

**H&ETQPAmine2:
Modelling Atmospheric Dispersion for Components from
Post-Combustion Amine-based CO₂ Capture**

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1. Executive Summary

This report has been compiled under Service H&ETQPAmine2 of the CO₂ capture Mongstad (CCM) project. The CCM project encompasses the planning and building of a large scale CO₂ capture plant (the CCP) next to Mongstad refinery on the Mongstad industrial site north of Bergen in Norway. It is planned that about 1.3 million tonnes per year of CO₂ will be captured from the flue gas of a Combined Heat and Power (CHP) plant. The amine-based CO₂ capture plant (CCP) process may result in potentially harmful emissions to air but the emissions, their behaviour in the atmosphere and that of their degradation products is not well understood. Another Service of the CCM is seeking to improve this understanding.

Service H&ETQPAmine2 of CCM is concerned with the CCP flue gas emissions and their fate in the atmosphere. Here we report on work carried out under the first call off of H&ETQPAmine2:

1. Recommend a model to be used to describe how emitted substances from the CCP can be expected to behave after release to the atmosphere
2. Carry out a case study of dispersion of emissions from an absorber stack, based on conditions at Mongstad
3. Identify model development needed to accomplish this in the short-term (within one year) and long-term (within 3 years)

These items are referred to as Sub-tasks 1, 2 and 3 and these are summarised in turn.

1.1. Sub-task 1: Model Evaluation

The aim of Sub-task 1 is to describe thoroughly the ADMS 4 dispersion model, how it can be used to model the emissions at Mongstad as it is currently, and its flexibility and capability to be modified in order to be more applicable to the special features at Mongstad and to be adapted in the light of future findings.

In carrying out Sub-task 1 we have described the relevant features of ADMS 4, outlined the potential for adding to, or adapting, ADMS 4 to reflect unique aspects of dispersion from the plant at Mongstad, described the model development process and quality control systems used by CERC, the validation of ADMS 4 and concluded by discussing other candidate models.

ADMS 4 is a model that has been and continues to be extensively validated, is developed to high standards of quality control and, with hundreds of users around the world, is fully supported and capable of being run by practitioners. It is an advanced Gaussian model, modelling dispersion in convective conditions using a skewed-Gaussian concentration distribution. It takes a far more physics-based approach than the engineering or empirical approach adopted by some Gaussian models. Plume rise is modelled using a Runge-Kutta solution to the integral conservation equations, NO_x chemistry is modelled using an adaptive time-stepping scheme and the falling drop wet deposition module uses a Runge-Kutta solution. This physics-based approach makes developments of the model within that same physical scheme possible. For instance, whilst the chemistry scheme in ADMS 4 models two reactions the scheme in ADMS-Urban models 8 for the Generic Reaction Set and 95 for the CBM scheme.

Other candidate models include AERMOD, CALPUFF, TAPM and NILU's PDF model. Each model has strengths for application at Mongstad:

- AERMOD, like ADMS 4, is a robust, widely-used advanced Gaussian mode. The AERMOD source code is available for anyone to develop. However, its empirical approach to modelling physical processes means that developments could not be made in a self-consistent manner without significant changes to the fundamental model. Its ozone-limiting chemistry scheme is a simple post-processing step and AERMOD has no capability to include the falling drop wet deposition scheme that is in ADMS 4.

- CALPUFF uses AERMOD in the near field so offers no additional advantages at that scale; it is recommended for use by US-EPA only for scales greater than 50km from the source. It uses a fully time-dependent puff model in the far field, which is slower than ADMS 4 or AERMOD. However, its met pre-processor, CALMET, allows a more robust treatment of the effects of surface variations than the AERMOD algorithms, it has a chemistry model which could probably be adapted for amine chemistry but it does not have advanced wet deposition algorithms (falling drop method) or calculations of in-plume humidity/water content.
- TAPM, **The Air Pollution Model** developed by CSIRO, nests a Lagrangian particle model within an Eulerian model. The Eulerian model has advanced chemistry and microphysical models and therefore may be suitable for development to model large scale impacts of the plant. However, the Lagrangian model includes neither chemistry (which is estimated from the Eulerian model when the Lagrangian model is used) nor deposition.
- NILU's Lagrangian probability density function (PDF) model is complex and computationally expensive compared with ADMS 4 and AERMOD. We are not aware that the PDF modelling approach has been through such extensive validation or scrutiny and, therefore, it does not seem appropriate to consider such a model for this study.

1.2. Sub-task 2: Case Study

A Case Study has been carried out to model the fate of emissions from a 50m high CCM stack using CERC's industrial dispersion model ADMS 4 and data provided to CERC by Gassnova. A baseline case was established modelling MEA emissions only from the CCM stack using meteorological data for 2007, no complex effects in ADMS 4, i.e. modelled assuming flat terrain, no deposition and no chemistry, and using mostly default values of model parameters. Sensitivity tests were then carried out to investigate the effect of changing model parameters within realistic ranges, of including additional modelling options and considering other sources and pollutants.

The tender specification stipulated a number of processes which require consideration, as well as processes which should be considered if possible. Tables 1.1 and 1.2 summarise how these have been considered in the Case Study.

Table 1.1: Processes required

Process	To be considered?	Details
Wet and dry deposition	Yes	The modelling included wet and dry deposition including spatially varying dry deposition velocity
Existing emission inventory for Mongstad region (several point sources)	Yes	Emissions of NO _x and SO ₂ from all relevant sources were modelled as one of the sensitivity tests
Local dispersion and deposition (less than 5km)	Yes	Local dispersion and deposition has been modelled at a high spatial resolution: 50m
Regional dispersion and deposition (more than 5km)	Yes	Regional dispersion and deposition has been over domains with extent 10kmx10km and 20kmx20km at grid resolutions of 100m and 200m respectively
Worst case meteorological / atmospheric conditions	Yes	Concentrations and deposition were calculated as long-term (annual) averages and short-term peaks (maximum hourly i.e. 100 th percentile)
On-site dispersion and deposition (10-1000m)	Yes	The choice of spatial resolution has been demonstrated. The highest resolution used in the Case Study was 50m but a resolution of 10m or even 1m can be used

Table 1.2: Processes to be treated if possible

Process	To be considered?	Details
Potential for particle formation	Demonstrated Future work	The ADMS 4 NO _x chemistry scheme was used. This is a simplified 2-reaction scheme. In the 8-reaction scheme or CBM-IV mechanism of ADMS-Urban, which could be implemented in ADMS 4, nitrate and sulphate particulate formation is calculated.
Influence on droplet formation	Demonstrated Future work	The plume visibility model in ADMS 4 calculates the formation of a condensed water plume; there is no capability for droplet formation of other chemicals at this stage, but the plume visibility module has the information required on water content to make this development possible.
Estimate of concentrations of given compounds in local/regional fresh water bodies	Demonstrated Future work	Calculation of deposition to a reservoir was demonstrated. Further information would be required to estimate the concentration in the water body.

The Case Study revealed model results were sensitive to the effect of on-site buildings (increasing ground level concentrations close to the stack) and to the effects of chemistry and wet and dry deposition. However, the species-dependent information for deposition and chemistry is not available for the sensitivity to these effects to be quantified.

The Case Study demonstrated the ability of ADMS 4 in its current form to model the emissions from CCP and to account for many of the important factors influencing dispersion.

1.3. Sub-task 3: Recommendations for model development

Sub-task 3 builds on the work carried out in Sub-task 1, the model evaluation and Sub-task 2, the Case Study, to assess the model development required to improve the accuracy and certainty of model results for the fate of emissions at Mongstad. Potential development tasks, further information required by the model and the proposed approach to validating the development are described. The time to complete each task and, hence, whether it can be delivered after 1 year or 3 years is reported.

The two key areas for which significant development would improve the modelling of amines and other species released at Mongstad are identified as: chemistry and deposition.

- Chemistry:** It is recommended that developments of increasing complexity be made to the model to include both gas phase and aqueous phase chemistry of amines. For the gas phase we recommend a simple degradation model (1 year), an enhanced degradation model (3 years) and a full chemical scheme for amines (greater than 3 years). We also recommend that the enhanced NO_x chemistry in ADMS-Urban be implemented in ADMS 4 for generation of sulphate and nitrate particulates (1 year). For the aqueous phase, based on the ADMS 4 condensed plume visibility module, we recommend simple (1 year) and advanced (3 years) schemes for uptake of amines in plume droplets and subsequent transformation into particulates.
- Wet and dry deposition:** For wet deposition we recommend adaptation of the ADMS 4 scheme for amines and ammonia: washout model (less than 1 year); pH limiting washout (1 year); falling drop method (3 years). For dry deposition the surface resistances used in the calculation of the deposition velocity require modification for amines.

The short-term (1 year) developments involve customisation and limited developments of the model for releases of amines and ammonia. Their implementation will remove the broad simplifying assumptions used in the Case Study (e.g. washout coefficients identical for all amines, instantaneous degradation of amines), however longer-term developments will be required to implement the most advanced scientific understanding into the model (in case of wet deposition) and more sophisticated chemical routines. It may be that this more advanced implementation is necessary fully to understand the extent to which the methodologies used in the shorter-term developments are sufficient or otherwise.

Developments of the chemistry module and the impact they will have on model results, depend on improved knowledge of the chemistry of amines and their degradation products in both gaseous and aqueous phases.

Developments to the wet deposition module depend on the availability of Henry's Law coefficients, disassociation coefficients and gas diffusion coefficients for all relevant amines and their products.

CERC has over 20 years experience in developing and supporting operational models and are experts in model evaluation techniques, currently leading the model evaluation work package of the EU 7th framework PASODOBLE project (www.myair-eu.org). CERC will bring this expertise to the Service and are confident that once agreed and specified and with necessary information supplied, development can be delivered on time and to the established quality of the ADMS 4 model.

2. Introduction

The CO₂ capture Mongstad (CCM) project encompasses the planning and building of a large scale CO₂ capture plant (the CCP) next to Mongstad refinery on the Mongstad industrial site north of Bergen in Norway.

At Mongstad it is planned that about 1.3 million tonnes per year of CO₂ will be captured from the flue gas of a Combined Heat and Power (CHP) plant. The CO₂ will be conditioned, compressed and sent by pipeline to geological storage under the Norwegian Continental Shelf. The amine-based CCP may result in potentially harmful emissions to air. There is limited knowledge regarding the behaviour in the atmosphere of the resulting amines and their degradation products. Investigation of the behaviour of amines and their products is one of the strands of the CCM project, which was initiated to investigate the unknowns associated with the CO₂ capture plant.

This report has been carried out under a different strand of the CCM project that is called H&ETQPAmine2. This part of the CCM project is concerned with the CCP flue gas emissions and their fate in the atmosphere.

The CCP reaction products will include: CO₂, NO_x, NH₃, amines, aldehydes, alkylamines and amides, with the potential for the release and/or subsequent formation of nitrosamines and nitramines. In order to understand the health and environmental risk of these emissions, the project aims to determine: how long the substances survive in the atmosphere; how far they travel; where they are most likely to be deposited; and what are their likely concentrations in the environment.

The Service under H&ETQPAmine2 has the following Objectives:

1. Recommend a model to be used to describe how emitted substances from the CCP can be expected to behave after release to the atmosphere;
2. Carry out a case study of dispersion of emissions from an absorber stack, based on conditions at Mongstad;
3. Identify model development needed to accomplish this in the short term (within one year) and long term (within 3 years);
4. Complete the recommended model development program; and
5. Utilise the developed model in site-specific emission dispersion evaluation.

The work commissioned covers Objectives 1, 2 and 3 above which are referred to as Sub-tasks 1, 2 and 3. Each is described in more detail below.

2.1. Sub-task 1: Model Evaluation

The objective of Sub-task 1 is to recommend a model to be used to describe how emitted substances from the CCP can be expected to behave after release to the atmosphere. The tender document requires for the Sub-task:

'A general introduction will be given to emission dispersion modelling, including presentation of different models, their strengths and weaknesses as well limitations when used under different emission conditions. This part of the Service shall recommend the type of model(s) to be used in the succeeding case study.'

Following the project kick-off meeting on 25th May 2010 it was agreed that ADMS 4 would be the model used by CERC in its Case Study and some amendment was made to the description of Sub-task 1 to reflect this as follows:

'Detailed description of ADMS 4 including modelling methodology, scientific approach, description of key features relevant to current study, strengths and weaknesses as well as limitations when used under different emission conditions; comparison of ADMS 4 with other likely candidate models; extent to which ADMS 4 is able to model the important processes and obtain credible results as it stands; potential to add/adapt ADMS 4 to reflect unique aspects of dispersion from the plant (e.g. amine chemistry).'

The aim of this task is, thus, to describe thoroughly ADMS 4, how it can be used to model the emissions at Mongstad as it is currently, and its flexibility and capability to be modified in order to be more applicable to the special features at Mongstad and to be adapted in the light of future findings.

Sub-task 1 is covered in Sections 3 to 8 of this report as follows:

- Section 3: ADMS 4 Model Description covering representation of sources in ADMS 4, meteorological input and output, parameterisation of the boundary layer, dispersion over flat terrain, the effects of buildings, spatial variation in surface effects of changes in surface elevation and surface roughness, wet and dry deposition, chemistry, plume visibility, model inputs and outputs.
- Section 4: Potential to add/adapt ADMS 4 to reflect unique aspects of dispersion from the plant
- Section 5: Model Coding process
- Section 6: ADMS 4 Model Validation; and
- Section 7: ADMS 4 and other candidate models

ADMS 4 is a model that has been and continues to be extensively validated, is developed to high standards of quality control and, with hundreds of users around the world, is fully supported and capable of being run by practitioners. It is an advanced Gaussian model, modelling dispersion in convective conditions using a skewed-Gaussian concentration distribution. It takes a far more physics-based approach than the engineering or empirical approach adopted by some Gaussian models. Plume rise is modelled using a Runge-Kutta solution to the integral conservation equations, NO_x chemistry is modelled using an adaptive time-stepping scheme and the falling drop wet deposition module uses a Runge-Kutta solution. This physics-based approach makes developments of the model within that same physical scheme possible. For instance, whilst the chemistry scheme in ADMS 4 models two reactions the scheme in ADMS-Urban models 8 for the Generic Reaction Set and 95 for the CBM scheme.

2.2. Sub-task 2: Case Study

A Case Study has been carried out to model the fate of emissions from a 50m high CCM stack using CERC's industrial dispersion model ADMS 4. The source, emissions, meteorological and ambient background data were provided to CERC by Gassnova.

A baseline case was established modelling MEA emissions only from the CCM stack using meteorological data for 2007, no complex effects in ADMS 4, i.e. modelled assuming flat terrain, no deposition and no chemistry, and using mostly default values of model parameters. Sensitivity tests were then carried out to investigate the effect of changing model parameters within realistic ranges, of including additional modelling options and considering other sources and pollutants. The sensitivity tests covered the following:

Additional model options

- topography
- spatially varying surface roughness
- buildings
- wet deposition
- dry deposition
- plume visibility
- NO_x chemistry, using background ambient concentration data

Parameters varied

- minimum Monin-Obukhov length
- Priestley-Taylor parameter
- albedo
- constant surface roughness
- latitude
- year of meteorological data
- output grid extent and resolution
- model parameters associated with spatially-varying surface roughness
- model parameters associated with wet deposition
- model parameters associated with dry deposition

Other sources and pollutants

- NO_x and SO₂ from the CCM, the Test Capture Plant (TCM), four refinery stacks and a flare

Results were provided as tabulated values of maximum annual and maximum hourly (100th percentile hourly) ground level concentrations and, when modelled, deposition flux. Contour plots of the annual average and 100th percentile hourly concentrations are given for the base case, for the changed output grid and the case of modelling a building. The contour plots were superimposed on digital base maps, which is the best way to show how impacts vary over the surrounding area.

As the treated flue gas is washed before release, the water content of the plume may be high. Plume visibility due to condensation of water vapour was modelled with the results reported in terms of the frequency and length of visible plumes from the stack.

One of the main concerns about the release of amines from CCP is the potential presence of nitrosamines, degradation products of amines, in drinking water reservoirs. As a demonstration of how this could be investigated by ADMS 4, an example was run to calculate dry and wet deposition to a reservoir taken to be 4km to the south of the CCM stack. ADMS 4 can calculate total deposition and, if algorithms for run-off, degradation in a body of water and rate of change of the water in the reservoir were supplied, could develop a calculation of the concentration of nitrosamines in the body of water.

The Case Study demonstrated the ability of ADMS 4 in its current form to model the emissions from CCP and to account for many of the important factors influencing dispersion. The model results were sensitive to the effect of on-site buildings and to the effects of chemistry and wet and dry deposition. However, the species-dependent information for deposition and chemistry is not available for the sensitivity to these effects to be quantified. Sub-task 2 is described in Section 9 of this report.

2.3. Sub-task 3: Recommendations for Model Development

Sub-task 3 builds on the work carried out in Sub-task 1, the model evaluation and Sub-task 2, the Case Study, to assess the model development required to improve the accuracy and certainty of model results for the fate of emissions from CCP. Potential development tasks, their likely impact on model results, the quality of the proposed approach, further information required by the model and the proposed approach to validating the development are described. The time estimated to complete each task and, hence, whether it can be delivered after 1 year or 3 years is reported.

Sub-task 3 reviews the model features described fully in Section 3:

- the representation of sources in ADMS 4
- meteorological input and output
- parameterisation of the boundary layer
- dispersion over flat terrain
- the effects of buildings
- spatial variation in surface effects of changes in surface elevation and surface roughness
- wet and dry deposition
- chemistry
- plume visibility
- model inputs and outputs

Informed by the findings of the Case Study sensitivity tests, the model features are categorised as satisfactory in their current state for modelling CCP, or that development would improve the modelling. The two features for which significant development would improve the modelling are identified as:

- i. chemistry
- ii. deposition

Developments of the chemistry module and the impact they will have on model results, depend on improved knowledge of the chemistry of amines and their degradation products in both gaseous and aqueous phases. Developments to the wet deposition module depend on the availability of Henry's Law coefficients, disassociation coefficients and gas diffusion coefficients for all relevant amines and their products. These data have been sourced for some representative amines, including MEA, but data for some amines and amine degradation products are not currently available.

Sub-task 3 is described in Section 10 of this report.

3. ADMS 4 Model Description

3.1. General methodology and scientific approach

The key factors determining the concentration of chemicals in the atmosphere and surface deposition of chemicals to the underlying surface are as follows:

- the rate of emission of the different chemical species from the source(s);
- the density relative to ambient air and momentum of any of the material in which the chemical is released which, assuming the release is buoyant relative to the ambient air, determines the 'plume rise';
- the speed and direction of the mean wind;
- the characteristics of the turbulence between the 'source' and the 'receptor';
- chemical transformations; and
- wet and dry deposition.

In this study, it is necessary for modelling to describe the fine details of the in-plume processes and the discrete nature of the plume. For such a task the most common approach is to use a Gaussian plume model. The essence of this approach is the assumption that the dispersing material can be represented by a continuous plume and, at any particular distance downstream from the source, the mean wind speed and direction and turbulence are broadly similar across the plume. Other assumptions are that the characteristics of the mean flow and turbulence are constant in time (i.e. constant for each hour for which meteorological data is available) and that the form of the distribution of concentration is assumed to be known and commonly Gaussian, hence the name of this model type.

Figure 3.1 shows a pictorial representation of a horizontal cross-section of a Gaussian plume. The wind is blowing from left to right. The blue line represents the distribution of the chemical concentration across the plume and the dashed line the dependence of the plume centre-line concentration on distance downstream.

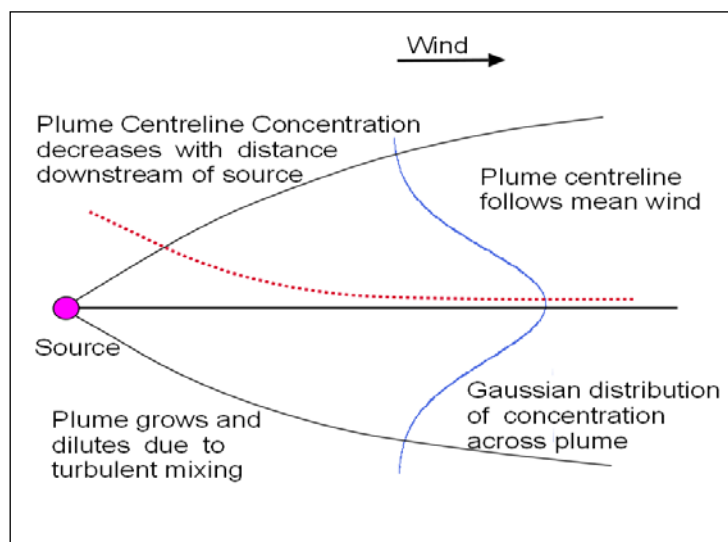


Figure 3.1: Pictorial representation of a horizontal cross-section of a Gaussian plume

In the simpler (first-generation) Gaussian plume models (e.g. R-91¹, ISC², CONDEP and CONCX³) the spread of the plume is related broadly to a weather type or stability class. The stability class is typically classified as being one of 'A' through to 'F' or 'G', where 'A' represents very unstable cases, 'D' neutral cases with no surface heating or cooling effects, 'G' the most stable cases and 'B', 'C', 'E' and 'F' the intermediate cases.

In order to overcome the shortcomings of the first-generation Gaussian models, ADMS 4 and other so-called second-generation models (e.g. OML⁴, AERMOD⁵), have been developed. These models use a more advanced approach in which the plume spread is related directly to the characteristics of the atmospheric turbulence. The boundary layer is parameterized in terms of two separate parameters, rather than just a single Pasquill stability category: namely the boundary layer height (which represents the height above the ground at which the air ceases to be turbulent); and the Monin-Obukhov length, a parameter related to generation of turbulence in the boundary layer. These parameters are estimated from standard meteorological data and the known surface properties (surface roughness, surface wetness represented as modified Priestley-Taylor parameter or Bowen ratio, and surface albedo).

In traditional Gaussian plume models, there is either no or only rudimentary allowance for the impact of buildings at the site of the emissions, effects of underlying topography or chemical transformation. However, ADMS 4 and some other second generation models may treat these effects. ADMS 4 also has a number of other advanced features which set it apart from other Gaussian models and make it a particularly suitable candidate for modelling the impacts of amine releases at Mongstad. These comprise the following:

- an integral plume rise model, which takes account of a fully 3-dimensional flow field;
- a building effects module, which calculates the impact of main site buildings on mean flow and turbulence and hence dispersion;
- a complex flow model, which calculates the impact of changes in terrain elevation and surface roughness on the mean flow and turbulence and hence dispersion;
- a dry deposition model, which may allow for spatial variation in the deposition velocity;
- a wet deposition model, including a falling drop method which explicitly calculates the rate at which the chemical species dissolve in raindrops and subsequent outgassing, if any, taking account of the chemical solubility, Henry's Law and chemical reactions within the drops. This model is currently set up for SO₂ and HCl but may be adapted for amines and ammonia;
- a condensed plume visibility model which calculates the in-plume water content and hence may be adapted for calculations of chemistry within droplets; and
- an in-plume chemistry model, which may be adapted for the consideration of amine chemistry.

In the next section we describe in more detail the features of ADMS 4 relevant to dispersion of amines and other emissions at Mongstad.

¹ Clarke, R.H., 1979: A model for short and medium range dispersion of radionuclides released into the atmosphere. NRPB Report NRPB-R91

² U.S. E.P.A., 1995: User's Guide for the Industrial Source Complex (ISC3) Models. Volume I: User Instructions (Report EPA-454/B-95-003a); Volume II: Description of model algorithms (Report EPA-454/B-95-003b), September 1995. U.S. E.P.A., Office of Air Quality Planning and Standards, Emissions Monitoring and Analysis Division, Research Triangle Park, NC 27711.

³ Karl, M., Brooks, S., Wright, R. & Knudsen, S., 2009: CO₂ and amines: Worst case studies on amine emissions from CO₂ capture plants (Task 6). NILU Ref: OR 78/2008

⁴ Olsen, H.R., Berkowicz, R. and Loftrom, P., 2007: OML: Review of model formulation. National Environmental Research, Denmark. NERI Technical Report No. 609, pp. 130, <http://www.dmu.dk/Pub/FR609>

⁵ Cimarelli, A.J., Perry, S.G., Venkatram, A., Weil, J.C., Paine, R.J., Wilson, R.B., Lee, R.F., Peters, W.D., Brode, R.W. and Paumier, J.O., 2004: AERMOD Description of Model Formulations. United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Emissions Monitoring and Analysis Division, Research Triangle Park, EPA-454-R-03-004

3.2. Features of ADMS 4 relevant to this study

This section presents the main details of the features of ADMS 4 which are relevant to the fate of pollutants released at Mongstad. The full specification of each of the model features may be found in the ADMS 4 Technical Specification⁶; see also Section 5 of this report. Figure 3.2 shows a schematic of the relevant model features.

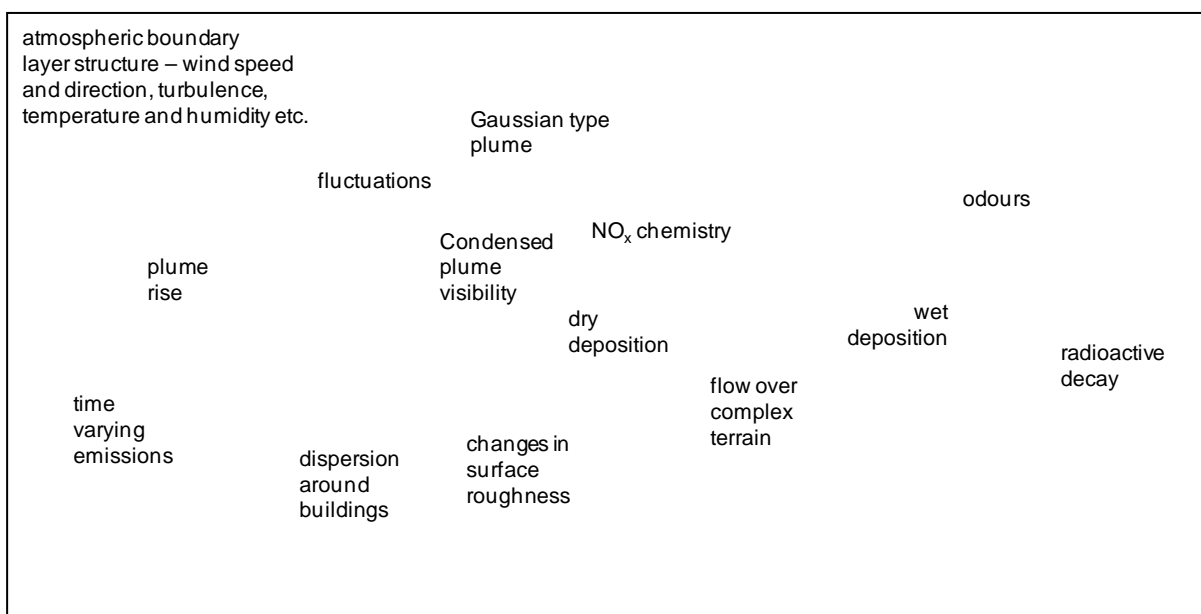


Figure 3.2: Schematic of ADMS 4 model features relevant to the study

3.2.1. Source representation

3.2.1.1. Sources types and emission rates

ADMS 4 is able to consider up to 300 point or jet sources, 30 area sources, 30 volume sources and 30 line sources. Each source may emit up to 10 pollutants, although more pollutants may be considered with coincident sources. Up to 10 particle sizes may be defined for each particulate emission. Pollutant emissions are specified in g/s. The model is thus able to account for all emissions at Mongstad.

3.2.1.2. Plume rise

The source momentum and buoyancy are important in determining the initial motion of the released material. The momentum of the source determines the initial direction of the material's motion. The buoyancy of the source determines whether there is a tendency for the material to rise (when it is less dense than the surrounding air) or fall (when it is denser than the surrounding air). A source is said to be 'passive' when these effects are not important. ADMS 4 takes account of releases with momentum and/or buoyancy using its integral plume rise model. The plume rise model solves the integral conservation equations for mass, momentum, heat and chemical species for the plume, taking account of entrainment and drag forces, using a Runge-Kutta method.

⁶ <http://www.cerc.co.uk/environmental-software/model-documentation.html>

3.2.2. Meteorological input and output

This section describes the types of meteorological data that can be input to ADMS 4. For each of the meteorologically related parameters (e.g. wind speed, wind direction, temperature) each line of input data describes the meteorological conditions for one or more hours, the conditions being assumed to be fixed for any given hour. The meteorology input module reads the data and uses the pre-processing algorithms to estimate values of the various meteorological quantities required for running the dispersion model.

Data are usually in the form of a chronological record, termed hourly sequential. Other data may have a certain weight or frequency associated with each line of meteorological data. Such data are usually not chronological and are termed *statistical*, as they have been statistically analysed.

The meteorological data from one surface meteorological observing site is typically input into the dispersion model; this data may be supplemented by data from other surface meteorological observing sites and/or from vertical profile data provided by radiosondes (weather balloons). The typical parameters supplied in hourly sequential meteorological data sets and used by ADMS 4 are:

- Day of the year (Julian day, 1-365 or 366)
- Hour of the day
- Wind speed (m/s) at a user-specified height
- Wind direction (° clockwise from north)
- Near ground surface temperature (°C)
- Cloud cover (oktas, 0-8)

The meteorological input dataset can contain a variety of input meteorological parameters (for a complete list of input parameters, minimum input requirements and output, see Appendix A).

3.2.3. Parameterisation of the boundary layer

3.2.3.1. Introduction

In ADMS 4, model algorithms are used together with observed meteorological data to calculate wind speed and turbulence at the locations required to calculate the transport and spread of the dispersing plume. The vertical profiles of mean wind and turbulence, that is, how they change with height above the ground, are dependent on the measured wind speed, heating (solar radiation) and cooling (long-wave radiation) at the surface, surface roughness, surface wetness and surface albedo.

3.2.3.2. Unstable and stable boundary layers

In the daytime, when the ground is heated by the sun, turbulence is generated both by the surface drag (the drag exerted on the air flow by objects on the ground) and by convection due to the surface heating. When generation of turbulence by convection is the dominant factor, conditions are said to be convective and the air in the atmosphere is said to be unstably stratified. At night-time, when the earth's surface is cooling, the air is said to be stably stratified. In such stable conditions vertical mixing is inhibited and there is little generation of turbulence.

In unstable conditions the plume mixes with the air and dilutes rapidly so that the chemical concentrations within the plume decrease rapidly with distance from the source. In stable conditions mixing is much slower and chemical concentrations decrease more slowly in the plume as it is transported downstream.

Figure 3.3 shows pictorials of plumes dispersing in unstable and stable conditions.

