

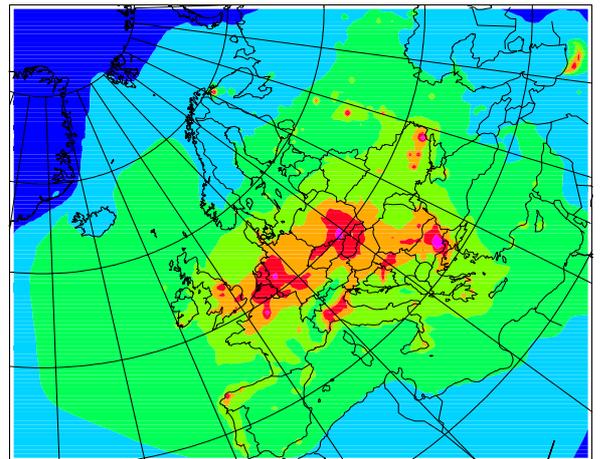
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Co-operative programme for monitoring
and evaluation of the long range
transmission of air pollutants in Europe

First Estimates of the Effect of Aerosol Dynamics in the Calculation of PM₁₀ and PM_{2.5}

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PM₁₀ Concentration



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in the calculation of PM₁₀ and PM_{2.5}**

by

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Preface and Acknowledgements

This note was prepared for the twenty-sixth session of the Steering Body to EMEP (Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe). It presents the latest development in the implementation of aerosol dynamics in the EMEP Unified model. This note carefully documents the processes and assumptions used in the development of the Aerosol model version UNI-AERO of the EMEP Unified model EMEP. Initial results on the distribution of aerosol mass and number concentrations, particles chemical composition and size distribution are presented here. The note is intended for use as UNI-AERO initial documentation reference.

The cooperation with Markku Kulmala and Liisa Pirjola at the Department of Physics at the University of Helsinki, Finland on the development of the aerosol dynamics module is gratefully acknowledged. Mr. Francis Binkowski at the US Environmental Protection Agency and Mr. Benedict Schell at the Ford Forschungszentrum Aachen, Germany are thanked for making a source code of the aerosol models available to MSC-W. Thanks are also due to Mr. Frank Stratmann and Mr. Ullrich Uhrner at the Institute of Tropospheric Research, Leipzig, Germany for providing the algorithm for nucleation parameterisation. The author highly appreciates all direct and indirect assistance and fruitful discussions with many scientists from the aerosol modelling and measurement community. This work has been supported by the Nordic Council of Ministers. All computations have been performed on a SGI Origin 3800 supercomputer at the Norwegian University of Science and Technology in Trondheim, Norway.

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Chapter 1

Introduction

Responding to the growing public concern on the adverse effects of atmospheric aerosols on the population health and the environment and the need to describe particles size distribution and composition, calculations of particulate matter (PM) has lately become one of the topic modelling activities at EMEP/MSC-W.

Previous calculations of particulate matter concentrations provided by EMEP were based only on mass estimate. PM₁₀ mass was calculated as the sum of Secondary Inorganic Aerosols (SIA) mass by the EMEP Eulerian Acid Deposition model, primary PM₁₀ by the Eulerian model for primary PM, and biogenic Secondary Organic Aerosols (SOA) from the Lagrangian Photo-oxidant model. The modelled PM₁₀ concentrations were in general lower than ambient PM₁₀ levels registered at EMEP sites and during several measurement campaigns. This was explained partly by the model underestimation of SIA and largely that not all aerosol components, in particular, such important natural atmospheric particles as mineral dust and sea salt, were included in the model estimates. Liquid water, which is an important component on hygroscopic particles, modifying the size distribution and affecting aerosols properties, were not considered either in the earlier aerosol modelling.

This note presents the progress in implementation of the aerosol dynamics module MM32 in the EMEP Unified Aerosol model version. In addition to PM mass, it calculates also particles number and size. MM32 uses a monodisperse approach for size distribution of internally mixed aerosols and accounts for particles formation by nucleation, their growth due to condensation and water absorption and coagulation processes. This note documents the EMEP Unified Aerosol model version and first calculation results on aerosol mass, number and size distribution in Europe.

Section 2 provides the description of the latest EMEP Aerosol model version. Firstly, the main features of the monodisperse aerosol dynamics module MM32 are presented and results of MM32 testing within a Lagrangian box-model are summarized. Then, a structure of the Unified Aerosol model version (UNI-AERO) is shown, and a detailed description is given to calculation in the model of the processes of aerosol formation, growth, interaction and removal.

Section 3 concerns initial testing with UNI-AERO of the aerosol dynamics effects on particle concentrations and its initial evaluation against the EMEP earlier Eulerian models. At first, effect of the aerosol dynamics is discussed with respect to primary PM_{2.5} and coarse PM. Then, concentrations of Secondary Inorganic Aerosols (SIA), namely SO₄, NO₃ and NH₄, calculated with the Aerosol model version are compared to those from the Unified Acid Deposition model version.

Section 4 gives preliminary analyses to the provisional PM₁₀ concentrations estimated with UNI-AERO. It also presents initial results on the aerosol mass, number and size distribution

and the chemical composition as calculated with the EMEP Aerosol model version. The calculation results are compared with some available measurements.

Finally, Section 5 summarises the remaining problems and gives a perspective on the further development of the EMEP Aerosol model version.

The recent model development has been aiming at building up a working version of aerosol model, which would allow for the complex of most essential components and processes. Therefore, preliminary or simplified parameterisations are used in the present model version to describe some of processes. However, the model is constructed in such a way that any process which affects the concentration and size distribution of particles can easily be modified or added as new or better parameterisation for this process becomes available.

Chapter 2

The EMEP Unified Aerosol model version (UNI-AERO)

The Aerosol model version (UNI-AERO) has been developed as a vital part of the EMEP Unified Eulerian model (EMEP Report 1&2/2002). All versions within the Unified model framework use the same advection and diffusion schemes, share the same meteorology and emissions treatment.

2.1 General description

The EMEP Unified Aerosol model version includes 14 chemical prognostic components:

gases – SO₂, H₂SO₄, NO, NO₂, HNO₃, PAN, NH₃

aerosols – SO₄, NO₃, NH₄, OC, EC, dust, sea salt.

Aerosol liquid water, H₂O, is a diagnostic component.

The Aerosol model version is based on the simplified gas-phase chemistry of the Acid Deposition model version. Aerosol dynamics are calculated on-line with the gas-phase chemistry, so that the actual gas-phase concentrations are used in the aerosol module and a feedback from the aerosol dynamics module is sent to the gas-phase module.

The aerosol dynamics module, that is called MM32, has been implemented in the EMEP Aerosol model version to account for particles formation, evolution and interaction. MM32 is a simplified and optimised version of the multicomponent monodisperse model MULTIMONO developed by the University of Helsinki in a close co-operation with EMEP/MS-CW. A detailed description of MULTIMONO can be found in Pirjola and Kulmala (2000) and of MM32 in Tsyro et al. (2002) and Pirjola et al. (2002). A monodisperse approach for representing the particles size distribution has been adopted in MULTIMONO and MM32. The monodisperse aerosol model was found physically sound and much faster as compared with modal and sectional models, (Pirjola et al, 1998). An essential advantage of the monodisperse approach is that it needs only two prognostic variables to per mode, i.e. mass M and number N. Therefore, the monodisperse aerosol model is computationally rather efficient and thus facilitated for long-term PM calculations. A recognised drawback of the monodisperse approach is the difficulty in modelling particles transfer to larger modes as particles grow (Section 2.3.5).

MM32 describes aerosol size distribution with four modes: nucleation (particles with diameters $d < 0.02 \mu\text{m}$), Aitken ($0.02 \mu\text{m} < d < 0.1 \mu\text{m}$), accumulation ($0.1 \mu\text{m} < d < 2.5 \mu\text{m}$), and coarse ($d < 10.0 \mu\text{m}$). It considers seven chemical components: sulphate (SO₄), nitrate (NO₃), ammonium (NH₄), organic carbon (OC), elemental carbon (EC), mineral dust, and sea salt (Table 1).

All particles within each mode are assumed to have the same size (monodisperse) and chemical composition (internally mixed aerosols). Thus, MM32 needs altogether 32

prognostic equations: 1 for particle number and 7 for chemical masses in each of the 4 modes (the number of prognostic equations can be reduced as not all of those aerosols are present in all the modes). Concentrations of PM_{2.5} and PM₁₀, as well as the total masses of aerosol components and aerosol chemical composition, can be easily calculated by adding up the relevant masses. It is noteworthy that UNI-AERO, with the aerosol dynamics module MM32 implemented in it, is flexible enough. It can be easily modified to calculate e.g. PM₁ concentrations if requested, providing there is necessary information on the size distribution of primary PM emission available.

Table 1. Prognostic variables in MM32: N-number and M-mass concentration.
(element present (X) or may be present (O) in the mode)

	N	M SO4	M NO3	M NH4	M EC	M OC*	M Dust**	M Sea salt	Water
Nucleation D < 0.02 μm	X	X				O			Diagnostic parameter
Aitken 0.02 < D < 0.1 μm	X	X	X	X	X	X	O	O	
accumulation 0.1 < D < 2.5 μm	X	X	X	X	X	X	X	X	
coarse 2.5 < D < 10 μm	X	X	X	O			X	X	

*) Only primary OC is currently considered

**) Only anthropogenic mineral dust is currently considered

In general form, prognostic equations for the evolution of particle number and mass due to aerosol dynamics are written as

$$\frac{\partial N_i}{\partial t} = (nucl_i) - coag_{ij} + EmN_i \quad (2.1)$$

$$\frac{\partial M_{Si}}{\partial t} = (nucl_i) + cond_{Si} \pm coag_{Sij} + EmM_{Si} \quad (2.2)$$

where N_i – particle number concentration in the size mode i (1/cm³), $nucl_i$ – rate of new particles formation by nucleation, $coag_{ij}$ – rate of the number loss due to intra- and intermode coagulation, M_{Si} – mass concentration of the aerosol component S in the size mode i (μg/m³), $cond_i$ – rate of the aerosol mass production due to gas condensation, $coag_{Sij}$ – rate of the mass production/loss due to intermode coagulation, EmN_i and EmM_i – emission rates for particle number and mass.

The prognostic equations are written for dry masses. Particles containing a fraction of hygroscopic components (SO₄, NO₃, NH₄ and sea salt) will change their sizes depending on the ambient relative humidity. As particles physical properties depend on their actual size, the "wet" diameter is used in calculations of aerosol dynamics and deposition. A current wet diameter D_i of the particles in each size mode is calculated as

$$D_i = \left(\frac{6}{\pi} \cdot \frac{M_i}{\rho_i N_i} \right)^{1/3} \quad (2.3)$$

where M_i is the total, including water component, aerosol mass in the size mode i , ρ_i is the average particle density in the mode i , which is updated at every time step depending on

particle chemical composition. The aerosol water content is a diagnostic parameter in the model (see Section 2.6).

The aerosol dynamics module was tested within a Lagrangian box-model, which provided meteorology and concentrations of gaseous H₂SO₄ and VOCs input to MM32. MM32 was compared with the sectional model AEROFOR2 (University of Helsinki) with 54 sections and verified against measurements available from the BIOFOR3 campaign in Hyytiälä, Finland (Tsyro et al., 2002 and Pirjola et al., 2002). The evaluation showed that for the most of conditions, MM32 was able to simulate the evolution of particles size and number with an acceptable for long-range modelling purposes accuracy, while being computationally efficient.

2.2 Model aerosol components

The EMEP Aerosol model version considers primary and secondary aerosols. Primary particles are those directly emitted in the atmosphere, while secondary aerosols are formed in the atmosphere through gas-to-particle conversion. In the model, emissions of particulate matter and homogeneous nucleation are sources for new particles production and thus increase both the particles number and mass concentration. Condensation of gaseous components on pre-existing particles contributes to the increase of secondary aerosol mass, but does not modify particles number. Primary particles calculated in the current UNI-AERO version include OC, EC and mineral dust from anthropogenic sources and sea salt aerosols. The secondary aerosols consist of SO₄, NO₃ and NH₄ formed from the emissions of gaseous precursors SO₂, NO_x and NH₃. The Secondary Organic Aerosols and natural dust (e.g. Saharan dust) are not presently included in the model.

