OR ../2009

CO_2 Capture Mongstad Project/H&ETQPAmine2

Modelling atmospheric dispersion for components from post combustion amine based CO_2 capture.

Svein Knudsen, Massimo Cassiani , Matthias Karl, Leiv Håvard Slørdal, Leonor Tarrasón

Contents

Page

Executive Summary 6

1 Introduction 8

2 Requirements for modeling the atmospheric dispersion of amine emissions 9
2.1 General requirements 9
2.2 Specific Requirements 10
2.2.1 Geographical extension 12
2.2.2 Early phase of dispersion 13
2.2.3 Meteorological processes 14
2.2.4 Chemical processes 15
2.2.5 Aerosol processes 17
2.2.6 Removal by dry and wet deposition 20

3 Evaluation of current models 21
3.1 Regional scale dispersion models 21
3.2 Embedded local scale dispersion models 22
3.3 Meteorological models 22
3.4 Chemistry processes 23
3.4.1.1 Chemistry solvers in 3-D models 23
3.4.1.2 Chemistry mechanisms in 3D-models 25
3.5 Aerosol Models 26
3.6 Overall evaluation for chemical and aerosol modules 26

4 Case study of the recommended model 27
4.1 Introduction 27
4.2 Air quality and water quality guidelines 28
4.3 Emissions 30
4.3.1 Emissions from CCM 30
4.3.2 Emissions from the other industries in the area 31
4.3.3 Chemical transformation rates for the emissions 31
4.4 Meteorology and meteorological model used. 32
4.5 Dispersion/deposition calculations 33
4.6 Sources and sinks of the emissions 38
4.7 Changes in the emissions 41
4.8 Discussion 41

5 Recommendations for amine chemistry dispersion model development 46

Appendix A Chemistry solvers for use in 3-D models 51

Appendix B Chemistry schemes for use in 3-D models 56

Appendix C Generic aerosol dynamics models 58

Appendix D Description of the dispersion models 62

Appendix E Embedded plume models 65
Gaussian plume dispersion models 65

- Lagrangian particle/puff and PDF model 65

Appendix F Meteorological models 67

Executive Summary

CCS with the use of amines has emissions to air. These emissions, although small, may pose a risk to the environment. It is not the amine itself , but the chemical reaction products formed after emissions that pose the risk. The present knowledge of the fate of amines in the environment is rather incomplete and exposure estimates are therefore uncertain. This report describes the available modelling tools, report the results from a case study based on current knowledge and gives a recommendation on R&D activities which are needed in order to reduce the overall uncertainty in the exposure estimates.

Worst case studies show exceedanses of the evaluation criteria in the following areas:

- Concentrations of nitrosamines/nitramine with short to medium exposure time at a local scale.
- Concentrations of nitrosamines/nitramine in drinking water due to wet deposition.

A better problem description is necessary to reduce uncertainty in the exposure estimates. The exposure estimates in the case study are connected to large uncertainties, to lower the uncertainty and thereby lowering the exposure estimates, it is recommended that the following processes are further developed:

- Include chemical reactions of amines in the modeling tool
- Increase the understanding of the processes from concentrations of amines in rain water to concentrations in surface/drinking water and include a more accurate assumptions in the model/evaluation.
- Improve the representation of precipitation(intensity, occurrence, amounts, geographical distribution)through observations

The following activities are recommended for the 1 year plan:

- Establish the chemical reaction scheme in the gas phase and prepare this for modeling.
- Conduct experiments for droplet/aerosol chemistry for MEA
- Conduct laboratory experiments to quantify the sources and sinks of the amines from concentrations in precipitation to concentration in surface water.
- Develop procedures for using measured precipitation to improve predicted precipitation
- Use the CMAQ model for scenario benchmarking calculations
- Start the development of the Plume in Grid formulations in a 3D modeling framework

Recommended activities for the 3 year plan are:

- Develop the gas phase chemical reaction model
- Develop the Droplet/aerosol model
- Merge these two models with the existing chemical model
- Include the chemical models in the modeling tools
- Test and make the WRF-CHEM/EMEP model operational.
- Develop the chemical plume model
- Test and make the chemical plume model operational.
- Build the chemical plume model into a plume in grid model where information flows from the plume model into the grid model.

CO_2 Capture Mongstad Project/H&ETQPAmine2
Modelling atmospheric dispersion for components from post combustion amine based CO_2 capture.

1 Introduction

Amine emission to air during Carbon Capture processes have been shown to impose a potential risk to human health and produce possible negative effects in the environment, as indicated in several "worst case studies" (Knudsen et al., 2009; Låg et al., 2009). Worst case studies are designed to evaluate possible risks and eliminate the effects that are not relevant to investigate. If the worst case studies show no possible effects then these can essentially be ruled out, however, if the worst case studies show exposure close to the evaluation criteria then these effects need to be investigated further. The worst case studies carried out until present show that non-desired effects on human health and adverse effects on the environment can potentially occur and that it is necessary that further research on these areas to increase precision on the estimates to get better evaluation of the estimated effects.

This report is aimed at developing a methodology to increase the precision of the tools to estimate the atmospheric dispersion of the emissions which will result in a better description of the fate of amine emissions to air. The report does not explicitly recommend methods to increase our understanding of the effects of amines and their oxidation products in human health, terrestrial ecosystems, aquatic organisms, corrosion, smell and climate, but focuses instead on the improvement of our present capacity to describe the fate of amines when emitted to air. It is envisaged that by improving the accuracy of the estimates of the atmospheric concentration of amines, we will allow for better input and increased accuracy in the evaluation of exposure from amine emissions.

Previous "worst case" studies show that limited information is available for the chemical reactions after the emissions have left the stack, and that no models are available which describe the physical and chemical processes that are necessary for estimating the exposure (Knudsen, et al., 2009; Berglen et al., 2008).

This report identifies the different requirements that are necessary for evaluation of the exposure, defines the processes that are necessary for fulfilling the requirements and evaluates the existing models and modelling tools. Recommendations on short term and long term development for modelling atmospheric dispersion for components from post combustion amine based CO_2 capture beyond "worst case" calculations is provided in Section 5 of this report.

2 Requirements for modeling the atmospheric dispersion of amine emissions

2.1 General requirements

Atmospheric chemical transport models are computational and numerical tools that quantify the various processes associated with transport of pollutants in the atmosphere. They reflect the current understanding on atmospheric dispersion. They are usually based on the continuity equation and trace the fate of pollution, their transport and dispersion in air, their chemical transformation and their removal both by dry and wet deposition.

Models are useful tools to test and increase our current understanding of the processes involved in atmospheric dispersion, and connect emissions to concentrations and mass fluxes. In combination with atmospheric monitoring, models provide us with a unique capability to test different hypothesis on the processes involved. As a supplement to measurements, models can test different scenarios and can derive predictions for the future.

The general requirements for atmospheric chemical transport (CTM) models can be summarized in the following five criteria. An adequate chemical transport model should be:

1) **Fit for purpose**
   This is the most significant requirement for a model or modeling system. The most challenging task for a modeling team is to define the type of model that is needed for a specific purpose. For instance, the requirements on accuracy are very different if the model results are to be used to derive a "worst case" estimate or if they are to be used to derive recommendations for the establishment of limit values within a policy control framework.
   The type of application of the model determines also the type of processes that need to be included in the modeling framework.

2) **Well Validated**
   This is an essential requirement for any modeling system as it relates to its actual ability to reproduce the observed conditions of air concentrations and depositions. Without documented and extensive validation, the model capabilities remain only a theoretical exercise. The model should be validated for many different situations, in different chemical, meteorological and spatial conditions, preferably for large spans of time. This requirement includes an implicit request on operability of the modeling framework as only operative models can produce results that can be validated with observations.

3) **Flexible**
   A model needs to be flexible to allow for the testing of different hypothesis. It should contain a reasonably friendly way to include new substances, new chemical reactions, new deposition processes,

removal mechanisms and interactions as these need to be investigated. The flexibility criteria involves also the choice of the spatial and temporal scales of the simulation and of the actual size of the model domain and its nesting capabilities. This flexibility requirement involves in many cases the need for a modular structure that allows the inclusion of new processes in the model framework.

4) **Transparent**
A model needs to be documented and transparent about the assumptions included in its formulation. It is recommended to use open source community models, that are open for the scientific community to review and improve their contents. Because of their openness and transparency such models are usually more robust, as errors/ mistakes in the formulation are easier to be identified when a large number of scientists uses the same modeling tool.

5) **Computationally effective**
This is to allow a timely calculation of many different scenarios. In many cases, specially for policy applications, a very large number of scenarios are necessary to determine cost-efficient solutions. Therefore it is necessary for the modeling tools to be computationally efficient in order to provide solutions in reasonable time spans.

These general requirements need to be further refined in view of the specific application of the chemical transport model. This involves in particular an analysis of what is requested for the modeling system to be "fit for purpose" since the type of application determines the processes that need to be included in the modeling framework. The specific requirements on the processes that need to be considered for modeling the dispersion of amines in air are given in the next section.

2.2 Specific Requirements

For the application in this report, namely to describe the fate in air of amines emitted under post-combustion Carbon Capture, a modeling system that involved a combination of experimental studies, box models, local scale dispersion model and nested regional scale chemical transport models was originally recommended back in 2008 (Berglen et al, 2008). This recommendation is still valid as we continue to assess considerable gaps in information about amines in air. Still, our understanding of the atmospheric dispersion of amines in air has improved in these two years and consequently our demands on the accuracy of the models has become more specific.

Initial modeling exercises for amine dispersion in air have aimed at a description of "worst case" situations. This is an appropriate first approach where simplifications in the transport and transformation processes of amines in air are assumed to produce an estimate of the maximum plausible risk. An example of this type of application is given in chapter 4. The conclusions from this type of applications is that for most amines and their oxidation products there is low risk

for high exposure to ecosystems and humans. This is not the case, however, for nitrosamines and nitramines, where results from "worst case" scenario applications indicate a potential risk for hazardous effects. Therefore, more refined estimates on the actual air concentrations and depositions of these two components should be carried out to increase the accuracy of the risk estimates.

This report provides specific recommendations to develop a modeling system that can produce more accurate estimates of the atmospheric dispersion of nitrosamines and nitramines. With this application in mind, this section identifies the specific requirements for the modeling system to be "fit for purpose".

Table 1 provides a summary overview of the specific requirements for the processes involved in the atmospheric dispersion and transformation of amines in air. Detailed comments on each of these process requirements follow at the end of the section.

Table 1: Specific process requirements for amine atmospheric dispersion models. Prioritized processes that require special development effort are highlighted in red.

Process	**Specific Requirements**
Geographical extension	From 100m to 300 Km from source, with nesting to larger areas
Emission treatment	Point sources and grid sources; emission lumping
Plume in grid treatment	High priority: should be included in the chemical transport model
Meteorology	3D model, same spatial and temporalresolution as above with possibility for data assimilation of observations
Meteorology-chemistry interactions	Low priority: both turbulence and cloud interactions with chemistry can be introduced in later stages
Nesting options	1-way nesting , 2-way nesting has lower priority
Gas Phase Photochemistry	Flexible numerical solvers (KKP or similar)
Aqueous Phase chemistry	Flexible numerical solvers (KKP or similar)
Gas-Particle partitioning	High Priority: EQSAM or similar
Amine chemistry	High Priority: Introduced stagewise
Aerosol model	Option to be coupled to chemistry model
Secondary organic aerosol	Option to be coupled to chemistry model, lower priority
Dry deposition	Simple vd approach for amine products
Wet depostion	High priority: Refined results from scavenging approach

2.2.1 Geographical extension

Amines are reactive compounds and readily form hundreds of products in the atmosphere. Among the theoretically predicted atmospheric degradation products from the reaction of amines (MEA, AMP, MDEA, and Piperazine) with atmospheric hydroxyl (OH) radicals are aldehydes, amides, imines, nitrosamines, nitramines, and nitramides (Bråthen et al., 2008). Amines may equally fast react with NO_3 radicals which are present in the atmosphere during night time. In the marine boundary layer halogen chemistry can be important.

Initial "worst case scenario" studies have indicated that although some aldehydes and amides are known to be very toxic compounds and have a high carcinogenic potential such as formaldehyde and acetamide (Låg et al., 2009), the expected atmospheric concentrations of aldehydes and amides forming in the oxidation of parent amines are however below critical exposure levels (Karl et al., 2008). Nitrosamines and nitramines have been identified to be a priority for further studies (Knudsen et al., 2009).

Nitrosamines are predicted to form in the atmosphere by OH-initiated oxidation of amines (Bråten et al., 2008). Nitrosamines are rapidly removed from the atmosphere due to their photolysis in sunlight (Chow, 1973) and their reaction with OH radicals is probably of minor importance. OH radicals are also only present in the atmosphere in daytime. In contrast to nitrosamines, it is expected that nitramines accumulate in the atmosphere due to their relatively low reactivity towards OH radicals (Grosjean, 1991).

The present understanding on the atmospheric cycling of amines indicates lifetimes of products ranging from a few minutes (nitrosamines) to several days (nitramines). This implies that the geographical scale of their dispersion in the atmosphere ranges from few meters to several kilometres (see Figure 1). Consequently, atmospheric chemistry dispersion models aiming to reproduce the dispersion of nitrosamines and nitramines should cover a geographical extension ranging from 100 m up to 300km from the source area. Dispersion beyond that distance may be treated through nesting with larger scale regional models.

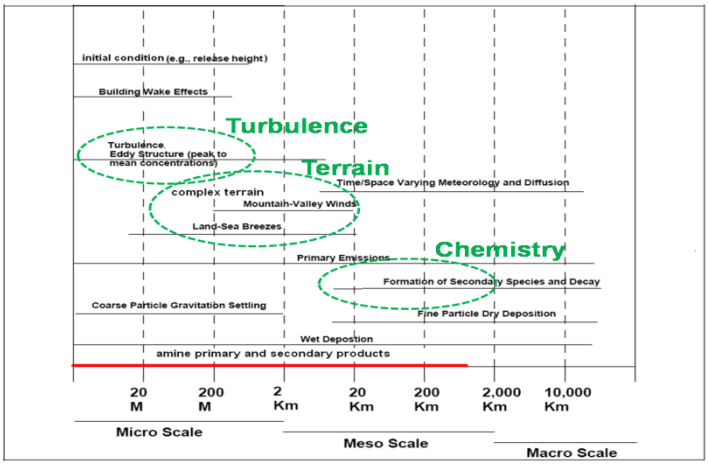

Figure 1: Geographical extension of different processes associated with amine primary and secondary products in the air.(adapted from the report: Federal Research and Development Needs and Priorities for Atmospheric Transport and Diffusion Modeling, FCM-R23-2004, NOAA)

2.2.2 Early phase of dispersion

Amine emissions to the air from post-combustion carbon capture are released from specific stacks. This means that these emissions will need to be treated in the modelling system as point sources. The CTM model will also have to deal with the emission of other pollutants (NO_x, SO_x, PM, VOC) that are released at the same time from the stacks. In addition, other area and stack emissions should also be considered in the calculations in order to provide enough information on the background air concentrations that influence the emission plume.

As indicated in Berglen et al, 2008, due to the short lifetime of amines in air, local scale models that can resolve the plume from the stack point are necessary to correctly describe the fate of amine emissions close to the source areas, that is, from the initial 100m to 5km. There is a variety of model types that are able to simulate this early phase dispersion processes, but with varying levels of physical consistency and accuracy. The simplest model is the Gaussian plume model while the more sophisticated are the Lagrangian particle probability density function (PDF) models. An intermediate level of physical consistency and complexity is the one found in Lagrangian puff dispersion models. The simplest approach, the Gaussian plume approach, considers mostly dispersion and does not consider the turbulence effects on chemical reactions. The approaches with intermediate consistency (Lagrangian puff formulations) take into account the chemistry but still do not consider the turbulence segregation effects. The most advanced methods (PDF models) integrate a sophisticate treatment of turbulence and chemistry.

Because of the short lifetime of nitrosamines in air, it is a requirement for the modelling system to be able to couple local scales plume models to a regional dispersion model so that dispersion from the stack to the regional scales will be correctly reproduced. Some amines such as piperazine and MEA are very reactive compounds and the time scale involved in the chemical reaction may result to be

comparable to the range typical of atmospheric turbulent phenomenon (few second to 10-15 minutes). This is a particularly complicated situation since it may require the modelling of the effects of turbulence on chemical reactions. For less reactive amines such as MDEA and AMP the chemistry-turbulence interactions may be less important.

However, since our focus is on nitrosamines and nitramines, the inclusion of interactions of turbulence with chemistry can be postponed for later stages in development of amine dispersion models. This is because the lifetime of nitramines is too long to be affected significantly by turbulence and also because nitrosamines rapid decay in the atmosphere is driven by photolysis rates and not by turbulence. As nitrosamines decay is mostly driven by photolysis it is not required at the moment to make use of the most sophisticated PDF models, because simpler formulations will still be adequate for a first model development stage.

2.2.3 Meteorological processes

The meteorological fields to be used as input for modelling the dispersion of amines in the atmosphere should be provided with the same geographical extension as the amine dispersion calculations, that is resolved from about 100m to 300 km from the sources. It is relevant also that the spatial resolution of the meteorological model fields is adequate for providing information on the dispersion of local scale air pollution, such as sea-breezes and terrain induced flows.

Since the modelling tools for amine dispersion should allow nesting from local to regional scales, it is an advantage to have meteorological models with inherent nesting capabilities. The meteorological information should in principle be provided by prognostic models in order to secure consistency in the meteorological input fields, but is also highly recommended that the meteorological models have the capability to assimilate meteorological observations. Numerical Weather Prediction (NWP) models have these capabilities, so that if suitable local meteorological measurements are available these may be integrated into the meteorological model through a nudging technique, allowing for improved wind field descriptions.

Necessary meteorological input data for chemical transport models (CTMs) are:

1. ***3D-Wind fields:*** Needed for estimating the advective transport of the atmospheric pollutant species.
2. ***Atmospheric stability and turbulence conditions:*** Needed for estimating the dispersion of the atmospheric species, and for describing the dry deposition process.
3. ***The humidity and cloud/rainfall distribution:*** Needed for the estimation of wet deposition and for the chemistry calculations.
4. ***Atmospheric temperature distribution and radiative conditions:*** Needed for the photochemistry scheme.

All of these input data can be extracted in various forms from existing mesoscale numerical prediction models. Examples of such models are presented in Chapter 3.3.

2.2.4 Chemical processes

The introduction of an amine chemistry mechanism is the highest priority requirement for the modelling system.

Current chemistry mechanisms used in 3-D atmospheric transport modelling do not include the chemistry of amines. Initial work has been done by Carter et al. (2008) who set up compressed mechanisms for several amines, among others for MEA and AMP. Carter et al. (2008) have added representations of the atmospheric reactions of 15 amines to the SAPRC-07 mechanism (Carter et al., 2007). A detailed chemistry mechanism has been developed for MEA in the frame of the project "CO2&Amines" (Bråten et al., 2008) and further refined results based on experimental data in the project "Atmospheric Degradation of Amines" (Nielsen et al., 2010). These results however are not reported in the peer review literature as yet. They have been used only to a limited extent in the "worst case scenario" reported in chapter 4, by applying fractional formation yields. A more detailed description of these chemical transformation results is recommended for the next development of the modelling system.

Comprehensive atmospheric chemistry models are computationally intensive because the governing equations are non-linear, highly coupled, and stiff. The ability to fully utilize current chemistry models remains severely limited by today's computer technology. The large computational requirements in the study of chemically perturbed environments arise from the complexity of the chemistry in the atmosphere (Jay et al., 1995). Integration of chemistry rate equations typically consumes as much as 90% of the total CPU time in 3-D CTMs. Addition of more chemical species and reactions to the chemistry scheme will enforce the need for faster chemistry solvers, and the interest in the toxicology of some of these chemical species requires a highly accurate solution.