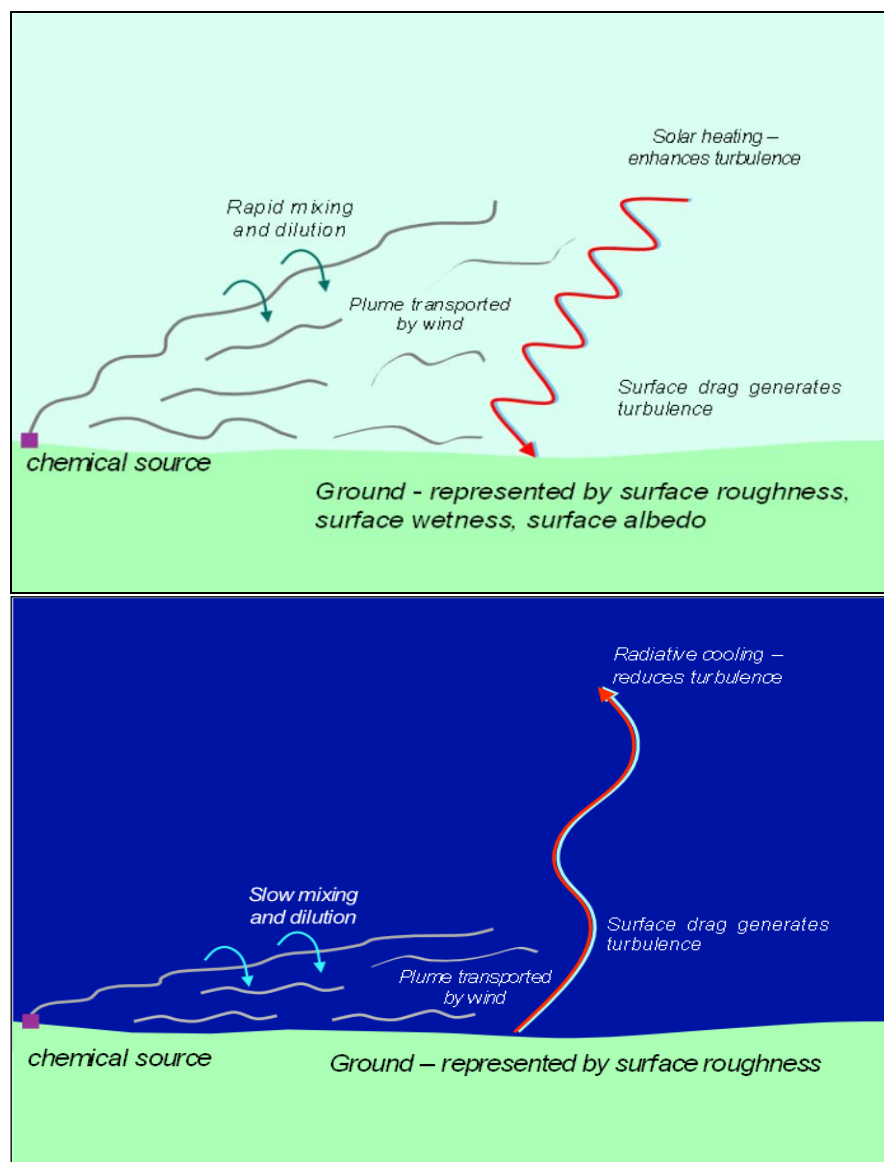


Figure 3.3: Pictorial of the dispersion of a surface release in (a) daytime unstable conditions and (b) night-time stable conditions. When the wind is strong, surface heating or cooling are less important and, in this case, the atmosphere is said to be neutrally stable

As discussed in Section 3.1, in ADMS 4 the boundary layer structure is characterised by the boundary layer height h and the Monin-Obukhov length L_{MO} and **not** by a Pasquill stability category.

In unstable (convective conditions), the Monin-Obukhov length is negative. The magnitude of the length is then a measure of the height above which convective turbulence, the turbulence caused by convective eddies, is more important than mechanical turbulence, the turbulence generated by friction at the Earth's surface. In stable conditions, the Monin-Obukhov length is positive. It is then a measure of the height above which vertical turbulent motion is significantly inhibited by the stable stratification.

Figure 3.4 shows the different regions of the boundary layer in terms of the parameters h/L_{MO} and z/h where z is height above the ground. Figure 3.5 shows the same information but with a dimensional vertical scale, z .

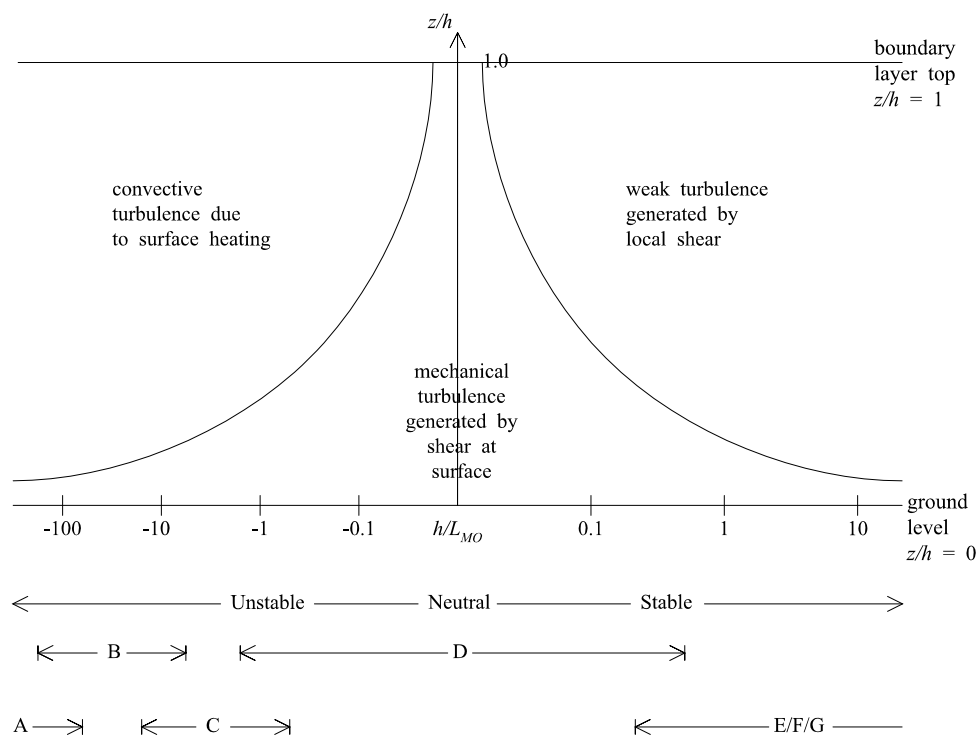


Figure 3.4: Non-dimensional schematic representation of variation of Monin-Obukhov length with atmospheric stability

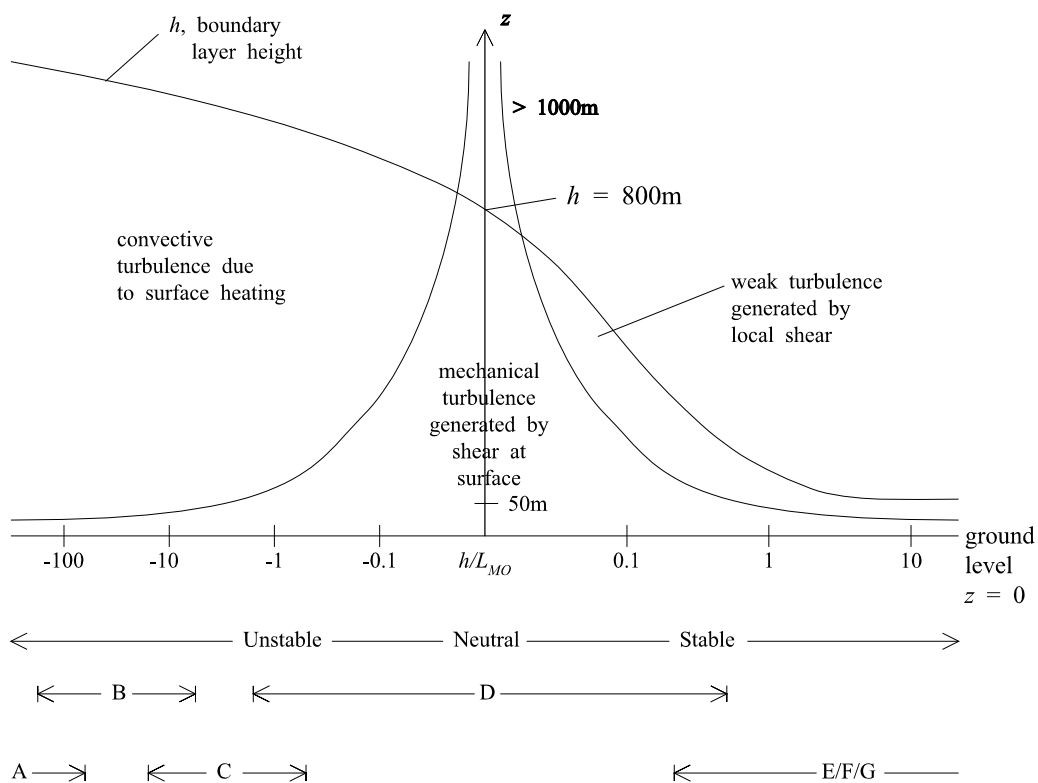


Figure 3.5: Dimensional schematic representation of variation of Monin-Obukhov length with atmospheric stability

3.2.3.3. Boundary layer structure variables

Taking the meteorological parameters described in Section 3.2.2 as input, ADMS 4 calculates vertical profiles of the boundary layer variables listed in Table 3.1. The vertical profiles are expressed as functions of z/L_{MO} and z/h and have been derived from experimental data^{7,8,9}. The profile of the boundary layer variables are used, in turn, by other modules such as the main dispersion module, plume rise module and plume visibility module.

Table 3.1: Boundary layer variables calculated by ADMS 4

Variable	Description
$U(z), \frac{dU}{dz}, \frac{d^2U}{dz^2}$	Mean wind speed (m/s) and its first (s^{-1}) and second derivatives ($m^{-1}s^{-1}$)
$\sigma_u(z), \sigma_v(z), \sigma_w(z)$	Root-mean-square turbulent velocities (m/s)
$\Lambda_v(z), \Lambda_w(z)$	Turbulent length scales (m)
$\varepsilon(z)$	Energy dissipation rate (m^2/s^3)
$T_L(z)$	Lagrangian time scale (s)
$N(z)$	Buoyancy frequency (s^{-1})
$T(z)$	Temperature (K)
$\rho(z)$	Density (kg/m^3)

3.2.4. Dispersion over flat terrain

3.2.4.1. Dispersion parameters

Field experiments and research have shown that the transverse spread, σ_y , and vertical spread, σ_z , of the plume vary with downwind distance from a point source in a way that depends on the atmospheric boundary layer height (h), the height of the source (z_s) and the height of the plume as it grows downwind.

There is no general theory or even generally accepted semi-empirical expression that describes the dispersion from a source at all heights within the boundary layer ($0 < z_s < h$) in all conditions of atmospheric stability and over the complete range of distances from the source to about 30-50 km downwind (typical maximum range of ADMS 4). In developing ADMS 4, the approach adopted was first to use formulae that have been developed and are broadly accepted for specific ranges of the parameters z_s/h , h/L_{MO} (stability) and x/h (downwind distance). Interpolation formulae have then been constructed to cover the complete parameter range. The basis for these formulae is set out in detail in the report by Hunt *et al.* (1988a).

3.2.4.2. The unstable and stable boundary layers

Field experiments of diffusion from elevated sources in the convective boundary layer (Briggs, 1985) confirmed earlier laboratory and computational studies (Lamb, 1982) that the form of the vertical profiles of concentration is skewed and significantly non-Gaussian; this skewed concentration profile is modelled by ADMS 4. Near the ground, the skewed distribution is important for modelling processes such as wet or dry deposition. It is also very important for evaluating maximum ground-level concentrations from elevated releases, since ignoring the non-Gaussian profile can lead to under-estimates of ground-level concentration from elevated sources.

⁷ Caughey, S.J. and Palmer, S.G., 1979: Some aspects of turbulence structure through the depth of the convective boundary layer. In Quart. J.R. Met. Soc., 105, pp. 811-827

⁸ van Ulden, A.P. and Holtslag, A.A.M., 1985: Estimation of atmospheric boundary layer parameters for diffusion applications. In J. Clim. Appl. Met., 24, pp. 1194-1207.

⁹ Hunt, J.C.R., Stretch, D.D. and Britter, R.E., 1988: Length scales in stably stratified turbulent flows and their use in turbulence models. In proceedings IMA Conference on Stably Stratified Flow and Dense Gas Dispersion, pp. 285-322. Ed. J.S. Puttock, Clarendon Press.

All the turbulence in the stable boundary layer is mechanically generated, i.e. there is no generation of turbulence due to convective motions. Usually, the level of turbulence decreases with height, as the relative effects of stratification increase, although it can be enhanced by wave motions at the top of the boundary layer. The distribution of the concentration profile is a Gaussian plume with reflections at the ground, and at the top of the boundary layer, if there is a boundary layer top inversion (i.e. sharp increase in temperature with height). ADMS 4 assumes that an inversion is present if conditions are neutral or convective, or if the meteorological pre-processor predicts an inversion.

In neutral conditions, the part of the plume that does not have sufficient momentum or buoyancy to penetrate the top of the boundary layer is effectively confined within the boundary layer, because material reaching the top of the layer is reflected downwards. Sufficiently far from the source, after parts of the plume have been reflected at the ground and at the top of the boundary layer, the vertical variation in concentration of the pollutant is so small as to be negligible. This is assumed to occur at the downwind distance where $\sigma_z = 1.5 h$. Downwind of this point, the plume is considered to grow horizontally as a vertical wedge extending from 0 to h so the variation with height, z , is ignored.

3.2.4.3. Low wind speed and calm conditions

At low mean wind speeds, the direction of the wind becomes more variable. In very unstable conditions this can arise, even when the geostrophic wind is well defined, because the turbulent fluctuations in the flow are large or comparable with the mean wind. In stable conditions, when the geostrophic wind is very small, both the mean and turbulent wind can be very small and below the lower limit of the measuring device. More usually, the measured wind at the surface is very light either with variable direction or with a consistent direction if the wind is being forced by thermal gradients or topography. The approach used in ADMS 4 for calm conditions is to calculate the concentration as a weighted average of a normal 'Gaussian' type plume (C_g) and a radially symmetric plume (C_r), where the weighting depends on the wind speed at a height of 10m (U_{10}).

3.2.5. Effects of buildings

3.2.5.1. Introduction

Close to a source when the plume spread is smaller than a representative building dimension the presence of the building can have a major impact on the transport of the plume, its spread due to changes in turbulence and hence the surface concentration. In particular, plumes affected by the building wake may be brought down towards the surface increasing surface concentrations near to the building. The ADMS 4 building module takes account of these effects and is described in the next section.

3.2.5.2. ADMS 4 Building Module

The building effects module is used to calculate the dispersion of pollution from sources near large structures. The building effects module has the following features:

- Up to 25 cuboidal or cylindrical buildings are defined by the user in terms of their height, length, width and orientation (latter two parameters are disregarded for cylindrical buildings). A main building is defined for each source. Then, for each wind direction the buildings are reduced to a single cuboidal effective wind-aligned building, whose height is a function of the height of the main building.
- The disturbed flow field consists of a re-circulating flow region or cavity in the lee of the building, with a diminishing turbulent wake downwind.
- Concentrations within the well-mixed re-circulating flow region are uniform and based upon the fraction of the release that is entrained.
- The concentration at a point further downwind is the sum of two contributions: a ground-level plume from the re-circulating flow region and an elevated plume from the unentrained remainder. The turbulent wake reduces plume height and increases turbulent spread.
- The concentration and deposition are set to zero within the user-defined buildings.

The building effects module interacts with the rest of ADMS 4, using the underlying concentration profiles, but with modified plume height and plume spread. The stages in the analysis of building effects are illustrated in Figure 3.6, while Figure 3.7 shows how a complex layout of buildings is treated.

One limitation of the building module is that it is based on experiments in which there was one dominant site building and several smaller surrounding buildings less important for dispersion.

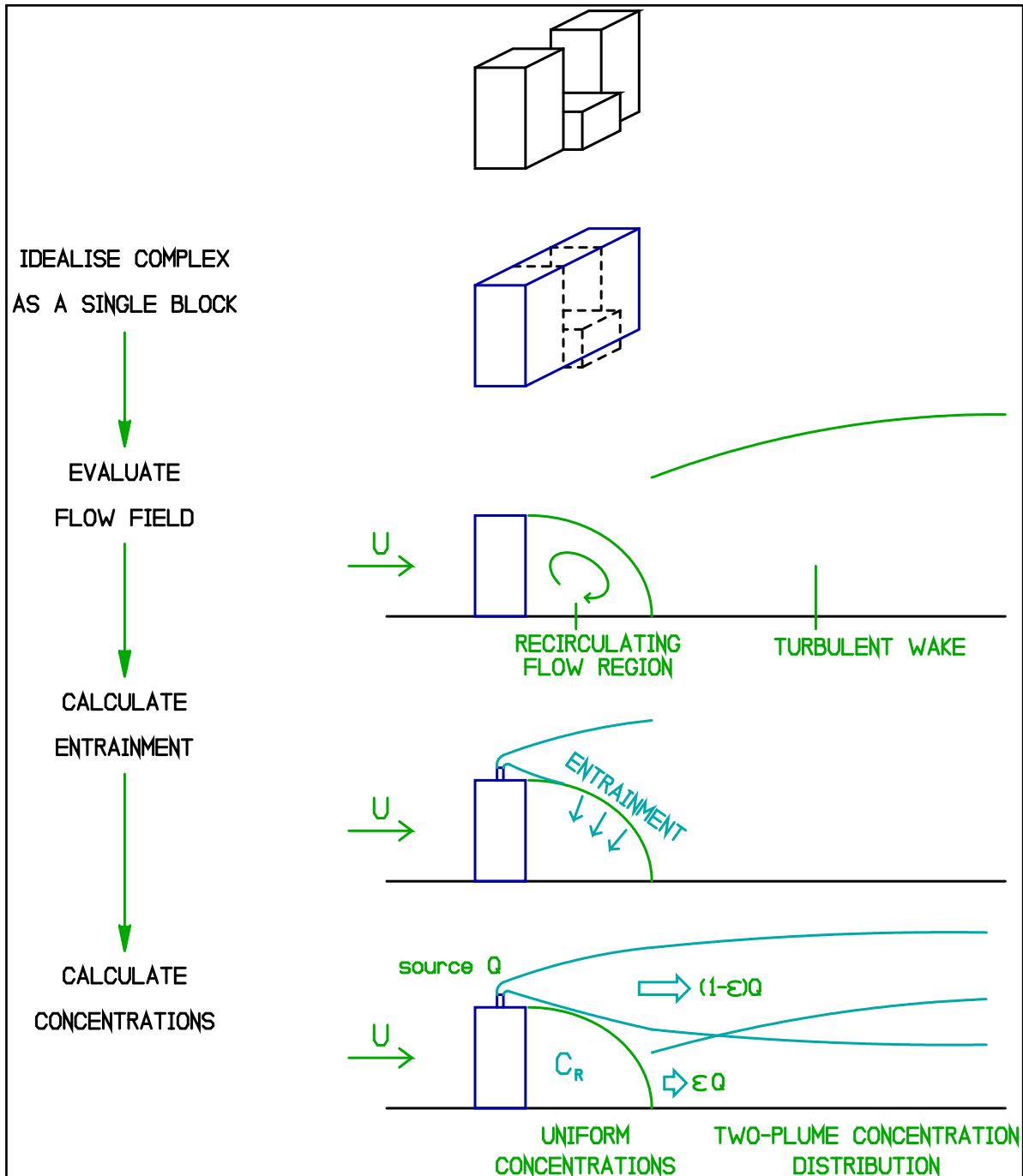


Figure 3.6: Stages in the analysis of building effects

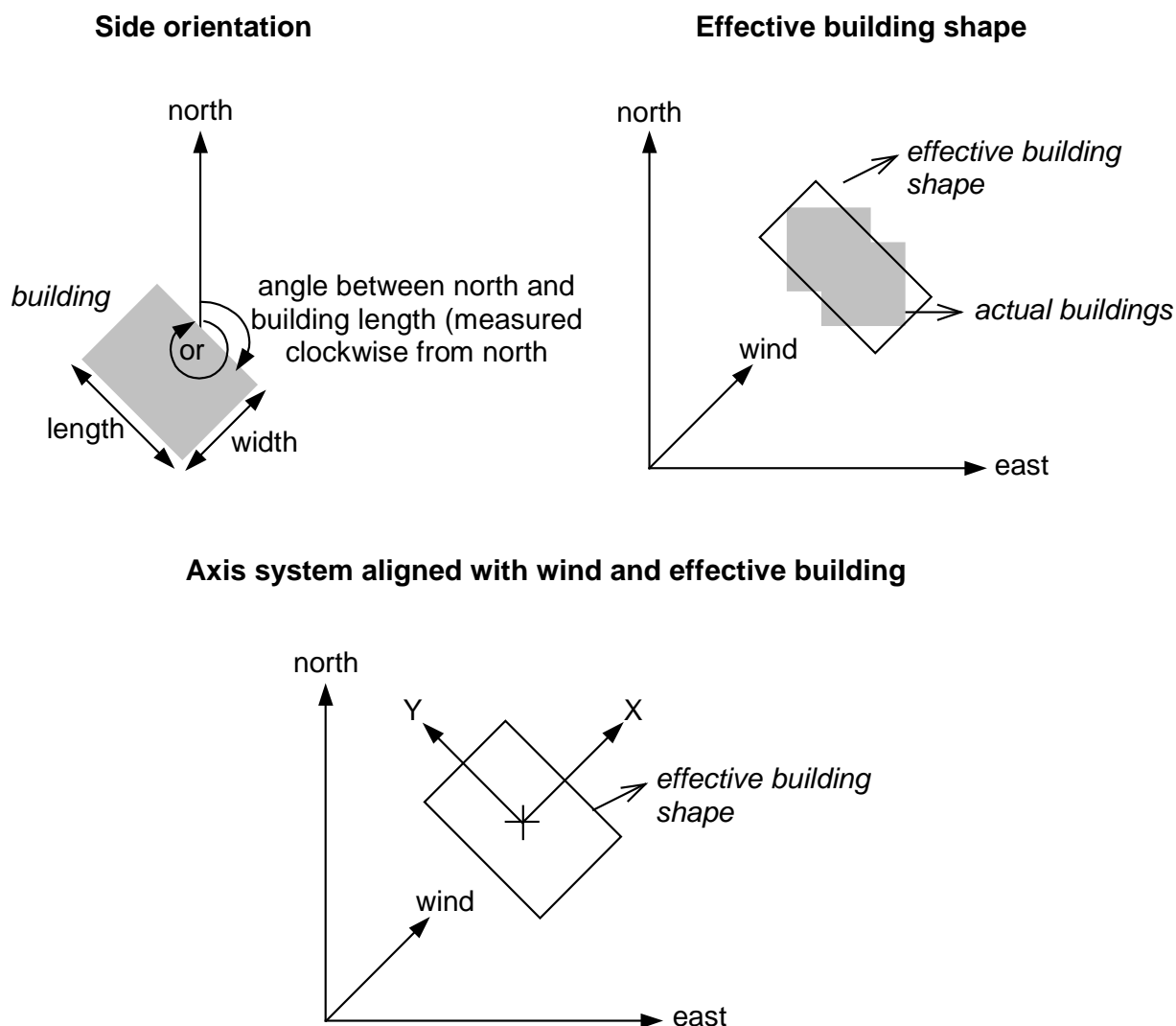


Figure 3.7: Building effects module definitions

3.2.6. Spatial variation in surface effects, surface elevation and surface roughness

3.2.6.1. Introduction

Over flat terrain the surface properties most relevant to the structure of the atmospheric boundary layer and, hence, dispersion are the surface roughness, surface wetness (described in ADMS 4 by the modified Priestley-Taylor parameter) and the surface albedo.

Surface roughness is an important parameter used to determine the impact of the surface features: buildings, trees, bushes etc., on the mean wind speed and the turbulence near to the surface. A high surface roughness (for example, trees or buildings) causes significant drag, thereby reducing the wind speed near the ground, generating high levels of turbulence and mixing and, hence, plume dilution. A low surface roughness (for example, a smooth water surface) causes little drag so low level (height) winds are generally faster than over a rough surface, leading to less turbulence and as a result less mixing of a plume.

Surface wetness refers to the amount of water on the surface or the amount of moisture in vegetation etc. This is important in determining how much heat from the sun is used for evaporation and how much, therefore, is not available for heating the surface and, hence, generating turbulence. If the surface wetness is high, a significant proportion of heat from the sun is used for evaporation so less heat is available for turbulence and mixing.

The surface albedo (reflectivity) is the fraction of incident radiation from the sun which is reflected by the surface. It is therefore also important in determining how much heat from the sun is available to heat the surface.

In ADMS 4 there is no allowance for spatial changes in surface wetness and surface albedo (although these are accounted for in the version of ADMS 4 developed to simulate urban heat islands¹⁰). However, effects of spatial changes in surface roughness and also changes in terrain elevation may be considered using the ADMS 4 complex terrain model FLOWSTAR as described in the next section.

3.2.6.2. Changes in surface elevation in ADMS 4

The complex terrain module applies a 3-dimensional flow and turbulence field to the dispersion modelling calculations. When variable terrain height is modelled, there are two possible flow field solutions. The flow field solution used depends on the meteorological conditions. The critical parameter for determining the flow field solution is the Froude number Fr , which is defined to be

$$(3.1) \quad Fr = \frac{U(h_{\max})}{N(h_{\max}) \times (h_{\max} - \bar{h})}$$

where h_{\max} is the height of the highest hill, \bar{h} is the mean height over the terrain, U is the flat terrain wind velocity value and N is the buoyancy frequency. The critical Froude number is unity.

At Froude numbers less than 1 the FLOWSTAR solution is used. At Froude numbers greater than or equal to 1 the solution is a weighted sum of the FLOWSTAR solution and a very stable flow solution that allows for plume impaction. Both the FLOWSTAR and stable solutions are described in more detail below.

When modelling the impact of spatially varying surface roughness in the absence of terrain only the FLOWSTAR solution is used by ADMS 4, the stable flow solution is never used.

Table 3.2 below summarises the Froude-number-dependent model behaviour.

Table 3.2: Summary of model behaviour when running the complex terrain option

Complex terrain modelling option	$Fr < 1$	$Fr \geq 1$
Variable terrain height, with or without variable surface roughness	Very stable flow solution (assuming a constant roughness value), weighted with the FLOWSTAR solution in the limit as $Fr \rightarrow 1$	FLOWSTAR solution
Variable surface roughness only	FLOWSTAR solution	FLOWSTAR solution

¹⁰ <http://www.lucid-project.org.uk/>

3.2.6.3. (i) FLOWSTAR

When $Fr > 1$, the flow field and turbulence values used in the dispersion modelling calculations are those output from the FLOWSTAR model. FLOWSTAR models air flow and dispersion over hills with roughness changes, including the effects of stratification. The model is described in some detail in Carruthers *et al.* (1988)¹¹ while the basis of the theory is presented in Hunt *et al.* (1988)^{12,13} and Hunt (1985)¹⁴.

The airflow model uses linearised analytical solutions of the momentum and continuity equations, and includes the effects of stratification on the flow. The hills modelled should have moderate slopes (say less than 1 in 3) but the model is useful even when this criterion is not met. The terrain height is specified at up to 16,500 points which are interpolated by the model onto a regular grid of up to 128×128 points. The best results are achieved if the points at which the elevation and/or surface roughness is specified are spaced regularly. The effects of roughness and terrain can be modelled separately. The airflow model has been extensively tested with laboratory and field data. Figure 3.8 shows a contour plot overlaid on complex terrain.

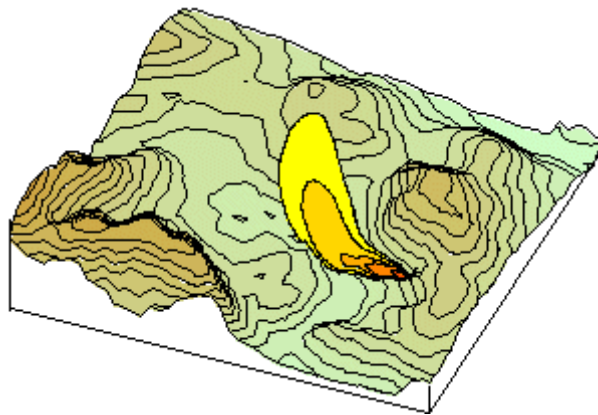


Figure 3.8: Example of the dispersion of a plume over complex terrain.

3.2.6.4. (ii) Very stable flow solution (variable terrain height, $Fr < 1$)

When very stable flows approach an isolated hill, the flow may divide into two regimes, with the air above a certain height h_c (the *dividing surface*) flowing over the hill in a terrain-following manner and the air below the dividing surface flowing around the hill in a 2-dimensional flow. This is shown in Figure 3.9.

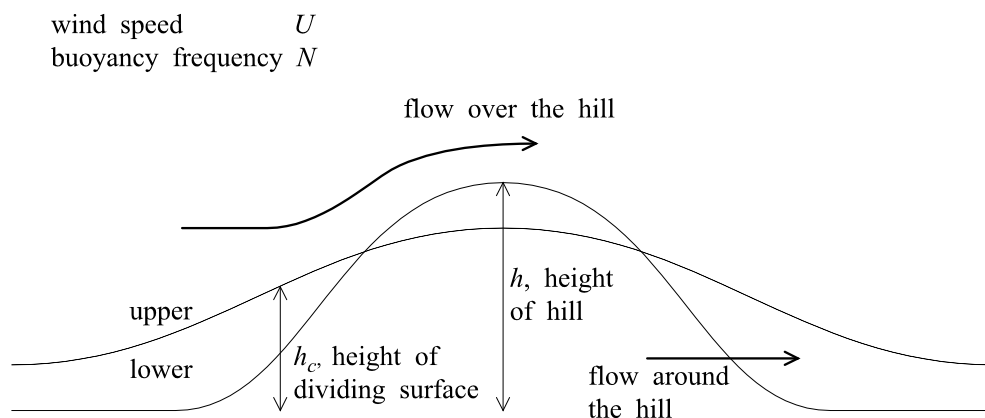


Figure 3.9: Effect of a hill on the flow in very stable conditions

¹¹ Carruthers, D.J. Hunt, J.C.R. and Weng, W.-S., 1988: A computer model of stratified turbulent airflow over hills – FLOWSTAR I. In Computer Techniques in Environmental Studies, pp. 481-492, Ed. P. Zanetti, Springer-Verlag

¹² Hunt, J.C.R., Leibovich, S. and Richards, K.J., 1988: Turbulent shear flow over hills. In Quart. J. R. Met. Soc., 114, pp. 1435-1470

¹³ Hunt, J.C.R., Richards, K.J. and Brighton, P.W.M., 1988: Stably stratified flow over low hills. Quart. J. R. Met. Soc., 114, pp. 859-886

¹⁴ Hunt, J.C.R., 1985: Turbulent diffusion from sources in complex flows. In Ann. Rev. Fluid Mech., 17, pp. 447-458

The height of the dividing surface is defined by an energy balance equation, which locates the lowest height at which the kinetic energy of an air parcel in the flow approaching the hill is equal to the potential energy attained by elevating an equivalent fluid parcel from this height to the top of the hill:

$$(3.2) \quad \frac{1}{2} U^2(h_c) = \int_{h_c}^{h_{\max}} N^2(z) \times (h_{\max} - z) dz.$$

The flow below the dividing surface is a 2-dimensional potential flow, with the exception of flow upstream of the hill in a thin layer close to the terrain. Above the dividing surface, the flow is terrain-following with the exception of flows where the Froude number approaches unity from below. In this parameter range, a weighted average of the FLOWSTAR and terrain-following flow fields is used.

3.2.6.5. Variable surface roughness

The FLOWSTAR model used within ADMS 4 includes the ability to calculate the effect on the flow and turbulence fields of spatially varying surface roughness. The model can be used for large changes in surface roughness, with an order of magnitude variation in surface roughness allowable with the approximations in the calculations. The surface roughness can be specified at up to 16,500 points. If variable surface roughness is being used in conjunction with variable terrain height then the terrain heights and surface roughness values should be specified over the same area but need not be at the same points.

A simple way of modelling a spatial variation in surface roughness in ADMS 4 is to specify a different, constant, surface roughness at the site at which the meteorological measurements are made from the constant value at the dispersion (source) site.

In addition, the constant values of surface roughness at the meteorological and dispersion sites may be varied hourly via the ADMS 4 *.met* input file.

3.2.7. Wet deposition

The uptake of gases in clouds and rain and their subsequent deposition at the ground in solution, is a complex kinetic process that must be simplified for inclusion in practical models of wet deposition. The wet deposition module in ADMS 4 allows users not only to model the amount of pollutant being deposited at the ground in solution, but also the corresponding depletion of the plume strength, as indicated in Figure 3.10.

