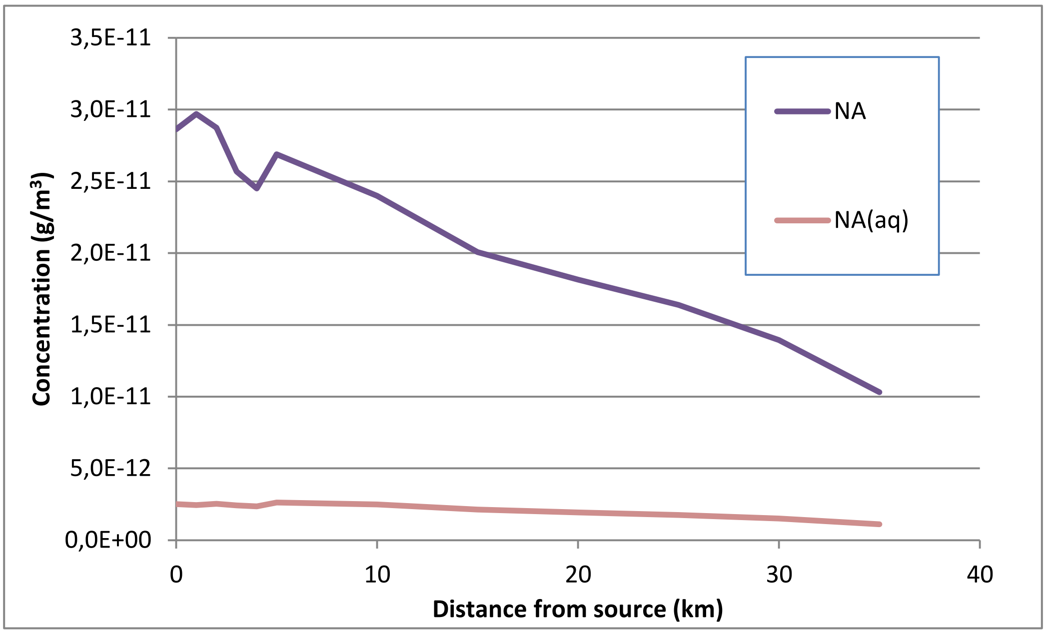
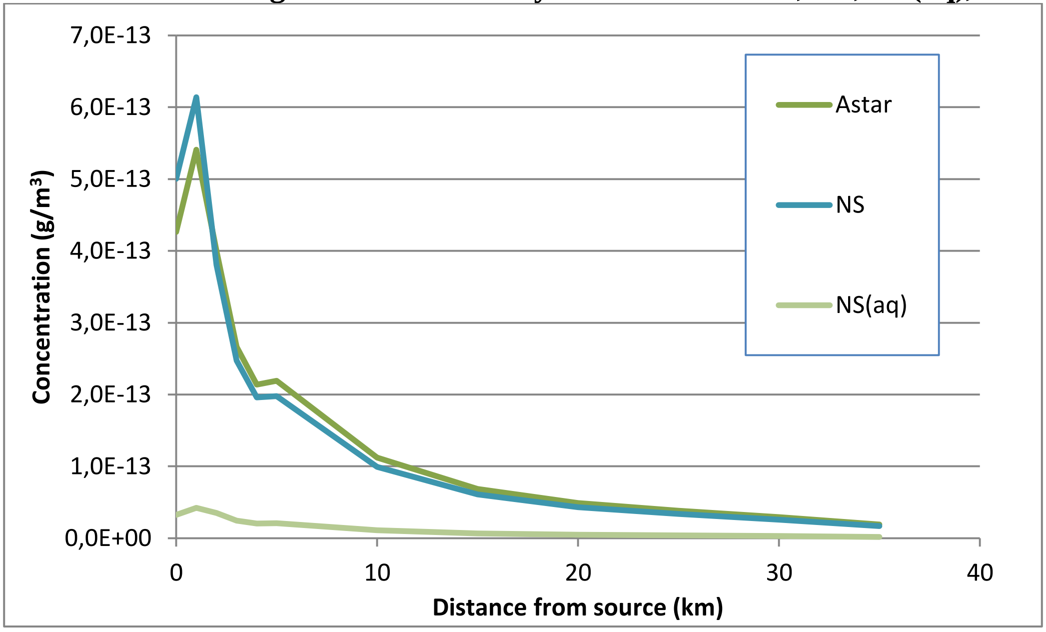


Figure 4.5 Case Study A: Concentration, NS, NS(aq), A*



Case Study A. Dilution-corrected Results (relative to ground level concentration at 0km)

Figure 4.6 Case Study A: Dilution-corrected, Tracer and Amine

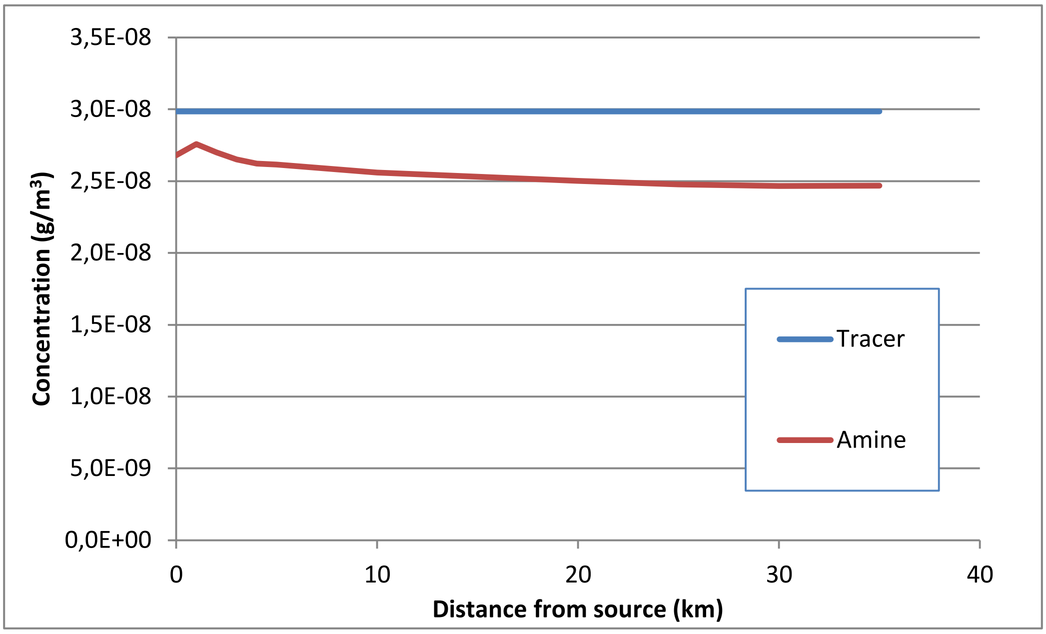


Figure 4.7 Case Study A: Dilution-corrected, NTP and Amine(aq)

