DET NORSKE VERITAS

Report for
Modelling for Atmospheric Dispersion of Components from post-combustion amine-based CO_2 capture

Gassnova SF
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EXECUTIVE SUMMARY

Background

The purpose of the CO_2 Capture Mongstad (CCM) Project is to plan and build a large scale carbon dioxide 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 carbon dioxide from the flue gas of a combined heat and power plant (CHP) using amine based capture technology. The design basis is the capture of approximately 1.3 million tonnes of CO_2 per year, which will then be conditioned and compressed for pipeline transport, to be sent to geological storage under the Norwegian Continental Shelf.

The CCM Project is currently at the early planning and development phase, organised jointly by Gassnova SF and Statoil, with funding from the Norwegian government. This report is submitted to Gassnova SF.

An amine based CO_2 capture plant may cause harmful emissions to the atmosphere. Amines and degradation products from reactions in the process and in the atmosphere are of particular concern to Gassnova SF / Statoil, but there is limited knowledge about the behaviour of such chemicals when discharged from large scale industrial processes (not commonly used particularly for large scale installations). As such Gassnova SF has launched several studies to be conducted during the capture plant development, in order to improve understanding and knowledge on these substances.

DNV have been contracted by Gassnova SF to conduct this study related to the atmospheric dispersion (and the ultimate fate) of components from post combustion amine based carbon dioxide capture for both primary (e.g. NO_x, NH_3) and secondary (e.g. nitrosamines and nitramines) pollutants.

Study Objectives

The objectives of this study are to:

- Recommend (after consideration of the strengths and weaknesses of existing air dispersion models) the most appropriate air dispersion model to be used to describe how emitted substances from the CCM facility behave after discharge to atmosphere.
- Conduct an air dispersion modelling case study for emissions from the CCM project, and consider the implications of the findings.
- Identify any air dispersion model development work needed both in the short (e.g. within 1 year) and long (e.g. within 3 years) term, to enable satisfactory environmental impact assessment of the atmospheric emissions from the CCM facility, of both the primary pollutants (e.g. amines, NO_x, NH_3) and secondary pollutants formed primarily as a result of chemical reaction in the atmosphere (e.g. nitrosamines and nitramines).

Model Evaluation

DNV investigated and summarised the state of the art in Air Quality Dispersion Modelling, considered the various strengths and weaknesses of the different models available, and recommended the most appropriate air dispersion model to be used to model the atmospheric pollutants emitted from the CCM facility (Dispersion Case Study).

In doing the above, DNV discussed the different types of meteorological models (diagnostic and prognostic) and atmospheric dispersion models (Gaussian Plume Model, Modified Gaussian Plume Model, Langrangian / Eulerian Model) that are available. Example models from each group were selected and evaluated.

Evaluation was carried out considering a wide range of parameters, both generic and specific, and a detailed comparison is provided within the body of the report. This evaluation was then used to recommend the most appropriate air dispersion model to describe how emitted substances from the CCM facility behave after discharge to atmosphere, both for the Case Study in this report, and for subsequent project stages.

Recommendation for Case Study

For the purpose of the preliminary evaluation in the Dispersion Case Study, which aims primarily at understanding the “area of interest” (i.e. the area where pollutant concentrations are above the defined air quality criteria) and estimating the timescale of the phenomena (i.e. residence time of pollutants inside the “area of interest”, which is an important factor when considering incorporating amine chemistry within existing dispersion models), the Gaussian Plume Model (ADMS) is recommended because:

- It allows the user to account for the main phenomena (plume rise, transport, dispersion, deposition, etc) in a simplified way.
- Input data is readily available.
- Short computational time, which allows the user to conduct sensitivity tests.
- Robust approach, also used for regulatory purposes.
- Output data is easily manageable.

Model selection for subsequent project stages

The model selection for the subsequent phase of the project concluded that either a Gaussian plume model (e.g. ADMS) or a Modified Gaussian Puff Model (e.g. the “CALPUFF Modelling System) is suitable, because:

- The area of interest is restricted to the near-mid field (up to 10-12 km), based on the assumed air quality criteria and the amine emission data supplied.
- The complexity of terrain features (near-mid field) in Mongstad area is medium.

- Both the models can address wet and dry deposition.
- Both models allow the calculation of the most important short term and long term atmospheric parameters to be compared with the Air Quality Standards.
- No potential significant benefits have been identified if the most refined and complex models (Eulerian/Lagrangian models) are used.

Despite both ADMS and CALPUFF Modelling System being suitable for the next phase of the study, the CALPUFF Modelling System has some additional benefits:

- ***If*** the timing of the chemical reaction/degradation of amines (to form nitrosamines/nitramines) is comparable with the timing for transport and dispersion into the area of interest (up to 10-12 km)
- CALPUFF is also capable of simulating pollutant transport in complex terrain.

Dispersion Case Study

The dispersion case study was conducted using ADMS 4, Version 4.1, a Gaussian plume air dispersion model. The sources considered were associated with the CCM facility, the TCM plant (pilot carbon capture and storage plant), and existing, key Mongstad refinery sources.

Point source emissions generated by the facilities include primary pollutants such as NO_x, SO_2, NH_3, MEA (mono ethyl amine) as well as secondary pollutants such as nitramines and nitrosamines (which are the most toxic and harmful, and are the key secondary pollutants of interest).

The key findings from the dispersion case study are:

- The maximum ground level concentrations predicted anywhere account for less than 5% of the identified air quality criteria for the *primary* pollutants.
- The extent of the area affected by *secondary* pollutants (nitrosamines/nitramines) is very dependent on the amine to nitrosamine/nitramine conversion rate assumed. The area affected is more than 10 km distance from the emission point when assuming 7% amine conversion. For a 0.3% conversion, there are no air quality criteria exceedances.

It should be noted that the ambient air quality criteria assumed for nitrosamines/nitramines are based on DNV's judgement of the limited information currently available. As the criteria will heavily influence the conclusions of such studies as this, it is recommended that results from toxicity and other studies currently ongoing are utilised in order to better understand the effect of amine degradation products, and to help establish air quality criteria.

Model Development Needs

DNV summarised the readily available literature on the atmospheric chemistry of amines, with the objective to provide guidance to the best strategy for developing an air dispersion model (to be incorporated within, or used in conjunction with, existing air dispersion models) to contribute to the environmental impact statement for the proposed CCM facility at Mongstad.

The key issue is the release of amines to atmosphere from the CCM facility and whether they, or their degradation products, form a significant environmental hazard.

The task was divided into two main sections, a literature review and a "route-map" for model development.

Literature Review

The literature review examined key information relating to the chemistry of amines and their degradation in the atmosphere, such as Release Parameters, Partition between phases, Yields, Reaction rates and Air quality criteria.

The present state of knowledge was found to be insufficient to allow a complete model of the environmental consequences of the proposed process to be built, and further research is necessary.

The review highlighted a number of knowledge gaps that are discussed in detail in the report, with the most important ones being:

- Better understanding of the differences between starting amines, and the implications upon the amine degradation products formed.
- The starting amine may be partitioned in either gas or aqueous phase; knowledge to date is concentrated on the gaseous phase, with partitioning into the water phase poorly examined.
- Improved understanding is required of the formation of amine degradation products, and their subsequent degradation.
- The criteria used for interpreting dispersion modelling results need to be carefully considered, as it fundamentally effects the conclusions and actions to be taken.

Route Map

The route map considers the findings of the literature review and proposes a high-level method for deciding the most suitable approach for the development of an air dispersion model for future implementation. It also suggests how model development needs would best be addressed both in the short and long term.

The central problem in the modelling of the air dispersion of possible pollutants released from the carbon capture facility is that of combining the modelling of the atmospheric dispersion with the atmospheric chemical processes. In principle, and in the general case, the modelling should reflect the fact that the dispersion and chemical reactions occur simultaneously. However, certain special cases may exist that could be exploited to simplify this process.

For instance, if the chemical processes can be shown to take place much faster than the dispersion process, then the chemical reactions can be regarded as essentially complete before the dispersion modelling begins. This is a significant simplification of the problem since it would allow the yield of the chemical reaction to be calculated outside of the atmospheric dispersion modelling programme (as assumed in the Dispersion Case Study of this document).

If the chemical processes can be shown to take place much slower than the dispersion process, then the dispersion process can be regarded as complete before the chemical reactions begin. Again, this represents a significant simplification since the primary pollutant (i.e. amine) may have diluted sufficiently such that the potentially dangerous amine degradation products (nitrosamine/nitramine) may also be diluted enough as to not pose a threat in the environment.

Existing models are examined in this study in the light of the above considerations, and a route map developed, each step of which represents increasing levels of sophistication and refinement. The latter steps (which may or may not be required, depending on a number of influencing factors) in the process include examination of atmospheric formation kinetics (of nitrosamines/nitramines) and their degradation kinetics; there are a variety of methods to undertake this, as follows:

- *Option 1: Program the chemistry into an existing dispersion model*
- *Option 2: Use existing dispersion models with post processing of results*
- *Option 3: Bespoke model of chemistry and dispersion*

These options are discussed and considered within the body of this report. Given the various data gaps for the different amine degradation mechanisms, the model development *Option 2: Use existing dispersion models with post processing of results* is considered by DNV to be the best and most efficient way forward at least for short term development. This option also has the additional benefit of not requiring additional validation (which may be necessary for Options 1 and 3).

To summarise, DNV recommend that Gassnova SF work with DNV and with specialist contract research organisations, such as NILU, to fill the identified data gaps in a systematic way such that an answer to the question of the environmental impact of CCS can be fully answered in the most cost-effective way.

1 INTRODUCTION

1.1 Background

The purpose of the CO_2 Capture Mongstad (CCM) Project is to plan and build a large scale carbon dioxide 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 carbon dioxide from the flue gas of a combined heat and power plant (CHP) using amine based capture technology. The design basis is the capture of approximately 1.3 million tonnes of CO_2 per year, which will then be conditioned and compressed for pipeline transport, to be sent to geological storage under the Norwegian Continental Shelf.

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DNV have been contracted by Gassnova SF to conduct a study related to the atmospheric dispersion (and the ultimate fate) of components from post combustion amine based carbon dioxide capture for both primary (e.g. NO_x, NH_3) and secondary (e.g. aldehydes, nitrosamines) pollutants.

1.2 Scope and Objectives

1.2.1 Overview

The key objective of this study is the evaluation of the potential health and environmental impact that can be caused by pollutants emitted to the atmosphere as a result of amine based CO2 capture.

The project ultimately aims to answer the following:

- How long do these substances survive in the atmosphere?
- How far do they travel?
- Where are they most likely to be deposited?
- What secondary pollutants may be formed along the dispersion pathway and what effects might these have?
- What will their concentrations in the environment be?

It should be noted however that this study does not provide definite answers to all the aforementioned questions (mainly because of data gaps). These will be addressed at a later phase of the project.
The scope does not include evaluation of the environmental risk due to non-routine events (i.e. accidents). Furthermore, the scope does not include evaluation of what receptors can potentially be affected or what the effects will be on these receptors.

1.2.2 Objectives and Scope Outline

The objectives of this study are:

- Recommend an air dispersion model to be used to describe how emitted substances from the carbon dioxide capture facility can be expected to behave after discharge to the atmosphere.
- Identify any air dispersion model development work needed to achieve the above on the short (e.g. within 1 year) and long (e.g. within 3 years) terms.

The scope includes an air dispersion modelling case study, modelling the emissions from an absorber stack. The model is based on local conditions in the Mongstad area and also considers the key emission sources from the Mongstad refinery and the TCM pilot carbon capture plant.

1.3 Report Layout

The remainder of this report is structured as follows:

- Section 2 outlines the findings from the model evaluation task. This is also supported by Appendix 1.
- Section 3 summarises the results of the dispersion case study. This is also supported by Appendix 2.
- Section 4 summarises the findings of the literature review conducted, as well as addressing model development needs. This is also supported by Appendix 3.
- Section 5 summarises the conclusions from the study.
- Section 6 provides the study recommendations.
- Section 7 includes the references.

2 MODEL EVALUTION

2.1 Introduction

The aim of this task was to:

- Investigate and summarise the state-of-the-art in Air Quality Dispersion Modelling.
- Consider and document the strengths and weaknesses of the various air dispersion models available.
- Recommend the most appropriate air dispersion model to be used to meet the study objectives, for both the short term (the dispersion case study in this report), and longer term (the next stage of the study).

This section summarises the above, details of which can be found in Appendix 1.

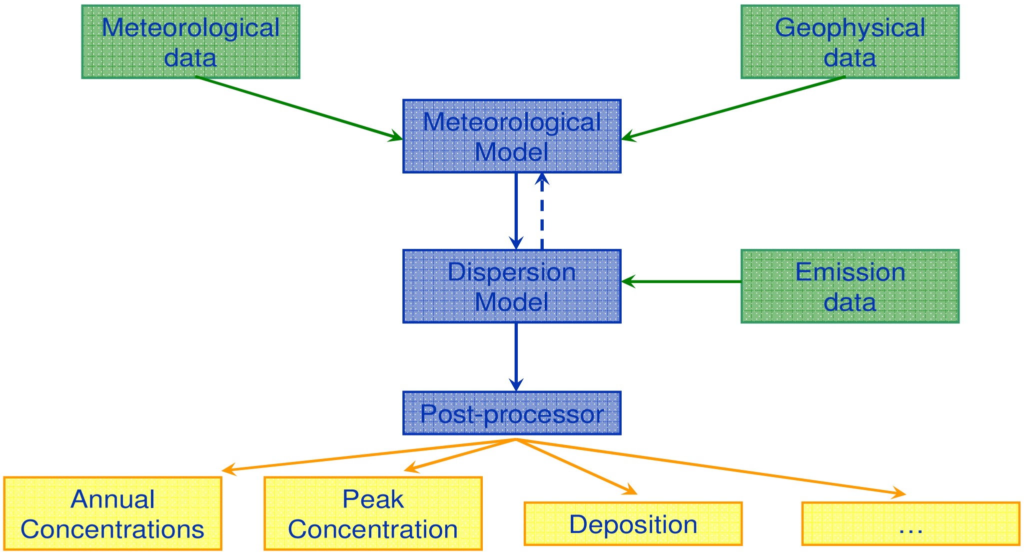
2.2 Model Chain

The fate of pollutants in the atmosphere is usually evaluated through a model chain, which typically comprises of (see

Figure 2.1):

- *Meteorological model*, aimed at calculating the 2D / 3D wind field, to be used as input by the dispersion model. Meteorological models require meteorological data and geophysical data (e.g. terrain features).
- *Dispersion Model*, aimed at simulating the fate of the pollutants into atmosphere, in terms of transport, dispersion, formation (chemical reaction) and removal (chemical reaction, dry and wet deposition).
- *The postprocessor* is aimed at giving results in a format suitable for the user, i.e. annual average concentration, 1-hour average 99.8th percentile, maximum concentration, deposition, etc.

Figure 2.1 - Model Chain



The most common meteorological and dispersion models are described below.

2.3 Meteorological Models

Pollutant dispersion models require, as input, the wind field to forecast the cloud transport and evolution. Therefore, the application of a meteorological model is a key point in evaluating the fate of pollutants into the atmosphere. Obviously, the accuracy of the plume cloud evolution and pollutant dispersion is strictly connected with the accuracy of the meteorological field simulation.