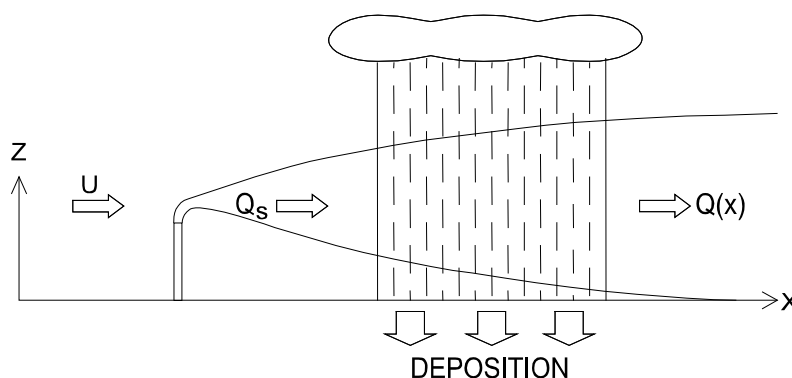


Figure 3.10: Wet deposition model

The type of wet deposition that can be modelled in ADMS 4 depends on the source and pollutant type. There are three different models as follows:

- wet deposition of all pollutants from all source types can be modelled using a washout coefficient;
- wet deposition of SO₂ and CO₂ from all source types can be calculated using a pH-limited washout coefficient; and
- wet deposition of SO₂ and HCl from point sources can be modelled using the falling drop method.

Using a washout coefficient to model wet deposition is a significant simplification of the processes involved, but the predicted values are relatively accurate when the uptake of pollutants is irreversible. However, when a pollutant is subject to significant 'outgassing' (i.e. where the pollutant passes back from the droplet to the atmosphere due to relatively low air concentrations of the pollutant in the local vicinity), wet deposition predicted by the washout coefficient methodology may be significantly over-estimated. In such cases, where possible, it is advisable to use the falling drop method.

3.2.7.1. Washout coefficient method

When wet deposition is modelled through use of a *washout coefficient* Λ , the amount of material incorporated into any falling rain or precipitation is ΛC per unit area per unit vertical distance per unit time, where C is the local airborne concentration.

Assuming irreversible uptake, the total wet deposition rate per unit horizontal area per unit time (F_{wet}) is found by integrating through a vertical column of air:

$$(3.3) \quad F_{wet} = \int_0^{\infty} \Lambda C dz$$

The pollutant remaining in the plume, or plume strength, Q , therefore decreases with downwind distance.

The following simplifications are made:

- uptake of pollutants is irreversible; uptake in rain does not lead to a *redistribution* of material in the plume;
- all plume material lies in or below rain cloud; furthermore no distinction is made between in-cloud scavenging (*rainout*) or below-cloud scavenging (*washout*);
- solution in raindrops does not lead to saturation except for SO₂ and CO₂ where a pH-limited value is calculated; and
- the rainfall rate is constant and uniform over the area of calculation.

The washout coefficient Λ is dependent on a large number of parameters, including the nature of the pollutant, rainfall rate, droplet size distribution and the pollutant concentrations in the air and in the raindrops. A value for Λ may be entered as a user-specified, constant value or as a function of the precipitation rate: $\Lambda = AP^B$, where A and B are user-specified constants and P is the precipitation rate in mm/hr.

3.2.7.2. pH-limited method

For some species, the amount of material removed by wet deposition may be limited by its solubility in rainwater and the pH of the raindrops. For acidic species such as SO₂, this has a significant effect near the source, where high gaseous concentrations and the low pH of the raindrops limit the uptake of material into the raindrops. In ADMS 4, a set of solubility coefficients and a chemical reaction scheme are used to calculate acidity within the raindrops and thus the effective solubility of pollutants for SO₂ and CO₂. An effective washout coefficient (Λ_{eff}) is then determined by estimating the amount of material absorbed by the raindrops. If this pH-limited washout coefficient Λ_{eff} is less than the value of Λ specified in the interface, the wet deposition flux is assumed to be pH-limited and Λ_{eff} is used. Otherwise the usual washout coefficient Λ is used.

3.2.7.3. Falling drop method

After passing through the plume centreline, raindrops often fall through some relatively 'clean' air before reaching the ground. If the pollutant in question undergoes outgassing (i.e. where the concentration gradient between the drop and the air causes the pollutant to pass back into gaseous form), the pollutant concentration within the drop at the ground will be reduced relative to the maximum concentration that was achieved at, or in fact often just below, the plume centreline. The acid gas of most interest that undergoes significant outgassing before the drop reaches the ground is SO₂.

Figure 3.11 gives an example of the change in concentration of a pollutant in a raindrop as it travels vertically through the plume when there is significant outgassing.

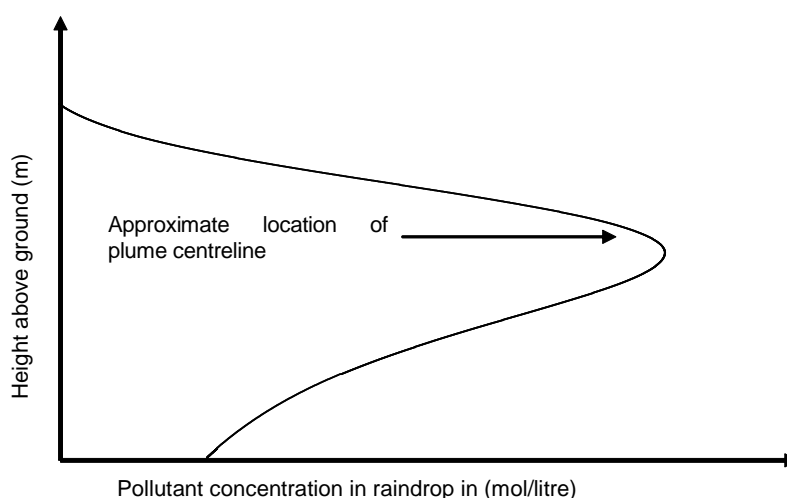


Figure 3.11: Pollutant concentration within a raindrop falling vertically through the plume, when significant outgassing occurs below the plume centreline

The key components of this process may be examined by using a model of a rain drop falling vertically through a plume of gaseous pollutant, with the assumption of kinetically controlled gas uptake into the drop and rapid solution equilibration within the drop. This model is applied to SO₂ and HCl in ADMS 4. The SO₂ and HCl are considered as a coupled system with the additional assumptions of electro-neutrality of the 'washed out' species and the initial pH of the drop is determined by dissolved CO₂ and other species in the 'clean air' entering the top of the plume.

3.2.8. Dry deposition

Dry deposition modifies the airborne concentration in two ways:

1. a reduction in plume strength (integrated flux of pollutant) Q with distance as material is removed from the plume at the surface, and
2. adjustment of the vertical profile because removal occurs of material at the surface. This is illustrated in Figure 3.12.

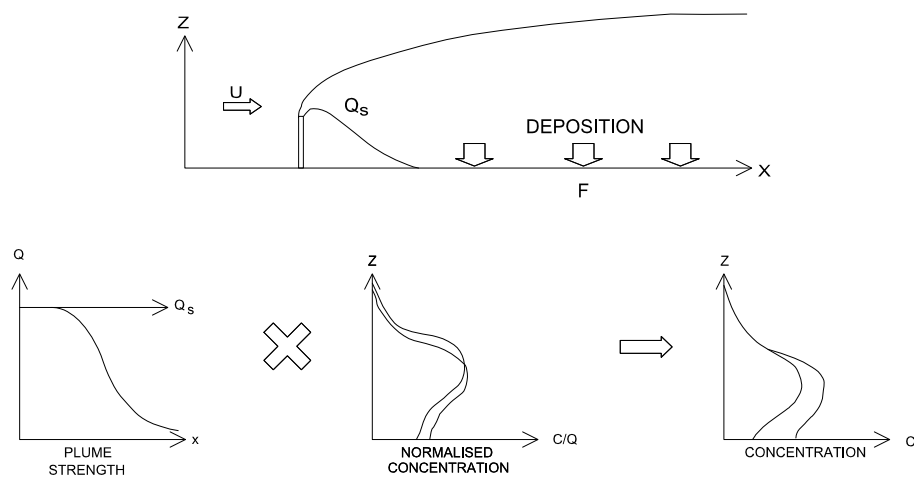


Figure 3.12: Dry deposition modifies the vertical profile of concentration; profiles of concentration and normalised concentration are shown

The rate of dry deposition is assumed to be proportional to the near-surface concentration, i.e.

$$(3.4) \quad F_{dry} = v_d C(x, y, 0)$$

where F_{dry} is the rate of dry deposition per unit area per unit time, $C(x, y, 0)$ is the predicted airborne concentration at ground level and v_d is the deposition velocity. This velocity contains a diffusive part (v'_d) commonly referred to as the deposition velocity itself, and an element due to the gravitational settling (v_s), the terminal velocity of a particle. They are related to the overall deposition velocity v_d by the equation:

$$(3.5) \quad v_d = \frac{v_s}{1 - \exp(-v_s / v'_d)}$$

When v_s is zero, $v_d = v'_d$ and when v'_d is zero $v_d = v_s$. These limits can be derived from equation (3.5), as well as making sense physically. One or both of v'_d and v_s may be known by the user and input directly to the model, or they can be estimated by the model on the basis of either gas type or particle size and density.

If v_d' is estimated by the model it is expressed as the reciprocal of the sum of three resistances:

$$(3.6) \quad \frac{1}{v_d'} = r_a + r_b + r_s$$

where r_a is the aerodynamic resistance, r_b is the sub-layer resistance and r_s the surface layer resistance, which can either be calculated by the model or input directly by the user.

These resistances depend on the pollutant species, nature of the surface and the wind speed. For particles $r_s = 0$, while for gases r_s is either input by the user or estimated by the model as 30 s/m for reactive gases (e.g. SO₂), 1000 s/m for unreactive gases (e.g. CO₂) and is infinite for inert gases. The terminal velocity v_s is always zero for gaseous pollutants, while for particles it is estimated from the properties of the particle.

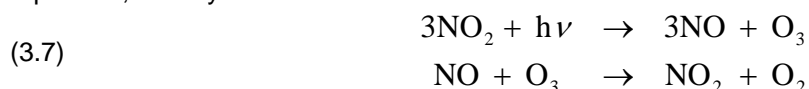
Spatially varying values of the deposition velocity or, for gases, the surface resistance can be entered in ADMS 4. If these data are supplied, the deposition at each point is calculated using the local deposition velocity and the plume depletion calculated using a weighted average of values across the plume.

Deposition velocity or, for gases, the surface resistance may be entered as seasonally or hourly varying values in ADMS 4.

3.2.9. Chemistry

The chemical scheme in ADMS 4 uses the reaction rates from the Generic Reaction Set of equations (GRS) (Azzi and Johnson, 1992; Venkatram *et al.*, 1994), a semi-empirical photo-chemical model which reduces the complicated series of reactions involving NO (nitric oxide), NO₂ (nitrogen dioxide), O₃ (ozone) and many hydrocarbons to just seven.

In ADMS 4, hydrocarbons are not included in the chemical scheme, which then reduces to just two equations, namely



where $h\nu$ is ultra-violet radiation. Equations (3.7) represent exact chemical reactions, which happen very quickly.

The model uses background concentrations of ozone, NO_x (nitrogen oxides) and NO₂. These values should be rural background values, i.e. values that do not take into account the effect of the sources being modelled. During the day, these background values will be adjusted in order to ensure that they are in chemical equilibrium.

At each receptor the NO_x may have originated from more than one source. A weighted mean age of pollutant is calculated for each downwind receptor. The minimum non-zero age is the value used in the chemistry scheme to calculate concentrations of NO_x and ozone.

3.2.10. Plume visibility

The ADMS 4 plume visibility module calculates the total water in the plume. This may be of particular relevance to the Mongstad study as it could provide input to an aqueous phase amine chemistry model and a cloud physics module to examine the impact of amines on drop development.

The plume visibility module uses the initial water content of the release and the humidity of the ambient air to determine whether the plume will be visible at each downstream distance. In addition, when plume visibility is chosen as a model option, the effect of water on the plume density and the heating and cooling effects of condensation and evaporation are taken into account in the plume rise module.

As input, the plume visibility module requires:

- surface humidity (as specific humidity q_0 or relative humidity RH_0) to be entered as a meteorological variable;
- surface temperature to be entered as a meteorological variable, since moisture properties of the atmosphere depend strongly on temperature; and
- the initial mixing ratio of the plume in kg/kg (i.e. the mass of water vapour per unit mass of dry release at the source).

Output includes the length and maximum liquid water content of each visible plume and, for long-term calculations, the frequency of visible plumes and visible plume 'groundings'. The liquid and gaseous water content of the plume at each point could provide input to a cloud physics module to examine the impact of amines on drop development.

3.3. Inputs and outputs of ADMS 4 relevant to this study

The basic ADMS 4 dispersion model calculates long-term and short-term concentrations and deposition fluxes from continuous point, jet (directional release), line, area and volume sources. Long-term output can be in terms of averages, rolling averages, percentiles or number of exceedences for direct comparison with air quality objectives and limits. Sources can be time varying on an hourly, period or seasonal basis.

The concentration can be calculated at any specified location and the resulting concentration can then be presented at each hour for that location as a time series or it can be presented as a contour plot covering the domain of interest.

The output grid can be specified in a Cartesian or Polar coordinate system. The grid spacing can be regular or variable. Results at up to 101 x 101 grid points can be output in a single model run. This means for a regular Cartesian grid, the model can output over an area of 1km x 1km at a resolution of 10m or a resolution of 50m over an area of 5km x 5km.

Links and extensions of ADMS 4 allow for visualisation of model inputs and results in the GIS packages ArcGIS and MapInfo, the contour-plotting package Surfer and the ADMS 4 Mapper. Examples of visualisation of inputs and outputs using the ADMS 4 Mapper are shown in Figure 3.13 and Figure 3.14.

Modelling parameters are input to ADMS 4 using a graphical user interface. The input file created by the model interface is saved with the extension *.apl*. There are a number of additional model input files that may be required by the model in order to run. These are most often comma-delimited text files in a simple format. The most common example of a file used by the model is the *.met* file, which contains the meteorological data required by the ADMS 4 met pre-processor. Other model files include the *.bgd* file that contains hourly values of background concentrations, the *.ter* and *.ruf* files that contain variable terrain height and surface roughness values respectively, and the *.asp* file that contains a list of additional output points.

Some model options are not available through the interface and require use of an auxiliary input file (*.aai* file). Options that required an *aai* file that are relevant to this project are:

- Spatially and temporally varying dry and wet deposition parameters;
- Falling drop scheme for wet deposition;
- Temperature and humidity output for point sources;
- Switch off stack downwash for certain sources; and
- Specify multiple output heights for gridded output.

A variety of output data is produced by ADMS 4 according to the run configuration. The majority of the ADMS 4 output files are in a text-based format. These can be opened using ADMS 4 utilities for line plotting and visualisation in GIS packages or viewed directly with a text editor such as Notepad, for example.

The main output files are *.plt* and *.pst* files for output at specified points for long-term results (annual averages and percentiles) and short-term results (hour-by-hour concentrations) respectively. Gridded output that can be used for contour plotting are output in *.glt* and *.gst* files for long-term and short-term results respectively.

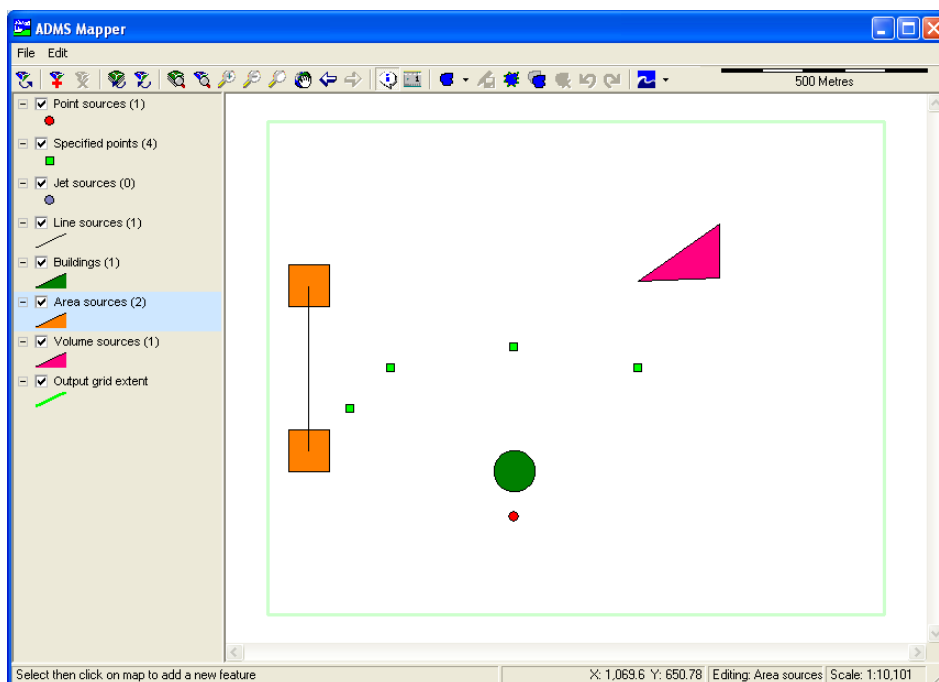


Figure 3.13: Model inputs visualised in the ADMS 4 Mapper

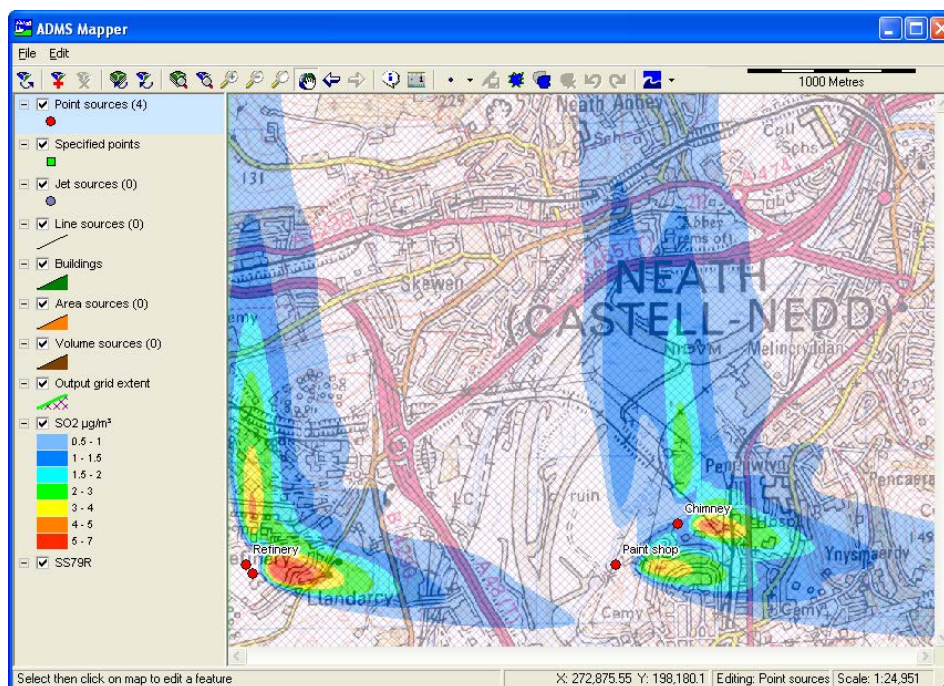


Figure 3.14: Contour plot using Surfer visualised in the ADMS 4 Mapper

4. Potential for development of ADMS 4 under H&ETQPAmine2

In this section we discuss the potential for ADMS 4 to consider processes specifically relevant to the Mongstad plant which are either not typically considered in dispersion models or for which there has been insufficient knowledge. These are as follows: potential for chemistry model development (i.e. reactions of amines and formation of nitrosamines and nitramines); potential for particle formation; influence of particle formation on droplet formation; and estimation of concentrations in local/regional fresh water bodies.

4.1. Potential for gas phase chemistry model development to include amine chemistry

The current version of ADMS 4 includes a generic chemistry scheme including photochemistry as described in Section 3.2.9 above. Different chemistry schemes may be introduced into the model, for example there is a version of the ADMS-Urban model for urban air quality which includes the CBM-IV mechanism. The ADMS 4 chemical scheme methodology is based on the approach of assuming that the 'chemistry' takes part 'in-plume' and that is impacted on by species mixed into the plume from the 'background' outside the plume but the 'background' is constant for each hour as specified by the user. ADMS-Urban has a regional chemistry model, however ADMS-Urban is not suited to the current study as it lacks some of the key in-plume processes, e.g. the falling drop method for wet deposition.

In conclusion, ADMS 4 may be readily adapted to include a gas phase chemistry model developed specifically for amine chemistry.

4.2. Potential for aqueous phase chemistry model development

The condensed plume visibility model within ADMS 4 provides a framework for the inclusion of an aqueous phase chemistry model. This could include the generation of aminium salts by displacement of ammonium.

4.3. Potential for particle development

Particle formation would be considered by gas phase and aqueous phase chemistry models, for example by the reaction of the gaseous amine with gaseous nitric and sulphuric acid to form aminium nitrate and sulphate particles, and evaporation of aminium sulphates formed in aqueous phase.

4.4. Influence of particle development on droplet formation

In the Task 3 report¹⁵ mechanisms are discussed by which amines may enhance early development of cloud droplets leading to rain, although this effect is not quantified. The plume visibility module in ADMS 4 calculates the moisture content of the dispersing plume. This could be used with a suitable cloud physics model to quantify the process of droplet formation. In high humidity/saturated conditions the enhanced deposition of amines relative to 'dry deposition', due to surface deposition of droplets, could also be modelled.

4.5. Deposition

The three different models for taking account of wet deposition in ADMS 4, namely washout coefficient method, pH-limited washout coefficient method and falling drop method, have been applied mainly to acid gases (for example SO₂ and, HCl). These models may be customised and developed for basic species including amines and ammonia. Similarly, the resistance-based dry deposition velocity formulation may be applied to amines and ammonia.

¹⁵ Bråten, H. B., Bukan, A. J., Bache-Andreassen, L., Solimannejad, M. & Nielsen, C. J., 2009: CO₂ and amines: Final report on a theoretical study on the atmospheric degradation of selected amines, NILU Ref: OR 77/2008

4.6. Estimation of concentrations in local/regional fresh water bodies

As it stands, the model can calculate the rate of deposition over specific areas, including freshwater bodies. The concentrations of species in the freshwater body will depend on water volume and mixing rates, the chemical processes within the water and water exchange rates. It would be straightforward to combine ADMS 4 deposition output with any available models that take account of these processes.

Examples of models that can take freshwater body processes into account are:

- Those used in the Norwegian lakes project:
http://www.aslo.org/lo/toc/vol_54/issue_6_part_2/2520.html
- MAGIC (Model of Acidification of Groundwater In Catchments):
<http://www.macaulay.ac.uk/recover/magic.htm>

4.7. Limitations under different dispersion conditions

The range of features of ADMS 4 and the potential for development have been presented in the previous sections. These show that ADMS 4 appears to fit key criteria both for the model to be used as it is and for it to be adapted to reflect the unique aspects of dispersion from the Mongstad plant, in particular the releases of amines. In considering a model it is important to present key features and advantages but also to be informed of potential limitations, and some discussion of that is presented at this point.

At this stage it is not possible to provide insight into model performance for the modifications which could be made (e.g. amine chemistry) so we will focus on the performance of the model for predicting dispersion and deposition of the primary pollutants (i.e. those which do not undergo chemical transformation). See also Section 7 on model validation.

Generally, the longer the averaging time the greater the accuracy of a model prediction. The most challenging conditions are low wind speed conditions where short-term peaks in concentration are required. In common with all other models ADMS 4 has lower accuracy in such conditions because the mean flow and turbulence may not be well specified. Other factors generally relevant to model accuracy and to ADMS 4 in particular are the following:

- The wind speed and turbulence levels derived using the meteorological algorithms have some uncertainty associated with them, as discussed above. Underestimation of wind speed leads to overestimates of concentration levels and vice versa.
- The wind direction at each of the sources may be different from that at the meteorological observing site; differences of typically 10 degrees (or more) being quite possible for the lowest wind speeds. This uncertainty will impact mainly on the location of the maximum short-term average concentrations modelled with little influence on the level of concentration calculated by the model. This uncertainty may be overcome by using local wind measurements.
- The dispersion model algorithms themselves, which assume that the plume disperses in a Gaussian type fashion and which relate the mixing in the plume to the ambient turbulence, necessarily have some uncertainty associated with them.
- Because of the random nature of atmospheric turbulence, there is always an inherent uncertainty in atmospheric dispersion processes (i.e. in the same meteorological conditions, a series of plumes released at the same spot will not disperse in an identical fashion). This effect is most relevant for time scales comparable with the turbulence time scales; the approximate size of the turbulent eddies divided by typical air speeds associated with them, which is typically measured in seconds or minutes. This effect is small for hourly and longer averages and has little or no impact for larger averaging times.

- The ADMS 4 model assumes that the meteorology for each site is steady in each hour. Thus the impact of rapid changes in meteorology within such hour periods cannot be accounted for. In addition, if concentrations of the emitted species or their degradation products are of relevance many hours after their release (i.e. well downstream), then there will be some loss of accuracy in the model predictions if there are significant changes in the meteorological conditions over the period. This is why for large scales (e.g. hundreds of kilometres) ADMS 4 is not suitable and fully time-dependent models are required.

5. Available model documentation

The model is accompanied by documentation describing the algorithms as well as practical documentation for users on getting started and using all the features of ADMS 4. The documentation comprises:

5.1. Technical Specification

A complete Technical Specification for ADMS 4 is available from the CERC web site¹⁶. The Specification comprises a set of papers, each of which describes a module or feature of ADMS 4. The papers are listed in Table 5.1.

Table 5.1: List of Technical Specification papers

Reference	Title
P04/05D/09	Standard properties in ADMS 4
P05/01P/09	The Meteorological input module
P07/01N/09	Output specification for mean concentration and deposition fluxes
P07/04E/09	Calculation of long term statistics
P07/05E/09	Calculation of exceedences using the Fluctuations module
P09/01U/09	Boundary-layer structure specification
P10/01V/09 P12/01V/09	Plume/puff spread and mean concentration module specifications
P10/02A/09	Stack downwash
P11/02O/09	Plume rise model specification
P13/01E/92	The Fluctuations Module
P13/03C/96	Averaging time and fluctuations in ADMS versions 1 and 2
P13/07E/09	Concentration fluctuations in ADMS 3, including fluctuations from anisotropic and multiple sources
P14/01O/09	Complex terrain module
P15/01H/09	Coastline module, the thermal internal boundary layer
P16/01S/09	Modelling of building effects in ADMS
P17/06B/95	Sources for radioactive decay data
P17/11C/09	Modelling radioactive decay
P17/12D/09	Modelling wet deposition
P17/13F/09	Modelling dry deposition
P18/02H/09	Simple chemistry
P20/01L/09	Calculation of γ -ray dose rate from airborne and deposited activity
P24/01H/09	Multiple sources, species and particle sizes
P25/03H/09	Implementation of area, volume and line sources
P26/01F/09	Plume visibility
P26/02A/09	Calculation of plume temperature and humidity
P29/01B/09	Calculating odour levels

Each paper describes the approach taken, the algorithms and, where relevant, the references are listed. The Technical Specification papers are updated to reflect technical changes and new features in the model.

¹⁶ www.cerc.co.uk/environmental-software/model-documentation.html#technical

5.2. ADMS 4 User Guide

The ADMS 4 User Guide can be downloaded from the CERC web site¹⁷. It is also installed with the model, from which the User Guide can be automatically launched in pdf format. The User Guide covers:

- Installation of the model;
- Use of the model's graphical user interface;
- How to use each model option;
- How to use the in-built utilities e.g. plotting, terrain data file creation;
- Worked examples;
- A summary version of the Technical Specification;
- References; and
- Air Quality limits and guidelines.

The User Guide is updated for each model release and either reissued or, for small changes, an Errata document or other supplement is issued.

5.3. User Guides for auxiliary software

User Guides for the various ADMS 4 auxiliary software are also installed with the model. They describe installation and use of the links to three Geographical Information Systems (GIS): ArcGIS, MapInfo and ArcView. There is a User Guide for the Mapper that is installed free with ADMS 4 for entering, viewing and editing the geometry of sources, buildings and receptors and a Guide for the Sentinel Security (dongles) that usually accompany the software.

5.4. Training material

Training material for ADMS 4 covers the fundamentals of the boundary layer and atmospheric dispersion and step-by-step worked examples for most of the modules of ADMS 4. The training material is used during the courses that are held regularly at CERC's premises or as requested at the user's premises. It can also be sold to users not attending a course for independent study.

5.5. Validation documents

Validation documents are published on the CERC web site¹⁸. They describe the data sets used, the modelling approach taken and present the results of ADMS compared with the monitored data. The ADMS model files are available on request so that anyone may re-run the scenarios.

¹⁷ www.cerc.co.uk

¹⁸ www.cerc.co.uk/environmental-software/model-documentation.html#validation

6. Model coding procedures

All software code planned development or modifications to ADMS arising from requests or software issues are subject to a quality assurance plan that includes the following items:

- There is a set of documents to which developers are referred for guidelines on writing high quality code.
- Source management software is employed to control the entire development process; CERC uses MKS Source Integrity developed by Mortice Kern Systems Inc. This system tracks all changes made to a project, thus ensuring a complete audit trail. It also helps manage group development by guaranteeing that only one developer at a time may change any given code module.
- Where possible, code that carries out the same function is shared between applications using whatever technology is most appropriate.
- Development and changes to code are controlled by a documentation system of Change Requests, Technical Reports, Code Reviews and Inspection Summaries:
 - **Change Request:** Changes to code are planned with at least one other person and must be agreed and approved by the line manager before work can commence.
 - **Technical Report:** The developer writes a Technical Report describing the changes made including a listing of all code module revisions affected. There is a section for describing all testing carried out to validate the changes.
 - **Code Review:** A code review with at least one reviewer and sometimes with a moderator is carried out. Necessary and advised changes are made, the Technical Report revised and, if necessary, another review of the code is carried out.
 - **Inspection Summary:** An Inspection Summary is written after the code review recording major and minor issues, comments and further actions.
- Any testing data and files are stored with the reposts so that retesting is possible.
- The final version of the Technical Report is signed off. All these documents are stored in electronic and paper copies.
- A Change Request Log records the Change Requests started with dates of their completion and signing off.
- The Change Request Log allows for centralised tracking of all completed and signed off code changes, which is used as part of the process for building final versions of all components for a release of a product.
- Issues raised, either by customers or internally, are logged electronically. Changes to the code to resolve issues are thoroughly tested at the time the change is made.
- Before release of a new product version, the results from the new code are compared with results from an older code version for the example files supplied, standard validation cases and other model runs.
- The installation program and results from the example files are tested on a test machine. The test machine can be networked or operated as standalone machine. It uses Norton System Commander and Norton Ghost to produce clean installations of various operating systems for testing which currently include Windows XP, Vista and Windows 7.

6.1. Handling of issues and quality improvement

Bugs, issues and suggestions for improvement may arise from internal or external users or as part of the development and review process. All contact from users are recorded in the *Helpdesk log* (an MS Excel spreadsheet), each helpdesk contact with its own unique number. If after a developer has looked into a *Helpdesk* query and they consider there is a bug, issue or suggestion for improvement, this is recorded in the *Issues* spreadsheet, each matter with its own unique number. Associated files and documents used in the investigation of the matter are stored under the unique number. Matters arising from the development and review process would be entered directly into the *Issues* spreadsheet and would not appear in the *Helpdesk log*.

The *Helpdesk log* and *Issues* spreadsheet are both reviewed at the weekly meeting of developers so that any helpdesk matters that should be transferred to the *Issues* spreadsheet are transferred and to check whether any item needs urgent attention in the form of issuing advice, clarification or a software patch. At this point the cause of the matter arising is discussed and if it is due to a failure of the review or other internal process action is taken following the meeting. If necessary, similar code changes will be checked and the software development advice documents updated.