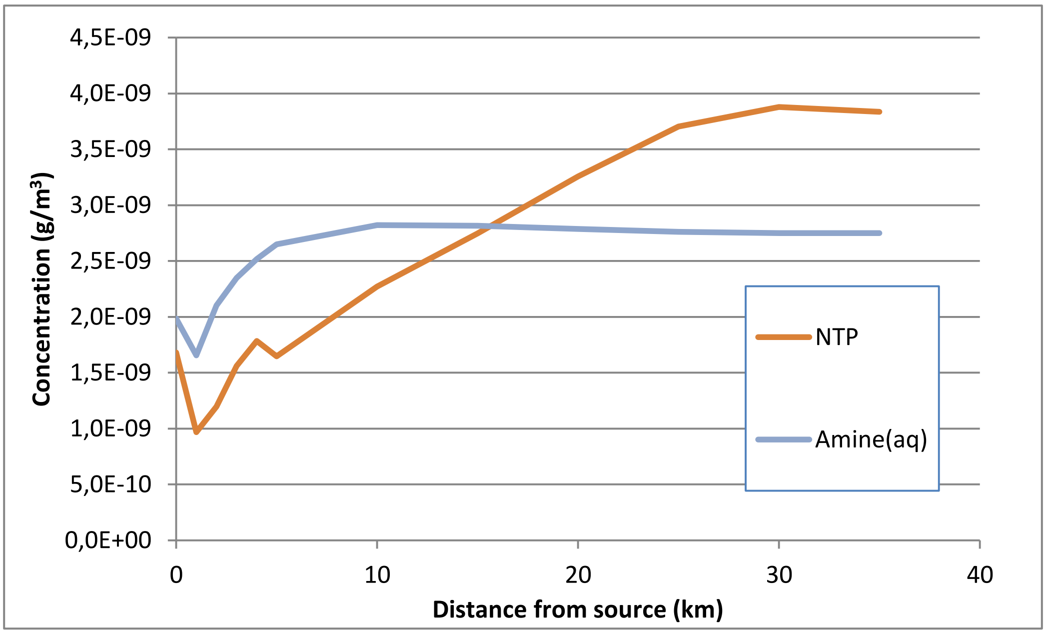


Figure 4.8 Case Study A: Dilution-corrected, NA and NA(aq)

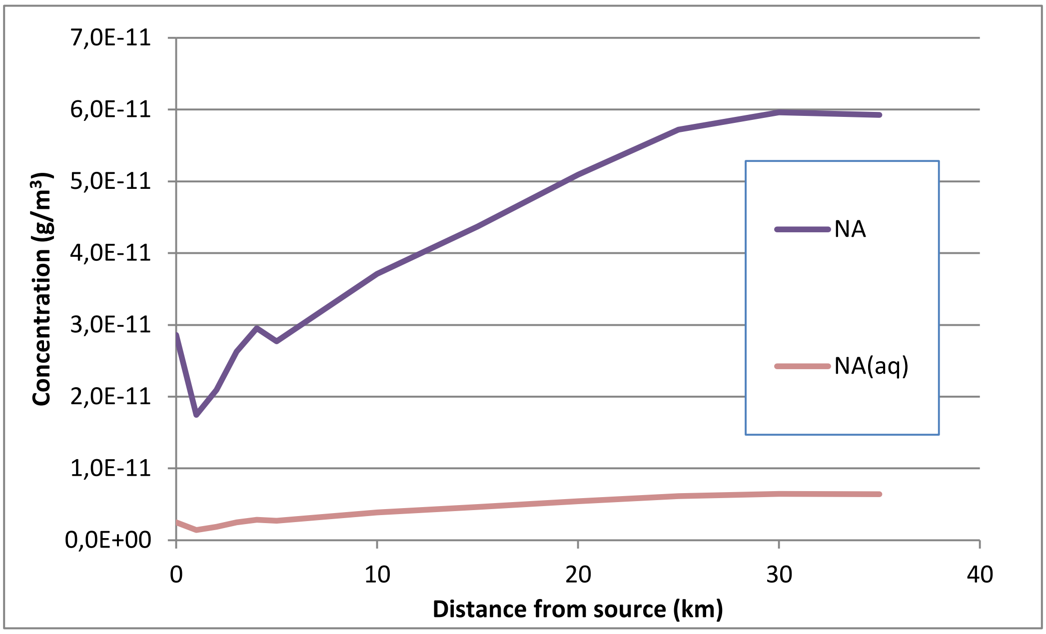
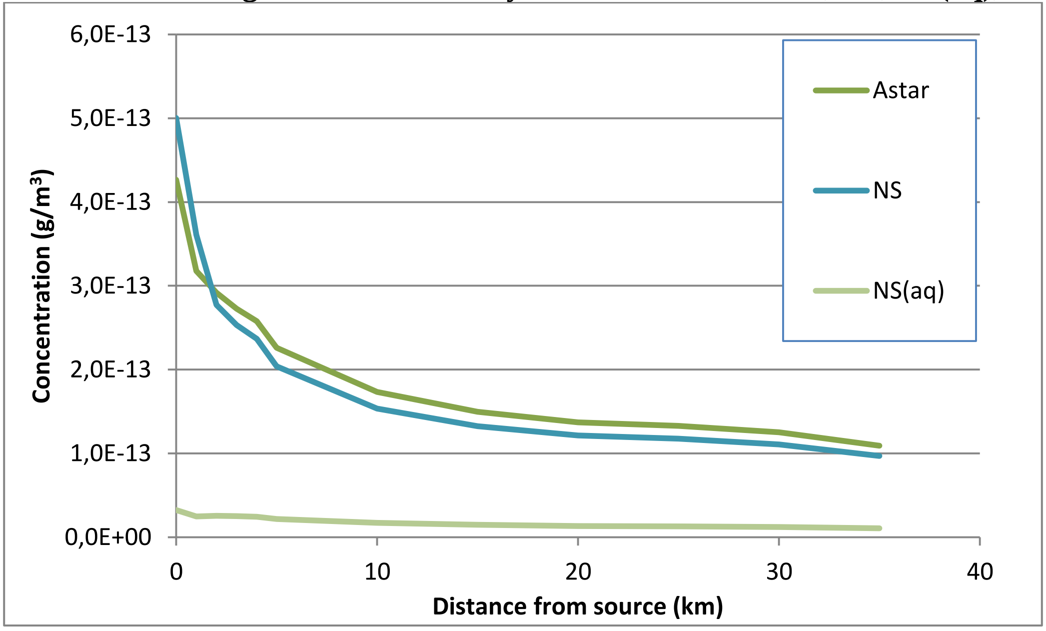