The meteorological models are able to perform a detailed description (with a varying level of detail) of physical reality through a set of equations and semi-empirical correlations, which simulate atmospheric phenomena.

Meteorological models can be distinguished in two broad categories:

- Diagnostic: a diagnostic meteorological model uses, as input data, monitoring data from detection units/weather stations. The model interpolates input data on the overall spatial domain by means of algorithms and semi-empirical parameterisations. As such, it is important that these weather stations be representative of the spatial domain. The most commonly used diagnostic model is CALMET, which is part of the “CALPUFF Modelling System”.
- Prognostic: a prognostic meteorological model consists of a system of partial differential equations in time and space. The model uses, as initial and boundary conditions, data that are the result of the interpolation of continuous measurements, obtained from synoptic meteorological station network, balloon probes and oceanic buoys. This allows the prognostic model to be able to forecast the spatial-temporal evolution of the meteorological field.

Examples of important prognostic limited area models are MM5, RAMS and WRF.

2.4 Atmospheric Dispersion Models

A pollutant dispersion model is a mathematical computer tool, which simulates the cloud evolution and the resulting pollutant concentration in a space-time domain, in the presence of one or more emission sources.

The dispersion model, as such, is an approximation of reality and its output and forecasts will not be the same as measured concentrations. According to the level of detail of the model, the forecast output will be more or less representative of reality.

Research over the years has lead to the development of different classes of dispersion models.

A primary distinction can be made between steady state and dynamic models. In the first ones, the time evolution of a pollutant dispersion phenomenon is considered as a sequence of almost steady state events: this kind of approach simplifies the model but its applicability decreases considerably, especially for accidental releases (typically time-varying) and large domains (characterised by non-homogeneous meteorological conditions). The second one simulates the evolution of the pollutant dynamically.

Steady state models are often used because of their simplicity and low run times, but they can have severe limitations for the analysis of complex systems.

DNV considers that existing air dispersion models can be categorised into three main categories:

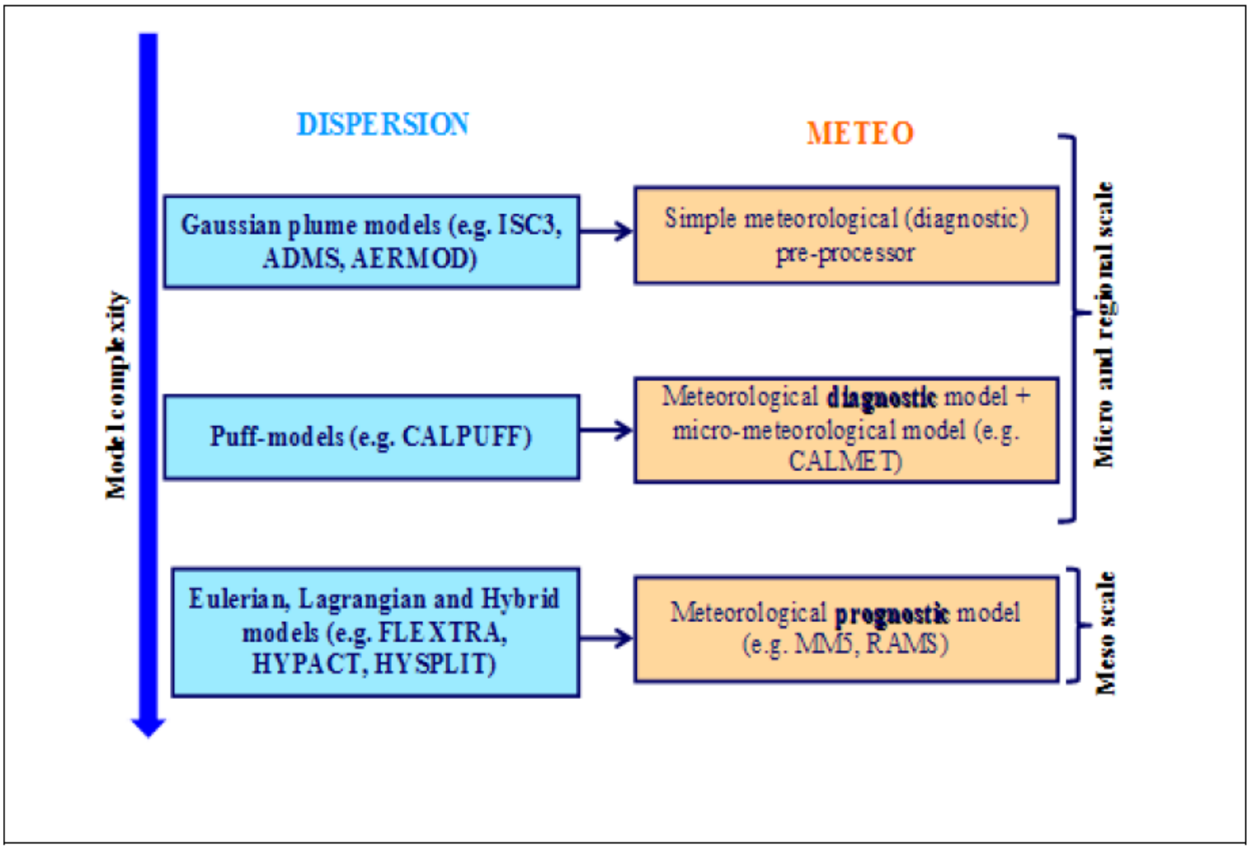
- **Gaussian Plume Model**: The Gaussian model is the most commonly used model type. It assumes that the air pollutant dispersion has a Gaussian distribution (i.e. the pollutant distribution has a normal probability distribution). Gaussian models are most often used for predicting the dispersion of continuous, buoyant air pollution plumes originating from ground level or elevated sources. Recent models combine a meteorological pre-processor with a Gaussian plume dispersion tool. This allows for a coarse characterisation of the (diagnostic) wind field in the area of interest. This can then account for terrain features, to an extent. The model running time is relatively fast and allows for a long term analysis. These models are suitable for the near / mid field effects (up to 60 km from the discharge points), if the terrain features are not too complex. Limitations are associated with non-continuous emission sources and calm wind conditions. Examples of Gaussian Plume models are ADMS and AERMOD.

- **Modified Gaussian Puff Model**: This category is similar to the above, but with some additional capabilities. The meteorological model allows for a more reliable 3-dimensional wind field analysis, and can be directly interfaced with Global Circulation Models (GCMs) and Local/Limited Area Models (LAMs). These models can simulate continuous releases, while the “puff” module / capability allows for the simulation of calm wind conditions as well as non-continuous / intermittent / instantaneous release sources. These models are suitable for simulating transport and dispersion in the near, mid and far field (up to 100km, depending on the complexity of the scenario). An example model from this category is the "CALPUFF Modelling System".

- **Lagrangian / Eulerian Model**: These models are considered "State of the Art" in air quality modelling. They are recommended for very complex terrain and climatic conditions and for applications where a high level of detail is required. Lagrangian dispersion models mathematically follow pollution plume particles as they move in the atmosphere, modelling the motion of the particles as a "random walk" process. The Lagrangian model then calculates the air pollution dispersion by computing the statistics of the trajectories of a large number of the pollution plume parcels. The most important difference between the two models is that the Eulerian models use a fixed three-dimensional Cartesian grid as a frame of reference rather than a moving frame of reference. These models are usually applied for short-term simulations, given the long run times required. These models can be used at their best when associated with a detailed (prognostic) meteorological model.

The simple schematic below (Figure 2.2) illustrates the main air quality modelling categories / types, as described above.

Figure 2.2 - Meteorological and Dispersion Models



2.5 Modelling Evaluation

Five approaches to modelling have been selected and evaluated for the purposes of this project (in order of increasing complexity and capability):

- Gaussian Plume Model (example selected is the ADMS model).
- Gaussian Plume Model (ADMS), associated with a diagnostic meteorological model (Flowstar).
- Modified Gaussian Puff model (CALPUFF), associated with a diagnostic meteorological model (CALMET).
- Modified Gaussian Puff model (CALPUFF), associated with a prognostic meteorological model (MM5 Meteorological LAM as refined/downscaled by Calmet).
- Lagrangian/Eulerian model (HYPACT hybrid Eulerian/Lagrangian dispersion model) associated with a prognostic meteorological model (RAMS Meteorological LAM).

The model comparison and evaluation is given in the table below Table 2-1. The model comparison / evaluation has been carried out considering a wide range of parameters. Some are generic capabilities, and some are specific capabilities required for this project. Weighing/importance factors are also included for each parameter, based on DNV judgement.

Note that some of the model capabilities have been simply addressed with a short judgement, as described below:

- ***Poor*** means that the model has no or poor capabilities to deal with the investigated parameter. If the parameter is of high or medium importance, an unsatisfactory performance is predicted.
- ***Basic*** means that the model is able to deal with the investigated parameter. However, if the parameter is of high importance, the model performance could be unsatisfactory.
- ***Fair*** means that the model has enough capability to deal with the investigated parameter, but it doesn't excel.
- ***Good*** means that the model performs very well.
- ***Very good*** means that the model excels.

Table 2-1 - Model Comparison

CAPABILITIES	**GAUSSIAN PLUME MODELS**		**PUFF MODELS**		**LAM + LAGRANGIAN / EULERIAN MODELS**	**Note**	**Evaluation**	**Weight / Importance**
	Gaussian (ADMS)	**Diagnostic + Gaussian (Flowstar + ADMS)**	**Diagnostic + Puff (Calmet + Calpuff)**	**LAM + Puff (MM5+Calmet+ Calpuff)**	**LAM + Hybrid (MM5 / RAMS+ Hypact)**			
Space scale	Near / middle field (up to 15-30km)	Near / middle field (up to 15-30km)	Near / middle field (up to 30-60km)	Near / middle field / far field (up to 50-100km)	Near / middle / far field and regional scale (theoretically, no limitation to space scale)	For less complex terrain, Gaussian / Puff models space scale can be extended.	The space scale depends on model capabilities and local conditions (complex terrain / land use). The values reported are based on expert judgment for the Mongstad area	High
Resolution	Up to 10,000 cells	Up to 10,000 cells	Up to 40,000 cells	Up to 40,000 cells	Potential for very high resolution, with implications on computational time	For all the models, the resolution is commensurate with the space scale.		Medium
Time scale	Short / long term	Short / long term	Short / long term	Short / long term	Short / long term	All models allow short and long terms air quality parameters to be assessed.		High
Time step	Not applicable (steady-state model)	Not applicable (steady-state model)	1 second to 1 hour	1 second to 1 hour	1 second to 1 hour			Medium (high for physical phenomena whose timing is comparable with transport /

CAPABILITIES	**GAUSSIAN PLUME MODELS**		**PUFF MODELS**		**LAM + LAGRANGIAN / EULERIAN MODELS**	**Note**	**Evaluation**	**Weight / Importance**
	Gaussian (ADMS)	**Diagnostic + Gaussian (Flowstar + ADMS)**	**Diagnostic + Puff (Calmet + Calpuff)**	**LAM + Puff (MM5+Calmet+ Calpuff)**	**LAM + Hybrid (MM5 / RAMS+ Hypact)**			
								dispersion)
Variable emission sources	Basic (only steady state or instantaneous sources)	Basic (only steady state or instantaneous sources)	Yes	Yes	Yes		Not relevant for this study, since all the relevant sources are anticipated to be steady-state.	Low
Computational time	Short (minutes to hours)	Short (minutes to hours)	Relatively short (days)	Medium (1-2 weeks) or high (2-3 months), depending whether LAM data are available from external sources	Medium (1-2 weeks) or high (2-3 months), depending whether LAM data are available from external sources		Gaussian and Puff models allow for relatively low computational time. The availability of LAM data is a key point for a detailed analysis.	Medium
Terrain features - General	Basic (only slopes)	Basic / Fair (slopes plus effects of slopes on wind field)	Fair / Good (3D wind field)	Very good (3D wind field)	Very good (3D wind field)		This is a potentially key capability for Mongstad area, especially if the pollutants involve the mid / far field	Potentially High

CAPABILITIES	**GAUSSIAN PLUME MODELS**		**PUFF MODELS**		**LAM + LAGRANGIAN / EULERIAN MODELS**	**Note**	**Evaluation**	**Weight / Importance**
	Gaussian (ADMS)	**Diagnostic + Gaussian (Flowstar + ADMS)**	**Diagnostic + Puff (Calmet + Calpuff)**	**LAM + Puff (MM5+Calmet+ Calpuff)**	**LAM + Hybrid (MM5 / RAMS+ Hypact)**			
Terrain features 1 - Effects on wind direction	No	Fair (semi-empirical algorithm)	Good (semi-empirical algorithm)	Very good	Very good			Potentially High
Terrain features 2 - Land use	Basic (only surface roughness)	Basic (only surface roughness)	Good (a wide range of parameters)	Good (a wide range of parameters)	Good (a wide range of parameters)			Potentially High
Terrain features 3 - Building effects	Fair	Fair	Fair	Fair	Good (if RAMS is applied for the “microscale”)	The application of MiscroSwift Model would lead to a very good characterisation.		Low
Wind field - General	Basic (one set of hourly data for all the computational domain)	Fair (data from a number of stations)	Fair/good (data from a number of stations, including radiosonde, turbulence measurements & 3D	Very good	Very good	This is a key capability for Mongstad area	Key capability for Mongstad area, especially if the pollutants involve the mid / far field	High in case of large / complex computational domain
Wind field 1 - Input data	Poor (1 hourly data for all the computational domain)	Poor (1 hourly data for all the computational domain)	Good (up to 20 met stations, including radiosonde data)	Very good (as beside + 3D wind field from LAM)	Very good (met stations, radiosonde, 3D data from GM)			High in case of large/complex computational domain
Wind field 2 - Model Engine	Basic	Semi-empirical correlations	Interpolation + semi-empirical correlations	Downscaling of LAM data via semi-empirical correlations	Physical 3D fluid-dynamic model			High in case of large / complex computational domain

CAPABILITIES	**GAUSSIAN PLUME MODELS**		**PUFF MODELS**		**LAM + LAGRANGIAN / EULERIAN MODELS**	**Note**	**Evaluation**	**Weight / Importance**
	Gaussian (ADMS)	**Diagnostic + Gaussian (Flowstar + ADMS)**	**Diagnostic + Puff (Calmet + Calpuff)**	**LAM + Puff (MM5+Calmet+ Calpuff)**	**LAM + Hybrid (MM5 / RAMS+ Hypact)**			
Wind field 3 - Output	Basic (2D wind field with capability to input a 3D wind field from another model)	3D wind field	3D wind field	3D wind field	3D wind field			High in case of large / complex computational domain
Chemistry	Basic	Basic	Fair	Fair	Good	No amine chemistry implemented in any model	A separate chemistry model needs to be developed and interfaced (or integrated) with dispersion model.	High
Wet and dry deposition	Yes	Yes	Yes	Yes	Yes	Generic approach - No amine chemistry implemented in any model	No major differences among selected models	Medium
Area / Volume sources	Yes	Yes	Yes	Yes	Yes			Low
Dense gas dispersion	Poor	Poor	Poor	Poor	Poor	All the selected models cannot directly simulate dense gas dispersion. They need coupling with a dense gas model in the near field.	No major differences among selected models	Low

