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DET NORSKE VERITAS

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Report for  
Deposition and Soil Transport  
Modelling of Components from post-  
combustion amine-based CO<sub>2</sub> capture

Gassnova SF

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**Summary:**  
 Final report for a deposition case study, conducted using the CALPUFF Modelling System, in order to investigate the behaviour of nitrosamines and nitramines in the environment. The modelling after deposition analysis is conducted by CEH (sub-contracted to DNV) using the EQC model.

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## EXECUTIVE SUMMARY

### *Overview*

The purpose of the CO<sub>2</sub> 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). Amine-based solvent technology is one technology option for CO<sub>2</sub> capture. The design basis is the capture of approximately 1.3 million tonnes of CO<sub>2</sub> per year, which will then be conditioned and compressed for pipeline transport, to be sent to geological storage under the Norwegian Continental Shelf. An amine-based CO<sub>2</sub> capture plant may cause harmful emissions to the atmosphere. Amines and their degradation products from reactions in the process and in the atmosphere are of particular concern to Gassnova SF and Statoil ASA (who are jointly organising the CO<sub>2</sub> Capture Mongstad Project, CCM), but there is limited knowledge about the behaviour of such chemicals when discharged from large scale industrial processes. As such Gassnova SF has launched several studies to be conducted during the capture plant development in order to improve understanding and knowledge of these substances. One of the studies is associated with the atmospheric dispersion and deposition (and the ultimate fate) of components from post-combustion amine-based carbon dioxide capture.

As part of Call-Off 01 conducted in 2010 DNV investigated the available air dispersion models and their suitability for simulating the dispersion and deposition of pollutants (amines and their degradation products of concern, namely nitrosamines and nitramines), from post-combustion amine-based carbon dioxide capture from the facilities associated with the CCM project. The scope also included a dispersion case study using one of these existing models as well as recommending model development work (short and long term) for meeting the study objectives.

This report constitutes part of Call-Off 02 which aims to achieve a better understanding of the role of different deposition routes, and higher precision in predicting the concentrations of harmful pollutants (specifically nitrosamines and nitramines) in drinking water from a known concentration of those pollutants in air.

For the simulation of dry and wet deposition the CALPUFF Modelling System, Version 6.4 has been used because:

- For alignment with the atmospheric chemistry modelling study which was undertaken in parallel to this study (incorporating simple amine chemistry in CALPUFF). DNV believes it is beneficial to use the same model for dispersion (including chemistry) and dry / wet deposition, since these phenomena influence each other.
- The “time” parameter is an important factor in the simulation of amine chemical reactions. It should be emphasised that ADMS (an alternative model to CALPUFF) 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 is not simulated). CALPUFF is a time-varying model, where the pollutant can be followed step by step



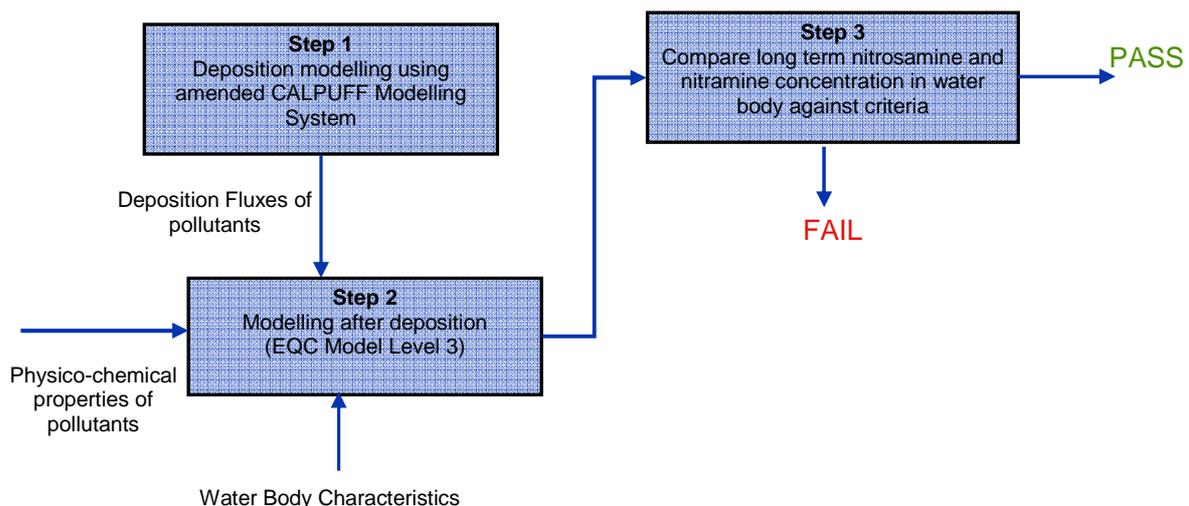
(minimum time step is 1 second) from the source to the receptor. This capability provides a good base for a more accurate implementation of an amine chemistry model using CALPUFF. Even though amine chemistry has not been considered for the purposes of this study (all emissions assumed to occur at source), it is noted that DNV is in parallel also conducting a study for implementing simple amine chemistry in CALPUFF (*DNV Report No. PP011013/1*). The amended model can be used at a later stage of the deposition study if more accuracy is required to predict the concentration of nitrosamines and nitramines in drinking water sources (i.e. by including amine chemistry in a deposition case study).

- CALPUFF also allows for more accurate simulation of pollutant transport in complex terrain areas. Within this context, the use of 3D LAM data as meteorological input would maximise this capability.
- Wet and dry deposition are also included in the CALPUFF model design specifications.

The CALPUFF Modelling System identifies the important water bodies affected and provides deposition fluxes of nitrosamines and nitramines for these. The Centre for Ecology and Hydrology (CEH) has provided the necessary specialist expertise for the better understanding of the transport and retention of the pollutants after they have been deposited to ground. Their analysis was conducted using the EQC (Equilibrium Criterion) Level III fugacity model.

A high-level flow-chart of the methodology used to estimate the long term nitrosamine and nitramine concentration in drinking water sources is provided in Figure 0-1.

**Figure 0-1: Summary of methodology for predicting pollutant concentration in water sources**



A deposition case study was run (based on emission information provided by CCM), followed by sensitivity analysis in order to identify the key deposition mechanism and the water bodies in the Mongstad area that can potentially be affected. This was followed by the CEH analysis investigating transport and retention of the pollutants after they have been deposited to ground in order to estimate the long term concentration of

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nitrosamines and nitramines in a water body (including sensitivity analysis in order to address uncertainties in the modelling).

### **Conclusions**

The key conclusions from the study are as follows:

- The methodology developed for estimating the concentration of pollutants (amine, nitrosamines and nitramines) in a drinking water source from a known concentration in air appears robust and can be readily used for an actual emission scenario, including more accurate information for the drinking water source. The methodology can also be easily modified if more accuracy in the prediction of the results is required (i.e. account for atmospheric amine chemistry in the model).
- Wet deposition is the driving deposition mechanism, whereas dry deposition is negligible in comparison in this relatively humid and wet study area (over an order of magnitude lower for equivalent deposition fluxes).
- Effectively, all the mass emitted for pollutants of interest (nitrosamines and nitramines) will be deposited via the wet deposition mechanism *during* precipitation hours.
- Peak deposition fluxes are observed in the near field (a few kilometres from the emission source).
- The base case model (after deposition) was not an actual real case; it was run primarily to test out the methodology for estimating pollutant concentration in drinking water sources and not to explicitly draw conclusions in relation to the currently available criteria. However, predictions suggest that (**if** the case was real, the assumptions correct, and the emissions and lake characteristics accurate):
  - assuming that primary degradation (degradation of the parent molecule to a first metabolite) removes any carcinogenic effect, the nitrosamine and nitramine concentrations in the lake water will be greater than the strictest suggested protective level for lifetime exposure through drinking water (4 ng/l, representing a negligible lifelong risk of 1 in a million of acquiring cancer), but less than the higher level of 40 ng/l (representing a minimal lifelong risk of 10 in a million of acquiring cancer).
  - If complete mineralization (ultimate degradation) of the molecule is required to remove the carcinogenic effect then both levels are likely to be exceeded.
  - Given that the case study is not based on actual emission data and the selection of the lake for detailed analysis does not correspond to the lake receiving peak flux, the results presented relative to criteria should be considered in this context.
- It should be noted however that because the nitrosamines or nitramines might be expected to form less carcinogenic compounds after primary degradation to a metabolite, consideration of the primary degradation rate may be justified for the purposes of this study (with ultimate degradation of interest as a sensitivity test).

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- The model results were also shown to be sensitive to the size of the lake with respect to the size of the catchment: the larger the lake the lower the predicted lake concentrations. This was because of the increased water volume in which the loading was diluted.
  - The model results were rather insensitive to all of the other parameter variations assessed. This included the organic carbon content of the soil, which was unimportant because of the low Koc values (partitioning coefficient normalised for organic carbon content of soil or sediment) estimated for these molecules. Given that the Koc values were estimated, it would be very useful to make measurements of the Koc in suitable representative soils.

However, it should be noted that there are some significant uncertainties and conservative assumptions related to the above conclusions.

The uncertainties are as follows:

- The degradation rates used in the modelling were, with the exception of NDMA, all estimated from the structures of the molecules using an adaptation of a method that was really only supposed to be qualitative. These values are therefore rather uncertain and the model was sensitive to them as was shown by the significant difference in the results found when primary and ultimate degradation rates are compared.
- Any change in the criteria could dramatically affect the results of the analysis relative to the comparison against these criteria. The criteria is currently based on NDMA which is considered a conservative estimate as NDMA is one of the more potent of this group of pollutants. However, it is again emphasised that the purpose of this study was to develop a methodology for estimating pollutant concentration in drinking water sources and not to explicitly draw conclusions in relation to the currently available criteria. Given that the case study is not based on actual emission data, the criteria have not yet been confirmed and the selection of the lake for detailed analysis (i.e. not corresponding to lake receiving peak flux) the results presented relative to the criteria should only be considered as indicative.
- Further refinement of the physico-chemical properties described above will provide more robust estimates and more confident prediction could then be made.
- The predicted deposition fluxes are highly dependent on the assumptions related to the pollutants scavenging coefficients, and on the study area weather.

The conservative assumptions are as follows:

- All degradation reactions of nitramines and nitrosamines in the atmosphere have been neglected for the purposes of the deposition modelling study (once formed these pollutants do not react further, which is a conservative assumption).
- The nitrosamine and nitramine deposition flux provided by DNV and utilised in this report is likely to be overestimated because it was estimated prior to the development of the simple atmospheric amine chemistry module within CALPUFF (as mentioned previously).

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### ***Recommendations***

The key recommendations from the study are as follows:

- Given that the nitrosamine and nitramine deposition flux predictions are likely to have been overestimated because the analysis was conducted prior to the development of the simple atmospheric amine chemistry module within CALPUFF, further deposition case study analysis should be conducted utilising the amended model. This would increase the accuracy of the study results.
- The assumptions related to the pollutants scavenging coefficients used for the wet deposition modelling should be confirmed. The data can be best confirmed through literature review, and if no information is available experimental investigation may be required.
- Improved estimates of degradation rates should be obtained through experiments with soil and water samples, and at temperatures typical of sites where deposition is expected. It would be useful to identify the degradation mechanisms, the metabolites and their potential carcinogenicity. This would increase the level of confidence in the modelling after deposition results. It is emphasised that because nitrosamines or nitramines might be expected to form less carcinogenic compounds after primary degradation to a metabolite, consideration of the *primary* degradation rate may be justified for the purposes of this study (with ultimate degradation rate of interest as a sensitivity test).
- The modelling after deposition results were rather insensitive to variations in the organic carbon content of the soil. This was unimportant because of the low Koc values estimated for these molecules. Given that the Koc values were estimated, it would be very useful to make measurements of the Koc in suitable representative soils. It is noted that some of the chemicals may be weakly positively charged at neutral pH and therefore the estimates made here might underestimate the actual value and therefore lead to an overestimate of lake concentrations. Experimental determination of the Koc values would show if this is in fact the case.

