Simulation of Coastal Atmospheric Processes including Aerosols

A contribution to subproject CAPMAN

K. Heinke Schlünzen and L. Klein

Meteorologisches Institut, ZMK, Universität Hamburg,
Bundesstr. 55, 20146 Hamburg, Germany

Summary

The dependence of the close–to-coast deposition on the meteorological situation and the relevance of atmospheric processes was studied with the aid of the atmospheric mesoscale transport and fluid model METRAS (Schlünzen, 1990; Schlünzen et al., 1996) and the chemistry transport model MECTM (Müller et al., 2000). The study region was the south-western North Sea, the simulations were performed for the 1998 measurement campaign of the ANICE (Atmospheric Nitrogen Inputs into the Coastal Ecosystem) experiment.

Aim of the Research

The mesoscale model system METRAS/MECTM is applied to simulate coastal atmospheric phenomena including the nitrogen transport and the composition of coastal aerosol.

METRAS is a multi-layer dispersion model which can generate three-dimensional meteorology fields. This model is coupled with the Chemical Transport Model (MECTM) which includes a gas phase chemistry (Stockwell et al., 1997) and the aerosol model SEMA (von Salzen and Schlünzen, 1999a, 1999b, 1999c). SEMA combines a thermodynamic equilibrium approach with a kinetic approach to predict the condensation and evaporation of gases at the surface of the aerosol.

With the model system scenario studies were performed to calculate the atmospheric nitrogen input to coastal waters in a spatial resolution of 8 km and a time resolution of minutes for the ANICE experimental days. At lateral boundaries and to initialise the model, results of larger scale models were used for the meteorology. The model results were compared with available routine data and with the measurements from the ANICE project for the box-model aerosol runs and the METRAS runs.

Activities During the Year

One of the most important components of any regional air quality model is its chemical mechanism. A transport-transformation model must include a gas phase chemical mechanism that incorporates all significant reactions, but must also be simple by comparison with the very complex chemistry of the real atmosphere. The most well known reactions in a photochemical model are the chemistry of ozone, nitrogen, and sulphur-containing species. Through a chain of photolytical reactions ozone reacts with H_2O to produce the hydroxy radical (HO) which in turn reacts with both inorganic and organic species. The reactions of HO with SO_2 and with NO_2 are the major gas phase sources of H_2SO_4 and HNO_3, which is a very important loss process for NO_x, and both play a role in the formation of coastal aerosols.

NH_3, after N_2 and N_2O is the most abundant compound of nitrogen in the atmosphere (Seinfeld, 1998). NH_3 can react with OH, but as it is highly soluble and reactive with atmospheric acids, that is the preferable route for the removal of the gas phase from the atmosphere. NH_3 and SO_2 are rapidly taken up by aerosols and are therefore relevant when investigating deposition in coastal areas.

The METRAS/MECTM system solves:

- Equation of 3D motion in a surface following co-ordinate system,
- Conservation of energy,
- Budget equation for water (gas, cloud, rain), and
- Budget equation for the tracer gases including emissions, transport, transformations and deposition.

The MECTM uses the Regional Acid Deposition Model (RADM2) gas phase chemical mechanism as described in Stockwell et al., 1990. The RADM2 uses a reactivity lumped molecular approach and includes the above mentioned gas phase reactions as well as alkenes and ketones. Alkenes (ie. Ethene, propene) are important constituents of the polluted and rural troposphere. They are very reactive species that have relatively high rate constants for reaction with HO radical, and they react with ozone to produce aldehydes. Ketones represent a significant sink of carbon since they are less reactive and are transported over long distances.

In the MECTM calculations are made with consideration to gaseous emissions, vertical and horizontal dispersion, chemical transformations, removal of species due to deposition. For solving the stiff chemical equation system the hybrid solver (Müller et al., 2000) was selected for use in the chemistry model so that it would be compatible with the aerosol modules used in later runs. In this solver, the iteration procedure is continued until the convergence criterion is satisfied for all species. The time step used in the chemistry is 220 - 260 s (3-4min).