CAPABILITIES	GAUSSIAN PLUME MODELS		PUFF MODELS		LAM + LAGRANGIAN / EULERIAN MODELS	Note	Evaluation	Weight / Importance
	Gaussian (ADMS)	Diagnostic + Gaussian (Flowstar + ADMS)	Diagnostic + Puff (Calmet + Calpuff)	LAM + Puff (MM5+Calmet+ Calpuff)	LAM + Hybrid (MM5 / RAMS+ Hypact)			
Plume visibility	Basic	Basic	Fair (specific algorithm for plume visibility)	Fair (specific algorithm for plume visibility)	To be checked			Low
Easy to use by third parties	Easy	Easy	Fair	Complicated	Complicated (very complicated if LAM needs to be run)		Gaussian and Puff models are more “user friendly”	Medium
Interface with other met/ dispersion models	Poor	Poor	Good	Good	Good			Medium
Easy to modify	Poor (the developer must be involved)	Poor (the developer must be involved)	Reasonable	Reasonable	Complicated			Medium
Cost	Low (estimated between GBP £2,000 to £5,000)	Low (estimated between GBP £2,000 to £5,000)	Free	Free	Free			Low
Regulatory (general - worldwide)	OK	OK	OK	OK	To be checked			High
Regulatory (Norway)	To be checked	To be checked	To be checked	To be checked	To be checked			High
Source code	License	License	Free	Free	Free			Low

CAPABILITIES	**GAUSSIAN PLUME MODELS**		**PUFF MODELS**		**LAM + LAGRANGIAN / EULERIAN MODELS**	**Note**	**Evaluation**	**Weight / Importance**
	Gaussian (ADMS)	**Diagnostic + Gaussian (Flowstar + ADMS)**	**Diagnostic + Puff (Calmet + Calpuff)**	**LAM + Puff (MM5+Calmet+ Calpuff)**	**LAM + Hybrid (MM5 / RAMS+ Hypact)**			
Programming Language	-	-	Fortran	Fortran	Fortran			Low
Operating System	Windows	Windows	Windows / Linux	Windows / Linux	Unix / Linux			Low

2.6 Model Selection

2.6.1 Site Description

The Mongstad Refinery area is characterised by:

- Terrain features are relatively complex in the near field. Within 5-6 km from the facilities, terrain elevation ranges from 0 (sea level) to 150m.
- Terrain features can be considered to be complex in the mid to far field (more than 10 km from sources). Terrain elevation can reach 1000 meters, with narrow fjords and valleys.
- Wind field is expected to be relatively homogeneous in the near field (up to 5 km from the source), but not in the mid and far field, following the complexity of terrain features.
- Land use is fairly complicated, both in the near and far field. The area is characterised by the presence of sea, coastline (complicated morphology), industrial area (refinery), and forests. The presence of the fjord and coastline is deemed to have a key influence on the wind field in the region, even if the "leading"/prevailing wind is mostly due to large scale atmospheric circulation.

2.6.2 Preliminary Evaluation

2.6.2.1 Purpose

Table 2-1 compares the five different modelling approaches identified.

For the purpose of the preliminary evaluation, which aims at understanding the spatial scale of the phenomena, the simplest approach is recommended and has been applied: "Gaussian Plume Model, ADMS". This approach is suitable for the preliminary assessment (i.e. Dispersion Case Study, see Appendix 2), because:

- It allows the user to account for the main phenomena (plume rise, transport, dispersion, deposition, etc) in a simplified way.
- Input data is readily available.
- Short computational time, which allows the user to carry out a number of tests and sensitivity analyses.
- Robust approach, also used for regulatory purpose.
- Output data is easily manageable.

The main findings of the dispersion case study focus on:

- Identification of the "area of interest" (i.e. the area where concentrations of pollutants are above or close to the defined air quality criteria).
- Estimated time scale of the phenomena (residence time of pollutants inside the "area of interest"). This is an important factor when considering incorporating amine chemistry within existing air dispersion models.
- Sensitivity on the amine conversion rate.
- Sensitivity on PBL parameters (mixing height).

2.6.2.2 Results

The key findings (see Appendices 2 and 3) from the dispersion case study and literature review are:

- The most important pollutants to be tracked are anticipated to be nitrosamines and nitramines (secondary product from amine degradation).
- The area of interest is still not clear, due to uncertainties in the chemistry (essentially the reaction/conversion rates of amine compounds in the atmosphere). However, sensitivity analysis indicates that the potential impact is limited to the near or mid field (from 2 km up to 10-12 km from the source, depending on the assumptions on amine conversion rate).
- The timescale for dispersion ranges from a few minutes to 2 hours, depending on chemical conversion rate (uncertain) and meteorological conditions (mainly wind speed). This is the time the pollutants spend inside the area of interest. After this time, the dilution is sufficient to make sure there are "no adverse effects". This means that the modelling activity should focus on the fate of pollutants within the first hour or two after the release.
- From the literature analysis, the formation and subsequent degradation of the nitrosamine and nitramine from amines is uncertain and requires further study to be understood. Initial review of readily available information suggests that the formation reactions of nitrosamines (from MEA) are relatively slow – see Appendix 3 (hours, with the conversion rate limited to no more than 1%).
- Sensitivity on conversion rate demonstrates that this is a key parameter, and additional investigations (laboratory analysis) are recommended.

2.6.3 Model selection for subsequent project stages

The model selection for the subsequent project stages has been based on:

- The model comparison / characteristics given in Table 2-1.
- The results of the literature review for amine reactions into atmosphere (see Appendix 3).
- The results of the preliminary evaluation/ dispersion case study, given in Appendix 2 and summarised above.

The general conclusion is that either a Gaussian plume model (e.g. ADMS) or a Modified Gaussian Pufff Model (e.g. the "CALPUFF Modelling System) can be considered suitable for the purposes of the next stages/phases of the project. This is because:

- The area of interest is restricted to the near-mid field (up to 10-12 km), based on the assumed air quality criteria and the amine emission data supplied.
- In the near-mid field the complexity of terrain features is medium.
- Both the models can address wet and dry deposition.
- Both the models allow the calculation of the most important short term and long term atmospheric parameters to be compared with the Air Quality Standards.

- No potential significant improvements have been identified if the most refined and complex models (Eulerian/Lagrangian models) are used.

Despite both ADMS and CALPUFF Modelling System being suitable for the purposes of the next phase of the study, the CALPUFF Modelling System has some additional benefits, as discussed below:

- ***If*** the timing of the chemical reaction/degradation of amines (to form nitrosamines/nitramines) is comparable with the timing for transport and dispersion into the area of interest (up to 10-12 km), the "time" parameter is an important factor in the simulation of amine chemical reactions. It should be emphasised that ADMS is a steady-state plume model, where the parameter "time" is not considered (i.e. the "history" of the pollutant from the source to the receptor cannot be simulated). CALPUFF is a time-varying model, where the pollutant can be followed step by step (minimum time step 1 sec) from the source to the receptor. This capability provides a good base for a more accurate implementation of an amine chemistry model using CALPUFF.
- Further to the above, CALPUFF also allows some improvements due the capabilities for simulating pollutant transport in complex terrain areas. Within this context, the use of LAM data (if readily available) as input could also be considered.

3 DISPERSION CASE STUDY

3.1 Introduction

This section outlines the dispersion case study conducted for the facilities associated with the CCM project, and:

- Summarises the case study, the various input data (emission, terrain and meteorological data), and the proposed air quality criteria.
- Presents and discusses the results from the dispersion case study.
- Provides a summary of the key findings from the dispersion case study.

More details regarding the dispersion case study can be found in Appendix 2.

3.2 Dispersion Case Study

3.2.1 ADMS4

The dispersion case study was conducted using ADMS 4, Version 4.1, a Gaussian plume air dispersion model. As discussed in Section 2.6.2 (and in detail within Appendix 1), this is considered adequate for the purposes of this preliminary assessment because:

- It allows the user to account for the main phenomena (plume rise, transport, dispersion, deposition, etc) in a simplified way.
- Input data readily available
- Short computational time, which allows the user to carry out a number of tests and sensitivity analyses
- Robust approach, also used for regulatory purpose
- Output data easily manageable (e.g. considering different amine conversion rates to secondary pollutants)

It is noted that none of the modelling approaches discussed in detail within Appendix 1 are capable of dealing with amine chemistry directly.

3.2.2 Emission Sources

The sources considered in the case study are briefly outlined below:

- Sources associated with the CHP (combined heat and power plant) Carbon Capture plant. These include emissions from the CHP stacks, as well as the CHP absorber overhead (the key emission source of interest).
- The source associated with the TCM plant (pilot carbon capture and storage plant) - the TCM absorber overhead.

- Sources associated with the existing Mongstad refinery. These include the main refinery emission sources, namely the residue catalytic cracker (RCC), the old refinery main stack, a second reformer stack and the calcination furnace stack.

The emission sources are summarised in the table below.

Table 3.1: List of significant air emission sources

Facility	Source Name / Description	No. of sources	No. of stacks
CHP	CHP Stacks	2	2
	CHP Absorber Overhead	1	1
TCM	TCM Absorber Overhead	1	1
Refinery	Residue catalytic cracker Stack (RCC)	1	1
	Old Main Refinery Stack (crude oil heater, reformer ovens, old steam boilers)	More than 3	1
	Reformer 2 Stack	1	1
	Calcination Furnace Stack	1	1

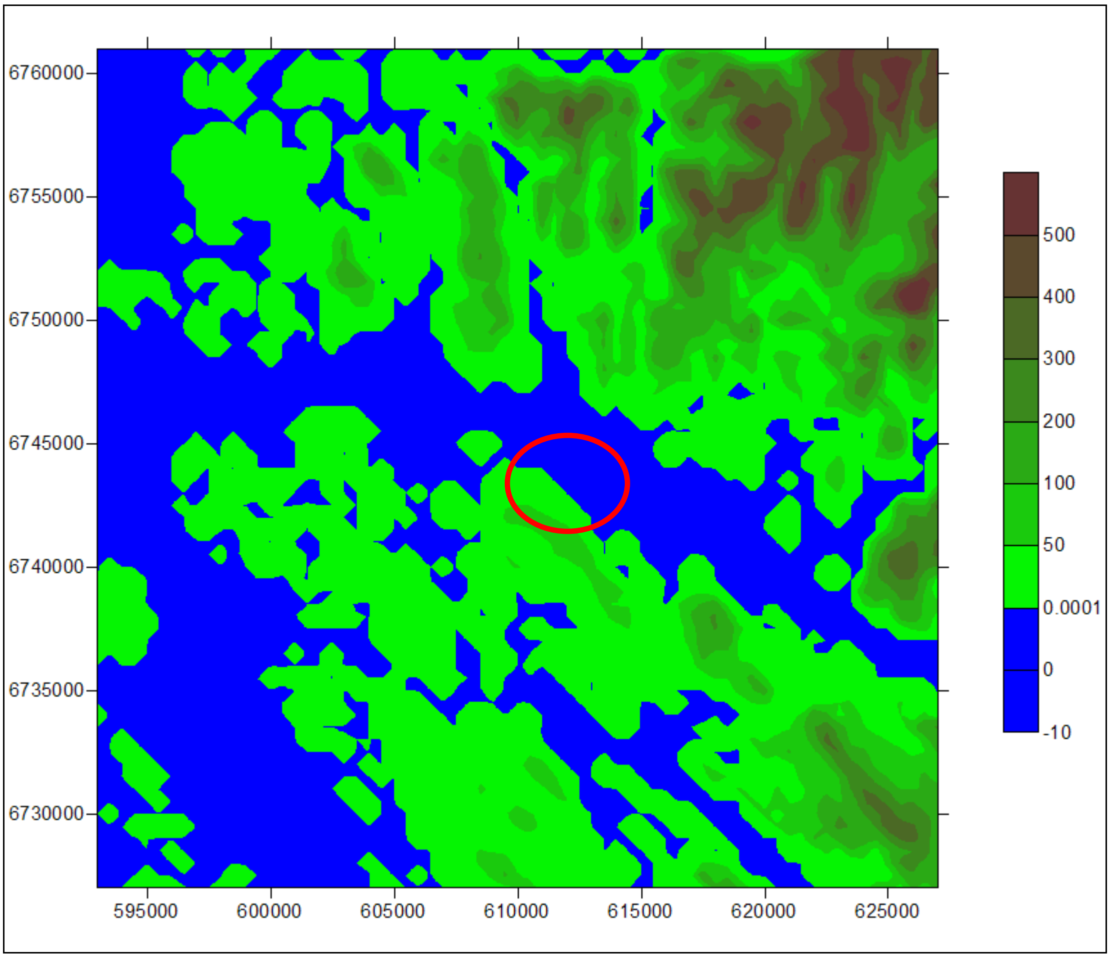
Point source emissions generated by the facilities include primary pollutants such as NO_x, SO_2, NH_3, MEA (mono ethyl amine) and possibly methylamine, as well as secondary pollutants such as methylamine acetaldehyde, nitramines and nitrosamines. Nitrosamines and nitramines are considered the most toxic and harmful to people and the environment, and are the key secondary pollutants of interest to this study.

Detailed emission data is provided in Appendix 2.

3.2.3 Terrain Data

For the purposes of this study, terrain data was purchased from East View Cartographic Inc. The red circle in the figure below indicates the approximate location of the Mongstad facilities. The dimensions of each grid cell are approximately 500 m x 500 m, ensuring that key variations in terrain are adequately represented. It can be seen that the Mongstad area and its immediate vicinity can be considered relatively “flat” (elevation of 50 m or less), with increasing elevation at greater distances.

Figure 3.1: Terrain data used in dispersion case study



3.2.4 Modelling Grid

Preliminary runs using 7 lines of meteorological data corresponding to the Pasquill-Gifford stability classes A to G were conducted in order to obtain an indication of the expected maximum concentrations (and under what type meteorological conditions they occur) in the area, though more importantly for setting an appropriate modelling grid for the study.

The criterion for doing this was set as the long term risk threshold concentration for exposure of the general population to nitrosamines in air (by inhalation) of 4 ng/m3.

These preliminary runs indicated that the area that can be affected is significantly less than 10 km from the release sources, assuming a maximum amine conversion to nitrosamines/nitramines of 0.3% (see Appendix 2, Section 3.1).

Based on the above outcome the calculation/modelling grid for the dispersion case study was set to approximately 14 km x 14 km, with the corresponding area covered by the terrain data set at 34 km x 34 km.