Figure 4.9 Case Study A: Dilution-corrected, NS, NS(aq), A*



4.4.2 Results: By Distance for Case Study B

Case Study B. Concentration Results

Figure 4.10 Case Study B: Concentration, Tracer and Amine

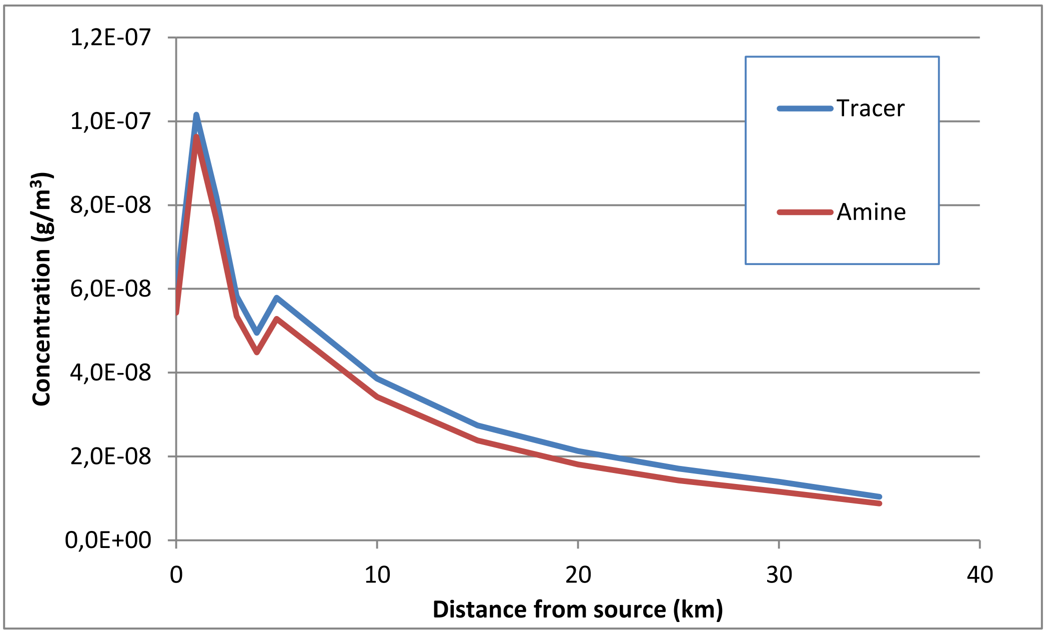


Figure 4.11 Case Study B: Concentration, NTP and Amine(aq)

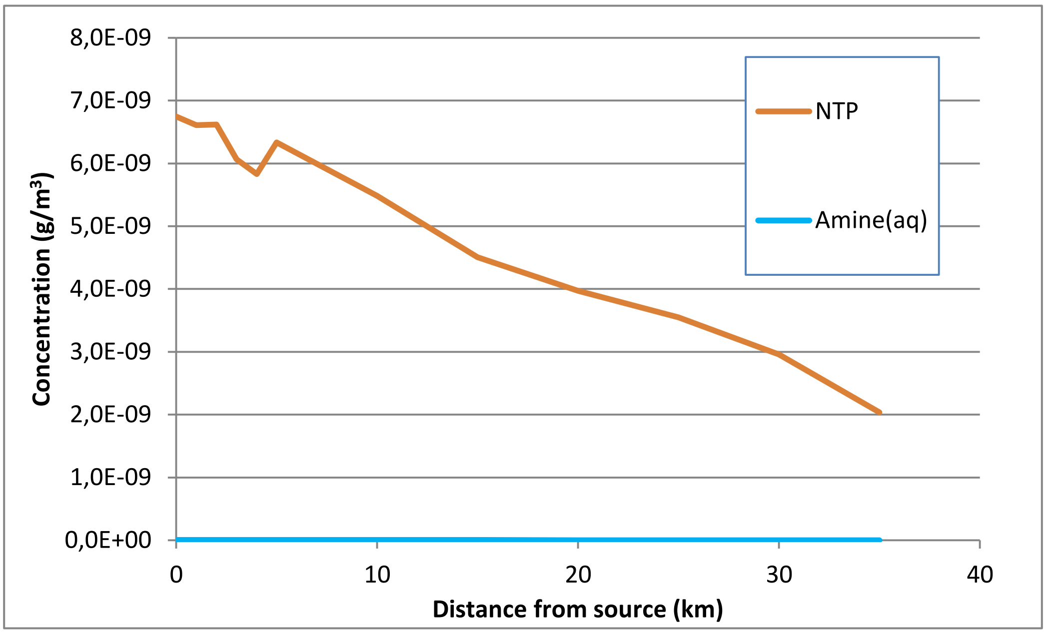


Figure 4.12 Case Study B: Concentration, NA and NA(aq)

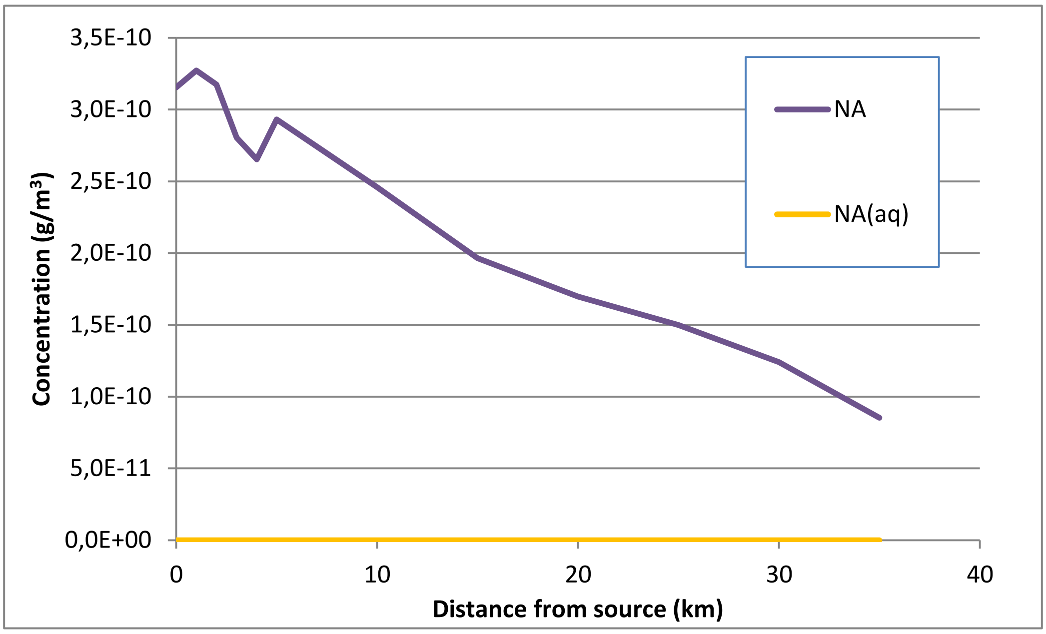
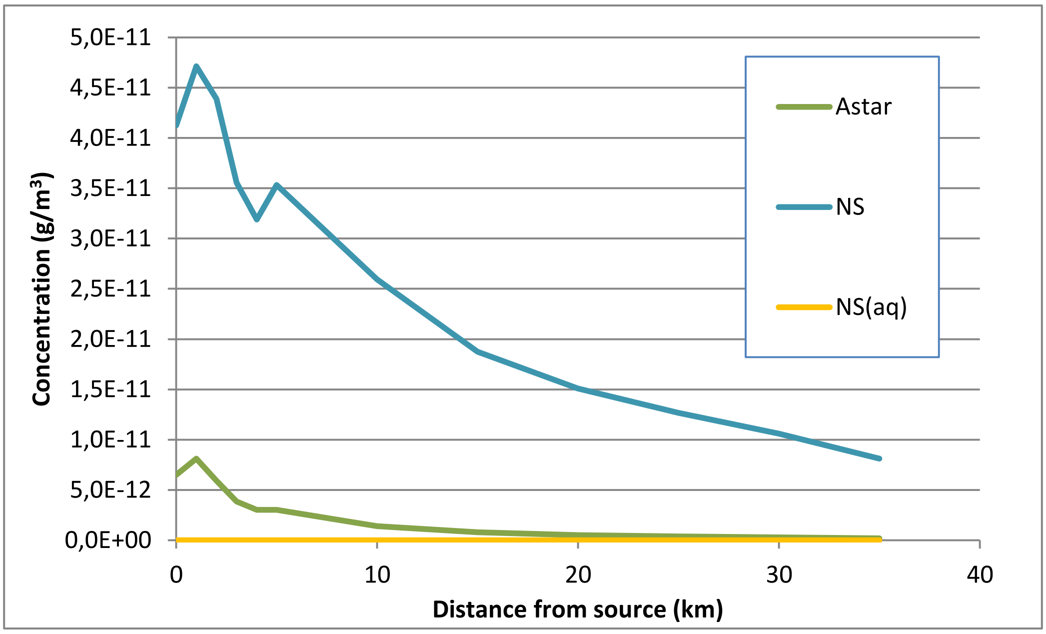