When a model release is planned, the *Issues* spreadsheet is the starting point for identifying the necessary and desirable model improvements. We involve users in shaping the development of new scientific or user features, holding consultations at the annual User Group Meetings. The feedback sheets and consultation responses from each User Group are analysed within a week of the meeting and matters taken up as helpdesk matters, entered in the *Issues* spreadsheet or not pursued further.

6.2. Experience transfer

Software development is carried out by staff who are appropriately trained by virtue of their qualifications, attendance at internal and external training courses and mentoring by senior colleagues. An annual review is the formal opportunity to track a member of staff's development and set appropriate targets for training, development and achievement. These matters can also be addressed between reviews and at the start of a new piece of work the member of staff's skills and training needs are considered. Staff are expected to develop from making straightforward changes as part of a pre-determined development plan to making more complex developments, contributing to the determination of the development plan and reviewing the work of others.

The standards to which we work and the processes used are documented, held centrally and explained to new developers. Holding centrally information not just on plans, inputs and outcomes but also the methodology is important in ensuring that knowledge is shared. As a company with staff with family responsibilities working flexible hours we continually pay attention to ensuring that every skill is held by more than one member of staff and hence skill and experience is transferred. The standards are reviewed regularly and updated as required.

7. ADMS Model Validation

CERC has participated in many evaluation and validation projects, being founding members of the Harmonisation initiative (www.harmo.org), hosting the 11th Conference in 2007 and hosting a dedicated workshop on model evaluation techniques. CERC co-ordinated the EU SMEDIS project to evaluate dense gas models scientifically and against field data¹⁹ and is leading the work package on model evaluation in the EU 7th Framework PASODOBLE project. Under PASODOBLE the current work on model evaluation will be reviewed and a toolkit for evaluation of local forecasting models developed. We also participate in the FAIRMODE initiative²⁰, (Forum for Air Quality Modelling in Europe). FAIRMODE is led by the European Environment Agency and aims to provide guidance on the use of air quality modelling, promote best practice in air quality modelling and assessment and to provide a central reference document for the application of models, with respect to the new EC directives on air quality (Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe).

7.1. Validation of ADMS

Validation of ADMS is routinely carried out and published. The aim of the validation is to assess the model's performance. As ADMS is a largely deterministic model, rather than largely empirical, validation encourages revisiting of scientific understanding, rather than simply making adjustments to fit the field data. The validation uses as many quality datasets as possible so that a wide range of model set-ups and meteorological conditions can be assessed. The validation data may be from field campaign data or wind tunnel data. When possible, the different modules (hills, buildings, etc.) are validated separately.

The validation usually makes use of the BOOT package which is used in model validation to make statistical comparisons of model results against observed data. BOOT is part of the Model Validation Kit that was developed under the series of conferences on Harmonisation Within Dispersion Modelling for Regulatory Purposes²¹. Results are presented numerically and graphically (scatter plots, quantile-quantile plots).

Figures 7.1 to 7.4 show example validation plots. Figure 7.1 shows an example scatter plot. In a scatter plot the modelled data at each time period is plotted against the observed data at the same time period. Figure 7.2 shows an example quantile-quantile plot. Like a scatter plot a quantile-quantile plot plots the modelled against the observed data. However, in a quantile-quantile plot the data are unpaired in time. The modelled and observed data are sorted independently and the new pairs of data plotted. Quantile-quantile plots show the overall model tendencies and the ability to model high and low values. They are useful when assessing a model's ability to predict concentrations for comparison with air quality standards that are usually based on annual statistics, rather than predicting accurate short-term concentrations under specific meteorological conditions.

Figure 7.3 shows an example box-and-whisker plot. A box-and-whisker plot shows the spread of ratio of modelled to observed data and can be used for comparing several models under different conditions. Figure 7.4 shows examples of a polar plot. A polar plot shows the distribution of average concentrations at a specific receptor point against the wind speed and direction. Polar plots are useful for gaining an insight into the behaviour of sources by indicating the location and nature of the important sources.

¹⁹ www.dnv.com/binaries/UDM_MER_v1.0_tcm4-76493.pdf

²⁰ <http://fairmode.ew.eea.europa.eu/>

²¹ www.harmo.org/Kit/default.asp

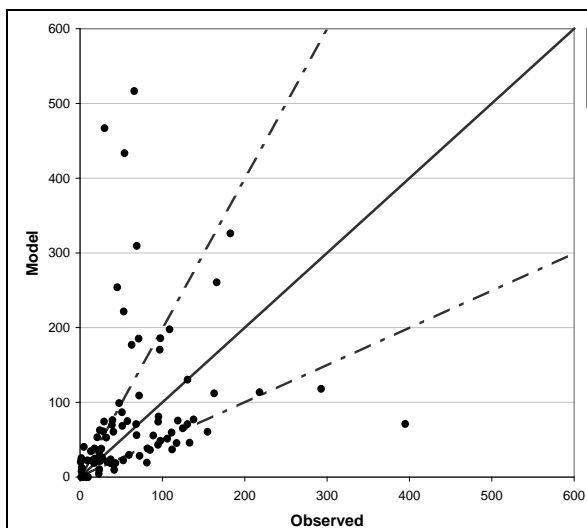


Figure 7.1 A scatter plot of modelled data against observed data

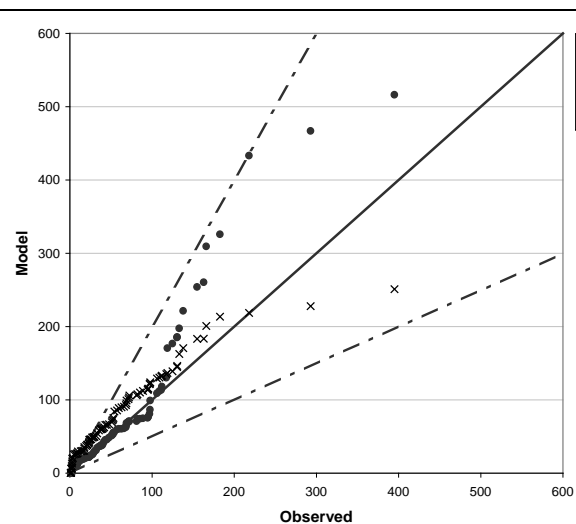


Figure 7.2 A quantile-quantile plot of two sets of modelled data compared with observed data

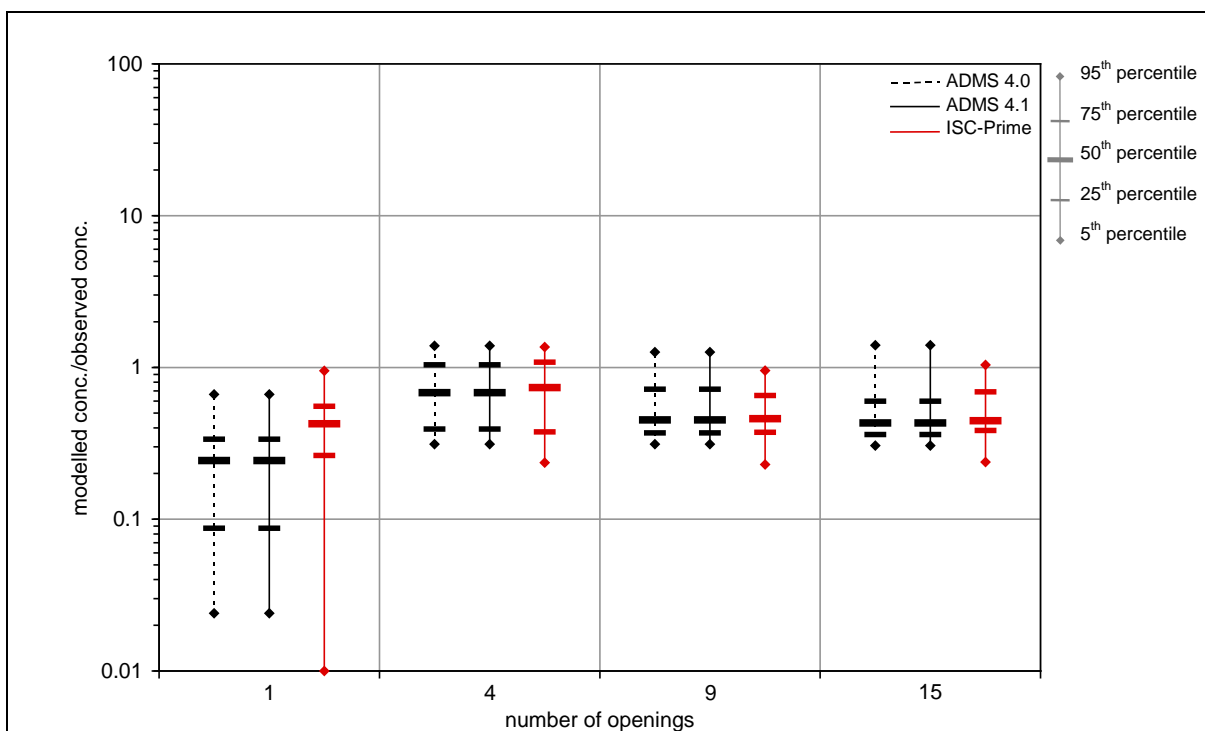
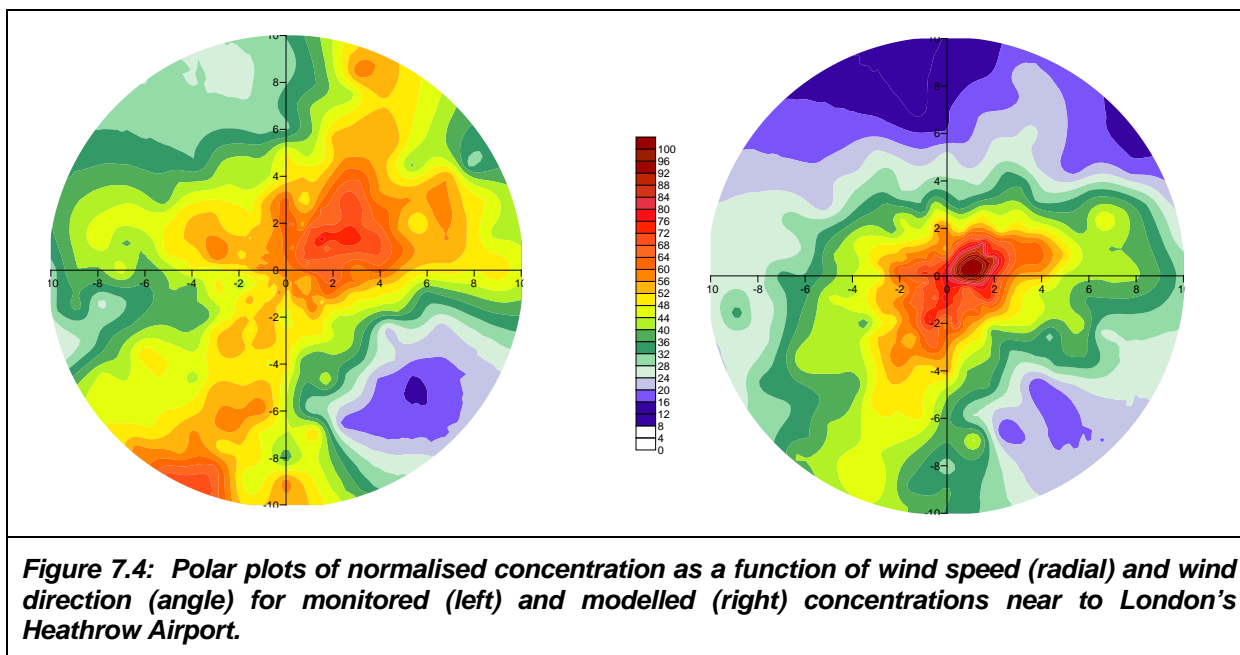


Figure 7.3: A box-and-whisker plot comparing two versions of ADMS with ISC-Prime and wind tunnel data for a building with various numbers of roof openings: 1, 4, 9, 15 openings.



7.2. Other model assessment

Other work to validate and assess model performance that CERC has carried out includes:

- Parametric studies, varying one model parameter at a time to check the expected physical behaviour;
- Running a set of standard runs with successive model versions, automatic calculation of the differences in output (maximum and mean), automatic contour plotting of output and automatic compilation of the contour plots from each version to display as pairs of plots in an animated gif;
- Comparison with other models such as AERMOD, ISC-Prime. Understanding the difference in the physics of each model means the results can be compared for expected differences and unexpected differences can be investigated further;
- Use of methods developed for the UK government's assessment of air quality at Heathrow that involved innovative, detailed analysis of monitoring and modelled data, for instance via polar plots (normalised concentration as a function of wind speed and wind direction) to understand the important physical processes and how the models represent them²²; and
- Use of methods developed in the US under the banner of the ASTM (American Society for Testing and Materials) to assess model performance in categories e.g. stability, rather than the usual space-time point comparison²³.

Validation documents are published on the CERC web site. They describe the data sets used, the modelling approach taken and present the results of ADMS compared with the monitored data. The ADMS model files are available on request so anyone may re-run the scenarios.

²² www.dft.gov.uk/pgr/aviation/environmentalissues/heathrowsustain/chapter2monitoringandmeasure2911

²³ <http://harmo.org/astm/Downloads/UGDesign2.pdf>

7.3. ADMS 4 validation studies

Given below is an outline of the validation studies that have been used for ADMS 4. These studies cover flat and complex terrain, with and without buildings. The studies cover both a variety of meteorological conditions and look at different averaging periods in different times.

- Flat terrain
 - *Kincaid, Indianapolis and Prairie Grass experiments*
- Buildings
 - *AGA experiment*
 - *Alaska North Slope tracer study*
 - *Bowline point site*
 - *EOCR study*
 - *Lee power plant wind tunnel study*
 - *Millstone nuclear power plant*
 - *Robins and Castro wind tunnel experiments*
 - *Snyder wind tunnel experiments*
 - *Warehouse fires wind tunnel experiments*
- Buildings & complex terrain
 - *Baldwin power plant*
 - *Martins Creek steam electric station*
 - *Cinder Cone Butte tracer experiments*
- Complex terrain
 - *Clifty Creek power plant*
 - *Hogback Ridge tracer experiments*
 - *Lovett power plant*
 - *Tracy power plant*
 - *Westvaco corporation*

7.4. ADMS-Urban and ADMS-Roads validation studies

The following validation studies have compared ADMS-Urban and/or ADMS-Roads model performance against field trial data. More generally, in modelling a town or city, the model set up includes a model verification step using, typically, the most recent monitoring data for one year. In this way ADMS-Urban model predictions are continuously tested against monitored data.

- *Validation of ADMS-Urban and ADMS-Roads against M4 and M25 motorway data*
- *Validation of ADMS-Roads using the Caltrans Highway 99 dataset*
- *Comparison of ADMS-Roads, CALINE4 and UK DMRB model*

8. ADMS 4 and other Candidate Models

Up to this point the focus has been on the ADMS 4 model features, the model's applicability for modelling the dispersion of releases at Mongstad and its potential to be adapted for special aspects of Mongstad. Here we make reference to other candidate models and, where appropriate, comment on their suitability to be utilised to model the releases at Mongstad. Note that, whilst we have sought to cover the most well-known, relevant models within the key model categories, there may be some omissions due to the huge number of models in use.

Modelling approaches may broadly be described according to the following categories:

- Gaussian-type models

These models express the concentration distribution according to a predetermined analytic formulation. The model type includes ADMS 4 and AERMOD and has been discussed in Section 3.1.

- Lagrangian models

These represent the released pollutant with a stream of particles or puffs transported by the mean flow and spread according to the statistical properties of the turbulence. They are better able to represent transient effects (rapidly varying meteorology or accumulation of pollution in low wind conditions) than plume models, however, they are more complex to run and may require much greater run times. Examples include the US-EPA model CALPUFF²⁴, the US models SCIPUFF²⁵, HYSPLIT²⁶ and the UK Met Office model NAME²⁷.

- Eulerian models

Eulerian models use an Eulerian grid to calculate both the flow and turbulence and the transport and diffusion of released material. This model type is able to include detailed treatment of chemistry and microphysics. However, being grid-based, with a minimum grid size typically of the order of 1km, Eulerian models are not able to resolve the fine details of the plume near the source and are therefore not suitable for looking at processes which are important at small scales, such as dispersion local to stacks. An example of this model type is the US-EPA model system WRF/CMAQ²⁸. Higher-resolution Eulerian models such as Computational Fluid Dynamics (CFD) or Large Eddy Simulation (LES) models have also been developed which may resolve the plume. Due to the computer run-time constraints, these models are not run routinely and cannot easily take account of important chemical or microphysical processes.

- Combined approach

Besides these main model types there are models which combine aspects of the different approaches. For example the TAPM model²⁹ nests a Lagrangian model for the near field within an Eulerian system for the far field, whilst the recent report by NILU for the Mongstad project *Report on models, model needs and requirements*³⁰ suggests a Lagrangian probability density function (PDF) model as a potential candidate model. This combines aspects of Gaussian and Lagrangian approaches.

The key requirements of a model for application to Mongstad are the following:

- (i) describes in-plume processes and characteristics in detail;
- (ii) runs in reasonable time so that long-term (annual) averages may be calculated for different scenarios;

²⁴ <http://www.src.com/calpuff/calpuff1.htm>

²⁵ <http://gcmd.nasa.gov/records/SCIPUFF-Model.html>

²⁶ <http://ready.arl.noaa.gov/HYSPLIT.php>

²⁷ <http://www.metoffice.gov.uk/research/modelling-systems/dispersion-model>

²⁸ <http://www.epa.gov/AMD/ModelDevelopment/twoway.html>

²⁹ <http://www.cmar.csiro.au/research/tapm/index.html>

³⁰ Berglen, T. F., Cassiani, M., Matthias, K. & Knudsen, S., 2008: CO₂ and amines: Report on models, model needs and requirements (Contribution to Task 5), NILU Ref: OR 50/2008

- (iii) allows for a range of processes including impact of on-site buildings on dispersion, complex terrain effects (e.g. variation in surface roughness, surface elevation), wet and dry deposition, in-plume chemistry);
- (iv) may be adapted in a reasonable time frame to the special characteristics of the Mongstad processes (e.g. amine chemistry, impact of amines on droplet formation); and
- (v) is developed for use by third parties; i.e. has a user interface which makes it practical to use the model by those other than those involved in developing the code and has been through rigorous verification and validation procedures.

Based on these criteria, and referring to the discussion of modelling methods above, it is possible to reach the following conclusions regarding the potential of models to be utilised and developed for the treatment of releases at Mongstad: advanced Gaussian-type models offer adequate spatial resolution and practicality; Lagrangian models also offer adequate spatial resolution however only some are practical for being run repeatedly for long-term assessment; Eulerian models are not suitable, either because of their lack of resolution or because of run-time limitations. In addition to ADMS 4, of the models mentioned above, those warranting further consideration therefore include AERMOD, CALPUFF, PDF approach (NILU) and TAPM.

AERMOD

AERMOD is a steady-state advanced Gaussian plume model that simulates air quality and deposition fields up to 30km. It was developed for the US-EPA, is open source and could be developed by those other than US-EPA. Developed after ADMS, it deals with many of the same features as ADMS 4 but often using very different methodologies, typically using more of an empirical-based than a physics-based approach. The model includes a building effects module, module for impacts of changes in surface characteristics, complex terrain module and a simplified chemistry model (ozone-limiting model). With the exception of the buildings effect module, the approaches used are generally simpler than those of ADMS 4.

Terrain is modelled in AERMOD using an atmospheric stability weighted sum of two idealised solutions: a plume impaction solution in very stable conditions and a terrain-following solution in neutral conditions. Dispersion from sources in the lee of hills is one of the weaknesses of the terrain modelling.

The AERMOD ozone-limiting chemistry is a simple post-processing calculation rather than a model of multiple chemical reactions, so it is not clear how AERMOD could be adapted to include advanced chemistry modules.

AERMOD does not include the advanced falling drop method for wet deposition nor the calculations of in-plume humidity/water content that would be the basis for looking at impacts of water droplets resulting from amines.

CALPUFF

CALPUFF is a multi-layer, multi-species, non-steady-state puff dispersion model that simulates the effects of time- and space-varying meteorological conditions on pollution transport, transformation and removal. CALPUFF can be applied on scales of tens to hundreds of kilometres, but is recommended by the US-EPA only for scales greater than 50km from the source. It includes algorithms for subgrid scale effects, such as terrain impingement, as well as longer-range effects such as pollutant removal due to wet scavenging and dry deposition, chemical transformation, and visibility effects of particulate matter concentrations.

CALPUFF nests algorithms from AERMOD in the near field (see previous section). Although slower to run than AERMOD (and ADMS 4) it offers more potential than AERMOD for Mongstad. In particular, its met pre-processor CALMET allows a more robust treatment of the effects of surface variations than the AERMOD algorithms and the (time-dependent) puff model has advantages over a plume model at larger distances from the source. It also has a chemistry model which could probably be adapted for amine chemistry. It does not have advanced wet deposition algorithms (falling drop method) or calculations of in-plume humidity/water content.

PDF Model (NILU)

In NILU's *Report on models, model needs and requirements*³⁰, a Lagrangian probability density function (PDF) model is put forward as the '*best option to ... fully describe the plume and plume chemistry with short averaging times.*' The PDF model is a Lagrangian particle dispersion model driven by meteorological data fields, analyses or forecasts, in Gridded Binary (GRIB) format from the ECMWF numerical weather prediction model. It was originally designed to calculate the long-range and mesoscale dispersion of air pollutants from point sources, for instance after an accident in a nuclear power plant.

The model includes routines to calculate radioactive decay and wet and dry deposition. The wet deposition treats in-cloud and below-cloud scavenging differently. The in-cloud scavenging for gases and particles depends on the height over which scavenging takes place and the liquid water content of the cloud. The below-cloud scavenging uses a washout coefficient approach which is the same as the ADMS 4 simple wet deposition models. Output from the model is gridded 3D concentration fields and 2D wet and dry deposition fields. Kernel estimates are made from the gridded output for specified receptor locations.

Lagrangian models are independent of a computational grid and have, in principle, no limit on resolution, but in practice the run times make their use impractical for generating comparable output to the Gaussian models. Their complexity often makes them unsuitable for non-expert users. The PDF model has been validated using data from long-range tracer and intercontinental air pollution transport studies.

This type of model is complex and computationally expensive. Despite the assertion made in the reference³⁰, it is not explained why the PDF approach is said to be superior to the use of advanced Gaussian models for this study.

TAPM

TAPM, *The Air Pollution Model* developed by CSIRO in Australia, nests a Lagrangian particle model within an Eulerian model. The Eulerian model has advanced chemistry and microphysical models and includes dry and wet deposition. It consists of a series of nested, grid-based solutions of the Eulerian equations for mean concentration and, optionally, the variance equations for advection, diffusion, chemical reactions and emissions. The gas-phase chemistry scheme used in TAPM is similar to the chemistry schemes in ADMS-Urban. It is a ten-reaction scheme for NO_x and SO₂, where the VOC (volatile organic compounds) can be aggregates of VOC species from the CBM-IV chemistry model. It has an aqueous-phase chemical reaction for SO₂ and particles.

On the inner-most grid of the Eulerian model a Lagrangian Particle Module is used to account for near-source effects such as gradual plume rise and near-source dispersion. The emitted mass is represented as a puff in the horizontal direction and as a particle in the vertical direction. In the Lagrangian model, chemistry is estimated from the Eulerian model; deposition is neglected; the effect of building wakes on plume rise and dispersion is modelled using an approach based on the PRIME model of AERMOD. The highest horizontal grid resolution of TAPM is 0.25km.

Summary

ADMS 4, AERMOD and CALPUFF have all been through a comprehensive validation process and, consequently, have been subject to high level of scrutiny. TAPM has been validated with respect to some of the same datasets as ADMS 4 and AERMOD whereas the PDF model has been validated with respect to longer-range data sets. Neither TAPM nor the PDF model have, to our knowledge, been subject to the same level of (international) scrutiny as ADMS 4, AERMOD and CALPUFF.

CALPUFF, TAPM and the PDF model can operate at domain scales greater than 50km. The ADMS 4 core dispersion model is valid for ranges up to around 50km, but the model has been used at distances up to 100km for calculating long-term average concentrations from fossil-fuelled power stations i.e. 200m tall stacks with very buoyant emissions. ADMS 4 can currently use mesoscale or CFD model flow fields as input and can, thus, be nested within a mesoscale model as AERMOD is nested within CALPUFF.

This ability was developed in response to users concerned with complex terrain and complex wind fields arising from the complex terrain or the urban environment.

Finally we note that the focus of this discussion has been on models which resolve and describe the detailed physical and chemical processes taking place within the plume. When regional scale effects (10s to 100s of kilometres) are of interest, other models including Eulerian models would need to be considered.

9. Case Study

The preceding chapters described how ADMS 4 is currently able to take into account many important features of the required modelling of the Mongstad site. The Case Study of Mongstad comprises a baseline case plus sensitivity tests that use all of the major features of ADMS 4.

Input data representing the Mongstad site were provided to CERC by GASSNOVA. The sources modelled include the Carbon Capture Mongstad (CCM), the Technology Centre Mongstad (TCM), four major refinery sources and a flare around the site. Figure 9.1 shows the location of the Mongstad site and the sources included in the Case Study.

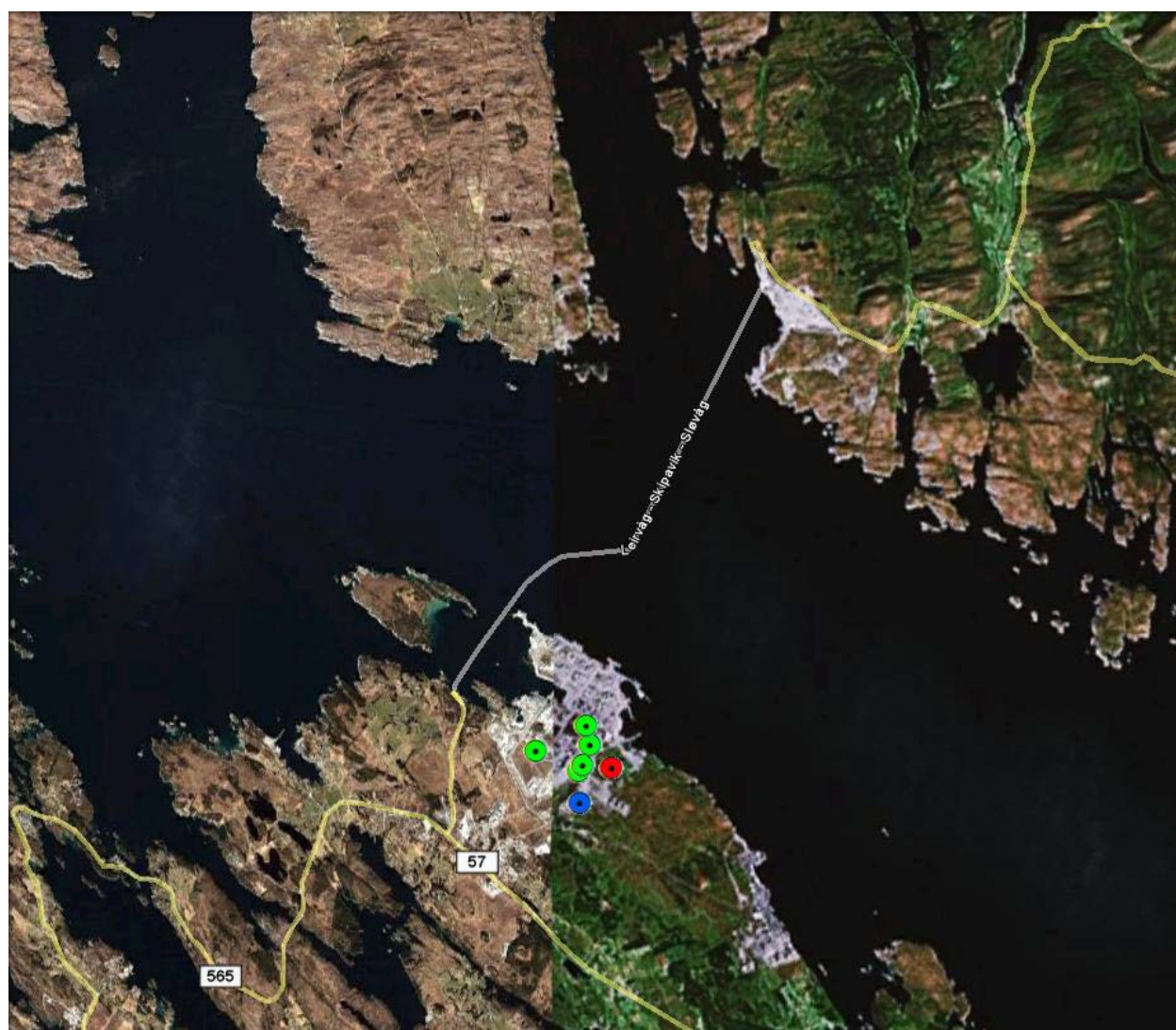
The baseline case includes the Carbon Capture Mongstad (CCM) source only and emissions of monoethanolamine (MEA) only. The baseline run uses meteorological data from 2007. Sensitivity tests were carried out for various model parameters and input data by varying these within realistic ranges. Where relevant, the sensitivity tests involve the other sources and emissions at Mongstad.

Maximum concentrations calculated over the model output grid are presented, including both the annual mean and the 100th percentile statistics, for the baseline and sensitivity tests. Where contour plots from the sensitivity tests show significant differences from the baseline, these contour plots have been included. Although ADMS 4 can output concentrations at any required height, the concentrations presented for this Case Study are all ground level concentrations.

Section 9.1 describes the analysis of data available from surrounding meteorological sites and the resulting data used for the dispersion modelling studies. The emissions data provided, and the processing carried out to produce the input data required for ADMS 4 are described in Section 9.2. Section 9.3 describes the baseline case. Section 9.4 outlines different model parameters and input data pertaining to the Mongstad site and includes sensitivity tests for each of these. Section 9.5 shows contour plots of varying output extents, while Section 9.6 gives results for different meteorological years. Modelling results for all amines and related compounds from the CCM and TCM stacks are given in Section 9.7. Sections 9.8 and 9.9 discuss deposition and plume visibility output. Modelling of the other sources at the Mongstad site is described in Section 9.10. Finally, a summary of the model run results is given in Section 9.11.

Figure 9.1: Aerial photograph of Mongstad, showing locations of modelled sources: Carbon Capture Mongstad (CCM, red), Technology Centre Mongstad (TCM, blue), and major refinery sources (green).