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## 1 INTRODUCTION

### 1.1 Background

The purpose of the CO<sub>2</sub> 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). Amine-based solvent technology is one technology option for CO<sub>2</sub> capture. The design basis is the capture of approximately 1.3 million tonnes of CO<sub>2</sub> 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 ASA, with funding from the Norwegian government. This report is submitted to Gassnova SF.

An amine-based CO<sub>2</sub> 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 ASA, but there is limited knowledge about the behaviour of such chemicals when discharged from large scale industrial processes. As such Gassnova SF has launched several studies to be conducted during the capture plant development, in the period up to the project sanctioning, in order to improve understanding and knowledge on these substances. One of the studies is associated with the atmospheric dispersion (and the ultimate fate) of components from post combustion amine-based carbon dioxide capture (CO<sub>2</sub>, NO<sub>x</sub>, NH<sub>3</sub>, amines, aldehydes, alkylamines, amides, nitrosamines and nitramines). The first part of the study (Call-Off 01, *DNV No. EP024442, Rev1, 5<sup>th</sup> October 2010, E-Room No. FM07-ADZ00-S-RA-0001, Rev3*), performed by DNV in 2010, investigated the air dispersion models available and their suitability for the CCM project, conducted a dispersion case study using one of these existing models, as well as recommended short and long term model development work for meeting the study objectives.

This report constitutes part of Call-Off 02 which aims to achieve a better understanding of the role of different deposition routes, and higher precision in predicting the concentrations of harmful pollutants (specifically nitrosamines and nitramines) in drinking water from a known concentration of those pollutants in air.

### 1.2 Scope and Objectives

#### 1.2.1 Objectives

One of the main findings from earlier studies, including DNV's call-off 01 work, was that wet deposition and the transport of pollutants (amines, nitrosamines and nitramines) from air by uptake in rain drops, deposition on land and run-off to drinking water sources were important, and currently not very well understood.

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As such, the key objectives of this study are:

1. Understand the role of the different deposition routes (specifically dry and wet deposition) in emission dispersion modelling.
2. Assess the relative importance of deposition as a part of the atmospheric processes occurring when amines, nitrosamines and nitramines are emitted, formed and dispersed from CO<sub>2</sub> capture plants. The influence of precipitation – intensity, frequency and probability – as well as watershed estimation and retention of pollutants in soil/ground are important factors that need to be better understood.

The key goal is to propose a methodology for estimating the concentration of pollutants (amine, nitrosamines and nitramines) in a drinking water source from a known concentration in air.

### 1.2.2 Scope

The scope for this study involves developing a methodology for evaluating the long term concentration of nitrosamines and nitramines (pollutants of interest) in one drinking water source in the vicinity of the Mongstad facilities (case study).

This was achieved via wet and dry deposition modelling of pollutants of interest in order to understand the key deposition mechanism and the relative importance of different influencing factors based on best available information. Once deposited, the subsequent run-off of those pollutants within a watershed to a drinking water source, and the retention/destruction in soil or water bodies within the watershed area was estimated using a fugacity model. In summary, fugacity can be described as the “escaping potential” of a compound from a particular media (e.g. soil, water, air).

This study does not involve any software development, but is focussed on developing a methodology that is specific and relevant to the pollutants of interest.

DNV understands that this study is not concerned with acidification and eutrophication resulting from the deposition of amines, nitrosamines and nitramines, but is focussed specifically on the concentrations of these pollutants, and their potential for human health impacts.

It is noted that a case study considering both the effects of deposition and atmospheric amine chemistry (using the modified atmospheric dispersion modelling software) is outside the scope of this study.

### 1.2.3 Project Organisation

All the work was conducted in DNV’s London offices with the deposition modelling performed using the CALPUFF Modelling System.

The Centre for Ecology and Hydrology (CEH) in the UK has provided the necessary specialist expertise for the better understanding of the transport and retention of the pollutants after they have been deposited to ground.

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CEH is part of the National Environmental Research Council NERC and is a science-led organisation, carrying out scientific research, operating three Science Programmes: Biodiversity, Water and Biogeochemistry.

### 1.3 Report Layout

The remainder of this report is structured as follows:

- Section 2 outlines the model descriptions for the models utilised to achieve the objectives of this study. This is also supported by Appendix 1.
- Section 3 summarises the results of the deposition case study. This is also supported by Appendix 2.
- Section 4 summarises the results of modelling after deposition. 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.

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## 2 DEPOSITION MODEL DESCRIPTION

### 2.1 Introduction

This section provides a summary description of air dispersion modelling tool used for conducting this analysis (i.e. CALPUFF Modelling System Version 6.4) and the reasons for its suitability and selection.

The above are discussed in further detail within Appendix 1, which also summarises the state-of-the-art in Air Quality Dispersion Modelling.

Furthermore the different deposition routes (dry and wet) and how these are modelled in CALPUFF are also briefly discussed.

### 2.2 Model Selection and Description

The general conclusion from the work conducted as part of Call-Off 01 was that either a Gaussian plume model (e.g. ADMS) or a Modified Gaussian Puff Model (e.g. "CALPUFF Modelling System") can be considered suitable for the purposes of the next stages/phases of the project.

DNV considers the CALPUFF Modelling System is preferable for this study because:

- 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 is not simulated). CALPUFF is a time-varying model, where the pollutant can be followed step by step (minimum time step is 1 second) from the source to the receptor. This capability provides a good base for a more accurate implementation of an amine chemistry model using CALPUFF. Even though amine chemistry has not been considered for the purposes of this study (all emissions assumed to occur at source), it is noted that DNV is in parallel also conducting a study for implementing simple amine chemistry in CALPUFF (*DNV Report No. PP011013/1*). The amended model can be used at a later stage of the deposition study when more accuracy is required in predicting the concentration of nitrosamines and nitramines in drinking water sources (i.e. by including amine chemistry in a deposition case study).
- Further to the above, CALPUFF also allows for more accurate simulation of pollutant transport in complex terrain areas. Within this context, the use of 3D LAM data as meteorological input would maximise this capability.
- Wet and dry deposition are also included in the CALPUFF model design specifications.

The CALPUFF modelling system has been proposed by the US EPA as a Guideline model for regulatory applications involving long range transport and near field applications, where non steady state effects (factors such as spatial variability in the meteorological fields, complex terrain, calm winds, fumigation, recirculation or stagnation and coastal effects) may be important ([http://www.epa.gov/scram001/dispersion\\_prefrec.htm](http://www.epa.gov/scram001/dispersion_prefrec.htm)).

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The CALPUFF Modelling System includes three main components which are briefly outlined below, and described in more detail within Appendix 1:

- CALMET is a meteorological model that develops hourly wind and temperature fields - as well as turbulence parameters - on a three-dimensional gridded modelling domain. It includes a micro-meteorological model for the characterization of the turbulence in the lower level of atmosphere.
- CALPUFF is a transport and dispersion model that uses puffs of material emitted from modelled sources for simulating dispersion and transportation processing along the way (including chemical transformations, dry and wet deposition). The model uses, as input, the 3D meteorological field generated by CALMET, which allows the spatial / temporal variations in the meteorological field to be accounted for.
- CALPOST is used to process the CALPUFF output files and permits the generation of concentration / deposition plot files which can be directly read by GIS tools and compared with Air Quality Standards.

## 2.3 Dry and Wet Deposition Modelling

### 2.3.1 Dry Deposition

Many complex processes are involved in the transfer and deposition of pollutants on a surface. The most important factors that influence dry deposition are:

- Properties of the depositing materials (size, shape and density for particles; diffusivity, solubility and reactivity for gases).
- Characteristics of the surface (roughness, type of vegetation, amount and physiological state).
- Atmospheric parameters (stability, turbulence intensity).

In terms of dry deposition mechanisms, deposition of particles is mainly controlled by gravitational settling and inertial impaction whereas deposition of gases is driven by turbulence and molecular diffusion. Deposition of small particles is complicated by the fact that they may be influenced by the processes affecting both gases and large particles.

Although it is not practical to fully include all the parameters mentioned above in a dispersion / deposition model, CALPUFF parameterises many of the most important effects based on atmospheric, surface and pollutant properties.

The CALPUFF dry deposition module is based on the so-called “resistance deposition model”, which evaluates the deposition velocity (and then the deposition flux) as the inverse of a sum of resistances plus, for particles, a gravitational settling term. Each resistance represents the opposition to transport of the pollutant through the atmosphere to the surface. The “resistance deposition model” is based on a multi-layer structure which includes the layer aloft, mixed, surface, deposition and vegetation layers. These are discussed in detail within Appendix 1 along with the model input information requirements.

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### 2.3.2 Wet Deposition

Many studies have shown that, during rain events, wet scavenging of soluble or reactive pollutants can be of the order of tens of percent per hour (Barrie, 1981; Slinn et al., 1978; Levine and Schwartz, 1981; Scire and Venkatram, 1985). Gaseous pollutants are scavenged by dissolution into cloud droplets and precipitation. For some pollutants (e.g. SO<sub>2</sub>) aqueous-phase oxidation can be an important removal pathway. Particle pollutants are removed by in-cloud scavenging (rainout) and below cloud scavenging (washout). For receptors located tens of kilometres from the source, wet scavenging can deplete a substantial fraction of the pollutant material from the puff.

The wet deposition module in CALPUFF is based on the scavenging coefficients, which depends on the characteristic of pollutants (mainly, solubility and reactivity), as well as the nature of precipitation (liquid / frozen).

Wet deposition flux at the ground (typically expressed in mg/m<sup>2</sup>/hr) is calculated by the model through the scavenging factor and the precipitation rate.

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## 3 DEPOSITION CASE STUDY

### 3.1 Introduction

This section:

- Outlines the case study, the various input data (emission, terrain and meteorological data), and presents the agreed drinking water quality criteria used for the assessment. The physico-chemical properties of pollutants of interest are also discussed.
- Presents the key results from the deposition case study, as well as the results of the sensitivity analysis conducted on key influencing factors.

The aim of the deposition study was to identify the deposition flux of pollutants at sensitive drinking water receptors, where more detailed analysis will be conducted (see Section 4). This forms part of the methodology developed for evaluating the potential long term nitrosamine and nitramine concentration in drinking water sources.

The dispersion case study was conducted using the CALPUFF Modelling System, Version 6.4, a Gaussian puff air dispersion model.

Detailed information regarding the deposition case study is provided in Appendix 2.

### 3.2 Deposition Case Study

#### 3.2.1 Emission Sources

One scenario for the CCS facilities was considered for the purposes of the deposition case study. The main emission source from the CCM plant at Mongstad (the CHP absorber stack) is considered to be the key source of interest. This is because amine emissions will only occur from the absorber.

As the key for this study is to examine the behaviour of amine by-products as they are deposited onto the ground or onto water bodies in the vicinity of the Mongstad area, it was not necessary to include other emission sources associated with the CCS facilities or the refinery.

Amine chemistry has not been considered for the purposes of this study (all emissions assumed to occur at the source based on literature values for maximum rural yields for nitrosamines and nitramines). It is noted that existing Mongstad refinery sources involve significant emissions of NO<sub>x</sub> and SO<sub>2</sub>. These may be included in the dispersion case study at a later stage if more accuracy is required in relation to the deposition flux evaluation (if the amine chemistry calculation is found to be very sensitive to the exact values for NO<sub>x</sub> and SO<sub>2</sub>).

The data for the CHP absorber stack emission source described above are summarised in Appendix 2 based on information provided by CCM. The deposition case study also makes certain assumptions on the maximum yield (in rural areas) of nitrosamines and nitramines from the different starting amines (MEA, DMA and MMA) based on the information provided. The nitrosamine / nitramine yield varies from 0.3% to 2.5% of the

corresponding amine emission rate. All emissions are assumed to occur at the source (i.e. no amine chemistry is explicitly modelled).

Figure 3-1 illustrates the location of the CHP absorber stack point emission source (in the green circle) included in the CALPUFF model in relation to other emission points at Mongstad refinery that are not considered in the deposition case study.