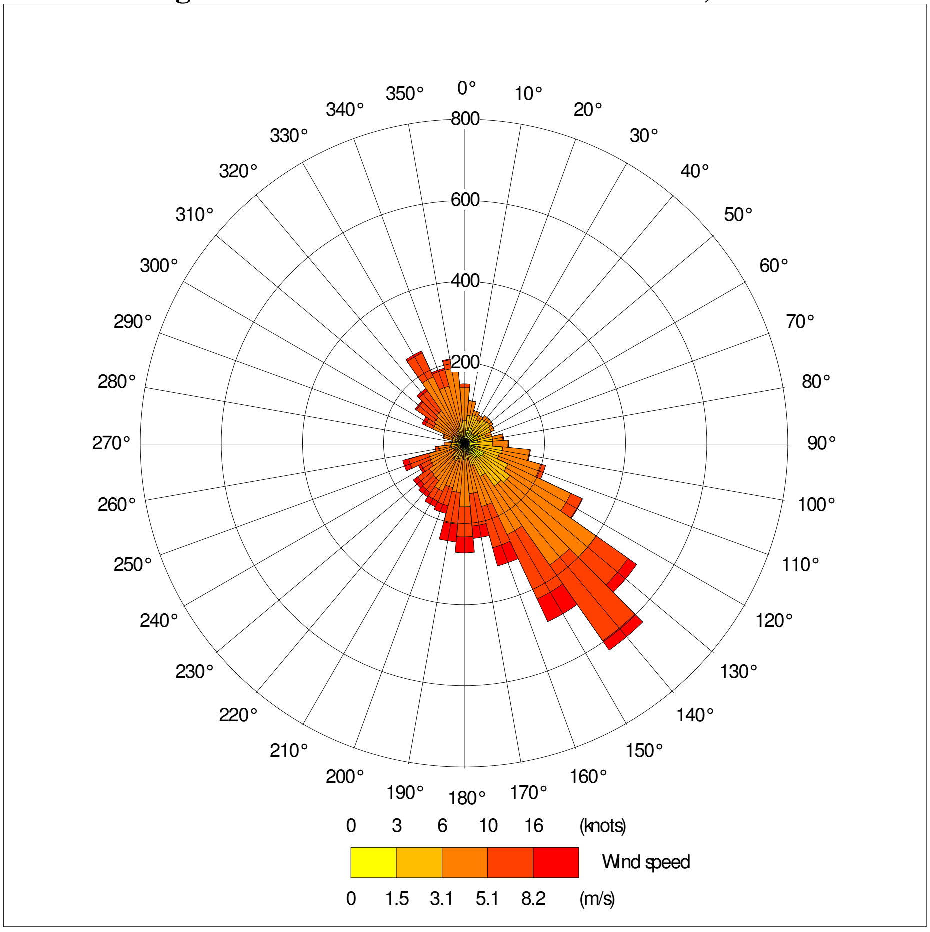
3.2.5 Meteorological Data

Two sources of data were examined by DNV when selecting the meteorological data for the dispersion case study:

- Data purchased from the National Oceanic and Atmospheric Administration (NOAA) for various monitoring stations in the vicinity of the Mongstad area.
- Wind rose data for Mongstad refinery as supplied by Gassnova SF / Statoil and measured on the roof of Control Building IP21.

After examination (see Appendix 2), it was considered that the meteorological data from station 01311099999 (Bergen airport) for 2009 was the best available for use in this study. The 2009 wind rose is provided in Figure 3.2 below, and is consistent with all other years (and with the Mongstad refinery data supplied).

Figure 3.2: Wind Rose for 013110999999, 2009



The information considered for the purposes of the case study includes hourly sequential data for:

- Julian Day Number (TDAY)
- Hour of the Day (THOUR)
- Wind speed (U in m/s)

- Wind direction (PHI in degrees)
- Cloud Cover (CL in units of eighths/octas)
- Temperature (T0C in degrees Celsius)
- Precipitation (P in mm/hour)

3.2.6 Air Quality Criteria

For primary pollutants the air quality criteria are based on limits set by Klif (Norwegian Climate and Pollution Agency, former SFT) for NO_2 and SO_2 and the UK Environment Agency for NH_3. For acetaldehyde, no established short or long term criteria could be found, hence occupational exposure limits are converted to short and long term criteria based on an approach using UK Environment Agency Guidelines.

The air quality criteria used for amines and secondary pollutants are based on available information in NILU reports. For nitrosamines:

- *"Long term risk threshold for exposure of the general population by nitrosamines through inhalation is 4 ng/m3 nitrosamines in air, corresponding to a* 10^{-6} *lifetime cancer risk"*

This corresponds in DNV's understanding, to a long term annual criterion. No information is provided in the available literature with regards to short term criteria, so DNV have assumed that the equivalent short term criterion is an order of magnitude greater.

For nitramines the same criteria is applied as nitrosamines in the absence of other data (this is considered pessimistic as acute toxicity data available suggest that nitramines could be an order of magnitude less toxic than nitrosamines).

The readily available information implies that the most toxic amine degradation products are nitrosamines and nitramines, hence this dispersion study focuses on these.

It should be noted that, particularly for amines and secondary pollutants, the suggested air quality criteria (against which the results are judged) are based on DNV's judgement of the limited information available, as there are currently no published ambient air quality criteria for amines or their degradation products. It is recommended that results from other studies currently ongoing are utilised in order to help establish air quality criteria relevant for environmental studies.

The limit values and proposed criteria used in this assessment are presented in Table 3.2 below.

Table 3.2: Maximum Permitted Ground Level Concentrations Criteria

Pollutant	Short Term (1-hour average) - µg/m3	Long Term (Annual) – µg/m3
NO_x[2]	200[3]	40[3] (30 for ecosystem)[3]
SO_2[2]	350	20
NH3	566	98
MEA	At least 10x LT	10
Acetaldehyde[4]	6,750	450
Methylamine	At least 10x LT	10 (equivalent to MEA)
Nitrosamines/Nitramines	At least 10x LT	4 ng/m^3 [1]

1 Equivalent value for nitrosamines assumed for nitramines (possibly pessimistic).
2 The criterion for NO_2 is based on the 99.8%ile, whereas for SO_2 it is based on the 99.7%ile.
3 As NO_2 ; it is assumed in the model that NO_2 corresponds to 10% of the resulting NOx concentration.
4 To determine Acetaldehyde criteria, occupational exposure limits {STEL 67,500$\mu g/m^3$, 8 hour limit 45,000 $\mu g/m^3$} are converted to short and long term criteria based on an approach using UK Environment Agency Guidelines (Technical Guidance Note E1). Annual average criterion is calculated as 1/100 of the 8-hour occupational exposure standard, whereas the 1-hour average criterion is calculated as 1/10 of the STEL (15 minute) value.

3.3 Results

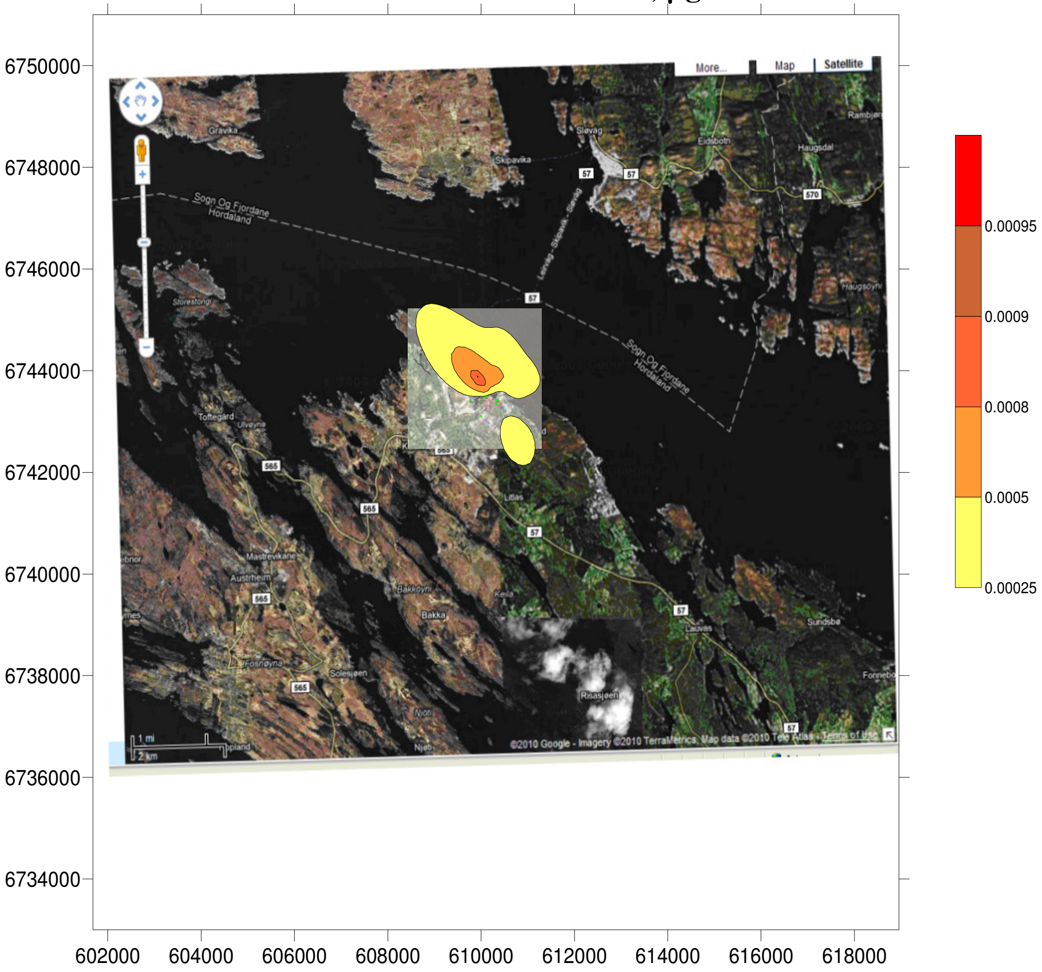
The case study was initially conducted without accounting for deposition, as this will result in the most pessimistic ambient air concentrations for the various pollutants considered (and also the largest possible affected area).

The modelling results were post-processed using the Surfer package to account for the different amine conversion to nitrosamines / nitramines found in literature:

- 0.3%, based on *Atmospheric Degradation of Amines – Gas phase photo-oxidation of MEA, NILU OR 8/2010.*
- 2% for nitrosamines, based on *Task 6: Amine Worst Case Studies, NILU OR 78/2008, N-108068, February 2009* (using TEA).
- 7% for nitramines, based on *Task 6: Amine Worst Case Studies, NILU OR 78/2008, N-108068, February 2009* (using TEA).

One long term air modelling ground level concentration contour plot is presented below as an example (many more are provided in Appendix 2), to provide an illustration of the resulting nitramine /nitrosamine concentrations in the surrounding environment. Results were obtained for both long term LT average (annual) and short term ST (1-hour average 100th percentile) GLCs. The peak GLCs for each pollutant modelled are also reported in Appendix 2.

Figure 3.3: Long Term Nitrosoamine/nitramines Ground Level Concentration Contours based on 0.3% conversion, µg/m^3



The resulting air quality results for NO_2, SO_2, NH_3, MEA and methyl amine, as well as the secondary pollutants such as nitrosamines/ nitramines (based on the three different amine conversion rates of 0.3%, 2% and 7%) are provided in Appendix 2, and can be summarised as follows.

Primary pollutants: NO_2, SO_2, NH_3, MEA and methyl amine

The maximum ground level concentrations predicted anywhere on the study grid as a result of the operation of the CHP, TCM and the Mongstad refinery account for less than 5% of the identified air quality criteria for the primary pollutants.

Secondary Pollutants: Nitrosamines and Nitramines

These secondary pollutants are formed as a result of chemical reactions in the atmosphere, and the resulting concentrations depend on the conversion assumed (literature provides three rates; 0.3%, 2% and 7%). It is also noted that a proportion of these secondary pollutants is emitted directly at the stack (as per the emission scenario information provided – see Appendix 2). The emissions at the stack are as follows, in comparison to the emissions as a result of chemical reactions in the atmosphere:

- For the 0.3% amine conversion, around 48% of the nitrosamine/nitramine mass emitted occurs at the stack/release point.
- For the 2% amine conversion, around 7% of the nitrosamine/nitramine mass emitted occurs at the stack/release point.
- For the 7% amine conversion, around 2% of the nitrosamine/nitramine mass emitted occurs at the stack/release point.

Based on 0.3% amine conversion to nitrosamines/nitramines:

- The identified LT and ST ambient air quality criteria for nitrosamines and nitramines are not exceeded anywhere on the modelled grid.
- The peak ST and LT concentrations are approximately 4 times less than criteria.

Based on 2% amine conversion to nitrosamines/nitramines:

- For the LT nitrosamine GLC results, the relevant criterion is exceeded at a distance of up to 1 km from the emission sources.
- For the ST nitrosamine GLC results, the relevant criterion is exceeded at a distance of up to 2 km from the emission sources.
- The peak GLCs exceed the assumed ambient air quality criteria by more than 30% for the ST values, and approximately 7% for the LT values.

Based on 7% amine conversion to nitrosamines/nitramines:

- For the LT nitramine GLC results, the relevant criterion is exceeded up to a distance of over 2 km from the emission sources.
- For the ST nitramine GLC results, the relevant criterion is exceeded up to a distance of over 10 km from the emission sources.
- The peak GLCs exceed the air quality criteria by a factor of approximately 4.5 for the ST values, and a factor of approximately 3.7 for the LT values.

A simple comparison between the peak air quality ground level concentrations of all pollutants for a run where deposition has been modelled and another where it has not indicates that:

- For ST air quality ground level concentrations the peak concentrations when deposition is considered are 5 to 8% lower than when deposition is not considered.

- For LT air quality ground level concentrations the peak concentrations when deposition is considered are 8 to 18% lower than when deposition is not considered.

3.4 Summary of Key Findings

The key findings from the dispersion case study are as follows:

- The maximum ground level concentrations predicted anywhere on the study grid as a result of the operation of the CHP, TCM and the Mongstad refinery account for less than 5% of the identified air quality criteria for the primary pollutants.

- The area that can be affected from dispersion of secondary pollutants from the facilities varies significantly depending on the amine to nitrosamine / nitramine conversion rate assumed. This conversion appears to depend on the amine itself (as well as other factors) and can vary from 0.3% to 7% (see Appendix 3).
- The extent of the area affected by nitrosamines/nitramines is more than 10 km distance from the emission point (when assuming 7% amine conversion). For a 0.3% conversion, no air quality criteria exceedances are observed.

It should be noted that:

- The results are based on the amine emission rates from the CCM and TCM facilities, which are related to the capacity of the CO_2 capture plan. For larger or smaller capture plans the results will vary according the exact amine emission rate (and capture plant capacity).
- The ambient air quality criteria assumed for amines and their degradation products (nitrosamines/nitramines) are based on DNV's judgement of available information, as there are currently no published ambient air quality criteria for amines or their degradation products. As the criteria will heavily influence the conclusions of such studies as this, it is recommended that results from toxicity and other studies currently ongoing are utilised in order to better understand the effect of amines and their degradation products, and to help establish air quality criteria.

4 LITERATURE REVIEW AND MODEL DEVELOPMENT NEEDS

4.1 Introduction

This section summarises the readily available literature of the atmospheric chemistry of amines that have potential use in carbon capture and storage. The objective is to provide guidance to the best strategy for ultimately producing / developing a model (to be incorporated within, or used in conjunction with, existing air dispersion models) that will contribute to the environmental impact statement for the proposed carbon capture scheme at Mongstad.

The key issue is the release of amines from the scrubbing stack at the facility and whether those amines or their degradation products form a significant environmental hazard.

This section summarises that, which is discussed in detail in Appendix 3.

The task was divided into two main sections, a literature review and a “route-map” for model development.

The literature review summarises the presently known information on the following aspects:

- Release Parameters
- Partition between phases
- Products / Further Products
- Yields
- Reaction rates
- Criteria (e.g. for air quality)

The subsequent “route map” section considers the state of completeness of this information and proposes a high-level method for deciding what strategy might be most suitable for the development of a suitable model for future implementation. It also suggests / identifies how model development needs would best be addressed, as well as proposing different options for model development (in the short and long terms).

4.2 Literature Review

4.2.1 Overview

The present review of literature relating to the chemistry of amines and their degradation products in the atmosphere has been undertaken with a view to informing the route map for model development.