2.2.1 Primary particles: treatment of PM_{2.5} and PM₁₀ emissions

Emissions of primary PM_{2.5} and PM₁₀ are taken from the 1995 emission inventory compiled by the Netherlands Organisation for Applied Scientific Research (TNO) within the CEPMEIP project (Co-ordinated European programme on Particulate Matter Inventories, Projects and Guidance) (Tarrason, 2002). Since no information on the emissions chemical speciation or particle size distribution is presently available, the same preliminary estimate on the composition of PM_{2.5} emissions as used in Andersson-Sköld and Simpson (2001) has been adopted in the present calculations. PM_{2.5} mass emissions in each source category have been apportioned between organic carbon (OC), elemental carbon (EC) and mineral dust as indicated in Table 2. OC and EC emissions have been distributed between Aitken and accumulation modes in the same proportion, so that 15% of the mass is assigned to the Aitken and 85% to the accumulation mode (e.g. Seinfeld and Pandis, 1998). All fine dust from PM_{2.5} emissions is assigned to the accumulation mode.

Emissions of coarse particles have been calculated as the difference between PM₁₀ and PM_{2.5} emissions. Primary coarse PM has been assumed to consist of dust particles and assigned to the coarse mode. Table 2 summarises the distribution of PM_{2.5} and PM₁₀ emission between the aerosol components and size modes as presently adopted in UNI-AERO.

Particles number emissions in the Aitken, accumulation and coarse modes have been derived from the mass emissions in the respective modes as

$$EmN_i = \frac{6}{\pi} \cdot \frac{EmM_i}{\rho_i D_i^3} \quad (2.4)$$

where EmN_i is the number emission in the mode i ($1/m^3 \cdot s$), EmM_i is the total mass emission in the mode i ($kg/m^3 \cdot s$), D_i is the diameter of the emitted particles, and ρ_i is the average particle density. The average particle density in each mode is found as the mass weighted mean density of aerosol components present in the mode. The diameters of primary emitted Aitken, accumulation and coarse particles are presently assumed constant and set to 0.05, 0.2 and 5 μm .

Table 2. Size and chemical speciation of primary PM emission (in %) and component densities (kg/m^3) used in UNI-AERO

PM _{2.5} Source sectors	OC	EC	Mineral dust
Power generation	33	33	33
Residential and other combustion	50	20	30
Industrial combustion	33	33	33
Industrial processes	0	20	80
Storage and handling	40	0	60
Heavy duty vehicles	40	50	10
Light duty vehicles	40	20	40
Motorised bikes	40	20	40
Passenger cars	40	20	40
Non-road transport	10	60	30
Agriculture	70	0	30
Waste incineration	33	33	33
Size distribution (Aitken/accum)	15 / 85	15 / 85	0 / 100
Coarse PM = PM₁₀ - PM_{2.5}	-	-	100
Density, ρ (kg/m^3)	2000	2200	2600

2.2.2 Secondary Aerosols: interaction between gas-phase and aerosol chemistry

Secondary Inorganic Aerosols (SIA) are the only secondary particles included in the present UNI-AERO version. SIA are formed in the atmosphere from the gaseous precursors through both irreversible and reversible processes. In the case of reversible process, UNI-AERO calculates the mass and composition of particles based on the assumption of a thermodynamic equilibrium for volatile compounds (e.g. ammonium, nitrate) in the gas and the aerosol phase. The existence of such equilibrium between atmospheric gas and aerosol phases is generally supported by field measurements except for large particles in rather clean environment and at low temperatures (Saxena *et al.*, 1986, Seinfeld & Pandis, 1998).

Calculation of gaseous H₂SO₄

As it was pointed above, gas-phase chemistry module in UNI-AERO is based on the chemical scheme from the Unified Acid Deposition model version (UNI-ACID). In order to calculate sulphuric acid (H₂SO₄) concentrations, which are necessary for modelling nucleation and condensation, the gas-phase and aqueous SO₂ oxidation processes need to be distinguished. Gaseous H₂SO₄ is formed in the gas-phase oxidation of SO₂ by hydroxyl radical OH. It contributes to the formation of new particles through homogenous nucleation and to the increase of SO₄ aerosol mass due to condensation on pre-existing particles. To account for H₂SO₄ loss due to the nucleation and condensation, H₂SO₄ concentrations are re-calculated at each time step after accomplishing aerosol dynamics calculations. The continuity equation for chemical tendency of H₂SO₄ can schematically be written as:

$$\frac{d(H_2SO_4)_g}{dt} = EmSO_4 + chem(H_2SO_4) - nucl - cond - Ddep_{H_2SO_4} - Wdep_{H_2SO_4} \quad (2.5)$$

Here $EmSO_4$ designates the fraction of SO_x emissions in the form of H_2SO_4 (presently 5 %), $chem(H_2SO_4)$ is the rate of H_2SO_4 production due to oxidation of SO_2 by OH, $nucl$ and $cond$ are the loss rates of H_2SO_4 due to nucleation and condensation on all pre-existing particles and $Ddep_{H_2SO_4}$ and $Wdep_{H_2SO_4}$ denote the rates of H_2SO_4 dry and wet deposition.

Calculation of total particulate SO_4

Aqueous phase oxidation (heterogeneous process) of SO_2 by H_2O_2 and O_3 (Bartnicki et al., 1998) produces particulate sulphate, which increases SO_4 aerosol mass. This SO_4 is added to the SO_4 mass formed due to H_2SO_4 nucleation and condensation, so that the continuity equation for the total mass of sulphate aerosol is written as:

$$\frac{d(SO_4)_a}{dt} = chem(SO_4) + nucl + cond - Ddep_{SO_4} - Wdep_{SO_4} \quad (2.6)$$

where $chem(SO_4)$ is the rate of SO_4 production due to the heterogeneous oxidation of SO_2 by H_2O_2 and O_3 , $nucl$ and $cond$ are the production rates of SO_4 due to H_2SO_4 nucleation and condensation (equal to the correspondent loss terms for H_2SO_4), and $Ddep_{SO_4}$ and $Wdep_{SO_4}$ denote the rates of SO_4 dry and wet deposition.

Calculation of SO_4 - NO_3 - NH_4 system

In order to treat the chemistry of the sulphate-nitrate-ammonia-water system the Model for an Aerosol Reacting Systems (**MARS**) has been implemented in UNI-AERO.

MARS (Saxena et al., 1986) is an equilibrium model based on fundamental thermodynamic concepts, formulated in a way consistent with the results of theoretical, laboratory and field studies. MARS was designed for the use in regional models and therefore combines computational efficiency with reasonable accuracy as compared to more comprehensive rigorous thermodynamic models. It can be applied for an entire range of atmospheric conditions (Zhang et al., 1999). The MARS-A version has been implemented in UNI-AERO to calculate the chemical composition of sulphate-nitrate-ammonium-water. MARS-A is used in the EPA Models-3 Modelling System (Binkowski and Shankar, 1995, Binkowski, 1999) and in the Modal Aerosol Dynamics model for Europe (MADE) (Ackermann *et. al.*, 1998).

The species treated in MARS are:

- gas phase – NH_3 , HNO_3 and H_2O
- liquid phase – SO_4^{2-} , HSO_4^- , NH_4^+ , NO_3^- , H^+ , H_2O
- aerosols – H_2SO_4 , NH_4HSO_4 , $(NH_4)_2SO_4$ and NH_4NO_3

Not all of these components are present in each particular gas-aerosol equilibrium. The chemical composition of the aerosol is determined by the total concentrations of SO_4^{2-} , NO_3^- and NH_4^+ , as well as the relative humidity and temperature. In MARS, all ambient ammonia is converted to ammonium up to an NH_4^+ -to- SO_4^{2-} molar ratio of 2.0, i.e. fully neutralised sulphate $(NH_4)_2SO_4$. Based on the NH_4^+ -to- SO_4^{2-} ratio and the ambient relative humidity, MARS divides the entire regime of aerosol species into several sub-domains.

In the **ammonia deficient regime** ($NH_4^+/SO_4^{2-} < 2$), the aerosol phase is acidic as there is insufficient ammonia to neutralise the sulphate. All available ammonia is taken up by the aerosol phase. The concentrations of dissolved nitrate are negligible at lower relative humidity

(Rh<60-70%), but increase significantly with the increase of relative humidity.

In the **ammonia rich regime** ($\text{NH}_4^+/\text{SO}_4^{2-} > 2$), sulphate is fully neutralised and an excess of gaseous ammonia is present. If nitric acid vapour is also present it will be neutralised by NH_3 to produce ammonium nitrate either in a particulate or aqueous form depending on the relative humidity. The process is reversible, and the concentrations of gaseous NH_3 and HNO_3 and solid or aqueous NH_4NO_3 are derived based on the equilibrium thermodynamics. The aqueous concentrations of ammonium nitrate depend also on the amount of water in the system, therefore estimation of the aerosol water content is performed (Section 2.6).

The calculated SO_4 , NO_3 and NH_4 aerosol masses, as well as liquid water, have been distributed in UNI-AERO between Aitken and accumulation modes. Presently, distribution of NO_3 , NH_4 and water between the Aitken and accumulation modes has been made according to the sulphate distribution.

2.2.3 Sea salt

Sea salt particles are among the most important natural primary particles and may significantly contribute to the aerosol mass and chemical composition. The generation of sea salt aerosol over ocean is driven by the surface wind. There are two main mechanisms for sea salt aerosol generation: bubble bursting during whitecap formation (indirect) and through spume drops under the wave breaking (direct). The latter mechanism is believed to be important source for particles larger than 10 μm and therefore not considered here.

A simplified bulk parameterisation for the production of sea salt aerosol is presently implemented in the EMEP Aerosol model version (Jonson *et al.*, 2000). It was derived based on the expression by Monahan *et al.* (1986) (see also Pryor and Sørensen, 1999) for sea salt particles generation rate as a function of their size, where the diameter of 6 μm was assumed for sea salt droplets. The production of sea salt aerosol P_{ss} ($\text{mg m}^{-2} \text{s}^{-1}$) is calculated as

$$P_{ss} = 0.007 \cdot (U_{10})^{3.41} \quad (2.7)$$

where U_{10} is the wind velocity at the height of 10 m, calculated from the surface wind stress assuming a logarithmic wind profile. All the sea salt particles are assigned to the coarse mode.

2.3 Aerosol dynamics

Continuity equations for the **number concentration** in all modes due to dynamic processes are

$$\begin{aligned} dN_1/dt &= Inuc - 0.5 K_{11}N_1^2 - K_{12}N_1N_2 - K_{13}N_1N_3 - K_{14}N_1N_4 \\ dN_2/dt &= -0.5 K_{22}N_2^2 - K_{23}N_2N_3 - K_{24}N_2N_4 \\ dN_3/dt &= -0.5 K_{33}N_3^2 - K_{34}N_3N_4 \\ dN_4/dt &= -0.5 K_{44}N_4^2 \end{aligned} \quad (2.8)$$

Here N_i (cm^{-3}) is the particles number concentration in the mode i , $Inuc$ ($\text{cm}^{-3} \text{s}^{-1}$) is the nucleation rate (i.e. number of particles, critical clusters, formed during 1s in a unit volume), K_{ij} ($\text{cm}^3 \text{s}^{-1}$) is the coagulation coefficient between particles in i and j modes ($i = j$ means coagulation of particles in the same mode, i.e. intramode coagulation, and $i \neq j$ means coagulation of particles from different modes, i.e. intermode coagulation). Indexes $i=1, 2, 3, 4$ refer to the nucleation, Aitken, accumulation and coarse mode, respectively.

Equations for the **mass** evolution due to dynamics processes are written for aerosol components present in each four size modes. As an example, continuity equations for the evolution of SO₄ mass are given here:

$$\begin{aligned}
 dM_1/dt &= Inuc \cdot n_a \cdot m_{h2so4} + C_1 \cdot m_{h2so4} N_{h2so4} N_1 & (2.9) \\
 &\quad - K_{12} N_1 N_2 \cdot m_{p1} - K_{13} N_1 N_3 \cdot m_{p1} - K_{14} N_1 N_4 \cdot m_{p1} \\
 dM_2/dt &= C_2 \cdot m_{h2so4} N_{h2so4} N_2 + K_{12} N_1 N_2 \cdot m_{p1} - K_{23} N_2 N_3 \cdot m_{p2} - K_{24} N_2 N_4 \cdot m_{p2} \\
 dM_3/dt &= C_3 \cdot m_{h2so4} N_{h2so4} N_3 + K_{23} N_2 N_3 \cdot m_{p2} - K_{34} N_3 N_4 \cdot m_{p3} \\
 dM_4/dt &= C_4 \cdot m_{h2so4} N_{h2so4} N_4 + K_{34} N_3 N_4 \cdot m_{p3}
 \end{aligned}$$

Here M_i ($\mu\text{g m}^{-3}$) is the SO₄ mass concentration in mode i , n_{h2so4} is the number of sulphuric acid molecules in a critical cluster, m_{h2so4} is the mass of a sulphuric acid molecule, $C_i N_{h2so4} N_i$ ($\text{molec/m}^3 \text{ s}$) is the condensation rate of sulphuric acid onto particles in the mode i , m_{pi} is the mass of an average sulphate particle in the mode i . Terms $K_{ij} N_i N_j \cdot m_{pi}$ designate the mass lost in the smaller mode i and gained by the larger mode j due to coagulation between particles in these modes. Evolution equations for the other aerosol component masses are written analogously, excluding nucleation and condensation terms.