**Figure 3-1: Location of CHP Point Emission Source for deposition case study**



### 3.2.2 Literature Review of physico-chemical properties

This section provides details of the key influencing factors for dry and wet deposition modelling conducted with the CALPUFF Modelling System. More detail is provided in Appendix 1.

The CALPUFF model requires the following inputs for deposition modelling for each pollutant:

- Wet deposition: Scavenging coefficient (measured in units of  $1/s$ ). This relates the solubility of a gaseous pollutant in a liquid (water in this case) with the 'speed' at which the pollutant is washed-out of the plume by precipitation.
- Dry deposition: Various parameters for each individual pollutant such as diffusivity, reactivity, resistance to vegetation.

Given that from the available information to date (and experience from call-off 01) wet deposition is expected to be the key driving deposition mechanism for amines and their degradation products, the emphasis was on identifying suitable values for scavenging coefficients in the literature.

#### 3.2.2.1 Wet Deposition

The solubility of a gas in a liquid can be expressed by Henry's law constant (H). There are various sources in literature (some based on experimental data) for the pollutants of interest of this study, namely amines, nitramines and nitrosamines.

As part of the scope of this work the CEH conducted a literature survey on the physico-chemical properties of pollutants of interest (see Appendix 3). One of the properties investigated was H. Information related to this property was also included in the CTCC report (*Theoretical evaluation of the fate of harmful compounds post emission, H&E TQP Amine, 256430116 – extracts from CTCC Report*) and the CERC call-off 01 report (*Modelling Atmospheric Dispersion for Components from Post-Combustion Amine-based CO<sub>2</sub> Capture, CERC No. FM867/R2/10, 11<sup>th</sup> October 2011*). The H constant values from different sources for the pollutants of interest are summarised in Table 3-1.

The H values from the CEH literature survey have been used for the purposes of the deposition study. This is mainly because the information from the CEH review is more comprehensive and covers the full spectrum of pollutants of interest. In addition the H values are generally similar to the other information sources (where data are readily available to DNV). High H values would result in high solubility of pollutants in water though it should be noted that this property is purely a thermodynamic constant (and is dependent on pressure and temperature). As such conclusions based only on this parameter with regards to the partitioning of pollutant between the gas and aqueous phases can be misleading.

**Table 3-1: Henry's Law Constants for Pollutants of interest**

Pollutant	Source of Henry's Law Constants			OR 2/2011
	CTCC <sup>##</sup>	CERC Report	CEH Literature Survey	
	(M atm <sup>-1</sup> )	(Mole / L atm) or (M atm <sup>-1</sup> )	(Mole / L atm) or (M atm <sup>-1</sup> )	
MEA	3.1 x 10 <sup>4</sup> to 6.2 x 10 <sup>6</sup>	6.2 x 10 <sup>6</sup>	3.1 x 10 <sup>4</sup>	Dry experiments only
DMA	31 to 60	N/A	5.65 x 10 <sup>1</sup>	
MMA	N/A	90 to 1.4 x 10 <sup>2</sup>	9 x 10 <sup>1</sup>	
Methylnitramine	N/A	N/A	1.43 x 10 <sup>3</sup> to 2.33 x 10 <sup>5</sup>	
Dimethylnitramine	N/A	N/A	3.13 x 10 <sup>2</sup> to 8.33 x 10 <sup>3</sup>	
Ethanolnitramine	N/A	N/A	2.86 x 10 <sup>5</sup> to 1.41 x 10 <sup>7</sup> <sup>(1)</sup>	
NDMA*	5.5 to 9.6 x 10 <sup>2</sup>	N/A	2.78 to 5.49 x 10 <sup>1</sup>	

Notes:

\* No "stable" yield of nitrosamines from MMA and MEA.

## Theoretical evaluation of the fate of harmful compounds post emission, H&amp;E TQP Amine, 256430116 – extracts from CTCC Report.

<sup>1</sup> Different values reported for other nitramines in literature (primarily lower).<sup>2</sup> H values generally expressed at 298 K and 1 atm pressure.

For comparison the Henry law coefficients for carbon dioxide and oxygen are 3.4 x 10<sup>-2</sup> and 1.3 x 10<sup>-3</sup> M atm<sup>-1</sup> respectively. This indicates the very high solubility of amines, nitrosamines and nitramines in water.

As discussed previously CALPUFF requires a scavenging coefficient for each pollutant for the purposes of modelling wet deposition. This relates the solubility of a pollutant with the 'speed' of removal from the plume by the rain droplets / precipitation. Experimental data for NO<sub>x</sub> and SO<sub>2</sub> (which are included as default values in the model) indicate that their H constant values are factored by 10<sup>-4</sup> to obtain the scavenging coefficients.

As such, and in the absence of experimental data, the same approach was used for the pollutants of interest for this study. It is emphasised however that this approach is only an assumption and should ideally be verified through experiments involving these pollutants.

It is also noted that sensitivity cases examining the effects of factoring the H constants values have been performed in order to understand how this affects the wet deposition mechanism (two orders lower than 10<sup>-4</sup> and, if appropriate, two orders of magnitude higher). In summary, for the purposes of this study the H values for each pollutant have been multiplied by 10<sup>-4</sup> (for the Base Case), 10<sup>-6</sup> (Sensitivity 1) and if appropriate by 10<sup>-2</sup>.

The results from this sensitivity analysis are presented and discussed in Section 3.3.2.

**Table 3-2: Scavenging Coefficients used for deposition case study**

Pollutant	Henry's Law Constant	Scavenging Coefficient (/s) <sup>1</sup>	
	g / l atm	Base Case	Sensitivity 1
MEA	1.88E+06	1.88E+02	1.88E+00
DMA	2.54E+03	2.54E-01	2.54E-03
MMA	2.79E+03	2.79E-01	2.79E-03
Methylnitramine	1.77E+07	1.77E+03	1.77E+01
Dimethylnitramine	7.50E+05	7.50E+01	7.50E-01
Ethanolnitramine	1.49E+09	1.49E+05	1.49E+03
NDMA	2.06E+03	2.06E-01	2.06E-03

Note: 1. Scavenging coefficients as estimated by DNV.

### 3.2.2.2 Dry Deposition

It is not anticipated that dry deposition will be a significant mechanism for the pollutants considered in the scope of this study based on information available to date because of the high solubility of nitrosamines and nitramines and the relatively high humidity and precipitation in the study area. As such the focus for this study was obtaining the best available information for wet deposition parameters.

For modelling dry deposition various parameters are required for each pollutant. These include diffusivity, reactivity, resistance to vegetation, aqueous phase dissociation (which refers to water bodies and not rain droplets / precipitation). Most of this information is based on experimental data for different pollutants.

CALPUFF has default values for NO<sub>x</sub> and SO<sub>2</sub> which cover a large range of values for diffusivity, resistance to vegetation and aqueous phase dissociation. Different model runs where the parameters for NO<sub>x</sub> and SO<sub>2</sub> were used for each of the pollutants of interest have been simulated to investigate the importance of the dry deposition route (i.e. one model run where the parameters for NO<sub>x</sub> have been used for all pollutants, and one run where the parameters of SO<sub>2</sub> were used).

The results from this analysis are presented and discussed in Section 3.3.2.

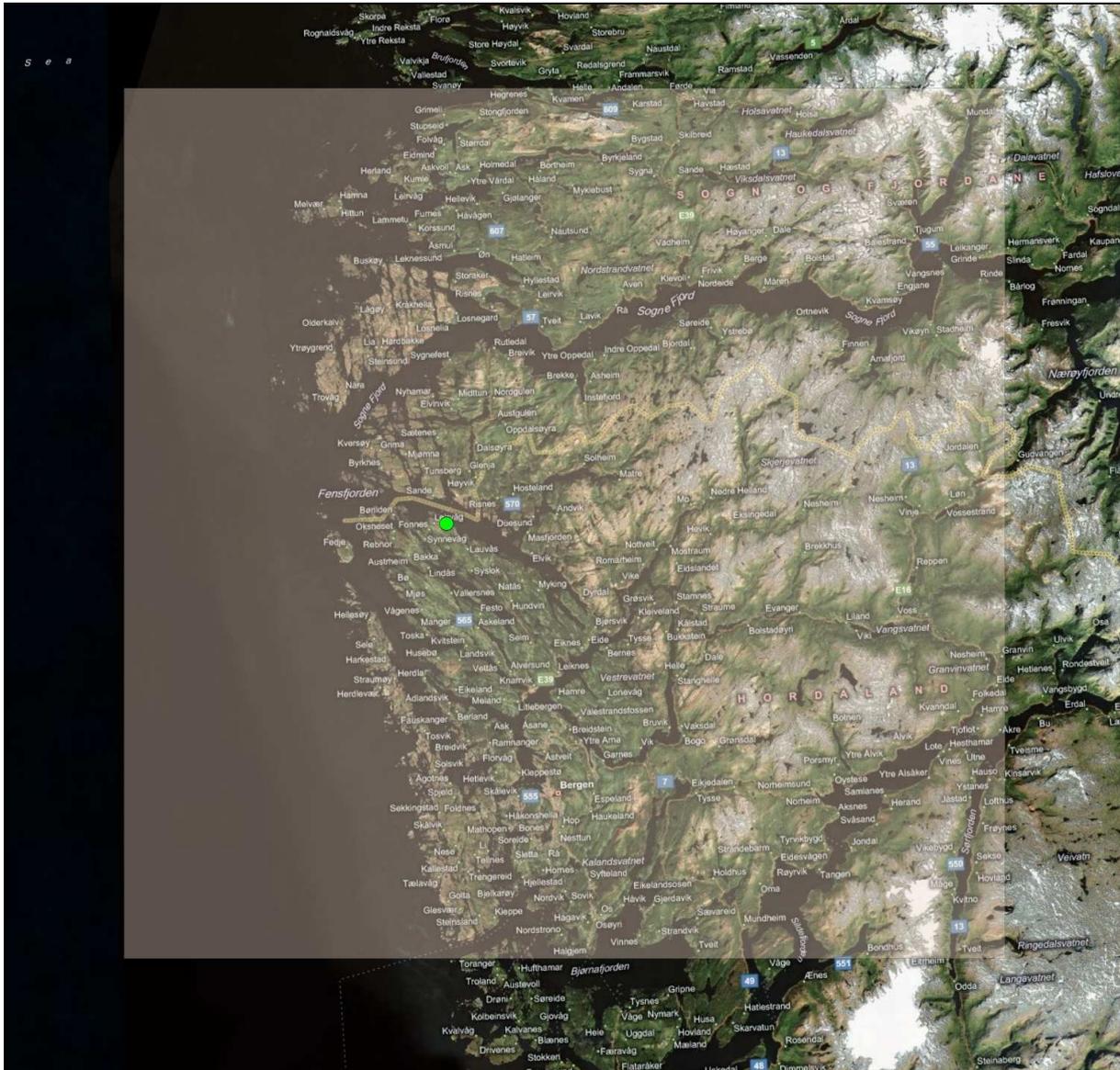
### 3.2.3 Area of Interest

On the basis of the coarse / preliminary simulations previously performed as part of call-off 01 with a simple “plume model”, the maximum extent of the potential “area of interest” for concentration / deposition effects was estimated to be 25 km from the release sources. On this basis, the extent of the computational domain for this study has been set to 35 km in each direction from the release sources, because of the following reasons:

- It is general good practice to work on a “computational” domain slightly larger than the “area of interest”
- The need to include two key weather monitoring stations (observational data) into the domain. These are discussed in Section 3.2.5.

This computational domain is shown in Figure 3-2, and has been characterised in detail in terms of terrain features and land use (see Section 3.2.6).