Figure 4.13 Case Study B: Concentration, NS, NS(aq), A*



Case Study B. Dilution-corrected Results (relative to ground level concentration at 0km)

Figure 4.14 Case Study B: Dilution-corrected, Tracer and Amine

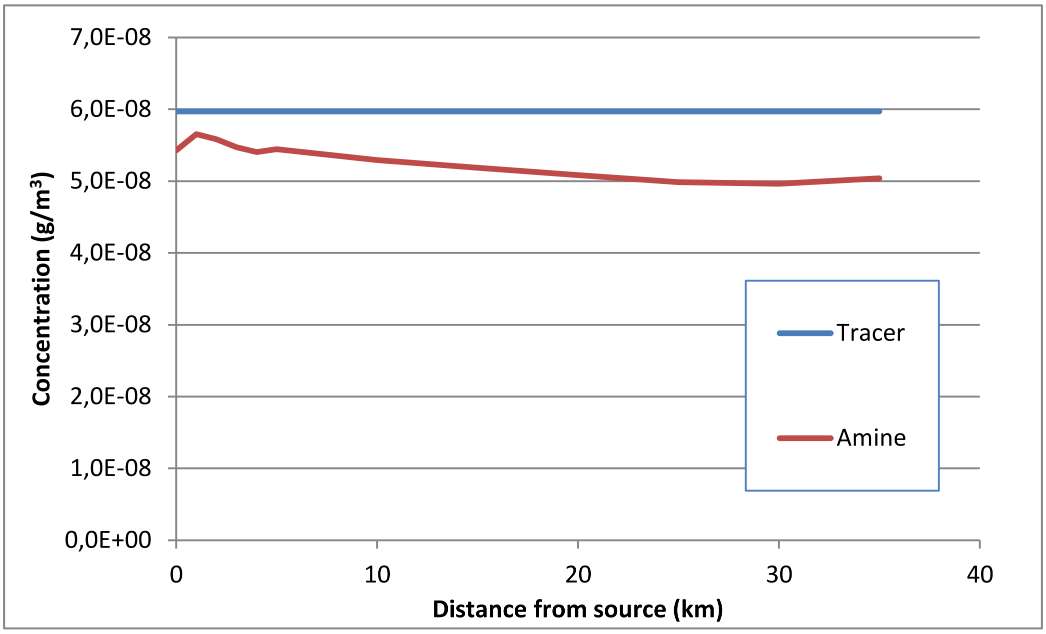


Figure 4.15 Case Study B: Dilution-corrected, NTP and Amine(aq)

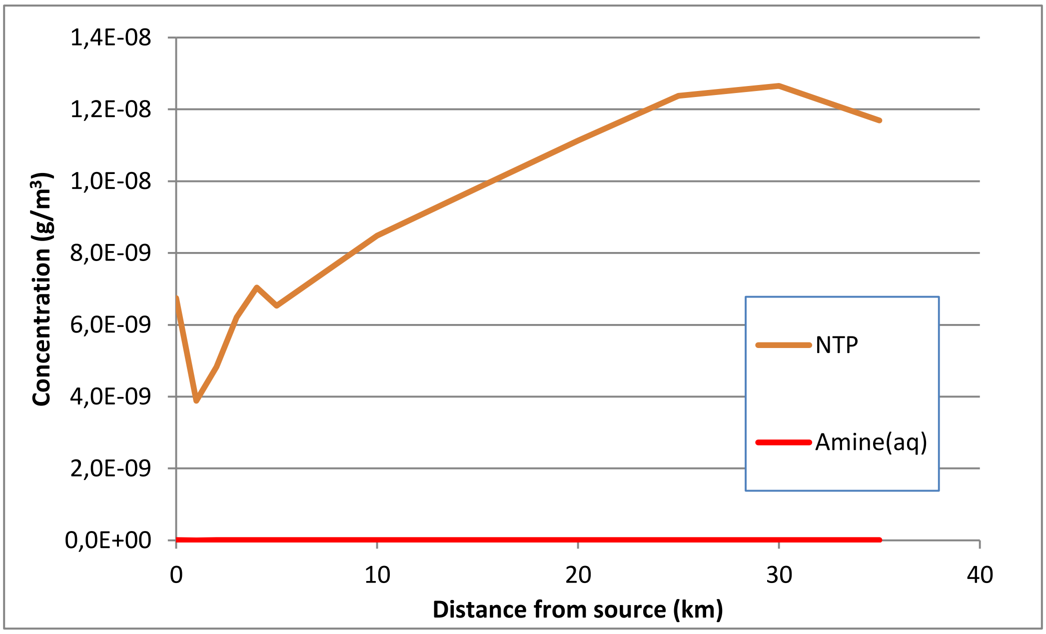


Figure 4.16 Case Study B: Dilution-corrected, NA and NA(aq)