An important requirement of large-scale 3-D models is the ability to perform simulations with acceptable run-times for any given simulation period, which typically range from between months to decades. Therefore simplifications have to be made for chemical reactions that occur in the atmosphere. For example, rather than including an explicit description of the hundreds of chemical species which are thought to occur in the troposphere, lumped chemical mechanisms have been developed (e.g. CBM-IV (Gery et al., 1989); RACM (Stockwell et al., 1997)) which have the ability to accurately capture the chemical evolution of the most abundant reactive gases (e.g. ozone) in the atmosphere.

In summary the following aspects of amine chemistry are of particular importance for atmospheric chemistry modelling of amines:

1. Removal of amines from the gas-phase;
2. Production and removal of harmful secondary products such as nitrosamines and nitramines;
3. Light-dependent chemistry (day and night) ;

4. Ozone production potential;
5. Particle formation potential;
6. Partitioning of amines to aqueous phase of aerosols and clouds;
7. Partitioning of secondary products to the particle phase.

Below follows a short summary of our present understanding of amine aqueous phase and particle phase chemistry. The requirement is to identify feasible ways to introduce such knowledge in a 3-dimensional chemical transport modelling framework.

Aqueous-phase chemistry

Monoethanolamine (MEA) is highly water soluble with a Henry's Law coefficient of $6.2x10^6$ M/atm (Bone et al., 1983), i.e. 5 to 6 orders of magnitude higher than that for sulphur dioxide or ammonia. Thus a large fraction of emitted amines will partition into the aqueous phase of aerosols and clouds. The lifetime of amines in water is expected to be in the range of 14 to 20 days (Hales et al., 1996), but experimental evidence on the chemical transformation of amines and its degradation products in water is lacking.

Nitrosamines, nitramines and amides produced in the gas-phase degradation of amines can become dissolved in the plume cloud droplets due to their generally good water solubility, immediately after their formation when escaping the stack of the CO_2 capture plant. The dimethyl and diethyl derivatives of nitrosamines are soluble in water (IARC, 1978). For instance, the highly carcinogenic compound N-Nitrosodimethylamine (NDMA) is very soluble in water. Moreover, it is well known that nitrosamines form in the aqueous phase nitrosation (reaction with aqueous HONO) of secondary amines (e.g. Smith and Loeppky, 1967) and tertiary amines (Loeppky et al., 1983). In general, nitrosamines are considered to be thermally stable in the condensed phase in alkaline or mildly acidic medium and hence do not decompose when temperatures increase. In prolonged contact with strong acids they decompose by hydrolysis (U.S. EPA, 1976). This has implications for the atmosphere, since strongly acidic aerosol occur only in extremely polluted conditions, e.g. in plumes from power plants. Thus in ambient continental and remote air, particulate nitrosamines can be considered stable towards thermal degradation. N-nitrosamines undergo photochemical decomposition in sunlight limiting their lifetime in the atmosphere, and this is expected also to occur on aerosol particles (Chow, 1973; U.S: EPA, 1976).

Major oxidants in the aqueous phase of aerosols and clouds are the hydroxyl and hydroperoxy radical (OH, HO_2), ozone (O_3) and hydrogen peroxide (H_2O_2). Free radicals such as OH and HO_2 can be scavenged from the gas phase by water droplets or produced in the aqueous phase (Herrmann et al., 2000). For the fate of amines in aerosols and clouds it is thus of great importance to know about their reaction rates with OH in the aqueous phase. Assuming an aqueous phase reaction rate with OH(aq) similar to that of ethanol, the lifetime of dissolved MEA in cloud droplets in a remote environment would be only 0.1 hours, rendering aqueous phase degradation competitive to gas-phase oxidation of amines. At present, aqueous phase chemistry (kinetics and product formation) of amines in droplets and clouds has not been studied.

Gas phase / particle partitioning

Gas phase aliphatic amines may play a significant role in secondary aerosol formation via photo-oxidation and gas-to-particle conversion in regions with high amine concentrations (Murphy et al., 2007; Angelino et al., 2001). Aerosol particles forming in the atmospheric oxidation of amines can be either organic salt particles or organic non-salt particles, the latter are commonly referred to as secondary organic aerosol (SOA) particles. Acid-base (gas-phase) reactions between amines and acids commonly present in the atmosphere (i.e. nitric acid and sulphuric acid) and in the emissions (e.g. from the power plant) appear to play an important role in the formation of the salt particles.

The tendency of amines to form particulate salts with nitric acid and sulphuric acid has a stabilizing effect on small nucleated clusters and thus enables their further growth. Organic salt formation potentially also enhances the hygroscopic growth of aerosol particles and facilitates their activation into cloud droplets (Smith et al., 2010). Contrary to primary and secondary amine, tertiary amines form significant amounts of organic non-salt particles. The discovery of trialkylamine-N-oxides in aerosols provided first evidence that gas phase oxidation products of alkyl amines can partition to the condensed phase of aerosol particles. Significant organic non-salt particles formation was observed in the oxidation of alkyl amines with the nitrate radical rendering amines a potential important night-time source of organic non-salt particles.

Members of the chemical class of nitrosamines range from high vapour pressure liquids to rather non-volatile solids. Measurements of potentially toxicological important N-nitroso and nitrite-containing compounds in both the fine particulate (PM2.5) and gas phase in samples collected in Provo, Utah, indicate that the majority of the N-nitroso and nitrite organic compounds present in fine particulate matter in the studied urban area are semi-volatile organic compounds (Ding et al., 1998). Little is known about the gas phase / particle partitioning behaviour of nitrosamines and nitramines. The potential of N-nitroso compounds to re-evaporate from the particles would increase the possible inhalation exposure and allows for the transportation of these hazardous compounds over longer distances before their release to the gas phase.

2.2.5 Aerosol processes

In the atmosphere, amine may contribute to particle formation and growth via the following processes:

1. Nucleation (stable clusters) involving amines and nitric acid or sulphuric acid;
2. Growth of particles by condensation of amines;
3. Growth of particles by condensation of low-volatility or oligomeric products that form in the atmospheric oxidation of amines;
4. Formation of secondary organic aerosol (gas phase/particle partitioning);
5. Mass transfer and into aqueous aerosols and dissociation in the liquid.

Secondary aerosol formation in the plume of the CO_2 capture plant by oxidation of emitted amines may contribute to the regional aerosol (see Figure 2). On the local scale aerosol particles from industrial sources might cause adverse health effects and impair visibility.

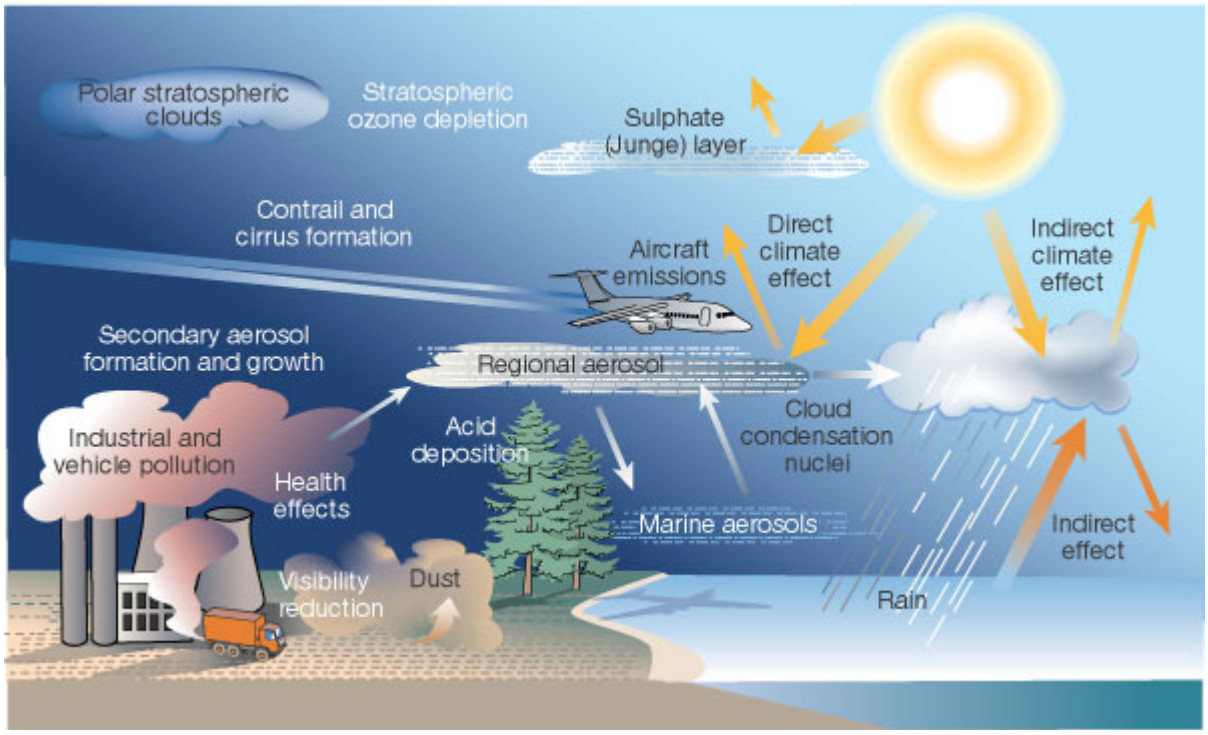

Figure 2: Atmospheric relevance of particles. Taken from Kolb (2002).

The region of Mongstad is strongly influence by winds from the sea and the aerosol can probably be characterized as mainly marine. Interaction of gas-phase amines and secondary products with the marine aerosol (e.g. heterogeneous reactions on sea-salt particles) are therefore of considerable interest. However little is known about these interactions.

As a starting point, the modelling effort should ignore such possible interactions and instead focus on the gas-to-particle conversion of emitted amines. Initial knowledge about these gas-to-particle conversion processes has been gathered in the last few years (e.g. Angelino et al., 2001; Murphy et al., 2007; Silva et al., 2008; Nielsen et al., 2010; Smith et al., 2010).

Requirements for modelling aerosol dynamics to include amine-specific particle formation and growth:

1. Aerosol dynamics processes solved in robust manner;
2. Possibility to add new aerosol compounds;
3. Possibility to include new nucleation process;
4. Possibility to add new condensation/evaporation processes;
5. Treatment of thermodynamic equilibrium in aqueous aerosols;
6. SOA module;
7. Treatment of CCN production.

Amines in the emission of the absorber unit (CO_2 capture plant) will be partly contained in water droplets generated by the wet scrubber and in fresh liquid droplets that formed after the flue gas leaves the stack. Solutions of amines are basic and thus emissions of amines will impact the pH of cloud and rain droplets. Amines are known to efficiently lower the surface tension of water droplets (Vázquez et al., 1997; Águila-Hernández et al., 2001; Águila-Hernández et al., 2007) and thereby facilitate the growth of aerosols (Karl, 2008). In detail, the presence of dissolved MEA in small water droplets will lower their surface tension and in consequence allow for growth out of the equilibrium state at lower ambient super saturation compared to pure water droplets or droplets containing equal amounts of sodium chloride. Dissolved MEA enhances the probability that very small water droplets can grow to fog/cloud droplet size (10-20 µm) and cause fog or cloud formation. Because of the surface tension depression resulting from dissolved MEA, cloud droplets can grow to larger droplets that can form rain drops.

Additionally, wash-out of droplets containing amines or amine salts from the plume cloud can contribute to severe corrosion affecting buildings and materials. Amines are used as corrosion inhibitors that can offer both cathodic protection by increasing pH and making proton reduction less favourable, and anodic protection by producing a passivation layer. However, as for ammonia, it is expected that, amines such as MEA can react with acids to produce alkyl ammonium salts (aminium salts). These salts may have similar atmospheric corrosion effects as inorganic ammonium salts, depending on their solubility and hygroscopic properties.

Organic salt formation from the reactive uptake of amines increases the effective van't Hoff factor of the solute, thereby decreasing the water vapour saturation required for a particle to develop into a cloud condensation nuclei (CCN). Reactive uptake into liquid droplets can also occur with gas-phase amines and it can thus be inferred that aminium salts will enhance the CCN activity of organic acids thereby contributing to haze, fog, and cloud droplet formation. Amine salts are also hypothesized to have contributed to significant hygroscopic growth observed in a plume from an animal husbandry area in California (Sorooshian et al., 2008). Acid-base reactions between amines and acids commonly present in the atmosphere (i.e. nitric acid and sulphuric acid) and in the emissions (e.g. from the power plant) play an important role in the formation of the salt particles. Depending on ambient temperature, relative humidity, and particle acidity the particle-bound amines could repartition to the gas phase (Murphy et al., 2007; Pratt et al., 2009).

In the aqueous phase of aerosols (aerosol droplets, fog droplets, cloud droplets, rain drops), chemical reactions can take place which produce low-volatility compounds thereby contributing to the growth of particles (growth of the condensation nuclei) after evaporation of the water phase. In clouds, this process is often referred to as cloud-processing of aerosol. Reactions occurring in clouds might also occur in non-activated aerosol solution droplets, however, with different efficiencies because of the larger ionic strength in such droplets (Raes et al., 2000).

2.2.6 Removal by dry and wet deposition

The removal of amines from the atmosphere is determined by photo chemical reactions and by dry deposition and wet deposition. Dry deposition is defined as uptake of pollutants on different surfaces and by vegetation. Wet deposition is defined as the removal of gas and particles by precipitation processes.

Dry deposition

The dry deposition of gasses and particles are dependent on concentration at ground level or close to the surface absorbing the gas or particle. The simplest and most commonly used formulation of dry deposition processes is through a deposition velocity formulation $Q_{dep}= C*V_d *t$, where Q_{dep} is the mass deposited C is the mean concentration of either gas or particulates at ground level, V_d is the deposition velocity and t is the integration time. The input to this calculation is concentration at ground level.

The next level is the resistance formulations where :

$dC/dt= -V_g.*C/z$

and

$V_g =1/(R_a+R_b+R_c)$

Where C is the concentration at reference height V_g is the deposition velocity and z is the reference height of the concentration. R_a is aerodynamic resistance , R_b is the quasi laminar boundary layer resistance and R_c is the surface resistance.

This formulation needs input of meteorology, and surface characteristics.

The case study(chpt 4.6) show that the simple dry deposition formulation is adequate and that the this process is represented adequately in the evaluated models.

Wet deposition

Wet deposition is mainly described through solvability of the compound in question and if there is rain in the geographical position of the pollutant. The wet deposition is normally computed as the integration of mass above a certain location when it is raining. Depending on the solvability of the substance in water all mass is deposited or a fraction or the mass is deposited if the solvability is low. This fraction is normally scaled through the precipitation intensity. The modelling is quite simple, but the meteorological model needs to provide time , space and intensity fields of precipitation. This is a challenging task for the meteorological models. This formulation or more advanced formulations of wet deposition is available in the evaluated models and is considered adequate. This is the same methodology that is used for the other work that NILU have been applying for wet deposition of hydroscopic substances from plumes from a local to regional scale.

The challenge is however to evaluate the effects of the deposition. The effects that need special attention from the worst case study is concentration in drinking water and surface water. This means that a better understanding of governing processes from the concentration in precipitation to drinking or surface water needs to be understood. Little is known today. The easiest way to get estimates of what happens in this process is through experiments. This can facilitate black box models for later studies of the processes.

3 Evaluation of current models

This chapter provides a short description of available atmospheric dispersion models susceptible for use in the envisaged improved accuracy atmospheric dispersion modelling system for amines from post combustion CO_2 capture.

An evaluation of the capabilities of these models is also provided in relation to the requirements and objective criteria identified in Chapter 2. We begin evaluating existing 3D regional scale dispersion models because these will be the backbone of the envisaged modelling system. The next sections indicate the capabilities of different process modules that can be incorporated as necessary to the application of refined estimates of amine atmospheric dispersion. The final section in this chapter provides an overall summary of the evaluation.

3.1 Regional scale dispersion models

The models described below are all well validated, flexible, transparent, open source models, except TAPM (TAPM, 2010), that is included here mostly for consistency with previous case studies on "worst case scenarios". As indicated in *Table 2*, none of the selected regional scale models is fit for the purpose of modelling amine atmospheric dispersion. This is because none of them has amine chemistry included in their present formulation. This however is not a problem, as relevant processes can be added to their basic model structure.

Table 2:. Summary overview of the regional scale dispersion models

Model	Fit for purpose	Well validated	Flexible	Transparent	Computationally efficient
CMAQ	-	+++	++	+++	++
CAMx	-	++	++	+++	++
WRF-Chem	-	+++	+++	+++	++
EMEP	-	+++	++	+++	+++
TAPM	-	++	o	-	o

Rating:

–	not feasible
o	poor
+	good
++	very good
+++	excellent / outstanding

For further information on the dispersion models see appendix D.

3.2 Embedded local scale dispersion models

The approximations used in CTM models are not necessarily valid close to the emission source, where the scalar and velocity field are not properly resolved by these models (e.g. few ten of meters compared to grid of few kilometres) and the actual chemical reaction rates are influenced by the effective ability of turbulence in mixing the reactant together. Therefore close to localized intense sources these models need to be coupled with plume in grid local dispersion models that will improve the above abrupt approximation in a manner related to their proper formulation.

The flexibility and modularity of the model will determine to what extent local scale plume models can be embedded in the regional scale models. As it was mentioned above, at present neither WRF-Chem nor EMEP have an embedded plume in grid module. TAPM uses a hybrid LPM approach with no treatment of chemistry, CAMx has an embedded, Lagrangian puff based, plume in grid model and CMAQ uses a embedded segmented plume in grid model.

A brief description of local scale dispersion models for the early dispersion phases from the stack is given in appendix E.

3.3 Meteorological models

There are at present a series of meteorological model that satisfy the requirements for input required in chapter 3.1. All of these model allow calculation of prognostic 3D meteorological input field with a spatial resolution down to 1x1km. A brief description of a selection of such models is given in appendix F..

Our recommendation is to select the WRF model (WRF, 2010; Skamarock et al., 2005) for further investigation in order to decide whether it fulfil the requirements needed for meteorological data in the amine dispersion modelling. The main reasons for selecting this model system are:

1. The WRF system is flexible, transparent, computationally efficient and is extensively validated, thus complying with our general requirements.
2. There exist an online user-support system and a growing WRF community worldwide from which knowledge and experience can be gained.
3. The WRF model has been offline coupled with CTM's like CMAQ(CMAQ, 2010) and there exist an online coupled version with an Eulerian CTM, WRF-Chem (WRF-Chem, 2010)
4. There are already preliminary WRF-activities at NILU, for instance on the coupling of WRF/EMEP and WRF/FLEXPART, and in the WRF/CHEM activity planned within the EXSIRA project.

3.4 Chemistry processes

The minimum requirements for the chemistry model for future implementation (1-year target) into atmospheric 3-D chemistry transport models are:

- Up-to-date atm. chemistry mechanism combined with a robust chemistry solver;
- Possibility to include amine-specific reactions and products;
- Flexible lumping scheme to add emission/chemistry of new compound groups;
- Possibility to add new photolysis reactions and reactions with NO_3;
- Include gas-phase/aqueous phase partitioning (Henry's Law coefficients);
- Coupling to aerosol model (incl. SOA).

In most cases the selection of a particular chemistry mechanism is coupled to the selection of the chemistry solver. The highest flexibility in terms of adding new reactions and compounds (here amine chemistry) is a kinetic pre-processor based approach, such as models that use the KPP kinetic pre-compiler. Rosenbrock solvers in combination with KPP enable high degrees of freedom in the implementation of chemical processes since they are able to cope with all time scales of chemistry. On the other hand, implementation of amine gas-phase chemistry into existing chemistry mechanisms requires knowledge about the applied lumping routines. This is difficult for all the existing chemistry mechanisms; it seems to be impossible for some (e.g. CBM-IV), while it seems feasible for others (e.g. SAPRC-07). In those models where the chemistry solver is adjusted to a particular mechanism (in the model code) inclusion of amine chemistry will be very difficult and will involve extensive testing for all typical atmospheric situations. Realistically, inclusion of amine chemistry is feasible, either by a) using strictly simplified reactions, e.g. max. 2 reactions per amine added to an existing chemistry mechanism that is solved with a dedicated (hard-coded) method, or by b) using a somewhat more detailed set of reactions together with a kinetic pre-processor. Both the need for high computational efficiency of the chemistry model and the planned timeframe of implementation lead to this recommendation.