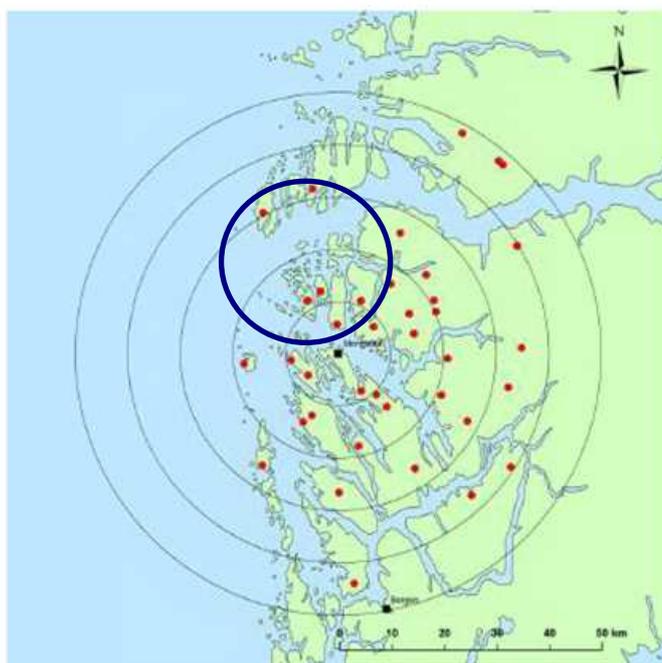
**Figure 3-2 - Computational Domain**



### 3.2.4 Sensitive Receptors in the Mongstad Area

The specific receptors included in the CALPUFF runs (i.e. locations at which long and short fluxes are provided separately as model outputs) are based on locations where NIVA has conducted aquatic monitoring in the Mongstad area. These are illustrated in Figure 3-3.

**Figure 3-3: NIVA Sampling Locations for Aquatic Monitoring**



*Sampling locations where NIVA has performed aquatic monitoring in the Mongstad area. Circles indicate distance from Mongstad in 10-km increments.*

The sampling locations in the blue circle in the figure above indicate the areas where the peak deposition fluxes are anticipated to occur. This is due to the prevailing wind direction in the Mongstad area which is from the South-East.

It is also noted that the two locations at the North-West of the blue circle also correspond to water bodies that CCM have indicated are of particular interest (Yndestal and Frøyset).

### 3.2.5 Meteorological Data

For the purposes of this study, the prognostic Local Area Model (LAM) meteorological model CALMET (part of the CALPUFF Modelling System) has been initialised with meteorological data from the prognostic model MM5, which in turn has been set up with the three-dimensional meteorological input arising from Global Circulation Model (GFS - NOAA). Figure 3-4 describes the “model chain” used for the meteorological characterisation of the area of interest around the Mongstad area.

MM5 has been run twice. The first run refined the resolution from 120km (GFS output) to 16km; the second run refined the resolution to 4km. The LAM output, for this study, is the 3D wind field for a 150x150km domain, with 4km horizontal resolution. The LAM model has been run by a third party (the meteorological data providers, Trinity Consultants Inc.). The LAM output is then used as input by CALMET, which allows for further refinement. In this case, a mesh of 500m resolution has been used, in order to allow the local terrain features to be properly simulated.

The dispersion case study was performed for a full year of data (2009, 8764 hours). This allows all the Air Quality Parameters to be evaluated for “long term” effects.

The meteorological data and the approach followed for refining these is described in more detail in Appendix 2.

In addition, local observational data have been introduced into the CALMET, in order to increase the “quality” of boundary conditions and make sure local phenomena (particularly the precipitation rates) are adequately captured in the final 3D wind field. The surface station data for 2009 have been supplied by the National Oceanic and Atmospheric Administration (NOAA) for various monitoring stations in the vicinity of the Mongstad site. Among the available data, the following stations have been selected, based on the quality and completeness of data, as discussed in Appendix 2:

- Takle
- Bergen Florida

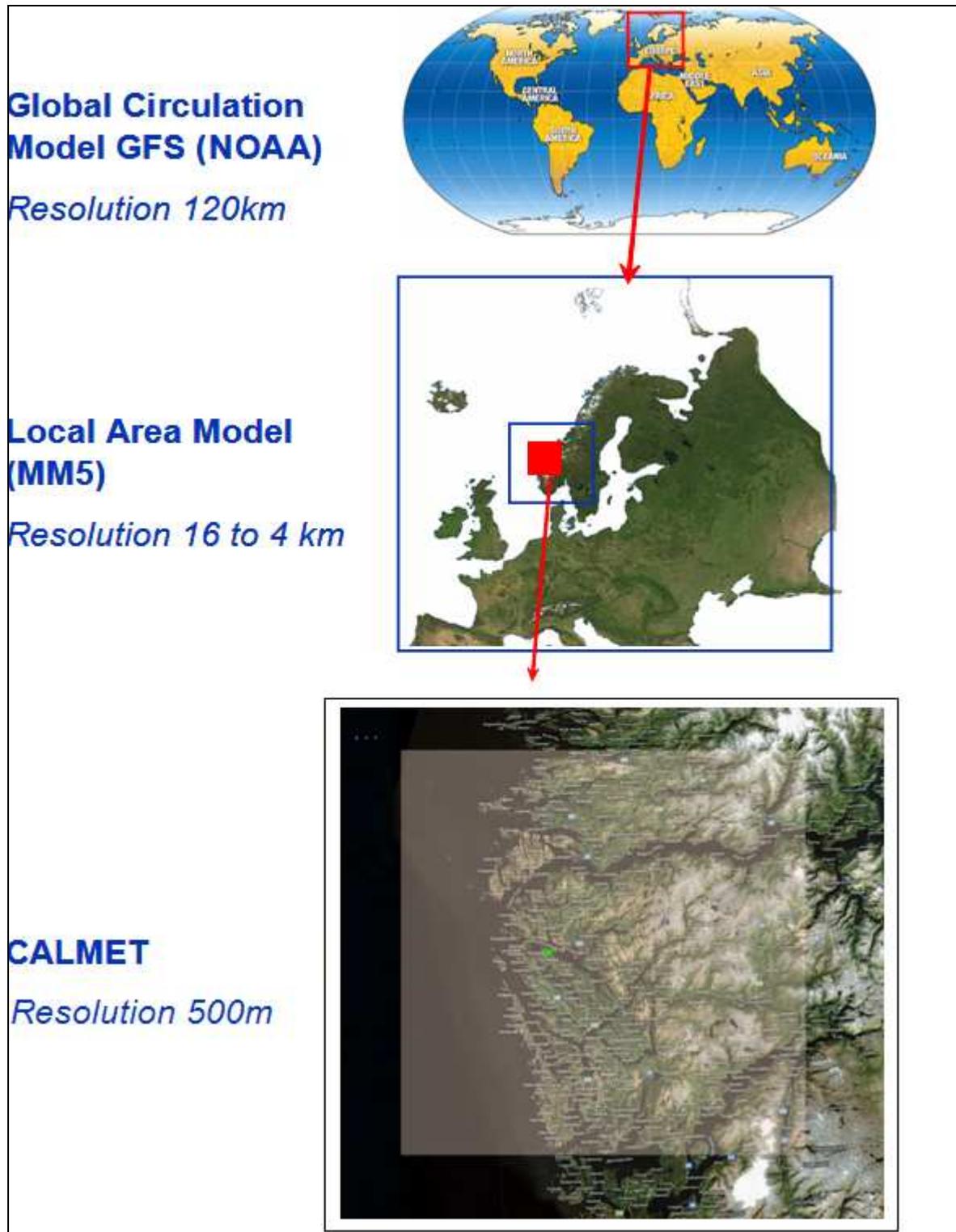
Precipitation data from the analysed meteorological stations, used as local observational data in the meteorological model, are given in Table 3-3. The rainfall / snowfall in 2009 match the historical data, which indicates an average per year in the range 2500-3000 mm. This confirms that 2009 is a robust choice for the simulation of pollutant rainout / washout (wet deposition).

**Table 3-3 - Precipitation Data**

Station	Year	Annual precipitation (mm)	Historical 1960-1990 (mm)
Takle	2009	2670	2500-3000*
Bergen Florida	2009	2930	2500-3000*

\* Source: <http://met.no/?module=Articles;action=Article.publicShow;ID=804>

**Figure 3-4 - Meteorological Simulation – Approach**



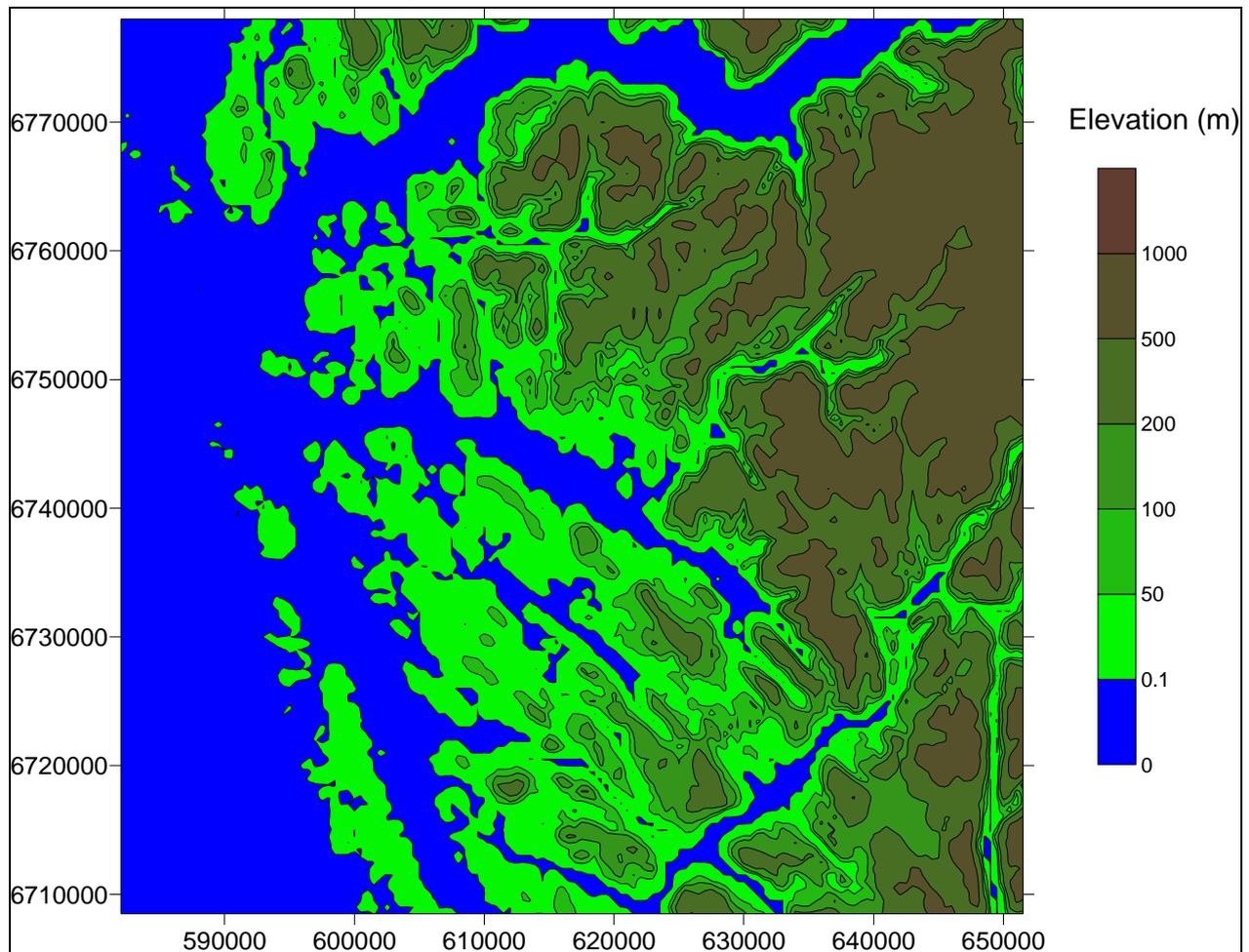
### 3.2.6 Terrain Data and Land Use

Terrain data is one of the main inputs of the meteorological model. Terrain influences local wind field and micrometeorological conditions, which in turn affect the cloud path, atmospheric turbulence and, ultimately, pollutant dispersion.

