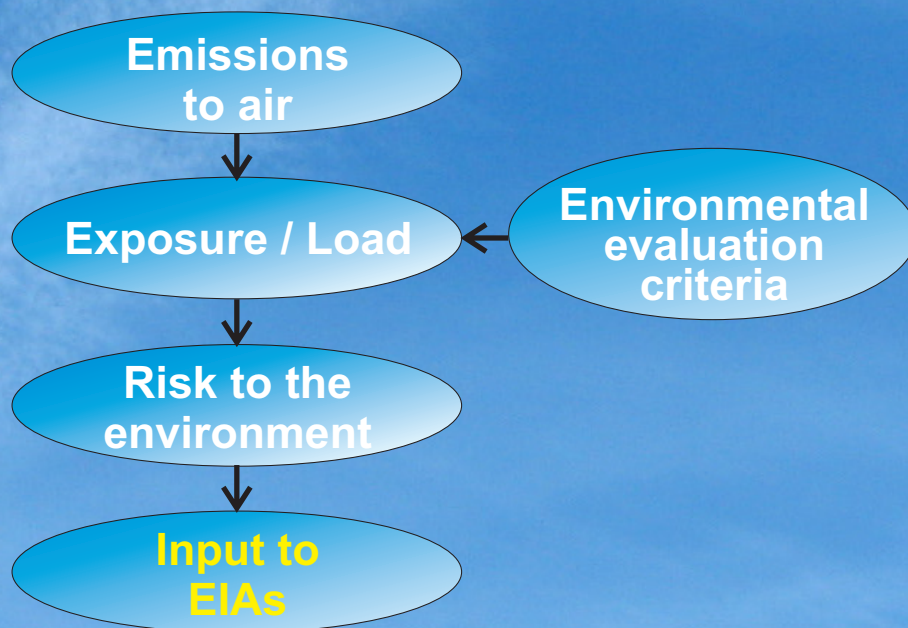




# Task 5.1 & 5.2 Report: Report on Models, Model Needs and Requirements

Phase I: CO<sub>2</sub> and Amines Screening Study  
for Environmental Risks



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of Public Health



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for Nature Research



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# **Report on models, model needs and requirements**

## **Contribution to task 5**

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## Preface

CO<sub>2</sub> capture and storage (CCS) has been proposed for two Norwegian gas-fired power plants as a measure to reduce CO<sub>2</sub> emissions to the atmosphere, thus reducing the main contributor to global warming. A leading technology for CO<sub>2</sub> capture is through the use of amines. The *CO<sub>2</sub> and Amines Screening Project* began with *Phase I* in May 2008. The project was initiated by NILU based on the results of an expert meeting in October 2007, and discussions with SFT. The expert meeting and the following Phase I project is based upon the concern that the emissions from CO<sub>2</sub> capture using amines could be potentially harmful to the environment and human health, and that the existing information regarding these subjects were quite limited, thus demanding further examination and analysis.

The project was graciously sponsored by the following:

- Gassnova SF (CLIMIT)
- Statoil Hydro ASA
- Shell Technology Norway AS

The following institutes participated in the project:

- Centre for Theoretical and Computational Chemistry (CTCC) Department of Chemistry at the University of Oslo, responsible for the theoretical study on the atmospheric degradation of selected amines (Task 3).
- The Norwegian Institute of Public Health (FHI), responsible for the effects to human health (Task 7).
- Norwegian Institute for Nature Research (NINA), responsible for the effects to terrestrial ecosystems (Task 8).
- Norwegian Institute for Water Research (NIVA), responsible for the effects on freshwater ecosystems (Task 9).
- Norwegian Institute for Air Research (NILU), responsible for project management/coordination, including the chemical screening report, models report, worst case study report, and the summary report (Task 4, 5, 6, and 10).

The project sponsors comprised the Steering Committee, which gave useful guidance to the project and its administration. The project sponsors function within the Steering Committee also gave them an active role in reviewing all project reports and documentation.



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## Summary and conclusions

*This report is a contribution to a series of report on the project “Environmental and Health effects from emission of amines to air from CO<sub>2</sub> capture”. The main topic of this report is to reveal the basic needs and requirements concerning models.*

The atmosphere is a very complex, non-linear system that basically behaves according to the principles of physics. To achieve a better understanding of the atmospheric processes one can use mathematical equations and simulations that represent these processes. This is the principle behind all models. The purpose of models are two-fold: One is to better understand all the processes of the atmosphere (chemistry, transport, clouds etc.). The other is, once the basic processes are known, to perform theoretical experiments that are too dangerous, not possible or too expensive to perform in the real atmosphere.

First this report describes and discusses the most important processes in the atmospheric cycle of amines (emissions, transport, chemistry and loss). These processes cover a wide range of scales, from typically  $10^{-9}$  m to  $10^6$  m for the spatial scale and  $10^{-3}$  s to  $10^6$  s for the time scale. This wide range of scales has to be taken into account when the choice of models or models concepts are made. Processes too small for the model scale have to be parameterized.

Based on the range of scales involved, NILU emphasizes three types of models or model concepts: box models, local small scale models, and regional transport models. Findings and results from smaller scale models should be included in the models at a larger scale, e.g. knowledge about processes from box models should be used in the local and regional models, either to parameterize sub-grid processes, or to calculate the processes specifically. The objectives of the modelling and the necessary results will decide which model that best is applicable. The need for accuracy is also important.

No known model has amine chemistry included. To include such chemistry is the first priority of this model development part. This means inclusion of gas phase chemistry, aqueous phase chemistry and aerosol chemistry.

Based on the analysis outlined in this report the conclusion is that, for box models, several types of models should be developed, each aimed at studying one specific problem (amine chemistry, aerosol formation, droplet formation etc.).

For small scale models the atmospheric lifetime of amines is crucial. If the lifetime is long ( $\tau \sim$ hrs.), then a Gaussian type dispersion model is suitable. If the lifetime is short, a dispersion model with chemistry should be applied, also with amines included. Moreover, if the lifetime is in the atmospheric turbulence time scales range, turbulence-chemistry interactions need to be included. Model types like Lagrangian PDF models (Probability Density Function), or meandering plume models would be applicable in the last case.



There are several models that are suitable for transport and deposition. The models have several levels of detail included and the model formulation is more or less suitable for including different schemes of photochemistry. This means that the dispersion models exist but chemical models need to be developed. The chemical models are dependent on information from large scale models for ambient concentrations. These ambient concentrations will typically come from large scale models. When the smaller scale models reach the size of the grid in the large scale models these large scale models will continue the dispersion and deposition. In this way the local scale is treated with sufficient accuracy. If long time scales are relevant, a regional model needs to be implemented, and get input from the smaller scale models. The local and the regional scale models can be run separately, and results from one model used by the other.

Concerning choice of regional models, a regional chemistry and dispersion model is sufficient. In this report three different models are listed; WRF-Chem, CMAQ-MM5, and FLEXPART. In any case amine chemistry should be included into such a model. WRF and WRF-Chem may be used in both cases, either as a weather forecast model, or with prescribed meteorology. This possibility to use prescribed meteorology or forecast mode is a strong advantage with WRF. However, in this report no definitive conclusion concerning regional model is drawn. All the three models listed are suitable, it depends on the objectives and the purpose of the study. More investigation and more knowledge is needed before model and model concept could be chosen.

The different models and model concepts can be coupled, i.e. run at the same time and exchange information during model run (both 1-way coupling and 2-way coupling). For instance, one box model may be used to calculate ambient air chemistry, another box model may be used to calculate plume chemistry, this can be coupled to a plume dispersion model that gets concentrations of the chemical components from a regional chemical-transport model. This is an example how models and model concepts can be coupled and run together.

# Report on models, model needs and requirements

## Contribution to task 5

### 1 Introduction

The overall main objective of this report is to study the effects of emissions of amines to air on the environment. For this we need a broad approach, and we will perform:

- theoretical studies
- laboratory studies
- model calculations
- measurements/observations/monitoring

Models are used to connect emissions to environmental load. Before the model is chosen the atmospheric processes that need to be described need to be assessed. Concerning models the objective is to make a predictive description of the emissions, dispersion, degradation and deposition of amines in the atmosphere, i.e. the processes in the atmospheric cycle of amines.

#### 1.1 Why models?

What is actually a model and why do we need it?