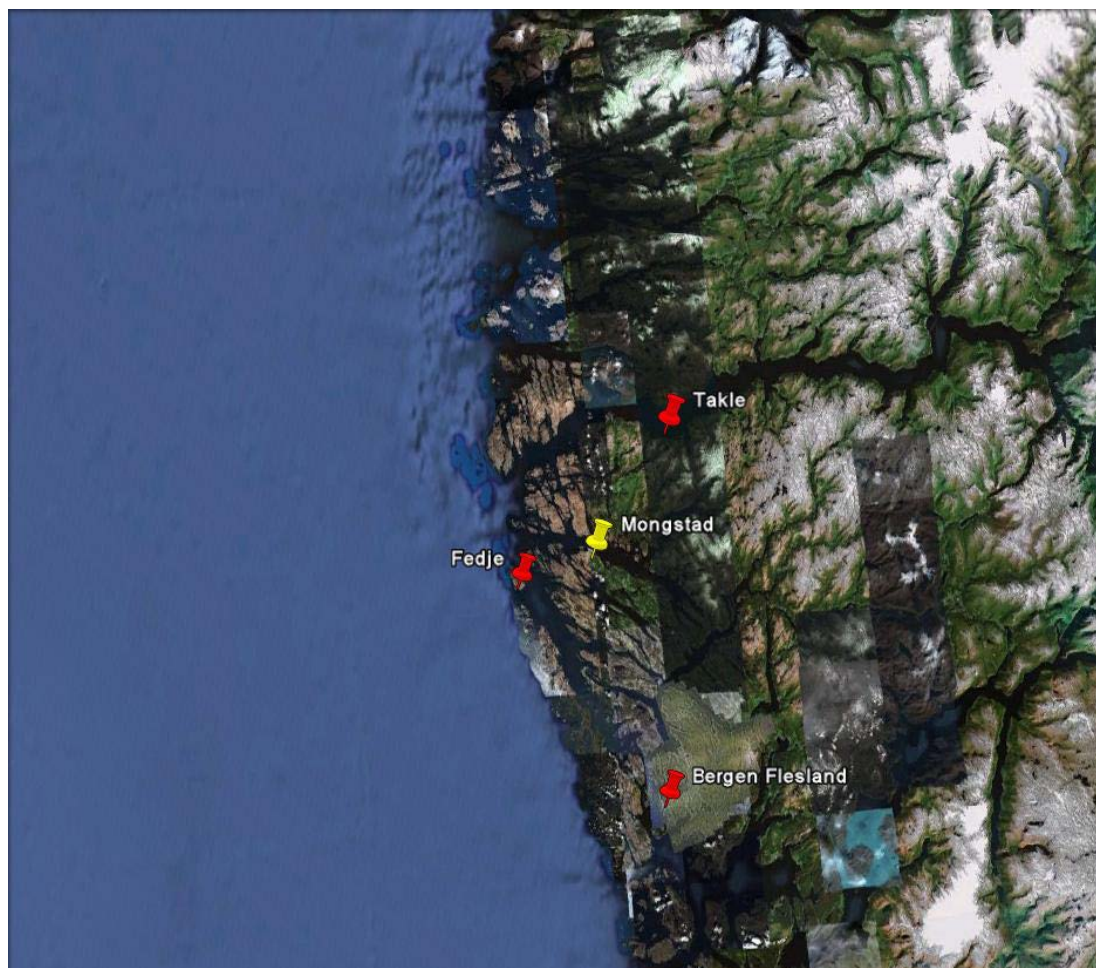
Scale: the distance across the fjord is approximately 3km.



9.1. Meteorological data

An initial screening of data available from the eKlima portal of the Norwegian Meteorological Institute³¹ resulted in a shortlist of sites that were potentially useful for modelling the Mongstad site. These were Fedje, Bergen Flesland and Takle, as shown in Figure 9.2.

Figure 9.2: Google Earth image showing Mongstad (yellow) and the three meteorological sites: Takle, Fedje and Bergen Flesland (red). Fedje is approximately 20km from Mongstad.



For dispersion modelling, meteorological data from the meteorological monitoring site closest to the dispersion site, the source, are usually selected, as they will tend to be the most representative. Exceptions to this can arise where an area is subject to coastline effects or major topographical effects such as the channelling of winds along valleys. A comparison of wind roses and mean wind speeds at the candidate sites plays a part in deciding how representative the meteorological site is of the dispersion site.

The availability of data at particular sites is another important consideration in selecting the source of meteorological data:

- Observations of necessary parameters, such as cloud cover, can be missing from a site. However, cloud cover shows less spatial variation than the other meteorological parameters required and therefore cloud cover data from one site can be used with other parameters from a second site.
- The extent of data capture must be considered. A large proportion of missing hours of data can be detrimental to the accuracy of the modelled results.

³¹ http://sharki.oslo.dnmi.no/portal/page?_pageid=73,39035,73_39049&_dad=portal&_schema=PORTAL

Table 9.1 summarises the site characteristics and data available from the candidate sites: their location; their location relative to both the Mongstad site and to the coast and the elevation of the site above sea level. Fedje is the nearest site but is more coastal than Mongstad. The other two sites, Takle and Bergen are 30km and 60km respectively from Mongstad and both are inland. All the sites are at a low elevation above sea level but are likely to be affected by nearby mountains, although the extent of the terrain effects has not been quantified.

Hourly wind speed, wind direction and temperature data were available from Fedje. The only other parameter available from Fedje was relative humidity that was reported intermittently and appeared to be of poor quality and therefore were not used. Hourly relative humidity data from Bergen Flesland were used in preference to the 8-hourly data from Takle. The most frequent cloud cover data were the 3-hourly data from Bergen Flesland. The alternative source of cloud cover data was Takle where it is reported 3 times a day (8-hourly). Precipitation data were not available from Fedje, were erratically recorded at Bergen Flesland and were available as 12-hourly averages at Takle. The data from Takle were, therefore, used.

Table 9.1: Summary of relevant properties of the meteorological sites

	Site name			Mongstad
	Fedje	Bergen Flesland	Takle	
Location (Lat, Long)	60.78, 4.72	60.283, 5.233	61.033, 5.383	60.808, 5.036
Relative location	20km west of Mongstad	60km south of Mongstad	30km north east of Mongstad	-
Coastal / inland	Coastal	20km inland	40km inland	15km inland
Height above sea level (m)	19	50	38	20
Relevant measured parameters	wind speed wind direction relative humidity* temperature	wind speed wind direction relative humidity temperature cloud cover precipitation**	wind speed wind direction relative humidity temperature cloud cover precipitation	-
Frequency of measurements	All hourly	Cloud cover (3-hourly) Precipitation (erratic) All others hourly	Precipitation (12-hourly) All others 3 times a day	-

*incomplete and poor quality; **erratic

Figures 9.3 to 9.7 compare the wind roses from Fedje, the nearest site, with a wind rose for a similar period from Mongstad. The Mongstad windrose was generated from meteorological measurements that were carried out at the Mongstad site for the period 26.11.2006 to 04.05.2010. These were supplied to CERC in a memo from Statoil.³² No further data from meteorological measurements at the Mongstad site were available for use by ADMS 4.

The wind roses from Fedje and Mongstad suggest that the direction of the wind at Fedje is indeed representative of that at Mongstad. The height at which the wind speed is measured at Fedje is 10m. At Mongstad the wind speed measurements are *assumed* to be at 10m, but may not be. The measurements were made on top of a building that is surrounded by other buildings and stacks. Therefore, although the wind roses suggest that the measured wind speeds are higher than those at Mongstad, the measurements at Mongstad are not of sufficient quality to be certain of this. It has, therefore, been assumed that wind speeds at Fedje are representative of those at Mongstad.

³² Internal memo, Statoil: Meteorological conditions at Mongstad . 21st June, 2010.

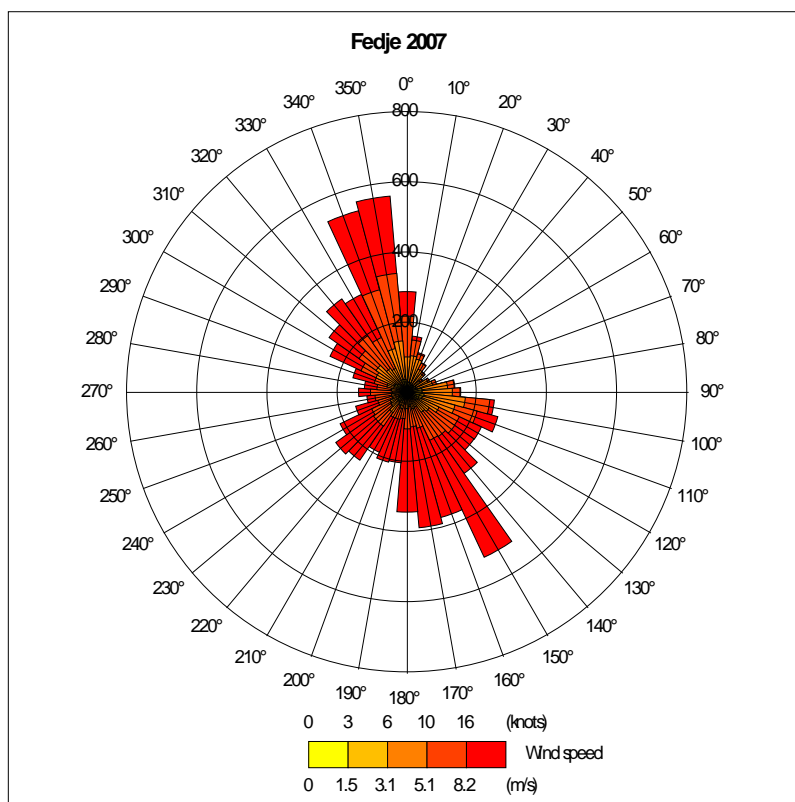


Figure 9.3: Wind rose for Fedje, 2007

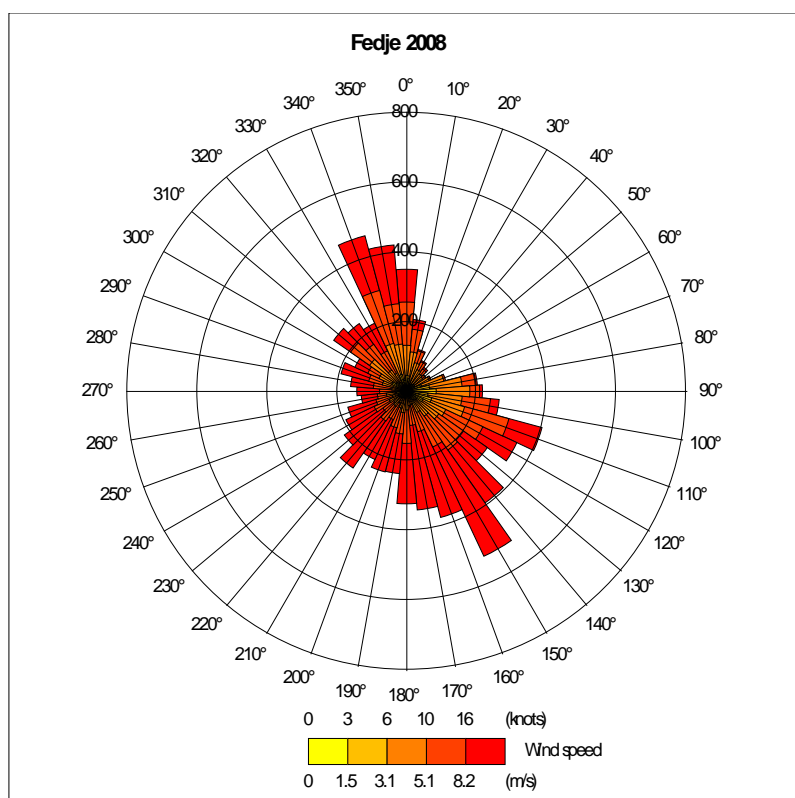


Figure 9.4: Wind rose for Fedje, 2008

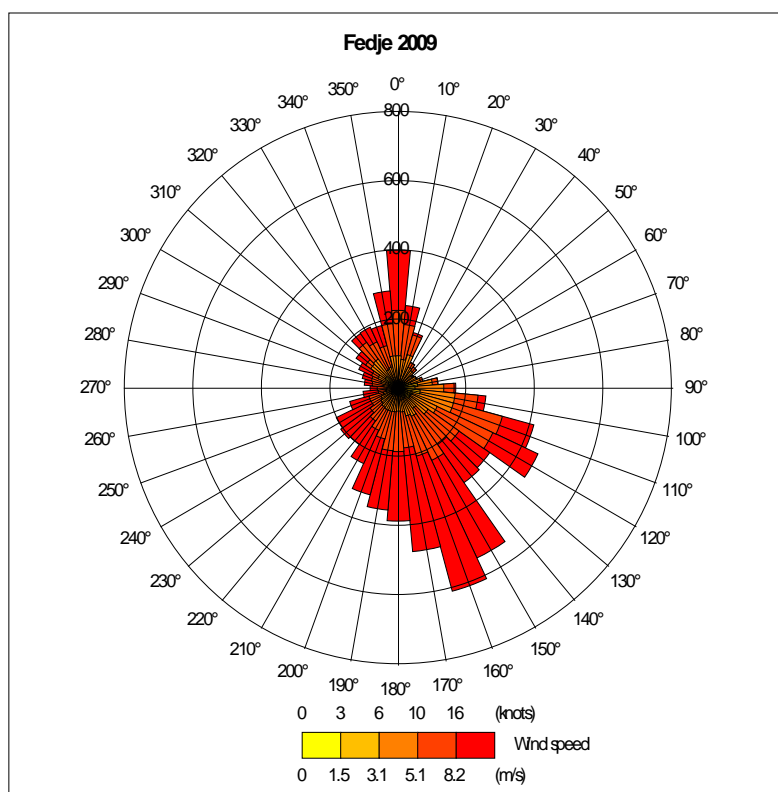


Figure 9.5: Wind rose for Fedje, 2009

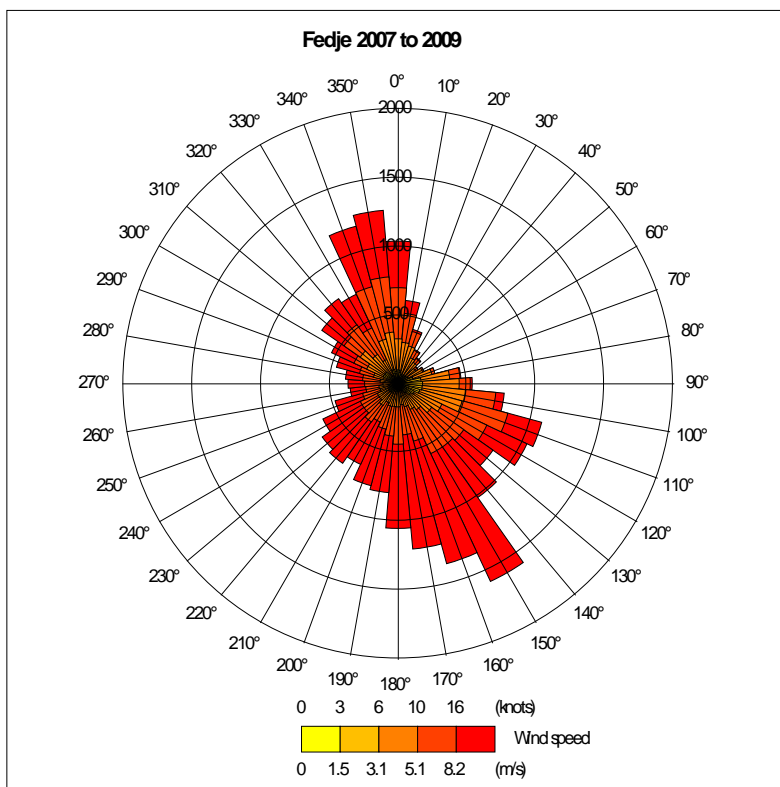


Figure 9.6: Wind rose for Fedje, 2007-2009

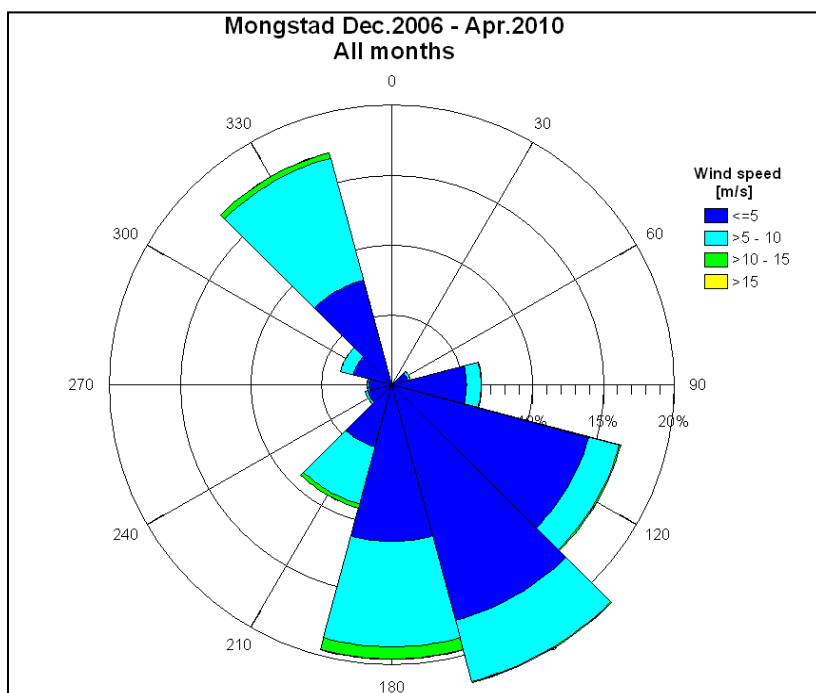


Figure 9.7: Wind rose for Mongstad, all months 2006 to 2010
(Statoil memo: Meteorological conditions at Mongstad, 21/06/10)

Following this analysis, the meteorological data chosen for the Case Study comprised:

- Hourly wind speed and wind direction from Fedje
- Hourly near-surface air temperature from Fedje
- Cloud cover from Bergen Flesland. The 3-hourly data were assumed to be constant for the following 3-hour period.
- Hourly relative humidity from Bergen Flesland
- Precipitation from Takle. The 12-hourly average precipitation measurements were assumed constant over the preceding twelve hours.

The data sources used are summarised in Table 9.2.

Table 9.2: A summary of meteorological sites used for each parameter

Parameter	Site used	Reasons for choice of site
Wind speed	Fedje	Closest site to Mongstad
Wind direction		Wind roses very similar to wind roses generated from measurements at Mongstad
Temperature		Closest site to Mongstad
Cloud cover	Bergen Flesland (3-hourly data)	No data at Fedje. The 3-hourly data were applied to the following 2 hours.
Relative humidity	Bergen Flesland	Data at Fedje were incomplete and sometimes of poor quality.
Rainfall	Takle (12-hourly data)	No data at Fedje, erratic data at Bergen Flesland. 12-hour total rainfall data were available from Takle and were spread equally over each 12-hour period.

Modelling more than one year of meteorological data can be important for investigating year-to-year variations. This inter-annual variation does not tend to significantly affect annual average concentrations, but can have a large effect on peak concentrations such as high percentile values. It is good practice to use data from the most recent complete years, so data from the years 2007, 2008 and 2009 were considered. 2007 was the baseline year.

Table 9.3 shows the statistics of the meteorological data for each year, as summarised by the ADMS 4 meteorological pre-processor. This includes the percentage of hours actually used by ADMS 4 in the model calculations; it can be seen that there is extremely good data capture and usage for all three years. When running ADMS 4, meteorological data may be present but not used if the wind speed measured at 10m, U_{10} , is below 0.75m/s. In this case the model skips the meteorological data for that hour unless the "Calms" option has been selected. The wind speed data for Mongstad shows very few hours with wind speeds at 10m lower than 0.75m/s and so the calms option has not been used in the Case Study.

Table 9.3: Summary of meteorological parameters used by ADMS 4

Year	Percentage data that can be used	Parameter	Minimum	Maximum	Mean
2007	95.3 %	Temperature (°C)	-3.9	23.3	8.3
		Wind speed at 10m (m/s)	0	25.2	7.7
		Cloud cover (oktas)	0	8	6
		Relative humidity (%)	21	100	81
		Rainfall (mm, annual)	3933		
2008	98.9 %	Temperature (°C)	-2.9	26.3	8.9
		Wind speed at 10m (m/s)	0	27.3	7.5
		Cloud cover (oktas)	0	8	5
		Relative humidity (%)	23	100	78
		Rainfall (mm, annual)	3377		
2009	95.9 %	Temperature (°C)	-4.8	26.5	8.0
		Wind speed at 10m (m/s)	0	24.3	7.4
		Cloud cover (oktas)	0	8	6
		Relative humidity (%)	19	99	79
		Rainfall (mm, annual)	2887		

9.2. Emissions data

9.2.1. CO₂ Capture Plant (CCM) and Test Capture Plant (TCM)

Data on the main stacks, the CCM and TCM, and their emissions were provided to CERC. The data are shown in Tables 9.4 and 9.5, respectively. For the TCM, two alternative sets of emission parameters and rates were provided corresponding to the two separate flue gas sources that will be tested in the TCM facility. It is anticipated the test facility will capture CO₂ from either source approximately 180 days a year each.

Table 9.4: Source parameters as provided

Parameter	CCM	TCM (Case 1)	TCM (Case 2)
Source height (m)	50	60	60
Source diameter (m)	-	1	1
Emission temperature (°C)	30	30	30
Emission velocity (m/s)	20.0	-	-
Volume flow rate (m ³ /s) at 30°C	645.2	13.2	16.1
Water mixing ratio (kg/kg)	0.027	0.027	0.027

The emissions from the CCM stack comprised amines plus a mixture of nitrosamines, nitramines and aldehydes that might be expected to form within the flue. Fewer pollutants were provided for the TCM stack. All emissions were provided as emission concentrations, in volumetric units (ppmv and ppbv).

Table 9.5: Emissions as provided

Pollutant	Units	Emission concentration		
		CCM	TCM (Case 1)	TCM (Case 2)
NO	ppmv	4.6	4.6	100
NO ₂	ppmv	0.5	0.5	5.0
MEA	ppmv	0.5	1.5	1.0
Ethanal (acetaldehyde)	ppmv	1.8	2.0	2.0
NH ₃	ppmv	2.6	3.0	3.0
Methylamine	ppmv	0.5	-	-
N-nitrosodimethylamine	ppbv	0.5	-	-
N-nitrosodiethanolamine	ppbv	0.5	-	-
Nitrosomorpholine	ppbv	0.5	-	-
Dimethylnitramine	ppbv	0.5	-	-
Ethanolnitramine	ppbv	0.5	-	-
Methylnitramine	ppbv	0.5	-	-
Dimethylamine	ppbv	0.5	-	-
Diethylnitramine	ppbv	0.5	-	-
Dimethanolnitramine	ppbv	0.5	-	-
2-(methylnitroamino)-ethanol	ppbv	0.5	-	-
Nitrosomethylethylamine	ppbv	0.5	-	-
Nitrosopiperazine	ppbv	0.5	-	-
1-methyl-N-nitroso-diethylamine	ppbv	0.5	-	-
Nitrosodiethanolamine	ppbv	0.5	-	-
Nitrosodiethylamine (NDEA)	ppbv	0.5	-	-

Tables 9.6 and 9.7 show the source parameters and emission rates, respectively, that were used as input to ADMS 4 for the modelling.

Source parameters not directly provided were calculated using assumptions when necessary. For the CCM:

- the diameter of the CCM was calculated from the volume flow rate and velocity values.

For the TCM, rather than model the two different emission cases, the data available were used to give one set of stack and emission parameters that would correspond to a worst case i.e. pessimistic concentrations:

- the higher value of volume flow rate was used to calculate emission rates as this would give higher mass emission rates for a worst case;
- the lower volume flow rate was used to calculate the velocity to give a lower exit velocity. This is a worst case for concentrations close to the stack; and
- the higher of the two emission concentrations for each pollutant was used in the calculation of the emission rate for a worst case.

For both the CCM and TCM:

- the stack locations were estimated from the site map provided, in conjunction with digital map data;
- emission concentrations were converted to emission rates in g/s using the volume flow rate information provided, the molecular weights shown in Table 9.7 and the ideal gas equation; and
- emissions were assumed to be constant and continuous throughout the year at the specified emission rate, i.e. no time-varying factors were applied to the emission rates.

Table 9.6: Emission parameters for CCM and TCM input to the ADMS 4 baseline modelling

Parameter	CCM	TCM
Source height (m)	50	60
Location (x,y)	284391,6747872	284034, 6747527
Source diameter (m)	6.6	1
Emission temperature (°C)	30	30
Emission velocity (m/s)	20.0	16.7

Table 9.7: Calculated emission rates for CCM and TCM input to the ADMS 4 baseline modelling

Pollutant	Molecular weight	Emission rate (g/s)	
		CCM	TCM
NO _x (as NO ₂)	46	4.34	2.06
MEA	61	0.82	0.06
NH ₃	44	1.19	0.033
Ethanal (acetaldehyde)	17	2.13	0.056
Methylamine	31	0.42	-
N-nitrosodimethylamine	74	0.0010	-
N-nitrosodiethanolamine	134	0.0018	-
Nitrosomorpholine	116	0.0016	-
Dimethylnitramine	90	0.0012	-
Ethanolnitramine	106	0.0014	-
Methylnitramine	76	0.0010	-
Dimethylamine	45	0.0006	-
Diethylnitramine	118	0.0016	-
Dimethanolnitramine	122	0.0016	-
2-(methylnitroamino)-ethanol	120	0.0016	-
Nitrosomethylethylamine	88	0.0012	-
Nitrosopiperazine	115	0.0015	-
1-methyl-N-nitroso-diethylamine	116	0.0016	-
Nitrosodiethanolamine	134	0.0018	-
Nitrosodiethylamine (NDEA)	74	0.0010	-

9.2.2. Other Mongstad sources

Data were provided to CERC for the other sources of emissions to air at Mongstad. Of these, only the major sources, the residue catalytic cracker, old main refinery stack, reformer stack, calcination furnace stack and two flares were modelled; minor sources with lower emissions were not modelled. The major sources were all modelled as point sources. Figure 9.8 shows the location of the CCM, TCM and other sources. Those sources modelled are labelled and indicated by green arrows.

The two flares were combined into a single source for modelling. In order to account for the buoyancy of the flame, an effective diameter and height were calculated, based on a calculated heat release value. Values for the temperature and efflux velocity of the flare emissions were assumed. All flare calculations and assumptions were based on guidance produced by the Ontario Ministry of the Environment, Canada.³³

The locations of the sources were determined from diagrams of the site layout. Emission and stack parameters were provided to CERC for each source and are given in Tables 9.8 and 9.9.

Emission rates for oxides of nitrogen (NO_x) and sulphur dioxide (SO₂) were provided as monthly emissions in tonnes for the year 2007. Data supplied for other years were incomplete. The emissions were assumed to be continuous and at a constant rate. The monthly variation was modelled using the monthly profile feature in the ADMS 4 .fac file, with a different monthly profile for each pollutant.

³³ Proposed guidance for air dispersion modelling, 2003. Ontario Ministry of the Environment / Lakes Environmental Consultants Inc.

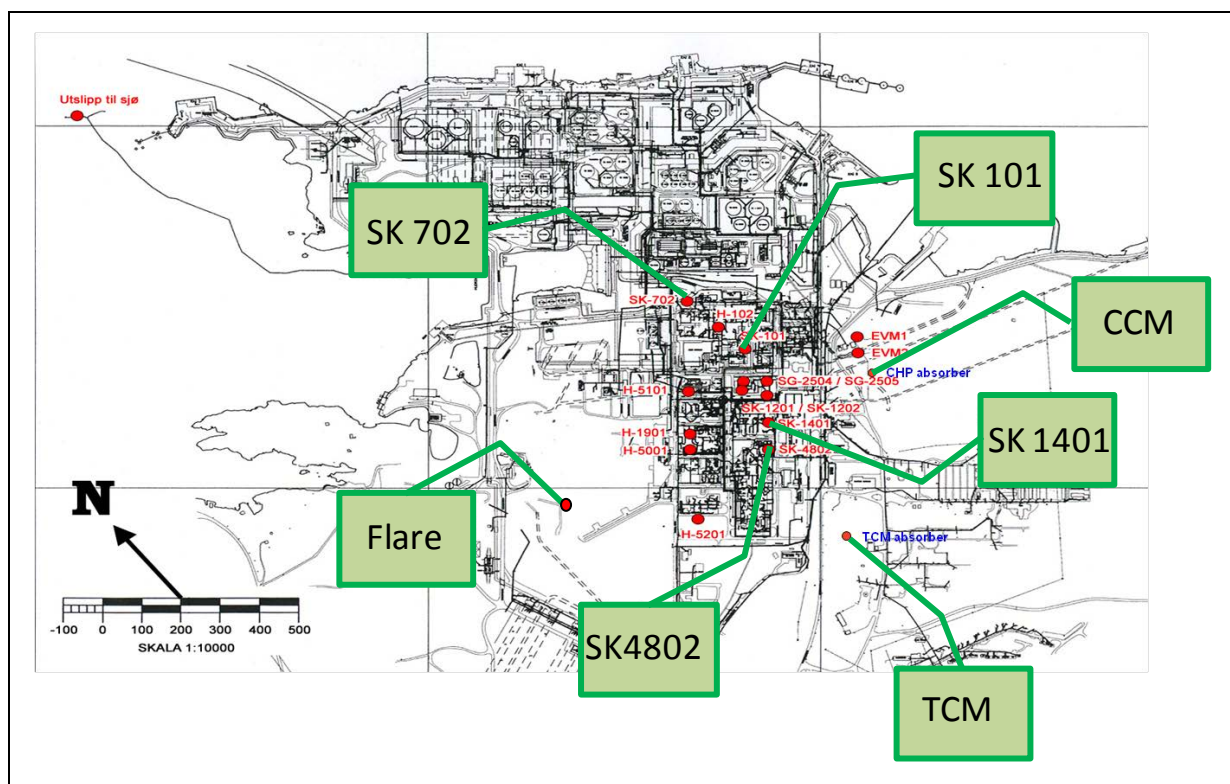


Figure 9.8: Location of the CCM, TCM and other sources at Mongstad. The sources modelled as part of the Case Study are labelled and indicated with green arrows.

Table 9.8: Parameters for major sources modelled

Parameter	SK4802	SK101	SK1401	SK702
Stack name/process	Residue catalytic cracker	Old main refinery stack (crude oil heater, reformer ovens, old steam boilers)	Reformer stack	Calcination furnace, petrol coke converted to anode material
Location (x,y)	284038, 6747857	284178, 6748130	284087, 6747918	284152, 6748335
Source height (m)	103	103	70	50
Source diameter (m)	2.8	7.6	2.4	1.4
Emission temp (°C)	120	275	550	60
Emission velocity (m/s)	29.2	4.2	14.4	15.8
NO _x emission rate (g/s)	29.7	11.9	2.8	2.8
SO ₂ emission rate (g/s)	5.2	5.8	2.8	0.2

Table 9.9: Parameters for the combined flare source (two flares combined)

Location (x,y)	283600, 6748100
Source height (m)	105
Source diameter (m)	1.5
Emission temp (°C)	1273
Emission velocity (m/s)	20
NO _x emission rate (g/s)	1.7
SO ₂ emission rate (g/s)	2.6

9.3. Baseline case

A baseline case was set up for the purposes of comparing results from model sensitivity tests and other model runs. The baseline case includes the Carbon Capture Mongstad (CCM) source only, as this is the major source for the CO₂ capture project, emitting around ten times more than the TCM facility. The CCM emission parameters given in Table 9.6 were used.

Only emissions of monoethanolamine (MEA) were modelled in the baseline case. Currently, the amines and their related compounds (nitrosamines, nitramines, etc) are treated identically in the model calculations; the current lack of information means that no compound-specific parameters can realistically be assigned to them. The resulting dispersion patterns will therefore be the same for each emitted compound. This means that only the emission rate is different for each, so MEA was chosen, due to its large emission rate, given in Table 9.5.

Meteorological data from 2007 is used in the baseline case. Model default values for many parameters are used, and complex effects are not included; complex terrain, buildings effects, chemical reactions or deposition calculations were not modelled.

A surface roughness length of 0.5m was used for the Mongstad site and surrounding area (dispersion site), and a value of 0.1m for the meteorological site. The latitude of the Mongstad site, 60.8 °N, was input. Model default values were used for other parameters defining the site characteristics: minimum Monin-Obukhov length (1m), Priestley-Taylor parameter (1), and surface albedo (0.23). The model output domain covered an area of 5km by 5km centred on the CCM, with a grid resolution of 50m.

Details of each of these parameters and complex effects are given in the following sections. Modifying the baseline run to produce a series of further runs provides a means of testing each parameter, complex effect and meteorological dataset individually, and the results of these model runs are also provided in the following sections.

The results of the baseline case are:

- the maximum annual average concentration of MEA on the grid was 0.09 µg/m³.
- the maximum 100th percentile hourly average concentration of MEA on the grid was 1.73 µg/m³.

Contour output for the baseline case is given in Figure 9.13.

9.4. Site location and characteristics

ADMS 4 uses a selection of parameters and modules to represent the area in which dispersion is modelled. These are:

- Complex terrain (hills);
- Surface roughness;
- Building and stack downwash effects;
- Minimum Monin-Obukhov length;
- Surface wetness;
- Surface albedo; and
- Latitude.

These parameters and the sensitivity tests carried out will be described in turn in this section.