An additional consideration in the mechanisms for amines is the fact that they are basic compounds that can react with atmospheric nitric acid (HNO_3) to form amine nitrate salts, which partition into the aerosol phase (Carter et al., 2008). This has to be considered while setting up the chemistry mechanism. It is highly recommended to enable a coupling of chemistry and aerosol models.

3.4.1.1 Chemistry solvers in 3-D models

The numeric solution of the transport and fate of chemical compounds in comprehensive three-dimensional atmospheric chemistry-transport models (here referred to as 3-D CTM) is usually done by an operator splitting approach. The chemistry operator of the continuity equation involves the solution at every grid point of the chemical kinetic equation:

$$\frac{dc}{dt} = P - L \qquad (4.4.1)$$

Where P denotes the chemical production term and L denotes the chemical loss term. For a chemical mechanism involving p chemically interacting species, we have coupled ordinary differential equation (ODE) system:

$$\frac{dn_i}{dt} = P_i(n) - L_i(n) \qquad (4.4.2)$$

where n is the vector of number densities n_i (i = 1, …p). A general characteristic of atmospheric chemistry systems is that they are *stiff*, that is, the chemical lifetimes of the species involved vary over many orders of magnitude. Characteristic chemical reaction times of atmospheric chemistry problems typically span 12 orders of magnitude (e.g. from 10^{-5} min^{-1} to 10^{7} min^{-1}) making its solution a formidable problem on a 3-D model grid.

For a more general nonlinear system (Eq. 4.4.1),

$$\frac{dc}{dt} = f(c) \qquad (4.4.3)$$

The so-called *Jacobian matrix* of the ODE system is defined as:

$$J = \frac{\partial f}{\partial c} \quad \text{with the elements } J_{i,k} = \frac{\partial f_i}{\partial c_k} \qquad (4.4.4)$$

The inverse of the eigenvalues of the *Jacobian matrix* correspond roughly to the characteristic reaction times of the reactive species. If τ_L and τ_S are the longest and shortest time scales over which the species vary (we will define these time scales below), then the *stiffness* can be defined as $s = \tau_L / \tau_S$. Numerical ODE solvers generally require time steps $\Delta t \sim \tau_S$, but we are interested in solutions integrated over time periods $\sim\tau_L$. Thus the number of time steps is of order s.

Stiff systems cannot easily be solved with *explicit* numerical solvers, such as forward Euler or Runge-Kutta, where the concentration at time $t+\Delta t$ is calculated solely on the basis of concentrations at previous time steps. In these solvers, the time step needs to be kept shorter than the lifetime of the shortest-lived species in order to maintain stability. This is not feasible for 3-D models due to tremendous computational time that would be needed to solve chemistry with a very small time step (e.g. $<10^{-5}$ min^{-1}).

Fully implicit, stiffly stable integration techniques have been developed and routinely used for such problems, the most relevant of these are the *Euler Backward Iterative (EBI)* solver and the *Gear* solver(Appendix A). Both are frequently used in 3-D models, but in the last decades, computationally faster solvers have been developed.

One approach to simplify chemical kinetics problems is the *pseudo steady-state* approximation (PSSA). For example, instead of solving the differential equations for short-lived species like O, OH, HO_2, and NO_3, one calculates and solves the corresponding PSSA algebraic equations. PSSA for short-lived species can also be used in combination with implicit solution of the remaining ODE system. Another example is to impose a fixed concentration of NO_x = NO+NO_2 while allowing the concentrations of NO and NO_2 to change; this can be done by replacing the chemical kinetic equation for either NO or NO_2 by the NO_x conservation equation.

An overview of widely applied chemistry solvers for use in 3-dimensional atmospheric models is provided in Appendix A. The fully implicit integration schemes EBI and Gear solver are very accurate and therefore widely used. Quasi Steady State Approximation (QSSA) solvers are the simplest approach for integration of the stiff ODE system that describes the chemical transformations and have been / are widely used in atmospheric 3-D CTM. Dedicated solvers of intermediate complexity are CHEMEQ and TWOSTEP, the latter is used in the EMEP model. Finally, in more recently developed models such as WRF-Chem, the Rosenbrock solvers in combination with a kinetic pre-compiler is used. This type of solvers allows for highest flexibility in terms of implementation of new chemical reactions.

3.4.1.2 Chemistry mechanisms in 3D-models

An important requirement of large-scale 3-D models is the ability to perform simulations with acceptable run-times for any given simulation period, which typically range from between months to decades. Therefore computational efficiency, parallelisation of the code over multiple processors and strict optimization procedures are necessary to avoid excessive load on shared computing facilities and achieve satisfactory runtimes. For this reason parameterisations are commonly used for the concise description of the processes that occur in the atmosphere. For example, rather than including an explicit description of the hundreds of chemical species which are thought to occur in the troposphere, lumped chemical mechanisms have been developed (e.g. CBM-IV (Gery et al., 1989); RACM (Stockwell et al., 1997)) which have the ability to accurately capture the chemical evolution of the most abundant trace gas species found in aged air-masses.

An overview of schemes of atmospheric chemistry reactions for use in 3-dimensional atmospheric models is provided in Appendix B. SAPRC-07 is the updated version of the previous SAPRC-99, and includes amine chemistry (Carter et al., 2007). CBM-IV and its updated version CB05 are based on the carbon-bond type aggregation of chemical compounds into group compounds ("lumped species"). The EMEP model has its own chemistry scheme which is rather detailed but has not been updated in recent years. WRF-Chem is often used together with the comprehensive atmospheric chemistry mechanisms RADM2

(Stockwell et al., 1990) and RACM (Stockwell et al., 1997); both adequate for regional air quality modelling.

3.5 Aerosol Modells

Treating aerosols in a large-scale modelling framework is always a compromise between the detail of description and computational efficiency. Sectional aerosol models used in 3-D model studies (e.g. Jacobson, 2001; Gong et al., 2003) reach generally a higher accuracy compared with the (modal) moment approach (Binkowski, F. S. and Shankar, 1995; Ackermann et al., 1998; Binkowski and Roselle, 2003) but are computationally more demanding. The drawback of the moment approach is that many of the processes such as aerosol formation and growth, cloud processing, and aerosol ageing in terms of its cloud nucleating properties, are difficult to simulate properly. There are several ways to improve the efficiency of a sectional aerosol model. Specifically, reduction of number of computational tracers, number of aerosol processes, and number of size bins is of major importance, as they affect the model efficiency severely. For a detailed explanation of the sectional versus the moment approach we refer to Appendix C.

Aerosol models are described in Appendix D and follow either sectional (using a discrete size distribution) or moment approaches (using a modal size distribution). Presented aerosol models contain up-to-date microphysical process descriptions of aerosol dynamics. It is also assessed whether the model treats SOA partitioning or not. Among the presented aerosol models some follow the moment approach: M7 (Vignati et al., 2004) and MADE/SORGAM (Schell et al., 2001); some follow the sectional approach: MAFOR (Karl et al., 2010a;b) and SALSA (Kokkola et al., 2008); some contain elements of a moment approach and bulk aerosol representation (CMAQ and CMAx aerosol modules); and one is a monodisperse model, MONO32 (Pirjola et al., 2003), which is implemented in the EMEP model.

3.6 Overall evaluation for chemical and aerosol modules

The recommendation is to include in the 3D chemical transport model a chemistry module capable to include the main reactions for nitrosamine and nitramines, with an effective chemical solver. In addition the model needs to have the capability of linking to an existing aerosol module where cloud-aerosol interactions can be further investigated. The third condition for the chemistry scheme is to allow for a formulation of the gas to particle equilibrium formulations. This implies that the thermodynamic equilibrium treatment of the SO_4-NO_3-NH_4-H_2O system in large-scale models has to be extended by the amine/aminium equilibrium (RNH_3, RNH_2, or RNH) as an additional multiphase compound, which can be treated in analogy to NH_4. It is recommended that laboratory studies are initiated to investigate the thermodynamic equilibrium over a wide range of atmospherically relevant temperature and relative humidity.

In Table 3 the different model-frameworks are presented which already incorporate treatment of gas-phase chemistry, aerosol dynamics processes, and thermodynamic equilibrium (of the SO_4-NO_3-NH_4-H_2O system). A ranking of these model framework is based on: degree of transparency and flexibility to implement amine chemistry and aerosol processes, degree of robustness/accuracy of the framework, and degree of experience that NILU/UiO have in usage and/or code modification of the different frameworks with respect to regional air quality modelling. The ranking is naturally subjective and it is determined to a large degree by the development experience with these model from the modelling team that would introduce these processes in the overall modelling framework.

Table 3: Overall evaluation of existing chemical and aerosol modules introduced in the different models

Ranking	3-D CTM (Host model)	Chemistry model	Aerosol Dynamics model	Thermo-dynamic Equilibrium model	*Implementation of amine chemistry. Estimated degree of*			
					Transparency	Flexibility	Original Validation	Development experience
1	WRF-Chem	RADM2 or RACM	MADE/ SORGAM	MADE/ SORGAM	+++	+++	++	++
2	EMEP MSC/W	EMEP/Two step	MONO32	EQSAM	+++	++	+++	++
3	CMAQ	SAPRC-07	Built-in	ISORROPIA	+++	+	++	o
4	CMAx	CMB IV	CF or CMU	ISORROPIA	+++	+	++	o
5	TAPM	Built-in	Built-in	Built-in	-	o	++	o

Rating:

–	not feasible
o	poor
+	good
++	very good
+++	excellent / outstanding

4 Case study of the recommended model

4.1 Introduction

The case study is aimed at identifying how the assessment of the possible effects of emissions of amines to air can be treated today. Rank the possible effects, to be able to focus on the effects that need to be addressed and investigated specifically, because they may pose a risk to the environment.

The case study focus on the understanding of the results and which gaps in the knowledge base that are most important to close for reducing uncertainty by

getting better precision in the estimation of exposure. The main processes that need to be solved in connection to the studies of exposure from the emissions of amines to air on the west coast of Norway are:

- Transport and dispersion of the pollutants
- Chemical reactions of the pollutants after emission
- Wet deposition of the substances.

The model needs "history" to describe the exposure from concentration and wet deposition. This means that the model needs to calculate the concentrations and the deposition taking into account earlier emissions. For the model this means that the model keep results from previous hours and calculate every hour of the year. The model also needs to take into account time and space dependent precipitation. TAPM is a model widely used internationally. The model was chosen because of the availability and that the input to the model is easy to achieve. The model solves the main features in a simple way. The model is a prognostic model for meteorology and a grid model for dispersion with a hybrid Lagrangian Particle Model for close to source evaluations. The model system is one of the few simpler modeling systems that predict precipitation. Precipitation is difficult to predict and therefore few models do. The disadvantages with the TAPM system is that the possibilities for chemical reactions is limited. Also the complexity of the meteorology in the west coast of Norway needs a better meteorological model giving input to the dispersion, photochemistry and deposition processes. TAPM have chemical schemes, but this is not sufficient for solving more complex photochemistry. The more complex models gives a higher flexibility of the chemistry. For the case study where chemistry is not solved by the modeling system the cost of going to a more complex system is not justifiable.TAPM must be seen as an intermediate model between the simple models and the more complex meteorological, dispersion and chemical models.

None of the models available contains amine chemistry. The chemical reactions is taken care of as bulk yields and given as a percentage of the emissions. These are then added to the emissions and treated as a tracer by the model. This is means that the model needs to describe transport, dispersion and precipitation taking into account previous emissions. TAPM have these features. Of the models available TAPM was evaluated as the most suitable for the case study of CCM on the large scale. For the local scale meteorological models are not so important. The wet deposition is also limited in this scale. Therefore the steady state Gaussian models have been used for calculations of concentration fields on the local scale. On the local scale the models CONDEP and CONCX have been used for estimating the local concentrations. These models are adequate for tracer studies on the local scale.

4.2 Air quality and water quality guidelines

The evaluation criteria for the compounds that are emitted or produced after emission to the atmosphere are not well known and investigations on the toxicity and possible effects are initiated to increase this knowledge. The evaluation criteria put forward here is where we have information. Nitrosamines and

nitramines are groups of substances. The evaluation criteria is set according to the most toxic substance.

The limits are divided in air quality limits and water quality limits and given in Table 4.

Table 4: Air quality limits for concentration in air for different compounds

Compound	Exposure	Toxicity	Safety Limit (Timescale)	Reference
MEA	Inhalation	Human health, subchronic	10 µg/m^3 (monthly avg.)	Låg et al., 2009
	Aquatic Env.	Algae/bacteria, chronic	7500 ng/l	Brooks and Wright (2008)
Nitrosamines	Inhalation	Human health, carcinogenic	1 µg/m^3 (8-hourly avg.)	German Regulation [c]
	Inhalation	Human health, carcinogenic	0.07 ng/m^3 (monthly avg.)	US EPA [d,g,i]
	Drinking water	Human health, carcinogenic	0,7 ng/l	US EPA [d]
	Aquatic Env.	Algae/bacteria, chronic	25 ng/l [e]	Brooks and Wright (2008)
Nitramines	Drinking water	Human health [f], carcinogenic	1 µg/l	Wollin and Dieter, 2005
	Aquatic Env.	Fish, chronic	200 ng/l [g]	Brooks and Wright (2008)
Formamide	Aquatic Env.	Invertebrate, chronic	24,000 ng/l	Brooks and Wright (2008)
Acetamide	Inhalation	Human health, carcinogenic	0.05 µg/m^3 (monthly avg.) [h]	California EPA (1999)

[c] German regulation for the group of nitrosamines, 8-hourly average.

[d] Long-term limit value for N-nitrosodiethylamine (DEN) corresponding to a 10^{-6} lifetime cancer risk, US Environmental Protection Agency, IRIS database: http://www.epa.gov/IRIS/subst/0042.htm.

[e] Safety limit derived for nitrosamine NDMA.

[f] Only drinking water safety limit established; inhalation risk was not considered in this work.

[g] Nitrosamine is a group of compounds and there is a range of toxicity for the different compounds. We have found levels of 0,02 and 0,07 ng/m^3. We have used 0,07 ng/m3 as a level for all nitrosamines. The Norwegian health authorities state that the level should be kept as low as possible.

[h] Based on a 10^{-6} lifetime cancer risk.

[i] http://www.epa.gov/ncea/iris/subst/0045.htm, section II.C.1. Summary of Risk Estimates).

[g] In addition to this The Norwegian Health Institute have stated that the exposure to nitrosamines should be kept at a minimum and that there are no lower limit of exposure.

4.3 Emissions

The CCM plant is located in one of the heaviest industrialized areas in Norway. There are several activities that emit pollutants to air. The main activity is the Mongstad refinery, the Combined Heat Plant (CHP) and the Technology Centre Mongstad (TCM). This report does not intend to give a complete overview of the emissions from these activities, but to the extent that these emissions will influence the effects of the emissions from CCM these emissions will be included and discussed. It is not taken into account the increase or decrease in emissions from the refinery or from the CHP from the CCM activity at Mongstad. The focus has been set to the non standard emissions.

4.3.1 Emissions from CCM

The emissions from the CHP are done through two stacks and these stacks will be used for emission of the flue gas after the CO_2 capture process. The physical emission parameters used in the dispersion calculations are described in table 1. The emissions are not real emissions but reflect an example of emissions according to today's knowledge. The emissions are given by the CCM project.

Table 5: Physical parameters for the stack

	unit	
Stack height	m	50
Stack diameter	m	6.6
Exit gas velocity	m/s	20
Exit gas temperature	ºC	30
Exit gas volume	m^3/s	640

The composition of the flue gas is given in Table 6 and *Table 7*. Table 6 give the content of traditional pollutants in the flue gas and *Table 7* give the emissions that are related to the CO_2 capture using amines in this case MEA.

Table 6: Content of traditional pollutants in the flue gas from CCM

Compound	value	Molecular weight	Unit g/s	Unit ton/y
CO_2	0,4 mol%	44	4700	150000
NO,	4,6 ppmv	29	3,6	113
NO_2	0,5 ppmv	45	0,61	19

Table 7: Emissions related to the use of amines.

Compound	value	Molecular weight	Unit g/s	ton/y
Monoethanolamine (MEA)	0,5 ppmv	61	0,82	25,9
Acetaldehyde	1,8 ppmv	44	2,13	67,3
NH3	2,6 ppmv	17	1,19	37,6
Methylamine	0,5 ppmv	31,06	0,42	13,2
Nitrosamines	3 ppbv		0.0087	0,272
Nitramines	3 ppbv		0,0085	0,268

Dimethylamine	0,5 ppbv	45,08	0,00061	0,019

4.3.2 Emissions from the other industries in the area

The TCM plant is the only other industry that has emissions of amines. The plant will be working with different technologies and the emissions are therefore uncertain. In this study the CCM project have given the emissions of MEA of 1.5-2 ppmv and Acetaldehyde of 2 ppmv. This corresponds to an emission rate of 0.031-0.058 g/s for MEA and 0.045-0.56 g/s of acetaldehyde. These emissions will come at the same time as the CCM emissions and could also impact in the same areas. The TCM plant is operating for 180 days a year.

4.3.3 Chemical transformation rates for the emissions

After the emissions have left the stack the emissions will be subject to chemical reactions. Since the modelling system treats the emissions of amines as inert substances it is necessary to estimate the chemical transformation and use these transformations as emission. This enables a first estimate of the exposure caused by chemical reactions and will be important in the evaluation of the importance of the chemical reaction scheme.

The following assumptions are done:

Atmospheric formation yields of MEA oxidation products were based on results from recent chamber experiments (Nielsen et al., 2010): 1% nitramines, 50% formamide, and 3% acetamide. Nitrosamines were not detected in the experiments.

Table 8: Fractional formation yields of degradation products (chemical compounds and compound classes) in the photo-oxidation of the parent amines. The fractions are used to calculate compound emissions from carbon capture

.

Solvent Amine	Nitrosamines	Nitramines	Acetamide	Formamide	Reference
MEA	0.00	0.01	0.03	0.50	Nielsen et al., 2010

Table 9: Emissions of pollutants related to the use of MEA (in kg/yr) from the CCM. Emission rates for the oxidation products are derived from the fractions given in the *Table 7*.

Scenario	MEA	Nitrosamines	Nitramines	Acetamide	Formamide
Case study	25.9	0	0,259	0,777	12.95

These emissions will be added to the direct emissions given in *Table 7*

In addition to the emissions from CCM, TCM will have emissions of amines. This means that there will be an addition of the TCM emissions to the emissions from CCM. The emissions from TCM are summarized in Table 10:

Table 10: Emissions of pollutants related to the use of MEA (in kg/yr) from TCM. Emission rates for the oxidation products are derived from the fractions given in the *Table 7*.

Scenario	MEA	Nitrosamines	Nitramines	Acetamide	Formamide
Unit	**ton/180 d**		**kg/180 d**	**kg/ 180 d**	**kg/180 d**
TCM	0.905	0	9,05	27,2	452.5

4.4 Meteorology and meteorological model used.

The CCM project has given a set of meteorological data to use for this study. The wind rose for the period December 2006 to April 2010 at Mongstad is given in Figure 3.

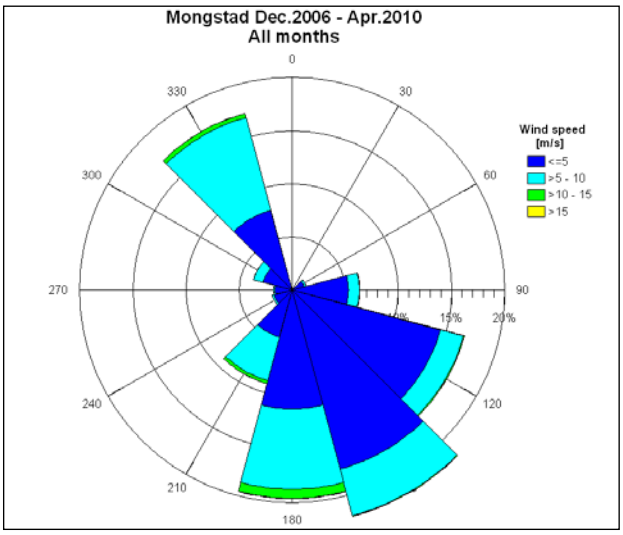

Figure 3: Wind rosette for Mongstad based on all presently available data from control centre IP21.