The atmosphere is a very complex, non-linear system. At the same time it behaves according to the basic principles of physics. That is the reason why mathematical equations can be used to represent the processes in the atmosphere, both the physical processes, i.e. meteorology (wind, temperature, rain and rainfall) and the chemical processes, i.e. gas phase chemistry, aqueous phase chemistry and aerosols.

An atmospheric model is a computer program that calculates and quantifies the various processes in the atmosphere. There are basically two main reasons for using a model; one is to do forecasting, e.g. weather or pollution forecasts. The other is to study the processes itself, how does the atmosphere behave? The second point is most applicable to our project. By using models processes can be studied in more detail. Models can also perform experiments that are perhaps dangerous and expensive to perform in the field. However, at some stage the model results must be compared to observations to validate model performance.

### 2 Processes important for the amine study

As shown in Figure 1, the atmospheric cycle of an amine molecule has four main stages, where stage two and three take places simultaneously;

- 1) emissions
- 2) transport/dispersion
- 3) chemistry/photochemical loss in the atmosphere

#### 4) deposition

To simplify further we say that this cycle is basically production, transport/degradation and loss.

This is a very simplified overview of the processes. More detail is needed and each stage is described below.

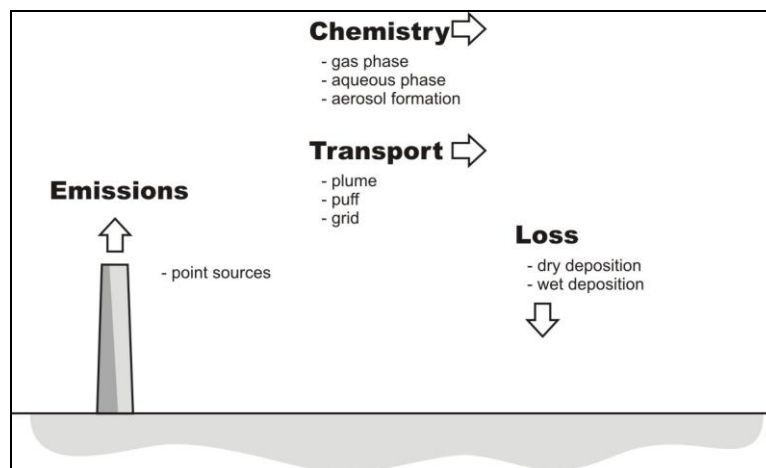


Figure 1: Atmospheric cycle of amines and photochemical loss products.

### 2.1 Emissions:

The amines studied in this project will be released through a stack. This means that we have one (or several) specific emission points emitting amines into the atmosphere. Atmospheric models/dispersion models usually “start” at the emission point. Processes that take place before the release to air are not taken into account in this report, for example in the scrubber or in the stack itself. Models usually need a parameterization of the emission condition and the emission rate of amines.

In addition to the emissions of amines, there will also be release of  $\text{NO}_x$ ,  $\text{NH}_3$ , VOC and water vapour from the stack. These compounds will, to a certain degree, affect local photochemistry. There will also be emissions of other pollutants from the stack. These are largely unknown.

### 2.2 Transport/dispersion

#### 1) Molecular diffusion

In a gas volume, molecules tend to go from areas with high concentrations towards areas with low concentrations.

#### 2) Turbulence

Turbulence is small-scale, irregular air motions characterized by winds that vary in speed and direction. Turbulence is important because it mixes the atmosphere and causes gases, water vapour, and aerosols to spread both vertically and horizontally. When a component is released from a stack, the concentration is

very high, and it will then be diluted and “spread out” in a plume, even if there is no wind. The concentration will decrease as the plume grows older.

### 3) Large scale advection

Advection is geographical transport in time and space by mean wind. Atmospheric components may be transported over large distances in relatively short time. For example, if the wind speed is 5 m/s and the wind direction is constant, air parcels are transported 18 km away during one hour, and 432 km away during 24 hrs. For components with medium and long atmospheric lifetime (longer than minutes/hours) the advective transport will then be important. For short-lived components like OH with a lifetime of  $\sim 0,1$  s, transport is negligible.

Diffusion, turbulence and advection are all processes that contribute to dispersion of pollutants released to the atmosphere. Concerning a CO<sub>2</sub> capture plant, pollutants will be released from one (or several) stacks and the dispersion will be what is characterized as a “point source plume dispersion case”.

## 2.3 Chemistry

Concerning chemistry it is convenient to separate between gas phase chemistry, aqueous phase chemistry and chemistry on aerosols. There will be two types of chemical regimes in the vicinity of the CO<sub>2</sub> capture plant; plume chemistry and ambient chemistry. In the plume there are high concentrations of amines, NO<sub>x</sub>, NH<sub>3</sub>, VOC, and water vapour from the stack. This plume chemistry is in a way “abnormal” since the concentrations are much higher than in ambient air and also different compounds. Gradually there will be entrainment of background air into the plume and the plume will be diluted. In ambient air there is “normal” photochemistry. At a certain distance from the stack ( $> \sim 10$ km), the plume and ambient air will be totally mixed. The effectiveness of this mixing is strongly dependent on meteorological conditions and therefore the turbulence regime.

### • Gas phase chemistry

Gas phase chemistry means chemical reactions between gas molecules. In the troposphere the NO<sub>x</sub>-VOC-O<sub>3</sub> cycle constitutes the most important parts of gas phase chemistry. CO<sub>2</sub>-capture plants will evidently be located at the ground and amines will then be emitted into the troposphere. OH is the most important daytime oxidant in the troposphere. The amines will enter into chemical reactions where there is a connection between the normal photochemistry and the amine plume photochemistry. The reactions can be classified as fast.

### • Aqueous phase chemistry

This signifies chemical reactions taking place in droplets, i.e. droplets in clouds or in falling rain. A molecule needs to be soluble in order to be taken up by a droplet, then only soluble components may be part of the aqueous phase chemistry. Many components dissolve when they enter water, some dissolve into ions (positive and negative ions). In short, aqueous chemistry differs from gas phase chemistry and needs to be treated separately.

### • Aerosol chemistry

Aerosol chemistry signifies two things: one is chemical reactions taking place at the surface of aerosols. This is much like aqueous phase chemistry since many

aerosols are soluble and water stick to its surface. The other is formation of aerosols from gas phase components, like e.g. oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  by OH, sulphate is very hygroscopic and stick easily to other components and will eventually form a particle.

## 2.4 Loss

Eventually all atmospheric gases and aerosols will be lost by deposition, either by dry deposition (uptake by vegetation or onto surfaces) or by wet deposition (uptake in droplets and removal by rain).

### • Dry deposition

Gases and aerosols may be deposited onto surfaces, like buildings or it may be deposited onto vegetation (see section 4.3). How easily a gas is deposited onto a surface or taken up by vegetation will vary from one gas to another. Some gases, like for example  $\text{O}_3$  (ozone) stick easily to surfaces, while others are not affected at all. Concerning uptake in vegetation through the plant stomata, this is strongly dependent on type of vegetation, meteorology and time of day, and if the vegetation in question is active. The degree of toxicity of gases to plants varies considerably. Some gases are very toxic, this is the case with e.g.  $\text{O}_3$  and  $\text{SO}_2$ , of which even low concentrations (ppb level) may harm leaves and affect photosynthesis.

### • Wet deposition

Only gases that are water soluble can possibly be lost by wet deposition. Wet deposition is expected to be the main deposition removal path for amines. The primary amines are soluble in water, and many of the identified photochemical loss products are also soluble in water. Wet deposition is effectively removing particles from the atmosphere.

## 3 The question of scale of the processes

### 3.1 Spatial scale

The processes we study in the atmosphere cover a large range of scales, from the molecular reactions in the nm range ( $10^{-9}$  m) to the mesoscale meteorological transport pattern at 1000 km scale ( $10^6$  m). Hence the spatial scale of the processes differs with at least 15 orders of magnitude (see Figure 2). We must take this into account when we define our needs and requirements concerning models.