The documents selected for review have been those recommended and provided by Gassnova SF / Statoil, supplemented with some on-line research including some input from the Royal Society of Chemistry. There is a concentration on overview documents and meta-studies, rather than primary research documentation.

The main objective of the review is to gain an understanding of the potential environmental hazards that the proposed carbon capture activity might lead to – whether the primary amines used in the carbon capture process or their degradation products constitute an environmental hazard. In particular, it is an objective of the present work to identify what data is required in order to be able to answer this question.

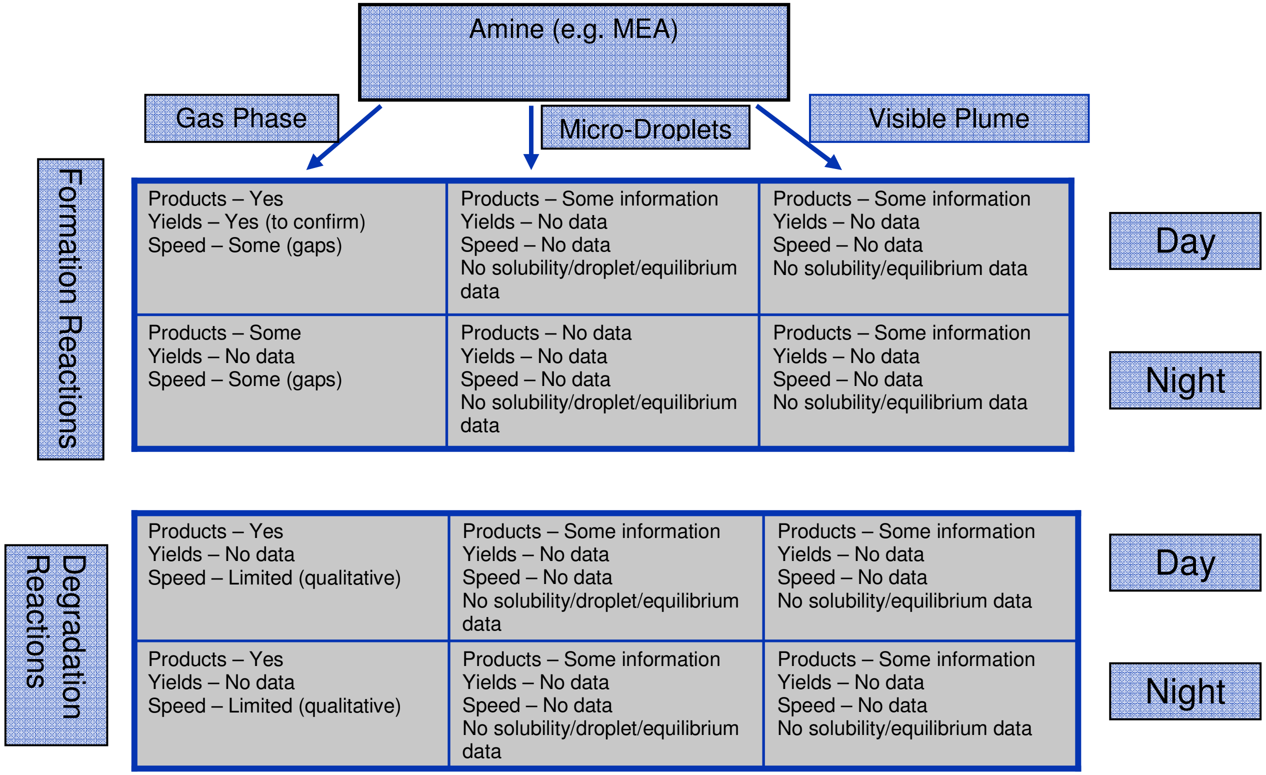
It is a further objective to attempt to place some boundaries around the problem and to explain what level of detail is likely to be required when pollutant modelling is finally undertaken.

In some areas, it has become clear that the present state of knowledge is not sufficient to allow a complete model of the environmental consequences of the proposed process to be built. In these cases, this shortfall is highlighted and the need for further research emphasised.

In this present review, there is a strong emphasis on the best-studied carbon-capture amine, Mono-ethanol-amine (MEA). Where clear differences between this starting amine and others are identified, this difference is highlighted.

Figure 4.1 shows (in schematic form) how the mass of starting amine (MEA in this case) may be partitioned (e.g. gas or aqueous phase) and the state of knowledge of the vital parameters in each case. The figure indicates the knowledge / data gaps for each partition / degradation mechanism. It can be seen that the knowledge to date is concentrated on the gaseous phase, while partitioning into the water phase is poorly examined. This is worth noting as uptake of MEA into the aqueous films is fast, as described below.

Figure 4.1: Overall partitioning of the mass of MEA



Amine (e.g. MEA)

		Gas Phase	Micro-Droplets	Visible Plume
Formation Reactions	Day	Products – Yes Yields – Yes (to confirm) Speed – Some (gaps)	Products – Some information Yields – No data Speed – No data No solubility/droplet/equilibrium data	Products – Some information Yields – No data Speed – No data No solubility/equilibrium data
	Night	Products – Some Yields – No data Speed – Some (gaps)	Products – No data Yields – No data Speed – No data No solubility/droplet/equilibrium data	Products – Some information Yields – No data Speed – No data No solubility/equilibrium data
Degradation Reactions	Day	Products – Yes Yields – No data Speed – Limited (qualitative)	Products – Some information Yields – No data Speed – No data No solubility/droplet/equilibrium data	Products – Some information Yields – No data Speed – No data No solubility/equilibrium data
	Night	Products – Yes Yields – No data Speed – Limited (qualitative)	Products – Some information Yields – No data Speed – No data No solubility/droplet/equilibrium data	Products – Some information Yields – No data Speed – No data No solubility/equilibrium data

4.2.2 Photo-Oxidation of Amines

The initial photo-oxidation reaction of amines in the atmosphere is a hydrogen abstraction by an atmospheric OH radical. The abstraction can take place from 4 possible sites on the MEA molecule: two in the CHOH group that lead to the same reaction products, one in the $–CH_2–$ group and one in the $–NH_2$ group [1, 2].

These four initial reactions are labelled as reactions (1) to (4) as in the following figure, which show the position from which the hydrogen atom has been abstracted by means of a dot over the position of the vacant binding site.

Figure 4.2: Initial reactions of MEA with OH radicals in the atmosphere

$$\begin{aligned}
NH_2CH_2CH_2OH + OH &\xrightarrow{k_1} NH_2CH_2CH_2\dot{O} + H_2O && (1)\\
&\xrightarrow{k_2} NH_2CH_2\dot{C}HOH + H_2O && (2)\\
&\xrightarrow{k_3} NH_2\dot{C}HCH_2OH + H_2O && (3)\\
&\xrightarrow{k_4} \dot{N}HCH_2CH_2OH + H_2O && (4)
\end{aligned}$$

These reaction routes are referred to as Branches 1 to 4, with Branches 1 and 2 being grouped together because of the similarity of the reaction products in those cases.

Figure 4.3: Photolysis reactions of MEA with OH radicals in the atmosphere

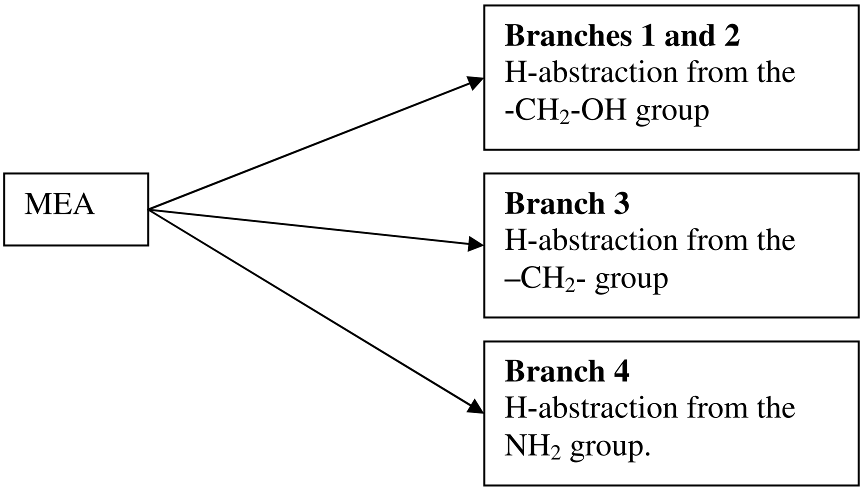
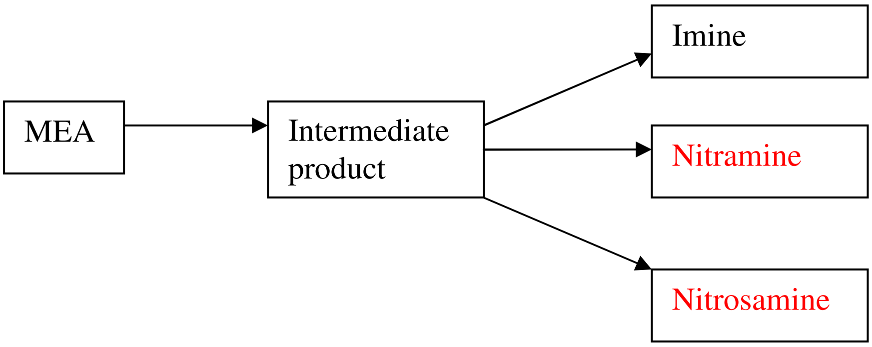


Figure 4.4 summarises the reaction scheme for the formation of nitramines and nitrosamines from MEA. Note that these MEA (and amines in general) degradation products appear to be the most important ones in terms of hazards to people / environment (based on toxicity and other information reviewed).

Figure 4.4: Reactions following hydrogen abstraction from the NH_2 group on MEA



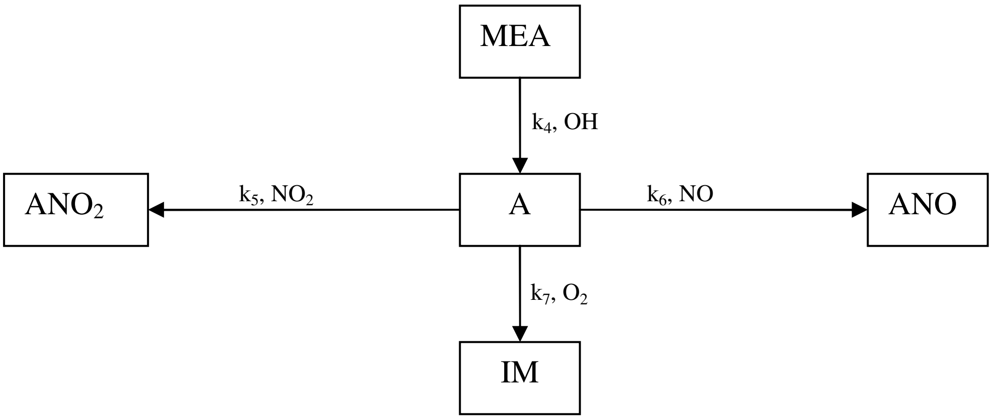
4.2.3 Reaction Rates

DNV has undertaken a preliminary investigation in the formation rates of nitrosamines and nitramines, based on currently available information.

The production of nitrosamine (ANO) and nitramine (ANO_2) are governed by the following reaction scheme (Figure 4.5). Note that this neglects any possible further degradation of the products. ANO is expected itself to further degraded in the presence of photochemically produced OH radicals, but ANO_2 may be relatively stable in the atmosphere with a lifetime in excess of 3 days.

The intermediate product (labelled “A”) is the radical $\dot{N}HCH_2CH_2OH$. The product labelled “IM” is the Imine $HN{=}CH\text{-}CH_2OH$.

Figure 4.5: Reaction scheme for the formation of ANO and ANO_2



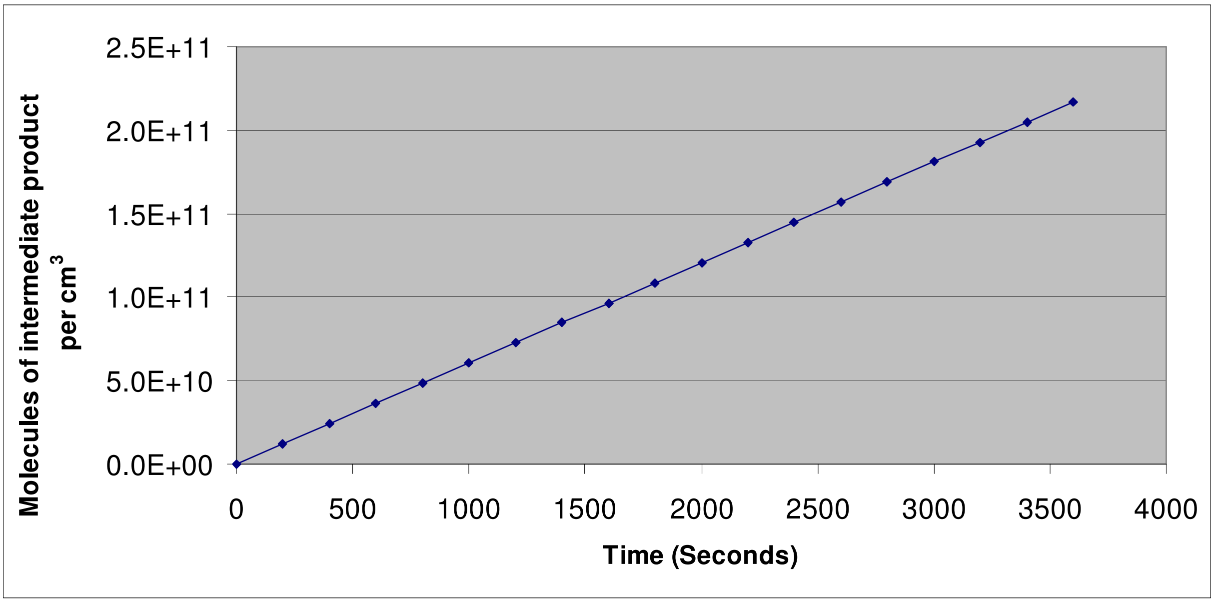
The Valencia experiments report [1] shows the kinetic constant k_4 to be 2.48×10^{-12} $cm^3.molecule^{-1}.s^{-1}$, stressing that this is based on a branching ratio for reaction (4) that is itself an upper limit (note that this is based on MEA as the starting amine).

The kinetic constants k_5, k_6 and k_7 are unknown, but it is known that the major product of the reaction is the Imine.

One way to gain insight into the rate of production of the damaging products ANO and ANO_2, therefore, is to model the growth of the intermediate product A. The rate of production of the products ANO, ANO_2 and IM will all be slower than this modelled growth.

DNV has conducted a simple analysis examining the growth of this intermediate product A (see Appendix 3), and with an initial concentration of $[MEA]_0 = 2.4\times10^{13}$ $molecules.cm^{-3}$ (which is 1ppmV at 1atm and 300K), and $[OH]= [OH]_0$ of 10^6 $molecules.cm^{-3}$ [1], the growth of the intermediate product A can be shown to be represented by the following figure (Figure 4.6), which displays the first hour of the evolution of the growth of the product A.

Figure 4.6: Growth of intermediate product "A"



Notes:
1. It is assumed that [OH] = 10^6 molecules.cm^{-3}.
2. Results produced using the Runge-Kutta-Fehlberg algorithm, order 4, tolerance = 10^5.