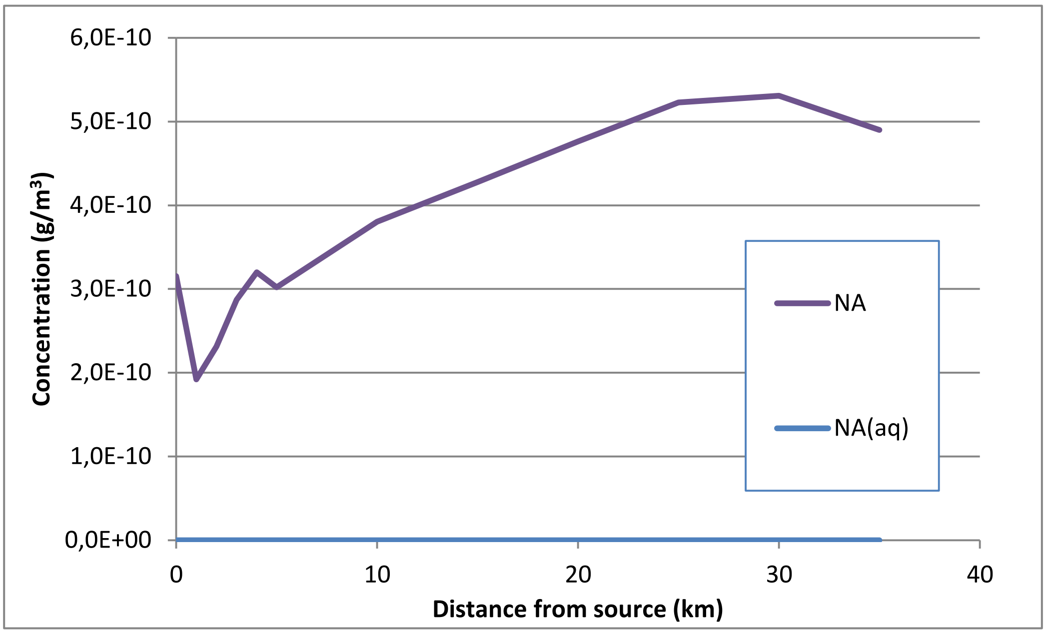
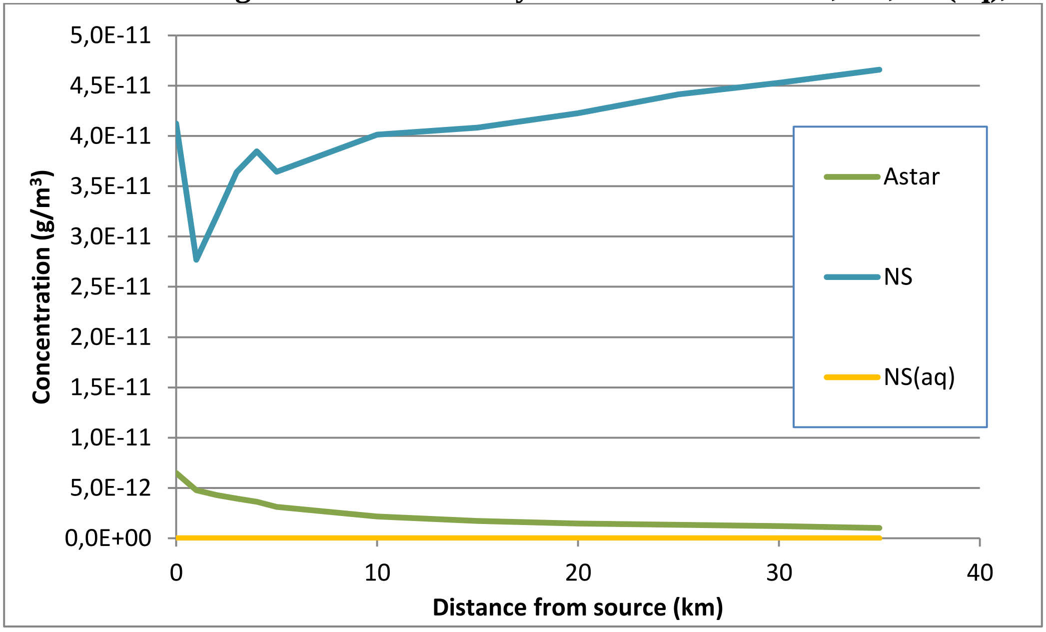


Figure 4.17 Case Study B: Dilution-corrected, NS, NS(aq), A*



4.5 Discussion of General Appearance of Results

The display of the results as a function of distance reveals more information about the chemical processes modelled so most of the discussion in this section will be based on the concentration vs. distance figures shown in Section 4.4.

One of the intentions behind showing the results in this way was to gain some insight into the progression of the chemistry with respect to time. This is of interest because the box model results are with respect to time rather than distance from a source. It is clear that because of the dispersive forces at work, there is a correlation between time and distance from the source in CALPUFF, although it has not been possible so far to extract data to establish how firm that correlation is. From a physical point of view however, it is clear that it must (in general) take longer for a species to be transported to a ground location far from the source than to one close to it. In uniform conditions of constant wind at all vertical levels, this relationship would be one-to-one and linear. The present results were averaged over a full year's worth of real meteorological data however and therefore the real relationship between distance from the source and the time elapsed since emission is less clear. However, DNV considers that the distance from the source is a useful surrogate for time since emission when considering the changes in the concentrations due to chemistry.

4.5.1 General Comments on the Concentration Profile Plots

Before discussion of the detailed results it is important to first note two specific observations seen in the plots in Section 4.4. In some of the dilution-corrected plots, the concentration curve reduces in the far field, see for example NTP in Figure 4.7. The chemistry scheme (Figure 2.2) cannot result in a loss of NTP by chemical reaction, so DNV conclude this must be some form of model edge effect (the final point is at the edge of the study boundary). DNV note that the effect is also seen slightly for the tracer species in the uncorrected concentration profiles (e.g. Figure 4.2 and Figure 4.10). The tracer does not undergo chemical transformation. It is concluded that this effect is a native characteristic of CALPUFF and is unrelated to DNV's new chemistry calculations.

Some superficially odd observations are also seen in the near field profiles (e.g. Figure 4.2 and Figure 4.10). The concentrations rise and fall as expected, then rise and fall again. DNV's first idea was that this was due to the relatively coarse resolution of the CALPUFF calculation grid (500m x 500m) and the simplicity of our approach to interpolation along the profile line (Figure 4.1), but we improved the interpolation method and the observation was not materially changed. However the observation is not always seen if the direction of the profile line (Figure 4.1) is changed. This leads DNV to assign this observation to a combination of terrain variations and complex meteorology data, though the coarse calculation grid could also be relevant. This conclusion is supported by the observation that the variations appear at the same distance from the source for all species and for each case study.

4.5.2 Concentration of Gas Phase Amine

Examining the results, the first impression gained from the way that the concentration of amine in the gas phase decreases as a function of distance from the source (and therefore, roughly speaking, time), is that dispersion is the dominant factor. In Figure 4.2 and Figure 4.10, it is clear that both the tracer species (which undergoes no chemical transformations) and the gaseous amine drop away in concentration in a very similar way, although the amine concentration decreases faster. The difference is due to losses in amine due to the chemical transformations. (In this report "chemical transformations" will normally include phase equilibria processes, for the sake of brevity.)