The data are also available as hourly data. To be able to do dispersion and deposition modeling it is in addition to the data given necessary to have information on dispersion parameters and precipitation simultaneously. This information is essential for the evaluation of dispersion and wet deposition. This means that the meteorology that is given is not adequate for running the models that are used for the estimation of exposure and evaluation of effects by NILU . To be able to answer the questions posed, meteorology was produced through the

model TAPM. TAPM is an integrated model consisting of a prognostic meteorological module using large scale weather predicting models as boundary conditions, thus eliminating the need to have site-specific meteorological observations (Hurley et al., 2005a). In our application the meteorological module was nested three times, from an initial domain of 600 x 600 km^2 (grid resolution of 15 km) down to a domain of 80 x 80 km^2 (2 km resolution) centred on the Mongstad plant. The region in which pollution concentrations and depositions were calculated is a 60 x 60 km^2 region (2 km resolution) within the smallest meteorological grid surrounding the plant. The inner 40 x 40 km^2 area was used to avoid the impact of domain border effects on the results. Initial and boundary conditions for the outermost grid were taken from the six-hourly synoptic scale analyses derived by the LAPS or GASP models from the Australian Bureau of Meteorology. Surface boundary data, such as topography, land use and sea surface temperature were taken from the US Geological Survey, Earth Resources Observation Systems (EROS) Data Centre Distributed Active Archive Centre (EDC DAAC) and the US National Centre for Atmospheric Research (NCAR).

The modelled period was the year 2007.

The seasonality of wind direction and wind speed at the met.no stations Takle, 30 kilometres northeast of Mongstad, and Fedje, an island, 18 kilometres to the west of Mongstad, were well reproduced by the dispersion model. Monthly averaged wind speed is underestimated by ca. 10-50% at both stations. TAPM systematically overestimated the monthly rainfall amounts during the year 2007 by up to a factor 2-3. The yearly rainfall pattern, however, was well captured by the model. The frequency of days with rain (rainfall amount >0.1 mm) in TAPM was about 20% higher than observed. The wind patterns are similar. This provided a full set of data for the dispersion calculations.

4.5 Dispersion/deposition calculations

Estimates of concentrations in air.

Concentrations close to the source

It is necessary to conduct special studies of the concentrations close to the source. This is because the TAPM model has a grid resolution of 2*2 km^2 and the concentrations field needs a better geographical resolution. TAPM can also be used for a better geographical solution, but steady state Gaussian models are adequate and easier to use. Concentrations close to the source is closely related to the design of the CCM plant and the structures in the vicinity. This means that the model that is applied for concentrations close to the source needs to take into account the building turbulence to evaluate the initial dispersion. The ideal is that the stack is tall enough for the emissions to travel in an elevation where these effects are not present. If this is not the case it is necessary to estimate the additional dispersion. It is also important that the model estimate downwash. This is the effect that flue gas can travel down the outside of the stack on the leeward side because of low pressure caused by the wind. It is also important that the model have possibilities of treating fumigation. Fumigation is if the plume travels above a very stable layer that suddenly breaks up and the plume is mixed down to

the ground causing high concentrations at a distance from the stack. This is typical for stacks close to the sea shore.

The model used here is are steady state Gaussian model called CONCX and CONDEP developed at NILU. This generic type of models is widely used and uses more or less the same formulations. The CONCX model predicts the hourly concentrations for a number of meteorological conditions as distance from stack. The model does include the above mentioned features. The user needs to use meteorological knowledge of the area to pick the critical situation. The CONDEP model uses meteorological statistics and predicts the yearly averaged concentrations in a predefined grid. The model can take into account topographic features.

Figure 4 show the hourly concentrations from CCM with an emission of 100 g/s with distance from the stack, and The concentrations shown in figure 4 is for an emissions of 100 g/s. The real emissions from CCM is different, but the dispersion parameters are equal. This means that the concentrations can be scaled with the ratio of the emissions. This means that if the emissions are 1g/s of a substance the resulting concentration is 1/100 the results in figure 4.

Table 11 the corresponding maximum values for the actual emissions.

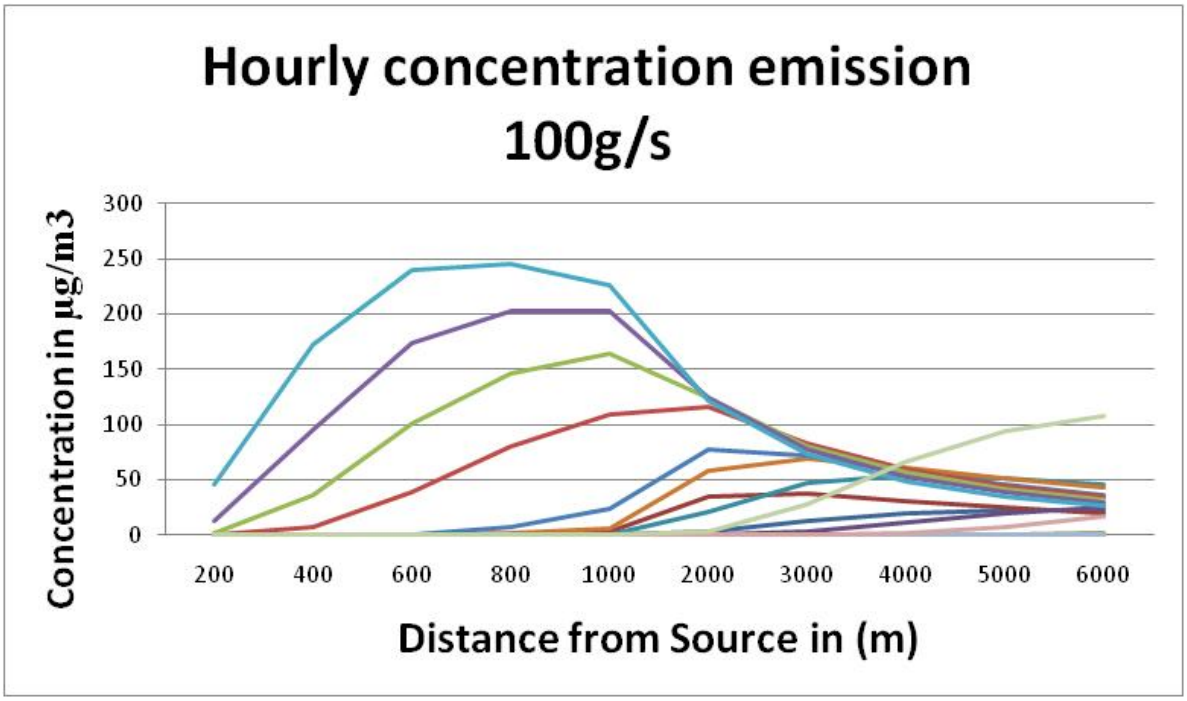

Figure 4*: Concentrations of an emission of 100g/s of a substance from the CCM plant. The coloured lines indicates different combinations of wind speed and atmospheric stability where strong winds and neutral atmosphere predicts is the highest concentrations close to the source and light wind with stable atmosphere is highest further from the source.*

The concentrations shown in figure 4 is for an emissions of 100 g/s. The real emissions from CCM is different, but the dispersion parameters are equal. This

means that the concentrations can be scaled with the ratio of the emissions. This means that if the emissions are 1g/s of a substance the resulting concentration is 1/100 the results in figure 4.

Table 11: Maximum hourly concentrations at ground level of the emitted pollutants from CCM.

Component	*Emission g/s*	*Max. Hourly conc. at ground level*
Monoethanolamine (MEA)	0,821806	0,21 µg/m^3
Acetaldehyde	2,134	0,53 µg/m^3
NH3	1,190944	0,30 µg/m^3
Methylamine	0,418447	0,10 µg/m^3
Nitrosamines*	0.008672	2,17 ng/m^3
Nitramines**	0,008521	2,13 ng/m^3
Dimethylamine	0,000607	0,15 ng/m^3

*Emissions only
** Emissions plus a factor of 0.01 on the MEA emission

This show that the maximum concentrations come at 500-1000 m from the stack. When comparing the hourly concentration of MEA to the short term inhalation German criteria of 1 µg/m^3 as an 8 hour limit for nitrosamines the predicted hourly concentration is a thousand times lower than this. The hourly maximum concentration predicted for nitrosamines is slightly over 2 ng/m^3. This means that the maximum hourly concentration is 500 times lower than the German 8 hour average limit. The other compounds are below the short term criteria.

The results for the yearly averaged concentrations of emissions of 100 g/s from the CCM stack for the year 2007 is shown in *Figure 5*.This shows that the maximum yearly concentration is estimated to 9 µg/m^3 with 100 g/s in emission. Table 2 give the corresponding concentrations for the emitted substances.

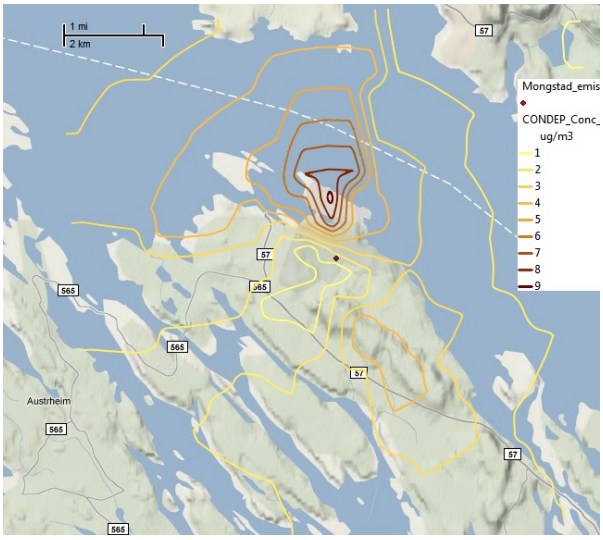

Figure 5 :Yearly concentrations with emission of 100 g/s for CCM at Mongstad for the year 2007. Unit µg/m3.

Table 12: Maximum yearly concentrations of the other pollutants emitted at Mongstad from CCM for 2007. Unit ng/m^3.

Substance	Emission	Max yearly concentrations
Monoethanolamine (MEA)	0,821806	73,96 ng/m^3
Acetaldehyde	2,134	192,06 ng/m^3
NH3	1,190944	107,18 ng/m^3
Methylamine	0,418447	37,66 ng/m^3
Nitrosamines	0.008672	0,78 ng/m^3
Nitramines	0,008521	0,77 ng/m^3
Dimethylamine	0,000607	0,05 ng/m^3

This shows that the yearly averaged concentration of nitrosamines is 10 times higher than the evaluation criteria 2000 m from the stack for monthly averages. The monthly modelled averages will be higher than this and therefore the exceedanse for the maximum month will be higher than 10 times. The concentrations will be higher than the evaluation criteria in most of the grid covering 100 km^2 around the stack.

Concentrations further than 5 km from the source

The Based on TAPM calculations for CCM, yearly mean concentrations (2007) of MEA in air were below 0.032 µg/m^3 inside the 40 x 40 km^2 study domain (Figure 6) and further from the stack than 5 km. Monthly mean concentrations of MEA in air reached maximum values of 0.032-0.16 µg/m^3. Highest levels were 5-15 km to the north of Mongstad. In most months, the simulated plume also impacted the region south-east of Mongstad at a distance of 2-20 km, but monthly average concentrations were below 0.05 µg/m^3.

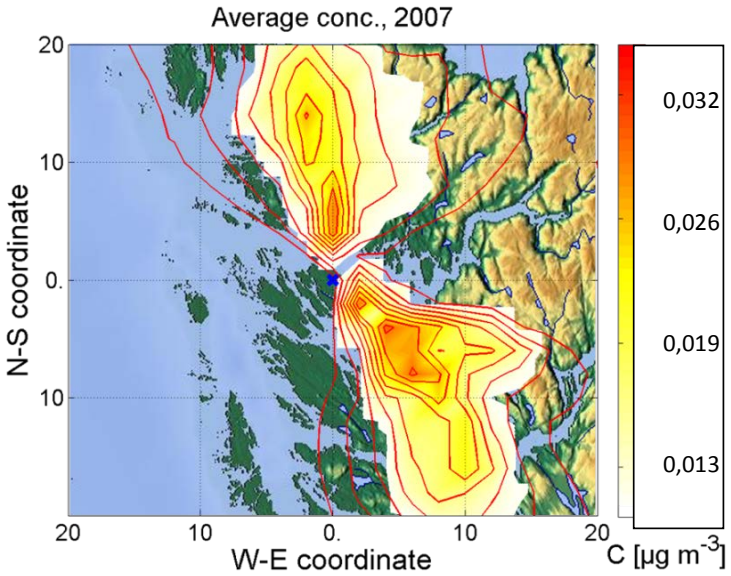

Figure 6 : *Predicted yearly mean MEA concentration in air (µg/m^3) in 2007 using meteorological data of 2007 in the 40×40 km^2 domain around CCM (blue cross). (Karl et al.,2010)*

The yearly average of short-term MEA concentrations in air - calculated from the modelled 8-hour average concentrations - in the 40×40 km^2 domain for the year 2007 are shown in Figure 7 . Highest values occur in April-June in an area 8-18 km southeast of CCM, where short-term MEA air concentrations reached up to 2,3 µg/m^3 .

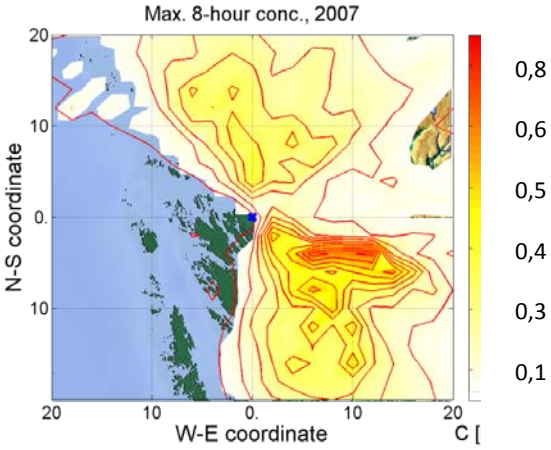

Figure 7: Maximum 8-hourly averages (2007) in the 40×40 km^2 domain around CCM (blue cross).Unit µg/m^3*(Karl et al.,2010)*

.

The concentrations of the other components are assumed to have the same dispersion patterns as MEA and the concentrations are given in Table 13.

Table 13:Maximum yearly , 8 hourly and monthly concentrations for the emitted substances outside 5 km.

Substance	Emission ton/yr	Correction factor	Max. yearly average µg/m^3	Max. 8 hour average µg/m^3	Max. monthly average µg/m^3
Monoethanolamine (MEA)	25,9	1,000000	0,032000	2,3000	0,160000
Acetaldehyde	67,3	2,598456	0,083151	5,9764	0,415753
NH3	37,6	1,451737	0,046456	3,3390	0,232278
Methylamine	13,2	0,509653	0,016309	1,1722	0,081544
Nitrosamines	0,272	0,010502	0,000336	0,0242	0,001680
Nitramines	0,268	0,010347	0,000331	0,0238	0,001656
Dimethylamine	0,019	0,000734	0,000023	0,0017	0,000117

There are one substance over the evaluation criteria. This is nitrosamines. The evaluation criterion from USEPA is 0.07 ng/m^3 as a monthly value. The model

predicts 0.33 ng/m^3 as a yearly maximum and 1.6 ng/m^3 as a maximum monthly average. These concentrations are respectively 5 and 23 times higher than the limit and therefore needs to be investigated further. The result is a significant exceedanse, partitioning of MEA and other emitted compounds into the liquid phase of the plume may lead to lower concentrations in the gas-phase when assuming that rapid (irreversible) chemical transformation occurs in droplets released from the stack. These concentrations are close to the source and the processes that influence these emissions needs to be fast. It is therefore fast chemical reactions that will have a possibility to influence these concentration estimates. These have not been taken into account. This indicates that it is necessary to specify the toxicity of individual nitrosamines to be more specific on the toxicity and then solve the photochemistry in the dispersion model together with a better representation of the precipitation so that the model can give estimates for the individual nitrosamines.

4.6 Sources and sinks of the emissions

Deposition

The main sinks of the pollutants is as described earlier is through chemical reactions and deposition. The deposition can be divided into two: dry deposition and wet deposition. The processes are described in chapter 2.2.6. The deposition from the CCM plant is described here.

Dry deposition

To evaluate the importance of dry deposition the most simple model have been evaluated for the maximum concentration of nitrosamines that were evaluated to be closest to the evaluation criteria. The estimate is done through the dry deposition velocity. The mass flux is defined by multiplying the average concentration with the dry deposition velocity and multiplying with the integration time. The dry deposition is estimated to be low compared to the wet deposition.

To illustrate the magnitude of the dry deposition a simple calculation have been done. If the concentration in a single point was equal to the criteria of 0. 07 ng/m3 and the integration time is 8000 h. The deposition velocity is normally 0.05 cm/s or less. We have used 0.05 cm/s as a deposition velocity. This results in a dry deposition of 0.1 µg/m^2 year. This is very low compared to the wet deposition. The flux is so low that the dry deposition can be neglected.

Wet deposition

In this study we have focuses on the wet deposition of MEA, Nitrosamines, nitramines, acetaldehyde, methylamine and dimethylamine. All these components are highly hydroscopic and therefore available for wet deposition. Wet deposition is modelled through a tracer. This means that the assumption made that all the emitted mass is available to wet deposition is a good assumption. For the

substances produced chemically after emission this is not the case. The chemical reactions will take time. The effect of this is that the mass of the chemically produced substance will have a time delay and the maximum exposure will come further from the plant. The levels will depend on the amounts produced chemically.

The annual wet deposition flux of MEA in the study domain is shown in *Figure 8*. The maximum wet deposition for the year of MEA inside the grid was 29 mg/m^2, and the grid-averaged wet deposition flux was 1.9 mg/m^2.

To check the validity of the wet deposition calculations a back of the envelope calculation is done. The yearly MEA amount that is deposited inside the study region predicted by the model corresponds to 14% of the total emitted amount, i.e. 3.6 t/yr MEA. Assuming, that all the deposition is done in a 30°-wide sector within 20 km distance of the plant the average deposition is 35 mg MEA/m^{2}yr inside the sector. If the occurrence of precipitation in one 30º sector is 10%, the average is 3.5 mg/m^2. The maximum deposition predicted by the model is 25 mg/m^{2}yr. This is within the range of the rough estimate presented here. The maximum deposition covers an area of 2*2 km^2 and the sector 104 km^2.

The estimates from (Karl et al in 2008) indicate a lower estimates (0.02-0.2 as average and 1-7 as maximum) than the two above . This is mostly caused by the gradients in the precipitation fields and that the current models calculate all hours of the year and therefore calculates deposition geographically.

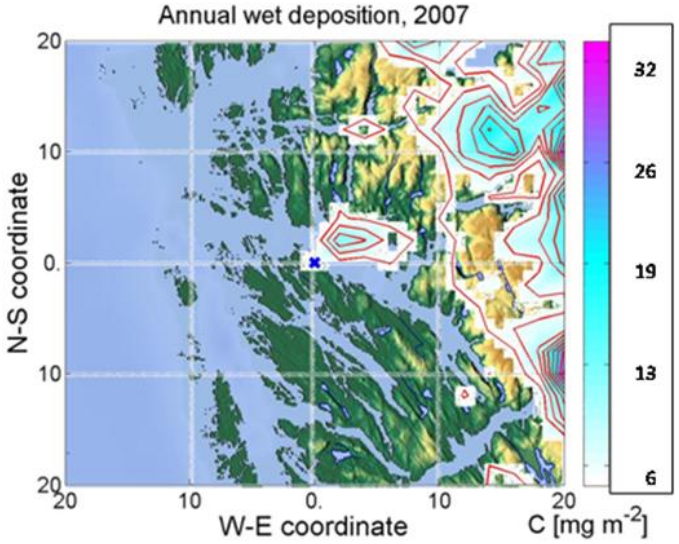

Figure 8: Predicted total wet deposition flux (in mg/m^2) of MEA for the year 2007 inside the 40x40 km^2 domain with CCM (blue cross). (Karl et al.,2010)

The evaluation criteria for wet deposition is based on content in water either drinking water or surface water. This evaluation is difficult and the worst case study have focused on concentration in precipitation. To get from wet deposition

to water quality it is necessary to know the concentration in the precipitation. This is not estimated in the model. We have gridded precipitation results from the meteorological model. The precipitation for 2007 was in average over the grid approximately 2000 mm. The precipitation in the location of the maximum deposition corrected for over prediction by the model is 2000 mm which is close to the average precipitation. Measurements of rainfall in the area show a large variation with approximately 1000-1500 mm over the sea and up to 8000 mm in the wettest areas in the mountains. The mean concentration of MEA in precipitation where maximum deposition occur is 2000 l/m^2 yr/29 mg/m^2 = 14.5 µg/l on average for the whole grid 1µg/l. All the precipitation is not affected by the plume and this means that this number easily and probably can increase by a factor 2. On the other hand nitrosamines are destructed by photolysis this means that the emitted nitrosamines are destructed in the daytime but not night time and can therefore be reduced by a factor two.