This almost linear relationship shows that the consumption of MEA is not the major limiting factor in this timescale, and yields only about 1% of the initial MEA concentration after 1 hour. The growth of ANO or ANO_2 will be slower still and the corresponding first-hour yield will also be lower than this 1% figure.

The true rate will be further limited by the 3-way branching between ANO_2, ANO and IM and by the concentrations of the reactants NO and NO_2.

IM is known to be a "major product" and the other two "minor products". Based on this, it would seem reasonable to assume that at least 50% of the yield is IM (though this would need to be backed-up by further experimental work and other studies). Therefore, a first-hour yield of 0.5% from MEA for both ANO and ANO_2 is still reasonably conservative.

For these reasons, the figure of 0.5% can be used as a conservative estimate of the yield of the damaging products ANO and ANO_2 in the first hour of release of MEA. This figure appears to be limited by the concentration OH radicals, not the availability of MEA, so constant replenishment of MEA does not present a threat to this conclusion.

Furthermore, it is known that ANO in particular degrades "fast" in sunlight, so the 0.5% yield from MEA is additionally conservative in the case of ANO (due to the subsequent degradation reactions that destroy ANO).

For modelling purposes, DNV considers that it would be reasonably conservative to assume that the full first-hour yield of 0.5% is produced before the reactants leave the stack, and dispersion modelling could proceed from that point for the first hour with confidence that the concentrations of the key pollutants is not higher than 0.5% of the initial concentration of MEA.

This conclusion is dependent on the quoted value for OH radicals presence in the atmosphere ($[OH] = 10^6$ OH ions/cm^3). If evidence can be found that this value is not unusually low, then the above approach can be used for the purposes of the next phase of this study.

It should be noted however that the above is only theoretical, and is based on formation reactions in the gas phase, excluding the aqueous phase (the bulk of information on amine chemistry is concentrated on the gas phase at this stage). The partitioning of MEA in the aqueous phase should also be considered (given the high solubility of MEA), as the information available indicates that it is much faster than the reactions in the gas phase. The current data gaps, discussed in Section 4.2.1, do not allow for a preliminary investigation of the fate of MEA in the aqueous phase at this stage (similar to the gas phase formation reaction example).

4.3 Model Development & "Route-Map"

4.3.1 Overview

The issues surrounding the development of a model for the environmental assessment of amines and their degradation products have been examined.

A "route map" towards the objective of a robust assessment of the environmental impact of each of the compounds of interest is laid out, showing what is required in principle at each step, what work has already been completed, what data is available, and what data is missing and should be the subject of further study.

4.3.2 General Considerations

The central problem in the modelling of the air dispersion of possible pollutants released from the carbon capture facility is that of combining the modelling of the atmospheric dispersion with the chemical processes.

In principle, and in the general case, the modelling should reflect the fact that the dispersion and chemical reactions occur simultaneously. That is, for every iteration the model should perform both dispersion and chemical calculations before passing the results on to the next iteration. This implies that the equations governing the chemical processes must be programmed into the dispersion software or a method is developed to perform these calculations outside of existing air dispersion modelling software. The dispersion models reviewed as part of the present study do not have amine specific chemical modules.

However, certain special cases may exist that could be exploited to simplify this process.

For instance, if the chemical processes can be shown to take place much faster than the dispersion process, then the chemical reactions can be regarded as essentially complete before the dispersion modelling begins. This is a significant simplification of the problem since it would allow the yield of the chemical reaction to be calculated outside of the atmospheric dispersion modelling programme (by reference to laboratory experiments for instance). The dispersion programme could then be used to model the dispersion of the product, or the results of the model post-processed to account for a yield factor. The latter is essentially the assumption that has been made in the Dispersion Case Study reported as Appendix 2 of this document (see Section 3).

If the chemical processes can be shown to take place much slower than the dispersion process, then the dispersion process can be regarded as complete before the chemical reactions begin. In this case, the chemical reactions would take place in the natural environment. Again, this represents a simplification since the concentration of the reactants other than the pollutant of interest can be regarded as constant during the course of the calculation.
If the chemical processes are indeed *found to be* much slower than the transport/dispersion processes, then the primary pollutant (i.e. amine) will have diluted sufficiently that the potentially dangerous amine degradation products will also be diluted enough as to not pose a threat in the environment.

4.3.3 Existing models

The qualities of two existing air dispersion modelling software packages, ADMS and Calpuff, that can be utilised for the purposes of future model development, have been discussed previously in Section 2.

ADMS is a “steady state” model that does not report the time evolution of the discharged gas, but rather reports the concentrations of pollutants as a function of position (note that there are capabilities within ADMS that allow, for single point sources and short-term averaging only, the estimation of various other plume properties such as temperature, travel time from the source, height etc). This means that if it is to be used to help model the dispersion of pollutants released at the Mongstad facilities, some strong assumptions must be justified first. That assumption is exactly the condition discussed in the previous section: that the chemical reaction takes place either much more quickly or more slowly than the transport / dispersion process. Whether this assumption can be justified in the case of the pollutants of particular interest for this study (nitrosamines and nitramines) is discussed in the sections below. It is also noted that ADMS includes modules of a kinetic-chemistry model for wet deposition of SO_2 and HCl, as well as NOx chemistry.

Calpuff is a non-steady state model that reports the evolution through time of the dispersion of compounds of interest, given an initial concentration, also as a function of position. Another feature of Calpuff is that it allows for chemical transformation options.

It is thought that it would be possible to use the output from Calpuff (or ADMS if the time parameter is not important in amine chemistry) as an input into a post-processing framework that implements the chemistry model.

Additionally the existing chemistry modules / options (not amine specific) in the dispersion models can be used for incorporating new chemistry models into them.

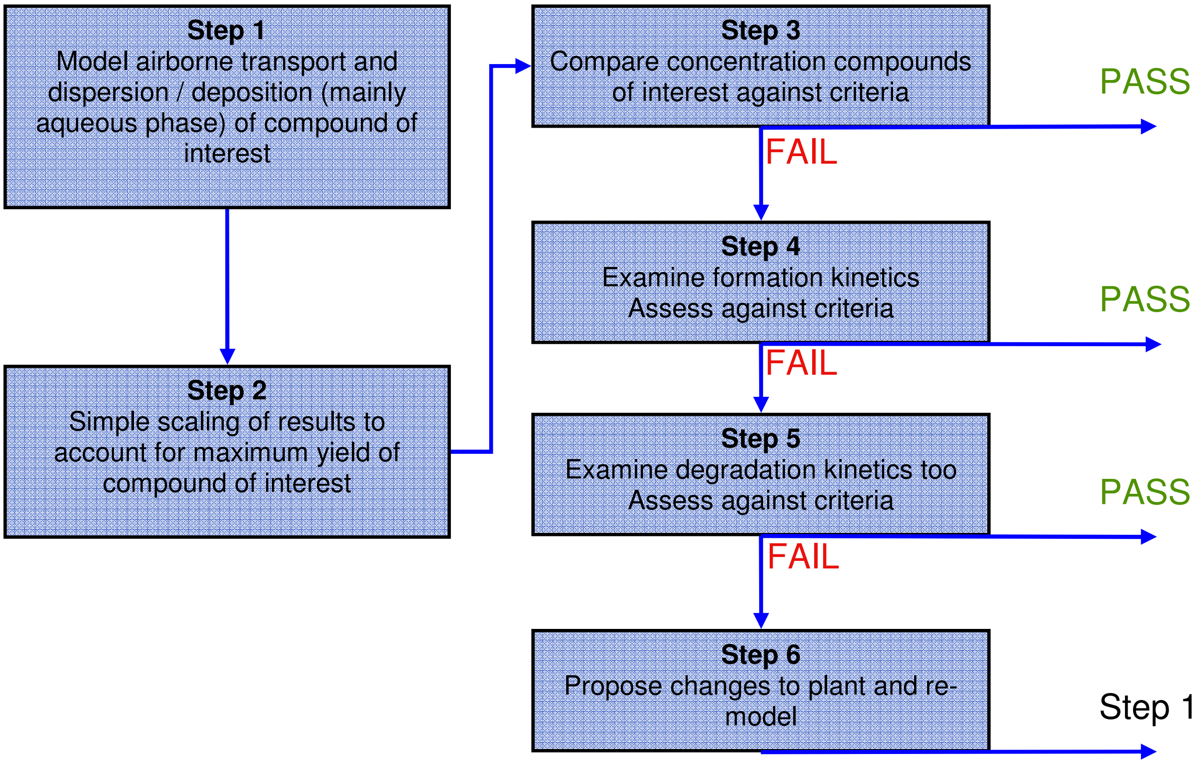
4.3.4 "Route-Map"

The following general scheme (Figure 4.7) is proposed for the overall assessment of pollutants potentially emitted by the facilities (including their degradation products). Some of these steps for some of the potential pollutants have been performed already, either as part of the worst case studies [3] or in the dispersion case study conducted as part of this study.

Each step in the scheme below represents an increasing level of sophistication and refinement. It is to be expected that proceeding through the steps of this assessment scheme will result in concentration estimates for the compounds of interest that are successively less and less conservative.

Since all the assumptions made for the crude approximation models are designed in such a way that the resulting concentrations will be over-estimates, there is no need to proceed to a subsequent Step for a particular compound of interest if it passes the criteria at any stage.

Figure 4.7: Route map for the overall assessment of pollutants



This scheme should be "interpreted" in conjunction with Figure 4.1, which illustrates the current knowledge and vital parameters for the different amine degradation mechanisms/schemes (e.g. gas phase degradation reactions at day and night).

Step 1

Inputs

- Identification of the compounds of interest and emission rates / other parameters
- Meteorological data for the study location
- Transport and dispersion model

Outputs

- Concentration contours (or deposition) of compounds based on the assumption that the compound is emitted/produced at a yield of 100% and remains un-reacted.

Current Status

This step has been performed at least twice for the study facilities, as part of the worst case studies [3] and as reported in Appendix 2 of this study. Existing air dispersion modelling software were used to conduct these studies.

A list of compounds of interest has been obtained from the various theoretical and experimental studies of atmospheric degradation of amines that have already been performed.

Step 2

Inputs

- All the inputs identified for Step 1
- Calculation of the maximum yield of the compound of interest under the conditions to be studied.

Outputs

- Concentration contours (or deposition) of each compound of interest under the assumption that the compound does not degrade once it has formed.

Current Status

The yields of the compounds of interest depend in principle on a number of factors. The following is not necessarily a complete list:

- Starting amine selected
- Concentration of OH radicals in the atmosphere
- Concentration of NO_x in the atmosphere
- Humidity
- Solar radiation and temperature

Yields for the compounds of interest have been reported in two experimental studies using two difference starting amines, the tertiary amine TEA, and the primary amine MEA (and discussed previously within this report). There are significant differences.

Implicit assumptions

The implicit assumption at this stage of the assessment is that the amine degradation products form quickly enough that no significant dispersion has taken place by the time that the bulk of the yield has been produced. This is a conservative assumption for the amine degradation products (i.e. it over-estimates the production of them) because the rate of production of the degradation products depends on the concentration of the reactants and any dispersion that takes place before reaction will slow that production and reduce the concentration of the degradation products.

Conversely, in the case of the starting amine itself, the assumption is that it remains un-reacted.

Since the starting amine is consumed in the production of the other compounds of interest, these assumptions are clearly contradictory. However, since the goal is to achieve a high degree of confidence that all compounds are distributed in the environment at acceptably low levels, they are justifiable.

Step 3

Step 3 is an assessment in which the outputs from Step 2 (essentially concentration or deposition contours of each compound of interest) are compared against identified criteria.

Inputs

- Criteria for all the compounds of interest must be established. Inhalation criteria, water quality criteria and deposition criteria (to land) are all of interest.

Outputs

Tolerability assessments for each compound.

Current Status

The status of the identification of suitable criteria for each compound of interest has been discussed in Appendix 3 and Section 3.2.6 of this report. The most notable gap in the presently-assembled knowledge is criteria for nitramines. Nitramines are known to be carcinogenic in rodents but the degree of carcinogenicity is expected to be lower than that for nitrosamines. A good first assessment criteria set would be to adopt that for nitrosamines. However, given the fact that the observed yields in smog chamber experiments was higher in the case of nitramines than for nitrosamines, this first approach may not be successful (i.e. maybe overly conservative).

Step 3 has already been performed for the compounds of interest as reported both in [3] and Appendix 2 of this study. The results for this study [3] are reproduced in the table below.

Note that the effects on ambient air quality have been discussed in Appendix 3.

Step 4

Step 4 of the route map for assessment involves dropping the assumption that amine degradation compounds of interest achieve their full yield very quickly relative to the time scale for dispersal.

It has been explained in earlier sections why this assumption is a conservative one and why it might therefore overestimate the concentrations of amine degradation products. Step 4 involves, therefore, the modelling of the formation and dispersion of those compounds that have been identified in Step 3 as requiring further study (i.e. FAIL). It is anticipated that this increase in the sophistication of the approach used to model the compounds of interest will result in lower estimates of their concentration in the atmosphere and of their rates of deposition.

Step 4 does not include the modelling of the further degradation of the compounds of interest. Modelling the further degradation may not, in fact, be a great increase in complexity, but this Step is defined separately in recognition of the fact that modellers may be forced to model formation without further degradation as a result of lack of data, and because criteria may be achieved without having to consider further degradation.

Inputs

- All the inputs identified for previous assessment steps
- Understanding of the reaction schemes that lead to the compounds of interest.
- Kinetic rate constants
- Ranges for the concentration of the reactants

Outputs

A refined estimate (now incorporating the formation kinetics of amine degradation) for each compound of interest (i.e. nitrosamines/nitramines) as concentration contours (or deposition).

Current Status and possible methods

A sufficient understanding of the reaction schemes for the gaseous phase is probably now in place to begin modelling effort, but information on the required kinetic rate constants is patchy. The reaction leading to nitramines (for example) is a two stage process and information regarding only one of the two required kinetic constants is presently available (- see Appendix 3). It is possible that once a working model of the process is established, the missing kinetic constant could be estimated from the experimental results already obtained.

The reaction speeds also depend on the concentrations of amine, OH and NOx. These can be estimated from the properties of the Mongstad development or results produced for a range of these concentration values.

In an effort to understand the formation (in essence the speed of the reaction) of the first stage of formation of nitramines (from MEA), where most kinetic data are available, DNV has conducted a simple analysis, detailed in Section 4.2.3.

There are a variety of possible methods that could be employed to implement a Step 4 assessment. None of these options is understood to have been implemented at present.

As identified by Section 4.2.1 (and Figure 4.1), there are significant data gaps for amine chemistry within the aqueous phase.

Option 1: Program the chemistry into an existing dispersion model

ADMS and CALPUFF already contain modules that perform some chemical calculations (e.g. NOx chemistry in ADMS). In principle, it should be possible to amend these chemistry modules to perform amine chemistry calculations simultaneously with dispersion. Some information on the current level of detail and required inputs (as well as the outputs) in the chemistry modules of ADMS and CALPUFF are briefly discussed below.

Note that the chemistry modules described below refer to NOx and SOx. However, it should be emphasised that the "MESOPUFF II" module described below (implemented in the CALPUFF Modelling System), even if developed for NOx chemistry, includes all the main chemical mechanisms (photochemical, aqueous and gas reactions) which are included in the amine chemistry.