The scheme of a computational structure of the EMEP Unified Aerosol model version is presented in Figure 1. Parameterisations for calculating the nucleation, condensation and coagulation rates are described below.

2.3.1 Nucleation

Homogeneous heteromolecular nucleation in the H₂SO₄-H₂O system is one of the main processes for new particles formation. Prediction of nucleation rates is still subject to large uncertainties. Calculated with presently available parameterisations, the nucleation rates can differ by several orders of magnitude. However, even though the errors in nucleation rates can be considerable, their effect on the number concentrations can be diminished due to rather fast coagulation of nucleation particles, which efficiently reduces their number. Furthermore, nucleation often occurs in the areas of large H₂SO₄ concentrations, i.e. large emissions. In such areas, particles emission and particles growth by condensation are believed to dominate the production of aerosol number and mass.

Different parameterisations for the rate of particle formation by nucleation have been implemented and are available for testing in UNI-AERO if desirable. Those are:

- Binary nucleation rate based on the revised classical theory for binary homogeneous nucleation for H₂SO₄-H₂O system (Kulmala *et al.*, 1998).
- A preliminary parameterisation for ternary H₂SO₄-NH₃-H₂O nucleation rate due to Korhonen *et al.* (1999).
- Binary nucleation rate used in the MADMAcS model at the Institute for Tropospheric Research in Leipzig (Berndt *et al.* 2000).

Based on the classical theory, rate of **binary** H₂SO₄-H₂O nucleation strongly depends on the H₂SO₄ concentrations and increases at lower temperatures and high relative humidity. Rather high H₂SO₄ concentrations are needed for the occurrence of significant binary nucleation. Nucleation bursts are more favoured to occur in areas with lower aerosol load, as nucleation competes against the condensation process for available H₂SO₄.

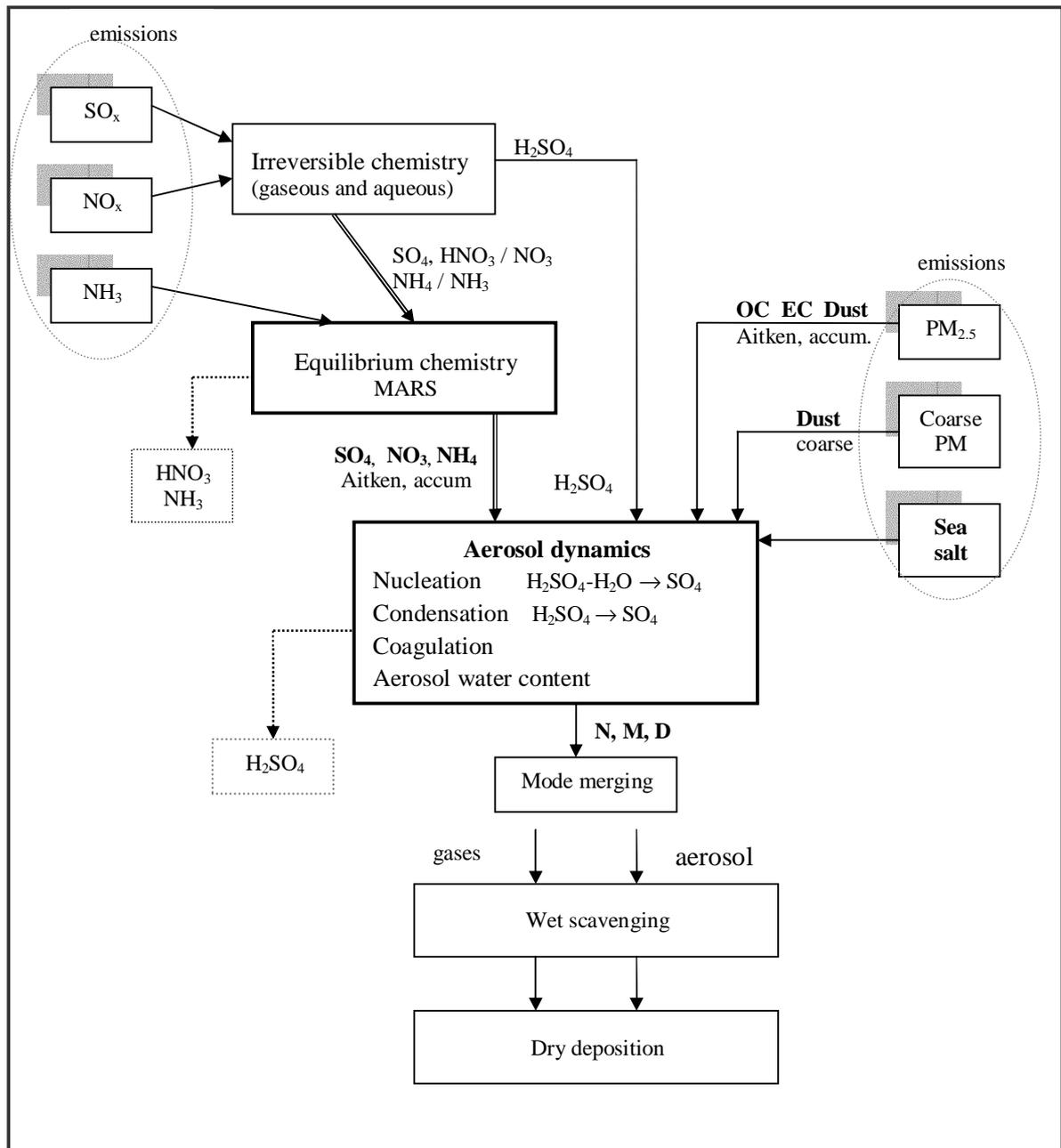


Figure 1: Schematic computational structure of the EMEP Unified Aerosol model version (UNI-AERO).

The revised classical theory, accounting for H₂SO₄ hydrates formation, was found to predict reasonably well binary homogeneous H₂SO₄-H₂O nucleation rates at a temperature of around 289K and relative humidities of 30-50 % (Viisanen et al., 1997). When tested within UNI-AERO, the parameterisation for binary nucleation by Kulmala *et al.* (1998) has calculated reasonable nucleation rates for warm months, but failed for cold months.

The classical theory for binary H₂SO₄-H₂O nucleation predicts too low nucleation rates at less favourable conditions (higher temperature, lower relative humidity and lower H₂SO₄ concentrations). The presence of ammonia is expected to enhance the nucleation process as the presence of NH₃ in particles considerably decreases the vapour pressure of H₂SO₄ at the particles surface. Therefore, **ternary** H₂SO₄-NH₃-H₂O nucleation is believed to be a more likely mechanism responsible for new particle formation in the atmosphere (Korhonen *et al.*, 1999). In very first tests performed with UNI-AERO, the preliminary parameterisation for ternary nucleation due to Korhonen has not managed to calculate adequately nucleation rates at all ambient conditions. In particular, the parameterisation has often predicted unreasonably high nucleation rates apparently due to their very strong dependence on the H₂SO₄ and NH₃ concentrations.

An empirical parameterisation for the rate of homogeneous nucleation of H₂SO₄-H₂O from the MADMAcS model at the Institute of Tropospheric Research, Leipzig has been implemented and used in the present calculations. A general form for the nucleation rate *Inuc* (m⁻³ s⁻¹) is

$$Inuc = (A \cdot [C_{h2so4}]^{na} \cdot [C_{h2o}]^{nw}) / (B + [C_{h2o}]^{nw}) \quad (2.10)$$

where $[C_{h2so4}]$ and $[C_{h2o}]$ are the concentrations of sulphuric acid and water, *na* and *nb* are number of sulphuric acid and water molecules in a stable critical cluster, *A* and *B* are empirical parameters. A critical for the onset of significant nucleation, H₂SO₄ concentration is calculated following Binkowski and Shankar (1995) as

$$C_{h2so4,crit} = 0.16 \exp (0.1T - 3.5Rh - 27.7) \quad (2.11)$$

$C_{h2so4,crit}$ is the critical gas-phase H₂SO₄ concentration, which produces a nucleation rate of 1 m⁻³ s⁻¹, *T* is the temperature and *Rh* is the relative humidity.

Newly formed particles have been assigned to the nucleation mode in UNI-AERO. Thus, homogeneous nucleation has increased the nucleation particle number and SO₄ mass in the nucleation mode. Formed by nucleation, particles coagulate very efficiently and/or can grow by condensation of gases to the Aitken size.

For long-range transport modelling purposes, nucleation process is important for predicting aerosol number concentrations, while its effect on the total PM mass is negligibly small. However, more tests are needed in order to analyse the effect of nucleation on the aerosol long-range number concentrations.

2.3.2 Condensation

Condensation of vapours is one of the main processes for atmospheric particles growth. Condensational growth increases the overall aerosol mass, while does not affect the number concentration. Sulphuric acid, due to its low volatility, will preferably reside in the aerosol phase (irreversible process). Below, the parameterisation for H₂SO₄ condensation on the surface of all particles is described. More volatile vapours, such as HNO₃, HN₃, organic vapour, H₂O, will tend to equilibrate between the gas and aerosol phase. Calculation in UNI-AERO of equilibrium concentrations of HNO₃, HN₃, HN₄NO₃ are performed with the thermodynamic model MARS, as described in Section 2.2.2, and parameterisation for

diagnosing the aerosol water is described in Section 2.3.4. Formation of secondary organic aerosol from the volatile organics has not yet been implemented in UNI-AERO.

The flux of condensing H₂SO depends on the difference between its ambient concentration and that at the particle surface. In the MM32 aerosol dynamics module, H₂SO₄ vapour pressure at the particle surface is currently assumed to be zero, which will result in maximum condensation flux. The continuum regime (see explanations to Eq. (2.13)) theory for condensation corrected for the free-molecular regime by a transitional correction factor is used to calculate the condensation rate (Fuchs and Sutugin, 1970, Pirjola *et al.*, 1999). The expression for condensation rate C_{cond} (molec m⁻³ s⁻¹) of H₂SO₄ to particles in mode i is written as

$$C_{cond} = C_i N_{h2so4} N_i, \text{ where } C_i = 4\pi r_i \beta_M D \quad (2.12)$$

Here, N_{h2so4} (cm⁻³) is the concentration of sulphuric acid molecules, N_i (cm⁻³) is the number concentration and r_i is the radius of particles in mode i , D is the diffusion coefficient. β_M is the transition correction factor calculated as

$$\beta_M = \frac{Kn+1}{0.377Kn+1 + \frac{4}{3}\alpha^{-1}Kn^2 + \frac{4}{3}\alpha^{-1}Kn} \quad (2.13)$$

where α is the accommodation coefficient set presently to unit, $Kn = \lambda_v/r$ is the Knudsen number, λ_v is the mean free path of vapour molecules. In the continuum regime ($Kn \leq 1$), $\beta_M = 1$ and in the free-molecular regime ($Kn > 10$), $\beta_M \sim \frac{3d}{4\lambda_v}$.

It can be noted that an effective condensational growth may decrease considerably the rate of particle coagulation. Smaller particles grow by condensation much faster than the larger ones, so that the size difference between them gradually decreases as condensation evolves, and thus coagulation process slows down (see Section 2.3.3).

2.3.3 Coagulation

Coagulation modifies the aerosol size distribution, and the overall effect is a reduction of particles number. This process is particularly efficient for smallest particles in the nucleation and Aitken modes, which rapidly coagulate with each other and especially to the larger particles. Currently, only coagulation due to particle Brownian motion has been accounted for in UNI-AERO. From MM32, Brownian coagulation coefficients are calculated due to Fuchs (1964). The Brownian coagulation coefficient K_{ij} (cm⁻³ s⁻¹) between particles in i and j modes is calculated for all size regimes, i.e. free molecular ($Kn > 10$), transition ($1 < Kn \leq 10$) and continuum ($Kn \leq 1$) by

$$K_{ij} = \frac{K_C^B}{\frac{R_i + R_j}{R_i + R_j + \sigma_{ij}} + \frac{4(D_i + D_j)}{(\bar{c}_i^2 + \bar{c}_j^2)^{1/2}(R_i + R_j)}} \quad (2.14)$$

where the Brownian coagulation coefficient in the continuum regime is:

$$K_C^B = 4\pi(R_i + R_j)(D_i + D_j),$$

here R_i and R_j are the radii of coagulating particles, D_i and D_j are their diffusion coefficients, and \bar{c}_i is the particle mean thermal velocity. The coagulation coefficient is smallest for particles of the same size and increases rapidly as the ratio between the particle diameters increases.