9.4.1. Complex terrain

Terrain effects can be modelled in ADMS 4 and this is described in more detail in Section 3.2.6.

9.4.1.1. Baseline case

The area immediately surrounding the Mongstad site is relatively flat. The baseline case therefore assumed flat terrain, no complex terrain was modelled.

9.4.1.2. Sensitivity tests

To test the sensitivity of the modelled results to the effects of the local topography, local terrain elevation data were incorporated in the modelling. Figure 9.9 shows a 3-dimensional plot of the local terrain. Note that in the 3-dimensional plot the vertical scale is exaggerated.

In ADMS 4 the extent of the terrain input to the model must be larger than that of the receptor grid in order to avoid edge effects in the modelling. The baseline model run has an output grid extent of 5km by 5km. The terrain data used for this run has an extent of 12km, with a resolution of 50m.

Table 9.10 shows the maximum concentrations predicted over the output grid, with and without the inclusion of terrain data. These values suggest that the terrain does not have a significant effect on predicted concentrations.

Table 9.10: Maximum annual mean and 100th percentile values over the output grid

	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
	Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
Complex terrain		
Without terrain (baseline)	0.09	1.73
With terrain	0.09	1.78

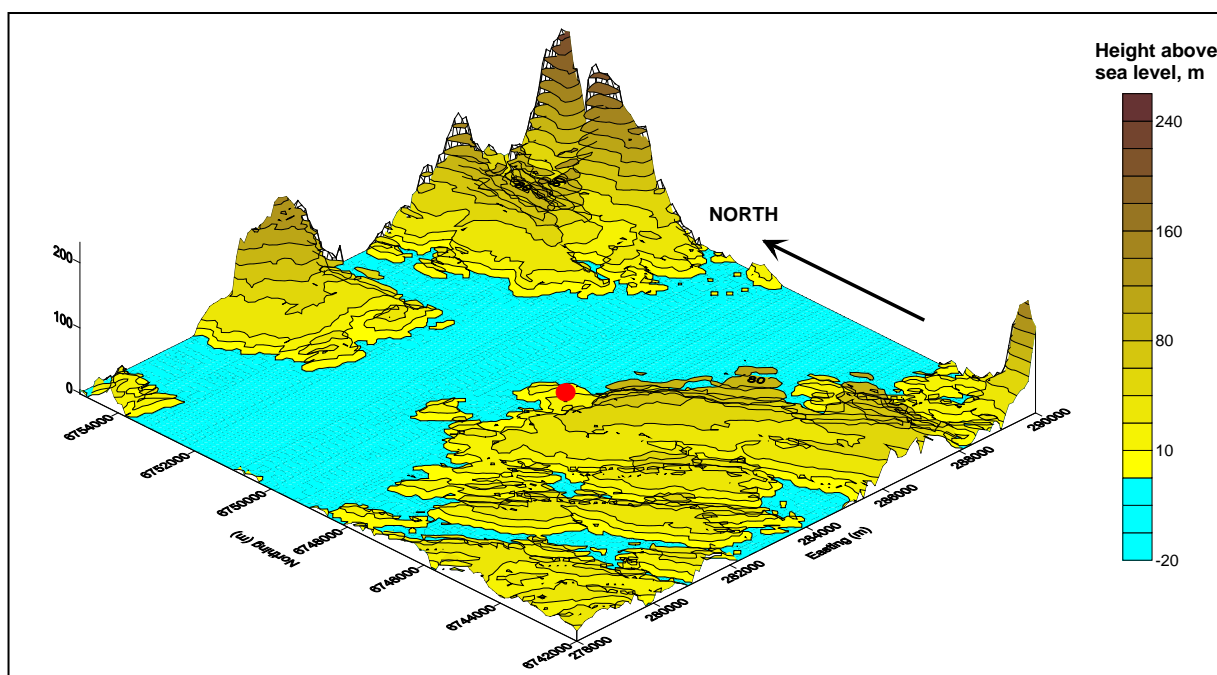


Figure 9.9: Plot of local terrain. Mongstad is marked with a red dot.

9.4.2. Surface roughness

A surface roughness length is used in the model to characterise the surrounding area in terms of the effects it will have on wind speed and turbulence, as described in Section 3.2.6. The surface roughness length values at the dispersion site can be:

- constant in time and space
- constant in space and hourly varying
- constant in time and spatially varying. In this case multiple values, usually several discrete values, are used to represent areas of land use. The spatially varying surface roughness is entered via the ADMS 4 .ruf file.

In addition to this, a different value can be input for the surface roughness length at the meteorological site compared with the dispersion site to account for any difference in land use at the meteorological site compared to the modelled area. The surface roughness length values at the meteorological site can be:

- constant in time and space
- constant in space and hourly varying

9.4.2.1. Baseline case

For the baseline case the surface roughness at the dispersion site was assumed to be constant in space and time and to take the value 0.5m. 0.5m was chosen to represent the mixture of land uses at the Mongstad site, with buildings and stacks surrounded by open land and water. For the meteorological site, a different surface roughness length value, constant in space and time and equal to 0.1m, was used.

9.4.2.2. Sensitivity tests

The sensitivity of the modelled concentrations to surface roughness values was tested in various ways:

- i. A different value, constant in space and time and equal to 0.2m, was used. The value at the meteorological site was kept at a constant value of 0.1m.
- ii. Spatially varying roughness lengths were used in ADMS 4, entered using a *.ruf* file. Four different values of roughness length were used: 0.001m for the sea and other water, 0.4m for the majority of the land, 0.6m for areas with a relatively high density of buildings and 1m for the Mongstad site. Figure 9.10 shows how these roughness points were distributed. The extent and resolution of the roughness data is the same as that of the terrain data. The value at the meteorological site was kept at a constant value of 0.1m.
- iii. Spatially varying roughness as in ii, with terrain modelled as well

The surface roughness was not varied temporally in this Case Study, but this feature of ADMS 4 might be appropriate for future modelling studies if the surface characteristics were significantly altered over the year due to factors such as foliage changes.

Figure 9.10: Visualisation of the spatially-varying roughness file. The light green points represent the main sources at Mongstad

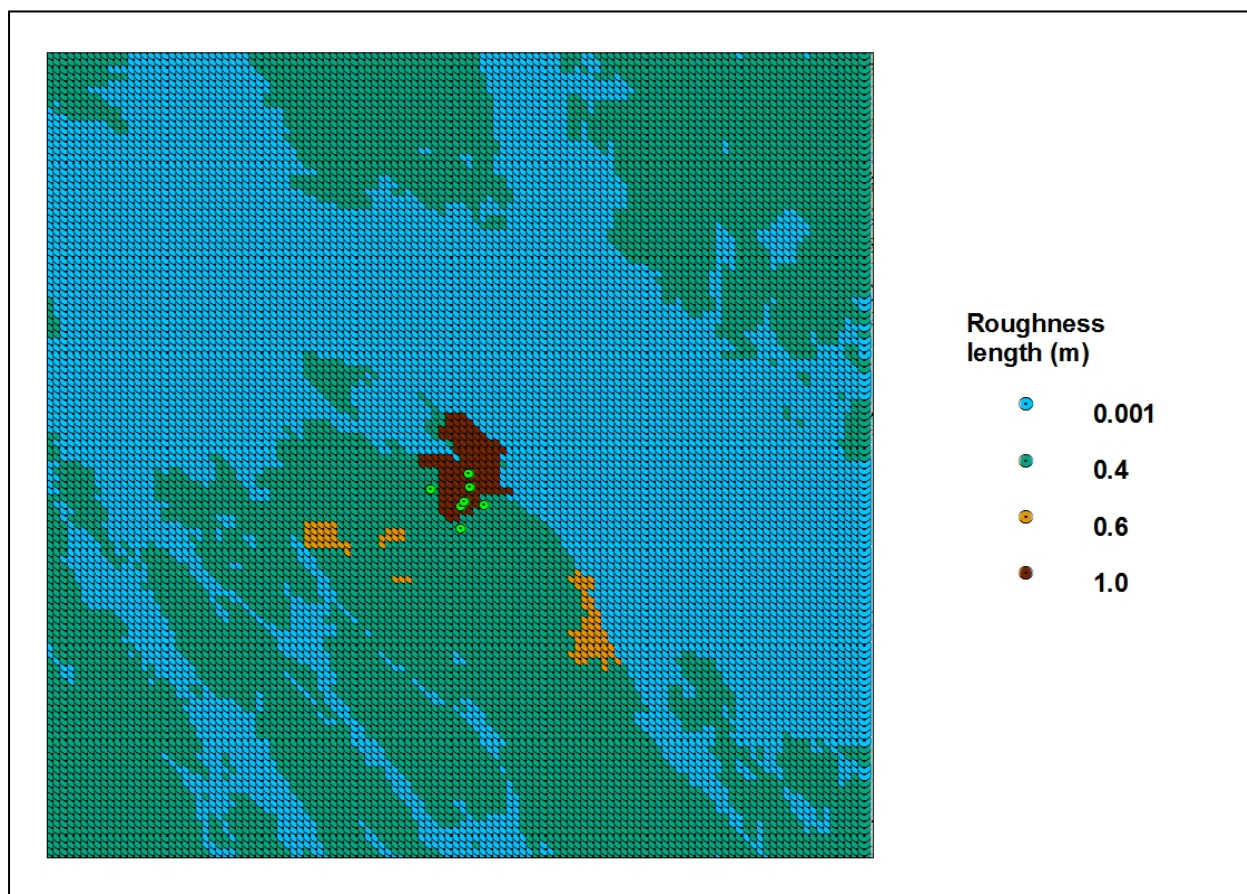


Table 9.11 shows maximum concentrations calculated over the output grid. It can be seen that the concentrations are reasonably sensitive to roughness parameters. It should be noted, though that the fixed value of 0.2m is likely to be unrealistic for the modelling site. The remaining three scenarios are likely to be much more representative of the site characteristics, and give very similar results.

Table 9.11: Maximum annual mean and 100th percentile values calculated over the output grid

Surface roughness length	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
	Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
Constant value of 0.5m at the dispersion site (baseline)	0.09	1.73
Constant value of 0.2m at the dispersion site (baseline)	0.08	1.76
With spatially-varying surface roughness length	0.08	1.81
With spatially-varying surface roughness length and terrain	0.08	1.84

9.4.3. Building and stack downwash effects

The modelling of building effects in ADMS 4 is described in Section 3.2.5. A related effect included in ADMS 4 is stack downwash, which accounts for the effect of the stack structure on the plume. Stack downwash reduces the effective release height, the reduction being greatest when the exit velocity is low and the wind speed is high. For most stacks, this effect is reasonably small, compared with the effects of buildings. For the CCM source, however, the stack has an unusually large diameter, and the effects are likely to be significant. Stack downwash is calculated by default in the model.

9.4.3.1. Baseline case

No building effects were included in the baseline case. Stack downwash was included in the baseline runs.

9.4.3.2. Sensitivity tests

Sensitivity tests were carried out to investigate the effect on modelled concentrations of modelling a building on the Mongstad site. No building dimensions were provided, so a generalised building was set up, with its dimensions based on discussions of a possible building geometry. The building parameters are shown in Table 9.12.

The maximum concentrations calculated over the modelled grid are shown in Table 9.13, both with and without the modelled building.

The maximum concentrations are much higher with the building modelled. With a building the maximum concentrations occur very close to the modelled building, as part or all of the plume can be entrained into the building cavity and the plume centreline can be brought towards the ground. As the maximum modelled concentrations are very different with building effects modelled, and occur in different locations, contour plots of the annual mean concentrations are shown in Figures 9.11 and 9.12, to illustrate the effect of the building on the plume dispersion.

Table 9.12: Building parameters

Parameter	Value
Location of centre	284391, 6747872
Height (m)	48
Length (m)	20
Width (m)	20
Angle of the length of the building from North (°)	0

Table 9.13: Maximum annual mean and 100th percentile values calculated over the output grid

Building effects	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
	Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
No buildings modelled (baseline)	0.09	1.73
Building modelled	0.89	8.99

Figure 9.11: Contour plot for run without building effects

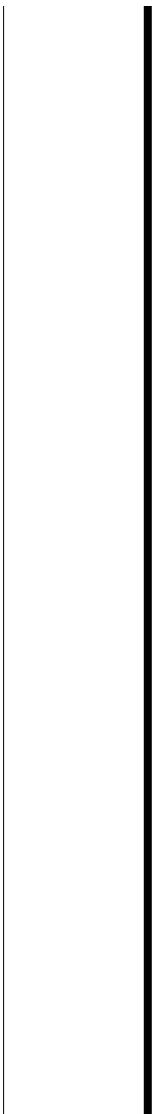


Figure 9.12: Contour plot for run with building effects



9.4.4. Minimum Monin-Obukhov length

In urban and suburban areas a significant amount of heat is emitted by traffic and by buildings at night time, after absorbing heat during the day. The heat emitted warms the air within and above a city. This is known as the urban heat island and its effect is to prevent the atmosphere in a built up area from becoming very stable. In general, the larger the area the more heat is generated and the stronger the effect becomes.

In ADMS 4, the stability of the atmosphere is represented partly by the Monin-Obukhov length (L_{MO}) parameter. In very stable conditions it has a positive value of between 1 metre and 20 metres, with conditions being most stable when L_{MO} is 1m, representing a rural area where conditions may become very stable indeed. In near-neutral conditions the magnitude of the Monin-Obukhov length is very large, and it can be a positive or negative value depending on whether the surface is being heated or cooled by the air above it. In very convective conditions the Monin-Obukhov length is negative with a magnitude of typically less than 20 metres.

The effect of the urban heat island is that, in stable conditions the Monin-Obukhov length will never fall below some minimum value; the larger the city, the larger the minimum value.

ADMS 4 allows the user to define a value of the Monin-Obukhov length at the meteorological site as well as at the dispersion site to account for any difference in the nature of the sites. In addition the Monin-Obukhov length at the dispersion site may vary hourly, with the values entered via the ADMS 4 *.met* file.

9.4.4.1. Baseline case

A constant, minimum Monin-Obukhov length of 1m (the model default) was used in baseline case for the value at both the dispersion site and the meteorological site.

9.4.4.2. Sensitivity tests

In the sensitivity tests only the value of minimum Monin-Obukhov length at the dispersion site was varied, as the sites from which the meteorological data was sourced are all rural sites, and therefore likely to be well-represented by a value of 1m.

In the sensitivity tests:

- the minimum L_{MO} value at the dispersion site was set to a constant value of 5m
- the minimum L_{MO} value at the dispersion site was set to a constant value of 10m. A value of 10m represents the environment of small towns with a population of less than 50,000. This is likely to be a large overestimate of the area around Mongstad, as the urban heat island effect is likely to be much smaller than this over the whole modelling area.

Table 9.14 shows the maximum values predicted over the output grid for the annual mean and 100th percentile of hourly averages. There is very little change in the modelled concentrations, even using the probably unrealistically large value of 10m for the minimum L_{MO} value.

Table 9.14: Maximum annual mean and 100th percentile values calculated over the output grid

Minimum L_{MO} (m)	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
	Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
1 (baseline)	0.09	1.73
5	0.09	1.73
10	0.09	1.73

9.4.5. Surface wetness

The Priestley-Taylor parameter represents the surface moisture available for evaporation, as described in Section 3.2.6.1. The Priestley-Taylor parameter must be between 0 and 3 and the default value is 1, corresponding to moist grassland.

In ADMS 4 a value of Priestley-Taylor parameter can be entered for the dispersion site and the meteorological site independently, to account for any difference in the surface moisture.

9.4.5.1. Baseline case

The baseline run has the model default value of 1 (moist grassland).

9.4.5.2. Sensitivity tests

The sensitivity of the modelled results to the value for the Priestley-Taylor parameter at the dispersion site was tested. The value for the meteorological site was not varied in these tests.

In the sensitivity tests:

- The Priestley-Taylor parameter at the dispersion site was set to 0.45 to represent a surface considerably drier than the default. A value of 0.45 is used for modelling North American Prairies
- The Priestley-Taylor parameter at the dispersion site was set to 1.5 to represent a surface considerably wetter than the default

Table 9.15 shows the maximum concentrations calculated over the model output grid. The results suggest that the modelled concentrations are reasonably sensitive to the Priestley-Taylor parameter, particularly the maximum concentrations, but the tested values represent a very wide range of conditions that would not be expected to occur at a single location. The value of 0.45, for example, would not be representative of the area around the Mongstad site.

Table 9.15: Maximum annual mean and 100th percentile values calculated over the output grid

Priestley-Taylor parameter	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
	Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
1 (baseline)	0.09	1.73
0.45	0.10	2.78
1.5	0.08	1.18

9.4.6. Surface albedo

The albedo characterises the reflectivity of the land surface, as discussed in Section 3.2.6.1. A value of 0.6 is used for snow-covered surfaces and a value of 0.23 is an average value used for non-snow covered surfaces.

In ADMS 4 values for the meteorological site and the dispersion site can be set independently of one another. The albedo at both sites can be varied hourly with the values entered via the ADMS 4 .met file. It would be possible, therefore, to use real snow cover data, to change the value of albedo from hour to hour.

In this Case Study the values of albedo for the meteorological site and the dispersion site were set to be the same, as the meteorological sites are sufficiently close to the Mongstad site that the snow cover is likely to be the same.

9.4.6.1. Baseline case

The surface albedo is assumed to be 0.23 (the model default value) for the baseline model runs.

9.4.6.2. Sensitivity tests

It is likely that the land surrounding Mongstad would be snow-covered for part of the year, which would increase the surface albedo. The sensitivity of the modelled results to the presence of snow cover was tested by varying the albedo value. The albedo for both the meteorological site and the dispersion site were set to 0.6, representing snow-covered ground, for the entirety of December, January and February. The value for the remainder of the year was set to 0.23 (the model default value). Constant snow coverage assumed for three months is an overestimate of actual conditions at Mongstad.

Table 9.16 shows the maximum concentrations calculated over the model output grid. It can be seen that varying the albedo has a relatively small effect on the modelled concentrations, even given the overestimated period for snow coverage assumed in the sensitivity test run.

Table 9.16: Maximum annual mean and 100th percentile values calculated over the output grid

Albedo	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
	Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
Constant value of 0.23 (baseline)	0.09	1.73
December, January and February: 0.6 Remainder of the year: 0.23	0.11	1.74

9.4.7. Latitude

Latitude is input to ADMS 4 and is used to calculate the angle of solar elevation which in turn affects the solar radiation, atmospheric stability and photochemistry.

9.4.7.1. Baseline case

The actual latitude of Mongstad of 61.808 degrees North was used.

9.4.7.2. Sensitivity tests

The latitude of Mongstad cannot, of course, be changed but the sensitivity to the location of the plant at this latitude rather than at another was investigated. A latitude of 70° North, representing the far north of Norway was chosen for the sensitivity test value.

Table 9.17 shows the maximum concentrations calculated over the model output grid. The results show that higher latitude gives lower concentrations in this case, but that the difference is relatively small.

Table 9.17: Maximum annual mean and 100th percentile values calculated over the output grid

Latitude	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
	Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
61° (baseline)	0.09	1.73
70°	0.09	1.51

9.5. Output extents

For the baseline run, concentrations were calculated on an output grid with extent 5km by 5km centred on the Mongstad site and a resolution of 50m.

ADMS 4 has flexible options for specifying the locations for model output. Output grids can be defined with regular spacing, with variable spacing e.g. high resolution near to the source and lower resolution further away. Receptors can be specified at a combination of gridded receptors and individually specified receptors. Up to 10,000 individual receptors may be defined by the user. Importantly, the model results predicted at any point are *independent* of the grid resolution.

To investigate the sensitivity of results to grid resolution the model was run with output grids of 10km by 10km, and 20km by 20km extents. The resolution of these output grids was 100m and 200m, respectively. Table 9.18 shows the maximum concentrations calculated over the model output grid. As the grid resolution increases around the area of maximum plume concentration, the maximum is better resolved and so the maximum concentration increases. As the grid resolution increased from 200m to 50m the maximum annual average concentration did not change significantly and the maximum hourly average concentration changed slightly.

Figures 9.13 to 9.15 show contour plots of the annual mean concentrations for each of the modelled extents.

Note that the model extent can be much larger than 20km, the largest extent modelled in this Case Study; see Section 3.2.4.1 for a discussion of the typical maximum range of ADMS 4.

Table 9.18: Maximum annual mean and 100th percentile values calculated over the output grid

Output extent	Output resolution (m)	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
		Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
5km by 5km (baseline)	50	0.09	1.73
10km by 10km	100	0.09	1.70
20km by 20km	200	0.09	1.65

Figure 9.13: Contour plot for 5km output grid

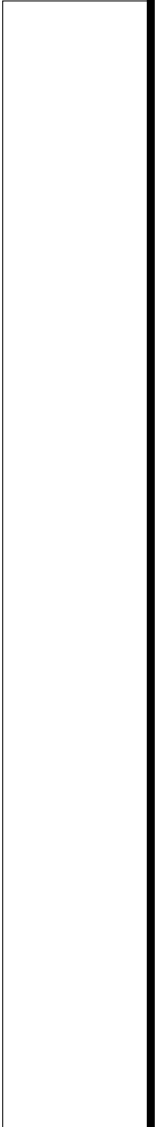


Figure 9.14: Contour plot for 10km output grid

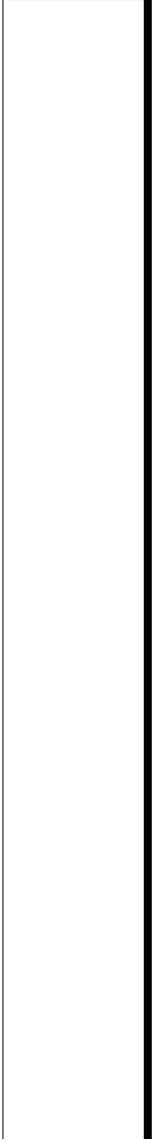
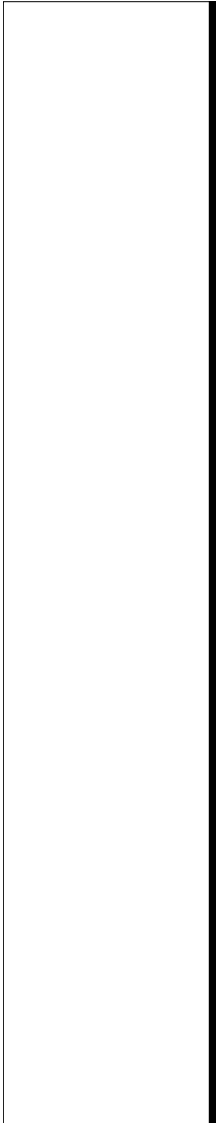


Figure 9.15: Contour plot for 20km output grid



9.6. Sensitivity to meteorology data

The baseline run used meteorological data for the year 2007. As described in Section 9.1, modelled concentrations can show significant inter-annual variation, so the baseline case was repeated using met data for the years 2008 and 2009.

Table 9.19 shows the maximum concentrations calculated over the model output grid. There are significant differences in the maximum values, even for the annual mean, which demonstrates the importance of modelling more than one year of meteorological data for a modelling study.

Figures 9.16 to 9.18 show contour plots of the annual mean concentrations for each of the modelled years of meteorological data. It can be seen that the different years of met data produce markedly different patterns of ground level concentrations. For the three years considered at Mongstad, the pattern of concentration using meteorological data from 2009 is significantly different from that using data for 2007 or 2008.

Table 9.19: Maximum annual mean and 100th percentile values calculated over the output grid

Meteorological data	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
	Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
2007 (baseline)	0.09	1.73
2008	0.09	1.91
2009	0.11	1.74

Figure 9.16: Contour plot for 2007 meteorological data

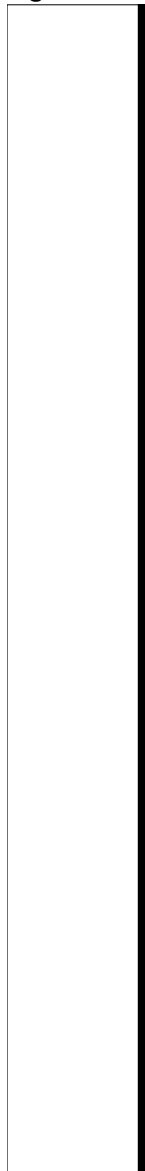


Figure 9.17: Contour plot for 2008 meteorological data

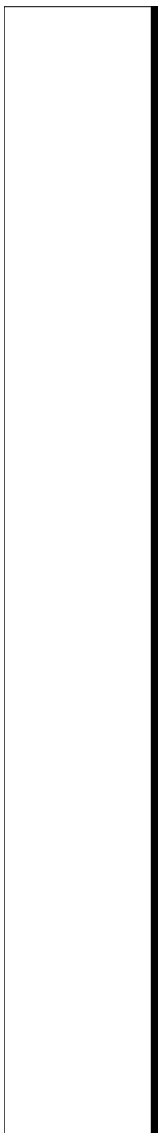
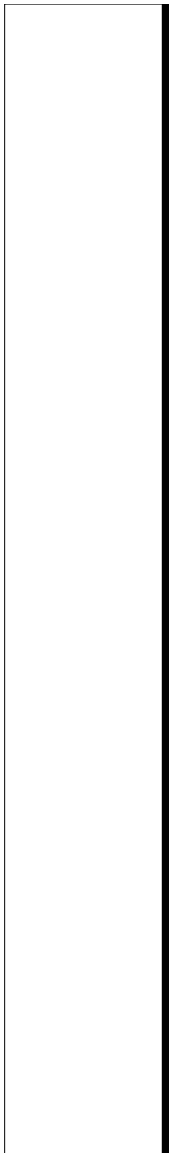


Figure 9.18: Contour plot for 2009 meteorological data



9.7. Emissions of all species from CCM and TCM stacks

The baseline case modelled only the MEA emissions from the CCM stack. In this section results of modelling emissions of all the species emitted from the CCM and TCM stacks are presented. The emissions are those given in Section 9.2.1.

Table 9.20 shows the maximum concentrations calculated over the model output grid. The dispersion patterns are the same for each of the species at this stage, as no specific properties were assigned to the different species, i.e. the modelling does not take into account chemistry or deposition effects.

In future modelling, if detailed parameters were available for each of the compounds as input to the ADMS 4 chemistry and deposition modules, the modelled concentrations would be compound-specific.

Table 9.20: Maximum annual mean and 100th percentile values calculated over the output grid for all pollutants

Pollutant	Annual mean (of hourly averages)		Maximum (100 th percentile of hourly averages)	
	CCM	TCM	CCM	TCM
NO _x	0.47	0.62	9.07	38.4
MEA	0.09	0.02	1.73	1.12
NH ₃	2.51	0.005	2.51	0.30
Ethanal (acetaldehyde)	0.23	0.02	4.49	1.04
Methylamine	0.046	-	0.89	-
N-nitrosodimethylamine	0.00011	-	0.0021	-
N-nitrosodiethanolamine	0.00020	-	0.0038	-
Nitrosomorpholine	0.00017	-	0.0033	-
Dimethylnitramine	0.00013	-	0.0026	-
Ethanolnitramine	0.00016	-	0.0030	-
Methylnitramine	0.00011	-	0.0022	-
Dimethylamine	0.00007	-	0.0013	-
Diethylnitramine	0.00017	-	0.0034	-
Dimethanolnitramine	0.00018	-	0.0035	-
2-(methylnitroamino)-ethanol	0.00018	-	0.0034	-
Nitrosomethylethylamine	0.00013	-	0.0025	-
Nitrosopiperazine	0.00017	-	0.0033	-
1-methyl-N-nitroso-diethylamine	0.00017	-	0.0033	-
Nitrosodiethanolamine	0.00020	-	0.0038	-
Nitrosodiethylamine (NDEA)	0.00011	-	0.0021	-

9.8. Deposition

The treatment of wet and dry deposition by ADMS 4 is described in Sections 3.2.7 and 3.2.8, respectively.

For the amines and related compounds, there is currently limited knowledge of parameters for modelling both dry and wet deposition. Therefore, only limited modelling of deposition was carried out for this Case Study, for illustrative purposes. The approach to the modelling of both wet and dry deposition of amines is very general, but can be refined in future as more information on the deposition behaviour of the amines becomes available. In ADMS 4 deposition parameters can be specified by the user for each species.

The results presented in this section are the deposition flux i.e. rate of deposition of material to the ground, and the ground level concentration. The ground level concentration when deposition is modelled is different from that when deposition is not modelled as there is less material in the plume (plume depletion) and, for dry deposition, there is a change in the shape of the plume that can affect concentrations.

9.8.1. Wet deposition

The washout coefficients used by ADMS 4 to calculate wet deposition are described in Section 3.2.7. In ADMS 4 washout can be modelled:

- i. by a constant value of washout coefficient λ
- ii. by a value of washout coefficient that depends on precipitation rate P : $\lambda = AP^B$ where A and B are constants; A represents the solubility of the material, and B the precipitation dependence.
- iii. for SO_2 and CO_2 by asking ADMS 4 to calculate a pH-limited washout coefficient
- iv. for SO_2 and HCl from point sources, using the ADMS 4 'falling drop' method.

Method ii, a washout coefficient dependent on precipitation rate, has been used in the wet deposition sensitivity tests. For all runs, an hourly precipitation rate, in millimetres per hour, was specified in the meteorological file for every hour. The precipitation data was derived from 12-hourly average measurements at Takle meteorological monitoring site, as described in Section 9.1.

9.8.1.1. Baseline case

In the baseline case wet deposition was not modelled.

9.8.1.2. Sensitivity tests

The sensitivity tests used method ii and investigated the effect of changing the values of the constants A and B :

- $A=0.0001$; $B=0.64$; these are the ADMS 4 default values;
- $A=0.0005$; $B=0.64$; this value of A corresponds to increased solubility; and
- $A=0.0001$; $B=1.28$; this value of B corresponds to increased precipitation dependence.

Table 9.21 shows the values of A and B used and the resulting maximum ground level concentrations due to depletion by wet deposition. It can be seen that the loss of material from the plume to wet deposition processes is likely to be significant.

Table 9.21: Maximum annual mean and 100th percentile values calculated over the output grid

Wet deposition parameters	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
	Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
No deposition modelled (baseline)	0.09	1.73
Washout coefficient A = 0.0001 Washout coefficient B = 0.64	0.10	1.28
Washout coefficient A = 0.0005 Washout coefficient B = 0.64	0.10	1.27
Washout coefficient A = 0.0001 Washout coefficient B = 1.28	0.10	1.28

Due to poor data capture for the precipitation data, fewer lines of meteorological data could be used when wet deposition was introduced, resulting in higher average ground level concentrations over the modelled period.

Table 9.22 shows the deposition rates calculated for each of the combinations of washout coefficient values. Note that it is not yet known which of these values would be most appropriate for modelling MEA (or other amines and their products); they are intended only to show the general sensitivity of the model to these parameters.

The results show that increasing the value of washout coefficient A by a factor of five makes a large difference to the maximum deposition rate whereas doubling the value of washout coefficient B has a much smaller effect. Washout coefficients A and B represent different properties of modelled compounds, and can be specifically set for different types of amines and related compounds.

Table 9.22: The maximum wet deposition rates calculated over the model output grid

Wet deposition	Maximum deposition rate ($\mu\text{g}/\text{m}^2/\text{s}$)
Washout coefficient A = 0.0001 Washout coefficient B = 0.64 (model default values)	0.050
Washout coefficient A = 0.0005 Washout coefficient B = 0.64	0.248
Washout coefficient A = 0.0001 Washout coefficient B = 1.28	0.069

Figure 9.19 shows a contour plot of the wet deposition rate of MEA calculated assuming the model default values.

9.8.2. Dry deposition

ADMS 4 allows dry deposition to be modelled in a variety of ways depending on the level of information available for each pollutant. Full details of the dry deposition modelling options and the associated parameters are given in Section 3.2.8. In summary the options are:

- user-specified values of deposition velocity or surface resistance constant in space and time
- user-specified values of deposition velocity or surface resistance constant in space and varying in time on an hourly or seasonal basis
- user-specified values of deposition velocity spatially varying in space and constant in time (when used with the complex terrain option)
- values of deposition velocity calculated on an hourly basis from the nature of gas (reactive/unreactive/inert) or the diameter and density of particles. The values vary from hour to hour as the wind speed varies

The deposition velocity is an important parameter for dry deposition calculations, but this information is not currently known for the amines and their products. In ADMS 4, if this information is not known, for a gas, the user can specify the nature of the gas: reactive, unreactive or inert. The model then calculates the surface resistance and hence the deposition velocity.