The other estimates of concentration in rain water for emissions from the CCM plant is given in *Table 14*.

Table 14: Estimation of content in precipitation for the emissions from CCM.

Substance	unit	Predicted conc. in prec. Average in grid	Max in grid
Monoethanolamine (MEA)	µg/l	1,000	14,500
Acetaldehyde	µg/l	2,598	37,678
NH3	µg/l	1,452	21,050
Methylamine	µg/l	0,510	7,390
Nitrosamines	µg/l	0,011	0,152
Nitramines	µg/l	0,010	0,150
Dimethylamine	µg/l	$7{,}5\ 10^{-6}$	0,011

The estimated concentration in precipitation can be evaluated towards the evaluation criteria for water quality. The precipitation concentration for nitrosamines is 50 % higher than the evaluation criteria for the average and in the maximum area more than a factor 100 higher. The uncertainty in the model predictions is large. This estimate is probably high, but can also be low. The evaluation above clearly indicates that more work needs to be done to give better estimates of the concentration of the precipitation. It also shows that nitrosamines are the critical substances for the emissions. This conclusion is however dependent on the chemical production and destruction, the existence of non known substances and the toxicity of the known substances are not changed dramatically.

Uncertainty

TAPM systematically overestimated the monthly rainfall amounts during the year 2007 by up to a factor 2-3. The yearly rainfall pattern, however, was well captured by the model. The frequency of days with rain (rainfall amount >0.1 mm) in TAPM was about 20% higher than observed. Due to the nature of the wet

deposition in the dispersion model, where the amines are assumed to be completely dissolved in the rain water, it is the frequency and timing of rainfall, rather than the quantity that determines the total wet deposition. In this regard it is expected that TAPM overestimates wet deposition by 20-30%.

4.7 Changes in the emissions

The case study is done with the use of MEA as the active amine. This is the case where most effort has been done to estimate the emissions and the chemical reactions and effects of the emissions. From previous studies it is known that the use of other amines in the capture process will have the potential of producing nitrosamines. The case study shows that nitrosamines are the substance that has the highest potential for causing effects. This means that changing the emissions to other amines will increase the uncertainty in the estimation of the exposurefrom the most critical substance and probably increase the exposure and that the environmental effects should be taken into account when choosing the capture amine in the process.

4.8 Discussion

Conclusion and discussion on Case study results

The conclusions and discussion will focus on the gaps in the model system used in the case study and justify the need for closing of these gaps. The need for closing the gaps will be dependent on the consequences the development have on the estimated critical exposure from the emission.

The main conclusions from the Case study are that possible effects can arise from the emissions from CCM. These are mainly connected to concentrations in air and water quality. There is also a large uncertainty in the evaluation criteria and the emission estimates, but this is beyond the scope of this report to discuss. The main problems are connected to the nitrosamines. For MEA the nitrosamines are emitted from the plant and not produced chemically after emissions. It is believed that this is not the case for other candidates of amines used for CCS. The concentrations are close to and above the guideline for inhalation and the estimations are more than 100 times exceeded for drinking water. There is little known on the behavior of nitrosamines in water and in vegetated surfaces. It is also known that nitrosamines is subject to photolysis and will thereby be destroyed by sunlight. This is not taken into account. The highlight is however that the problems with concentrations in air and effects on water quality cannot be ruled out and it is necessary to improve the accuracy of the modeling tools to improve the estimation of probability of effects.

The weakest part of the modeling system in the case study is the non treatment of chemistry. To have a good knowledge of the chemistry it is possible to estimate the sources and the sinks for the specific nitrosamines that are present. It might be possible that the majority of the nitrosamines are destructed soon after emission and therefore not pose a threat. It is also possible that because of the mixture that is emitted, nitrosamines are formed. Another possibility is that the substances that are formed have very different toxicity from what is assumed here. The life time

of the amines are also of importance. This is therefore evaluated as the main source of uncertainty.

The modeling is adequate when it comes to transport. The chemical reactions are so fast that the chemistry will need to be solved. There are indications that the plume can have a droplet fall out depending on the humidity in the surrounding air and the vapor content in the plume. This can cause severe corrosion damages to surrounding structures.

In addition to this the modeling system needs to estimate the deposition correctly. The deposition is dominated by the wet deposition. This means that the precipitation field needs to be determined. Both the time resolution and the geographical resolution need to be sufficient to describe the rain correctly. This is a difficult task to model. A 2*2 km^2 grid resolution and an time scale of 1 hour as used here will be adequate. The timing of the rain and the concentration of the components in the rain water is important. The concentration in rain water needs to be estimated for a good estimate of concentration in drinking water . This means that the model needs to have good representation of cloud physics. The main uncertainty is however in how the connection from precipitation to surface water is done. This part of the evaluation needs to be understood better.

Plume dispersion will cover several geographical scales. The models that exist today do not have the resolution to describe the processes in the plume from local scale that have a dimension of tens of meters up to regional scale covering several hundred kilometers horizontally and several thousand meters in the vertical. Models describing the local scale from meters up to approximately 5-10 km exist. However these models have a problem including photochemistry and none of them have amine chemistry. Models for larger scales also exist. These models do not represent the first part of the plume well. This is shown in the fact that two models have to be used for estimations in the case study. These models can be used separately as long as the chemical reactions are not important. When chemical reactions are important the models needs to be coupled so that the local model feeds information into the larger scale model.

The main non desirable effects of the amine emissions from the case study are connected to the sources and sinks of the different components. Emission and photochemical reactions are the main sources the main sinks are photochemical reactions, removal through wet deposition and dry deposition. The case study is done through a suite of models. The model system can be split into the following sub models.

Meteorological model

To describe the meteorology at Mongstad it is important to take into consideration the processes that are caused by the fact that the plant is situated in an area with sea land effects and effects of topography. This means that the model needs to include these processes and have a spatial resolution that reflects this. The transport of the pollutants is well represented in the case study. The transport is described geographically and has a time resolution of 1 hour. The precipitation is however grossly overestimated. To reflect the orographic effects it is necessary to reflect the differences of 1000 mm precipitation at sea and the 8000 mm

precipitation in Gulen. The timing of the precipitation is also important and the model is not verified against actual precipitation. This needs to be done. The model needs to estimate the precipitation on a hourly scale. The precipitation field needs to be accurate to estimate the wet deposition.

Dispersion
The challenge here is to connect the different geographical scales and use a formulation that can support chemical reactions in the atmosphere. The case study does not handle this satisfactorily. It is known from several studies of large and regional scale models that the concentrations in the grid cell with emissions do not represent the emissions in the cell well. The longer the distance from the stack the better the models perform. This is because of geographical resolution. This means that a coupled model is needed if information needs to be transferred from one scale to the next.

The dispersion with TAPM can handle local scale and regional scale but not at the same time. Therefore the CONCX and CONDEP models are used for the local scale . These models have a good resolution close to the source.

The representation close to the source takes into consideration the main source characteristics such as building turbulence and plume rise in addition to the normal dispersion. The dispersion is also evaluated as satisfactory.

It is also evident that the emissions from CCM are in an industrial area and that there are other plumes in the area and the TAPM and CONCX model is not able to treat interactions between the plumes.

Chemistry
It is shown through the case study and other studies that concentrations of the products formed by amines in the atmosphere after released from the stack and in precipitation can cause non desirable effects both to human health and the environment as such. This is for drinking water and the concentration in air. This means that the sources of the active amine in the capture process are not the main concern, but the substances that are formed chemically and emitted or formed chemically after emission. This conclusion is drawn on the knowledge of MEA as the active capture component. The conclusion will also hold for use of other active amines but some of the alternatives the effects of the active amine come in addition. The chemistry for the different alternatives of active amines will have different chemical reaction schemes.

When looking into the chemical processes that take place after the emissions have left the stack it is important that the chemistry is dependent on the composition of components in the atmosphere that the emissions are emitted into. The chemical reactions will to some extent compete for the same molecules and it is therefore important to solve the amine chemistry at the same time as the “normal” chemistry.

When released from the stack the plume contains water droplets that are caused by the cooling of a humid plume. This is the visible part of the plume. Most of the amines that are emitted are hydroscopic and the main mass will probably be

contained in the water droplets. The plume will gradually be dispersed and the humidity in the plume will decrease and the droplets containing aerosols and pollution will evaporate, but will still contain some water. This means that the aerosol processes are important. Amines will also lower the surface tension in the droplet so that the droplet will have a larger volume and this will favor having droplets in the plume for a longer time.

The concentration on the particle and in the water is completely different than for the concentrations in air and it is therefore important that the chemical model handles both the gaseous and the aerosol/water phase of the chemistry. It is probable that the chemistry is different and the yields in the aerosol/water phase could be very different than the gas phase.

This show that there is a need for first including photo chemistry because the substances that is formed after emission are important for excluding non desirable effects and to describe the chemically produced substances in the atmosphere it is necessary to include gas and aerosol/water chemistry and solve this simultaneously with the photochemistry taking place in the surrounding atmosphere. The model needs to be embedded into a dispersion model.

Dry deposition
Dry deposition is not estimated in the case study. Dry deposition is driven by the concentration of the compounds at ground level. The emissions from CCM are through a stack. When released from a stack the concentration of pollutants at ground level is low. The mass that is available for deposition is therefore low and is considered not important for the estimation of effects. Dry deposition becomes important when several sources are emitting and collectively creates concentrations at ground level that makes dry deposition an important contributor.

Wet deposition
To be able to remove substances through precipitation (wet deposition) it is necessary for the pollutants to be in contact with the clouds and rain. In addition to this the pollutants must be absorbed by the water droplets. There are three main zones; these are above cloud, in cloud and under the cloud. The case study treats the emissions as a tracer. The substances are considered to be washed out by rain completely when it is raining because of the large affinity to water. If the pollutants are not hygroscopic the wet deposition is not effective and the pollutants needs to undergo a chemical transformation to be available for deposition. This is the case with NO and NO_2.

The second part of the wet deposition is the representation of the precipitation. There are three important characteristics of wet deposition of amines at Mongstad and the vicinities. These are:

- representation of precipitation amount geographically.
- frequency of the precipitation geographically.
- intensity of the precipitation.

The model needs to have good time resolution of precipitation to estimate when the deposition takes place. The geographical resolution determines when the

deposition takes place. The intensity is not so important because of the model formulation that all mass is deposited when raining.
The Case study does not represent chemistry and is therefore weak in describing the availability. On the precipitation side the Case study has both the time resolution and the geographical resolution necessary but the intensity is not well described. The main uncertainty is connecting concentration in precipitation to concentrations in drinking water and surface water.

Conclusion
The case study highlights that the concentrations in air of nitrosamines can cause non desirable exposure. In this case the nitrosamines are given as emissions. Nitrosamines can also form in the atmosphere. For MEA experiments suggests that nitrosamines will not be formed in the atmosphere by gas phase reactions.

The amines and pollutants emitted are hygroscopic and therefore have a tendency to be transferred into the liquid phase of aerosols and clouds. Little is known about the fate of these substances in the liquid phase. It is likely that the emitted substances are in the water phase some time after emission. Exposure to concentrations in air and to concentrations in precipitation has to be considered.

If rain water is used as drinking water this will have a concentration of approximately 100 times the acceptable drinking water level. There are three main areas that can affect these conclusion. These are:

- Reduction of emissions
- Better evaluation criteria
- Better exposure estimates.

To be able to improve accuracy in the exposure estimates it is important to improve the description of the chemical reactions to better estimates the quantities of the different substances in the atmosphere and include these in the model formulation. The chemical reactions must be coupled to the background chemistry in the surrounding air and the turbulent mixing of atmospheric oxidants into the plume directly after release from the stack has to be included. This will give better estimates of concentrations in air. The concentration of the substances in precipitation strongly depend on the concentrations in air. When the chemical reactions are included the concentration in precipitation can be fairly well estimated. The TAPM model over estimates the amounts of rain but relatively accurately represents the precipitation patterns. The representation of precipitation in time and space needs to be improved and is currently a weak point in all large-scale models.

To give a better estimate of the concentration of drinking water from concentration in precipitation is necessary. For this more detailed information about the exposed aquifers has to be included and the possibility of abiotic and biotic degradation of compounds in water and soil has to be investigated by predictive tools and experimental studies.

The combining of scales, simultaneous treatment of several plumes and interaction of plumes is also important.

5 Recommendations for amine chemistry dispersion model development

The recommendation is to make use of a suite of models. This means further development of existing 3D chemical transport models of recognized capabilities to account for amine relevant processes and use of box models and laboratory chamber experiments to test the implementation of these processes. The recommendation is to focus the development to include processes relevant for the atmospheric dispersion of nitrosamines and nitramines and get these models operational .

Areas that need attention

The findings in the case study show that there are two main areas that need to be addressed in a modeling tool for estimation of exposure from amine emissions. These are:

- Concentrations of nitrosamines/nitramine with short to medium exposure time at a local scale.
- Concentrations of nitrosamines/nitramine in drinking water.

In order to understand better the origin of these concentrations, the following processes need to be investigated:

- Chemical reactions of amines
- Understanding of the processes from concentrations of amines in rain water to concentrations in surface/drinking water
- The representation of precipitation(intensity, occurrence, amounts ,geographical distribution)

These processes are not well understood or represented in the models and therefore introduce uncertainty in the modeling of exposure. It is therefore recommended to focus on increasing knowledge and implement this into the modeling tools to reduce uncertainty in the worst case estimates.

Chemical reactions of amines

Amines are shown to be very reactive when emitted to air. It is also shown that the chemistry is dependent on the air that the amines are released into and that there are interactions with the “background air”. This means that the chemical models need to solve the amine chemistry embedded into a well known “background chemistry”. For MEA it is shown that the gas phase chemistry does not produce nitrosamines. It is however not necessarily true that nitrosamines are

not produced in the atmosphere after emission. This is because the emissions probably will be in the droplet phase given that the substances are hydroscopic and the humidity in the plume will cause formation of droplets after emission. This is seen as a cloud in connection to the stack. This means that the majority of the emissions will be in a droplet form. Droplets contain aerosols and when the drop is evaporating the aerosol will be likely to contain a water film and the emissions will be contained by the particle or particle with a water film. These chemical reactions will be different from the gas phase reactions. It is therefore important to understand the chemistry and to include this understanding in the modeling tools.

The recommendation is to include in a 3D chemical transport model a chemistry module capable to include the main reactions for nitrosamine and nitramines, with an effective chemical solver. In addition the model needs to have the capability of linking to an existing aerosol module where cloud-aerosol interactions can be further investigated. The third condition for the chemistry scheme is to allow for a formulation of the gas to particle equilibrium formulations. This implies that the thermodynamic equilibrium treatment of the SO_4-NO_3-NH_4-H_2O system in large-scale models has to be extended by the amine/aminium equilibrium (RNH_3, RNH_2, or RNH) as an additional multiphase compound, which can be treated in analogy to NH_4. It is recommended that laboratory studies are initiated to investigate the thermodynamic equilibrium over a wide range of atmospherically relevant temperature and relative humidity.

If other amines are used for CC the specific amine needs to be investigated because the different amines behave differently in the atmosphere.

From Precipitation to drinking water

The process from concentration of amines in precipitation to concentrations in drinking water is complex and the understanding of this is limited. This process is however vital for the evaluation of the drinking water quality and this is probably where the largest uncertainty lies. The assumption that the concentration in drinking water is equal to the concentration in precipitation is weak and it is therefore necessary to find a better assumption. Better assumptions needs more knowledge.

Prediction of precipitation.

The representation of precipitation in the meteorological models needs to be improved. Precipitation is the driver of the wet deposition and it is therefore important to have correct estimates of precipitation on an hourly basis. It was found in the case study that the representation of the precipitation needs to be improved.

1 year plan

It is proposed that during the first year the modeling system is initially implemented and made operational to allow for building the modeling tool in the next phase. This must be coordinated with other initiatives and projects dealing

with the same processes. We recommend that the present knowledge on MEA to be gathered and structured to be introduced in a 3D dispersion modeling system.

To gain knowledge on the droplet /aerosol phase chemistry it is necessary to conduct experiments. These experiments are needed to be able to build an adequate chemical model that takes into account the gas phase and the droplet/aerosol chemistry. These experiments can be done in chambers specially designed for these purposes. There are several chambers available worldwide.

To gain knowledge on the process from rain water to surface/drinking water experiments in the laboratory and analysis of samples from the ExSIRA project on content in water from the irrigation experiments should be done. This will enable a better estimate of sources and sinks for this process and reduce uncertainty. This empirical results can be made into a box model that after validation, can then be included in the 3D modeling system.

The evaluation of existing models presented in Chapter 3 identified three possible modeling systems that were good candidates for future more refined amine dispersion calculations. It is proposed to implement different CMAQ scenario runs during the first year of development. This is to provide a first benchmarking for more accurate dispersion of amines in the atmosphere. It is also important to evaluate if the atmospheric reactions of 15 amines is adequate for the purpose of evaluating the effects of amine emissions. It is also recommended that experiments designed to quantify the fate of the different compounds either emitted or produced in the atmosphere from content in precipitation to drinking and surface water is done to facilitate box models for estimation of impact from wet deposition. On the short time horizon this is probably the activity that will reduce uncertainty in the effect evaluation.

To be able to estimate the short term concentrations a plume in grid model is needed. The introduction of such type of module in the 3D framework is necessary in order to improve the estimate of the short-term near source exposure estimate. With this formulation, the model could be able to resolve the chemistry with sufficient resolution for plume description. This will enable the description of the sources and sinks in the plume. The emphasis should be on the fast reactions because of the relative short travel time to maximum ground level concentrations.

A summary of the recommended activities in the first year:

- Establish the chemical reaction scheme and prepare this for modeling.
- Conduct experiments for droplet/aerosol chemistry for MEA
- Conduct laboratory experiments to quantify the sources and sinks of the amines from concentrations in precipitation to concentration in surface water.
- Develop procedures for using measured precipitation to improve predicted precipitation
- Use the CMAQ model for scenario benchmarking calculations
- Start the development of the Plume in Grid formulations in a 3D modeling framework

3 year plan

The three year plan will build on the 1 year plan and use these results to implement the chemical reaction in the modeling tools chosen. To do this the following bullet points are recommended:

- Develop the gas phase chemical reaction model
- Develop the droplet/aerosol model
- Merge these two models with the existing chemical model
- Include the chemical models in the modeling tools
- Test and make the large scale model operational.
- Develop the chemical plume model
- Test and make the chemical plume model operational.
- Build the chemical plume model into a plume in grid model where information flows from the plume model into the grid model.

The content of the 3 year plan is dependent of the findings in the earlier stages. This means that the importance of the chemical reactions in the different phases needs to be assessed before a chemical model is developed. The amount of work necessary for including the processes will naturally depend on this. This work must also be coordinated with initiatives through other bodies and institutions to avoid double work. It is also important that the development of the models facilitate the inclusion of other chemical reactions because the amine that is chosen for CC is not necessarily MEA and the chemistry for other amines will be different from this.