ADMS 4

ADMS 4 has the ability to calculate the chemical reactions in the atmosphere between nitric oxide, nitrogen dioxide and ozone (NO, NO_2 and O_3 respectively), and therefore the resulting concentrations of each of these pollutants in the plume.

The chemical scheme uses the reaction rates from the Generic Reaction Set (GRS) of equations [8,9], a semi-empirical photo-chemical model which reduces the complicated series of reactions involving NO, NO_2, O_3 and various hydrocarbons to just seven.

Hydrocarbons are not included in the ADMS 4 chemical reaction scheme, which then reduces to the following equations:

$NO + O_3 \rightarrow NO_2 + O_2$ (1)

$NO_2 + hv$ (ultra-violet radiation) in the presence of oxygen $\rightarrow NO + O_3$ (2)

The reaction coefficient for equation (1) depends on the air temperature, whereas the photo-dissociation coefficient for equation (2) depends on the solar radiation.

This chemistry module also uses the background level concentrations of NO_x, NO_2 and O_3 to initialise the chemistry scheme. The main assumption in this calculation scheme is that the background pollutants are mixed instantaneously into the plume.

The NO_x chemistry calculations are performed after all plume dispersion (and wet/dry deposition if applicable) calculations have been conducted for all pollutants and sources. This is because the total concentrations are required in order to model chemistry correctly.

CALPUFF

CALPUFF has the capability of modelling the linear chemical transformation effects in a manner consistent with the “puff” formulation in the model.

Three options are available within the CALPUFF chemical module for dealing with chemical processes:

1. A pseudo-first-order chemical reaction mechanism for conversion of SO2 to SO_4^{2-} and NOx to NO_3^-. This mechanism is based on the chemical transformation scheme used in the MESOPUFF II model [10] and incorporates the most significant dependencies of spatially and temporally varying environmental conditions on the transformation rates.
2. The ARM3 scheme [11], which treats the NO and NO_2 conversion process in addition to the NO_2 to total NO_3^- and SO_2 to SO_4^{2-} conversions, with equilibrium between gaseous HNO_3 and ammonium nitrate aerosol.
3. User specified 24-hour cycles of the transformation rates. This allows the simulation of the diurnal, time-dependent behaviour of the transformation rates (note however that the transformation rates are spatially uniform).

The first two options use ozone concentrations (and solar radiation intensity) as surrogates for the OH radical concentration during the day, when the gas phase free radical chemistry is active. Hourly observations of ozone concentrations at one (or preferably more) monitoring stations is a model input requirement.

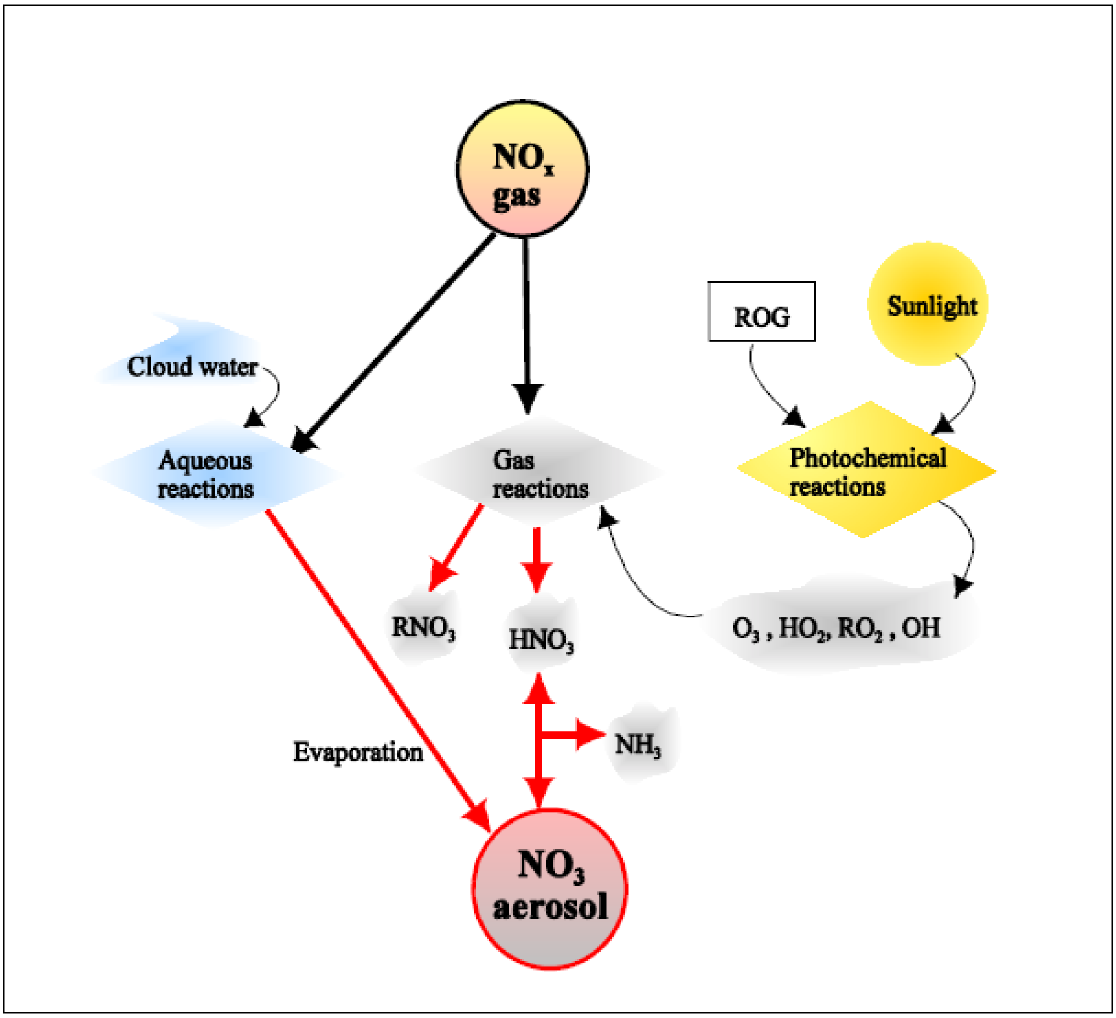
The following sections provide a brief summary of the two first chemical mechanisms/options.

1. MESOPUFF II Chemical Mechanism

The chemical processes included in this option are the conversion of sulphur dioxide to sulphate and the conversion of nitrogen oxides to nitrate aerosol. The chemical pathway for nitrogen oxide and aerosol formation is illustrated in **Figure 4.8**.

Oxidation may occur by gas and aqueous phase reactions. The gas phase reactions for both SO_x and NO_x involve free radical photochemistry and are therefore coupled to the oxidation of reactive organic gases (ROG).

Figure 4.8: NO_x Oxidation Pathways



2. ARM3 Chemical Mechanism

This is based on a condensed pseudo-first-order chemical scheme. The mechanism assumes low background volatile organic compounds (VOCs) concentrations; hence it should be considered prudent to use this option for relatively clear, non-urban areas.

The rate of sulphate and nitrate production is estimated by calculating the steady-state OH radical concentration, which is the primary SO_2 and NO_2 oxidiser.

Option 2: Use existing dispersion models with post processing of results

Use ADMS or CALPUFF as a source of pollutant concentration and temperature / other data (also time if deemed necessary which is only a Calpuff output), which is output to a spreadsheet and then joined to a bespoke secondary chemistry spreadsheet calculation model.

The secondary chemistry model would be a solution of the chemical reaction equations using first principles and probably numerical methods to yield solutions to the differential equations to a known precision.

Such a hybrid model could be calibrated against ADMS or CALPUFF by examining, for example, the special case of the NO_x chemistry that is already built into those software products.

The following aims to elaborate further on some of the characteristics of this option, noting however that certain assumptions are made in order to provide an example of input data required and the expected outputs and their interpretation.

Given the various data gaps in amine chemistry (which are discussed in detail in Section 5.4), at this stage it is only the gas phase formation reactions of nitrosamines and nitramines (as an example of data requirements / outputs) that is elaborated. This is because most of the existing experimental and literature data are related to the formation reaction of secondary pollutants in the gas phase (with MEA as the starting amine). It should however be noted that the key data gaps identified would all need to be addressed in order to have a better and full understanding of amine chemistry and adequately address all the key issues, including for example degradation of secondary pollutants.

Having said that, the approach when building a chemistry model (and the model structure) using this option will be largely the same independent of the particular amine chemistry issue that is aimed at (e.g. formation or degradation of secondary pollutants). If adequate data are available for representation of the different amine chemistry issues, they could all be addressed using the same overall chemistry model.

However, it should be noted that when these data become available, each amine chemistry stage should be looked at individually (and not necessarily through a full chemistry model development) in order to verify whether, for example, the subsequent degradation of nitrosamines requires to be addressed in such way (e.g. it may be a much slower reaction than the equivalent formation one, hence can be ignored for the purposes of dispersion/chemistry modelling). In other words, the spreadsheet will be aimed at investigating only the reaction stages / mechanisms which are significant within the time / space framework relevant to the dispersion.

Existing dispersion models (ADMS and CALPUFF) can provide suitable background data for the amine chemistry modelling. In particular, the set of data could include (but not limited to) the following:

- Ground level concentrations.
- Dry/wet/total deposition.
- Temperature, solar radiation and relative humidity.
- Concentration along the plume centreline.
- Trajectory of plume centreline.

It is noted that these data can only be provided for a single point source for each ADMS run (model limitation).

The above data can be provided by the models in two different formats:

- In the simplest case, the above data are provided as a "steady-state snapshot", for each meteorological condition (ADMS, CALPUFF). This means that only the final distribution of pollutants (for each meteorological condition) is available. Hence, the "history" of the pollutants (in terms of path, age, travel time, etc) is not available.
- In the most refined case, the data are provided as subsequent time-steps (transient evolution of the plume). This means that the "history" of each pollutant particle is tracked. Note that this option is available only in CALPUFF (which is a time-dependent model) and, generally, in all Lagrangian models.

Depending on the reaction mechanisms, and the kinetics associated with each mechanism, the "history" of pollutants (i.e. the parameter "time") could become an important factor in the chemistry model development. In this case, the interface with the CALPUFF model would provide more suitable background information.

In order to create a post-processing chemistry tool, the various formation reaction constants discussed in Section 4.2.3 (k4, k5, k6 and k7) would be required as input data. The rate constants for the formation of nitrosamine (k6) and nitramine (k5) would be the most important information to be obtained, since as identified earlier they appear to be the most important amine degradation products. The concentration of OH radicals in the Mongstad area would also form a key input.

This chemistry model would in essence be a solution of the chemical formation reaction equations using first principles and probably numerical methods, utilising the data obtained from the aforementioned 3rd party studies as well as the background data provided by existing air dispersion models (ADMS or CALPUFF).

Solving these equations would then provide the growth profile (and hence yield factors from MEA emissions) of these secondary pollutants against time or distance from the emission sources (based on the MEA emission data provided). From these, the ground level concentrations of nitrosamines/nitramines contour plots can be produced, which will then be compared against the applicable criteria.

A simple schematic of this process is shown in Figure 4.9. The MEA concentration downwind of the emission source (blue line) is supplied by the dispersion model (ADMS, CALPUFF), together with the main atmospheric parameters. Based on these background data (and accounting for the reaction mechanisms), the chemistry model is able to calculate the "nitrosamines yield" parameter (violet/purple line), taking into account both formation and degradation mechanisms, as shown in the figure, if all the necessary data are available. Note that the "nitrosamines yield" parameter is space-varying, i.e. depends on the distance from the source (if the CALPUFF model is used for background data, this parameter is both space / time varying). Then, the nitrosamines yield parameter is used to factor-down the MEA concentrations (see red arrows in the figure), in order to obtain the actual concentration of nitrosamines (green line).

A simple schematic of the conceptual steps in the overall process is provided in Figure 4.10 (i.e. an example Option 2 "solution"). Note that this example only deals with the gas phase formation reactions of nitrosamines and nitramines.

Figure 4.9: Chemistry Model

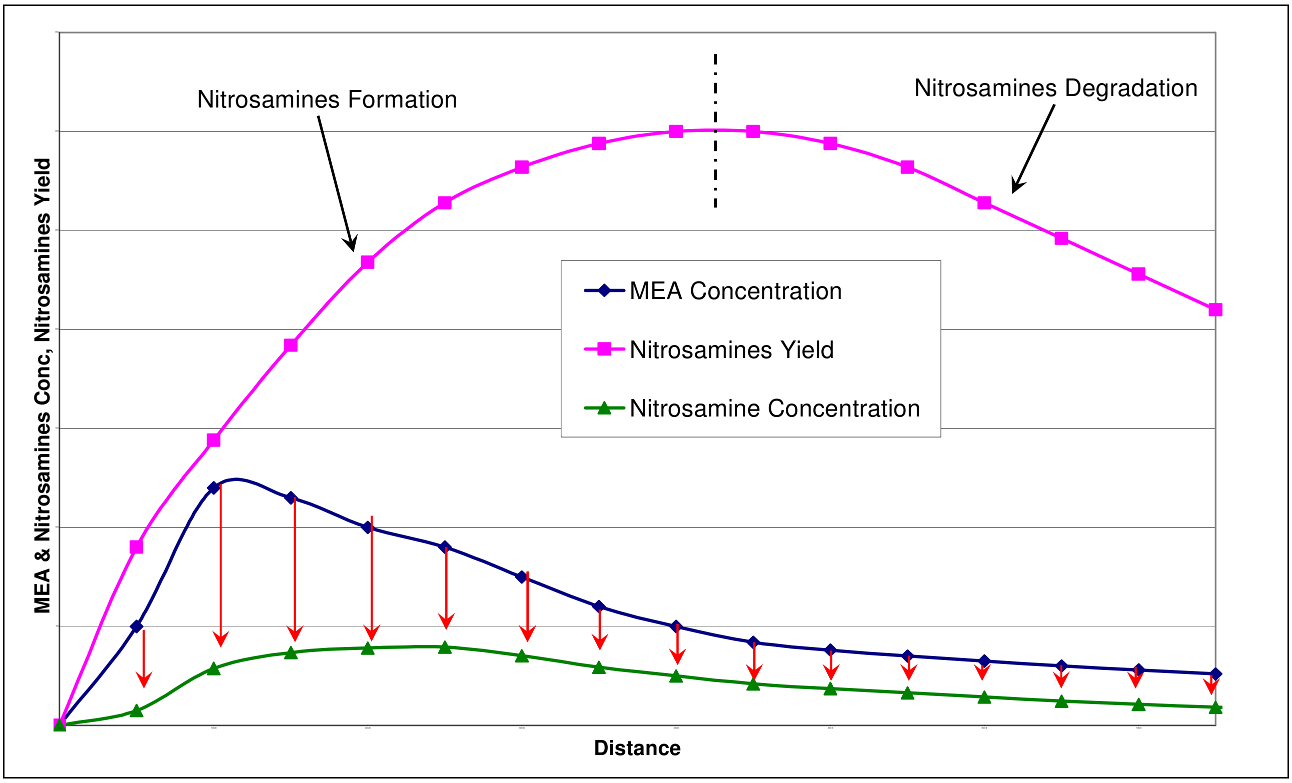
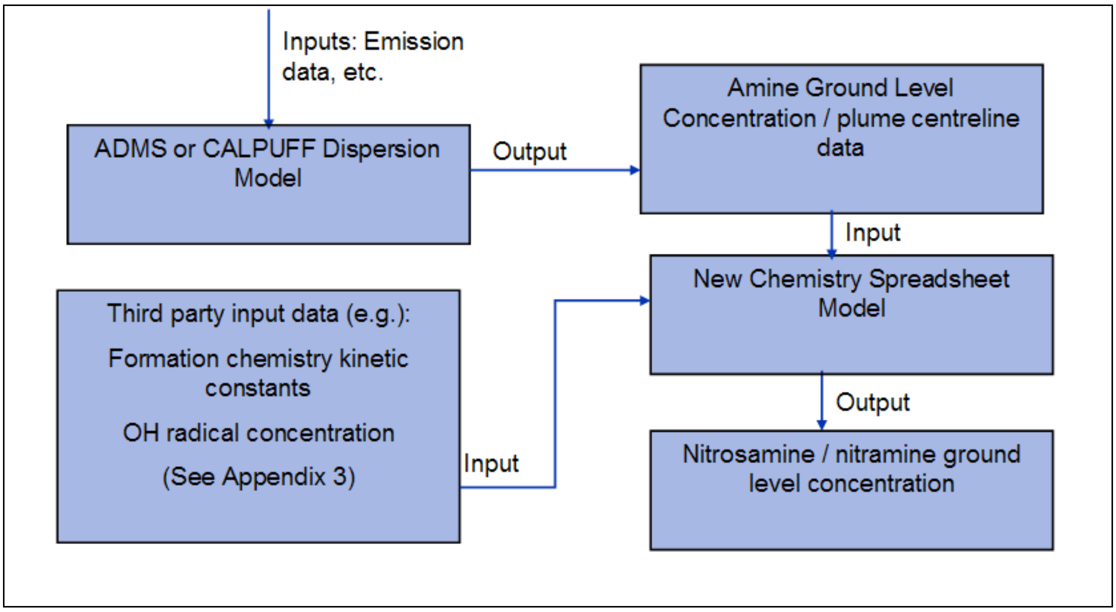


Figure 4.10: Schematic of an example of an Option 2 "solution"



Option 3: Bespoke model of chemistry and dispersion

This option is the possibility of creating a bespoke model to conduct chemical reaction equations *and* dispersion. In this case, the full set of differential equations defining the reactions and dispersion would be solved explicitly, probably with numerical methods.