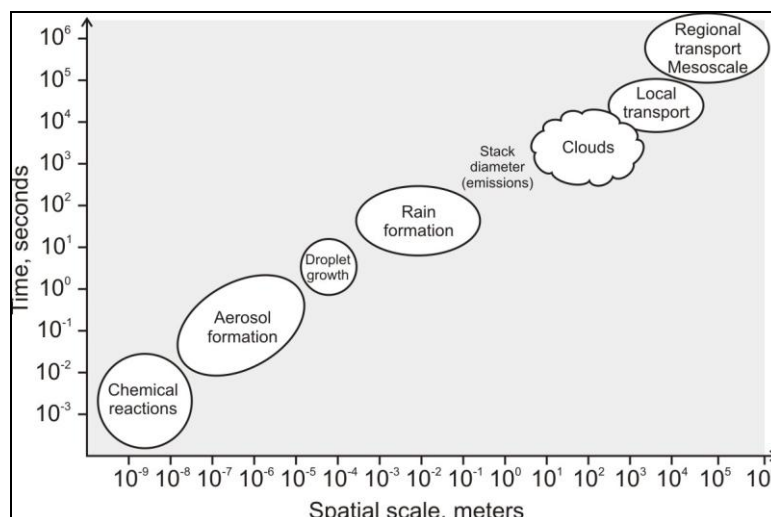


Figure 2: Range of scales important for the amine processes.

### 3.2 Time scale

Also for the time scale there is a wide range in the scale of the processes (Figure 2), at least 9 orders of magnitude. Time scale ranges from the scale of chemical reactions ( $10^{-3}$  s) up to mesoscale transport time ( $\sim 1-2$  week, i.e.  $10^6$  s).

As shown in Figure 2 the spatial scale and the time scale are closely related. Small scale processes take place at a short time scale, like molecular reactions at  $10^{-9}$  m and  $10^{-3}$  s. Large scale meteorological transport processes take place at a  $10^6$  m spatial scale and  $10^6$  s time scale.

The time step used in the model runs must be appropriate for the time scale of the processes described. For example, for a model that calculates chemical reactions the time step must be much shorter than for a model that calculates long range transport.

### 3.3 Parameterizations

As already shown, the scale of the processes vary with 10-15 orders of magnitude. To make a model that represents all processes in detail would require huge computer resources and is therefore not feasible. E.g. processes at molecular scale ( $10^{-9}$  m scale) cannot be represented in a model with a large model domain ( $10^6$  m), simplifications and parameterizations must be made. The term parameterization signifies to represent processes too small for the model grid (“sub-grid processes”) by using simplifications.

To give an example; if a model covers a  $1\text{ m} \times 1\text{ m} \times 1\text{ m}$  volume, the droplet formation may be represented in detail by using relative humidity, cloud condensation nuclei (CCN) concentrations and size distribution, Köhler curve etc. However, if a model domain is  $1000\text{ km} \times 1000\text{ km}$  this detailed method cannot be used, and further simplifications are needed. One way is e.g. to assume that if relative humidity is over 100%, formation of droplets occur. This will not be totally correct, but a good approach.

### **Grid size**

In a numerical model the model domain is often divided into a grid, so-called Eulerian grid. This means that numerical values (quantities) are calculated at discrete points in space. The grid resolution, i.e. distance between these discrete points, will depend on the scale of the process we want to study. For example, to study processes in a plume the resolution will be 1 m, while in a global transport model 200 km resolution would be more appropriate. The choice of grid size is a question of computer time vs. level of detail, and the processes that need to be described. For example will studies of the chemical processes have a smaller grid than studies of regional transport.

## **4 Effects and output**

While running models there are several possible types of output (output defined as the parameters the model actually calculates, i.e. the model results). The choice of output is dependent on the processes or the effects that are investigated in the model. Output is needed to describe the connections between emissions and environmental load. Below some possible effects of amines emissions are listed together with the subsequent desired model output.

### **4.1 Health effects**

Consequences for public health of emissions of amines are normally evaluated through concentrations and deposition. This means that concentrations in air (most important at the ground level), and concentrations in rain water and tap water are most crucial. The threshold values for exposure of people towards amines are different for acute and chronic effects. For acute effects, the maximum concentration is important, while for chronic effects the average concentration is the aim. In addition, there is a need to detect both exposure **and** effect, i.e. critical level where the compound causes damage, e.g. to DNA.

### **4.2 Smell**

Some amines have a very strong smell, for instance a smell similar to rotten fish. Even though this smell is not toxic, it may be disagreeable and cause nuisance. To find the effect of amines concerning smell, concentrations in air with short averaging time must be determined. Concentrations can then be compared with threshold values for smell. These threshold values may be found in the literature.

### **4.3 Effects on vegetation**

Uptake of amines and their degradation products by vegetation is dependent on concentrations in air at ground level. This is the process where a component is taken up through the stomata of plants, called dry deposition by vegetation. Once taken up by the plant, a gas can be toxic to the plant tissue. This is the case with for example O<sub>3</sub> (ozone) and SO<sub>2</sub>. How amines affect vegetation is not well known, but this will be studied further.

Uptake by vegetation also needs information about the vegetation type, temperature, sunlight and humidity, these three latter to determine whether the plants' stomata are open or not, but this can be parameterized in the model.

#### 4.4 Effects on aquatic organisms

Amines and the degradation products may have an effect on aquatic organisms. To study these effects, there is a need to calculate the concentration of amines and products in cloud droplets and rain droplets, i.e. wet deposition. This information will then be input to studies on effects on aquatic organisms.

#### 4.5 Corrosion

Degradation of materials (corrosion) may also be one important effect of emissions of amines to air. To study this, knowledge of long time average concentrations in air as well as of concentrations and pH in rain is needed.

#### 4.6 Climate effect

Will emissions of amines affect climate? The radiative properties of amine molecules are considered to be weak and the atmospheric lifetime is short, hence the so-called direct effect is negligible. But amines may affect the properties of cloud droplets and thereby have an indirect effect. To determine the indirect effect changes in cloud droplet size, cloud droplet concentration and cloud cover are needed.

#### 4.7 Other types of output

For a quality control and to assist in understanding of the processes, information on total load of the components, lifetime of the components, fluxes (total emissions, total deposition, dry deposition, wet deposition etc.), and budget (should sum up correctly) are needed.

#### 4.8 Conclusion modeling needs

The different environmental effects and required model output are described above. In this subsection the findings will be summarized and put into perspective. One important point using models is to find maximum load. Concentrations of the different substances must be calculated on a short term as well as on a long term basis, to study e.g. acute effects and chronic effects respectively (timescale ranging from minutes to annual mean).

In Figure 1 the atmospheric cycle of amines and the most important processes are shown. Here these processes are related to the requirements concerning models.

Chemistry: The chemistry must be described using a chemistry scheme. All three types of chemistry, i.e. gas phase, aqueous phase and aerosols, must be included. How sophisticated and detailed this scheme should be depends on the objectives. If chemistry and chemical reactions are to be studied, then a detailed scheme is required. If e.g. regional transport is the main concern, then simplifications in the chemistry scheme could be made.

Plume (transport): Near the emission point (the stack) it is crucial to get knowledge about what happens inside the plume. Hence a model should be able to describe and resolve the plume properly. Plume chemistry, entrainment of ambient air, transport and dispersion will be important in this respect.



Regional transport: amines and photochemical products have a lifetime of hours to days in the atmosphere. It can then be transported several hundred kilometers away before it is lost by deposition. There is a need for a model that can calculate regional transport of amines. At the same time, such a model must be able to resolve the plume from the stack (see previous point).

Wet deposition: Deposition is the ultimate loss of atmospheric constituents. The amines used in CO<sub>2</sub> capture plants and many of its photochemical products are very soluble. Wet deposition is therefore evaluated to be the most important loss process. A model must be able to represent the wet deposition properly. Cloud data and precipitation are needed, but also calculations of aqueous phase chemistry to get concentration of amines in cloud water and rain water. This process can be simplified depending on the precision needed.

Dry deposition: Even though amines are very soluble, there may be some loss by dry deposition to vegetation and on surfaces. The model chosen for regional transport studies should also have a dry deposition scheme included (describing surface type, deposition velocities, etc.).

## 5 Existing models

The fundamental question concerning choice of model is the question of scale. In general, based on the range of scales, one single tool and modeling approach cannot be considered as optimal. This diversity in scale is exacerbated by the several possible impacts to be investigated covering ecological aspects as well as human health and living standards.