Anthropogenic emissions for both point and area sources were obtained from the University of Stuttgart, Institute for Energy Economics and the Rational Use of Energy. These include emissions from industry, residential, and a mobile emissions inventory (including running losses, cold-starts, etc) as well as agriculture (NH_3 emissions). The data was aggregated to the METRAS grid and converted to the units that would be necessary for the gas phase chemistry reactions.

The biogenic emission factors are calculated in MECTM by a program which uses the land use classification data and the emission factors from McKeen et al. (1991). A biogenic emission inventory data file was created with the factors stated in kilogram per model grid cell per hour.

In order to accurately model and predict the effects of air pollution, photo-dissociation reaction rate estimates must be made. The simulation accuracy of the entire chemical system is highly dependant upon the accuracy of the photolysis rates, which are the primary source of radicals in the atmosphere. The current approach taken for setting photolysis rates in the METRAS/MECTM was based on the System for Transfer of Atmospheric Radiation (STAR) model developed by Ruggaber (1994). It included two stages of processing: (1) a table of clear-sky photolysis rates was calculated for 21 different gases using a pre-processor which calculates the rates for each photolysis reaction and each hour based on meteorological information extracted from the METRAS runs; and (2) photolysis rates were interpolated from the pre-generated table by the MECTM based on grid cell location and model time. These rates are then matched to the RADM2 mechanism in the chemical transformations during the chemistry run.

The results of the model runs were validated against observations using a series of programs developed for that purpose. These programs interpolated the METRAS results to the locations

of the observation stations and then various statistical methods were applied. The results of this analysis have been discussed in the the previous CAPMAN annual report (Schlünzen et al., 2000). In section 4 the results of the deposition study are discussed.

Principal Results and Main Conclusions

There are four main factors governing dry deposition in the atmosphere:

- concentration in the atmosphere,
- atmospheric turbulence,
- chemical properties of the depositing species, and
- nature of the surface/receptor.

The turbulence near the ground affects the deposition rate to the surface, the solubility and chemical reactivity at the surface may influence the uptake, and surfaces may be non-reactive for gas absorption/adsorption. They may be smooth enough for particles to bounce off, or as in the case of vegetation, may be highly susceptible to deposition. In the model, consideration is given to atmospheric transport processes as well as to removal mechanisms and the physical and physiochemical properties of gases.