Figure 4.6 and Figure 4.14, in contrast, shows an *estimate* of the chemical transformations alone. This is accomplished by dividing the concentrations at each distance from the source by the degree to which the inert tracer compound has undergone dilution. (This is why the tracer compound is constant). Together these results show that chemical reactions are responsible for only a small proportion of the loss of amine concentration. That is, at the low concentration of emitted amine, the dispersion processes reduce this concentration much faster than chemical transformation processes. This conclusion is consistent with the Phase 1 report /2/.

By comparing the total amounts of tracer compound and amine observed at all the ground level receptors in the study area (proportional to the “average” figures in Table 4.3), enables an estimate of the total proportion of the amine that has been consumed by chemical reactions to be made. This figure is 22% for Case A and 25% for Case B.

It is interesting to compare this chemical loss of amine to the loss of amine in the box model (Figure 3.2). In Figure 3.2, even after the gaseous and aqueous phases have equilibrated (after about 0.5h), there is a much greater loss of amine due to the reactions with OH radicals and the other chemical reactants compared to that seen in the CALPUFF calculations. This difference is to be expected because:

- In the CALPUFF calculations, the effect of dispersion has 2 effects. First it reduces the concentration of amine by dispersion. Second it reduces the rate of loss of amine by chemical reactions because these rates are dependent on the absolute concentration of the amine. This means that in addition to dilution, the rate of the amine chemistry is also slowed down and much less chemical transformation occurs.
- The Case A and Case B studies shown here include a time-dependency that severely reduces the availability of OH radicals. The night-time first order reaction rate is calculated to be just over 1/10 of the maximum reaction rate with the sun closest to its zenith (using reaction rates and counter species concentrations from Table 2.1). Therefore, the incorporation of the true sun zenith angles as included in the full CALPUFF model is very significant. A further test case (Case 0) that removes this effect by removing the time-dependency has been run and indeed shows increased loss of amine due to chemistry. This is reported in Appendix 1.

The first of these two factors demonstrates the necessity of modelling the dispersion and chemistry simultaneously, as opposed to imposing a box-model derived yield factor for each chemical pathway onto a standard dispersion model (which will always over-estimate the concentration of NA and NS formed).

4.5.3 Concentration of Gas Phase Nitrosamine and Nitramine

In Case B, nitrosamine rises very much more slowly than nitramine and, in contrast to the box model results, shows no apparent rise and fall shape beyond the near field. Nitrosamine is regulated by the destruction mechanism corresponding to the reaction rate k_6 and by the reduction of the precursor concentration by dilution. A small “rise and fall” shape can be observed in the dilution-corrected graphs if very high (unrealistic) concentrations of NO are forced into the model. However for the Case B chemistry parameters the dispersion processes dominate and this masks the rise and fall behaviour that might be expected from the chemistry equations alone.

In contrast, the chemical scheme does not allow for the destruction of NA (k_{14} = 0.0) and so the concentration NA would continue to grow because of chemical transformation (whilst A and NS is still available) in the absence of dispersion, but is actually observed to reduce because of the dominance of dispersion processes over chemical transformation processes.

In Case A, the primary amine is allowed to undergo internal re-arrangement to imine (NTP) via the fast step represented by k_{13} (see Section 2.3). The peak concentration of NS for Case A (Figure 4.5) is therefore a factor of 75 times lower than that seen for Case B (Figure 4.13) (in Case B k_{13} is set to zero because the secondary nitrosamine cannot perform this rearrangement reaction).

4.5.4 Concentration of Aqueous Phase Amine

These observations are based on the Case A study because very little transition to the aqueous phase is observed in Case B. The aqueous phase of amine rises sharply from zero as the phases equilibrate (

Figure 4.3). Its concentration reaches a peak at about 2km from the source and then adopts a shape that is very similar to the gaseous amine curve. This corresponds with expectation since it remains in lagging equilibrium with the concentration of the gaseous phase amine from that point onwards.

4.5.5 Concentration of Astar (A*)

Finally, Figure 4.5 and Figure 4.13 shows the calculated absolute concentration of the reactive intermediate A*. This is observed to be higher in the near field and then reduces with distance from the source. DNV note that a standard assumption often used by chemists to solve systems of rate equations is to assume that the concentration of the reactive intermediate is in steady state. Whilst this assumption is usually justified in closed systems (though even in the box model results the concentration of A* does decay with time, see Figure 3.4), the results presented here indicate that this is not a valid assumption for open systems where the species both disperse and react simultaneously.

4.6 Results for Case 00

In the third case study, Case 00, the emission conditions modelled in Phase 1 of the present project are replicated as closely as possible taking account of the many changes between Phase 1 and Phase 2. Where conflicts between Phase 1 and Phase 2 methods existed, then the newer methods used in Phase 2 were applied to Case 00. The emission profile for this case study was a mixture of three different amines, plus a small quantity of the nitrosamine of dimethylamine (NDMA), as shown in the Table 4.6. MEA and its daughter species were assumed to have high solubility in water (like in Case A), whereas MMA and DMA and their daughter species were assumed to have lower solubility (like in Case B). Other input parameters were as given in Table 2.1.

Table 4.6 CHP Emission Profile for Case 00

Species Name	Formula	Molecular Weight (g/mole)	Emission Rate (g/s)
Nitric oxide	NO	30	3.72
Nitrogen dioxide	NO_2	46	0.62
Monoethanolamine	"MEA"	61	1.64
Dimethylamine	"DMA"	45	0.06
Monomethylamine	"MMA"	31	0.08
Nitrosdimethylamine	"NDMA"	74	0.0005

The concentrations assume an exit height of 65m, an exit velocity of 20m/s, an exit diameter of 6.52m and an exit temperature of 30°C, exactly as for Case A and Case B.

This case study was included mainly as a demonstration of the modified modelling system's ability to model multi-amine emission cases and for continuity with Phase 1 of the work stream. The modified CALPUFF model can, at the moment, only calculate chemistry for one amine system at a time. Thus the results for Case 00, which has 3 amine systems (MMA, DMA and NDMA, MEA), were calculated separately and then combined together in a post-processing step. This is possible because the different amine systems (amines and their degradation products) do not interact (react together across the amine systems) at these very low concentrations.

The results for this study are presented here only in the form of the summary statistics.

Table 4.7 Summary of Results for Case 00

		A (ng/m^3)	NA (ng/m^3)	NS (ng/m^3)	A(aq) (ng/m^3)	NA(aq) (ng/m^3)	NS(aq) (ng/m^3)
Case 00	**Peak**	64.3	0.0458	0.0188	4.35	0.00350	0.000226
	Average	2.45	0.00950	0.000586	0.259	0.000928	0.00000175

Note the concentration of the aqueous species are in arbitrary units because the amount of available moisture is unknown.

These results, along with the results for Case A and Case B, are discussed in Section 4.8.

4.7 Air and Drinking Quality Criteria

The primary objective of this report is to develop and demonstrate an enhanced air dispersion model with sufficient capability to represent the diverse chemical and physical processes of interest. Nevertheless, it is instructive to compare some of the results obtained to proposed environmental quality criteria as this will be the ultimate application of the work performed.