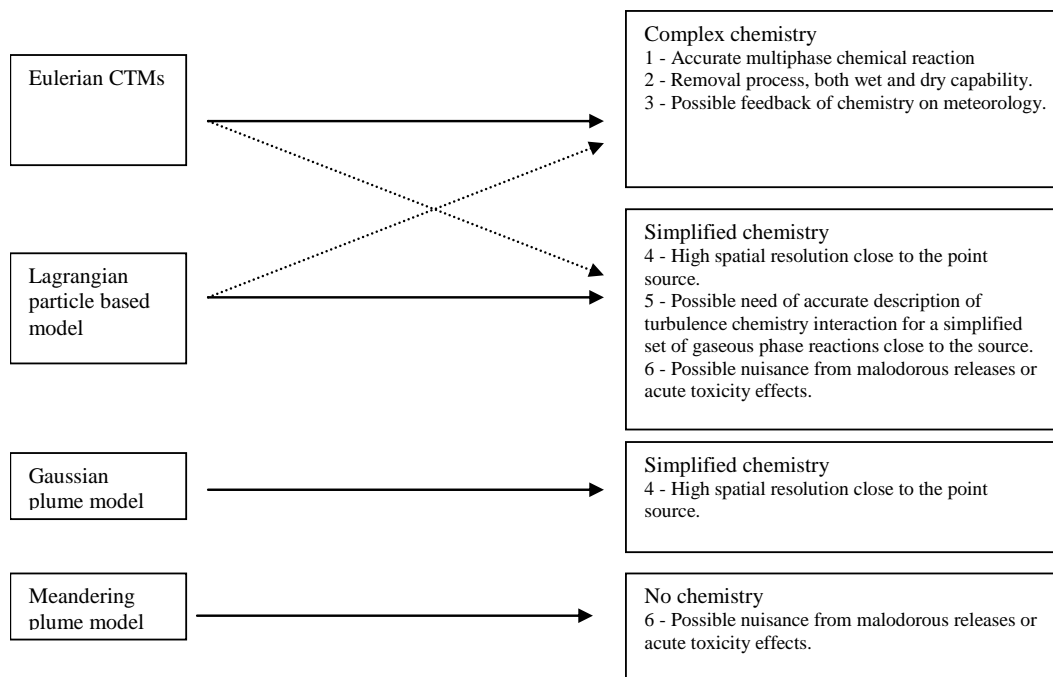


Figure 3: Diagram showing model types and their application. See sections 5.2 and 5.3 for description of model types.

As shown in Figure 3 different classes of models have been selected for different tasks. Eulerian chemical transport models (CTMs) are the optimal tools (indicated by continuous lines) for the first three points (multiphase reactions, removal processes and feedback on meteorology); these models have very sophisticated treatment of chemistry but a somewhat inadequate approach to turbulence related effects. Advanced Lagrangian particles model are the optimal tools for the plume description, plume chemistry and short averaging times. Simplified meandering plume model could also be eventually used to evaluate concentration fluctuations in the case where chemistry could be neglected in the short range dispersion.

In the diagram, dashed line indicates what we consider non-optimal paths, i.e. it is possible to handle these points with the indicated tools but this would require much more computational resources (Eulerian CTMs) or large development work (Lagrangian models).

Based on what is said so far, three types of models or model concepts are proposed, ranging from molecular scale up to regional scale. These main concepts are **box models, local small scale models and regional transport models**. In the following section, these model concepts will be described in detail. The different models and model concepts are discussed with respect to the processes, effects and output.

NILU, NIVA and NINA have developed a model concept called EIF-Air (Environmental Impact Factor- Air). This concept is based on the INPUFF model and calculates dispersion and wet deposition of sulphur and nitrogen. If the purpose of a model run is to calculate the wet deposition of N and discuss possible eutrophication, then the EIF-Air concept is suitable. Effects on vegetation by emissions of amines with regard to eutrophication will be studied in this project (task 9 performed by NINA). However if the purpose of a model run is to get concentrations of amines and degradation products in air and droplets, then the EIF-Air concept is not suitable.

## 5.1 Box models

These types of models include the processes from molecular reactions ( $10^{-9}$  m) up to droplet formation ( $10^{-3}$  m, 1 mm). The purpose of such a model is to study processes, in order to get some basic understanding and new knowledge. They are mainly used for studying chemical processes in the atmosphere, but could also be used for droplet formation.

### 5.1.1 Gas phase and aqueous phase box model

These models are used to study gas phase and aqueous phase reactions in detail. The two phases may be calculated either separately or simultaneously. The purpose is to see what kind of chemical reactions and chemical components are the most important, what photochemical loss products would be expected in the oxidation and what are the expected concentrations of these oxidation products.

One example of such a model is the box model module of the OsloCTM2 (Berglen et al., 2004). It covers the basic tropospheric chemistry with  $\text{NO}_x$ -VOC-

O<sub>3</sub> chemistry. In addition, the sulphur cycle is included as an option (gas and aqueous phase). Amines are not included in these box models at the moment, but need to be incorporated.

Dep. of Chemistry at the University of Oslo has developed a model that predicts degradation products of amines. This model is described in detail in a separate report from this project.

### **5.1.2 Aerosol box model**

There are two objectives for aerosol models:

- 1) Uptake of amines/condensation of organic vapours from amine oxidation to particles.
- 2) Growth of water droplets by additives of amines.

The first group of models (objective 1) may give us information about e.g. aerosol composition, aerosol mass, and aerosol size. The models aimed at studying the second objective may give us information about aerosol water mass, droplet formation, and droplet size distribution. Both types of models could be (or should be) used to study the processes taking place in a small volume. If chamber experiments are to be conducted, model studies should be performed prior to the experiments to give information and knowledge.

The information we obtain from box models and chamber experiments are very useful for dispersion models. Either we can include the scheme from the box models directly, or we can use the results from the box model to parameterize the processes at a scale that is too small for the dispersion models.

There are several aerosol models available today. However, no model with amines included has been found. When amines are to be included in a chemistry scheme, a box model should be used as a test before this amine scheme is put into a dispersion model.

## **5.2 Local scale dispersion models**

These are models covering a scale from  $10^{-3}$  m up to  $10^4$  m, i.e. from droplet size up to local scale, that can resolve the plume. These models must be able to simulate plume processes (chemistry, aerosols and droplets), as well as dispersion and transport of the plume. Several types of local scale dispersion models may be applicable.

### **5.2.1 Gaussian type dispersion models**

CONDEP (Bøhler, 1987) is currently used at NILU. It is a steady-state Gaussian dispersion model, with no chemistry or simple chemistry, that calculates annual mean concentrations based on average meteorological conditions (wind and stability, so-called "typical weather"). A vast number of this type of models exist, both for long time averages and short time averages. These models treat emissions for each averaging time independently and no evolution in time of the plume is available.

### 5.2.2 Lagrangian particle/puff transport model

A trajectory model follows plume parcels (“puffs”) as these parcels move around in the atmosphere, transported by advection (wind). In a model run, the model calculates the trajectory of a large number of parcels (up to 100.000 different parcels). Chemistry and aerosol processes take place while these parcels move around. The models take into account emissions that are done in hours before the current hour and have “history” included.

Lagrangian particle models are usually used for non-reactive scalar transport, a good example is FLEXPART, they are more accurate than Eulerian models with regards to dispersion. In practice, a large ensemble of marked fluid particles is tracked in the domain using a resolved velocity field and adding sub grid scale (SGS) and/or turbulent fluctuations. The particles are tracked according to a system of stochastic differential equations for the particle velocity and position,

$$du'_i = a_i(\mathbf{x}, \mathbf{u}', t)dt + b_{ij}(\mathbf{x}, t)d\zeta_j \quad (1)$$

$$dx_i = \langle u_i \rangle + u'_i dt \quad (2)$$

The coefficients are defined based on the scales of motion that should be represented. More specifically the coefficients can be defined to account for the boundary layer turbulence or for mesoscale meandering (e.g. FLEXPART). The resolved velocity field can be generated by any meteorological model or generated in a pre-processor step (see e.g. COST Action 710 – final report). The concentration is then usually obtained using a box counting or some kernel approach.

This leads to the related modelling approach called Lagrangian puff model (e.g. SCIPUFF, HYSPLIT, CALPUFF). In this case puffs are tracked in the domain instead of particles. Therefore care must be taken of correctly expanding the puff around centre of mass (i.e. not double counting dispersion). The trajectory is described in a way similar to the one for a particle. Concentration is obtained in any point by superimposing different puff contribution. These models have algorithms to split and merge puffs based on the local grid to better account for 3D variability.