The computational domain has been divided into 140x140=19600 cells (cell size 500m), each of them associated with a terrain elevation (see Figure 3-5). This level of detail is considered to be adequate to properly reproduce the terrain effects on local scale.

Figure 3-5 also highlights that the area is characterised by relatively complex terrain. In particular, the presence of important reliefs and the water bodies are deemed to have a strong influence on local winds.

**Figure 3-5 - Terrain Features**



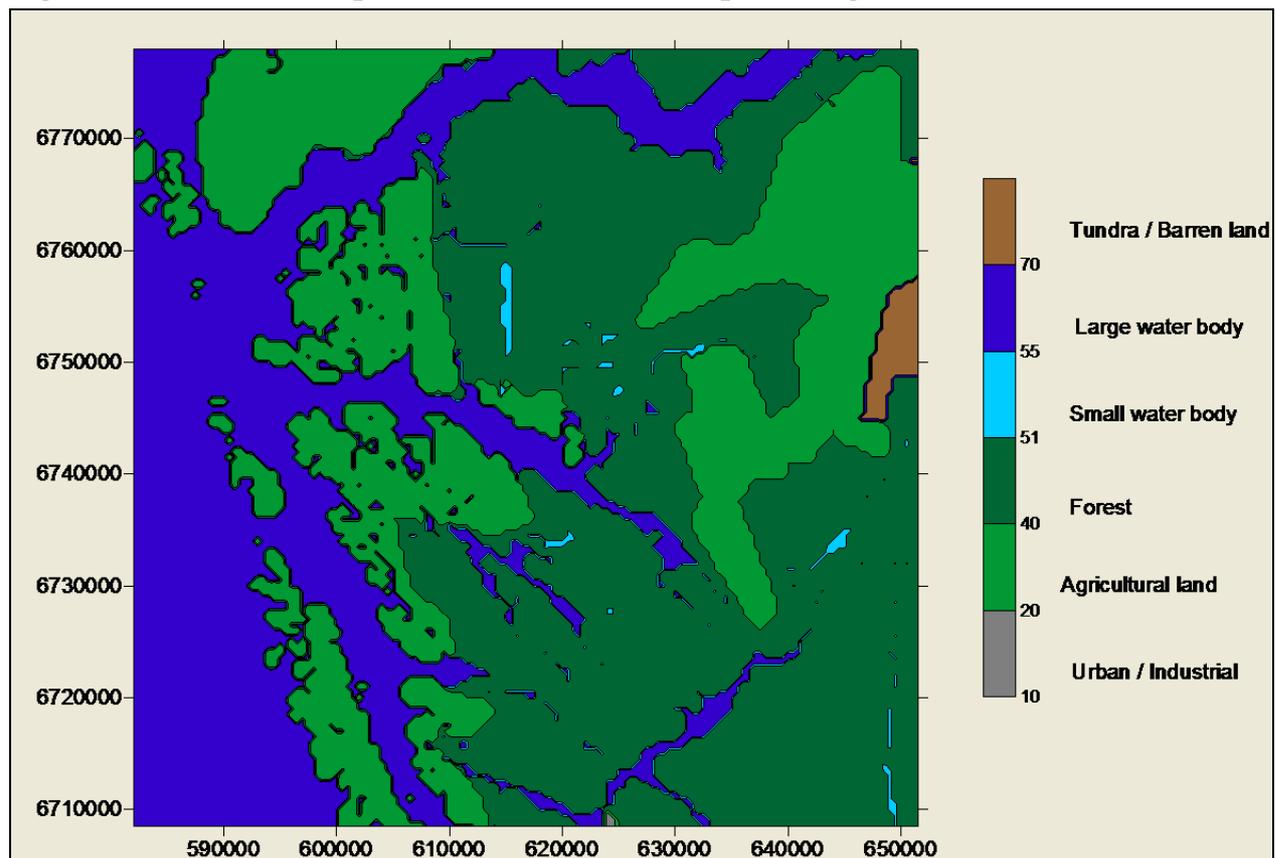
In addition to the terrain data, land use is a key input to the meteorological model. Land use influences local micrometeorological conditions, which in turn affect local atmospheric turbulence and, ultimately, pollutant dispersion.

The following land-use categories have been used in CALMET:

- Large water body
- Small water body
- Agricultural land
- Urban land
- Forest land
- Barren land / Tundra

The computational domain has been divided into 140x140=19600 cells (cell size 500m), each of them associated with a land use categories (see Figure 3-6).

**Figure 3-6: Land Use map – One value for land use per each grid cell of 500x500m**



### 3.2.7 Drinking Water Quality Criteria

This study only considers deposition of nitrosamines and nitramines and their potential long term concentration in drinking water sources. Amines have not been explicitly considered in this study given that the drinking water criteria associated with them are much less stringent than the criteria for nitrosamines and nitramines.

The drinking water quality criteria against which the results are judged are based on the Norwegian Institute of Public Health (NIPH) recommended values. The basis for this is the evaluation study conducted by NIPH as per the Climate and Pollution Agency (Klif) request (*Health effects of amines and derivatives associated with CO<sub>2</sub> capture: Nitrosamines and nitramines*). The NIPH study is based on evaluation of existing risk estimates related to N-nitrosodimethylamine (NDMA) for air and drinking water, and included an evaluation of the EPA / IRIS risk estimates.

The NIPH evaluation has calculated the concentration of nitrosamines (NDMA) in water associated with risks (to humans) in the range of  $10^{-5}$  to  $10^{-6}$ . This means that life-long exposure at the indicated levels would result in an excess life-long risk of cancer of either  $10^{-5}$  or  $10^{-6}$ . The recommended tolerable nitrosamine concentrations are summarised in Table 3-4. As limited information is available on health effects of nitramines, NIPH has suggested that the risk estimate for NDMA is also used for exposure to nitramines. This may be conservative as NDMA is likely to be more potent than any of the nitramines.

These values correspond, in DNV's understanding, to a long term annual criterion. The emphasis for this study is the long term results given that the criteria refer to the life-time risk of cancer.

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

**Table 3-4: NIPH recommended tolerable drinking water quality criteria**

Pollutant	Drinking Water Quality <sup>1</sup>
	Long Term (Annual) – ng/l
Nitrosamines/Nitramines	40 <sup>2</sup> / 4 <sup>3</sup>

Notes:

1 The cumulative nitrosamine and nitramine concentration (in drinking water) is judged against the recommended criteria.

2 Corresponds to a life-long risk of cancer level of  $10^{-5}$ .

3 Corresponds to a life-long risk of cancer level of  $10^{-6}$ .

However, it should be emphasised that the purpose of this study was to develop a methodology for estimating pollutant concentration in drinking water sources and not to explicitly draw conclusions in relation to the currently available criteria. As such, given that the case study is not based on actual emission data, the criteria are early in their development and the selection of the lake for detailed analysis (i.e. not corresponding to

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lake receiving peak flux) the results presented relative to the criteria should only be considered as indicative.

### 3.3 Results

#### 3.3.1 Overview

This section summarises the results from deposition case study as well as the sensitivity to the key parameters. The aim of the deposition analysis is to identify the pollutant deposition flux at a water body in the vicinity of the Mongstad facilities to conduct detailed analysis of the potential long term concentration of nitrosamines and nitramines in drinking water sources.

The results are presented as follows:

- Section 3.3.2 summarises the influence of the key assumptions in relation to the input data for dry and wet CALPUFF model input parameters for the pollutants considered.
- Section 3.3.3 summarises the results of the deposition case study in terms of long and short term deposition flux results.
- Section 3.3.4 summarises the details of the water body (receptor) selected for further analysis in terms of deposition fluxes for each pollutant of interest as well as area, depth, inflow, outflow etc.

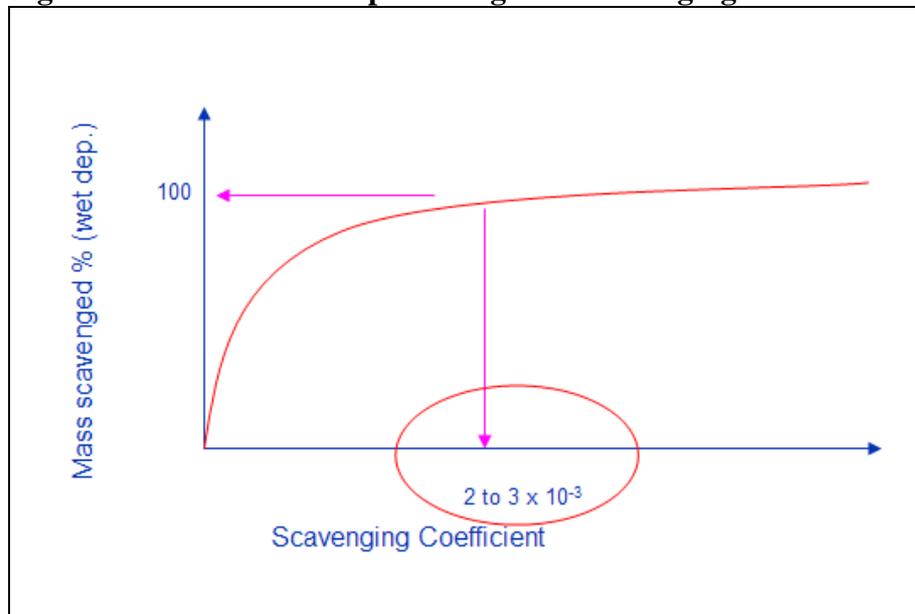
#### 3.3.2 Influence of dry and wet deposition inputs

##### 3.3.2.1 Wet Deposition

The key input in the CALPUFF model for wet deposition is the scavenging coefficient for the pollutants of interest (i.e. amines, nitrosamines and nitramines).

The results from the analysis conducted using different values for the scavenging coefficients, as discussed in Section 3.2.2.2, indicate that:

- The results indicate that for coefficient values in the region of 2 to 3 x 10<sup>-3</sup> / s almost complete wash-out (100% of the mass emitted) and deposition of the pollutant occurs during precipitation. This is irrespective of the pollutant and is illustrated by
- Figure 3-7. Given that the assumed coefficient values for nitrosamines and nitramines are much greater than 3 x 10<sup>-3</sup> / s, full deposition (i.e. 100% washout) of the emitted mass is expected for all pollutants during precipitation.
- The above is further illustrated for NDMA where the long term wet deposition results indicate that around 50% of the mass emitted at the source is deposited via the wet deposition mechanism. The precipitation data from two monitoring stations in the area (Tackle and Bergen Florida), which are direct inputs to the CALPUFF model, indicate that around 50-55% of the hours in 2009 include precipitation (i.e. rainfall hours). This is discussed further in Section 3.2.5.

**Figure 3-7: 'Wet' Mass deposited against Scavenging Coefficient**

As such the deposition base case run was conducted using the scavenging coefficient for NDMA for all pollutants of interest (primarily nitrosamines and nitramines) which results in complete deposition of pollutant during precipitation hours. This is considered conservative for the purposes of this analysis given that it is based on experimental data for other pollutants (NO<sub>x</sub> and SO<sub>2</sub>) and only on literature data for the pollutants of interest (nitrosamines and nitramines).

### 3.3.2.2 Dry Deposition

As discussed previously, it is not anticipated that dry deposition will be a significant mechanism for the pollutants considered in the scope of this study based on information available to date (i.e. high solubility for nitrosamines and nitramines and high humidity and precipitation in the study area).

As discussed in Section 3.2.2.2, different model runs where the CALPUFF model default parameters (diffusivity, reactivity etc) for NO<sub>x</sub> and SO<sub>2</sub> were used for each of the pollutants of interest have been simulated to investigate the importance of the dry deposition route. Note that these are based on experimental data.

The results from the analysis indicate that:

- Long term deposition results (for NDMA and ethanolnitramine) indicate that 0.6% to 2% of the emitted mass is deposited when using the NO<sub>x</sub> and SO<sub>2</sub> dry deposition parameters respectively.
- The dry deposition route is considered negligible compared to wet deposition equivalent (over an order of magnitude less in terms of deposition fluxes).