Of all the primary or secondary pollutants released by the proposed process, nitrosamines and nitramines have the strictest proposed environmental quality criteria. Thus this report will focus only on this comparison.

The proposed environmental quality criteria are based on the Norwegian Institute of Public Health (NIPH) recommended values. The basis for this is the evaluation study conducted by NIPH in response to the Climate and Pollution Agency (Klif) request /8/. The NIPH study is based on evaluation of existing risk estimates related to N-nitrosodimethlyamine (NDMA) for air and drinking water, and included an evaluation of the EPA / IRIS risk estimates.

The NIPH evaluation has calculated the concentration of nitrosamines (NDMA) in air and water associated with risks (to humans) in the range of 10^{-5} to 10^{-6}. This means that life-long exposure at the indicated levels would give an excess life-long risk of cancer of either 10^{-5} or 10^{-6}. The recommended tolerable nitrosamine concentrations are summarised in Table 4.8. As limited information is available on the health effects of nitramines, NIPH has suggested that the risk estimate for NDMA is also used for exposure to nitramines. This may be conservative as NDMA is likely to be more potent than any of the nitramines.

DNV understands that these values correspond to a long term annual criterion. The emphasis for this study is the long term results given that the criteria refer to the life-time risk of cancer.

DNV also understands that results from other studies currently on-going are utilised in order to help establish environmental quality criteria relevant for environmental studies. These values are considered as guidelines and criteria have not yet been officially set by Klif.

Table 4.8: NIPH recommended tolerable drinking water and air quality criteria

Pollutant	**Drinking Water Quality[1]**	**Air Quality[1]**
	Long Term (Annual) (ng/l)	**Long Term (Annual) (ng/m^3)**
Nitrosamines/Nitramines	40 [2] / 4 [3]	0.3 [4]

Notes:
1 The cumulative nitrosamine and nitramine concentration (in air or drinking water) should be judged against the recommended criteria.
2 Corresponds to a life-long risk of cancer level of 10^{-5}.
3 Corresponds to a life-long risk of cancer level of 10^{-6}.
4 Corresponds to a life-long risk of cancer level below 10^{-5}.

4.8 Comparison of Pollutant Concentrations to Air Quality Criteria

The peak ground level annual average concentrations observed within the study area for Case A, Case B and Case 00 are shown in Table 4.9. Also shown is the peak of the sum of NS and NA in both the gas phase and the aqueous phase. It is not clear if NA and NS in the (micro) aqueous phase should contribute against the air quality criteria shown in Section 4.7, but since the aqueous phase is inhalable DNV assume that it should (the responsible authority should clarify this point). It should be noted that, in general, the peak values for the individual species do not occur at the same location, thus “sum of the peaks” is greater than the “peak of the sums”.

Table 4.9 also compares the “peak of the sums” (the maximum combined concentration of NS and NA in the gaseous and the aqueous phase at any location) to the air quality criteria described in Section 4.7.

Table 4.9: Summary Statistics for Nitramine and Nitrosamine over Study Area

Case study	**Peak Gas Phase Nitramine (ng/m^3)**	**Peak Gas Phase Nitrosamine (ng/m^3)**	**Peak Aqueous Phase Nitramine (ng/m^3 equivalent)**	**Peak Gas Aqueous Nitrosamine (ng/m^3 equivalent)**
Case A	0.0374	0.000749	0.00316	0.0000489
Case A peak of summed values	0.0413			
Peak of summed values relative to $0.3ng/m^3$	14%			
Case B	0.426	0.0606	0.0000322	0.00000417
Case B peak of summed values	0.486			
Peak of summed values relative to $0.3ng/m^3$	162%			
Case 00	0.0458	0.0188	0.00350	0.000226
Case 00 peak of summed values	0.0632			
Peak of summed values relative to $0.3ng/m^3$	21%			

Note: “Peak” refers to the greatest modelled concentration observed across the receptor locations.

Comparing Case A and Case B, the high molecular weight of the heavy secondary amine, the greater chemical stability of the secondary nitrosamine ($k_{13} = 0s^{-1}$) and the faster reaction rate (k_{OH}) have all resulted in a much greater burden of potentially harmful compounds in mass terms for Case B.

Furthermore, the high transfer of amine from the gaseous to aqueous phase in Case A has allowed the amine to be “hidden” from the chemistry that produces the potentially harmful compounds until such time as dispersion has taken effect, as expected. Therefore lower concentrations of nitramine and nitrosamine are seen in Case A, relative to Case B.

The concentration of the harmful species generally decreases as a function of distance from the source (Figure 4.4, for example). This is due to the overwhelming effect of dilution, as can be seen by comparing Figure 4.4 to Figure 4.8 in which steady chemical production is seen for nitramine, whereas growth of nitrosamine is limited by chemical instability ($k_{13} > 0s^{-1}$) in Case A as seen in Figure 4.9, consistent with the input parameters chosen for these case studies.

The significance of the absolute values of these concentrations of harmful compounds will be discussed in the conclusion of the present report.

4.9 Discussion of Conservatism in the Case Studies

The calculations reported as Case A, Case B and Case 00 all retain elements of conservatism within them, as noted here:

- The literature states that NOx reacts preferentially with $OH^{\cdot}$ and in so doing could limit the availability of $OH^{\cdot}$ in the near field of the emission plume where the NOx concentration is highest and where most amine transformation chemistry occurs. This effect is not included in the current version of the modified CALPUFF model.
- Similarly, the presence of Volatile Organic Compounds (VOCs) will also compete for $OH^{\cdot}$ and hence reduce the concentration of $OH^{\cdot}$ available to react with amine. Since VOCs are present in the natural background, this effect may already be included in the measurements of $OH^{\cdot}$ concentration observed at Mongstad.
- As noted in Section 2.3, the modified model does not reduce the concentrations of counter species due to chemical reaction.
- The branching ratios and initiating rate constants (k_1, k_{10}, k_{11}, k_{12})assumed in the case studies are all set to conservatively compared to literature values.
- Oxidation processes which might destroy NA and NS are not represented in the modified model.
- Case B does not allow any significant equilibration to the aqueous phase, which is probably conservative as most amines are soluble in water.

All the above factors will result in *over-prediction* of the concentration of NS and NA formed

4.10 Application to Real Systems

The modified CALPUFF model developed by DNV and described above can evaluate the ground level concentrations of amines and amine degradation products for any one emitted amine plus degradation products (provided that the chemistry can be represented by Figure 2.2). If the chemistry differs from the scheme shown in Figure 2.2, DNV considers that a modification of the

DE system representing the scheme is probably a relatively simple matter thanks to the very general method that has been used in this implementation.