Such a model could also be calibrated against ADMS or CALPUFF by examining the special case of the NOx chemistry that is already built into those software products.

Further discussion of benefits for these options is given in Section 6.

Step 5

This step involves all the processes of step 4, plus the additional element of a model of the subsequent fate of the amine degradation products in the atmosphere or in aqueous solution. If the difficulties of step 4 can be solved satisfactorily, then it is likely that from a technical point of view, step 5 will not be significantly more difficult.

The barrier to completing a step 5 assessment might be lack of information regarding the subsequent fate of the amine degradation products.

Since all previous assessment steps made the assumption that the compounds of interest persisted in the environment indefinitely, this step certainly represents a refinement of the final concentration estimates leading to assessments that are more likely to pass the various acceptance criteria.

Inputs

- All the inputs identified for previous assessment steps.
- Kinetic constants for the subsequent reactions of the amine degradation compounds and other products of interest

Outputs

A refined estimate (now incorporating the subsequent reaction kinetics) for each compound of interest as concentration contours (or deposition).

Current Status and modelling options

The modelling options are essentially the same as they are for Step 4, with the complication that the differential equations for the chemistry contribution now must include terms for the subsequent lifetime of the compounds of interest.

The status of Step 5-level model development is the same as for Step 4: none has been developed.

Step 6

Step 6 involves a change in the physical characteristics of the proposed carbon capture plant or the mode of its operation. Examples might include changing the starting amine, raising the stack height, restricting the throughput of the carbon capture unit to limit the amine emissions to a certain annual value, etc.

5 SUMMARY AND CONCLUSIONS

This section provides a summary of all the work that was performed by DNV for the purposes of this study. It uses the main results from Appendices 1, 2 and 3 as the basis for describing what we have learned and "why we recommend what we recommend" for future work on this complex problem.

Consistent with previous work, the main concern is the formation of nitrosamine (especially) and nitramine by secondary reactions in the discharge plume. These chemicals are considered to be highly toxic even in very low concentrations.

5.1 Key Influencing Factors

The main influences that may affect the outcome of an environmental assessment include:

- The discharge conditions from the CCS plant. Lower discharge concentration of amine, higher discharge points and greater thermal lift or discharge momentum would all reduce the environmental impacts of amine emission.
- The type of amine used in the CCS, since this can affect the relative yield of nitrosamine and nitramine products compared to less toxic degradation products, and it can affect how the amine partitions with moisture in the air (i.e. how it is distributed between gaseous and aqueous phases).
- The affinity of the amine to moisture and the amount of water vapour in the discharge stream and in the ambient air, since this affects the amount of amine and amine degradation products that is quickly lost from the air by deposition mechanisms.
- The flux of sunlight (day versus night, weather conditions), since OH radicals (the main degradation reaction initiators) are mainly formed by photo-chemical reactions.
- The concentration of natural or industrial hydrocarbons in the air, because relatively high concentrations will reduce the concentration of OH radicals and hence reduce the rate of the initial amine degradation reaction step.
- The concentration of nitrogen oxides, because without these nitrosamine and nitramine cannot be formed.
- The rate of formation of nitrosamine or nitramine from the amine discharged. This is likely to vary with the exact amine used, and how this amine partitions between gaseous and gaseous but associated with water molecules ("micro-droplet" phase), since rates of reaction could be very different. The concentration of NO and / or NO_2 is also important.

- The rate of degradation of nitrosamine and nitramine in the discharge plume (gas phase and aqueous phase), since if these reactions are fast, then the concentration of nitrosamine and nitramine may always stay low and acceptable.

In broad terms, there are 2 strategies that can be used to address this problem:

1. Having identified all the influencing factors and obtained data to quantify them, a model could be built to calculate the answer. This would be a difficult and expensive task.
2. Data and logical reasoning is used to provide an answer.

It is possible that the second strategy could provide a clear answer, but the problem is more complex than anticipated and significant data gaps still exist, which would need to be filled if either strategy is to succeed.

The work that DNV performed for this study is summarised below.

5.2 Model Evaluation

DNV investigated and summarised the state-of-the-art in Air Quality Dispersion Modelling, and considered the strengths and weaknesses of the various air dispersion models available.

5.2.1 Preliminary Evaluation

Five different modelling approaches were identified by DNV, and for the purpose of the preliminary evaluation (Dispersion Case Study), which aims at understanding the spatial scale of the phenomena, the simplest approach was recommended and applied: Gaussian Plume Model, ADMS.

5.2.2 Model selection for subsequent project stages

The general conclusion for the model selection for the subsequent project stages is that either a Gaussian plume model (e.g. ADMS) or a Modified Gaussian Pufff Model (e.g. the “CALPUFF Modelling System) could be considered suitable for the purposes of the next stages/phases of the project. This is because:

- The area of interest is restricted to the near-mid field (up to 10-12 km), based on the assumed air quality criteria/yield factors of secondary pollutants and the amine emission data supplied.
- In the near-mid field the complexity of terrain features is medium.
- Both the models can address wet and dry deposition.
- Both the models allow the calculation of the most important short term and long term atmospheric parameters to be compared with the Air Quality Standards.
- No potential significant improvements have been identified if the most refined and complex models (Eulerian/Lagrangian models) are used.

Despite both ADMS and CALPUFF Modelling System being suitable for the purposes of the next phase of the study, the CALPUFF Modelling System has some additional benefits (discussed in the body of this report) if the timing of the chemical reaction/degradation of amines (to form nitrosamines/nitramines) is comparable with the timing for transport and dispersion into the area of interest (up to 10-12 km).

5.3 Dispersion Case Study

The dispersion case study conducted by DNV used an existing dispersion model (namely ADMS 4) focused mainly on the gas phase side of the amine degradation reactions. This is mainly because the literature data available currently focuses primarily on these amine reactions in the atmosphere.

The dispersion case study results indicate:

- The maximum ground level concentrations predicted anywhere on the study grid as a result of the operation of the CHP, TCM and the Mongstad refinery account for less than 5% of the identified air quality criteria for the primary pollutants (e.g. MEA, NH_3, NO_x).
- The assumed criteria for nitrosamines and nitramines can be exceeded for distances up to 10-12 km from the emission sources. Note however that this is based on the assumption that the worst reported literature yield applies at the emission point (7% amine conversion to nitramine, experimental literature data based on TEA as the starting amine). As such, based purely on air dispersion models existing today, the emissions from the proposed CCM facilities are a probable cause of environmental concern. It should be noted however that yields appear to be specific to the starting amine, which is not known at this stage for the Mongstad facilities. Note that based on a 0.3% conversion to nitrosamine, no air quality criteria exceedences are observed.
- The criteria used for the purposes of the dispersion case study must also be verified in light of the results of other studies currently ongoing. Irrespective of this particular dispersion study, the issue of criteria particularly for the amine degradation products (mainly nitrosamines and nitramines) are of key importance as their exact value bounds the overall area that can be affected.
- With regards to the liquid / aqueous phase reactions the data gaps are bigger than for the gas phase (particularly with regards to solubility, equilibrium and kinetic data; see Figure 4.1).
- A preliminary run has been conducted for the purposes of the dispersion case study, to account for deposition. In the absence of other data, the deposition parameters assumed for the amines and their by-products (nitrosamines and nitramines only in the case study) are the recommended ADMS values for ammonia (see Appendix 2).

A comparison between the peak ground level concentrations of all pollutants for a run where deposition has been modelled and another where it has not indicates that:

  - For short-term ground level concentrations the peak concentrations when deposition is considered are 5 to 8% lower than when deposition is not considered.
  - For long-term ground level concentrations the peak concentrations when deposition is considered are 8 to 18% lower than when deposition is not considered.
- Based on information available in literature (*Konsekvenser for utslipp fra Energiverk ved Statoil Mongstad, NILU Report O-103063, January 2005)* the existing Nitrogen and Sulphur background deposition rates in the Mongstad area currently exceed the tolerable limit criteria for both fertilisation and acidification. Literature also indicates that these high background Nitrogen and Sulphur deposition rates are primarily due to long distance transportation of air pollutants, and not as a result of Mongstad refinery emissions, which are negligible in comparison.

  The additional Nitrogen contribution from amines and their degradation products is expected to be much less than the emissions from the refinery itself because of the relatively low emission rates of amine.

- It is also understood that the key concern with regards to deposition for emissions from the CCM and TCM facilities is associated with the potential levels of nitrosamines in drinking water, as some criteria for different kinds of nitrosamines are available from literature. As no information was available for freshwater sources in the immediate vicinity of the facilities, it was difficult to assess the effect of potential deposition of nitrosamines (see Appendix 2 for more details).

5.4 Key Data Gaps

The key areas where information appears to be incomplete are:

- How amines partition between gaseous and aqueous phases. For the Valencia experiments [1] they attempted to perform photo-chemistry experiments with 20% relative humidity. These experiments failed because all the MEA partitioned quickly to the aqueous phase on the surfaces of the reactor. The CCS discharge stream will be at least 2% moisture by volume which is comparable to the moisture levels considered in the Valencia experiments (based on the data supplied for the dispersion case study), so it is not clear how MEA will partition under these conditions. This is a significant data gap.
- If the MEA does partition to some sort of aqueous phase, then there is very little information about if or how quickly nitrosamine or nitramine may form in that aqueous phase. This is a significant data gap (see Figure 4.1).
- Improved understanding of the formation of amine degradation products.

- Irrespective of whether the MEA stays in the gas phase or partitions to an aqueous phase, it is unknown how quickly any nitrosamine or nitramine may degrade once formed. Indications are that the gas phase degradation of nitrosamine is very fast (at Valencia they failed to find any nitrosamine – this could be because it was not formed, or it could be because it degraded very rapidly). It is anticipated that nitramines will be relatively stable (lifetime of more than 3 days) in the atmosphere, but this subject remains a significant data gap.
- The criteria used for interpreting dispersion modelling results need to be verified, particularly for the amine degradation products (nitrosamines and nitramines), because the criteria used fundamentally effects the conclusions and actions to be taken.
- Better understanding of the differences between starting amines, and the implications upon the amine degradation products formed.

6 RECOMMENDATIONS

For the purposes of model development, a better understanding of the reaction speed of amine degradation reactions is required (that is, the data gaps indicated above must first be filled). However, the following comments can be made (Note that the main body of the report includes a route map to facilitate):

- **If** the formation reactions of the key amine degradation products (nitrosamines and nitramines) is much faster than the transport/dispersion time and they can be considered relatively stable afterwards, then the reaction can be considered as complete at the emission source. A simple yield factor can be applied to the amine emission for estimating the secondary pollutant emission rates.
- **If** the formation reactions on the other hand are very slow compared to the transport/dispersion time, then the primary pollutant (i.e. amine) will have diluted sufficiently such that the potentially dangerous amine degradation products will also be diluted enough as to not pose a threat in the environment.
- The above do not require any further model development (existing models can deal with the various issues), other than information to back-up the reaction speed arguments (e.g. very fast).
- A preliminary investigation into the formation kinetics of nitrosamines and nitramines (Section 4.2.3) has shown that if the ambient concentration of OH radicals can be shown to be less than 10^6 ions/cm^3, then the first-hour yield of both nitrosamines and nitramines is less than 0.5% of the concentration of the starting amine (MEA in this case). This conclusion could be used to provide an upper bound for the assumed yield in the modelling approaches described above, for the first hour of transport after release. The case studies already performed with much more pessimistic yield assumptions limit the affected area to a region smaller than that expected to be covered by a 1-hour wind transport area. If the 10^6 ions/cm^3 upper bound for ambient OH radicals concentration can be justified, then this approach may remove the need for more sophisticated modelling that combines formation kinetics and dispersion simultaneously.
- The above are also highly dependent on the ambient air quality criteria assumed for the various pollutants as well as the transport/dispersion time. The dispersion time is dependent on the potential area that can be affected by emissions from the facilities (and hence the criteria as well). For example the “area of interest” of 10-12 km for the dispersion case study considered is based on the assumption of a 7% nitrosamine yield from amine (while not undergoing any further degradation reactions). An important factor is also the subsequent degradation reactions of these secondary pollutants.
- The deposition effects of nitrosamines in drinking water will need to be considered when information on the presence of freshwater sources within 15 km from the facilities are available, as well solubility and kinetic data.
- Given the various data gaps for the different amine degradation mechanisms, the model development Option 2 discussed in the body of this report (“Use existing dispersion models with post processing of results”) is considered by DNV to be the best and most efficient way forward at least for short term development. This option also has the additional benefit of not requiring additional validation, which may be required for Options 1 and 3 by regulatory

authorities prior to accepting them (these options involve incorporating chemistry within existing models). This is because it will only use outputs from already validated models. A spreadsheet solution may not be the most robust solution but it will allow for a quicker and more efficient incorporation of the data currently available (as well as data that will become available in the near future).

- Option 3 which involves the creation of a bespoke module(s) within existing models, conducting the chemical reactions and dispersion, is not recommended at this stage (time/cost consuming), prior to more data becoming available in order to make a more informed decision.

To summarise, DNV recommend that Gassnova SF work with DNV and with specialist contract research organisations, such as NILU, to fill the identified data gaps in a systematic way such that an answer to the question of the environmental impact of CCS can be fully answered in the most cost-effective way.

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