The above results confirm that dry deposition is negligible compared to wet deposition. However, this is highly dependent on the scavenging coefficient assumptions made for

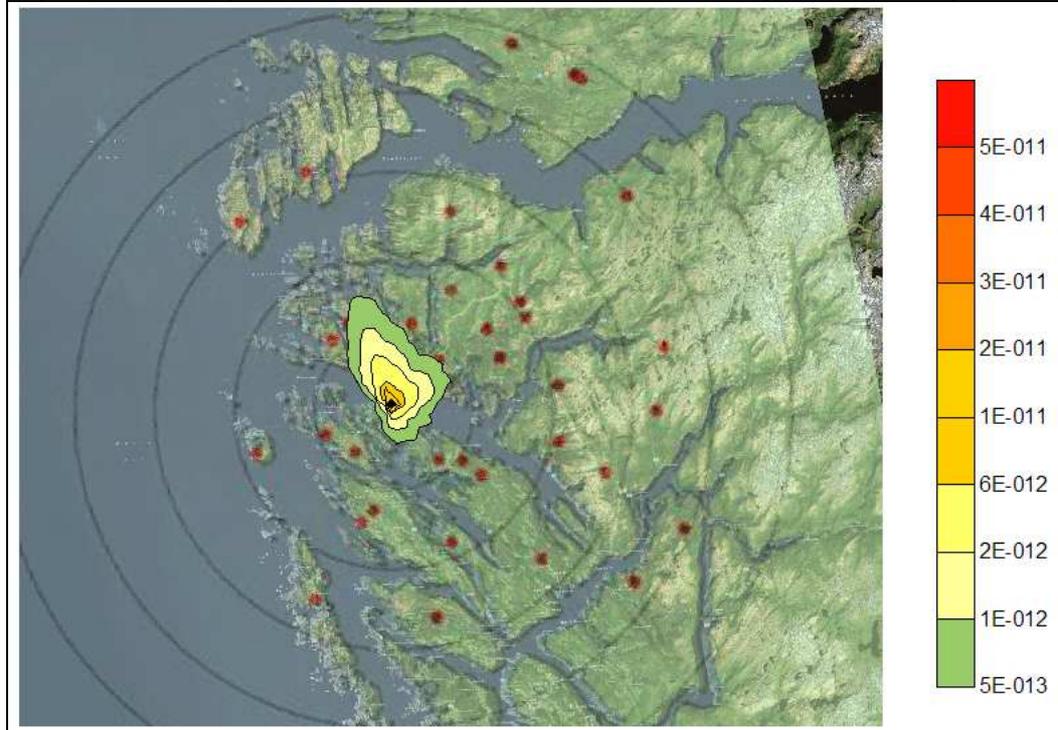
the purposes of the wet deposition analysis, the weather in the study area, and also the use of NO<sub>x</sub> and SO<sub>2</sub> default parameters for the dry deposition analysis.

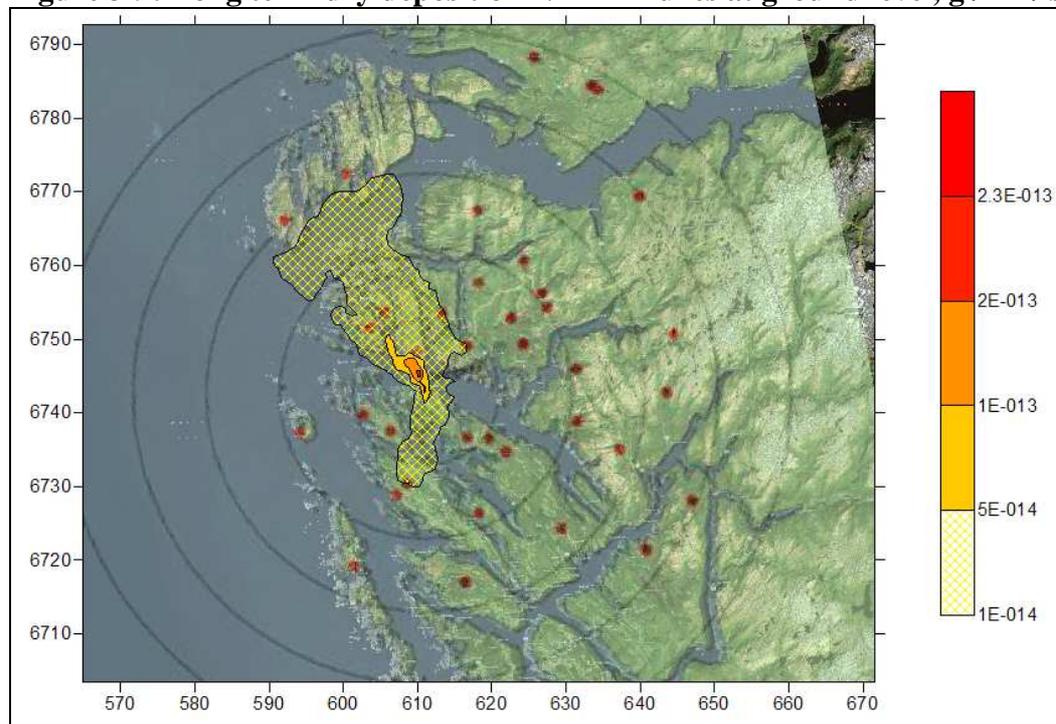
### 3.3.3 Deposition Case Study Results

The deposition case study results are presented in terms of long term results (ground level deposition flux contours) for NDMA for wet and dry deposition, as follows:

- Figure 3-8 illustrates the ground level long term wet deposition results for NDMA.
- Figure 3-9 illustrates the ground level long term dry deposition results for NDMA.

**Figure 3-8: Long term wet deposition NDMA fluxes at ground level, g / m<sup>2</sup> / s**



**Figure 3-9: Long term dry deposition NDMA fluxes at ground level, g / m<sup>2</sup> / s**

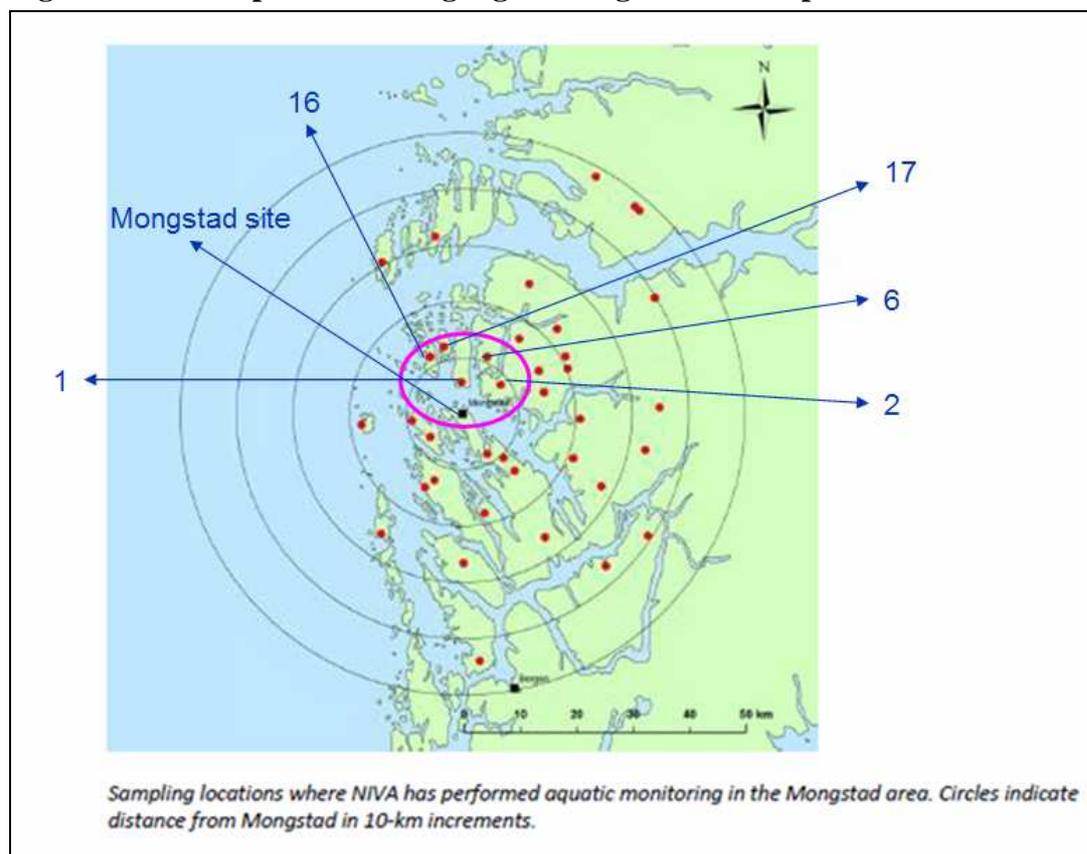
From the results presented above it can be seen that:

- The peak long term wet deposition flux anywhere on the grid is around  $5 \times 10^{-11}$  g / m<sup>2</sup> / s and occurs within a few kilometres from the emission source. The effects of wet deposition are relatively localised in the immediate vicinity of the CCS plant (around 15 km from the source). This is highlighted by the fact that deposition fluxes of up to two orders of magnitude lower are observed within 15 km from the release source. This means that the wet deposition mechanism is fast (though note that this result is heavily influenced by the scavenging coefficient assumptions made, as well as the weather in the study area). Note that the long term ground level concentration contours for NDMA (as illustrated in Appendix 2) indicate that concentration levels that differ by two orders of magnitude are within 30-35 km from the release sources. This further indicates that the effects of wet deposition are relatively localised.
- The peak long term dry deposition flux anywhere on the grid is around  $2.3 \times 10^{-13}$  g / m<sup>2</sup> / s. These occur within a few kilometres from the emission source. In general it can be seen that the dry deposition fluxes are two orders of magnitude lower than wet deposition equivalent values. This indicates the significance of the wet deposition mechanism compared to dry deposition which is negligible in comparison.
- The deposition flux results for the other pollutants of interest (i.e. nitramines) are similar, and the values are directly related to the ratio of emission rate of the pollutant against the emission rate of NDMA assumed at the CHP absorber source. For methylnitramine the ratio is approximately 1 (i.e. the equivalent deposition fluxes will be the same as for NDMA), for dimethylnitramine is 3 and for ethanoldinitramine is 10.
- It should be noted that no conclusions can be drawn from the above results in relation to the potential long term concentration of nitrosamines / nitramines in drinking water

sources. The aim of the deposition case study was to identify potentially affected water sources that would be carried forward for more detailed analysis (see Appendix 3 for modelling after deposition results).

Based on the long term deposition results presented above the water bodies indicated in Figure 3-10 have been identified as receiving the peak fluxes (only wet deposition has been considered as this is the main deposition route).

**Figure 3-10: Receptors receiving highest long term wet deposition fluxes**



Based on time-series plots (short term results) for each of the above receptors (which are provided in Appendix 2) indicating the wet deposition flux for every hour of the simulation (i.e. 8764 hours in 2009), the following can be said:

- The highest short term wet deposition flux occurs at ‘Lake’ 1 and is at least twice as high as for any of the other receptors (around  $1.8 \times 10^{-10} \text{ g / m}^2 / \text{s}$ ).
- ‘Lake’ 1 also receives the highest number of hours with wet deposition flux.
- No particular time of year appears to dominate the wet deposition mechanism.

In summary ‘Lake’ 1 receives the highest wet deposition fluxes and the highest number of ‘wet flux’ hours in 2009, and as such this receptor should be considered for detailed analysis in order to evaluate the worst case concentration of nitrosamines and nitramines in drinking water sources.

In order for the detailed analysis to be conducted certain lake characteristics, as well as the wet deposition fluxes for all the pollutants of interest will be required. The lake characteristics have been sourced from NVE, as discussed below.