If multiple amines need to be assessed, and assuming the reactions schemes for different amines do not interact together, there are two choices:

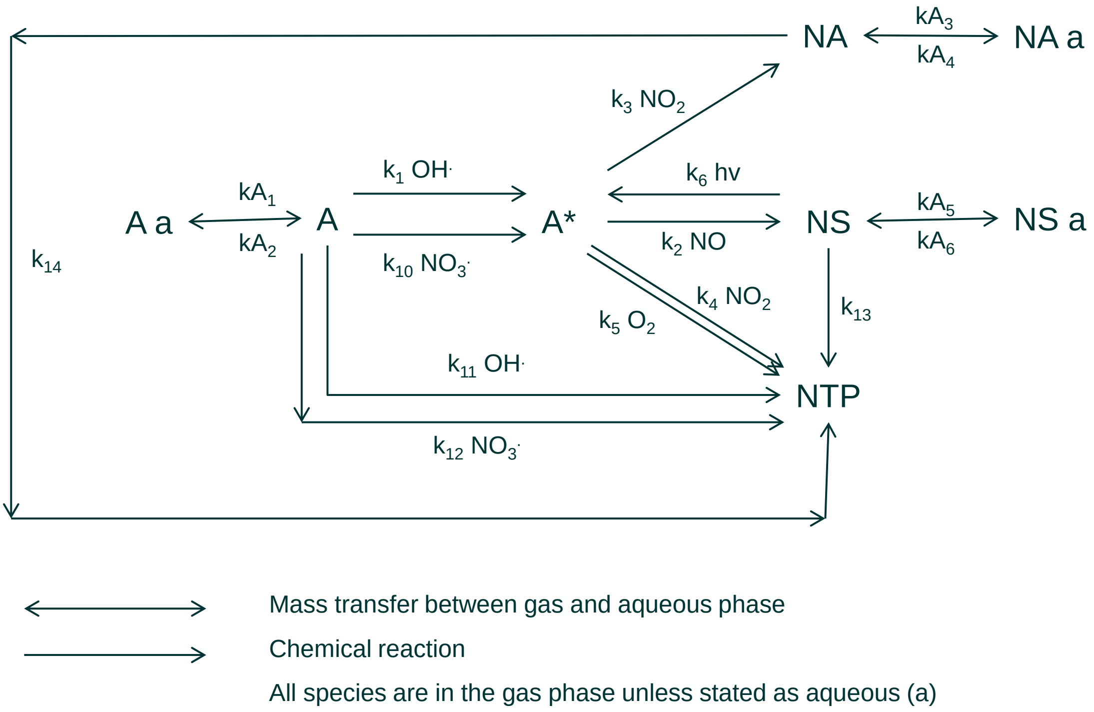
- CALPUFF could be further modified to be able to accept variables for multiple amines. This is, essentially, a code administrative task that will expand the number of variables that CALPUFF can handle at any one time.
- The present version of CALPUFF can be run multiple times to evaluate each amine in turn. This was the option used in Section 4.6 above.

If the chemistry schemes for the different amines do interact with each other, then the work required may be more complicated, but should not be insurmountable.

5 CONCLUSIONS

A general amine chemistry capability has been successfully added to the CALPUFF atmospheric dispersion modelling system. It performs chemical reactions according to the general scheme shown below.

Figure 5.1 The generalised amine chemistry scheme incorporated into CALPUFF



All reaction rates shown in this scheme are editable by the user as are the constants used in the calculation of counter species concentrations. Modifications to the way in which those calculations are made are probably relatively easy to make given knowledge of the CALPUFF code architecture. In particular, a link to the CALPUFF-generated OH-radical concentration could be restored easily if required.

The concentrations of the species in the scheme are determined by the solution of a system of ordinary differential equations with known initial conditions. This initial value problem is solved by a numerical technique known as the Rosenbrock method, a standard technique in numerical analysis that has been shown to be suitable for “stiff” problems of this type. The required accuracy for each invocation of the DE solver can be set by the user.

The behaviour of the implemented gas phase amine chemistry in the updated CALPUFF model is robust (no problems have yet been observed). The chemistry module added to CALPUFF has been extensively tested by comparison with a box model developed in MathCad using various competing numerical methods and exact solutions for certain special cases and no problems have been observed in the results obtained.

The box model, and therefore the model as appended to CALPUFF, behaves as expected with respect to all input parameters, be they counter-species concentrations, emission rates or reaction rate constants. Evidence has been provided in the present document showing that the model meets expectations in the general characteristics of its output.

All these factors, together with the expected emission rates can now be altered quickly and easily by the user, so this modelling system can be used efficiently to model cases in which altered assumptions are made. This was the main objective of this work and this has been achieved.

Three main case studies were run and the results presented in this report. Two of the case study results (A and 00) are about a factor of 5 lower than the air quality criterion used (that is, they are compliant). However Case B (the worst case) exceeded the air quality criterion by 60% (ratio of predicted concentration to criterion of 1.6). All these case studies continue to include conservatism in a number of parameters and modelling assumptions as discussed in the main report.

Uncertainties surrounding the solubility and rate of phase transfer for amines, nitramines and nitrosamines remain particularly important as the difference between the results for the Case A and Case B indicate.

6 REFERENCES, ACRONYMS AND ABBREVIATIONS

6.1 References

/1/	DNV Call-Off 01, "Modelling for Atmospheric Dispersion of Components from post-combustion amine-based CO_2 capture", 5th October 2010.
/2/	DNV Call-Off 02, Phase 1 Report, "Atmospheric Chemistry Modelling of Components from post-combustion amine-based CO_2 capture", 5th October 2011.
/3/	DNV Call-Off 02, Deposition Report. "Deposition and Soil Transport Modelling of Components from post-combustion amine-based CO_2 capture", 22 August 2011.
/4/	Tel-Tek Report Number 2211030-NP05 v2, "Atmospheric Chemistry – Nitrosamine Photolysis", 28.10.2011.
/5/	Tel-Tek Report Number 2211030-DC06 v2, "Atmospheric Chemistry – Dark Chemistry", 01.11.2011.
/6/	Tel-Tek Report Number 2211030-DC01 v2, "Specification of Atmospheric Dark Conditions", 16.09.2011.
/7/	Norwegian Institute for Air Research, "Atmospheric Degradation of Amines", CLIMIT project no. 201604, OR 2/2011.
/8/	Norwegian Institute of Public Health (NIPH) Health effects of amines and derivatives associated with CO2 capture: Nitrosamines and nitramines.

6.2 Acronyms and Abbreviations

3D	3-Dimension(al)
A	Amine
CCM	CO_2 Capture Mongstad
DE	Differential Equation
DMA	Dimethylamine
DNV	Det Norske Veritas Limited
IVP	Initial Value Problem
LAM	Local Area Model
MEA	Monoethanolamine
MMA	Monomethylamine
NA	Nitramine
NDMA	N-nitrosodimethlyamine
NILU	Norwegian Institute for Air Research
NIPH	Norwegian Institute of Public Health
NS	Nitrosamine
NTP	Non-Toxic products (mainly imine initially)
ODE	Ordinary Differential Equation
VOC	Volatile Organic Compound

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