The following algorithm for the mode allocation of coagulating particles has been presently adopted in UNI-AERO. When **intermodal coagulation** occurs, particles from the smaller mode coagulate to particles in the larger mode. The intermode coagulation results in the reduction of both number and mass in the mode where particles coagulate from (typically nucleation and Aitken modes). While in the mode where particles coagulate to (accumulation and coarse modes), the mass increases only slightly because small particles bring a rather small mass. The number concentration in this mode remains unchanged. If coagulating particles belong to the same mode (**intramode coagulation**) they will continue in the same mode after coagulation. Intramode coagulation reduces only the number concentration, but does not affect the mass.

Coagulation by Brownian motion is a dominating process for sub-micron particle. However, for larger particles, with diameter exceeding a few micrometers, gravitational coagulation and turbulent shear coagulation should also be taken into account.

2.3.4 Aerosol water content

Depending on the fraction of soluble components, particles can be less or more hygroscopic. Hygroscopic particles can contain significant amounts of water. Sulphate, nitrate, ammonium and sea salt are the soluble and hygroscopic components included in the Aerosol model version. A certain fraction of organic components can be hydrophilic. However, it is difficult to determine this fraction and for simplicity reason it has been assumed that the organic components are insoluble. This assumption should be revised in the future.

In UNI-AERO, hygroscopic particles are assumed to be in a stable equilibrium with the surrounding relative humidity, so that they grow by absorbing water at higher relative humidity and shrink as water evaporates at lower humidity. The aerosol water content is considered in the model as a diagnostic parameter and calculated based on a scheme developed by Binkowski and Shankar (1995).

Water content of aerosols has been calculated using empirical polynomials (Tang and Munkelwitz, 1994) for the mass fraction of solute as a function of water activity. In this scheme, the amount of water in the scheme depends on the ratio of total NH_4 to total SO_4 and on the ambient relative humidity. Polynomials for ammonium nitrate and ammonium sulphate have been taken from Chan *et al.* (1992).

Water mass in each mode has been computed at every time step based on the particles chemical composition and relative humidity. The water mass has been added to the particles dry mass to determine the actual PM mass in each mode. This PM mass determines then the wet diameter used in the aerosol dynamics and in the dry and wet deposition routines. Consistently, the particle density is recalculated as the mass weighted average of the densities of all (including aerosol water) aerosol components in each mode.

2.3.5 Mode merging

The scheme tested in this work is based on the "mode merging by renaming" algorithm by Binkowski (1999). To apply this method, a log-normal particles size distribution has been imposed within each size mode. Constant values for standard deviations of particle distribution have been assigned in each mode based on observation data (e.g. Jaenicke, 1993, Kulmala *et al.*, 2000). As the diameter (D) in a mode exceeds the upper limit (D_l), the geometric mean diameter for log-normal size distribution in the mode is calculated as:

$$\bar{D}_g = \frac{D}{\exp(0.5 \ln^2 \sigma_g)}$$

where D_g is the geometric mean diameter and σ_g is the geometrical standard deviation. The complementary error function is then used to find the fractions of particles greater (F_N) and smaller (PH_N) than the limit value as:

$$F_N = 0.5 \cdot \operatorname{erfc}(x_N) \quad (2.15)$$

$$PH_N = 0.5 + (1 + \operatorname{erf}(x_N)) \quad \text{with} \quad x_N = \frac{\ln(D_i/D_g)}{\sqrt{2 \ln \sigma_g}},$$

where D_i is the mode upper limit diameter. Then, the portions of number and mass concentrations transferred to the larger mode ($i+1$) and remaining in the mode i are calculated and new concentrations are found as

$$\begin{aligned} N_{i+1} &= N_{i+1} + N_i \cdot PH_{Ni} & M_{i+1} &= M_{i+1} + M_i \cdot PH_{Mi} \\ N_i &= N_i \cdot F_{Ni} & M_i &= M_i \cdot F_{Mi} \end{aligned} \quad (2.16)$$

From this information, new diameters are re-calculated in each of the modes.

2.4 Dry and wet removal

UNI-AERO uses the common formulation for dry deposition and wet scavenging in the EMEP Unified model. A rather simple parameterisation of dry and wet removal rates depending on the particle size have been adopted in the present version of UNI-AERO.

The loss of mass or number ΔC_{ddep} due to **dry deposition** is calculated in each size mode as:

$$\Delta C_{ddep} = -C \frac{vd_h}{\Delta z} \quad (2.17)$$

Here, C is the mass or number particle concentration in a mode, Δz is the thickness of the model lowest layer and vd_h is the dry deposition velocity at the middle of the lowest layer found using

$$vd_h = \frac{vd_{1m}}{\left[1 + \frac{vd_{1m}}{C_H |\vec{v}_H|} \right]}, \quad \text{and} \quad C_H/|v_H| = u_*^2 / (0.74 \cdot |v_H|) \quad (2.18)$$

where C_H is the drag coefficient, $|v_H|$ is the horizontal wind speed at the middle of the lowest layer of the model, and vd_{1m} is the dry deposition velocity of particles in a mode at 1m. Dry deposition velocities at 1 m height have been assigned to the particles in each size mode as indicated in Table 3. The most recent modifications in the dry deposition routine in the Unified model, described in the EMEP/Report 1/2002, have not yet been applied in the Aerosol model version.

Table 3. Particle dry deposition velocity at 1 m (vd_{1m}), in-cloud scavenging efficiency (ε) and sub-cloud collection efficiency (E)

	nucleation mode	Aitken mode	Accumulation mode	coarse mode
Vd_{1M} (cm/s)	1.0	0.5	0.1	1.5
ε	0.0	0.2	0.7	0.7
E	0.4	0.3	0.1	0.4

A simple description for the cloud processing of aerosol has been used in present calculations. As it was briefly described in Section 2.2.2, UNI-AERO calculates SO_4 formation through

heterogeneous oxidation of SO₂ by H₂O₂ and ozone in clouds. This production of sulphate aerosol increases the SO₄ mass in accumulation mode.

The aerosol mass is depleted due to **wet deposition**. Loss of aerosol mass/number (ΔC_{wet}) due to the **in-cloud** wet scavenging in each mode is expressed as:

$$\Delta C_{wet} = -C \frac{WP}{\Delta z} \cdot \varepsilon \quad (2.19)$$

where C is the mass or number particle concentration in the mode, W is the scavenging ratio set to $7 \cdot 10^5$, P ($\text{kg m}^{-2} \text{s}^{-1}$) is the precipitation rate, Δz is the thickness of the cloud layer, and ε is the in-cloud scavenging efficiency in the mode. The in-cloud scavenging efficiency depends on the aerosol solubility and size. In the current UNI-AERO version, average scavenging efficiencies are prescribed to particles in each size mode, independently on their chemical composition as indicated in Table 3.

Such aerosol processes in clouds like particles activation, collection of the interstitial aerosols by droplets and particles production due to the cloud evaporation have not yet been accounted for in the present Unified Aerosol model version.

Loss of particle mass/number concentrations due to the **sub-cloud** precipitation scavenging in each mode is calculated due to Scott (1979) as:

$$\Delta C_{wet} = -C \frac{AP}{V_{dr}} \cdot \bar{E} \quad (2.20)$$

where C is the mass or number particle concentration in the mode, V_{dr} the raindrop fall speed ($V_{dr}=5 \text{ m s}^{-1}$), $A = 5.2$ is the empirical coefficient, and E is the size-dependent collection efficiency of aerosols by the raindrops (Table 3).

Chapter 3

Initial tests on the effect of aerosol dynamics

In the following, initial sensitivity tests to systematically determine the effect of different processes in calculations of PM concentrations with the Unified Aerosol model version is presented. This exercise can also be considered as an initial evaluation of the UNI-AERO soundness against the earlier EMEP Eulerian models for primary PM and SIA.

3.1 Calculations of primary PM concentrations

The objective of this study is to evaluate the effect of aerosol dynamics on concentrations of primary PM. For this purpose, a series of tests has been performed, where primary PM_{2.5} and PM₁₀ concentrations have been calculated using two different models. The first model is the EMEP Eulerian model for primary PM used in Tsyro (2001) and Tarrason *et al.* (2000). The model was called AEROMADE and calculated primary PM_{2.5} and PM₁₀ concentrations based on atmospheric emissions, transport and removal by dry and wet deposition. Only two size classes, namely fine, or PM_{2.5}, and coarse particles, were defined. Particles were considered chemically inert and non-interacting, i.e. no aerosol dynamics processes were included. Size dependent dry and wet deposition velocities were used for fine and coarse particles (Table 4).

The second model for these tests is the Eulerian Unified Aerosol model version (UNI-AERO) described in Chapter 2. To make the Aerosol model version compatible with AEROMADE, all gaseous emissions and boundary conditions have been set to zero, and all chemical processes have been excluded. In this case, coagulation is the only aerosol dynamic process taking place. Size-dependent dry and wet deposition velocity/efficiency have been applied in each size mode. As indicated in Table 4, the dry and wet removal characteristics for accumulation particles in UNI-AERO coincide with those for PM_{2.5} in AEROMADE.

Table 4. Dry deposition velocities (Vd), efficiencies of particles in-cloud collection (ϵ) and sub-cloud scavenging (E) used in the sensitivity tests for primary PM.

	Removal param.	Aitken	accumulation	coarse	PM _{2.5}	Coarse PM
AEROMADE	Vd (cm/s)				0.1	1.5
	ϵ				0.7	0.7
	E				0.1	0.4
UNI-AERO Case1	Vd (cm/s)	0.5	0.1	1.5		
	ϵ	0.2	0.7	0.7		
	E	0.3	0.1	0.4		
UNI-AERO Case2	Vd (cm/s)	0.1	0.1	1.5		
	ϵ	0.7	0.7	0.7		
	E	0.1	0.1	0.4		

The calculations have been based on the 1995 emissions of $PM_{2.5}$ and PM_{10} from the CEPMEIP inventory (Tarrason, 2002). Emissions of coarse PM have been found as the difference between PM_{10} and $PM_{2.5}$ emissions. In UNI-AERO, emissions of primary PM have been distributed between OC, EC and dust and different size modes according to Table 2. Thus, the aerosol system in UNI-AERO consists of OC and EC particles in the Aitken and accumulation mode, and mineral dust in the accumulation and coarse modes, i.e. 3 components and 3 size modes.

Below, effects of various parameters on primary PM concentrations are discussed based on the calculations for January 1999.

Total effect

$PM_{2.5}$ concentrations calculated with the Aerosol dynamics model version are found to be lower compared to those AEROMADE. As shown in Figure 2a, the differences between $PM_{2.5}$ concentrations with AEROMADE and UNI-AERO range between 2 % to 10 %. On the other hand, the concentrations of coarse PM (not shown here) do not appear to be visibly affected by accounting for aerosol dynamics. This result could be anticipated as processes determining the concentrations of coarse PM are in effect similar in both models. Therefore we focus here on the effects of aerosol dynamics on primary $PM_{2.5}$ concentrations

To distinguish the effects of different factors on the concentrations of primary $PM_{2.5}$ the systematic analysis of the differences between the models needed. For this purpose, the following sensitivity tests have been performed.

Test 1: Effect of different emission treatment

AEROMADE uses the grid cell total emissions, which are imposed a vertical distribution and monthly variation. UNI-AERO operates with the emissions of $PM_{2.5}$ and coarse PM classified by source sectors. The model applies vertical distribution and monthly, weekly and daily variation to each emission source category. In addition, UNI-AERO distributes $PM_{2.5}$ emissions between OC, EC and dust in Aitken and accumulation modes as was shown in Table 3. These components are advected individually, which may cause some numerical differences.

To identify differences in PM concentrations due to the differences in emission treatment, coagulation rates between all particles in UNI-AERO have been set to zero. In addition, we assume in UNI-AERO the same dry deposition velocity and scavenging efficiency for particles in the Aitken and accumulation modes (Table 4, Case 2). This means that correspondent dry and wet removal rates for $PM_{2.5}$ and coarse PM particles are the same in AEROMADE and UNI-AERO.

Figure 2b shows that the differences in $PM_{2.5}$ concentrations by AEROMADE and UNI-AERO are largely within 1 % and associated primarily with large source areas of primary $PM_{2.5}$ emissions.