The recommendation is to, during the second and third years, carry out a separate implementation of the amine dispersion in a different modelling framework, for instance WRF-CHEM or WRF+EMEP. The comparison of the two model implementations will lead to a better estimate of the uncertainties expected in amine dispersion and risk estimates. The model formulations will also allow for different processes to be assessed. This can also lead to development of new box models and experiments to verify the box models.

The development of these type of models cannot be limited to three years. On the long term beyond the 3-year development, it is recommended to develop and perform a dedicated local-scale model study of the multiphase partitioning of amines emitted from the capture plant. In this study a multiphase chemistry/aerosol box model (for example MAFOR) that includes chemistry and aerosol processes of amines (either in detail or as parameterized schemes) should be coupled to a Lagrangian-type local-scale plume model.

Related projects

The ExSIRA project is a CLIMIT KMB project for 3 years. One of the tasks in the project is to develop a modelling tool for including gas phase chemistry. This project is done in collaboration between NILU, and UiO. There is a PhD. Scholar ship included. The project is in the initial stages. The time schedule is from October 2010 to approximately October 2013. The content of the modeling activity is to make the WRF-CHEM model operational and to prepare the model

for including gas phase amine chemistry. Then gas phase chemistry will be included according to the present knowledge.

Appendix A

Chemistry solvers for use in 3-D models

Euler Backward Iterative (EBI)

The backward Euler method is a first-order implicit finite difference solver. The implicit finite difference method is unconditionally stable and mass-conserving, and it can be made as accurate as desired by adjusting the size of the (chemistry) time step Δt. There is no constraint on stability associated with the shortest time scales of the system, since species with lifetimes $\tau_i << \Delta t$ will simply adjust to a quasi steady-state at time $t+\Delta t$ defined by $P_i(n(t+\Delta t) = L_i(n(t+\Delta t)$. The backward Euler method was further developed into the Euler Backward Iterative (EBI) solver by (Hertel et al., 1993) making use of the PSSA of short-lived species and is for example used in combination with the chemistry mechanism CBM-IV (Carbon Bond Mechanism IV) in the 3-D CTM TM5 (Krol et al., 2005). The EBI solver is therefore computationally very efficient, but a considerable drawback is that the iterative solution is adapted to the particular chemistry scheme (Sandu et al., 1997b).

Gear solver

For 3-D models, the most popular and accurate chemistry solver is the Gear solver named after its inventor *Charles Gear*. The Gear solver is an implicit finite difference method of variable order s (up to $s = 6$) where the results at previous time steps back to $t-(s-1)\Delta t$ are used to optimize the finite difference expression of dni/dt at time $t+\Delta t$. Gear solver codes include an efficient machinery to choose the time step and order of the method in order to optimize computational performance given user-specified error criteria. As in the first-order implicit finite difference method, the solution involves the inversion of the *Jacobian matrix* at every time step and iteration. But the higher order of the method, by providing a better definition of the trajectory towards the solution, allows for longer time steps and less frequent recalculations of the Jacobian. Popular variants of the Gear solver are LSODE (the "Livermore Solver") solver and its successor VODE ("Variable coefficient Ordinary Differential Equation) solver or DVODE (an open source solver).

QSSA solver

QSSA solvers are explicit in a sense that the loss matrix *L* is diagonal (by approximation) and no system of algebraic equations needs to be solved (no inversion of the Jacobian). Although their relative error can be large, their absolute error is small and QSSA solutions are in many cases (scenarios) close to the exact solution even for rapidly varying compounds like NO because QSSA-based methods preserve quite well the overall behaviour of the analytical solution (Jay et al., 1995). The performance of QSSA methods can usually be further improved by using lumping techniques which lead to the mass conservation of group of species. QSSA solvers have been successfully employed in 3-dimensional atmospheric chemistry transport models which require small computation times and where the precision of resulting concentrations is less important (due to much larger errors of the chemical rate constants). QSSA solvers are attractive because of small computational times and easy coding. The main weakness is their relatively low accuracy. Thus more advanced QSSA-based methods have been developed, among them CHEMEQ, a hybrid algorithm (Young and Boris, 1997).

CHEMEQ

One of the first dedicated, explicit methods for solving chemical equations in comprehensive transport-chemistry models is the hybrid algorithm by Young and Boris (1997). In CHEMEQ chemical species are divided into a category of stiff species and a category of non-stiff species. Each category is integrated with a special *predictor-corrector* algorithm. The explicit Euler method (used as the *predictor*) and an explicit trapezoidal method (used as the *corrector*) are employed to solve the non-stiff part, while the stiff part is integrated with a modified midpoint scheme. The *asymptotic method* (*predictor-corrector* algorithm) is numerically stable and does not require the solution of algebraic systems (meaning no expensive inversions of the *Jacobian*) for the advancement of the solution to the next time step.

TWOSTEP

TWOSTEP is an efficient QSSA solver that has been adapted to the particular chemistry scheme of EMEP (Verwer and Simpson, 1995). It is based on variable time step size, and a two-step backward differentiation formula. The classical Gauss-Seidel (or Jacobi) iteration technique is used for solving the non-linear system of chemistry equations. The two-step method enables the use of very large time step sizes. Of the dedicated explicit solvers (QSSA, CHEMEQ, TWOSTEP) included here, TWOSTEP was found to perform the best (Sandu et al., 1997a). It should be noted that TWOSTEP is advocated for gas-phase problems only, but has been extended to solve coupled chemistry-aerosol chemistry in EMEP MSC-W (Pirjola et al., 2003). A general disadvantage of TWOSTEP (and other dedicated solvers) is that changes of the chemistry mechanism (for instance to include amine chemistry) necessitate a reconsideration of the numerical solving scheme as well, and at best require straight-forward extension of the existing solver coding and at worst require a complete redesign of the solver.

Rosenbrock solvers

The performance of an integration method largely depends on its order of consistency and its stability properties. Consistency conditions are found from a formal Taylor expansion of the local error (truncation error). Rosenbrock (1963) proposed to generalize the linearly implicit approach (Euler backward, Gear) to solver methods using more numerical *stages* in order to achieve a higher order of consistency. Rosenbrock methods are attractive for a number of reasons (Sandu et al., 1997b). Like fully implicit methods, they preserve exact conservation properties due to the use of the analytic *Jacobian matrix*. Rosenbrock methods are easy to implement because they do not require an iteration procedure. Because of the multi-stage nature, computational costs for a Rosenbrock method (for one time step) are often high compared to a (multistep) Gear method. However, if a Rosenbrock code solves the whole problem efficiently in fewer steps than a Gear code needs, then the CPU time for the whole integration can become much less than for a Gear method. The use of Rosenbrock solver ROS3 is advantageous for coupled gas-phase/aqueous phase chemistry problems. Gas-liquid interactions are rapid and thus not feasible for integration with explicit solvers (QSSA, etc.). Use of Rosenbrock solvers in combination with the kinetic pre-processor KPP (Damian et al., 2002; Sandu et al., 2003; Sandu and Sander, 2006) makes this type of solvers the most flexible one (independent of particular chemistry schemes). The software tool KPP automatically generates FORTRAN (or C) code of the chemistry solver based on a given sheets of chemical species, reactions and rate constants. In addition KPP improves computational efficiency by automatically reordering the equations in order to exploit the sparsity of the Jacobian matrix. The ROS3/KPP is used for the integration of chemical equations in MAFOR (gas-phase + aqueous phase chemistry).

Appendix B

Chemistry schemes for use in 3-D models

SAPRC-07

SAPRC-07 (Carter et al., 2007), the updated version of the SAPRC-99 mechanism, was completed in August, 2007 (see http://www.cert.ucr.edu/~carter/SAPRC/). A condensed version of SAPRC-07 became available in January, 2010, for implementation into CMAQ (U.S. EPA's Community Multiscale Air Quality model). This mechanism was evaluated against the result of ~2400 environmental chamber experiments carried out in 11 different environmental chambers, including experiments to test mechanisms for over 120 types of VOCs. The performance of the mechanism in simulating the chamber data was comparable to SAPRC-99, with generally satisfactory results for most types of VOCs but some increases in biases in simulations of some mixture experiments. SAPRC-07 is also designed to retrieve VOC reactivity scales which are important with respect to ozone production potential of individual VOCs. Carter et al. (2008) have added representations of the atmospheric reactions of 15 amines to the SAPRC-07 mechanism. Among the comprehensive chemistry mechanisms presented in this chapter, SAPRC-07 is the most advanced and most detailed state-of-the-art chemistry scheme.

CBM-IV/CB05

U.S. EPA sponsored the development of the Carbon Bond mechanism version IV (CBM-IV) in the late 1980's for use in urban and regional photochemical modelling and Gery et al. (1989), published the mechanism. CBM-IV was developed mainly for urban smog and regional atmospheric modelling. This mechanism is a hybrid of detailed chemistry, surrogate approximations, and lumped or generalized chemistry designed to simulate the features of urban smog chemistry. Detailed chemistry is used for the description of inorganic and carbonyl species and the chemistry of ethene, isoprene, and formaldehyde. Many peroxy radicals have been lumped into a single XO universal peroxy radical. The lumping method of carbon-bonds is used mainly for alkanes (paraffins) and alkenes (olefins). Molecular surrogates toluene and xylene are used for higher aromatic compounds. For instance, a complex molecule with both aromatic and alkene structures might be represented with a combination of TOL, OLE, and

PAR surrogates (i.e. model species). Also, some of the rates and the stoichiometries of some incorporated reactions depend upon the atmospheric composition of reacting hydrocarbons. The most recent version of the mechanism is CB05 (Yarwood et al., 2005) which incorporates significant improvements to the mechanism, in particular when evaluated with smog chamber experiments. These improvements include increasing complexity regarding isoprene degradation, differentiating between acetaldehyde and the higher aldehydes, introducing a new formation route for organic nitrates in polluted atmospheres, and also the introducing a lumped species to represent terpenes. Due to the non-transparent (and old-fashioned) way of lumping in Carbon Bond Mechanisms it seems not feasible to include amine chemistry into this scheme.

EMEP-chemistry

The chemistry mechanism of EMEP MSC-W oxidant model (Simpson, 1992; Simpson et al., 1993; Simpson, 1995; http://www.emep.int/UniDoc/node10.html) is rather detailed and includes 68 chemical compounds (inorganic and organic) and 140 chemical or photochemical reactions and is capable of simulating rural, urban, and marine conditions (Pirjola and Kulmala, 1998). It also includes an isoprene mechanism based upon Paulson and Seinfeld (1992). The assignment of emitted species to the EMEP model species are based upon the detailed VOC inventory and follows the method given in Andersson-Sköld and Simpson (1999). The chemical equations are solved using the TWOSTEP method developed and tested by Verwer and Simpson (1995). The aerosol model MONO32 implemented in EMEP MSC-W uses a two-step method to integrate the prognostic equations of particle number and mass concentrations (Verwer and Simpson, 1995).

WRF-Chem/KPP

WRF-Chem is often used together with the comprehensive atmospheric chemistry mechanisms RADM2 (Stockwell et al., 1990) and RACM (Stockwell et al., 1997); both adequate for regional air quality modelling. The RADM2 mechanism represents organic chemistry through a reactivity aggregated molecular approach (Middleton et al., 1990). Similar organic compounds are grouped together into a limited number of model groups through the use of reactivity weighting ("reactivity-weighted lumping"). The aggregation factors for the most emitted Volatile Organic Compounds (VOCs) are given in Middleton et al., (1990). In the successor RACM the reactivity-weighted was done in a more consistent and transparent fashion, to allow further extension of the chemistry scheme. A KPP-embedded Rosenbrock solver is used in WRF-Chem for the chemistry mechanisms RADM2, RACM, coupled RACM/SORGAM. A pre-processor for WRF-Chem has been developed that automatically generates the interface routines between the KPP-generated modules and WRF-Chem, based on entries from the WRF-Chem registry files and the KPP input files. This WRF/Chem-KPP coupler is automatically executed during code compilation and considerably reduces the effort to add chemical compounds and/or reactions to existing chemical mechanisms.

Appendix C

Generic aerosol dynamics models

An aerosol particle is characterized by its shape, size, and chemical composition. Models generally assume that particles are *spherical*; this is strictly correct only for liquid particles, but for solid particles it can be viewed as an operational approximation, as the irregular shape is approximated by a sphere with equivalent radius.

To model the chemical composition of the aerosol size distribution function ($n(r)$) has to be constructed and assumptions about the mixing of chemical components within individual aerosol particles have to be made. In this context, a "chemical component" refers for example to sulphate, soot, organic, soil dust, or sea salt aerosol. One can then characterize the aerosol size distribution by the *number size distribution function* $n_N(r)$ (particles μm^{-1} cm^{-3}) such that $n_N(r)dr$ represents the number of particles per cm^3 of air in the radius size range $[r, r+dr]$.

An *external aerosol mixture* is one where there is no mixing between particles of different chemical components, that is, where each individual particle is made up of a single component. An *internal aerosol mixture* is one where there is complete mixing between particles of different chemical components so that all aerosol particles of a given size have the same chemical composition. The true mixing state of the atmospheric aerosol lies between these two extremes. For computational convenience, models often assume external or internal aerosol mixtures as limiting cases for describing aerosol evolution. External mixtures are represented in models by constructing separate size distribution functions for each chemical component of aerosol.

Sectional versus moment approach

The *number size distribution function* can be integrated to determine the total number concentration, total mass concentration, and other features of the aerosol over selected size ranges or over the entire size distribution.

The local evolution of the aerosol size distribution which accounts for condensational growth and coagulation between aerosol particles can be written in terms of the general (chemistry) continuity equation as:

$$\frac{\partial n_N(v)}{\partial t} = \left[\frac{\partial n(v)}{\partial t}\right]_{condensation/evaporation} + \left[\frac{\partial n_N(v)}{\partial t}\right]_{coagulation} + P - L \quad \text{(A.1)}$$

The two terms *P* and *L* summarize all terms of emission, deposition (dry and wet), nucleation as well as chemical production and loss. The first two terms on the right-hand side describe the evolution of the aerosol size distribution, while the other terms describe sources and sinks of particles. **Equation (A.1)** including all terms affecting the size distribution is commonly referred to as the *general dynamic equation* (GDE) for aerosols.

One generally assumes the aerosol size distribution to be a log-normal distribution (**Figure A.1**), representing the normal distribution of the logarithm of (*n(r)*):

$$n_N(\ln(r)) = \frac{dN}{d\ln r} = \frac{N}{(2\pi)^{1/2}\ln\sigma_g}\exp\left[\frac{-\ln(r/r_g)}{2\ln^2\sigma_g}\right] \quad \text{(A.2)}$$

In **Eq. (A.2)**, *N* is the total number concentration of particles, r_g is the *geometric-mean diameter* of the aerosol population, and σ_g is the *geometric standard deviation* of the distribution which is defined such that about 68 percent of the area under the lognormal distribution lies within one geometric standard deviation of the geometric-mean diameter. For a monodisperse aerosol, σ_g = 1; for typical log-normal approximations of the atmospheric aerosol, σ_g is in the range 1.5-2. Observed aerosol size distributions can in general be represented fairly well as a sum of lognormal distributions.

The numerical solution to the *general dynamic equation* for aerosols in atmospheric models is done by either of two approaches, the *sectional method* or the *moments method*. In the *sectional method* one divides the aerosol size distribution into discrete size bins and discretizes **Equation (A.1)** over each size bin (**Figure A.1**). This approach can be made as accurate as one likes, but a drawback is that a large number of size bins (of the order of 100) is needed to provide an acceptable resolution of the size distribution. Consequently, sectional methods become computational expensive.

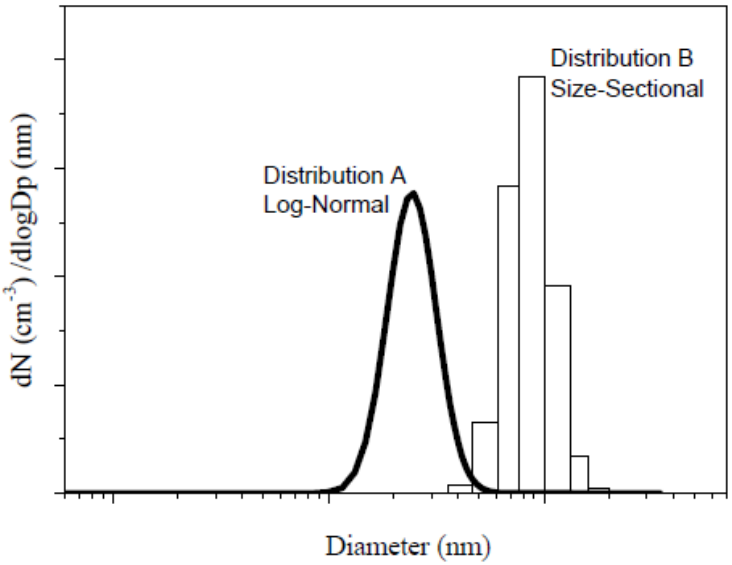

Figure A.1*: Two different schematic aerosol size distributions; one represented as a log-normal distribution, the other a size-sectional distribution.*

An alternate approach is the *moment method*, where one decomposes the size distribution in terms of its normalized moments M_i such that

$$M_i = \frac{\int_0^\infty r^i n_N(r)dr}{\int_0^\infty n_N(r)dr} \qquad \text{(A.3)}$$

Any size distribution can be decomposed in terms of these normalized moments:

$$n_N(r) = \sum_{i=0}^{\infty} \alpha_i M_i$$

The coefficients α_i are in units of cm^{-i}.

For typical aerosol size distribution functions, which are relatively smooth, one can capture most of the detail with just a few moments. Thus the moments offer a computationally economical representation of the aerosol size distribution in terms of only a few variables. A difficulty, however, is expressing the different processes of the GDE in terms of their moment equivalents. This requires some assumption about the shape of the aerosol size distribution; commonly a log-normal distribution is assumed (**Equation (A.2)**).

SOA models

Most SOA models utilize this partitioning theory for predicting SOA absorptive mass. Some models, particularly those with multiple aerosol species (as most of the current aerosol dynamic models), calculate explicitly the

condensation/evaporation driving force, which is the difference between the species concentration in the bulk gas and the concentration just above the particle surface (Jacobson 1997; Meng et al. 1998; Pirjola and Kulmala 2000). Hybrids of the partitioning and condensation methods also exist, where partitioning theory is used to calculate the gas-phase concentration above the particle surface, which is then implemented into a condensation-like flux equation (Bowman et al. 1997).

Appendix D

Description of the dispersion models

- **CMAQ**
  Reference: (http://www.cmaq-model.org/)

CMAQ (Community Multiscale Air Quality) – Multi-scale, multi-pollutant model developed by US EPA (http://www.cmaq-model.org). Different chemical mechanisms (CB-IV, CB05, SAPRAC-99 and RADM2) and solvers (EBI, SMVGEAR) are available. The model is embedded within the Models-3 framework, which includes interfaces to prepare for instance emissions (SMOKE), initial (ICON) and lateral boundary conditions (BCON). Note that the model is usually used for United States calculations and the use of the model in Norway implies the interface with the local emissions inventory. The University of Hertfordshire, UK adapted the emission processor SMOKE to include European (from EMEP and EPER) scale anthropogenic emissions. The modeling system (coupled with WRF or ARPS) can be used to investigate regional- to local-scale air quality. Only one-way nesting is permitted. The model has an embedded segmented plume, plume in grid, treatment that use the same gaseous chemical mechanism of the main Eulerian solver.

- **CAMx**
  Reference: http://www.camx.com/files/CAMxUsersGuide_v5.20.pdf.

The Comprehensive Air quality Model with extensions (CAMx) is an open source Eulerian photochemical dispersion model developed by ENVIRON. The model allows for an integrated assessment of gaseous and particulate air pollution over many scales ranging from urban to continental. CAMx simulates the emission, dispersion, chemical reaction, and removal of pollutants in the troposphere by solving the pollutant continuity equation for each chemical species on a system of nested three-dimensional grids. It contains five chemical mechanisms, four of them based on the Carbon Bond Mechanism version 4 (CB-IV) and the other one on the SPARC99. Other important features are: the two-way nested grid structure, several chemical kinetics solver options, horizontal advection solver options, an advanced photolysis model. The model has an embedded, Lagrangian puff based, plume in grid model which allows a separate advancement of

chemistry in the plume using the same chemical mechanism of the main Eulerian solver.