The 'inert' gas type represents the noble gases, such as argon; the 'non-reactive' gases are those that are not expected to undergo significant chemical reaction with the surface, and the 'reactive' gas type is intended for gases that are expected to undergo significant chemical reaction with the surface.

9.8.2.1. Baseline case

In the baseline case dry deposition was not modelled.

9.8.2.2. Sensitivity tests

Two options were used:

- specifying a deposition velocity = 0.02 m/s, constant in space and time
- specifying the pollutant, MEA, as a reactive gas for ADMS 4 to calculate the deposition velocity on an hourly basis. MEA was specified as reactive due to its expected chemical reactivity

Table 9.23 shows the resulting maximum gridded ground level concentrations due to depletion by dry deposition.

Table 9.23: Maximum annual mean and 100th percentile values calculated over the output grid

Dry deposition parameters	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
	Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
No deposition modelled (baseline)	0.09	1.73
Nature of gas = Reactive	0.08	1.67
Constant deposition velocity = 0.02 m/s (UK Environment Agency recommended value for ammonia, short vegetation)	0.08	1.65

Table 9.24 shows the deposition rates calculated for each of the dry deposition scenarios. Modelling the MEA as a reactive gas gave similar deposition rates in this case to those modelled using recommended values for ammonia. However, species-dependent dry deposition information is required for the accurate modelling of amines, nitrosamines, nitramines and aldehyde compounds.

Table 9.24: The maximum dry deposition rates calculated over the model output grid

Dry deposition	Maximum deposition rate ($\mu\text{g}/\text{m}^2/\text{s}$)
Nature of gas = Reactive	0.002
Deposition velocity = 0.02 m/s (UK Environment Agency recommended value for ammonia, short vegetation)	0.002

Figure 9.20 shows a contour plot of the dry deposition rate of MEA calculated assuming a reactive gas.

Figure 9.19: Contour plot for 2009 wet deposition (default parameters)

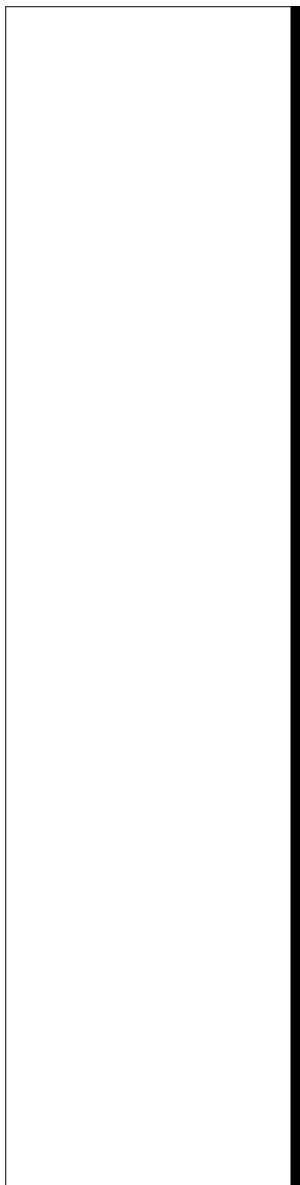


Figure 9.20: Contour plot for 2009 dry deposition of MEA (reactive gas)



9.8.3. Example scenario: Nitrosamine deposition to a local freshwater body

When material is deposited it can pass into bodies of water, into the sea, into the soil or vegetation. If deposited onto land the substance can dissolve and run off the land into bodies of water. Nitrosamines are thought to pose a potential risk to human health through contamination of drinking water reservoirs so deposition to and run off into water bodies are important mechanisms to consider. ADMS 4 currently has no means of calculating the fate of materials after deposition, but an example scenario was run to illustrate how this might be investigated using ADMS 4.

N-nitrosodimethylamine (NDMA) was selected as an indicative nitrosamine and was modelled using the baseline model run with both dry and wet deposition included in addition. The modelled emission rate from the CCM source, 0.0010 g/s, was that given in Table 9.7. For this scenario, it was assumed that no further production of this compound occurs in the atmosphere and that no degradation (such as photolysis) occurs in the atmosphere.

A specified receptor point, located 4km to the south of the CCM stack, was used to represent a theoretical water body. This point does not correspond to a real reservoir location, but was selected for illustrative purposes only. Note that this single point could be extended to a grid of several points to cover the lake in more detail; a single point was used here for simplicity.

For the deposition modelling, the nature of the gas was set to 'reactive' for the dry deposition, and the model default values (Washout coefficient constant A = 0.0001 and Washout coefficient constant B = 0.64) for the wet deposition.

ADMS 4 gives a 'total deposition' value when both wet and dry deposition are run, allowing the cumulative deposition rate to the surface of the water to be output.

Table 9.25 shows the calculated deposition rate at the specified receptor point, representing the rate of deposition of NDMA to the surface of the reservoir. In this case the maximum dry deposition rate was greater than the maximum wet deposition rate, but of the same order of magnitude. The deposition rate (in $\mu\text{g}/\text{m}^2/\text{s}$) could be used to estimate a concentration in the reservoir, if appropriate information about the reservoir volume, catchment area, etc. were known.

Table 9.25: The deposition rates of NDMA calculated at the reservoir surface

Deposition	Deposition rate ($\mu\text{g}/\text{m}^2/\text{s}$)
Dry deposition	2.49×10^{-8}
Wet deposition	1.49×10^{-8}
Total deposition	3.98×10^{-8}

Note that the wet and dry deposition values calculated here are of the same order of magnitude.

9.9. Plume water content / visibility

As the treated flue gas is washed before release, the resulting plume will contain water vapour, so plume visibility due to condensed water in the plume was calculated. ADMS 4 calculates plume visibility using the water content in the plume and the hourly values of relative humidity in the atmosphere as additional inputs to the dispersion modelling.

The plume visibility module is useful for two main applications: to assess the location, extent and duration of plumes that are visible to nearby residents, and to calculate the water content of the plume at any given location, in order to provide information for any calculation of amines and their products onto water droplets.

For future studies, the ADMS 4 plume visibility module can use user-defined specific humidity profiles, entered via the .prf file, to reflect local conditions, which could change the predicted length and frequency of the visible plumes.

9.9.1. Plume visibility results

9.9.1.1. Baseline case

Plume visibility was not modelled in the baseline case. It was assumed there was no liquid water in the plume.

9.9.1.2. Sensitivity tests

The treated flue gas of the CCM and TCM is washed before release from the stacks. The resulting plumes therefore contain water vapour. The sensitivity tests modelled the presence of liquid water in the emissions from the CCM and TCM. The water mixing ratio for both the CCM and the TCM was the provided value of 0.027kg/kg (a water emission concentration value 2.3 mol%).

Tables 9.26 and 9.27 provide a summary of the predicted visible plume results for the CCM and for the TCM. The results show that even though visible plumes are likely to be present for most of the hours of the year, the lengths of the visible plumes from both stacks are not expected to be very large. The largest calculated visible plume length was only 327m, and the average values are much lower.

Table 9.26: Plume visibility – CCM

Year	Number of hours with visible plume	% hours with visible plume	Average length of visible plume (m)	Maximum length of visible plume (m)
2007	7903	95.0	35	229
2008	7479	87.8	36	327
2009	7546	92.7	35	270

Table 9.27: Plume visibility – TCM

Year	Number of hours with visible plume	% hours with visible plume	Average length of visible plume (m)	Maximum length of visible plume (m)
2007	7928	95.3	7	56
2008	7608	89.3	7	81
2009	7636	93.8	7	69

9.10. Modelling of other major Mongstad sources

In section 9.2.2 the stack and emission parameters from the major sources at Mongstad, other than the CCM and TCM, were given.

9.10.1. Baseline case

In the baseline case the only source modelled was the CCM stack and the only pollutant modelled was MEA.

9.10.2.Sensitivity tests

A run was carried out to calculate total concentrations of oxides of nitrogen (NO_x) and sulphur dioxide (SO_2) from the CCM, TCM and the other major Mongstad sources. The supplied data shows zero emissions of SO_2 from the CCM and TCM.

Maximum annual mean concentrations calculated over the output grid are given in Table 9.28, for each of the modelled meteorological years.

Table 9.28: Maximum annual mean values calculated over the output grid

Year	Modelled concentrations ($\mu\text{g}/\text{m}^3$)	
	NO_x	SO_2
2007	2.76	0.71
2008	2.62	0.67
2009	3.31	0.87

9.10.2.1. NO_x chemistry

Concentrations of NO_x and NO_2 could be of interest for several reasons; they can contribute to nitrogen deposition (together with the nitrogen deposited from the amines and related compounds), and the concentrations of NO_x in a plume can have a significant effect on the chemical reactions of amines.

The ADMS 4 chemistry module currently models the photochemical reaction of NO_2 and NO . The chemistry module of ADMS 4 and the more advanced chemistry module of ADMS-Urban are described in Section 3.2.9. The chemistry module requires representative local background data to be input.

The ADMS 4 NO_x chemistry module was used to calculate concentrations of NO_2 from the CCM, TCM and other major sources. Although background data was sourced, this was received too late for inclusion in the modelling. Instead, a constant (annual average) value of 25ppbv for the background ozone was assumed, to represent the area surrounding the Mongstad site. For future model runs, the sourced background data could be used to better represent the background concentrations of ozone, as well as including background values for NO_2 and NO .

Table 9.29 shows the maximum annual mean concentrations calculated over the output grid for each of the modelled meteorological years. By comparing the maximum modelled concentrations of NO_2 with the maximum concentrations of NO_x in Table 9.28, it can be seen that the NO_2 makes up around half of the maximum NO_x concentrations. Note that this percentage relates to the maximum ground level concentrations only; the percentage will vary with distance from the sources.

Table 9.29: Maximum annual mean values calculated over the output grid

Year	Modelled NO_2 concentrations ($\mu\text{g}/\text{m}^3$)
2007	1.49
2008	1.29
2009	1.64

9.11. Summary of model runs

This section summarises the model results relating to MEA concentrations, to show the impact on modelled concentrations of including complex effects and varying model parameters.

Table 9.30 shows a summary of maximum modelled concentrations for the various complex effects investigated in this Case Study.

Table 9.31 shows a summary of the sensitivity test results for the various parameters tested in this Case Study.

Table 9.30: Maximum annual mean and 100th percentile values calculated over the output grid. Summary of complex effects model runs

Complex effect	Details	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
		Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
Baseline run	No terrain No spatially-varying roughness No buildings modelled	0.09	1.73
Complex terrain	With terrain	0.09	1.78
Surface roughness	With spatially-varying roughness	0.08	1.81
Building	With a general building included	0.89	8.99

Table 9.31: Maximum annual mean and 100th percentile values calculated over the output grid. Summary of sensitivity tests for various model parameters

Parameter details	Concentration of MEA ($\mu\text{g}/\text{m}^3$)	
	Annual mean (of hourly averages)	Maximum (100 th percentile of hourly averages)
Minimum L_{MO} (m)		
1 (baseline)	0.09	1.73
5	0.09	1.73
10	0.09	1.73
Priestley-Taylor parameter		
1 (baseline)	0.09	1.73
0.45	0.10	2.78
1.5	0.08	1.18
Albedo		
Constant value of 0.23 (baseline)	0.09	1.73
December, January and February: 0.6 Remainder of the year: 0.23	0.11	1.74
Latitude		
61° (baseline)	0.09	1.73
70°	0.09	1.51
Meteorological data		
2007 (baseline)	0.09	1.73
2008	0.09	1.91
2009	0.11	1.74
Wet deposition		
Washout coefficient A = 0.0001 Washout coefficient B = 0.64	0.10	1.28
Washout coefficient A = 0.0005 Washout coefficient B = 0.64	0.10	1.27
Washout coefficient A = 0.0001 Washout coefficient B = 1.28	0.10	1.28
Dry deposition		
Nature of gas = Reactive	0.08	1.67
Constant deposition velocity = 0.02 m/s (UK Environment Agency recommended value for ammonia, short vegetation)	0.08	1.65

Modelling the presence of a building significantly affects the predicted maximum ground level concentrations. The maximum concentration in the presence of a building would be near to the building and to the stack and hence likely to occur on-site. When modelling on-site and near field concentrations it would be important to model those buildings likely to affect the plume dispersion.

The model parameters fall into several categories:

- **Latitude, meteorological data:** These are fixed for the site and particular year under consideration. Year-to-year the changing meteorology can significantly affect the patterns of concentration and maximum short term concentrations. No further information or development is required.
- **Minimum L_{MO} , Priestley-Taylor parameter:** The model results were not sensitive to changing these parameters within a range that would be suitable for Mongstad. No further information or development is required.
- **Albedo:** The model results showed some sensitivity to changing albedo. Detailed or approximate information on snow cover could be used in future modelling.
- **Wet and dry deposition:** The model results for concentration did not show great sensitivity to the changes made but the deposition fluxes to the surrounding area were sensitive. The deposition parameters are highly substance-dependent and more information would be required for future modelling.
- **Plume visibility:** The plume visibility module calculates the liquid water content of the plume which is important for environmental assessment purposes. In addition the module could be developed to assist in an enhanced treatment of wet deposition and/or chemistry within water droplets.
- **Chemistry:** NO_x chemistry was modelled as this is the current chemical scheme in ADMS 4. Further information on amine chemistry could lead to the development of an amine chemistry module so that the fate of the amines and their reaction products, their concentration and deposition, can be more accurately modelled.

10. Recommendations for Model Development

10.1. Introduction

Sub-task 3 builds on the work carried out and previously presented, from Sub-task 1, the model evaluation of ADMS 4 and Sub-task 2, the Case Study of the application of ADMS 4 to emissions at Mongstad. Using that work and work from other studies, such as Phase 1 of the NILU “CO₂ and Amines Screening Study for Environmental Risks” project, we assess the model development required to improve the treatment of the fate of amines together with the other chemicals released at Mongstad.

In the following section, Section 10.2, we discuss the key processes that are required in a model for an appropriate treatment of the dispersion and fate of the amines and hence list those aspects of ADMS 4 that we recommend be developed both on relatively short (1 year) and longer (3 years) timescales. In the subsequent sections we describe the recommended developments in some detail followed by some comments on the proposed approach to validating the developments. We also discuss the accompanying requirements for new data and improved scientific understanding, e.g. gaseous amine chemistry, where these are not currently available.

10.2. ADMS 4 model features and developments required for the treatment of amines

In Sub-task 1 the features of the ADMS 4 dispersion model, its validation, quality control for its development and comparison with other candidate models were described. The Case Study and sensitivity tests of Sub-task 2 demonstrated the ability of ADMS 4, in its current form, to model the fate of amines emitted from Mongstad and the parameters to which model results are most sensitive. The relevant model features for the modelling of amines on the local to regional scale (up to 50-100km from the source) were:

- the representation of sources in ADMS 4: point, area, line, volume and jet sources are modelled with or without plume rise. This requires no further development.
- meteorological input and output: the data required by ADMS 4 are available from meteorological monitoring sites around Mongstad. Measurements of specific humidity, cloud cover and rainfall, preferably at a time resolution higher than 12 hours, at Mongstad or Fedje would improve the input data, ensuring they are representative of the site.
- parameterisation of the boundary layer: the ADMS 4 approach using Monin-Obukhov length and boundary layer height scaling needs no further development.
- dispersion over flat terrain: the advanced Gaussian-type approach with Runge-Kutta solution of the integral equations of conservation for plume rise needs no further development.
- the effects of buildings: the modelling of buildings is adequate. Including on-site buildings in the modelling is something to which near field modelled concentrations are very sensitive. If near field concentrations are important, input data on the site buildings is required.
- spatial variation in surface effects of changes in surface elevation and surface roughness: the ADMS 4 approach need no further development.
- gas phase chemistry: subject to information being available, reactions for amine chemistry can be incorporated into ADMS 4, using the existing ADMS 4 chemistry framework. To model the creation of nitrate and sulphate particles the 8-reaction NO_x scheme from ADMS-Urban or other more advanced schemes could be included in ADMS 4.
- Aqueous phase chemistry and plume visibility: the ADMS 4 approach needs no further development for the modelling of condensed water visible plumes, but could be developed to model aqueous phase chemistry and in-plume microphysics (droplet growth and evaporation).

- wet and dry deposition: modelling of wet and dry deposition would benefit from improved knowledge of the physical parameters for amines and their products and from use of a falling drop model of wet deposition for amines and ammonia. An algorithm for stomatal surface resistance could be included in the dry deposition algorithms subject to the information available on the behaviour of amines and nitrosamines.
- model inputs and outputs: the ADMS 4 approach that allows easy input of data and a link to contour plotting in ArcGIS, MapInfo or Surfer, needs no further development.

Table 10.1 summarizes these required model features and the development required together with enhanced data requirements. It can be seen from Table 10.1 that ADMS 4 already deals appropriately with all the dynamical aspects of the dispersion of amines, but that aspects connected with the chemical and physical properties of amines require further development, in particular chemical transformation and deposition processes.

In the following sections we consider in turn detailed recommendations for the development of:

- a. chemistry modules for amines (both gaseous and aqueous phases, including particulate formation);
- b. modification of the deposition algorithms in ADMS 4 to take account of the properties of amines; and
- c. other miscellaneous items: accumulation of amines in lakes and accounting for the ice phase including snow.

Table 10.1: ADMS 4 model features, development required and enhanced data requirements for the modelling of amines

Model features	ADMS 4 features	Development required?	Enhanced data required?
Source representation	Comprehensive treatment of source types	×	×
Source emission rates	User-specified	×	✓ Refined emission rates required.
Meteorological input	User-specified data	×	✓ Local cloud cover, rainfall & humidity
Atmospheric boundary layer structure	Based on Monin-Obukhov length / boundary layer height scaling	×	×
Dispersion over flat terrain	Advanced second-generation Gaussian type model	×	×
Effects of buildings on dispersion	ADMS 4 buildings module	×	✓ Data for on-site buildings
Complex terrain effects	ADMS FLOWSTAR module allows for variable surface elevation and roughness	×	×
Chemistry	Includes NO _x chemistry	✓ Addition of amine chemistry; Implementation of NO _x schemes from ADMS-Urban including particulate formation	✓ Local background measurements
Wet deposition	Washout coefficient or falling drop method	✓ Modifications required for amines and their products	✓ Washout and Henry's Law coefficients, and acid-base disassociation coefficients
Dry deposition	Resistance formulation	×	✓ Estimate for deposition velocity of amines and their products.
Other items	Features not currently included in ADMS 4.	✓ Accumulation in lakes, ice phase including snow	✓ To be determined

10.3. Chemistry

10.3.1. Current state of knowledge of amine chemistry

The chemical reactions of amines present a challenge to dispersion modelling, as amines are transformed not only through complex photochemical reactions in the gaseous form, but also through potentially rapid partitioning into solid and liquid phases. Add to this the fact that there could be many different parent amine species, and the result is a complex picture.

There is currently a very incomplete picture of the chemical reactions and the rates of reaction in all three phases (gaseous, particulate, aqueous), and it is recognised that substantial research needs to be carried out before detailed chemical reaction schemes may be constructed for use as/with models. Indeed one of the Primary Recommendations of the 'CO₂ and Amines Screening Study for Environmental Risks' NILU project³⁴ is that development of models to specifically incorporate amines "should begin after chemical pathways/reactivity has been well established".

Recent projects have nevertheless produced some solid information about the atmospheric fate of the amines likely to be used in CO₂ capture projects. For the gaseous chemistry, we know that the most important process is the reaction with hydroxyl (OH) radicals. Not only do the amines themselves react with OH radicals, but their products will also react with OH, producing complex, branched reaction pathways. The main products expected are aldehydes, amides, nitrosamines, and nitramines, of which nitrosamines and nitramines are of particular interest due to their known harmful effects to human health and to ecosystems. Investigations have led researchers to suggest that the timescales of the reactions of other species (notably nitrosamines, nitramines and alcohols) with OH radicals are such that they should be considered for inclusion in amine degradation schemes in models.

Amines are generally very soluble, so their uptake into water droplets and the resulting aqueous chemistry is likely to be significant. The studies at the European Photochemical Reactor in Valencia³⁵ suggest that this is likely to be a very important and rapid process for monoethanolamine (MEA), the solubility of which is five to six orders of magnitude higher than that of ammonia or sulphur dioxide.

It is also understood that the uptake of nitrosamines and nitramines into water droplets could be important processes. Nitrosamines are generally soluble in water if they have three carbon atoms or less and nitrosamines will be very soluble if they have hydroxyl groups (i.e. if they have alcohol groups).

Amines have the potential to attach to particulate matter in the atmosphere. It is likely, for example, that the amines will replace ammonia in ammonium salts to form the analogous aminium salts. It is possible that further chemical reactions, such as oxidation processes, could occur within these particles.

10.3.2. Recommendations for gas phase chemistry model development

In the NILU worst case modelling study³ and our calculations of Sub-task 2, no chemical reactions of amines were considered. Instead, assumed concentrations (and hence emission rates) of amines and important products were specified at source and dispersed and deposited without reaction. For the inclusion of chemistry in ADMS 4 we suggest three phases of development of different levels of complexity:

- (i) a relatively simple scheme assuming constant degradation rates for representative amines and important products
- (ii) a more advanced version of (i) in which a dependence of degradation rates on estimates of OH, solar intensity etc is included
- (iii) a detailed chemistry scheme.

Some details of each of the proposed developments are given in the following sections.

³⁴ Knudsen, S. et al., 2009: Summary Report: Amine Emissions to Air during Carbon Capture. NILU Ref OR 8/2009

³⁵ Nielsen, C.J. et al., 2010. Atmospheric Degradation of Amines (ADA) Summary Report: Gas phase photo-oxidation of 2-aminoethanol (MEA). CLIMIT project no. 193438

10.3.2.1. Simple degradation scheme for amines

In this scheme the degradation of amines will be accounted for using the set of the four representative amines (MEA, AMP, MDEA, PIPA) discussed in the NILU reports³ as a basis. The scheme will include degradation of these products and formation and subsequent degradation of important products (i.e. those toxic compounds formed in the greatest amounts) using simple estimates of decay rates. The key degradation pathways and estimates of decay timescales will be informed by current knowledge and ongoing and imminent investigations such as the studies at the European Photochemical Reactor, EUPHORE, which focus on each of the main, representative amines under pseudo-natural conditions.

The timescale for this development is one year.

Information required: key degradation pathways and estimates of decay timescales for MEA, AMP, MDEA and PIPA. Some current knowledge to be supplemented by results from ongoing and imminent investigations.

10.3.2.2. More advanced degradation scheme for amines

This development will use the same approach as 10.3.2.1 above, but employ more advanced estimates of degradation rates, for example dependence on estimates of OH concentration, NO_x concentration and parameters such as solar elevation and temperature. The details of the important degradation pathways and reaction rates will again be informed by current knowledge and ongoing and upcoming investigations, but the longer three year timescale proposed should allow a much greater input from new studies of amine chemistry being undertaken. As part of this development the more advanced NO_x chemistry scheme used in ADMS-Urban, including nitrate particulate formation, will also be implemented.^{36,37}

An important requirement for an enhanced degradation scheme is background monitoring of O₃, NO_x, NH₃ etc. There are two background monitoring sites located in the west of Norway, at Sandve and Kårvatn. Sandve is located around 200km to the south of Mongstad, while Kårvatn is located around 300km to the north east of Mongstad. Ozone is measured on an hourly basis at both Sandve and Kårvatn, and NO₂ is measured at Kårvatn on a daily basis only. Data from these sites could be used, but measurements at or near to the Mongstad site would give a better representation of background levels and allow a more accurate input of background concentrations into this model. An alternative is for a regional model to be used for background data.

The timescale for this development is within 3 years.

Information required: degradation of amines as a function of ambient concentrations, solar insolation and temperature. Hourly background concentration data representative of Mongstad.

³⁶ ADMS Urban Technical Specification, document P18/03

³⁷ ADMS Urban Technical Specification, document P18/04

10.3.2.3. Detailed amine chemistry model

The most comprehensive methodology for studying the chemical transformation of amines is the utilization of a detailed chemical scheme. Development of such a scheme for inclusion in ADMS 4 will require a fuller understanding of the important reaction pathways and their rates than is currently available. Even then, because of the complexities of amine chemistry, it is likely that a simplified scheme will need to be employed.

The timescale for such a development is significant and likely to be over three years.

Information required: detailed chemical reaction scheme for amines.

10.3.2.4. Implementation of proposed schemes into ADMS 4

The ADMS suite of models has been developed in such a way that different ADMS models can include different chemical schemes, for instance the 8-reaction Generic Reaction Set (GRS)³ for NO_x and 95-reaction Chemical Bond Model (CBM)⁴ are currently available in ADMS-Urban but not ADMS 4. Implementation in ADMS 4 of each of schemes described above is, therefore, relatively straightforward once the schemes themselves have been written.

10.3.3. Recommendations for wet phase chemistry model development

The gases released at Mongstad will have significant water content and, in addition, the ambient air frequently has high humidity. Therefore, as the condensed plume visibility calculations of Sub-task 2 have shown, the dispersing plumes frequently contain liquid water in the form of small cloud drops. These droplets are likely to form on cloud condensation nuclei (CCN) which are entrained into the plume at the stack exit, (typically ammonium sulphate, ammonium nitrate or sodium chloride), emitted from the stack or formed at the stack exit. As amines are very soluble and they also displace ammonium from ammonium sulphate³⁸, there is a strong likelihood that amines in the plume will dissolve in the cloud droplets and subsequently displace ammonium resulting in formation of aminium sulphate which will be in particle form after the cloud droplets have evaporated.

It is recommended that modelling of these processes occurring in the condensed plume be undertaken at two levels of complexity as follows:

10.3.3.1. Basic model for aqueous phase chemistry in plume

In this model significant simplifying assumptions are made. Where the condensed plume model of ADMS 4 shows the presence of 'significant' condensed plume, we will assume complete and instantaneous displacement by amines of the ammonium component of ammonium sulphate estimated to be within cloud droplets as CCN. Thus the rate of generation of aminium sulphate particles and hence loss of amines may be estimated.

The timescale for this development is one year.

Information required: details of the particulate concentration, distribution and chemical content of particles (if any) released from the stack. Data on ambient particle concentrations at Mongstad and their chemical composition. Estimates of background ammonium sulphate concentration.

³⁸ Bzdek, B.R., 2010: Amine exchange into ammonium bisulphate and ammonium nitrate nuclei. Atmos. Chem. Phys. Discuss., **10**, 45–68.

10.3.3.2. Advanced model for aqueous phase chemistry

In this development the detailed micro-physical and chemical processes associated with the condensed cloud drops are included within the model. This will include droplet growth and evaporation, the rate of uptake of amines into cloud droplets, their subsequent dissociation taking account of other species (e.g. ammonia) and chemical reaction with the droplets. The model for uptake of amines and their dissociation will draw on the falling drop model for wet deposition discussed in Section 3.2.7.3.

The timescale for this development is 3 years.

Information required: behaviour of amines in cloud droplets. Details of the particulate concentration, distribution and chemical content of particles (if any) released from the stack. Data on ambient particle concentrations at Mongstad and their chemical composition. Estimates of background concentration of ammonium sulphate, ammonium nitrate and NH_3 .

10.3.3.3. Aqueous phase chemistry – other considerations

A NILU study³⁹ discusses the tendency for CCN containing amines ‘activating’ at a lower humidity than would be the case without amines because of the hygroscopic nature of amines and their tendency to reduce the surface tension at the droplet surface. There is a suggestion that this can accelerate the development of rain size droplets. However, as most rain in northern latitudes is initially formed in the ice phase (which subsequently melts during descent), this mechanism may only be relevant to drizzle formation and then only if the impact of the amines is to significantly reduce the **number** of CCN ‘activated’ so that they subsequently grow faster before coalescence. The above report provides no evidence for this, however the processes could be modelled in the context of ADMS 4 using a drop growth model for droplet condensation and coalescence.

The timescale for this development is 3 years

Information required: behaviour of amines in cloud droplets. Details of the particulate concentration, distribution and chemical content of particles (if any) released from the stack. Data on ambient particle concentrations at Mongstad and their chemical composition. Estimated background concentration of ammonium sulphate and ammonium nitrate, NH_3 .

10.3.4. Recommendations for gas to particle conversion/aerosol chemistry

Gas to particle conversion is accounted for in the previous sections 10.3.2 and 10.3.3 as follows:

- (i) generation of particulate nitrate from NO_x emissions through the inclusion of the more advanced NO_x chemistry model in ADMS 4;
- (ii) generation of particles from amines including in the gaseous phase amine model (10.3.2.2); and
- (iii) generation of ammonium sulphate by displacement of ammonium in ammonium sulphate included in 10.3.3 for the aqueous phase. This will be included for low humidity by appropriate modification of this aqueous phase model.

³⁹ Karl, M. Amines and Rainfall Impact of Amines on Rainfall from Plume Clouds (Task 5.3). 2009. NILU Ref: OR 74/2008

10.4. Deposition

The wet and dry deposition models of ADMS 4 have been described in Sub-task 1 and also used in the Case Study (Sub-task 2). In the following sections on wet deposition (4.1) and dry deposition (4.2) we make recommendations for the modification of the models so that they may be used specifically for amines.

10.4.1. Recommendations for wet deposition model development

Figure 10.1 gives an overview of the processes that lead to wet deposition of pollutants in the air. The magnitude of the Henry's law and acid-base disassociation coefficients govern the quantities that will be present in a particular form; high values of the Henry's law and disassociation coefficients lead to the highest rates of deposition for a given rainfall rate. Table 10.2 gives the Henry's Law and disassociation coefficients for ammonia and for some representative amines, including MEA, but data for some amines and amine degradation products are not currently available.

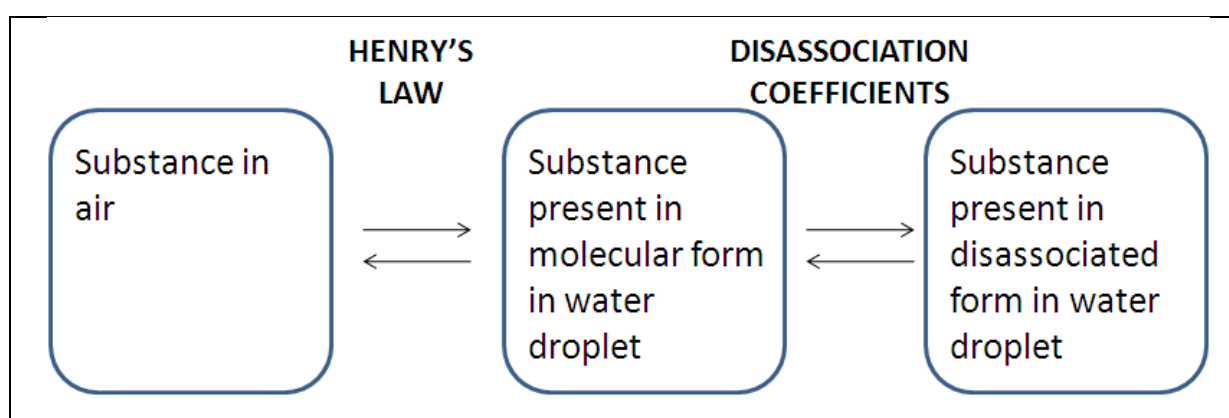


Figure 10.1: Overview of processes that lead to wet deposition

As described in Sub-task 1 there are currently three methods for modelling wet deposition in ADMS 4. Two of the methods apply the classical approach with empirically determined 'washout' coefficients (estimated from field studies and the Henry's Law constants), and the third method solves the full set of coupled equations that govern the system. The methods are summarised below:

- The simplest method for treating wet deposition is to use a washout coefficient for each chemical species dependent on the rainfall rate. A spatial variation of this parameter can be included in the model.
- In order to take some account of the change in pH within the droplet brought about by the disassociation of the pollutant, the washout coefficient method is applied in conjunction with a pH limiting method for SO₂ and CO₂.
- A more advanced method (falling drop method) includes a kinetic model for the uptake of gases at the water surface; this method is currently applied to SO₂ and HCl.