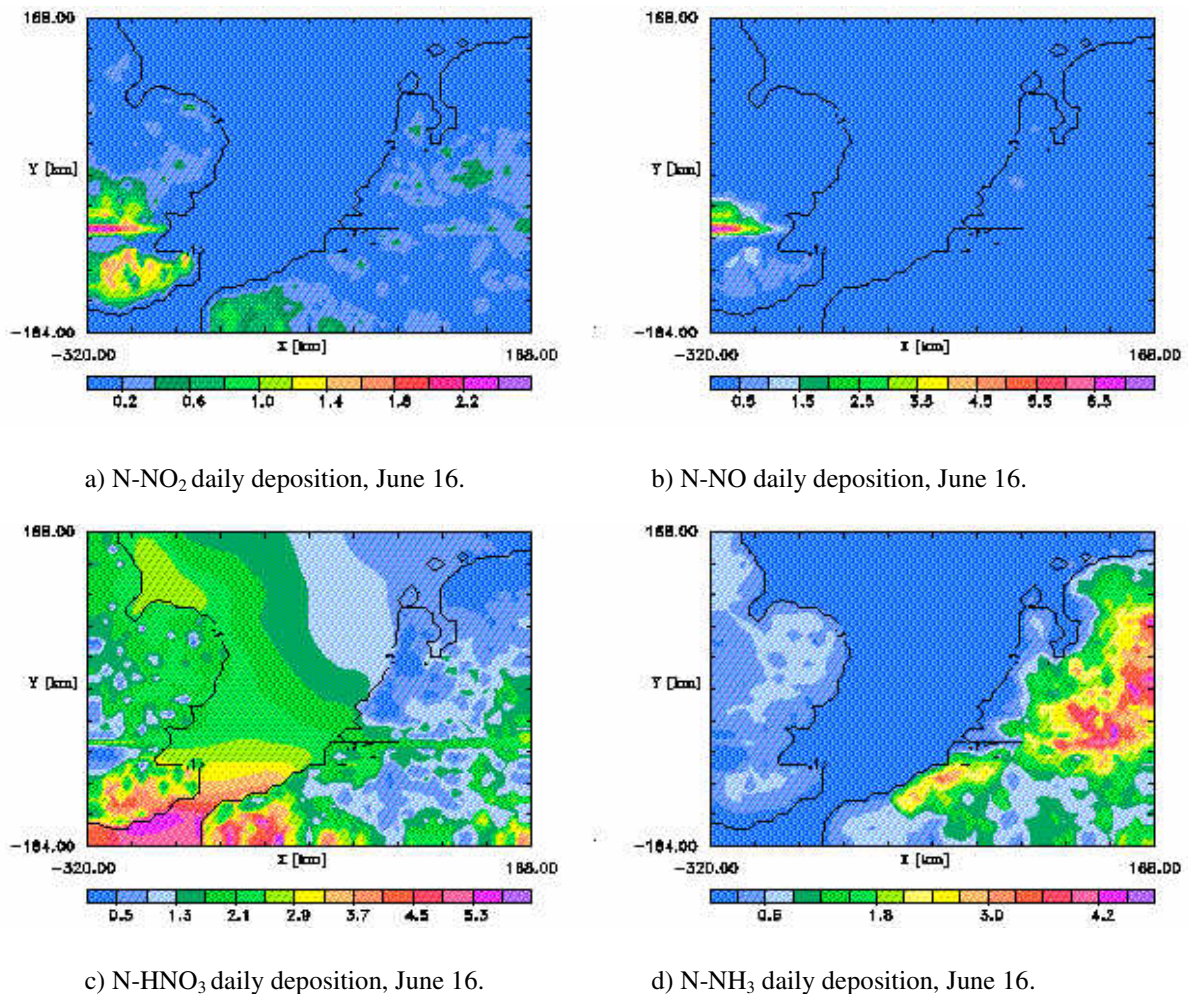a) Daytime, 14:00, June16, 1998.   b) Night-time, 23:00, June 16, 1998.
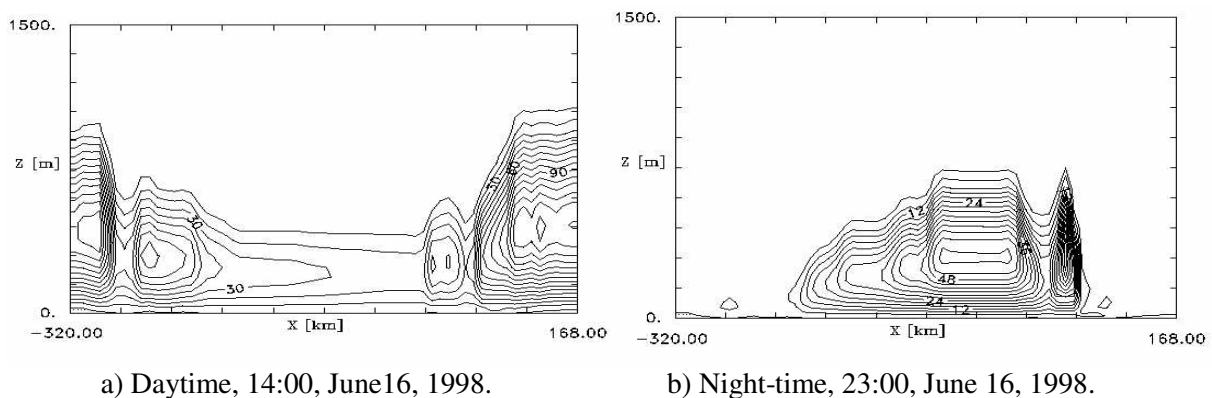
Fig 1. Vertical cross-section to 1500m height of vertical exchange coefficients during the day (a) and during the night (b). The North Sea lies in the middle and is bounded by England and the Netherlands. (not to scale)

The MECTM/METRAS system was run for the period of June 16-20, 1998. The 3-dimensional model allowed for simulating complex atmospheric flows. Dispersion and deposition processes in the coastal region are made complex by the flow changes resulting from the abrupt difference in surface characteristics between land and water which can best be simulated by using a 3-D model system. One example of the differences which strongly affect the atmospheric flow is the roughness length. The sea surface roughness is at least several orders of magnitude smaller than the agricultural land in the region so the mechanically generated turbulence is lower. There is also a difference in thermal convection which is partly due to land being warmer than the North Sea so there is more vertical motion in the atmosphere above. These inconsistencies between land and sea contributes to more vertical mixing of pollutants over land than over water. This was well simulated by the MECTM (*Fig 1*). During the day there is intense vertical mixing over land which compensates the higher emissions coming from urban areas like London, and agricultural areas like those located in the Netherlands.