Test 2: Effect of aerosol dynamics (coagulation)

In this test, dry and wet removal rates for $PM_{2.5}$ and coarse PM particles have been harmonized in UNI-AERO and AEROMADE, as in Test 1 (Table 4, case 2). Particle coagulation has been taken into account in UNI-AERO. The resulting differences between $PM_{2.5}$ concentrations from the two models are practically the same as in Test 1 (Figure 2b), meaning that no significant effect of coagulation on the $PM_{2.5}$ mass is found. This is as

expected because when Aitken particles coagulate to the accumulation mode in this test, they do not change their physical properties, as removal efficiency is assumed the same in the Aitken and accumulation mode. Furthermore, coagulation between accumulation and coarse particles is negligibly slow therefore it does not affect the concentrations of $PM_{2.5}$ and coarse PM.

Another test has been performed to evaluate the importance of **coagulation**. UNI-AERO has been run with and without coagulation being accounted for, and then PM concentrations from those runs have been compared. The results have shown that neglecting coagulation has reduced the overall $PM_{2.5}$ concentrations within 1 % (not shown here). This is because in the case without coagulation Aitken particles do not coagulate to the accumulation particles, but remain in the Aitken mode and are removed from the atmosphere faster compared to the run with coagulation. Thus, accounting for particles coagulation results in a slight increase of the $PM_{2.5}$ mass. Coagulation has apparently no effect on the coarse PM mass.

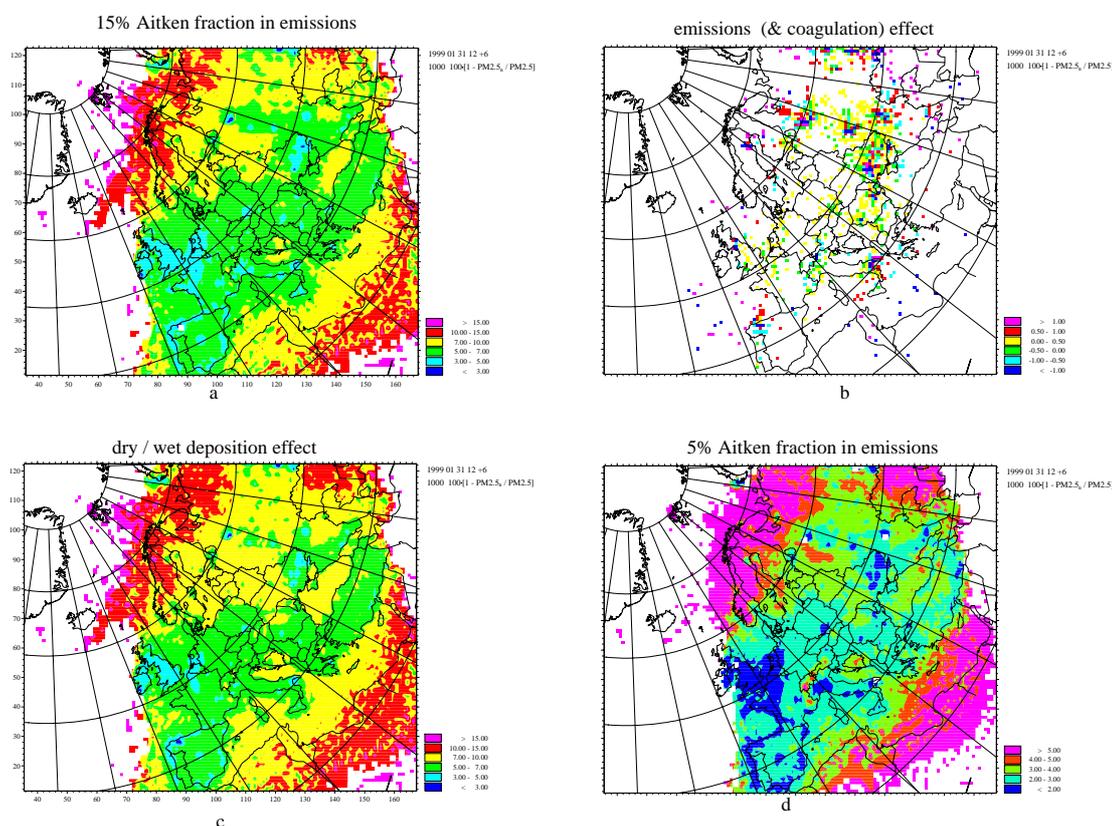


Figure 2: Differences between primary $PM_{2.5}$ concentrations calculated with AEROMADE and UNI-AERO: a) total effect, b) effect of emission and coagulation, c) effect of size-dependent removal, d) effect of emission size distribution.

Test 3: Effect of dry and wet removal

In this test, no aerosol dynamics has been included in UNI-AERO, but different dry and wet removal rates have been used for Aitken and accumulation particles. (Table 4, case 1). Namely, Aitken particles have been assigned larger dry deposition velocity and sub-cloud

scavenging efficiency, while in-cloud wet scavenging of Aitken particles has been less efficient than for particles in the accumulation mode.

The differences between $PM_{2.5}$ concentrations calculated with AEROMADE and UNI-AERO vary from 4-7 % in the Western and Central Europe up to 15 % in the Eastern Europe and Russia (Figure 2c). Lower $PM_{2.5}$ concentrations from UNI-AERO are apparently due to more efficient removal of Aitken particles.

These differences in $PM_{2.5}$ concentrations appear larger than the differences shown in Figure 2a, when both size-resolved deposition and aerosol dynamics were included in UNI-AERO. The reason for that is that the differentiation of removal rates for Aitken and accumulation modes, on one hand, and coagulation process, on the other hand, have opposite effects on $PM_{2.5}$ concentrations. Size-dependent particle removal results in the decrease of $PM_{2.5}$ concentrations, while this decrease is slightly diminished due to the effect of particle coagulation.

Test 4: Effect of the size distribution of emission

The above tests imply that $PM_{2.5}$ concentrations calculated with the Unified aerosol model version are dependent on the relative distribution of $PM_{2.5}$ mass between Aitken and accumulation modes in the model, as these have different removal characteristics. To that effect, calculations with UNI-AERO have been repeated with the fraction of Aitken particles in $PM_{2.5}$ emissions reduced from 15 % to 5 %. In this case, the differences between $PM_{2.5}$ concentration calculated with AEROMADE and UNI-AERO have been reduced from 4-10 % to 2-5 %, as shown in Figure 2d.

Summarising, in the case of primary PM, when other aerosol components are not present, coagulation is the only effective aerosol dynamics process. As expected, accounting for the aerosol dynamics makes practically no effect on the mass of coarse PM, while $PM_{2.5}$ concentrations calculated with size-resolved UNI-AERO are lower than those from AEROMADE. Size-dependent dry and wet deposition of particles has been identified as the most important cause for the reduction of primary $PM_{2.5}$ concentrations. Coagulation of Aitken and accumulation particles has made only a very small effect on $PM_{2.5}$ concentrations, slightly increasing them. Ultimately, concentrations of primary $PM_{2.5}$ calculated by Unified aerosol model version are on average 2-15 % lower compared to $PM_{2.5}$ from the mass model.

It should be highlighted that the effect of size-dependent removal rates on primary $PM_{2.5}$ concentrations have been shown to depend on the fraction of Aitken particles. Therefore, appropriate information on the size distribution of primary PM emissions is essential for accurate PM modelling. Another source for the uncertainty of results to be pointed out is dry deposition velocity and wet scavenging efficiencies used for particles of different size.

3.2 Differences in SIA from UNI-AERO vs. UNI-ACID

Concentrations of secondary inorganic aerosol, sulphate SO_4 , nitrate NO_3 and ammonium NH_4 , have been compared as calculated with the Unified Aerosol (UNI-AERO) and Acid Deposition (UNI-ACID) model versions. It is important to remember that these results are preliminary and need to be further analysed.

In UNI-AERO, total SO_4 , NO_3 and NH_4 concentrations are found as the sum of SO_4 , NO_3 and NH_4 masses in the Aitken and accumulation mode. From UNI-ACID, SO_4 is the total sulphate ($SO_4 + (NH_4)_{1.5}SO_4$), NO_3 is in the form of ammonium nitrate, and NH_4 is the total ammonium from $(NH_4)_{1.5}SO_4$ and NH_4NO_3 .

Differences in the model formulation of several processes are expected to cause differences in the SIA concentrations predicted by UNI-AERO and UNI-ACID. The following processes are different in UNI-AERO compared to UNI-ACID:

1. UNI-AERO accounts for aerosol dynamic processes
2. UNI-AERO uses the thermodynamic equilibrium model MARS for partitioning volatile components between the gas and aerosol phase (for UNI-ACID see Barticki *et al.*, 1998)
3. UNI-AERO uses size-dependent dry deposition and wet scavenging rates, while UNI-ACID uses constant values for all SIA, which are the same as for accumulation mode particles in UNI-AERO.

Figure 3 shows 1999 annual mean SIA concentrations calculated with the two model versions. The geographical distribution of the respective components looks rather similar, while some differences can be seen in the concentration levels. The differences between model results appear to vary from month to month. As an example, monthly means in September 1999 of SO₄, NO₃ and NH₄ concentrations calculated with UNI-ACID and UNI-AERO are shown in Figure 4.

UNI-AERO calculates higher than UNI-ACID annual mean concentrations of SO₄ (Figure 3a). The differences in SO₄ concentration show seasonal variation, being rather small in the warm period (Figure 4a) and larger in winter months. These results are not exactly as expected and more testing is needed to verify and explain the differences.

Overall concentrations of NO₃ from UNI-AERO are consistently lower, while concentrations of gaseous HNO₃ higher (not shown here), compared to those calculated with UNI-ACID (Figures 3b and 4b). In other words, the MARS equilibrium model used in UNI-AERO appears to distribute less of the total NO₃ to the particle phase and more to the gas phase than UNI-ACID does. This can partly be explained that in MARS, SO₄ gets fully neutralized by ammonia to ammonium sulphate (NH₄)₂SO₄ as long as there is available NH₃. On the other hand, in UNI-AERO, ammonium sulphate is assumed to be a mixture of the equal portions of ammonium sulphate and ammonium bisulphate. Thus, in UNI-AERO one SO₄ molecule binds two NH₃ molecules, while in UNI-ACID it binds 1.5 NH₃ molecules. This results in a larger NH₄ portion in the form of ammonium sulphate and less ammonia available to form ammonium nitrate.

Annual mean NH₄ concentrations are slightly lower as predicted by UNI-AERO (Figure 3c). For other months, NH₄ calculated by UNI-AERO is lower than that from UNI-ACID in warm (Figure 4c) and higher in cold months (NH₃ concentrations compares oppositely).

The comparison shows that there are certain differences between SIA calculated by the Aerosol and Acid Deposition model. As it was pointed out above, there are a number of causes for those differences. A series of sensitivity tests on the model results are needed with respect to all relevant chemical and physical processes in order to explain their individual effects on calculated SIA concentrations.

Summing up, the aerosol concentrations from the Unified Aerosol model version presented here are only provisional. Comparison of the Aerosol model version with the Acid Deposition model version is a preliminary evaluation of the physical soundness of UNI-AERO. The results from the two model versions for SIA are in a reasonable agreement, though discrepancies varying seasonally are found for individual components. These results need further analysis and the disagreements should be explained at the next stage of model evaluation. It should be highlighted that the EMEP Aerosol dynamics model is still under

development and testing. A thorough evaluation of the effects and importance of different processes involved in the aerosol formation, dynamics and transport will continue.