The recommendations for model development comprise adaptation/modification of each of the three methods to the species emitted at Mongstad especially amines and also ammonia. The proposed developments are described in turn below. In addition, a new, simple method for modelling the wet deposition of NO_x has been proposed.

Where relevant, the discussions include references to ammonia (NH_3), not only because ammonia is released from the stack, and potentially from other facilities on the Mongstad site (e.g. the “chilled ammonia process,” another carbon capture technique that will emit ammonia) but also because its Henry’s Law and acid-base disassociation coefficients are similar to some of the amines for which coefficients have been collated, for example methylamine. But note that ammonia’s behaviour will be different from other species, such as MEA and ethylenediamine, as relatively, these have very large Henry’s Law coefficients.

As mentioned above, the magnitude of the Henry’s Law and disassociation coefficients govern the behaviour of the species; it is therefore important that these data are available for each of the relevant amines and their degradation products in order for calculations of wet deposition to be undertaken. Available data for some examples of amines and their degradation products, and for ammonia, have been collated and presented in Table 10.2. This shows that the dataset is not currently complete. Referring to the table we see that, where known, the disassociation coefficients (K_b) of the amines are relatively small. For example, whereas sodium hydroxide, a base that disassociates readily, has a K_b value of $O(10^{-1})$, the K_b values of ammonia and the amines are $O(10^{-4})$ or smaller. This means that these species do not readily disassociate, and will outgas back into clean air below the plume. The exceptions to this are the amines that have very high Henry’s Law coefficients, for example MEA (ethanolamine) and ethylenediamine. For the pollutants that outgas readily, using the basic washout coefficient approach to modelling is likely to overestimate the amount of wet deposition that occurs.

Table 10.2: Summary of Henry's Law constants (H_a) and acid-base dissociation coefficients (K_b) for amines and ammonia

Substance	Formula [CAS number]	H_a (mol/ L atm)	Reference	K_b	Reference
Ammonia	NH ₃	5.8		1.77×10^{-5}	
Methylamine	CH ₃ NH ₂	3.6×10^1 9.0×10^1 1.4×10^2	Wilhelm et al. [1977] ⁴⁰ Christie and Crisp [1967] ⁴¹ Bone et al. [1983] ⁴²	4.4×10^{-4}	Lawrence [2004] ⁴³
Ethylamine	C ₂ H ₅ NH ₂ [75-04-7]	1.0×10^2 3.5×10^1 8.1×10^1	Butler and Ramchandani [1935] ⁴⁴ Wilhelm et al. [1977] Christie and Crisp [1967]	4.3×10^{-4}	Lawrence [2004]
Propylamine	C ₃ H ₇ NH ₂ [107-10-8]	8.0×10^1 6.7×10^1	Butler and Ramchandani [1935] Christie and Crisp [1967]		
Butylamine	C ₄ H ₉ NH ₂ [109-73-9]	6.6×10^1 5.8×10^1	Butler and Ramchandani [1935] Christie and Crisp [1967]		
Pentylamine	C ₅ H ₁₁ NH ₂	4.1×10^1	Christie and Crisp [1967]		
Hexylamine	C ₆ H ₁₃ NH ₂	3.7×10^1	Christie and Crisp [1967]		
Dimethylamine	(CH ₃) ₂ NH [124-40-3]	3.1×10^1 5.7×10^1	Wilhelm et al. [1977] Christie and Crisp [1967]	4.4×10^{-4}	Lawrence [2004]
Diethylamine	(C ₂ H ₅) ₂ NH [109-89-7]	3.9×10^1 1.5×10^1 1.3×10^2 3.9×10^1	Christie and Crisp [1967] Yaws and Yang [1992] ⁴⁵ USEPA [1982] ⁴⁶ Meylan and Howard [1991] ⁴⁷		
Dipropylamine	(C ₃ H ₇) ₂ NH	1.9×10^1	Christie and Crisp [1967]		
Dibutylamine	(C ₄ H ₉) ₂ NH	1.1×10^1	Christie and Crisp [1967]		
Trimethylamine	(CH ₃) ₃ N [75-50-3]	9.6	Christie and Crisp [1967]		
Triethylamine	(C ₂ H ₅) ₃ N	6.7	Christie and Crisp [1967]		

⁴⁰ Wilhelm, E., R. Battino, and R. J. Wilcock. Low-pressure solubility of gases in liquid water. Chem. Rev., 77, 219–262, 1977

⁴¹ Christie, A. O. and D. J. Crisp. Activity coefficients on the n-primary, secondary and tertiary aliphatic amines in aqueous solution. J. Appl. Chem., 17, 11–14, 1967

⁴² Bone, R., P. Cullis, and R. Wolfenden. Solvent effects on equilibria of addition of nucleophiles to acetaldehyde and the hydrophilic character of diols

⁴³ Lawrence, S. A. Amines: synthesis, properties and applications Cambridge University Press, 2004 pp.315-316

⁴⁴ Butler, J. A. V. and C. N. Ramchandani. The solubility of nonelectrolytes. Part II. The influence of the polar group on the free energy of hydration of aliphatic compounds. J. Chem. Soc., pages 952–955, 1935

⁴⁵ Yaws, C. L. and H.-C. Yang. Henry's law constant for compound in water. In C. L. Yaws, editor, Thermodynamic and Physical Property Data, pages 181–206. Gulf Publishing Company, Houston, TX, 1992

⁴⁶ USEPA. Air and steam stripping of toxic pollutants. Tech. Rep. EPA-68-03-002, Industrial Environmental Research Laboratory, Cincinnati, OH, USA, 1982

⁴⁷ Meylan, W. M. and P. H. Howard. Bond contribution method for estimating Henry's law constants. Environ. Toxicol. Chem., 10, 1283–1291, 1991

Table 10.2: continued

Substance	Formula [CAS number]	H _a (mol/ L atm)	Reference	K _b	Reference
Ethylenediamine	H ₂ NCH ₂ CH ₂ NH ₂	5.9 x 10 ⁵	Westheimer and Ingraham [1956] ⁴⁸		
Hexamethyleneimine	(CH ₂) ₆ NH	1.6 x 10 ²	Cabani et al. [1971b] ⁴⁹		
Ethanolamine (MEA)	HOC ₂ H ₄ NH ₂ [141-43-5]	6.2 x 10 ⁶	Bone et al. [1983]	4.0 x 10 ⁻⁵	Karl [2009] ³⁹

⁴⁸ Westheimer, F. H. and L. L. Ingraham. The entropy of chelation. J. Phys. Chem., 60, 1668–1670, 1956

⁴⁹ Cabani, S., G. Conti, and L. Lepori. Thermodynamic study on aqueous dilute solutions of organic compounds. Part 1. — Cyclic amines. Trans. Faraday Soc., 67, 1933–1942, 1971b

10.4.1.1. Washout coefficient method

The first development will be to derive improved washout coefficients for the different chemical species so that they may be used with ADMS 4. This is an improvement on the Case Study (Sub-task 2) approach where standard washout coefficients were used, which were constant for all species.

The timescale for this development is less than one year

Information required: washout coefficients for amines, supplied or may be derived from existing information.

The washout coefficient Λ is dependent on a large number of parameters, including the nature of the pollutant, rainfall rate, droplet size distribution and the pollutant concentrations in the air and in the raindrops. Washout coefficients are empirically determined, derived from field studies and Henry's Law.

In ADMS 4, a value for Λ may be entered directly by the user or estimated by the system, in one of the following ways:

- by specifying a constant value Λ , which is then independent of the precipitation rate input to the meteorological input module
- by specifying constants A and B which give a washout coefficient dependent on precipitation rate of the form

$$\Lambda = AP^B$$

In ADMS 4 the default values of A and B are $A = 10^{-4} \text{ s}^{-1}$ and $B = 0.64$, appropriate for a very soluble species.

Washout coefficients need to be estimated for amines and ammonia, as discussed below.

Washout coefficients for ammonia and amines

The following section summarises the state of knowledge with regard to the washout coefficients for ammonia, ammonium and amines.

Ammonia

An estimate for a constant washout coefficient for ammonia⁵⁰ is:

$$\Lambda_{\text{NH}_3} = 9 \times 10^{-6} \text{ s}^{-1}$$

The literature also suggests that the characteristics of the washout of ammonia are similar to those for SO_2 , which has been well documented⁵¹. For example, their 'scavenging ratios', which are proportional to the washout coefficient and defined as the mass of pollutant per unit volume of water divided by the mass of pollutant per unit volume of air, show similar behaviour on month-by-month time scale (Hicks⁵²).

The scavenging ratios of NH_4^+ and SO_4^{2-} are in the ratio of approximately 1:2. This is consistent with the estimates of $\Lambda_{\text{SO}_4^{2-}}$, which for an annual precipitation rate of 1000 mm/yr is given in CLAG⁶ as:

$$\Lambda_{\text{SO}_4^{2-}} = 2.6 \times 10^{-5} \text{ s}^{-1}$$

⁵⁰ CLAG (1994). Critical Load of Acidity in the United Kingdom (1994). Summary Report of the Critical Loads Advisory Group. Institute of Terrestrial Ecology, Penicuik, Midlothian.

⁵¹ Acid Deposition in the United Kingdom 1992-1994, Fourth Report of the Review Group on Acid Rain, DETR, June 1997

⁵² Hicks, B.B., 2005. A climatology of wet deposition scavenging ratios for the United States. Atmospheric Environment, **39**, 9, 1585-1596

Amines

Data for scavenging ratios for some amines and NH_4^+ are given in Gorzelska and Galloway⁵³, and summarised below in Table 10.3 below.

Table 10.3: Summary of scavenging coefficients from Gorzelska and Galloway (1990)

Substance	Scavenging coefficient
Methylamine CH_3NH_2	500
Ethylamine $\text{C}_2\text{H}_5\text{NH}_2$	500
Ethanolamine $\text{HOC}_2\text{H}_4\text{NH}_2$	500
Ammonium NH_4^+	400

CERC is not aware of standard precipitation-dependent washout coefficients for amines. However, they may be derived from the precipitation-independent washout coefficients and information underlying the scavenging ratio data (e.g. Gorzelska and Galloway).

10.4.1.2. pH Limited method

The second proposed development for wet deposition will be to include algorithms to adjust the washout coefficients dependent on droplet pH specifically to include allowance for amines and their degradation products and ammonia in the current ADMS 4 module.

The timescale for this development is one year.

Information required: Henry's Law coefficient and disassociation coefficient for all relevant amines.

As the concentration in the plume increases, there is a pH-dependent limit on how much gaseous pollutant can be transferred into the water droplet. This limit can be estimated for a particular pollutant if the following are known:

- The Henry's Law coefficient for the pollutant; and
- The acid/base disassociation coefficient for the pollutant.

10.4.1.3. Falling drop method

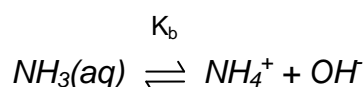
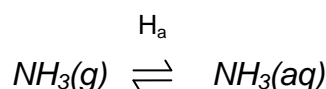
The third proposed development for wet deposition will be to adapt the falling drop method for amines and ammonia.

The timescale for this development is less than three years.

Information required: Henry's Law coefficient, disassociation coefficient and gas diffusion coefficient for all relevant amines. Gas diffusion coefficients can be estimated, for example using the US EPA tool <http://www.epa.gov/athens/learn2model/part-two/onsite/estdiffusion-ext.html>.

⁵³ Gorzelska, K. and Galloway, J.N. Amine Nitrogen in the Atmospheric Environment over the North Atlantic Ocean. Global Biogeochemical Cycles 4 No. 3, 309-333, 1990.

When NH_3 dissolves in water, the dominant chemical processes can be described by the following two equations:



In the first equation, $\text{NH}_3(\text{g})$ is the gas phase ammonia, i.e. the NH_3 present at the drop surface, the constant of proportionality is the Henry's Law constant H_a , and for the second equation, the coefficient is the acid-base disassociation coefficient K_b . The values of H_a and K_b are given in Table 10.2.

As can be deduced from the fact that K_b is of $\text{O}(10^{-5})$, most of the ammonia remains in molecular form in the aqueous phase, rather than disassociating into ions. This means that it will readily outgas from the droplets back to the atmosphere.

Total solubility is given by the equation:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3(\text{g})]} = H_a K_b.$$

The equations for the amines would be similar to these for ammonia, as they are also bases. Consideration of more than one chemical species requires solution to the electro-neutrality equation.

10.4.14 Washout of NO_2

A significant amount of NO_x is emitted from the CCM and TCM stacks and therefore wet deposition of NO_2 also needs to be considered (the wet deposition of NO is negligible). However the aqueous concentration of NO_2 in water droplets readily reaches equilibrium with the atmospheric concentration, and the ionisation of the NO_2 molecules is relatively slow. This means that:

- the washout coefficient method will overestimate the wet deposition of NO_2 ; and
- whilst it would be possible to include NO_2 in the falling drop method, a simpler approach would be to calculate the wet deposition of NO_2 from the ground level atmospheric concentration, using the Henry's Law coefficient.

This suggested approach represents a special case for wet deposition of NO_2 and is equivalent to the method that is applied in ADMS 4 to model dry deposition. It is straightforward to apply to ADMS 4.

The timescale for this development is less than one year

10.4.2. Recommendation for dry deposition model development

In the Case Study (Sub-task 2) a uniform deposition velocity was employed. It is recommended that spatially varying dry deposition velocities be derived for amines based on a surface resistance formulation which may be spatially varying. This task is for the derivation of appropriate input data to the model, not modification to the model code.

The timescale for this development is less than one year.

Information required: understanding of stomatal response to amines.

ADMS 4 represents the dry deposition flux (rate of deposition per unit area) F_{dry} by:

$$F_{\text{dry}} = v_d C(z = 0)$$

Where $C(z=0)$ is the near-surface concentration and v_d is known as the ‘deposition velocity’ and is a function of the pollutant species. In ADMS 4, the deposition velocity can be entered directly, including a temporal or spatial variation if required. In addition, the model is able to estimate values of the deposition velocity from user-entered values of the surface resistance parameter; again these can be temporally or spatially varying.

The equation is generally a good approximation for predicting the dry deposition for a number of pollutants. For the case of ammonia, however, v_d is concentration-dependent and is significantly reduced at high pollutant concentrations. It is thought that this is because leaf stomata close when concentrations of ammonia are high, leading to reduced deposition at the leaf surface.

The recent UK Environment Agency guidance⁵⁴ on the modelling of ammonia gives suggested concentration-dependent values for v_d for ammonia; these are summarised in Table 10.4 below. Implementation of the model for amines will require consideration of whether high concentrations of amines also cause leaf stomata to close.

Table 10.4: UK Environment Agency recommended ammonia deposition velocities

Ammonia concentration ($\mu\text{g}/\text{m}^3$)	<10	10-20	20-30	30-80	>80
Deposition velocity (m/s)	0.02 (short vegetation) 0.03 (tall vegetation)	0.015	0.01	0.005	0.003

10.5. Other miscellaneous issues

10.5.1. Accumulation in water bodies

ADMS 4 may be used to calculate deposition onto surfaces including freshwater lakes. Calculation of accumulated quantities of amines requires estimates of chemical degradation in the water body and the rate at which water in the freshwater body is replenished. Information on this will be required in order to construct an accumulation model.

The timescale for this development is less than one year.

⁵⁴ Guidance on modelling concentration and deposition of ammonia emitted from intensive farming, UK Environment Agency Air Quality Modelling and Assessment Unit, March 2010

10.5.2. Impact of ice and snow on aqueous phase chemistry and deposition

A literature study will be conducted to determine the state of knowledge of ice phase chemistry and “washout” by snow. Where appropriate the study will inform modification of aqueous phase models and “washout” coefficients. This is relevant during periods of snow or when cloud droplets may freeze. As cloud droplets may remain in liquid form at temperatures well below freezing point we anticipate that the latter effect is likely to be unimportant.

The timescale for this development is less than one year.

10.6. Validation of model developments

The validation that can be carried out to test new developments will depend on the available datasets. As many of the processes and physical properties have not been investigated previously, validation will depend heavily on data generated by the CCM project. Generally, there is never the large number of data sets that model developers would like in order to test each model feature independently. Therefore, verification of the model, verifying that the model results follow the trend predicted by a physical understanding of the processes involved and demonstrating the expected sensitivity will be an important complement to the validation.

The exact nature of the validation and verification activities will depend on the available data. However, they will include:

- Comparison with data such as chemical composition of rain drops, cloud drops, ground water, concentrations of NO_x, ammonia and so on;
- Comparison with amine concentration measurements; and
- Model sensitivity studies, i.e. investigating the effect of changes.

In the absence of data, parametric studies will be carried out to make sure the model is behaving in a physical way and shows the expected sensitivity to changes in parameters. Comparisons with specialist models may confirm trends:

- Parametric studies to assess trends in model results
- Comparison with specialist models

Data requirements

Provision of the data listed below would assist the model validation.

Meteorological data

- hourly precipitation data close to or at a site representative of Mongstad
- hourly relative humidity close to or at a site representative of Mongstad
- hourly cloud cover close to or at a site representative of Mongstad

Air quality data

- background (rural) O₃, NO_x, NO₂: hourly or 3-hourly
- background (rural) sulphate, H₃, VOC: hourly, 3-hourly or 8-hourly

Anticipated impact of model changes

The impact of the developments is difficult to quantify at this stage as the impact of improving the modelling of gaseous and aqueous phase chemistry and wet and dry deposition will depend on the reaction rates, pathways and physical parameters that are currently unknown or not yet modelled. To give an idea of the potential impact, Figure 10.2 shows the effect of introducing the falling drop method for wet deposition on wet deposition of SO₂ from six large fossil fuel power stations in Nottinghamshire in England. Using a pH-limiting approach to wet deposition of SO₂, the maximum annual average wet deposition rate was predicted close to the stacks. After the falling drop method was implemented the maximum rate was predicted to occur approximately 10km from the stacks and to be much reduced.

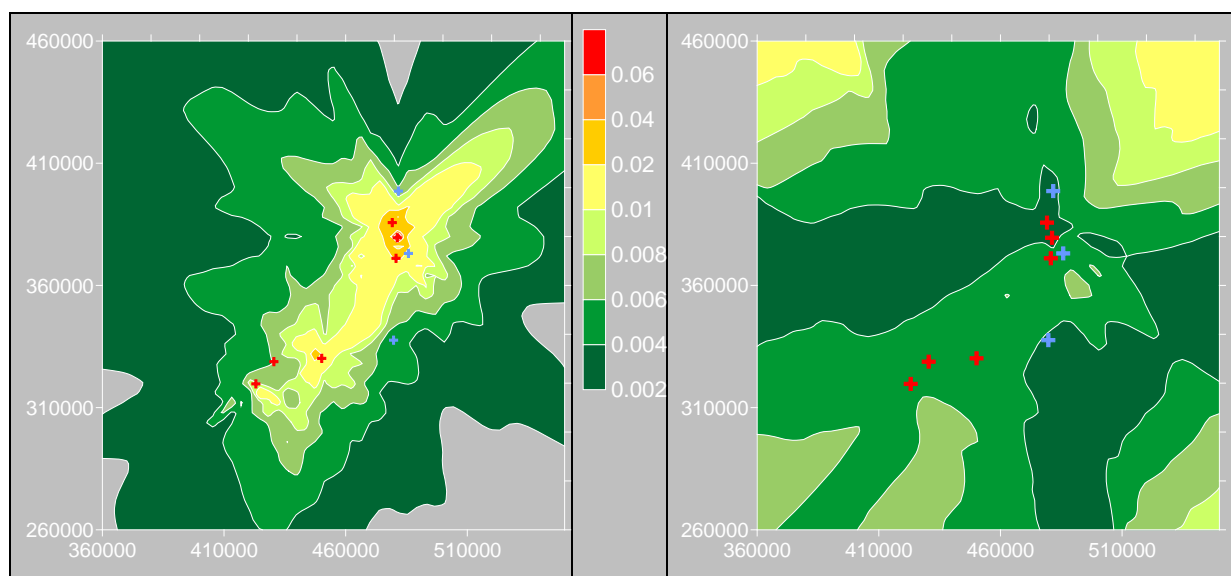


Figure 10.2: Annual average deposition rate of SO₂ in Nottinghamshire, England without the falling drop method (left) and with the falling drop method (right). Each power station is shown by a red + and the domain size in 20km x 20m. Units of deposition are µg/m²/s.

10.7. Conclusions

A review of work carried out for Sub-task 1, the model evaluation of ADMS 4 and Sub-task 2, identified those model features in ADMS 4 that could be developed to improve the treatment of dispersion, deposition and fate of amines and other species from Mongstad. Model features that could be improved by improved input data were also identified. This summary is presented in Table 10.5.

Sections 10.2 to 10.6 above considered each of the model features identified for potential development:

- chemistry modules for amines (both gaseous and aqueous phases, including particulate formation);
- modification of the deposition algorithms in ADMS 4 to take account of the properties of amines; and
- other miscellaneous items: accumulation of amines in lakes and accounting for the ice phase including snow.

Different levels of complexity have been considered for improving the modelling of chemistry and deposition. After describing each potential development we have estimated whether it would be a short term (1 year) or long term (3 years) development and listed the information and data required to complete the development. In Table 10.5, two timescales for development are listed. The first timescale assumes that there will be a delay before the information and data required to implement each scheme are available or where a more advanced scheme (e.g. falling drop method) is implemented after a simple scheme. The second, shorter, timescale assumes that the required information and data will be available at the start of the development.

ADMS 4 is a model that has been and continues to be extensively validated, is developed to high standards of quality control and, with hundreds of users around the world, it is fully supported and capable of being run by practitioners. It is an advanced Gaussian model, modelling dispersion in convective conditions using a skewed-Gaussian concentration distribution. It takes a far more physics-based approach than the engineering or empirical approach adopted by some Gaussian models and represents a substantial advance relative to these models. In particular the physics-based approach makes possible the development of the model to account for new physical processes or more complex schemes within a consistent framework.

The ADMS 4 core dispersion model is valid for ranges up to around 50km, but the model has been used at distances up to 100km for calculating long-term average concentrations from fossil-fuelled power stations i.e. 200m tall stacks with very buoyant emissions. ADMS 4 can currently use mesoscale or CFD model flow fields as input and can, thus, be nested within a mesoscale model. This ability was developed in response to users concerned with complex terrain and complex wind fields arising from the complex terrain or the urban environment.

ADMS 4 combines the benefits of a widely-used, operational model that has been subject to extensive validation and scrutiny with the potential for development within its existing framework.

CERC has over 20 years experience in developing and supporting operational models and are experts in model evaluation techniques, currently leading the model evaluation work package of the EU 7th framework PASODOBLE project⁵⁵. CERC will bring this expertise to the Service and are confident that once agreed and specified and with necessary information supplied, development can be delivered on time and to the established quality of the ADMS 4 model.

⁵⁵ PASODOBLE MYAIR Services, website, www.myair-eu.org

Table 10.5: Summary of recommendations

Recommendations for:	Developments	Timescale (assuming delay waiting for information)	Timescale (assuming no delay waiting for information)
Gas phase chemistry model development	Simple degradation scheme	1 year	1 year
	More advanced degradation scheme	≤ 3 years	1 year
	Detailed amine chemistry model	> 3 years	2 years
Wet phase chemistry model development	Basic model for aqueous phase chemistry in plume	1 year	1 year
	Advanced model for aqueous phase chemistry	3 years	2 years
	Aqueous phase chemistry – other considerations	3 years	2 years
Wet deposition model development	Washout coefficients	≤ 1 year	≤ 1 year
	pH-limited method	1 year	1 year
	Falling drop method	≤ 3 years	1.5 years
	Washout of NO ₂	≤ 1 year	≤ 1 year
Dry deposition model development	Derive spatially-varying dry deposition velocities	≤ 1 year	≤ 1 year
Accumulation in water bodies	Accumulation in water bodies	1 year	1 year
Consideration of ice/snow	Effect of ice/snow on aqueous phase chemistry/deposition	1 year	1 year

Appendix A: Input and output meteorological variables of ADMS 4

The complete list of possible meteorological input variables is shown in Table A.1. The first three columns are alternative forms of the variable names that may be used in creating meteorological data files. As ADMS 4 matches the string to identify a variable the user may want to use short versions of the variable names (columns 1 and 3) in order to avoid making errors in typing. Names from different lists may be used in the same meteorological input file, e.g. using U for wind speed and CLOUD for cloud cover in the same file is fine.

The most common type of input data will be sequential data (or data for a single hour) giving wind speed, direction, cloud cover, time of day, time of year, temperature and possibly precipitation, relative humidity and sea surface temperature. Such data are supplied by national meteorological services and are available for worldwide sites from the US NOAA (National Oceanic and Atmospheric Administration)⁵⁶.

National meteorological services can often also provide statistical met data sets. These data sets usually cover a long period e.g. 10 years and give the frequency of conditions occurring in certain ranges of wind speed, direction, surface sensible heat flux, boundary layer height (or depth) and precipitation. Statistical data are not usually used for regulatory or permitting studies.

Note that Pasquill-Gifford stability categories cannot be directly input into the model (although of course values of U , ϕ , L_{mo} and h may be), nor are they output. In ADMS 4 the boundary structure is characterised by the two parameters, h and L_{MO} . Values of these parameters corresponding *approximately* to the Pasquill-Gifford categories are shown in the data file *r91a-g.met* and below in Table A.2.

The minimum meteorological data requirement for ADMS 4 is:

- wind speed (this would normally be a near-surface wind, but could be a geostrophic wind or friction velocity. In each case, the height of wind must be entered, which would typically be 10 m for the near-surface case and should be 1000 m and 0 m for the geostrophic and friction velocity cases, respectively);
 - wind direction;
- plus *one* of the following:
- reciprocal of Monin-Obukhov length;
 - surface sensible heat flux; or
 - cloud cover, time of day and time of year.

The variables output by the ADMS 4 meteorological pre-processor are listed in Table A.3.

⁵⁶ <http://www.ncdc.noaa.gov/oa/ncdc.html>

Table A.1: Variables that may be input into the meteorological input module

Short name	Long name	Abbreviated name	Units
WIND SPEED	WIND SPEED	U	m/s
UG/USTAR	GEOSTROPHIC WIND SPEED/FRICTION VELOCITY	UGSTAR	-
WIND DIRN	WIND DIRECTION (DEGREES)	PHI	°
DIRN CHANGE	GEOSTROPHIC MINUS SURFACE WIND DIRECTION (DEGREES)	DELTAPHI	°
HEAT FLUX	SENSIBLE HEAT FLUX	FTHETA0	W/m ²
1/LMO	1/MONIN-OBUKHOV LENGTH	RECIPLMO	m ⁻¹
BL DEPTH	BOUNDARY LAYER DEPTH	H	m
CLOUD	CLOUD AMOUNT (OKTAS)	CL	oktas
SOLAR RAD	INCOMING SOLAR RADIATION	SOLAR RAD	W/m ²
TEMPERATURE	TEMPERATURE (C)	T0C	°C
N ABOVE BL	BUOYANCY FREQUENCY ABOVE BOUNDARY LAYER	NU	s ⁻¹
DELTA THETA	TEMPERATURE JUMP ACROSS BOUNDARY LAYER TOP	DELTATHETA	°C
PRECIP	PRECIPITATION RATE (MM/HOUR)	P	mm/h
SEA TEMP	SEA SURFACE TEMPERATURE (C)	TSEA	°C
DELTA T	TEMPERATURE OVER LAND MINUS SEA SURFACE TEMPERATURE	DELTAT	°C
SIGMA THETA	SIGMA THETA (DEGREES)	SIGMATHETA	°
S HUMIDITY	SPECIFIC HUMIDITY	S HUMIDITY	kg/kg
R HUMIDITY	RELATIVE HUMIDITY (PERCENT)	RHUM	%
RH ABOVE BL	RELATIVE HUMIDITY ABOVE BOUNDARY LAYER (PERCENT)	RH ABOVE BL	%
DRH/DZ	D(RELATIVE HUMIDITY)/DZ ABOVE BOUNDARY LAYER (PERCENT/M)	DRH/DZ	%/m
LAT HT FLUX	LATENT HEAT FLUX	LAT HT FLUX	W/m ²
WIND HEIGHT	WIND MEASUREMENT HEIGHT	WIND HEIGHT	m
Z0 (M)	ROUGHNESS LENGTH (MET SITE)	Z0 (M)	m
Z0 (D)	ROUGHNESS LENGTH (DISPERSION AREA)	Z0 (D)	m
ALBEDO (M)	ALBEDO (MET SITE)	R	-
ALBEDO (D)	ALBEDO (DISPERSION AREA)	ALBEDO (D)	-
ALPHA (M)	MODIFIED PRIESTLEY-TAYLOR PARAMETER (MET SITE)	ALPHA	-
ALPHA (D)	MODIFIED PRIESTLEY-TAYLOR PARAMETER (DISPERSION AREA)	ALPHA (D)	-
HOUR	HOUR	THOUR	-
DAY	DAY	TDAY	-
YEAR	YEAR	YEAR	-
FREQUENCY	FREQUENCY	FR	-
FREQUENCY FOR MONTHS xx TO xx, HOURS xxxxxx TO xxxxxx (GMT + xxxxxx)	FREQUENCY FOR MONTHS xx TO xx, HOURS xxxxxx TO xxxxxx (GMT + xxxxxx)	MONTHS xx TO xx, HOURS xx TO xx	-

Table A.2: Values of wind speed, Monin-Obukhov length (L_{MO}) and boundary layer height (h), which may be used to represent approximately Pasquill-Gifford categories A-G.

U (m/s)	L_{MO} (m)	$1/L_{MO}$ (m ⁻¹)	h (m)	h/L_{MO}	Pasquill-Gifford Category
1	-2	-0.5	1300	-650	A
2	-10	-0.1	900	-90	B
5	-100	-0.01	850	-8.5	C
5	∞	0	800	0	D
3	100	0.01	400	4	E
2	20	0.05	100	5	F
1	5	0.2	100	20	G

Table A.3: Output variables from the meteorological input module

Variable	Description
u_*	Friction velocity (m/s)
U_g	Geostrophic wind speed (m/s)
U_g^*	Geostrophic wind speed normalised by the friction velocity
ϕ_0	Surface wind direction (angle from which wind blows in degrees measured clockwise from north, e.g. 270° is a westerly wind) (°)
ϕ_g	Geostrophic wind direction (angle from which wind blows in degrees measured clockwise from north) (°)
$\Delta\phi$	Geostrophic wind direction minus surface wind direction (°)
ϕ	Wind direction (as obtained from the meteorological input data set) (°)
ϕ_{sec}	Wind direction used by the model for this meteorological data line for long-term calculations, which may differ from the input value if the data are in sectors (°)
w_*	Convective velocity scale m/s (if $F_{\theta_0} > 0$, $w_* = (g F_{\theta_0} h / \rho c_p T_0)^{1/3}$; if $F_{\theta_0} \leq 0$, $w_* = 0$)
F_{θ_0}	Surface heat flux (W/m ²)
K	Incoming solar radiation (W/m ²)
$1/L_{MO}$	Reciprocal of the Monin-Obukhov length (m ⁻¹)
h	Boundary layer height (m)
N_u	Buoyancy frequency above the boundary layer (s ⁻¹)
$\Delta\theta$	Temperature jump across the boundary layer top (K)
T_0^c	Near-surface temperature (°C)
P	Precipitation rate (mm/h)
ΔT	Near-surface temperature over land minus sea surface temperature (°C)
σ_θ	Standard deviation of mean wind direction (°)
q_0	Surface specific humidity (kg/kg)
λ_E	Surface latent heat flux (W/m ²)
RH_u	Relative humidity just above the boundary layer (%)
$d(RH_u)/dz$	Relative humidity lapse rate above the boundary layer (%/m)

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