Lagrangian particle/puffs models can be used in conjunction with Eulerian CTMs to describe sub grid scale (SGS) dispersion (Plume in grid), thus improving close to the source spatial resolution for point sources. However, it must be remarked that this does not solve any issue related to the closure of the chemical term  $\langle R_\alpha \rangle$ , but only to the closure of the SGS flux term  $\langle \phi'_\alpha u'_j \rangle$ . (see Appendix A).

These models can be opportunely modified to account for chemistry. The set of reaction treated is usually limited to what is not well described by an Eulerian CTMs close to the point source (e.g. NO<sub>x</sub> / O<sub>3</sub> chemistry). The improvement is only related to the spatial resolution of the flux term, not to the approximation involved in the treatment of the interaction between chemistry and turbulence (Plume in grid approach).

In general these models could be used, if it is established that turbulence–chemistry interaction may be neglected (point 5 in Figure 3), but a higher spatial resolution is necessary close to the source (point 4 in Figure 3) with respect to the Eulerian CTMs.

### 5.2.3 *Meandering plume model*

This class of models can be used to evaluate concentration fluctuations if non-reactive scalar are considered. This is a simplified approach compared to the precedent models, nonetheless they are recommended by Wilson (1995) in his monograph on dispersion of toxic and flammable vapour. These models can therefore be applied to the problem of evaluation of dispersion of malodorous materials. They require the a-priori knowledge of the mean concentration field that must be established by different models (e.g. the Lagrangian particle models discussed below in section 5.2.4). From the mean concentration they are able to extract information on the fluctuations, making some assumption on the instantaneous behaviour of dispersing plumes. A numerical based improved version of this approach (Cassiani et al. 2002) allows the use of this technique to more general terrain and stability conditions with respect to standard meandering plume models. It can be used only in flat terrain and neutral conditions. We remark that this approach can be used only if the scalar can be considered non-reactive and for a single point source. The output will be short term averages.

### 5.2.4 *Lagrangian probability density function (PDF) model*

This is the most advanced treatment of dispersion and chemical reaction available in the literature. (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. For example the most simplified approach use the following differential equation for the particle concentration evolution

$$d\phi_\alpha = -\frac{1}{t_m}(\phi_\alpha - \langle \phi_\alpha(\mathbf{x}) \rangle)dt + R_\alpha(\phi)dt + S_\alpha dt \quad (3)$$

No closure is necessary for  $R_\alpha$  or any non linear term which are handled exact (see Appendix A). This is because the model acts directly on “instantaneous” stochastic realizations of the concentration field not on the averaged value. No other modelling approach can ensure this level of consistency. It should also be remarked that this approach gives access to the full concentration probability density function (pdf)  $f(\phi)$ . These models are therefore optimal if concentration fluctuations must be considered (odours).

These models also use a 3D Eulerian grid to compute the mean concentration field used in Eq. (1), although the advection, dispersion and chemistry are treated at any particle location separately.

The only shortcoming of these models is the computational time required. However, they are less expensive than a very refined (i.e. Large Eddy Simulation level) Eulerian CTM that could give a comparable level of information. Here, contrary to CTMs, the averaged velocity field  $\langle u_i \rangle$  can be obtained from relatively coarse scale meteorological models since all the atmospheric boundary layer turbulence information is contained in the stochastic model equations.

NILU is among the few research groups having experience with this class of models (e.g. Cassiani et al. 2005a,b , 2007a,b) and a Lagrangian pdf model is considered to be the best options to construct a Plume in grid model for short range dispersion, able to fully describe the plume and the plume chemistry with short averaging times (see Figure 3).

### **5.2.5 Fotoplume**

The FOTOPLUME model (e.g. Solberg 1998) is a point source dispersion model developed at NILU. It is used to simulate the dispersion and the chemical reactions downwind of large emission sources. Both nitrogen oxides and VOCs are released in relatively high concentrations, in the exhaust gases from e.g. gas turbines, where the concentration of nitrogen oxides are several hundred parts per million. Subsequent dilution with the surrounding air is determined by the atmospheric turbulence, which causes the plume to increase its width and height, until it is more or less evenly dispersed within the mixing layer within a few hours. The lateral dimensions are also increased, within the same time frame, up to a few kilometres. In order to describe the chemical reactions of the nitrogen oxides and the volatile organic compounds emitted from large point sources, it is considered important to describe this mixing with the external air as correctly as possible. The formation of ozone by photochemical reactions depends critically on the concentrations of nitric oxide and nitrogen dioxide in relation to the concentrations of the other reacting species. The model is a Lagrangian model, but instead of the puff or particle, an expanding Eulerian grid is used. This enables the model to have sufficient resolution to describe the plume locally and to solve the chemical reactions. It is straight forward to include a new chemical reaction model into this dispersion model. The model needs a larger scale model to produce the boundary conditions for the ambient air surrounding the plume.

### **5.2.6 Plume in grid**

Plume in grid is a third method to represent sub-grid dispersion. For small plumes with scale less than the grid size, we calculate this separately as plume dispersion. Once the plume reach the grid scale we include the plume in the grid.

In practice, concentration is transferred from the particle/puff to a local grid based on local grid volume and used in chemical reactions. Then mass is transferred back to the particle/puff from the grid based on some heuristic concepts to advance the advection/dispersion of the scalars.

## **5.3 Regional transport models.**

These are models with scale from  $10^4$  m up to  $10^6$  m. The aim of these models is to calculate transport and dispersion of atmospheric pollutants (gases and aerosols). Chemistry, aerosol processes and droplet formation may be included, but parameterized to account for small scale features.

### **• The principle of nested models**

Nested models have a finer resolved domain within a more coarse resolved model domain. The coarse domain ideally covers the whole Earth, and then the finer resolved domain covers a region like Europe. The parent domain could also be Northern Europe, and the domain around a megacity like London could be resolved on a smaller scale (see Figure 4). Concerning this project, for instance Scandinavia could be the parent domain gradually nesting down to a domain near the plant resolved on a  $1 \text{ km} \times 1 \text{ km}$  grid. In nested models information from the coarse domain has to be passed to the finer domain, for example the boundary conditions for meteorological and chemical fields. A one-way nested model is a model in which information is passed only from the parent to the nested domain. A two-way nested model is a model in which information is passed in both directions.



*Figure 4: Example of nested grid in the WRF model, gradually nesting in on the London Metropolitan Area. The outer domain has a grid size of 81 km, the second domain has 27 km grid size, the third 9 km, and the fourth 3 km grid size. The innermost domain with 1 km grid size is not shown. Source: WRF Domain Wizard.*

### **5.3.1 Velocity field modeling**

Before going further a brief account of two selected meteorological models able to produce detailed local to mesoscale and larger wind field are given. These are the necessary basis of accurate dispersion calculations. They have been selected

because they are well documented, used by several users in the world and successfully coupled with advanced Eulerian CTMs.

#### • 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 (see section 5.3.2 below).

#### • WRF

WRF, Weather Research and Forecasting – Limited-area model (in contrast to global) developed as a community model (<http://www.wrf-model.org>) (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 kilometers. The model includes horizontal nesting capabilities allowing for Large Eddy Simulations (LES) of the planetary boundary layer but to our knowledge it has not been tested at very fine resolution for which ARPS should be more reliable. 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 the CMAQ description in section 5.3.2) and it can be used coupled with an embedded Eulerian CTM, WRF-Chem (also section 5.3.2).

### 5.3.2 *Standard Eulerian chemical transport models (CTMs)*

This is a broad class of model applied for modelling atmospheric dispersion in a wide range of spatial scales, commonly from the planetary scale down to a 1 km grid resolution and less. One example of model belonging to this class is EMEP model for large scale or CMAQ for multi scale applications.

These models assume a standard gradient diffusion, K, closure of the SGS flux term (e.g. Seinfeld and Pandis, 2006),

$$\langle \phi'_\alpha u'_j \rangle = -K_{jk} \frac{\partial \langle \phi_\alpha \rangle}{\partial x_j} \quad (4)$$

This relation is in general not true in the atmosphere but can be a good approximation in two cases



- i) very small volume average of both the original velocity field and scalar field, (i.e. LES level accuracy)
- ii) far from any localized source but only if the required resolution is coarser than both the fluid dynamic and the scalar grid.