Deposition values for hourly and daily amounts were calculated. *Fig. 2* shows the daily deposition values for various nitrogen compounds. The highest concentration modelled was clearly N-NO, but the greatest amount deposited to the waterway is $N-HNO_3$ due to its

solubility in water. The high values of N-NH$_3$ deposited over land are largely a result of the emissions from the agricultural regions in the modelled area.

a) N-NO$_2$ daily deposition, June 16.

b) N-NO daily deposition, June 16.

c) N-HNO$_3$ daily deposition, June 16.

d) N-NH$_3$ daily deposition, June 16.

Fig 2. Daily deposition values for various nitrogen compounds, June 16, 1998 (mol/m^2/day).

Deposition differs over water and over land due to the different surface resistances that are present. The ANICE model area comprised mainly sea surface and agricultural land use and the effect of the different surfaces on deposition can be seen. The less soluble species have greater deposition over land (i.e. N-NO$_2$), while the more soluble species such as N-HNO$_3$ deposited over the water as well as land. The greatest deposition occurred downwind from the London urban area as a results of the high concentration of emissions in that region at 16 June, 1998.

Aim for the Coming Year

The aims for the coming year are to continue the analysis of the effect of chemical reactions on deposition amounts and patterns. This includes investigating the effect of both wet and dry aerosols on deposition.

Acknowledgements

References

McKeen, S. A., E.-Y. Hsie, M. Trainer, R. Tallamraju, and S.C. Liu (1991). A Regional Model Study of the Ozone Budget in the Eastern United States. *J Geophys. Res.* **96**: 10,809-10,845.

Müller, F., K.H. Schlünzen and M. Schatzmann (2000). Test of numerical solvers for chemical reaction mechanisms in 3D air quality models. *Environmental Modelling Software*, **15**, 639-646.

Ruggaber, A., R. Dlugi and T. Nakajima (1994). Modelling Radiation Quanitities and Photolysis Frequencies in the Troposphere. *J. Atmo. Chem.* **18**:171-210.

Schlünzen, K.H. and L. Klein (2000). Simulation of coastal atmospheric processes including aerosols. *CAPMAN annual report 1999, International Scientific Secretariat, GSF-Forsachungszentrum für Umwelt und Gesundheit GmbH, Munich, Germany,* 63-67.

Schlünzen, K.H. (1990). Numerical studies on the inland penetration of sea breeze fronts at a coastline with tidally flooded mudflats. *Beitr. Phys. Atmosph.* **63**: *243 - 256.*

Schlünzen,K.H., K. Bigalke, C. Lüpkes, U. Niemeier and K. von Salzen (1996). Concept and realization of the mesoscale transport- and fluid-model 'METRAS'. *Meteorologisches Institut, Universität Hamburg, METRAS Techn. Rep.* **5** *pp 156.*

Seinfeld, J.H. and S.N. Pandis (1998). Atmospheric Chemsitry and Physics. Wiley,. New York.

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

Von Salzen, K., and K.H. Schlünzen (1999a). A Prognostic Physico-Chemical Model of Secondary and Marine Inorganic Multicomponent Aerosols: Part I. Model Description. *Atmospheric Environment* **33**: 567-576 .

Von Salzen, K., and K.H. Schlünzen (1999b). A Prognostic Physico-Chemical Model of Secondary and Marine Inorganic Multicomponent Aerosols: Part II. Model Tests. *Atmospheric Environment* **33**:1543-1552 .

Von Salzen, K., and K.H. Schlünzen (1999c). Simulation of the dynamics and composition of secondary and marine inorganic aerosols in the coastal atmosphere. *J.Geophys. Res.***104**, 30,201-30,217.