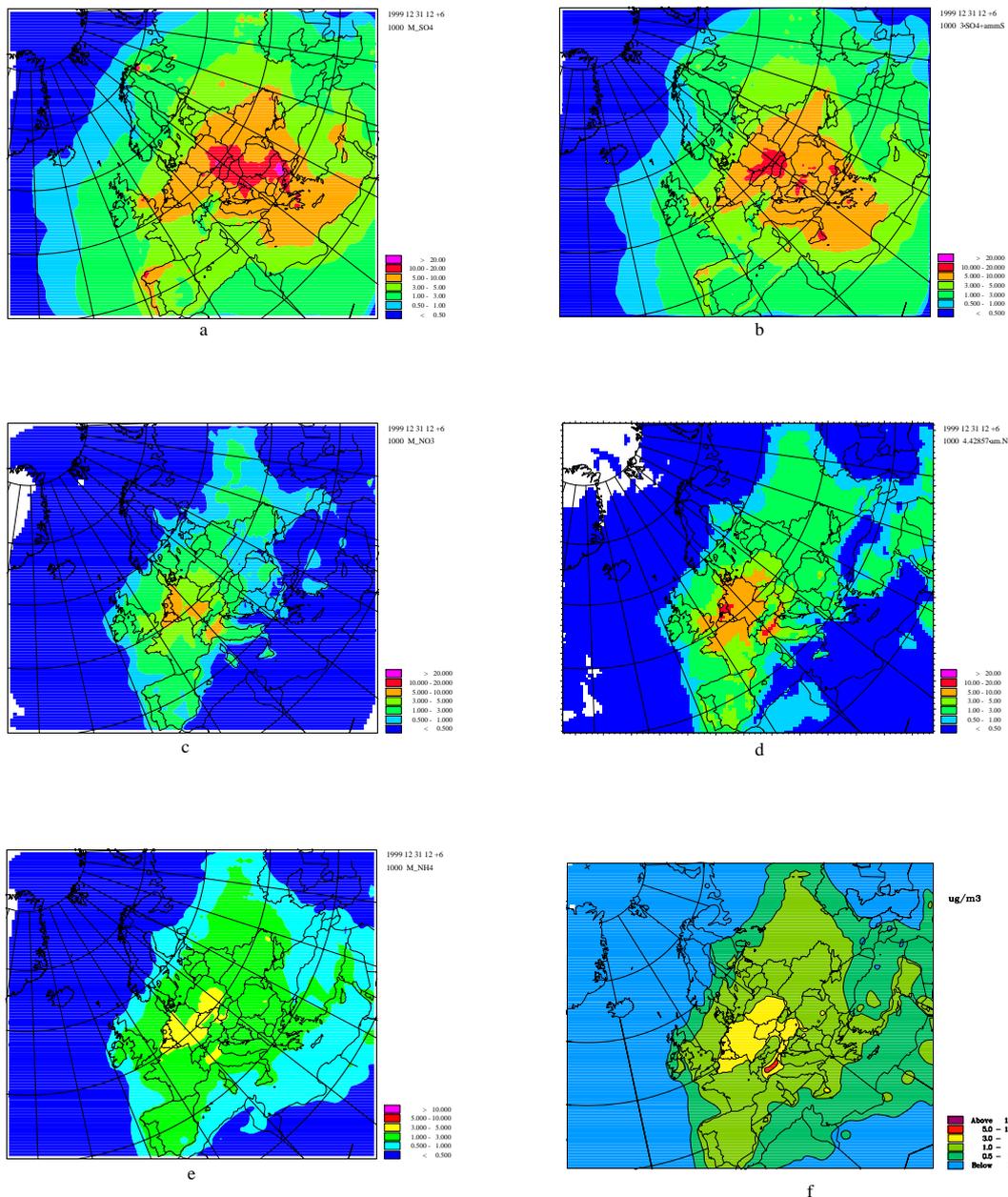


Figure 3: Annual mean concentrations of SIA calculated for 1999 by UNI-AERO: a) SO₄, c) NO₃, e) NH₄, and by UNI-ACID: b) SO₄, d) NO₃, f) NH₄.

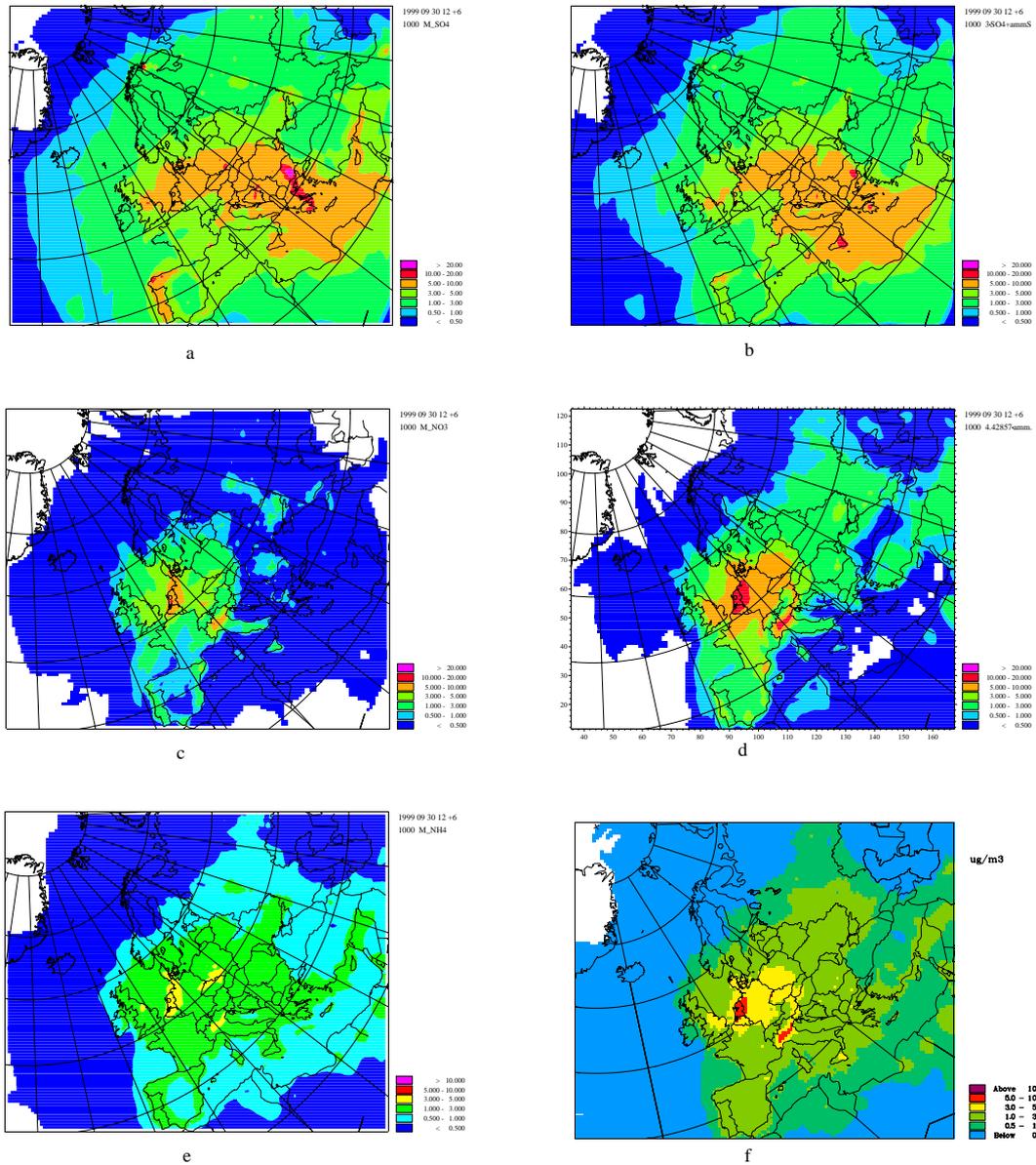


Figure 4: Monthly annual concentrations of SIA calculated for September 1999 by UNI-AERO: a) SO₄, c) NO₃, e) NH₄, and by UNI-ACID: b) SO₄, d) NO₃, f) NH₄.

Chapter 4

Preliminary results on the aerosol mass, number and size with UNI-AERO

The EMEP Unified Aerosol model version provides calculations of aerosol mass, chemical composition, as well as particles number concentration and size distribution. Concentrations of the aerosol components and preliminary results on the particles number and size are presented in this section. It is important to keep in mind that all model results presented in the note should be regarded as interim and subject to possible changes as work on model development and testing progresses.

4.1 Distribution of particle mass and number concentrations and aerosol chemical composition

4.1.1 Concentrations of PM_{2.5} and PM₁₀

Initial distributions of PM_{2.5} and PM₁₀ concentrations in 1999 calculated with the Unified Aerosol model version are presented in Figures 4a and 4b. Concentrations of PM_{2.5} are derived as the sum of all aerosol components in nucleation, Aitken and accumulation mode, and PM₁₀ is the sum of PM_{2.5} concentrations and coarse aerosol mass. For comparison, Figure 4d shows the total PM₁₀ concentrations calculated for the same year with the EMEP Eulerian models for primary PM and SIA (Tsyro, 2001). The differences between PM₁₀ concentrations from UNI-AERO and the Eulerian models should not be related to only accounting for aerosol dynamics in UNI-AERO. They are also due to profound refinement of the description of other processes in the EMEP Unified model. Among the main changes is improvement of the parameterisation of turbulent mixing and of the wet scavenging scheme. Simpler formulation for dry deposition has been used in the present calculations. For more information on the Unified model development and verification see the EMEP Report 1-2/2002.

Figure 5a shows that overall PM₁₀ concentrations calculated with UNI-AERO are higher than PM₁₀ values from the last year calculations (Figure 5d). Sea salt was not considered in the previous years PM modelling, while it contributes to the total PM₁₀ mass in UNI-AERO. To make the old and new results more compatible, sea salt mass has been subtracted from the PM₁₀ mass by UNI-AERO. Figure 5c reveals that the general level of PM₁₀ concentrations from UNI-AERO is higher compared to the earlier calculations with the EMEP Eulerian models. Annual mean in 1999 concentrations of PM_{2.5} predicted by UNI-AERO are shown in Figure 5b.

The inclusion of sea salt particles results in an additional increase of the PM mass, especially in coastal areas. Due to accounting in UNI-AERO for the sea salt contribution the model manages to predict for Scandinavia higher PM₁₀ concentrations, which were unexplainably low calculated previously with the mass models. In the south of Norway PM₁₀ modelled

concentrations has increased from 1-3 to 5-15 $\mu\text{g}/\text{m}^3$, which compares better with measurements. For example, the model predicts PM_{10} of 10 $\mu\text{g}/\text{m}^3$ in Kirkeness, while measured annual mean in 2000 PM_{10} concentration is 7.9 $\mu\text{g}/\text{m}^3$ (this value could be higher as monthly means in January and February are believed to be measured too low (EMEP/CCC-Report 5/2001)). Significant increase in PM_{10} concentrations due to the sea salt contribution is found in the United Kingdom, where modelled PM_{10} concentrations up to 30 $\mu\text{g}/\text{m}^3$ can be found. In Central Europe, the general PM_{10} level has increased, e.g. from 5-15 $\mu\text{g}/\text{m}^3$ to 10-20 $\mu\text{g}/\text{m}^3$ in France, Germany and Poland.

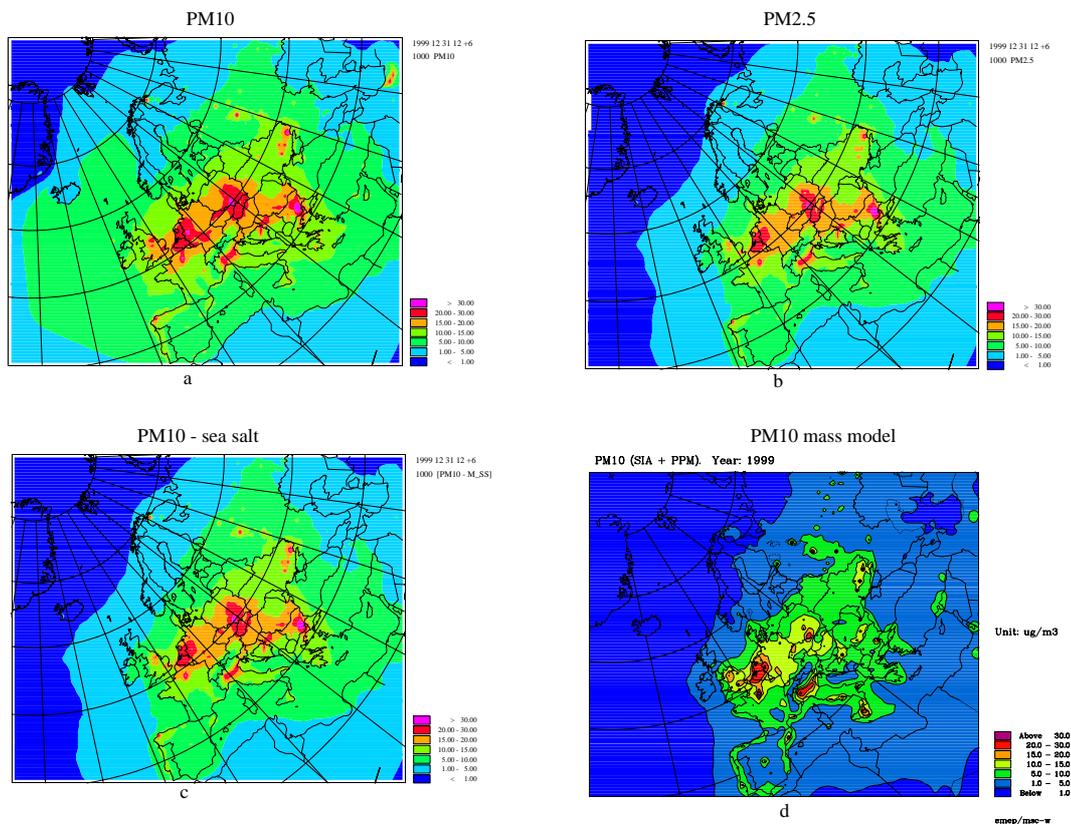


Figure 5: Concentrations of PM_{10} and $\text{PM}_{2.5}$ calculated for 1999 with UNI-AERO: a) PM_{10} , b) $\text{PM}_{2.5}$, c) PM_{10} without Sea salt contribution, and with the EMEP Eulerian models: d) PM_{10} .