These models assume also the following closure for the chemical term

$$\sum_{\beta=1}^M \eta_{\alpha\beta} k_{\beta} \left\langle \prod_{\gamma=1}^N \phi_{\gamma}^{n_{\gamma\beta}} \right\rangle = \sum_{\beta=1}^M \eta_{\alpha\beta} k_{\beta} \prod_{\gamma=1}^N \langle \phi_{\gamma} \rangle^{n_{\gamma\beta}} \quad (5)$$

This relation is general not true but can be a good approximation in two cases

- i) very small volume averaging, see above,
- ii) chemical reactions with time scale much slower than both the turbulence time scale and the characteristic time scale associated with the grid resolution (SGS time scale). See the discussion in sections 5.2.4 and 5.2.6.

In other words Eulerian CTMs neglects the dynamical and chemical perturbations generated by the scales smaller than the spatial and temporal resolution of the model. These perturbations lead to significant effects on the simulated temporal variation and spatial distribution of reactive species and cause errors of the calculated atmospheric composition if they are not taken into account (e.g. Ebel et al. 2007). This is particularly true in the planetary boundary layer (PBL) (e.g. Vilà-Guerau de Arellano et al. 2004) since chemical reactions of non-premixed reactants in a turbulent and diffusive medium are well known to be less efficient than those of perfectly mixed ones. Several studies have been devoted to evaluate the importance of these effects (Georgopoulos and Seinfeld 1986; Vilà-Guerau de Arellano et al. 1990, 2004; Schumann 1989; Sykes et al. 1994).

However, Eulerian CTMs have the most complete treatment of chemical reactions, in gaseous phase as well as aqueous, aerosol, and particulate and they usually include removal processes both wet and dry.

#### • CMAQ

CMAQ (Community Multiscale Air Quality) – Multi-scale, multi-pollutant model developed by US EPA (<http://www.cmaq-model.org>) (see e.g. Byun and Schere, 2006). Different chemical mechanisms (CB-IV, CB05, SAPRAC-99 and RADM2) and solvers are available. The model is embedded within the Models-3 framework of EPA, which includes interfaces to prepare for instance emissions (SMOKE), initial (ICON) and lateral boundary conditions (BCON). Note that the University of Hertfordshire, UK adapted the emission processor SMOKE to include European (from EMEP and EPER) and UK (from NAEI) scale anthropogenic emissions as well biogenic emissions. The modeling system (coupled with MM5, WRF or ARPS) can be used to investigate regional- to local-scale (including urban scale) air quality. Only one-way nesting is permitted.

This model fully accounts for multi-phase chemical reactions and deposition (see points 1 and 2 in Figure 3 above). But currently it neglects chemical feedback to meteorology (point 3) and cannot be used for that purpose. Depending on the resolution used to provide the velocity field the model having high enough spatial

resolution accurate description of turbulence chemistry interaction may be included (points 4 and 5 in Figure 3), but at the expense of very intensive calculations, feasibility should be eventually evaluated carefully. It is theoretically possible to use this model to compute fluctuations but feasibility and results should be carefully evaluated. Currently this approach is not considered optimal for the investigation of plumes with chemistry and short term fluctuations in concentrations.

We recommend its use for the regional to urban scale. Since it is not embedded inside a meteorological model CMAQ can use independent grid resolution if necessary (e.g. coarser to save computational time). The model should be integrated by some kind of plume in grid treatment of the point source to account for chemical reactions, plume representation and short term concentration fluctuations (point 4,5, and 6 in Figure 3). However, the standard available plume in grid treatment in CMAQ is not adequate for this purpose and should be replaced by something developed at NILU (see the discussion in sections 5.2.4 and 5.2.6).

- **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 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 fully accounts for large scale dispersion, multi-phase chemical reactions, removal (deposition), and feedback on meteorology (points 1, 2 and 3 in Figure 3). Depending on the resolution used to provide the velocity field the model can potentially treat plumes with chemistry and short term fluctuations in concentrations, but at the expense of very intensive calculations, feasibility and results should be eventually evaluated carefully. We do not recommend this approach for plumes with chemistry and short term fluctuations in concentrations.

Similarly to CMAQ this model should be integrated by some kind of plume in grid treatment of the point source to account for plumes with chemistry (point 4 and 5 in Figure 3, high spatial resolution near the source, and turbulence-chemistry interactions, respectively). The Plume in grid should be developed at NILU (see the discussion sections 5.2.4 and 5.2.6).

- **OsloCTM2** is a global Chemical Tracer Model (CTM) developed at the University of Oslo (Berglen et al., 2004). It is a global gridded model using meteorological input data from the IFS model at ECMWF. It may be run with various spatial resolution, from T21 ( $5^{\circ}625 \times 5^{\circ}625$ ) down to  $1^{\circ} \times 1^{\circ}$  ( $55 \text{ km} \times 111 \text{ km}$  at  $60^{\circ}$ ). The model includes both tropospheric and stratospheric chemistry, as well as sulphur chemistry, sea salt, mineral dust, an aerosol module (EQSAM), Black Carbon/Organic Carbon, and Secondary Organic Aerosols (SOA). The OsloCTM2 has then gas phase chemistry, aqueous phase chemistry

and aerosol module included. However no amine chemistry is included at the moment.

### **5.3.3 Lagrangian transport model FLEXPART**

FLEXPART (see <http://transport.nilu.no/flexpart>) is a Lagrangian particle dispersion model that has been developed by Stohl et al. (1998, 2005) and is now used at more than 40 institutes from 17 countries. The model simulates the transport of passive tracers by calculating the trajectories of a multitude of so-called particles using the resolved winds and parameterizations for turbulence and convection. It does not yet include any chemical processes but is a highly accurate transport model and contains detailed wet and dry deposition schemes. FLEXPART has been coupled with the ECMWF model and MM5 but could be easily coupled with WRF and ARPS.

FLEXPART can be straightforwardly used if the chemical species of interest could be assumed non-reactive. In this case would be preferable to CTMs model for modelling the transport.

As mentioned, FLEXPART can also be modified in a straightforward way to account for transport at local scale of non-reactive scalar with high accuracy and may be used as a starting point to build a Plume in grid particle model including chemistry based on the approach explained in Chock and Winkler (1994).

In summary the current available FLEXPART does not fulfil any of the points in Figure 3 if the scalar is considered reactive but it can be an excellent alternative if the scalar can be considered non-reactive (i.e. very long chemical life time, or very short dispersion time).

The model may be extended to become a Plume in grid chemical transport model to enhance the spatial resolution available from Eulerian CTMs close to the point source and thus fulfil point 4 above (high spatial resolution close to the source).

## **6 Model development, requirements and needs**

In the previous section a description of the models that exist today was given. In this section the needs and requirements for model development in the next phase of the project will be pointed out.

Possible models and model concepts have been discussed. In the previous section three model concepts based on the different scales involved were proposed (see Figure 2). These three were box models, local small scale models and regional transport models.

In short, box models treat chemical reactions, local small scale models treat dispersion of the plume and short time scale chemical reactions in the plume, and regional models treat transport and the more long lived compounds.

No models with amines included have been found at the moment. So one obvious task would be to include amines and amine chemistry in existing models.

## 6.1 Box models

A 0-dimensional box model is used to study processes in detail. Obtain knowledge is the main purpose of such models. At a later stage, when the various processes are well known, these box models may be included into a 3-d model.

### • Gas phase, aqueous phase and aerosol box model

Little knowledge about the amine chemistry is available, both concerning gas phase, aqueous phase and aerosol phase chemistry. Dep. of Chemistry, University of Oslo (DCUO) has developed a model to determine possible chemical reactions in the photochemistry of amines (reported separately). Based on the results from this model, a chemistry scheme including the main oxidation pathways should be developed. Typical concentrations of the oxidants may be taken from a large scale Chemical Tracer Model (CTM). A chemistry scheme like this should cover a) gas phase chemistry, especially with OH oxidation at day-time, b) aqueous phase chemistry, and c) chemistry taking place on the surface of particles (resembles aqueous phase chemistry).

Numerous chemistry schemes exist, but none with amines included. One option here is to include amines in an already existing scheme, rather than develop a scheme from basic. The scheme used in OsloCTM2 is already mentioned. If one wants to study the eutrophication caused by amines (from the  $\text{NH}_3$ -group) the EQSAM scheme (Metzger, 2004) may be a starting point. The EQSAM scheme is based on equilibrium considerations (sea salt, sulphate, ammonia/ammonium, and nitrate) and calculates aerosol concentration in fine mode and coarse mode. With some modifications it could be possible to include amines into the EQSAM scheme.