- **WRF-Chem**
  Reference: http://www.acd.ucar.edu/wrf-chem/

WRF/Chem (WRF coupled with Chemistry) – Multi-scale, multi-pollutant model developed collaboratively by several groups (NOAA/NCEP, NOAA/ESRL, NCAR) Many choices of chemical mechanisms (e.g. RADM2, CBM-Z) are available. The model is embedded within the WRF framework and is fully coupled with the dynamical core. It is used in the US and Europe for semi-operational simultaneous forecasting of weather and air quality and has been evaluated with retrospective simulations. WRF/Chem allows for both 1-way and 2-way nesting. This model does not have presently an embedded plume in grid module.

- **EMEP**
  Reference: http://www.emep.int/OpenSource/index.html

The Unified EMEP model is an open source community model developed by the Norwegian meteorological institute (Simpson et al., 2003, Fagerli et al., 2004). The model is used under the Convention on Long-range Transboundary Air Pollution to determine the origin of air pollutants and is widely recognized as a reference model for source allocation purposes. It has been extensively validated, also with respect to atmospheric aerosols (Tarrason et al., 2007, Yttri et al, 2007, Tarrason and Nyiri, 2008; Tsyro, 2008,).
The Unified EMEP model is 3-dimensional atmospheric dispersion model. The air pollutants under consideration are those involved in ecosystem and health damages, in particular sulphur oxides, nitrogen oxides, ammonia, ground level ozone and atmospheric particles. The model has 20 vertical layers in σ-coordinates and has generally been used with a $50*50km^2$ horizontal resolution in the EMEP polar stereographic grid. The model's numerical structure currently allows a flexible choice of the horizontal resolution, domain extension and map projection, so that it can now work down to 5x5km resolution. The treatment of aerosol dynamics in the EMEP model is based on the mono-disperse MONO32 model (Pirjola et al. 2003, Pirjola and Kulmala 2000) and accounts in the aerosol model for particle nucleation, condensation and coagulation processes. The model describes the aerosol size distribution with four modes: nucleation, Aitken, accumulation, and coarse. All particles within each mode are assumed to have the same size (thus the characterization of the model as mono-disperse) and the same chemical composition (internally mixed aerosols). The model calculates particle mass and number distributed in the four modes as well as aerosol chemical composition. The secondary formation of organic aerosol (SOA) may also be included in the model as there are available formulations of these processes (Andersson-Sköld and Simpson, 2001). A flexible design of the aerosol model allows easy modification of the definitions of size modes and to include different types of natural and anthropogenic sources, thus enabling different applications of relevance for amine dispersion. EMEP does not presently have an embedded plume in grid module.

- **TAPM**
  Reference: http://www.cmar.csiro.au/research/tapm/

The atmospheric dispersion and deposition calculations can be made with "The Air Pollution Model" (TAPM) developed by CSIRO, Australia (Hurley et al., 2005a; TAPM, 2010). TAPM is an integrated model consisting of a prognostic meteorological module and a set of air quality modules to calculate air pollution concentrations and deposition. TAPM has been shown to have a very good performance for the prediction of extreme pollution statistics, and performs well for non-reactive tracer compounds and also for reactive pollutants for a variety of sources such as industrial stacks and surface or urban emissions (Hurley et al., 2001, 2003; 2005b; Luhar and Hurley, 2003). A complete description of the model can be found in Hurley (2008), available through the TAPM URL (TAPM, 2010). TAPM carries out dispersion and transport using either the gridded Eulerian model (EGM) or a Lagrangian Particle Model (LPM), which is coupled to a Plume Rise Module (PRM) and a building wake model (BWM). The LPM provides a more detailed description of the atmospheric dispersion near to source than does the EGM but does not include any chemistry or deposition processes, with the exception of decay processes. After the particles in the LPM have travelled a specified time the mass from the plume is placed in the EGM. It is in the EGM that chemical and deposition processes are accounted for. Concentrations and depositions are based on the sum of both the EGM and the LPM concentrations. The Eulerian model can be run in either tracer mode, chemistry mode, or dust mode. In tracer mode, the only chemical reaction is an optional exponential decay. In chemistry mode, gas-phase photochemistry is based on the semi-empirical mechanism called the Generic Reaction Set (GRS)

Appendix E

Embedded plume models

Gaussian plume dispersion models

A typical Gaussian dispersion model is CONDEP and CONCX (Bøhler, 1987) and is currently used at NILU. They are steady-state dispersion models with no chemistry or simple chemistry that calculates mean concentrations based on average meteorological conditions (wind and stability). A large number of this type of models exists, both for long time averages and short time averages.

- ***Lagrangian particle/puff and PDF model***

A Lagrangian model follows notional air parcels (particles or puffs) as these parcels move around in the atmosphere, transported by mean advection and dispersed and/or expanded by turbulence. In a model run, the model calculates the trajectory of a large number of parcels, with number ranging from thousands for puff models to millions for particle models. In Lagrangian particle models the particles are tracked according to a system of stochastic differential equations for the particle velocity and position (e.g. Thomson, 1987)

$$du_i^{'} = a_i(\mathbf{x}\ , \mathbf{u}^{'}, t)dt + b_{ij}(\mathbf{x}\ , t)d\zeta_j$$
$$dx_i\ = \langle u_i \rangle + u_i^{'}\ dt$$

The *a* and **b** coefficients are defined based on the scales of motion that should be represented. The chemicals concentration is then usually obtained using box counting or kernel approaches. In Lagrangian puff model (e.g. SCIPUFF, , Sykes and Henn, 1995; CALPUFF, http://www.src.com/calpuff/calpuff1.htm) puffs are tracked in the domain instead of particles and therefore care must be taken of correctly expanding the puff around the centre of mass. The trajectory of the centre of mass is modelled in a way similar to the one for a particle but including only a fraction (or none) of the turbulent energy spectrum since the other energy fraction (or all the energy) goes in the expansion process. A segmented plume model work similarly to a puff model but do not account for along wind turbulent dispersion. Concentration is obtained in any point by superimposing different puff contribution. These models have algorithms to split and merge puffs based on local grid to better account for 3D variability.

Lagrangian particle/puffs models can be used in conjunction with Eulerian CTMs to describe SGS dispersion (plume in grid) thus improving close to the source spatial resolution for point sources. These models can be opportunely modified to account for chemistry. For particle models the chemistry take place on an opportunely generated grid (e.g. Chock and Winkler 1996) or using Kernel (e.g. Pagnini 2009) while for puffs the chemistry is calculated in the puff (e.g. Karamchandani et al. 2002).

A particularly advanced type of Lagrangian particle models is the Lagrangian particle probability density function model. This is the most advanced treatment of dispersion and chemical reaction available in the literature (e.g. Cassiani et al. 2005, 2007). These models treat dispersion similarly to standard Lagrangian particle models but they also include additional equations for the concentration vector and explicitly model the micro mixing with background air surrounding the plume.

Appendix F

Meteorological models

● WRF

Reference: http://www.wrf-model.org

WRF, Weather Research and Forecasting – Limited-area model (in contrast to global) developed as a community model (Skamarock et al., 2005). This next-generation community based model is mainly developed at NCAR and NOAA in USA. The modelling system is designed for both operational forecasting and atmospheric research needs for a broad spectrum of applications across scales ranging from a few meters to thousands of kilometres. The model includes horizontal nesting capabilities allowing for Large Eddy Simulations (LES) of the planetary boundary layer. We note that WRF has naturally replaced MM5 (Mesoscale model 5) for most of the on-going studies. It is straightforward to be coupled with CMAQ thanks to the MCIP interface in the Models-3 framework (see http://www.cmaq-model.org/) and it can be used coupled with an embedded Eulerian CTM, WRF-Chem (http://www.acd.ucar.edu/wrf-chem/). The WRF model is designed to be a flexible, state-of-the-art, portable code that is efficient in a massively parallel computing environment. A modular single-source code is maintained that can be configured for both research and operations. It offers numerous physics options, thus tapping into the experience of the broad modeling community. Advanced data assimilation systems are being developed and tested in tandem with the model. WRF is maintained and supported as a community model to facilitate wide use, particularly for research and teaching, in the university community. It is suitable for use in a broad spectrum of applications across scales ranging from meters to thousands of kilometres. Such applications include research and operational numerical weather prediction (NWP), data assimilation and parameterized-physics research, downscaling climate simulations, driving air quality models, atmosphere-ocean coupling, and idealized simulations (e.g. boundary-layer eddies, convection, baroclinic waves). With WRF as a common tool in the university and operational centres, closer ties will be promoted between these communities, and research advances will have a direct path to operations in scales ranging from 1x1km and beyond.

● ARPS

Reference: http://www.caps.ou.edu/ARPS/

The Advanced Regional Prediction System (ARPS) is a non-hydrostatic mesoscale meteorological model developed at the University of Oklahoma, USA (Xue et al., 2000, 2001). The finite difference equations of the model are discretized on the Arakawa C-grid, employing a terrain following co-ordinate in the vertical direction. Advection is solved with a 4th order central differencing scheme and leapfrog time stepping. Turbulence is represented by the 1.5 order TKE model, and parameterizations for the convective boundary layer. ARPS contains detailed parameterizations for cloud microphysics, cumulus convection, and radiation transfer. The model has nesting capabilities, allowing large-scale atmospheric features to enter the domain through the lateral boundaries. The code can be used to describe flow over complex terrain down to few meters resolution when working in Large-Eddy Simulation (LES) mode using several possible SGS closure. It has been successfully coupled with CMAQ (http://www.cmaq-model.org/).

● COAMPS

Reference: http://www.nrlmry.navy.mil/coamps-web/web/home/

The Coupled Ocean/Atmosphere Mesoscale Prediction System (COAMPS™) is a mesoscale model developed at the Naval Research Laboratory (NRL) Marine Meteorology Division (MMD). COAMPS represents state-of-the-art analysis (including the Nowcast capability) and short-term (up to 72 hours) forecast tool applicable for any given region of the Earth in both the atmosphere and ocean. The atmospheric component of COAMPS can be used for real-data or for idealized applications. The atmospheric model uses nested grids to achieve high resolution for a given area; it contains parameterizations for subgrid scale mixing, cumulus parameterization, radiation, and explicit moist physics. Examples of mesoscale phenomena to which COAMPS has been applied include mountain waves, land-sea breezes, terrain-induced circulations, tropical cyclones, mesoscale convective systems, coastal rainbands, and frontal systems. The COAMPS model domain typically covers a limited area over the Earth. The model grid resolution may range from a few hundred kilometers (synoptic scale) to approximately 100 meters. The actual dimensions applied depend on the scale of phenomena that the user is interested in simulating. COAMPS can be run with any number of nested grids, with the requirement that the horizontal grid resolution in any mesh be one-third that of the next coarser mesh. The COAMPS atmospheric system consists of two major components – analysis and forecast. The COAMPS analysis executable is run first to prepare the initial and boundary files used in the forecast model. The COAMPS forecast executable performs time integration of the model numerics and physics. It then outputs prognostic and diagnostic fields in pressure, sigma, or height coordinates. Options for running the analysis and forecast are specified through several Fortran namelists.

● MC2/GEM (with application of the MSC/RPN Physic Parameterization Package)

Reference: http://collaboration.cmc.ec.gc.ca/science/rpn.comm/

MC2: Mesoscale Compressible Community NWP Model

The Mesoscale Compressible Community [MC2] model is a state-of-the-art atmospheric model widely used by Environment Canada, Canadian Universities,

and others worldwide. The model is an extension of the fully compressible limited area model developed by Tanguay, Robert and Laprise [Tanguay et al. 1990; Laprise et al. 1997] in the mid-1980's at MSC-RPN and Université du Québec à Montréal (UQAM). The numerics of the model are based on a sophisticated semi-Lagrangian, semi-implicit time stepping procedure, which allows for comparatively large time steps despite the presence of rapidly propagating sound waves [Tanguay et al. 1990; Benoit et al. 1997a]. The high-resolution MC2 model allows the explicit numerical simulation of moist convection. It is equipped with a sophisticated microphysic package (KY scheme, Kong and Yau 1997). The need for such refined schemes, with their so-called ice-phase microphysics, was clearly demonstrated for topographically forced flow (e.g. Benoit et al. 1997b).
For efficiency it is designed to run on massively parallel computers using the Message Passing interface [MPI], allowing it to run on simple Linux-PC as well as super-computers. The model dynamic core is completed by a full set of physical parameterizations.
GEM: Global Environmental Multiscale NWP Model
The GEM Model (version 3.2.0) is now available for testing. The GEM version 3.2.0 is connected to Physics version 4.2. The RPN.COMM GEM NWP model is evolving at a fast pace with people from MSC/RPN working on the development of the dynamical core, physical parameterizations, and side tools, and from contributions
MSC/RPN Physic Parameterization Package
The RPN Physics Library consists of a set of parameterizations of the most important physical processes in the atmosphere and at the surface, and provides a unified library environment on which dynamical models can easily interface. The physical parameterizations modify the model basic variables, by adding tendencies due to various physical processes. These processes are either unresolvable by the model dynamics (e.g., turbulent transfers), unresolved (e.g., deep convection, gravity wave drag), or simply missing from the basic dynamic equations (e.g., radiation, surface processes, condensation).

● TAPM
Reference: http://www.cmar.csiro.au/research/tapm/
The meteorological part of TAPM (The Air Pollution Model) is an incompressible, non-hydrostatic, primitive equation model with a terrain-following vertical coordinate for three-dimensional simulations. The model solves the momentum equations for horizontal wind components, the incompressible continuity equation for vertical velocity, and scalar equations for potential virtual temperature and specific humidity of water vapour, cloud water/ice, rain water and snow. The Exner pressure function is split into hydrostatic and non-hydrostatic components, and a Poisson equation is solved for the non-hydrostatic component. Explicit cloud microphysical processes are included. The turbulence terms in these equations have been determined by solving equations for turbulence kinetic energy and eddy dissipation rate, and then using these values to represent vertical fluxes by a gradient diffusion approach, including counter-gradient terms. A vegetative canopy, soil scheme, and urban scheme are used at the surface, while radiative fluxes, both at the surface and at upper levels, are also included. A disadvantage with TAPM is that the model is only available as an executable. This means that the general requirement on transparency and flexibility is not satisfied.

References

Ackermann, I.J., Hass, H., Memmesheimer, M., Ebel, A., Binkowski, F.S. and Shankar, U. (1998) Modal aerosol dynamics model for Europe: Development and first applications. *Atmos. Environ., 32,* 2981-2999.

Águila-Hernández, J., Trejo, A. and Gracia-Fadrique, J. (2001) Surface tension of aqueous solutions of alkanolamines: single amines, blended amines and systems with nonionic surfactants. *Fluid Phase Equilibr., 185,* 165-175.

Águila-Hernández, J., Trejo, A. and García-Flores, B.E. (2007) Surface tension and foam behavior of aqueous solutions of blends of three alkanolamines, as a function of temperature. *Colloid. Surface. Physicochem. Eng. Aspects, 308,* 33-46.

Andersson-Sköld, Y. and Simpson, D. (1999) Comparison of the chemical schemes of the EMEP MSC-W and IVL photochemical trajectory models. *Atmos. Environ., 33,* 1111-1129.

Andersson-Sköld, Y. and Simpson, D. (2001) Secondary organic aerosol formation in Northern Europe: A model study. *J. Geophys. Res.*, 106, 7357-7374, doi:10.1029/2000JD900656.

Angelino, S., Suess, D.T. and Prather, K.A. (2001) Formation of aerosol particles from reactions of secondary and tertiary alkylamines: Characterization by aerosol time-of-flight mass spectrometry. *Environ. Sci. Technol.*, *35*, 3130-3138.

ARPS (2010): http://www.caps.ou.edu/ARPS/

Baird, C. and Cann, M. (2004) Environmental chemistry. 3rd ed. New York, Freeman.Benoit, R., M. Desgagné, P. Pellerin, S. Pellerin, S. Desjardins and Y. Chartier, 1997a: The Canadian MC2: a semi-Lagrangian, semi-implicit wide-band atmospheric model suited for fine-scale process studies and simulation. *Mon. Wea. Rev.*, 125, 2382-2415.

Benoit, R., M.K. Yau, A. Tremblay, F. Gayrard, S. Chamberland, 1997b: Sensitivity of selected MAP episodes to the modelling of cold phase of precipitation. *MAP newsletter*, 7, 18-20.

Binkowski, F.S. and Roselle, S.J. (2003) Models-3 community multi-scale air quality (CMAQ) model aerosol component 1. Model description. *J. Geophys. Res., 108,* 4183, doi:10.1029/2001JD001409.

Binkowski, F.S. and Shankar, U. (1995) The regional particulate matter model 1. Mode description and preliminary results. *J. Geophys. Res., 100,* 26191-26209, doi:10.1029/95JD02093.

Bone, R., Culls, P. and Wolfenden, R. (1983) Solvent effects on equilibria of addition of nucleophiles to acetaldehyde and the hydrophilic character of diols. *J. Atm. Chem. Soc., 105,* 1339-13443.

Bowman, F.M., Odum, J.R., Seinfeld, J.H. and Pandis, S.N. (1997) Mathematical model for gas-particle partitioning of secondary organic aerosols. *Atmos. Environ., 31,* 3921-3931.

Bråten, H.B., Bunkan, A.J., Bache-Andreassen, L., Soliman nejad, M. and Nielsen, C.J. (2008) Final report on a theoretical study on the atmospheric degradation of selected amines. Kjeller, Norwegian Institute for Air Research (NILU OR 77/2008).

Cassiani, M., Franzese, P. and Giostra, U. (2005) A PDF micromixing model of dispersion for atmospheric flow. Part I. Development of the model, application to homogeneous turbulence and to neutral boundary layer. *Atmos. Environ., 39,* 1457-1469.

Cassiani, M., Radicchi, A. and Albertson, J.D. (2007) An efficient algorithm for scalar pdf modeling in incompressible turblent flow; numerical analysis with evaluation of IEM and IECM micromixing models. *J. Comput. Phys., 223,* 519-550.

Carter, W.P.L. (2007) Development of the SAPRC-07 chemical mechanism and updated ozone reactivity scales. Final report to the California Air Resources Board, Contract No. 03-318. Riverside, CA, Center for Environmental Research and Technology, University of California. URL: www.cert.ucr.edu/~carter/SAPRC.

Carter, W.P.L. (2008) Reactivity estimates for selected consumer product compounds. Final Report, Contract No. 06-408. Riverside, CA, Center for Environmental Research and Technology, University of California.

Chock, D.P. and Winkler, S.L. (1994) A particle grid air quality modeling approach, 2. Coupling with chemistry. *J. Geophys. Res., 99,* 1033-1041.

Chow, Y.L. (1973) Nitrosamine chemistry: reactions of aminium radicals. *Acc. Chem. Res., 6,* 354-360.

CMAQ (2010): http://www.cmaq-model.org/

COAMPS (2010): http://www.nrlmry.navy.mil/coamps-web/web/home/

Damian, V., Sandu, A., Damian, M., Potra, F. and Carmichael, G.R. (2002) The kinetic preprocessor KPP - a software environment for solving chemical kinetics. *Comput. Chem. Eng., 26,* 1567-1579.

Ding, Y., Cui, W., Lee, M.L. and Eatough, D.J. (1998) Fine particulate N-nitroso and nitrite organic compounds in the atmosphere. *Appl. Occup. Environ. Hyg., 13,* 432-38.

Gery, M., Whitten, G.Z., Killus, J.P. and Dodge, M.C. (1989) A photochemical kinetics mechanism for urban and regional scale computer modelling. *J. Geophys. Res., 94,* 18925-18956, doi:10.1029/JD094iD10p12925.