4.1.2 Mass concentrations of aerosol components

Annual mean in 1999 concentrations of primary aerosols considered in UNI-AERO, namely organic and elemental carbon, anthropogenic dust and sea salt are presented in Figure 6. It shows that distribution of these aerosol components reflects the distribution of their emission sources. OC, EC and dust originate from primary PM emissions, so that their calculated distribution and relative concentrations are determined by the chemical speciation and particle size distribution for PM emissions adopted in the model. Fine OC and EC aerosols come from $\text{PM}_{2.5}$ emissions. Therefore their spatial distributions are rather similar, with largest concentrations in central Europe, while predicted OC concentrations are in general higher than EC concentrations. Primary anthropogenic dust has both fine and coarse component. The contribution of coarse dust particles is particularly large in the Eastern Europe, Russia and

Ukraine. Presently, all sea salt aerosols have been assigned to the coarse mode. It is efficiently deposited so that its concentration decreases relatively fast as it is transported from the sea on land. Concentrations of Secondary Inorganic Aerosol, SO_4 , NO_3 and NH_4 , were presented in Section 3.

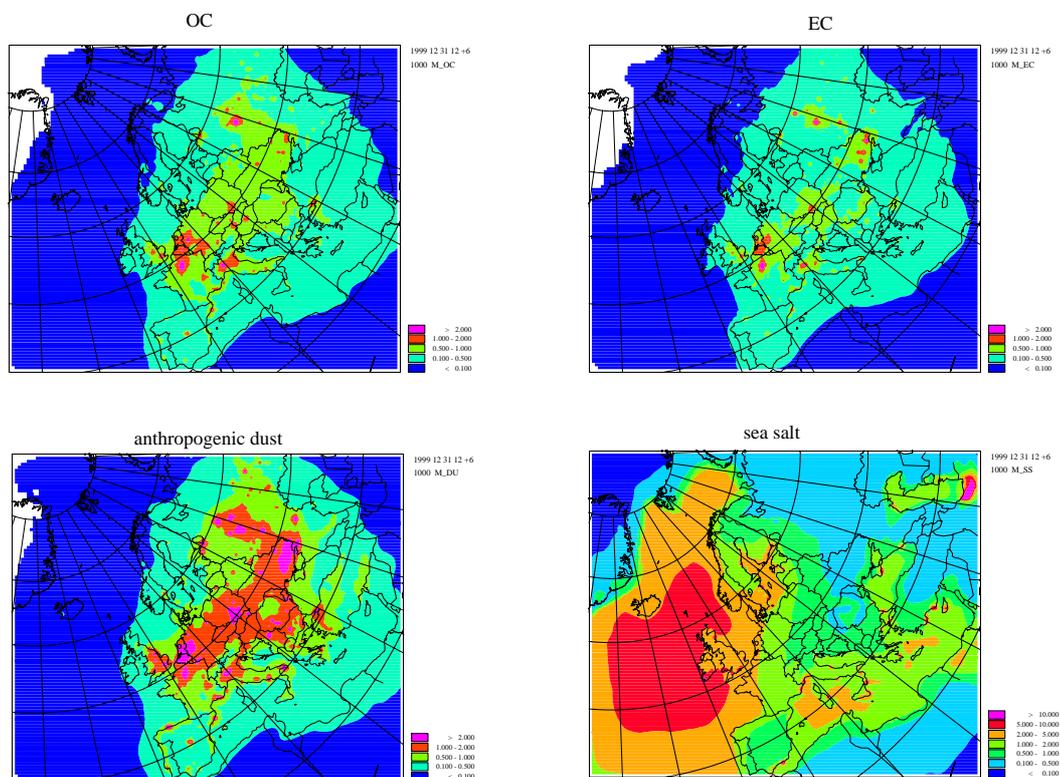


Figure 6: Concentration distributions calculated with UNI-AERO for: a) primary anthropogenic organic carbon, b) elemental carbon, c). anthropogenic mineral dust, and d) sea salt.

Relative contributions of different aerosol components to the total PM_{10} mass are shown in Figure 7. SO_4 is clearly the dominating aerosol component, accounting for from 30-50 % of PM_{10} concentrations in western, central and northern Europe to 50-70 % in Eastern Europe and parts of Russia. NO_3 is the next important components to the ambient aerosol. Its contribution to the PM_{10} mass is largest in central Europe (20-30 %) and decreases to 5-15 % in the Eastern Europe and Russia, and to below 5 % in the Northern Europe. NH_4 contributes with 5-20 %. Contributions of carbon particles vary from 3 to 15 % for primary OC and from 1 to 7 % for EC. Largest contribution of anthropogenic dust is found in Ukraine (exceeding 60 % in some grid squares), Russia, and Turkey.

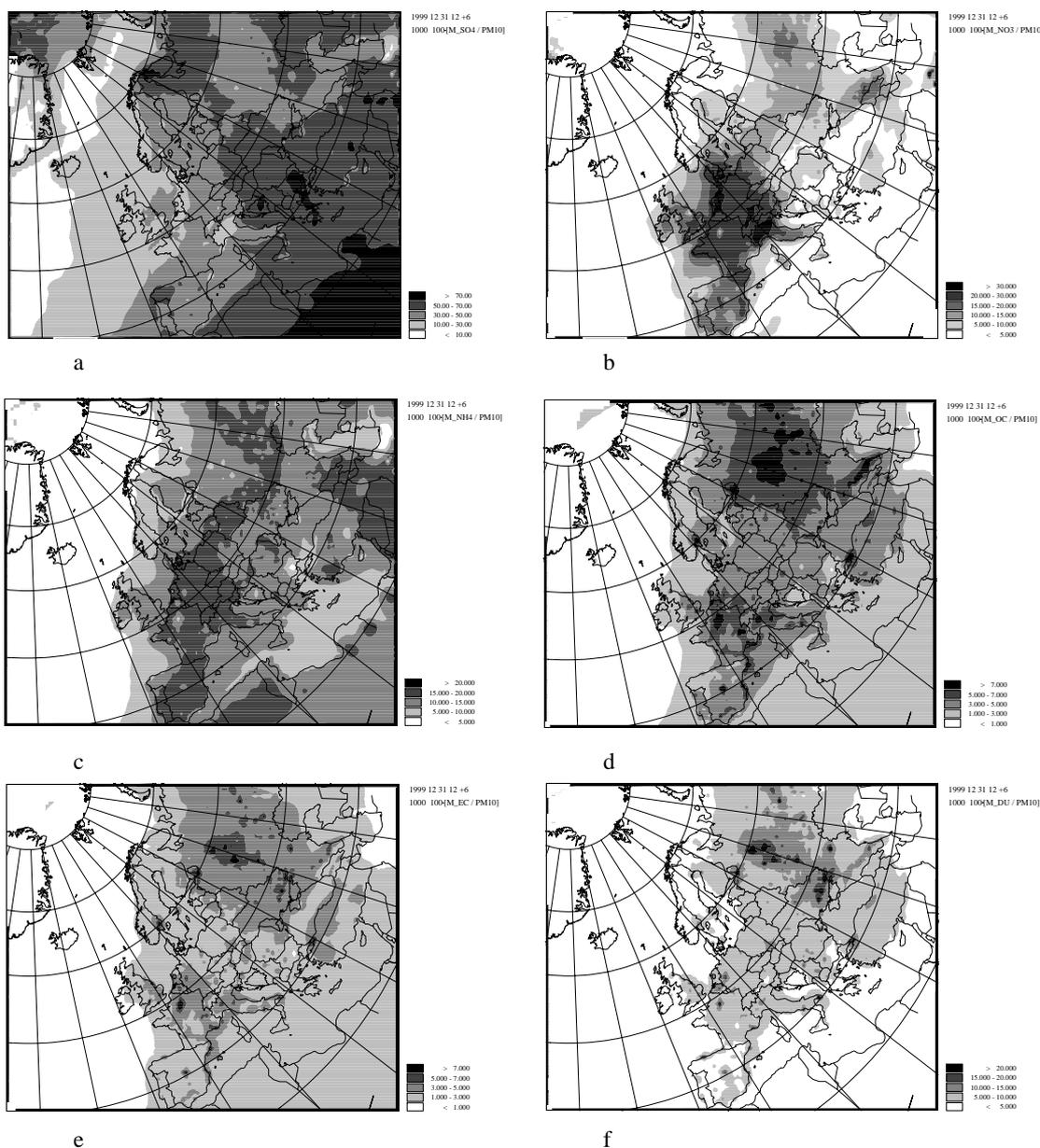


Figure 7: Relative contribution of different aerosol components to the PM₁₀ concentrations: a) SO₄, b) NO₃, c) NH₄, d) primary OC, e) EC, and f) anthropogenic dust.

4.1.3 Number concentrations

Annual mean concentrations of the aerosol total number calculated with UNI-AERO are presented in Figure 8a. Large number concentrations are associated with the areas of new particles production from emissions and/or nucleation.

The distribution of nucleation particle number is highly uneven (Figure 8b). Maximum number concentrations of nucleation particles occur where the conditions are favourable for nucleation bursts, i.e. high H₂SO₄ concentrations, lower temperatures, higher relative

humidity and low number of pre-existing aerosols. Number distribution of Aitken and accumulation mode particles (Figures 8c and 8d) reflects the distribution of the main emission sources. Compared to the accumulation mode aerosol, the field of Aitken particles number concentrations exhibits rather sharp gradients from source areas due to the relatively efficient dry and wet removal of Aitken particles and their coagulation to the accumulation mode. On the other hand, accumulation mode particles are very slowly removed from the atmosphere and their coagulation to the coarse aerosols is negligible. Therefore they can be transported to larger distances.

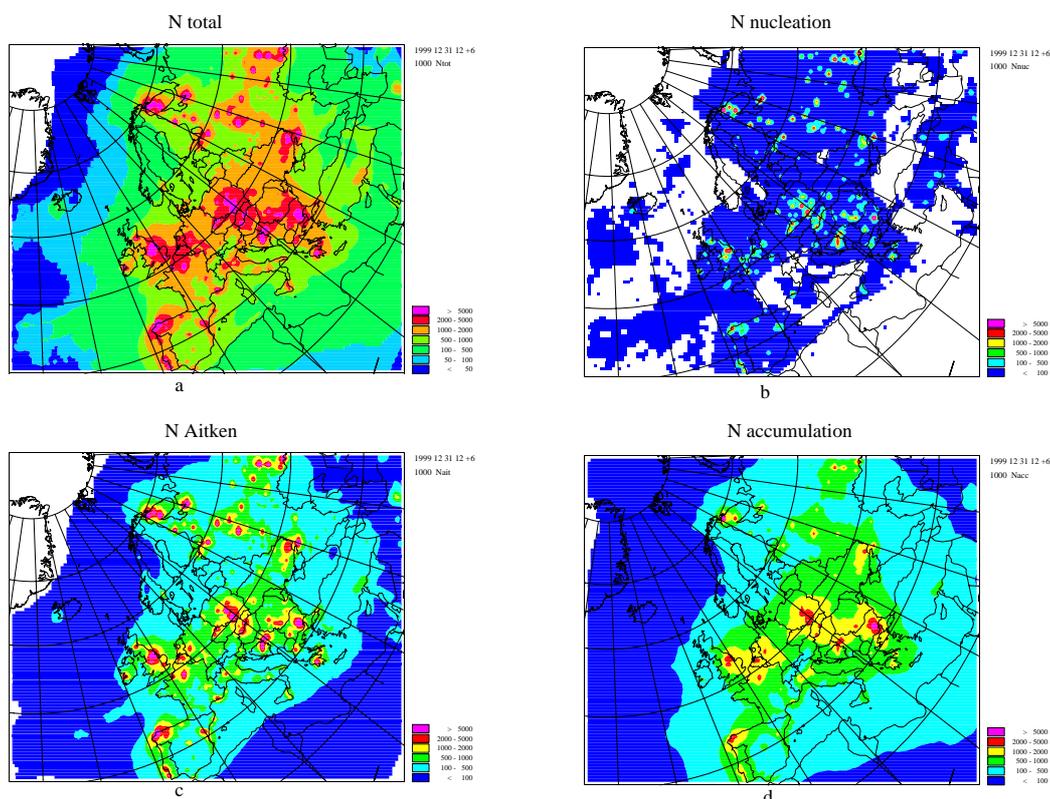


Figure 8: Modelled annual mean in 1999 total number concentration (a) and number concentrations of (b) nucleation, (c) Aitken and (d) accumulation mode particles.