Our main recommendation is then to take an existing chemistry scheme and include amines. When such a scheme does function properly, it may be included into the dispersion model.

### • Droplet formation box model

Amines affect the surface properties of water and thereby may modify the droplet formation. The theory behind these mechanisms are well known (Köhler theory). In phase I of the project NILU developed a simple scheme for droplet formation. This scheme may be developed further and modified so that it can be included into the dispersion model. If cloud chamber experiments are to be conducted, the scheme should be elaborated to fit with the actual experiment.

Our recommendation is to develop further the already existing rain or droplet scheme.

## 6.2 Local small scale models

Gaussian dispersion models, like CONDEP described in section 5.2.1 is considered to be too simple for our purpose, but it may be used for preliminary investigations. More sophisticated models exist today, like Lagrangian particle models, meandering plume models, Lagrangian PDF models (sections 5.2.3 and 5.2.4). FOTOPLUME is also an option where NILU has expertise (section 5.2.5). Whether chemistry should be included or not depends on the lifetime of the

amines emitted from the plant. If the lifetime is long compared to the spatial scale, e.g.  $\tau >$  several hrs and model domain 10 km, then most of the amines will not degrade within the model area. In that case we do not need chemistry. But if the lifetime  $\tau$  is short, e.g.  $\tau \sim$  minutes, then we need to include chemistry to determine the degradation products within the model domain as well. To determine how fast the processes develop and the lifetime of the components we may use a box model as described in section 6.1. The timescale of the mixing between the plume and the ambient air is also important (see Appendix A).

These small scale dispersion models will basically give concentrations in air and deposition as output. Based on the output from wet removal process we may also calculate amine concentration in rain water.

Our recommendation is then:

Use NILUs expertise to adopt Lagrangian PDFs or meandering plume models to our problem. To include amine chemistry should also be considered. Whether full chemistry or some simplified scheme should be included remains an open question, simplified chemistry scheme means e.g. fixed concentrations of oxidants.

### **6.3 Regional transport models.**

Some degradation products of amines have lifetimes  $\tau$  of the order of days, for example PAN-like compounds. These components emitted will then be transported a few hundred kilometers away before they are removed by deposition (see Figure 2 for the question of scale). In this project there is no need for a global model covering the entire globe. The OsloCTM2 model mentioned in section 5.3 is not suitable, it has a too coarse resolution and requires too much computing time. A regional model will be more adequate for our purposes.

An important question is also whether amines affect the meteorological conditions of the atmosphere. Findings from other tasks in this project will give us the answer to that. If the answer is yes, then a model with feedback between chemistry and meteorology should be chosen (e.g. WRF-Chem). If the answer is no, then this feedback is not needed and a broader range of models will be suitable.

Several types of regional models are described in section 5.3; WRF-Chem, CAMQ-MM5, and FLEXPART. All these models have strong and weak points, advantages and disadvantages. Which model to use depends strongly on the specific problem to be solved, the purpose of the model, the effects one wants to study, and the desired output.

If amine chemistry is included, these three models listed here will give concentrations in air, concentrations in cloud water/rain water, dry deposition, and wet deposition as output. If a cloud droplet formation scheme is included the model can also CALCULATE the cloud droplet output needed for climate purposes.

### **Our recommendation:**

The three models listed above are all suitable for regional studies of amines and amine degradation products. At the moment no definitive conclusion is drawn concerning choice of model or model concept. NILU has modeling expertise concerning all these types of models. The models need to work together with a sub grid model to resolve the plume phase. Based on the findings from other parts of this “Environmental and Health effects from emission of amines to air from CO<sub>2</sub> capture”, the needs and requirements for regional models will be more specified and one of these three models will be chosen.

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# **Appendix A**

## **Basic concepts of models**





The starting point to describe the evolution of chemical concentrations in the atmosphere is the advection and diffusion equation of reactive scalars (e.g. Seinfeld and Pandis 2006),

$$\frac{\partial \phi_\alpha}{\partial t} + u_j \frac{\partial \phi_\alpha}{\partial x_j} = \Gamma \frac{\partial^2 \phi_\alpha}{\partial x_j \partial x_j} + R_\alpha(\Phi) + S_\alpha \quad (1)$$

Where  $\phi_\alpha$  is the concentration of the chemical species,  $u_j$  is the j-component of the wind velocity,  $\Gamma$  is the molecular diffusivity and  $S_\alpha$  represents sources and sinks excluding chemical reaction, e.g. emission and deposition.

$R_\alpha \left( = \sum_{\beta=1}^M \eta_{\alpha\beta} k_\beta \prod_{\gamma=1}^N \phi_\gamma^{n_{\gamma\beta}} \right)$  represent a general chemical reaction,  $\eta_{\alpha\beta}$  is the stoichiometric coefficient for species  $\alpha$  in reaction  $\beta$ ,  $k_\beta$  is the reaction rate constant for reaction  $\beta$  and  $n_{\gamma\beta}$  is the reaction order of species  $\gamma$  in reaction  $\beta$ .

First we underline that in the equation 1 a velocity field must be supplied. The velocity field is highly unpredictable and for a complete description would require the solution of the Navier-Stokes equation for all the possible degrees of freedom. This is clearly an impossible task for atmospheric application since the number of degrees of freedom involved, is estimated to be proportional to  $R_e^{9/4} \left( R_e = \frac{UL}{\nu} \right)$

with  $R_e \sim 10^9$  and more in the atmospheric boundary layer. To simplify the problem statistical treatment of the equations is needed. The usual way is to apply volume, time or ensemble average to the equations. For example we can define:

-Volume average:  $\bar{u}(x,t) = \int u(x-r,t)G(r)dr$

- Ensemble average discrete:  $\langle u(x,t) \rangle = \frac{1}{N} \sum_{n=1}^N u^{(n)}(x,t)$

$G(r)$  is the spatial kernel and  $N$  is the number of realizations in an ensemble.

We briefly note that in large to mesoscale applications volume average are usually invoked while in small scale application, involving 3-D turbulence, ensemble and volume average are used depending on the approach. This may generate some inconsistency, since an ensemble average potentially include any scale of motion, thus care must be taken to avoid double accounting of scale explicitly resolved in the fluid dynamic (velocity) field.

Application of ensemble average to equation (1) gives

$$\frac{\partial \langle \phi_\alpha \rangle}{\partial t} + \langle u_j \rangle \frac{\partial \langle \phi_\alpha \rangle}{\partial x_j} = \Gamma \frac{\partial^2 \langle \phi_\alpha \rangle}{\partial x_j \partial x_j} + \langle R_\alpha(\Phi) \rangle + \frac{\partial \langle \phi'_\alpha u'_j \rangle}{\partial x_j} + \langle S_\alpha \rangle \quad (2)$$

A formally equivalent equation arises with application of volume average. Even with the a-priori knowledge of the averaged velocity field we immediately see that if nonlinearity is involved the chemical reaction are unclosed, i.e.

$$\langle R_\alpha \rangle = \sum_{\beta=1}^M \eta_{\alpha\beta} k_\beta \left\langle \prod_{\gamma=1}^N \phi_\gamma^{n_{\gamma\beta}} \right\rangle \neq \sum_{\beta=1}^M \eta_{\alpha\beta} k_\beta \prod_{\gamma=1}^N \langle \phi \rangle_\gamma^{n_{\gamma\beta}} .$$

The third term on the right of Eq.(2) is a flux and it is unclosed as well. If ensemble average is applied this should be interpreted as turbulent fluxes while if volume average is applied this is a sub grid scale (SGS) flux. Similar closure issues arise in the momentum equations in relation to the flux term. For example applying volume averaging to a simplified Navier-Stokes (no buoyancy and Coriolis forces) we have,

$$\frac{\partial \bar{u}_i}{\partial t} + \bar{u}_j \frac{\partial \bar{u}_i}{\partial x_j} = -\frac{1}{\rho_0} \frac{\partial \bar{p}}{\partial x_i} + \nu \frac{\partial^2 \bar{u}_i}{\partial x_j \partial x_j} - \frac{\partial}{\partial x_j} (\overline{u_i u_j} - \bar{u}_i \bar{u}_j) \quad (3)$$

Where the last term on the right is the SGS momentum flux and it is clearly unclosed.

To solve equation (2) and/or (3) a model of the unclosed quantities must be used. This is the general closure problem of turbulent flow modelling and it is present for any averaged equation.