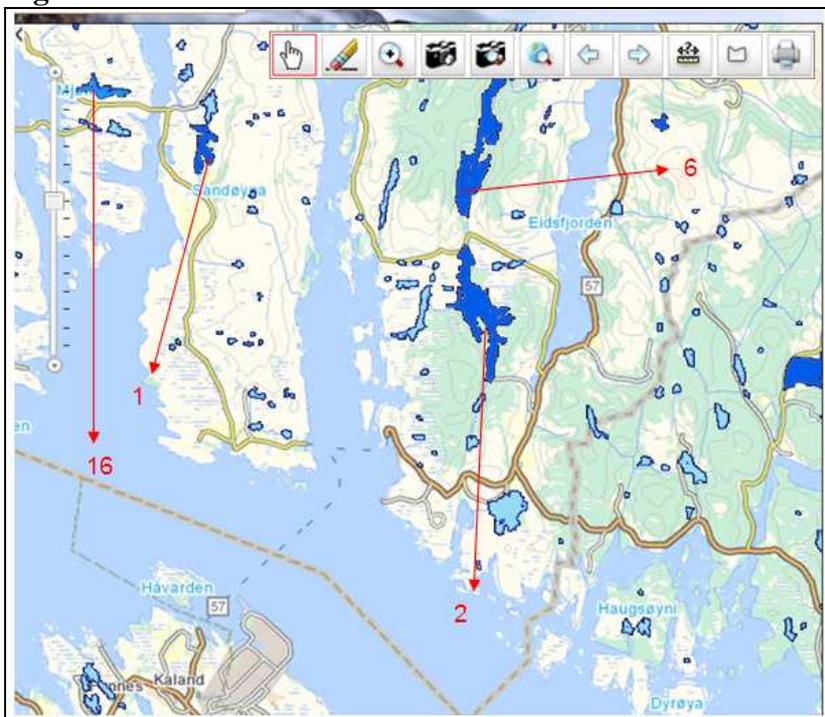
### 3.3.4 Receptor for detailed analysis after deposition

The Norwegian Water Resources and Energy Directorate has developed a national Norwegian lake database for lakes (Innsjødatabasen) with surface area larger than 2500m<sup>2</sup>. The necessary lake information for the detailed analysis has been sourced from this database (<http://nve.no/en/Water/NVEs-geographic-databases/The-National-Lake-Database-Innsjodatabasen/>).

The NIVA sampling locations for which results have been presented in the previous section have been investigated in order to obtain information such as lake area size, depth, inflow and outflow.

The lakes for which NVE information is available, in the vicinity of the Mongstad area are illustrated in Figure 3-11. The figure also attempts to match these lakes with the NIVA sampling locations (Lake IDs as indicated in Figure 3-10). Note however that the NVE database does not appear to correspond to the NIVA sampling locations.

**Figure 3-11: NVE Lake Locations**



Despite the apparent discrepancies between the NVE database and the NIVA sampling locations, an attempt was made to match the receptors considered in the deposition case study and the available information on lake characteristics. This is summarised in Table 3-5.

**Table 3-5: NVE Lake Information**

Lake ID	Name	NVE Identification No.	NVE REGINE No. #
1	Midtbøvatnet	068-25961-L	068.2
2	Langevatnet	068-26006-L	068.1Z
6	Svardalsvatnet	068-25912-L	068.1Z
16	Mjømnevatnet	068-25939-L	068.3

# REGINE is the Norwegian National Catchment Database. It divides Norway into major and subordinate reference units along river systems, basin boundaries and the coastline.

Further investigation of the information on the NVE database indicates that the lake characteristics required for the purposes of this analysis are only available for Lake ID 6 (Svardalsvatnet).

CCM have indicated that it is not necessary to use exact information for lake characteristics for the purposes of this study, as the key aim of the study is to test a methodology for evaluating the long term concentration of nitrosamines and nitramines in drinking water sources. As such it was decided to use the lake characteristics for Svardalsvatnet and the peak wet deposition flux results for receptor 'Lake' 1 in order to evaluate potential nitrosamines / nitramines concentration in drinking water sources.

The lake characteristics used for the purposes of the detailed evaluation and the long term wet deposition flux (i.e. annual average) summary are provided in Table 3-6 and Table 3-7 respectively.

**Table 3-6: Svardalsvatnet lake characteristics (NVE information)**

Parameter	Value
Lake Area (km <sup>2</sup> )	0.8
Depth (m)	25-49
Inflow (l / s km <sup>2</sup> )	92.8
Catchment Area for inflow (km <sup>2</sup> )	3.4
Outflow (l / s km <sup>2</sup> )	83.1
Catchment Area for outflow (km <sup>2</sup> )	9.8

Note that flow data is based on the period 1961-1990.

**Table 3-7: Peak Long Term Wet Deposition Flux summary at selected Receptor ('Lake' 1)**

Pollutant	Cumulative Wet Deposition Flux (g / m <sup>2</sup> / year)	Average Wet Deposition Flux (g / m <sup>2</sup> / s)
Methylnitramine	9.66E-05	3.06E-12
Dimethylnitramine	3.58E-04	1.13E-11
Ethanolnitramine	1.01E-03	3.21E-11
NDMA	1.06E-04	3.36E-12



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The above information was supplied to CEH for performing the modelling after deposition in order to evaluate the long term nitrosamine and nitramine concentration in a drinking water source.

The results from this analysis are presented and discussed in Section 4.

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## 4 MODELLING AFTER DEPOSITION

### 4.1 Introduction

This section describes how the deposition flux to ground of nitramines and nitrosamines (as determined in the previous section) was subsequently used to estimate the potential contamination levels in lakes that are used for drinking water.

CEH were subcontracted to DNV to lead this part of study, and their report is provided in full in Appendix 3, and summarised briefly below.

The study was conducted in the following stages:

- The physico-chemical properties of the nitrosamine and nitramine pollutants were determined by literature review where possible or based on the chemical structure of the compounds.
- These polluting compounds were then investigated to assess their potential fate in the environment using a modelling approach.
- A case study catchment was used to assess the concentrations of nitramines and nitrosoamines in a specific drinking water supply lake, based on an estimate of pollutant deposition flux to ground as provided by DNV.
- The modelling also investigated the sensitivity of the predicted drinking water concentrations to various model parameters used to simulate the case study catchment.

### 4.2 Physico-chemical data used for modelling

The data used in the modelling (e.g. water solubility, vapour pressure, Henry's Law constant, partition coefficients) came from two sources:

- firstly from a review of the published literature;
- secondly from the EPISuite™ software (United States Environmental Protection Agency 2003). EPISuite™ allows the calculation of basic physico-chemical data from the structure of the chemical compound of interest, through a series of independent sub-models. In addition, it has a database of physico-chemicals parameters which has been assembled from published and industry sources.

Degradation rates are obviously important in determining the fate and persistence of compounds in the environment as represented by the various model compartments. It is important to note that most of the degradation rates used in this study were estimated from the EPISuite™ software. Two values are given:

- Ultimate degradation (i.e. complete mineralization of compound, usually to CO<sub>2</sub> and water)
- Primary degradation, in which the compound is degraded to its first metabolite or by-product.

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Detailed data collected for these compounds and used in the modelling assessment are provided within Appendix 3.

## 4.3 Modelling

### 4.3.1 Model Description

A level III fugacity model was used to predict the distribution and concentrations of the selected nitramines and nitrosamines in the lake catchment. The model is briefly outlined below.

Fugacity ( $f$ , units of Pa) can be described as the “escaping potential” of a compound from a particular media (e.g. soil, water, air). It is linearly related to the chemical concentration ( $C$ , mol/m<sup>3</sup>) in the media through the fugacity capacity ( $Z$ , mol/m<sup>3</sup>Pa) of the medium for that chemical such that  $C = fZ$ . The  $Z$ - value quantifies the relative affinity of the chemical for a particular medium. At equilibrium all the fugacities in the system are equal and the ratio of the  $Z$  values for two media is equal to the partition coefficients of that chemical in those media. For example the air-water partition coefficient ( $K_{aw}$ ) equals the concentration of the chemical in air to the concentration of the chemical in water which at equilibrium equals  $Z_A/Z_W$  (Mackay D. ,2001. *Multimedia Environmental Models: The Fugacity Approach*. 2nd edn. Lewis Publishers, Boca Raton, USA).

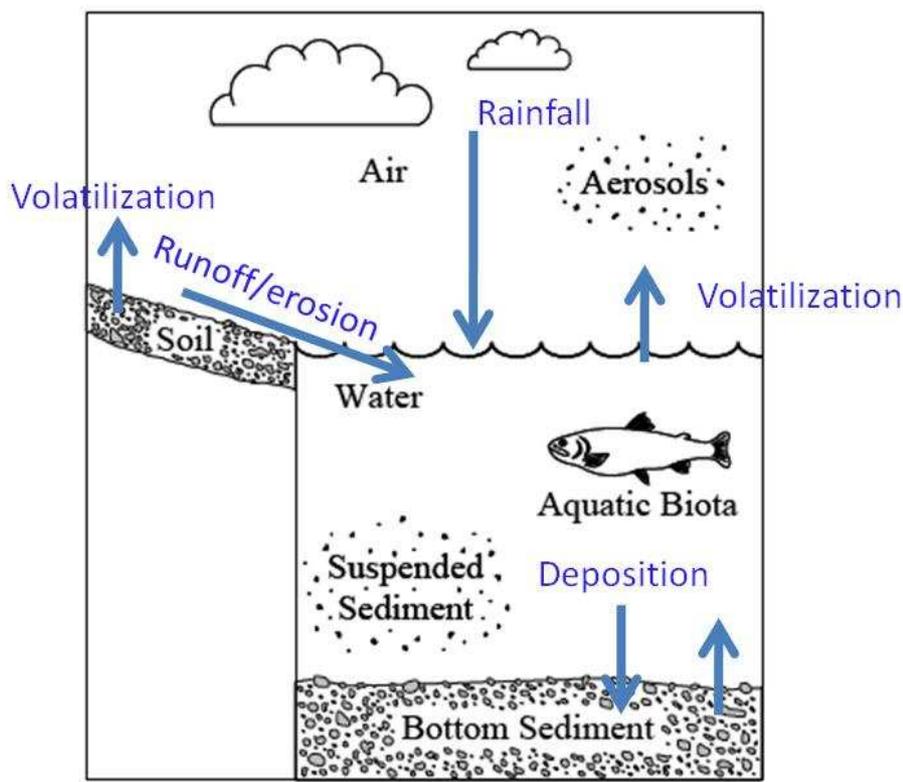
There are four types of fugacity models call levels I-IV because they are of increasing complexity. Level I are steady-state, equilibrium models with a fixed quantity of chemical introduced into the system: Level II as level I, but with a continuous discharge of the chemical with inputs and outputs of the chemical in balance: level III a non-equilibrium version of level II because it includes inter media transport and level IV a non-steady-state version of level III.

The level III model is generally considered appropriate for the initial assessment of potential environmental concentrations at particular locations. This calculation is of the steady state distribution of a chemical, in an environment not at equilibrium. The chemical is continuously discharged at a constant rate into the chosen environmental media, and achieves a steady-state condition at which input and output rates are equal. This involves calculating the rates of degradation and advection, from half-lives or rate constants, and advective flow rates and considering the emission. Inter-media transport processes (e.g. wet deposition, evaporation, or sedimentation) are included. The media receiving the emissions are very important and have a controlling influence on the overall fate of the chemical. When applied to a case study the level III model will give predictions of chemical concentrations in the various media, the dominant losses by reaction and advection, the inter-media transfers and an estimate of the residence time of the chemical in the environment being modelled.

The model enables the environment into which the chemicals are released to be completely defined by the model user.

The model considers four main compartments: air, soil, water and sediment with three sub-compartments: suspended sediments, fish and aerosols as illustrated in Figure 4-1.

**Figure 4-1: Configuration of model compartments in Level III fugacity model & the main transport pathways between compartments. Adapted from Cahill et al (2003).**



Emissions of chemicals can be made into one or more of the three main compartments (air, soil or water). The chemical is then distributed between the sub-compartments in a manner defined by the physico-chemical properties of the chemical and the environment.