4.1.4 Number and mass size distribution

The Aerosol model version predicts the size distribution of particle mass and number. An example is presented in Figure 9, which shows the average in September 1999 distributions of aerosol mass and number between the size modes at two different locations. The first location is chosen on the border between Germany and Czech Republic and characterised by efficient particle formation by nucleation and production of Aitken particles due to large direct emissions. The second location, the Hungarian site K-puszt, is located in an area with considerably lower emissions. Therefore PM here is characterised by much smaller fraction of newly formed and larger fraction of the “aged” particles. This is well reflected in the particles number distribution. In the first location, more that 50 % of particles is in the Aitken mode, and there is a considerable number of nucleation particles. While in the second site, the

nucleation mode is empty, and about 60% of the particles is in accumulation mode. This aerosol has apparently been transported over some distance to this site, so that the Aitken particles have coagulated to the accumulation ones. As to the aerosol mass, in both areas about nearly 95 % mass is found in the accumulation mode, and 4-5% of the mass are due to coarse particles. The contribution of nucleation and Aitken mode particles to the total aerosol mass is negligibly small.

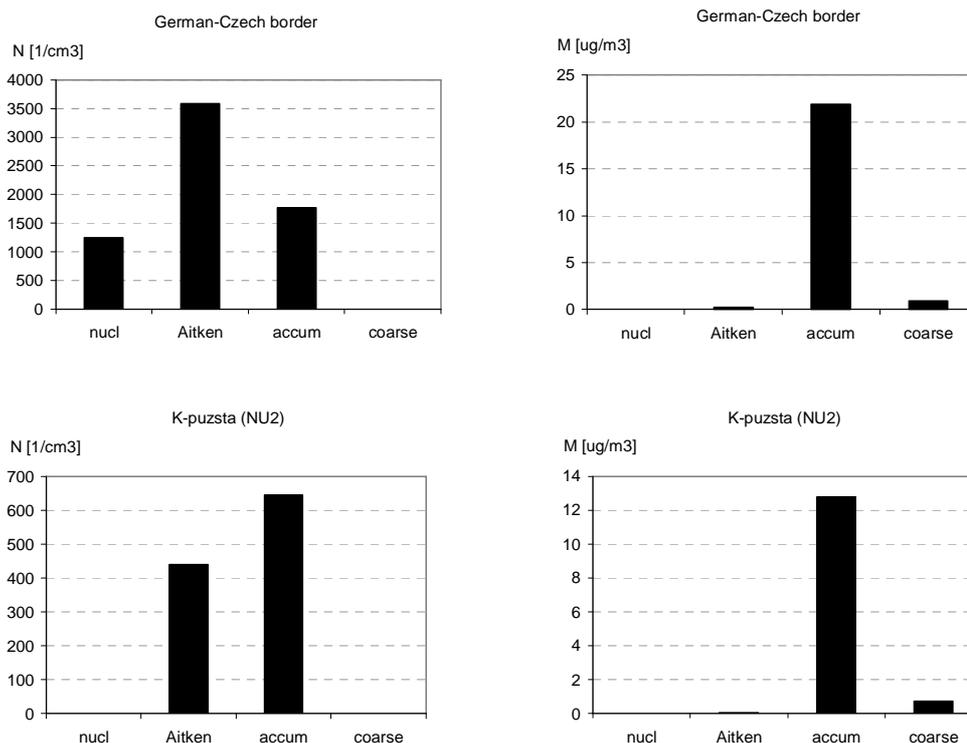


Figure 9: Number and mass size distribution as calculated with UNI-AERO.

The importance of a correct description of the primary PM emissions was already pointed when analysing the effect of aerosol dynamics on primary PM concentrations. Model results on the number and mass distribution between different size modes depends as well on the size distribution of mass and number applied for emitted particles. Therefore, expert information on the emission size distribution will facilitate more accurate modelling the aerosol size and number.

4.2 Comparison of UNI-AERO results on PM₁₀ mass and chemical composition with available measurements

Verification of UNI-AERO against available measurements is an essential requirement for progress in model development. In this note, a preliminary comparison of some modelled parameters with available measurements is included.

Figure 10 compares PM₁₀ concentrations in 1999 calculated with UNI-AERO and measured at EMEP sites. PM₁₀ concentrations with the Unified Aerosol model version compare better with measurements at all Swiss and most of German sites than the earlier results with the EMEP Eulerian mass models (EMEP Report 5/2000). For a number of German stations UNI-AERO slightly overestimates PM₁₀. However, there is still a considerable underestimation by the model of PM₁₀ concentrations in a number of Spanish stations. In Spain, the pollution episodes with very high PM₁₀ concentrations (sometimes exceeding 100 µg/m³) are associated with the transport of Saharan dust. Therefore in Spain and other areas with a large dust component, accounting for natural dust and its re-suspension is crucial for the accurate predicting of PM concentrations.

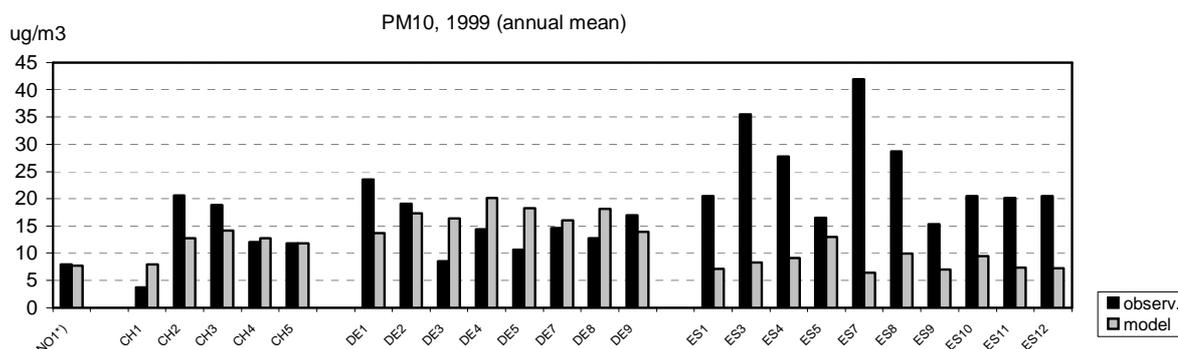


Figure 10: Calculated with UNI-AERO and measured at EMEP stations annual mean concentrations of PM₁₀ in 1999 (* in 2000 in Birkenes)

Aerosol chemical composition at two sites predicted by UNI-AERO is presented in Figure 11. There also is shown PM₁₀ composition measured at the same sites during different campaigns. The modelled and measured particles composition cannot be directly compared as the measurements were made in different years and time periods than the model calculations and different than in the model chemical components were analysed. Therefore, this comparison has not been meant for a rigorous validation of the UNI-AERO prediction. However, it can give some indication on the adequacy of model results.

Unfortunately, no appropriate measurements on the aerosol number concentrations are presently available to MSC-W for model verification and development purposes. Collecting representative measurement data on the size distribution of PM mass and number for verification of model results is among the future works.

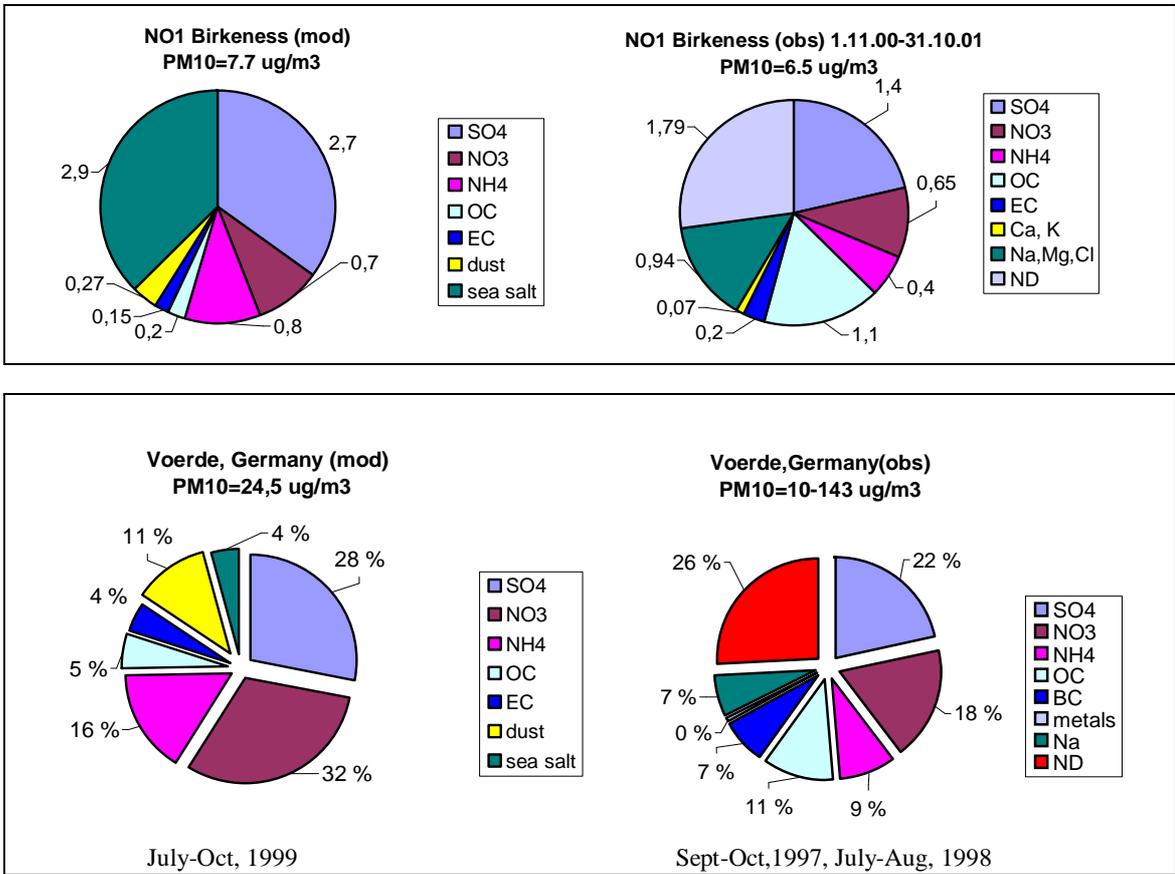


Figure 11: Chemical composition of PM₁₀ as calculated for 1999 by UNI-AERO and measured in Birkenes, Norway (Tørseth et al., 2002) and in Voerde, Germany in 1997-98 (Kuhlbusch et al., 1999).

Chapter 6

Remaining problems and perspective works

A new aerosol dynamics model, the EMEP Unified Aerosol model version (UNI-AERO), has been under development at EMEP/MSC-W. This note contains a careful documentation of the latest UNI-AERO version.

Preliminary calculation results on aerosol mass, number, chemical composition and size distribution are presented here. A series of sensitivity tests on the effects of implementation of aerosol dynamics on PM concentrations are discussed in the note. Initial comparison of UNI-AERO results with the earlier EMEP models and available measurements shows a reasonable soundness of the Aerosol model version. However, UNI-AERO needs a thorough verification and further testing. All results presented in this note must be considered provisional and therefore interpreted carefully.

Below, we highlight the remaining problems and define the areas of future works on the EMEP Aerosol model development, testing and verification.

1. Continue sensitivity tests to analyse the effect of individual chemical and physical processes on aerosol concentrations, in particular on SIA concentrations
 - Aerosol dynamics
 - Equilibrium chemistry – MARS
 - Initial and background conditions
2. Further development and improvement of:
 - Nucleation (testing different parameterisations)
 - Condensation (e.g. Kelvin effect)
 - Coagulation (including turbulent shear and gravitational coagulation)
 - Coupling between gaseous and aerosol chemistry
 - Modes merging (aerosol growth to larger modes)
3. Implementation of:
 - Natural aerosol (Saharan dust)
 - Particles re-suspension
 - Secondary Organic Aerosol
 - Size-resolved particle dry deposition depending on the land-use and meteorological conditions and gravitational settling
 - Cloud processing of aerosol (heterogeneous sulphur chemistry, scavenging of interstitial Aitken particles and their enhanced coagulation to the accumulation particles, activation of accumulation mode aerosols, new particles formation due to cloud evaporation)
 - Size-dependent sub-cloud wet scavenging
4. Model verification:

- Collection of available measurement data, appropriate for model verification. Measurements on particles mass, number concentration and size distribution, as well as their chemical composition are needed for credible model verification.

5. Need for improvements on emission input data information.

As concluding remarks, the modelling work suffers from missing emissions speciation and monitoring data. A number of parameters have to be covered by assumptions in view of the lack of available information. But the processes determined by these parameters have to be included in the model in order to ensure its physical soundness. There is a strong need for measurement data for verification on the calculated particle mass, number concentrations, chemical composition and size distributions

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