An important point to be recognized is related to non linear chemical reaction; in general the closure of this term is simply to assume.

$$\sum_{\beta=1}^M \eta_{\alpha\beta} k_\beta \left\langle \prod_{\gamma=1}^N \phi_\gamma^{n_{\gamma\beta}} \right\rangle = \sum_{\beta=1}^M \eta_{\alpha\beta} k_\beta \prod_{\gamma=1}^N \langle \phi \rangle_\gamma^{n_{\gamma\beta}}$$

But in doing this any effect of turbulence on chemistry is neglected. To understand this point we introduce the following Damköler numbers,  $Da_k = t_k / t_c$ , ratio of Kolmogorv turbulent and chemical reaction time scale and  $Da_t = t_T / t_c$ , ratio of integral turbulent and chemical reaction time scale. Based on these numbers and the relative concentration of two chemical species A and B we can, following Vila' Guerau de Arellano et al. (2004), explain the behavior of the interaction between chemistry and turbulence.

Figure 1, below, shows the effects of turbulence specifically for the reactant A. For the slow chemistry regime,  $Da_k < 1$ , turbulence is able to mix the reactants uniformly. For  $Da_k < 1 < Da_t$ , a moderate chemistry regime, the larger turbulent scales are unable to mix the reactants uniformly, and the segregation between them causes either a reduction

or enhancement of the reaction rate. In this regime, one can expect that once the species are mixed by the large scales, the mixing at smaller scales will proceed faster than the chemical reaction, since  $t_t$  is always larger than  $t_k$ . As a consequence, the reactivity is not limited by the small-scale turbulence. For  $Da_k \gg 1$  (fast chemistry regime) turbulence controls the chemical reactions at all the turbulent scales. If  $r < 1$ , similar limitations due to turbulence can be expected for species B.

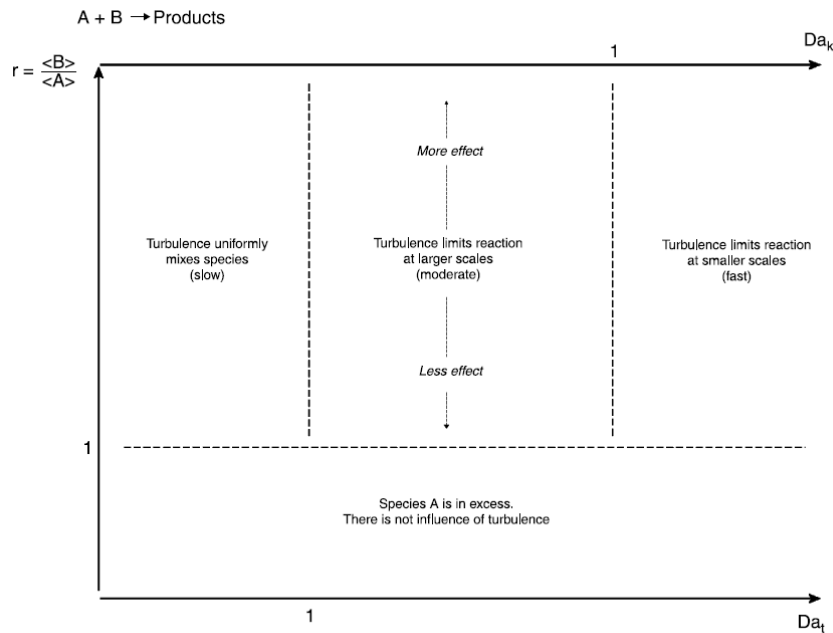
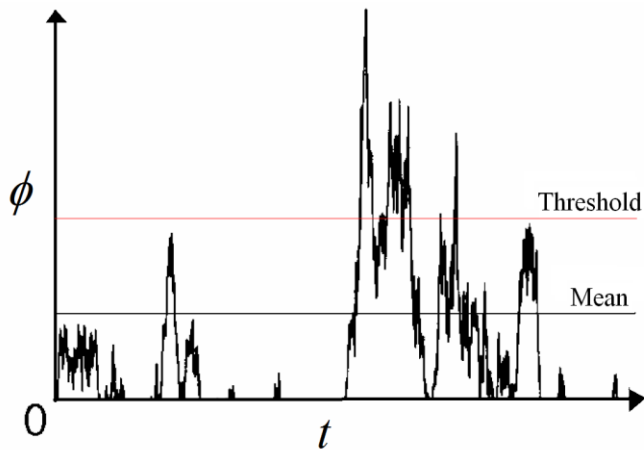


Figure A1. Chemistry turbulence interaction in non linear chemical reaction.

The following table from Vila' Guerau de Arellano et al. (2004) shows time scales for some chemical reactions and atmospheric phenomena

Approximate time scale (s)	Chemical species	Atmospheric phenomena
$10^{-1} - 1$	OH, HO <sub>2</sub> (HO <sub>x</sub> )	Turbulence
$10^2 - 10^3$	NO, NO <sub>2</sub> (NO <sub>x</sub> )	Thermal updrafts
$10^3 - 10^4$	CH <sub>2</sub> O, Isoprene	Convection, thunderstorms
$10^5 - 10^6$	H <sub>2</sub> O, SO <sub>2</sub>	Synoptic weather fronts
$10^7$	O <sub>3</sub> , CO	General circulation
$10^8 - 10^9$	CH <sub>4</sub>	Climate changes

We note that other non-linear phenomenon such as the sensitivity of human to malodorous materials or acute toxicity effect on humans must account for turbulence fluctuations to be correctly evaluated. In particular non linear response to pollutant concentration require the knowledge of the both the mean field  $\langle \phi \rangle$  and the fluctuation from this mean field. A measure of the fluctuation is for example the standard deviation  $\sigma_\phi$ , a complete description is provided by the probability density function (PDF)  $f(\phi)$  of the concentration (e.g. Wilson 1995, Cassiani et al. 2005). The following Figure shows the behaviour of a scalar in turbulent flow and highlight which error can occur in evaluating thresholds related effects based on mean quantities.



Synthesizing the main arguments in this introduction are that i) the modelling of dispersion is tightly connected with the modelling of the 3D velocity (wind) field, ii) the modelling of dispersion requires some averaging procedure, iii) care must be taken to consider which averaging procedure is used and at what scale, iv) averaging introduce a closure problem related to the non linear function of concentration and finally, v) simplified closure usually used in Eulerian CTMs neglect the effect of fluctuations on non-linear processes.

From now on we will use a single notation for the averaging,  $\langle \rangle$ , and we will speak in general of average, volume average or ensemble average as required. It is understood that we have well in mind the subtleties in connecting models formulated starting with different original averaging assumption.



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ABSTRACT This report gives an overview of models, model processes, and the needs and requirements concerning models to be applied in the project "Amines, emissions to air". The atmospheric cycle of amines, i.e. emissions, transport, chemistry and loss, is revealed and discussed. The question of scale is given special attention. Based on the wide range of scales involved, NILU suggests three different types of models or model concepts: box models, small scale local models, and regional large scale models. For every model concept, existing models are described. No model has amine chemistry at the moment. To include amines in existing models will be first priority. For each of the three model types, NILU recommends possible models to use. Concerning regional large scale models, the WRF-Chem, CMAQ-MM5, or FLEXPART models are recommended, with amine chemistry included.			
NORWEGIAN TITLE Rapport om modeller, modellkrav og spesifikasjoner. Bidrag til del 5			
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ABSTRACT (in Norwegian) Denne rapporten gir en oversikt over modeller, modellkrav og spesifikasjoner som er aktuelle for prosjektet "Aminer, utslipp til luft". Den atmosfæriske syklen til aminer er beskrevet og diskutert: utslipp, transport, kjemi og tap. Spørsmål om skala er viet spesielle oppmerksomhet. Basert på inndeling av skala for de forskjellige prosessene foreslår NILU å bruke tre forskjellige modeller/modelltyper: boksmoell, småskala lokal spredningsmodell og regional kjemi-transportmodell. For hver av disse modelltypene er eksisterende modeller beskrevet. Ingen nåværende kjente modeller har kjemi med aminer inkludert. Å inkludere aminer i allerede eksisterende modeller vil derfor være første prioritet. For alle tre modelltyper foreslår NILU mulige modeller som kan brukes. Angående regionale kjemi-transportmodeller anbefales WRF-Chem, CMAQ-MM5 eller FLEXPART med aminkjemi inkludert.			

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