The chemical is transported between compartments by a number of advection processes (indicated by the arrows labelled in blue on Figure 4-1). Some of these advection processes (outflow from the lake, bulk mass of air) can remove the chemical completely from the modelled environment. Within the model compartments/sub-compartments the chemical can be removed by a first order degradation process characterised by a degradation half life. The combination of the advection of the chemical through the model environment and the degradation of the chemical within the environment gives an estimation of the clearance rate for the chemical from the modelled environment.

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## 4.3.2 Model Parameterisation

### 4.3.2.1 Base Case

The model was parameterised to calculate environmental concentrations in the Svardalsvanet catchment located to the North East of Mongstad (latitude 60.9°, longitude 5.07°). Long term annual deposition flux data was provided by DNV (using CALPUFF) for four compounds that could potentially be deposited on the Svardalsvanet catchment; Methylnitroamine, N,N –Dimethylnitroamine, 2-(nitroamino)ethanol and NDMA. The deposition fluxes in g/m<sup>2</sup>/s were converted into loadings to the lake and soil compartments based on their surface areas; 0.8 km<sup>2</sup> for the lake in a total catchment area of 9.8 km<sup>2</sup> (see Section 3.3.4).

The environmental values used in the modelling (e.g. lake parameters, rainfall, soil and sediment data) were based on measured data where available, otherwise model default values were used. The depth of the lake was calculated from data supplied to ensure that the lake volume calculated in the model matched the actual lake volume. The median rainfall (provided by DNV) was 2300 mm/y, but since this resulted in a flow less than the median outflow from the lake of 83.1 l/s/km<sup>2</sup>, even assuming 100% runoff, the rainfall (called rain rate in the model) was set to be equal to a value that would produce this runoff amount, 2628 mm. The soil water runoff rate was also set to this value. The residence time for water in the lake was estimated from the lake volume divided by the outflow, and the residence time of the air in the air compartment overlying the catchment to a height of 1000 m was suggested by DNV based on approximate calculations.

Soil organic matter data was obtained by inspection of the Harmonised World Soil Database, from where the dominant soil group was a Lithic Leptosols (40%) a moderately well draining sandy loam soil with an organic carbon content of 1.4% by weight and a pH in water of 7.5.

### 4.3.2.2 Sensitivity Analysis

Because of the uncertainty about some of the environmental parameters used to describe the catchment, the sensitivity of the model results to variations in some of the parameters was explored (e.g. change in lake size, rainfall rate, degradation rate, soil organic content). This was done using a simple approach in which each parameter to be changed was increased or decreased by a certain amount and the model run again with only that parameter changed with respect to the baseline model. The exception to this was that for some environmental parameters the changes were run for both primary and ultimate degradation rates.

## 4.4 Results

Full details of the model results and the sensitivity tests are provided in Appendix 3, but are summarised briefly below.

### 4.4.1 Base Case

Results were obtained for two degradation rates representing:

- Primary degradation to the first metabolite or by-product (fast).
- Ultimate (complete) degradation of the compounds (a slower process).

It is clear that the slower degradation rates result in a higher proportion of the polluting compounds being in the lake water and higher concentrations in the potential drinking water supplies.

The total nitramines and nitrosamines concentration for lake water was predicted to be 81.3 ng/l when considering ultimate degradation, and 17.6 ng/l when the rate was taken for simple degradation to the first metabolite.

Two risk criteria levels have been derived for such pollutants in drinking water: 4 ng/l and 40 ng/l depending on whether a safety factor (with reference to the lifetime cancer risk level) of  $10^{-6}$  or  $10^{-5}$  is used.

Neither of the simulated base cases met the more stringent standard, but when the faster degradation was considered the calculated total met the less stringent standard. However, it should be noted that the base case modelling run was not an actual real case; it was run primarily to test out the methodology for estimating pollutant concentration in drinking water sources and not to explicitly draw conclusions in relation to criteria, particularly as emissions, lake parameters etc. are not yet fully defined.

### 4.4.2 Sensitivity Analysis

Sensitivity analyses were conducted on a number of parameters and the model run again with only that parameter changed with respect to the baseline model. The sensitivity analyses and the outcomes are summarised in the table below.

**Table 4-1: Summary of the results of sensitivity testing of the case study model**

Parameter Altered	Effect on resulting Nitrosamine & Nitramine Lake Concentrations	Reason for Effect
Increased lake size by 300% in same catchment size	Decrease of 62% and 64% for ultimate and primary degradation respectively	Greater dilution of nitrosamine & nitramines as a result of increased water volume.
Decreased lake size by 50% in same catchment size	Increase of 73% and 84% for ultimate and primary degradation respectively	Lower dilution of nitrosamine & nitramines as a result of increased water volume.
Increase rainfall and runoff by 50%	Increase of 1% and 10% for ultimate and primary degradation respectively	More of the nitrosamine & nitramines are moved from the catchment to the lake
Decrease Rainfall and Runoff by 50%	Decrease of 0% and 14% for ultimate and primary degradation respectively	Less of the nitrosamine & nitramines are moved from the catchment to the lake
Increase Rainfall by 50% no change in runoff	No effect	Water flows through the catchment are unchanged
Increase in degradation half life	41% decrease under primary	More of the nitrosamine & nitramines are



<b>Parameter Altered</b>	<b>Effect on resulting Nitrosamine &amp; Nitramine Lake Concentrations</b>	<b>Reason for Effect</b>
in soils by 75%	degradation (ultimate degradation not tested)	removed in the soil compartment
Increase organic carbon content of soils by factor 24.3	2% decrease under primary degradation (ultimate degradation not tested)	None of the nitrosamine & nitramines has a high Kow, so there is only a small interaction with the soil even at high organic carbon contents.
Increase lake suspended sediment concentration by factor of 10	No effect	Little or no interaction with the lake suspended sediment due to the low Kow (octanol-water partition coefficient for pollutants) of the nitrosamine & nitramines
Decrease height of air column above the catchment by 70%	No effect	Air compartment is not an important sink of nitrosamine & nitramines in the model
Increase residence time of air over catchment by 100%	No effect	As above.

In summary, model results were found to be sensitive to the lake size (because changing the water volume changes the degree of dilution), and to degradation rates, but were relatively insensitive to the other parameters examined (such as rainfall rate, soil organic content, lake suspended sediment concentration, residence times).

## 5 SUMMARY AND CONCLUSIONS

This section provides the summary and conclusions from the deposition case study as well as the analysis after deposition. These are included below.

### *Deposition Case Study*

- Wet deposition is the driving deposition mechanism, whereas dry deposition is negligible in comparison in this relatively humid and wet study area (over an order of magnitude lower for equivalent deposition fluxes).
- Effectively, all the mass emitted for pollutants of interest (nitrosamines and nitramines) will be deposited via the wet deposition mechanism *during* precipitation hours.
- However, it should be noted that the above are highly dependent on the assumptions related to the pollutants scavenging coefficients, and on the study area weather.
- Peak fluxes are observed in the near field (a few kilometres from the emission source).

It should also be noted that:

- The deposition fluxes are likely to have been overestimated given that amine chemistry has not been considered for the purposes of this analysis, and all emissions are assumed to occur at source based on maximum nitrosamine and nitramine yields (for rural areas) from the available literature (as provided by CCM).
- All degradation reactions of nitramines and nitrosamines in the atmosphere have been neglected (once formed these pollutants do not react further, which is a conservative assumption).

### *Modelling after Deposition*

- The base case model (after deposition) was not an actual real case; it was run primarily to test out the methodology for estimating pollutant concentration in drinking water sources and not to explicitly draw conclusions in relation to the currently available criteria. However, predictions suggest that (**if** the case was real, the assumptions correct, and the emissions and lake characteristics accurate):
  - The base case model predictions suggest that assuming that primary degradation (degradation of the parent molecule to a first metabolite) removed any carcinogenic effect, the nitrosamine and nitramine concentrations in the lake water will be greater than the strictest suggested protective level for lifetime exposure through drinking water (4 ng/l, representing a negligible lifelong risk of 1 in a million of acquiring cancer), but less than the higher level of 40 ng/l (representing a minimal lifelong risk of 10 in a million of acquiring cancer).
  - If complete mineralization (ultimate degradation) of the molecule is required to remove the carcinogenic effect then both levels are likely to be exceeded.
  - Given that the case study is not based on actual emission data and the selection of the lake for detailed analysis does not correspond to the lake receiving peak flux, the results presented relative to criteria should be considered in this context.

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- It should be noted however that because the nitrosamines or nitramines might be expected to form less carcinogenic compounds after primary degradation to a metabolite, consideration of the primary degradation rate may be justified for the purposes of this study (with ultimate degradation rate of interest as a sensitivity test).
  - The degradation rates used in the modelling were, with the exception of NDMA, all estimated from the structures of the molecules using an adaptation of a method that was really only intended to be qualitative. These values are therefore rather uncertain and the model was sensitive to them as was shown by the difference in the results found when primary and ultimate degradation rates are compared.
  - The model results were also shown to be sensitive to the size of the lake with respect to the size of the catchment: the larger the lake the lower the predicted lake concentrations. This was because of the increased water volume in which the loading was diluted.
  - The model results were rather insensitive to all of the other parameter variations assessed. This included the organic carbon content of the soil, which was unimportant because of the low K<sub>oc</sub> values (partitioning coefficient normalised for organic carbon content of soil or sediment) estimated for these molecules. Given that the K<sub>oc</sub> values were estimated, it would be very useful to make measurements of the K<sub>oc</sub> in suitable representative soils.
  - However, it should be noted that there are some significant uncertainties in the study:
    - Any change in the criteria could dramatically affect the results of the analysis relative to the comparison against these criteria. The criteria is currently based on NDMA which is considered a conservative estimate as NDMA is one of the more potent of this group of pollutants.
    - The nitrosamine and nitramine deposition flux provided by DNV and utilised in this report is likely to be overestimated because it was estimated prior to the development of the simple atmospheric amine chemistry module within CALPUFF (as mentioned previously).
    - Further refinement of the physico-chemical properties described above will provide more robust estimates and a more confident prediction could then be made.
    - The lake used in this case study does not actually receive the peak flux, but was used for methodology development purposes only.

The key conclusion from the study is that the methodology developed for estimating the concentration of nitrosamines and nitramines in drinking water sources, based on a known concentration in air, appears robust and can be used for an actual assessment (i.e. based on 'real' emission data and water body characteristics). Furthermore, the methodology can be expanded to account for amine atmospheric chemistry if more accuracy is required.

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## 6 RECOMMENDATIONS

The following recommendations are made:

- Given that the nitrosamine and nitramine deposition flux predictions are likely to have been overestimated because the analysis was conducted prior to the development of the simple atmospheric amine chemistry module within CALPUFF, further deposition case study analysis should be conducted utilising the amended model. This would increase the accuracy of the study results.
- The assumptions related to the pollutants scavenging coefficients used for the wet deposition modelling should be confirmed. The data can be best confirmed through literature review, and if no information is available experimental investigation may be required.
- Improved estimates of degradation rates should be obtained through experiments with soil and water samples, and at temperatures typical of sites where deposition is expected. It would be useful to identify the degradation mechanisms, the metabolites and their potential carcinogenicity. This would increase the level of confidence in the modelling after deposition results. It is emphasised that because nitrosamines or nitramines might be expected to form less carcinogenic compounds after primary degradation to a metabolite, consideration of the *primary* degradation rate may be justified for the purposes of this study (with ultimate degradation of interest as a sensitivity test).
- The modelling after deposition results were rather insensitive to variations in the organic carbon content of the soil. This was unimportant because of the low Koc values (partitioning coefficient normalised for organic carbon content of soil or sediment) estimated for these molecules. Given that the Koc values were estimated, it would be very useful to make measurements of the Koc in suitable representative soils. It is noted that some of the chemicals may be weakly positively charged at neutral pH and therefore the estimates made here might underestimate the actual value and therefore lead to an overestimate of lake concentrations. Experimental determination of the Koc values would show if this is in fact the case.

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