Gong, S.L., Barrie, L.A., Blanchet, J.P., von Salzen, K., Lohmann, U., Lesins, G., Spacek, L., Zhang, L.M., Girard, E., Lin, H., Leaitch, R., Leighton, H., Chylek, P. and Huang, P. (2003) Canadian aerosol module: A size-segregated simulation of atmospheric aerosol processes for climate and air quality models 1. Model development, *J. Geophys. Res., 108,* D4007, doi:10.1029/2001JD002002.

Grosjean, D. (1991) Atmospheric chemistry of toxic contaminants. 6. Nitrosamines: Dialkyl nitrosamines and nitrosomorpholine. *J. Air Waste Manage. Assoc., 41,* 306-311.

Hales S.G., Philpotts, C.J. and Gillard, C. (1996) A respirometer with improved sensitivity for ready biodegradation testing. *Chemosphere, 33,* 1247-1259.

Herrmann, H., Ervens, B., Jacobi, H.-W., Wolke, R., Nowacki, P. and Zellner, R. (2000) CAPRAM2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry. *J. Atmos. Chem., 36,* 231-284.

Hertel, O., Berkowicz, R., Christensen, H. and Hov, Ø. (1993) Test of two numerical schemes for use in atmospheric transport-chemistry models. *Atmos. Environ., 27A,* 2591-2611.

IARC (1978) Some N-nitroso compounds. Lyon, International Agency for Research on Cancer (IARC monographs on the evaluation of carcinogenic risk of chemicals to humans, vol. 17) pp. 177-189.

Jacobson, M.Z. (1997) Numerical techniques to solve condensational and dissolutional growth equations when growth is coupled to reversible aqueous reactions. *Aerosol Sci. Technol., 27,* 491-498.

Jacobson, M.Z. (1999) Studying the effects of calcium and magnesium on size-distributed nitrate and ammonium with EQUISOLV II. *Atmos. Environ., 33,* 3635-3649.

Jacobson, M.Z. (2001) Global direct radiative forcing due to multicomponent anthropogenic and natural aerosols. *J. Geophys. Res., 106,* 1551-1568, doi:10.1029/2000JD900514.

Jacobson, M.Z. (2005) Fundamentals of atmospheric modeling. 2nd ed. New York, Cambridge University Press.

Jay, L.O., Sandu, A., Potra, F.A. and Carmichael, G.R. (1995) Improved QSSA methods for atmospheric chemistry integration. Iowa City, Department of Mathematics, University of Iowa (Technical report, 67).

Karamchandani, P., Seigneur, C., Vijayaraghavan, K. and Wu, S.Y. (2002) Development and application of a state-of-the-science plume-in-grid model. *J. Geophys. Res., 107,* 4403, doi:10.1029/2002JD002123.

Karl, M., Wright R. F., Berglen T. F., and Denby B. (2010) Worst case study to assess the environmental impact of amine emissions from a CO_2 capture plant, submitted to *Int. J. Greenhouse Gas Control*,

Karl, M. (2008) Amines and rainfall. Impact of amines on rainfall from plume clouds. Kjeller, Norwegian Institute for Air Research (NILU OR 74/2008).

Karl, M., Brooks, S., Wright, R. and Knudsen, S. (2008) Worst case studies on amine emissions from CO_2 capture plants (Task 6). Kjeller, Norwegian Institute for Air Research (NILU OR 78/2008).

Karl, M., Gross, A., Leck, C. and Pirjola, L. (2007) Intercomparison of dimethylsulfide oxidation mechanisms for the marine boundary layer: Gaseous and particulate sulfur constituents. *J. Geophys. Res., 112*, D15304, doi:10.1029/2006JD007914.

Karl, M., Gross, A., Leck, C. and Pirjola, L. (2010a) New particle formation in the High Arctic: Observations and model simulations. *Geophys. Res. Abstr., 12*, EGU2010-8393.

Karl, M., Gross, A., Leck, C. and Pirjola, L. (2010b) A new flexible multicomponent aerosol dynamic model to study the marine boundary layer. I. Model development and evaluation. *Submitted to Tellus B.*

Knudsen, S., Karl, M., Randall, S. (2009). Summary report: Amine emissions to air during carbon capture. Phase I: CO2 and amines screening study for effects to the environment. Kjeller, Norway (NILU TR 04/2009).

Kong, F.-Y., and M.K. Yau, 1997: An explicit approach to microphysics in MC2. *Atmos. Ocean*,**35**, 257-291.

Korhonen, H., Lehtinen, K.E.J., Pirjola, L., Napari, I., Vehkamäki, H., Noppel, M. and Kulmala, M. (2003) Simulation of atmospheric nucleation mode: A comparison of nucleation models and size distribution representations. *J. Geophys. Res., 108*, 4471, doi:10.1029/2002JD003305.

Kolb, C.E. (2002) Atmospheric chemistry: Iodine's air of importance. *Nature, 417*, 597-598.

Kokkola, H., Korhonen, H., Lehtinen, K.E.J., Makkonen, R., Asmi, A., Järvenoja, S., Anttila, T., Partanen, A.-I., Kulmala, M., Järvinen, H., Laaksonen, A. and Kerminen, V.-M. (2008) SALSA - a Sectional Aerosol module for Large Scale Applications. *Atmos. Chem. Phys., 8*, 2469-2483.

Krol, M., Houweling, S., Bregman, B., van den Broek, M., Segers, A., van Velthoven, P., Peters, W., Dentener, F. and Bergamaschi, P. (2005) The two-way nested global chemistry-transport zoom model TM5: algorithm and applications. *Atmos. Chem. Phys., 5*, 417-432.

Laprise, R., C. Caya, G. Bergeron and M. Giguere, 1997: The formulation of the Andre Robert MC2 (Mesoscale Compressible Community) Model. *Atmosphere Ocean*, 35, 195-220.

Låg, M., Andreassen, Å., Instanes, C. and Lindemann, B. (2009) Health effects of different amines and possible degradation products relevant for CO_2 capture. Oslo, Norwegian Institute of Public Health (FHI Report, 2009:3). URL: http://www.fhi.no/dav/de810a615a.pdf [Accessed: 2010-09-09].

Langmann, B., Varghese, S., Marmer, E., Vignati, E., Wilson, J., Stier, P. and Dowd, C.O. (2008) Aerosol distribution over Europe: A model evaluation study with detailed aerosol microphysics. *Atmos. Chem. Phys., 8,* 1591-1607.

Loeppky, R.N., Outram, J.R., Tomasik, W. and Faulcon, J.M. (1983) Rapid nitrosamine formation from a tertiary amine: The nitrosation of 2-(N,N-Dimethylaminomethyl)pyrrole. *Tetrahedron Lett., 24,* 4271-4274.

MC2/GEM (2010): http://collaboration.cmc.ec.gc.ca/science/rpn.comm/

Meng, Z., Dabdub, D. and Seinfeld, J.H. (1998) Size-resolved and chemically resolved model of atmospheric aerosol dynamics. *J. Geophys. Res., 103,* 3419-3435.

Middleton, P., Stockwell, W.R., Carter, W.P.L. (1990) Aggregation and analysis of volatile organic compound emissions for regional modeling. *Atmos. Environ., 24A,* 1107-1133.

Murphy, S.M., Sorooshian, A., Kroll, J.H., Ng, N.L., Chhabra, P., Tong, C., Surratt, J.D., Knipping, E., Flagan, R.C. and Seinfeld, J.H. (2007) Secondary aerosol formation from atmospheric reactions of aliphatic amines. *Atmos. Chem. Phys., 7,* 2313-37.

Nenes, A., Pilinis, C. and Pandis, S.N. (1998) Continued development and testing of a new thermodynamic aerosol module for urban and regional air quality models. *Atmos. Environ., 33,* 1553-1560.

Nielsen, C.J., D'Anna, B., Dye, C., George, C., Graus, M., Hansel, A., Karl, M., King, S., Musabila, M., Müller, M., Schmidbauer, N., Stenstrøm, Y. and Wisthaler, A. (2010) Atmospheric Degradation of Amines (ADA). Summary report: Gas phase photo-oxidation of 2-aminoethanol (MEA) CLIMIT project no. 193438. Kjeller, Norwegian Institute for Air Research (NILU OR 8/2010).

Odum, J.R., Hoffmann, T., Bowman, F., Collins, T., Flagan, R.C. and Seinfeld, J.H. (1996) Gas-particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol., 30,* 2580-2585.

Pagnini, G. (2009) The kernel method to compute the intensity of segregation for reactive pollutants: Mathematical formulation. *Atmos. Environ., 43,* 3691–3698.

Pankow, J.F. (1994a) An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmos. Environ., 28,* 185-188.

Pankow, J.F. (1994b) An absorption model of the gas/particle partitioning involved in the formation of secondary organic aerosol. *Atmos. Environ., 28,* 189-193.

Paulson, S.E. and Seinfeld, J.H. (1992) Development and evaluation of a photooxidation mechanism for isoprene. *J. Geophys. Res., 97,* 20703-20715, doi:10.1029/92JD01914.

Pirjola, L. and Kulmala, M. (1998) Modelling the formation of H_2SO_4-H_2O particles in rural, urban and marine conditions. *Atmos. Res., 46,* 321-347.

Pirjola, L. and Kulmala, M. (2000) Aerosol dynamical model MULTIMONO. *Boreal Environ. Res., 5,* 361-374.

Pirjola, L., Kulmala, M., Wilck, M., Bischoff, A., Stratmann, F. and Otto, E. (1999) Effects of aerosol dynamics on the formation of sulphuric acid aerosols and cloud condensation nuclei. *J. Aerosol Sci., 30,* 1079-1094.

Pirjola, L., Tsyro, S., Tarrasón, L. and Kulmala, M. (2003) A monodisperse aerosol dynamics module, a promising candidate for use in long-range transport models: Box model tests. *J. Geophys. Res., 108,* 4258, doi:10.1029/2002JD002867.

Pratt, K.A., Hatch, L.E. and Prather, K.A. (2009) Seasonal volatility dependence of ambient particle phase amines. *Environ. Sci. Technol., 43,* 5276-81.

Raes, F., Van Dingenen, R., Vignati, E., Wilson, J., Putaud, J.-P., Seinfeld, J.H. and Adams, P. (2000) Formation and cycling of aerosols in the global troposphere. *Atmos. Environ., 34,* 4215-4240.

Rosenbrock, H.H. (1963) Some general implicit processes for the numerical solution of differential equations. *Comput. J., 5,* 329-330.

Sandu, A. and Sander, R. (2006) Technical note: Simulating chemical systems in Fortran90 and Matlab with the Kinetic PreProcessor KPP-2.1. *Atmos. Chem. Phys., 6,* 187-195.

Sandu, A., Verwer, J.G., Blom, J.G., Spee, E.J., Carmichael, G.R. and Potra, F.A. (1997a) Benchmarking stiff ODE solvers for atmospheric chemistry problems-I. implicit vs explicit. *Atmos. Environ., 31,* 3151-3166.

Sandu, A., Verwer, J.G., Blom, J.G., Spee, E.J., Carmichael, G.R. and Potra, F.A. (1997b) Benchmarking stiff ODE solvers for atmospheric chemistry problems II: Rosenbrock solvers. *Atmos. Environ., 31,* 3459-3472.

Sandu, A., Daescu, D. and Carmichael, G.R. (2003) Direct and adjoint sensitivity analysis of chemical kinetic systems with KPP: Part I – theory and software tools. *Atmos. Environ., 37,* 5083-5096.

Schell B., Ackermann, I.J., Hass, H., Binkowski, F.S. and Ebel, A. (2001) Modeling the formation of secondary organic aerosol within a comprehensive air quality model system. *J. Geophys. Res., 106,* 28275-28293, doi:10.1029/2001JD000384.

Silva, P.J., Erupe, M.E., Price, D., Elias, J., Malloy, Q.G.J., Li, Q., Warren, B. and Cocker, D.R. (2008) Trimethylamine as precursor to secondary organic aerosol formation via nitrate radical reaction in the atmosphere. *Environ. Sci. Technol., 42,* 4689-4696.

Simpson, D. (1992) Long-period modelling of photochemical oxidants in Europe. Model calculation for July 1985. *Atmos. Environ., 26A,* 1609-1634.

Simpson, D. , Andersson-Sköld, Y. and Jenkin, M.E. (1993) Updating the chemical scheme for the EMEP MSC-W oxidant model: current status. Oslo, Norwegian Meteorological Institute (EMEP MSC-W Note 2/93).

Simpson, D., Guenther, A., Hewitt, C.N. and Steinbrecher, R. (1995) Biogenic emissions in Europe 1. Estimates and uncertainties. *J. Geophys. Res., 100,* 22,875-22,890, doi:10.1029/95JD02368.

Skamarock, W. C., Klemp, J.B., Dudhia, J., Gill, D.O., Barker, D.M., Wang W. and Powers, J.G. (2005): A description of the advanced research WRF Version 2. Boulder, Col., National Center for Atmospheric Research (NCAR/TN-468+STR). URL: http://www.mmm.ucar.edu/wrf/users/docs/arw_v2.pdf.

Smith, P.A.S. and Loeppky, R.N. (1967) Nitrosative cleavage of tertiary amines. *J. Am. Chem. Soc., 89,* 1147-1157.

Smith, J.N., Barsanti, K.C., Friedli, H.R., Ehn, M., Kulmala, M., Collins, D.R., Scheckman, J. H., Williams, B.J. and McMurry, P.H. (2010) Observations of aminium salts in atmospheric nanoparticles and possible climatic implications. *Proc. Natl. Acad. Sci. U.S.A., 107,* 6634-6639.

Sorooshian, A., Murphy, S.N., Hersey, S., Gates, H., Padro, L.T., Nenes, A., Brechtel, F.J., Jonsson, H., Flagan, R.C. and Seinfeld, J.H. (2008) Comprehensive airborne characterization of aerosol from a major bovine source. *Atmos. Chem. Phys., 8,* 5489-5520.

Stockwell, W.R., Middleton, P., Chang, J.S. and Tang, X. (1990) The second generation regional acid deposition model chemical mechanism for regional air quality modeling. *J. Geophys. Res., 95,* 16343-16367.

Stockwell, W.R., Kirchner, F. and Kuhn, M. (1997) A new mechanism for regional atmospheric chemistry modeling. *J. Geophys. Res., 102,* 25847-25879.

Sykes, R.I. and Henn, D.S. (1995) Representation of velocity gradient effects in Gaussian puff model. *J. Appl. Meteorol., 34,* 2715-2723.

Tanguay, M., A. Robert, and R. Laprise, 1990: A semi-implicit semi-Lagrangian fully compressible regional forecast model. Mon. Wea. Rev., 118, 1970-1980.

TAPM (2010): http://www.cmar.csiro.au/research/tapm/

Thomson, D.J. (1987) Criteria for the selection of the stochastic models of particle trajectories in turbulent flows. *J. Fluid Mech., 180,* 529-556.

Tsyro, S. (2005) To what extent can aerosol water explain the discrepancy between model calculated and gravimetric PM10 and PM2.5? *Atmos. Chem. Phys., 5,* 515-532.

U.S. EPA (1977) Scientific and technical assessment report on nitrosamines. Washington, U.S. Environmental Protection Agency, Office of research and Development (EPA-600/6-77-001).

Vázquez, G., Alvarez, E., Navaza, J.M., Rendo, R., Romero, E. (1997) Surface tension of binary mixtures of water + monoethanolamine and water + 2-amino-2methyl-1-propanol and tertiary mixtures of these amines with water from 25°C to 50°C. *J. Chem. Eng. Data, 42,* 57-59.

Verwer, J.G. and Simpson, D. (1994) Explicit method for stiff ODEs from atmospheric chemistry. Amsterdam, Centre for Mathematics and Computer Science (CWI report, NM-R9409).

Vignati, E., Wilson, J. and Stier, P. (2004) M7: An efficient size resolved aerosol microphysics module for large-scale aerosol transport models. *J. Geophys. Res., 109,* D22202, doi:10.1029/2003JD004485.

Vignati, E., Karl, M., Krol, M., Wilson, J., Stier, P. and Cavalli, F. (2010) Sources of uncertainties in modelling black carbon at the global scale. *Atmos. Chem. Phys., 10,* 2595-2611.

WRF (2010): http://www.wrf-model.org/

WRF-Chem (2010): http://www.acd.ucar.edu/wrf-chem/

Xue, M., K. K. Droegemeier, and V. Wong, (2000): The Advanced Regional Prediction System (ARPS) - A multiscale nonhydrostatic atmospheric simulation and prediction tool. Part I: Model dynamics and verification. Meteor. Atmos. Physics., 75, 161-193.

Xue, M., K. K. Droegemeier, V. Wong, A. Shapiro, K. Brewster, F. Carr, D. Weber,Y. Liu, and D. –H. Wang, (2001): The Advanced Regional Prediction System (ARPS) - A multiscale nonhydrostatic atmospheric simulation and prediction tool. Part II: Model physics and applications. Meteor. Atmos. Physics., 76, 134-165.

Yarwood, G., Rao, S., Yocke, M. and Whitten, G.Z. (2005) Final Report . Updates to the carbon bond mechanism: CB05. RT-04-00675. Novato, CA, Yocke and company.

URL: http://www.camx.com/publ/pdfs/CB05_Final_Report_120805.pdf [Accessed: 2010-09-09].

Young, T.R. and Boris, J.P. (1997) A numerical technique for solving stiff ODEs associated with the chemical kinetics of reactive flow problems. *J. Phys. Chem., 81,* 2424-2427.

Zhang, K., Wan, H., Wang, B., Zhang, M., Feichter, J. and Liu, X. (2010) Tropospheric aerosol size distributions simulated by three online global aerosol models using the M7 microphysics module. *Atmos. Chem. Phys., 10,* 6409-6434.

Norwegian Institute for Air Research
P.O. Box 100, N-2027 Kjeller, Norway
Associated with CIENS and the Environmental Research Alliance of Norway
ISO certified according to NS-EN ISO 9001

REPORT SERIES [Skriv rapporttype]	REPORT NO. OR ../2009	ISBN: 978-82-425-[Skriv ISBN-nr] (printed) 978-82-425-[Skriv ISBN-nr] (electronic) ISSN: 0807-7207 ISSN: 0807-7185	
DATE	SIGN.	NO. OF PAGES 78	PRICE NOK 150.-
TITLE CO2 Capture Mongstad Project/H&ETQPAmine2 Modelling atmospheric dispersion for components from post combustion amine based CO2 capture.		PROJECT LEADER Svein Knudsen NILU PROJECT NO. O 110082/	
AUTHOR(S) Svein Knudsen, Massimo Cassiani , Matthias Karl, Leiv Håvard Slørdal, Leonor Tarrasón		CLASSIFICATION * B CONTRACT REF. Lars Bergersen eROOM number	
REPORT PREPARED FOR [Skriv tekst]CCM			

ABSTRACT
Carbon capture by the use of amines from power plants have emissions to air. Amines react chemically in the atmosphere after emission. The substances produced can pose a risk to the environment and human health. This report is a review of existing modeling tools , a case study of the emissions and a recommendation on future development aimed at reducing uncertainty in the exposure estimates.

NORWEGIAN TITLE
CO2 fangst Mongstad prosject /H&ETQPAmine2

KEYWORDS		
CCS	Spredningsberegninger	Strategi

ABSTRACT (in Norwegian)
Karbonfangst ved bruk av aminer fører til utslipp til luft. Aminene reagerer kjemisk i atmosfæren og danner stoff som kan være et problem for miljøet. Denne rapporten er en gjennomgang av modeller som egner seg for analyse av dette problemet, et eksempel på dagens muligheter for å estimere eksponering samt en anbefaling av hvordan usikkerheten kan minskes for å få bedre estimater av eksponering.

** Classification*
A Unclassified (can be ordered from NILU)
B Restricted distribution
C Classified (not to be distributed)

REFERENCE:
DATE: [Skriv dato]
ISBN: 978-82-425- (printed)
978-82-425- (electronic)

NILU is an independent, nonprofit institution established in 1969. Through its research NILU increases the understanding of climate change, of the composition of the atmosphere, of air quality and of hazardous substances. Based on its research, NILU markets integrated services and products within analyzing, monitoring and consulting. NILU is concerned with increasing public awareness about climate change and environmental pollution.

Norwegian Institute
for Air Research